The American Ceramic Society

38th International Conference & Exposition on Advanced Ceramics and Composites

ABSTRACT BOOK

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The American Ceramic Society
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Introduction

This volume contains abstracts for more than 900 presentations during the 38th International Conference & Exposition on Advanced Ceramics and Composites in Daytona Beach, Florida. The abstracts are reproduced as submitted by authors, a format that provides for longer, more detailed descriptions of papers. The American Ceramic Society accepts no responsibility for the content or quality of the abstract content. Abstracts are arranged by day, then by symposium and session title. An Author Index appears at the back of this book. The Meeting Guide contains locations of sessions with times, titles and authors of papers, but not presentation abstracts.

How to Use the Abstract Book

Refer to the Table of Contents to determine page numbers on which specific session abstracts begin. At the beginning of each session are headings that list session title, location and session chair. Starting times for presentations and paper numbers precede each paper title. The Author Index lists each author and the page number on which their abstract can be found.

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Monday, January 27, 2014

Plenary Session

Room: Coquina Salon D

9:00 AM

(ICACC-PL-001-2014) From the Rattler Test to Modern Fracture Mechanics: A Perspective on Toughness (Invited)

S. Wiederhorn*, National Institute of Standards & Technology, USA

In this talk, we project backwards to a time when there was no materials science, no fracture mechanics and no way to characterize or modify the microstructure of materials in a controlled way. There were no universal mechanical test machines and no standard means of establishing how a material would perform under a given load regime. Yet the needs for mechanical reliability were there, just as they are today. In this talk we review some of the problems encountered at the beginning of the 20th century that are still problems today. We shall show how the development of fracture mechanics and modern techniques of microstructural analysis have enabled the solution of mechanical problems associated with the use of ceramics in modern applications. In the course of the lecture we will trace the development of fracture mechanics from the early 20th century to the present day and the replacement of performance tests with design criteria based on fracture mechanics analysis.

9:40 AM

(ICACC-PL-002-2014) Building Bridges in Materials Science and Technology: An Important Issue for Solving Basic Problems in Modern Society (Invited)

J. A. Varela*, University of Sao Paulo State, Brazil

With the world population at 7 billion and growing we are stretching the limits of the earth's natural resources. To achieve our global goals of environmental health and economic development it is crucial that we find new and effective ways to use science and technology to meet our expanding energy needs while reducing gas emissions to minimize climate change. This is a global challenge and each nation must find its own individualized means to contribute solutions to this problem. Those challenges need more collaboration among worldwide scientists as well as an open science. Our recent knowledge in nanoscience and nanotechnology, in particular functional oxide semiconductors, has opened many doors for solving key technological problems. Developing new materials is multidisciplinary field and building bridge for scientists and engineers is an important issue to have more efficient materials solution for the future of humankind. There are several ranges of forming networks for scientists in Materials Science including those in the same research institution, among different research institutions, between research institutions and industries (for innovation), and at different countries. Funding Research Institutions are extremely important for building the network in all those ranges. Forming those network involve moving of scientists and students, and joint projects. Then the collaboration among funding agencies of the same and different countries are fundamental for building networks. I will give a brief overview of recent nanostructured functional semiconductors and a success example of FAPESP, the São Paulo State Foundation for Research in building collaboration with other Funding Agencies in Brazil and abroad, as well as with Universities and Companies all around the world. These collaborations have been important in establishing the bridge among scientists of São Paulo State in Brazil and colleagues of universities and companies in many countries.

10:40 AM

(ICACC-PL-003-2014) The Need and Potential of Porous Ceramic Materials (Invited)

W. Cutler*, Corning Incorporated, USA

A substantial amount of work over many decades has been aimed at developing understanding to create defect-free, fully dense ceramic bodies. However, there is an equal need for understanding and industrialization of porous ceramic bodies with well-engineered pores. The talk will provide an overview of specific aspects of porous materials including: Commercial uses, materials selection, porosity creation, processing, characterization and properties. Specific examples will be provided from pollution control and filtration sectors.

11:20 AM

(ICACC-PL-004-2014) Nanostructured Metal Oxides in Gas Sensing Applications: Challenges and Perspectives (Invited)

U. Simon*, RWTH Aachen University, Germany

The talk will address the challenge of identifying structure-property relations and descriptors for a rational design of gas sensing materials consisting either on semiconducting nanoparticles or ion-conducting nanoporous materials. Selected examples will (i) demonstrate the potential of high throughput experimentation in search of new selective gas sensors, and will (ii) introduce zeolites as a chemically variable class of nanoporous proton conductors, which can be tuned for optimized in particular for exhaust gas monitoring.

2nd Pacific Rim Engineering Ceramics Summit

Pacific Rim Ceramic Technologies: Trends and Directions I

Room: Coquina Salon C

Session Chairs: Kouichi Yasuda, Tokyo Institute of Technology; Hisayuki Suematsu, Nagaoka University of Technology

1:30 PM

(ICACC-PRECS-001-2014) Consolidation of cBN-based composites by spark plasma sintering (Invited)

T. Goto*, M. Kitiwan, A. Ito, J. Zhang, IMR Tohoku University, Japan

WC-Co composite are most common cutting tool materials, whereas W is a rare and localized element. Although cBN-based composite is a promising material to substitute WC-Co, they are commonly consolidated by ultra-high pressure with additives. SPS (spark plasma sintering) is a candidate process to densify cBN-based composite at a moderate pressure, while the transformation of cBN to hBN is a critical issue. By modifying cBN surface to retard the transformation combined with a hard and ductile matrix, high performance cBN-based composites can be consolidated by SPS. TiN-TiB2 is a quasi-binary eutectic system and can be more densified than monolithic TiN and TiB2. The TiN-TiB2 system is a candidate matrix for the cBN-based composite. The phase transformation of cBN under SPS condition can be retarded by SiO2 coating on the cBN powder. The cBN powder surface was coated with SiO2 (SiO2/cBN) about 50 nm in thickness by chemical vapor deposition (CVD) using tetraethylorthosilicate. The relative density of SiO2/cBN -TiN-TiB2 composite at cBN content of 50 vol% was 92.4% at 1873K. With increasing cBN from 10 to 60 vol%, the hardness of cBN-TiN-TiB2 composite matrix decreased 21.9 to 15.4 GPa and the fracture toughness (KIC) increased from 3.2 to 5.1 MPa m1/2. The harness of cBN phase was 52.7 to 69 GPa. The combination of CVD and SPS is effective to obtain dense cBN-based composites.

*Denotes Presenter

2:00 PM

(ICACC-PRECS-002-2014) Control of Electrical Resistivity in Liquid-Phase Sintered Silicon Carbide Ceramics (Invited)

Y. Kim*, K. Lim, The University of Seoul, Republic of Korea; K. Kim, Konkuk University, Republic of Korea

The electrical properties of β-SiC ceramics were found to be adjustable through appropriate aluminum and nitrogen co-doping. Polycrystalline β-SiC specimens were obtained by hot pressing SiC powder mixtures containing nitride(s) and oxide(s) as sintering additives in a nitrogen atmosphere. The electrical resistivity of the SiC specimens, which exhibited n-type character, increased with nitrogen doping and decreased with aluminum doping. The increase in resistivity is attributed to Al-derived acceptors trapping carriers excited from the N-derived donors. The results suggest that the electrical resistivity of the β-SiC ceramics could be varied in the range of 10^{6}-10^{-3} Ω.cm by manipulating the compensation of the two impurity states. The photoluminescence (PL) spectrum of the specimens was found to evolve with the addition of dopants. The presence of N-donor and Al-acceptor states within the band-gap of 3C-SiC could be identified by analyzing the PL data.

2:20 PM

(ICACC-PRECS-003-2014) Synthesis of Novel Materials Utilizing Extreme Conditions Obtained by Pulsed Power Technologies (Invited)

H. Suematsu*, Nagaoka University of Technology, Japan; Y. Tokoi, Nagaoka National College of Technology, Japan; T. Suzuki, T. Nakayama, K. Niihara, Nagaoka University of Technology, Japan

Inertial confinement fusion research has yielded pulsed power technologies, which include pulsed high voltage and large current sources and active species. These technologies can offer unique chemical reactions to form novel materials. We have been working on synthesis and preparation of functional materials under the extreme conditions mainly obtained by the pulsed power technologies. In the presentation, some examples with the benefit utilizing the extreme conditions, which include passivated Ti nanosized powders prepared by pulsed wire discharge, Cr(N,O) hard coatings deposited by pulsed laser deposition in nitrogen active species, and $CSr_2Ca_2Cu_3O_y$ superconductor synthesized at low temperatures using high-pressure- phase $Sr_2Ca_2Cu_3O_y$ precursor, are shown.

2:40 PM

(ICACC-PRECS-004-2014) Smart Powder Processing to Produce Advanced Ceramics (Invited)

M. Naito*, Osaka University, Japan

Smart powder processing stands for green and sustainable powder processing technique that creates advanced materials with minimal energy consumption and environmental impacts. Particle bonding technology is a typical smart powder processing technique to make advanced composites. Using the features, desired composite particles can be successfully fabricated. Particle bonding can also be applied to synthesize nanoparticles without extra heat assistance by only one-pot processing. By the combinations of both process of nanoparticle synthesis and its bonding, unique nanocomposite granules are favorably created. Therefore, the assembling of these composite particles and granules lead to the control of nano/microstructure of advanced materials.Furthermore,the particle bonding process can be also applied to bond nanoparticles with substrate to form mechanically deposited porous films. In this paper, the particle bonding process and its applications for making advanced ceramics will be explained. On the other hand, by carefully controlling the bonding between different kinds of materials, separation of composite structure into elemental components is also possible, which leads to the development of novel technology for recycling composite materials and turns all of them to high-functional applications. In this paper, the development of novel recycling method of glass-fiber reinforced plastics will be introduced.

3:20 PM

(ICACC-PRECS-005-2014) Grain Boundary Structures and Plasticity of Ceramics (Invited)

Y. Ikuhara*, Univ.Tokyo/JFCC//Tohoku Univ., Japan

It has been known that grain boundary (GB) sliding plays an important role for the plastic deformation of ceramic materials during creep tests. In this case, the behavior of GB sliding is strongly dependent on the GB characters such as misorientation angle between two adjacent crystals and GB plane, however, such effect has not been clarified yet. In addition, this effect in much influenced by dopant segregation at GBs. In this study, in order to clarify the atomistic mechanisms of GB sliding and its dopant effect, bicrystal studies have been performed to find the relationship between the atomic structures, chemistry and GB sliding behavior of Al2O3 ceramics. All of the samples were characterized by Cs-corrected STEM and HRTEM, and the detailed atomic structures were quantitatively determined by combining the experimental results and the theoretical studies. It has been also reported that several ceramic crystals can be plastically deformed by dislocation slip like metals. In this study, the nanoindentation experiments were conducted for several crystals and their bicrystals inside transmission electron microscopy (TEM). The interaction between the introduced lattice dislocations and the GBs were directly observed. The dislocation-GB interaction and its dependence on the GB characters will be discussed in detail.

3:50 PM

(ICACC-PRECS-006-2014) Challenges in Model Development for Estimating Internal Stress of Ceramic Laminates during Sintering (Invited)

K. Yasuda*, Tokyo Institute of Technology, Japan

Laminates are the most important categories of ceramic products such as multilayer capacitor, thin film/substrate system, and ceramic coating. During sintering of the laminates, internal stress may occur in each layer, due to the differences in sintering strain and thermal expansion strain between the layers. The author has already developed the elastic model for estimating the internal stress during sintering, based on these two strains. In this presentation, the author makes a challenge to extend this model into elasto-plastic, viscoelastic and viscous materials .Discussion is made for the materials having continuous composition change like functionally gradient materials also.

4:10 PM

(ICACC-PRECS-007-2014) The Development of Environmental Barrier Coatings for SiC/SiC Ceramic Matrix Composites: Challenges and Opportunities (Invited)

D. Zhu*, NASA Glenn Research Center, USA

Environmental barrier coatings (EBCs) and SiC/SiC ceramic matrix composites (CMCs) systems will play a crucial role in future turbine engines for hot-section component applications because of their ability to significantly increase engine operating temperatures, reduce engine weight and cooling requirements. The development of prime-reliant environmental barrier coatings is a key to enable the applications of the envisioned CMC components to help achieve next generation engine performance and durability goals. This paper will primarily address the performance requirements and design considerations of environmental barrier coatings for turbine engine applications. The emphasis is placed on current candidate environmental barrier coating systems for SiC/SiC CMCs, their performance benefits and design limitations in long-term operation and combustion environments. Major technical barriers in developing advanced environmental barrier coating systems, the coating integrations with next generation CMC turbine components having improved environmental stability, cyclic durability and system performance will be described. The development trends for turbine environmental barrier coating systems by utilizing improved compositions, state-of-the-art processing methods, and simulated environment testing and durability modeling will be discussed.

4:30 PM

(ICACC-PRECS-008-2014) Control of Mass-transfer through Grain Boundaries in Alumina Protective Layer by Dopant Configurations in TBCs (Invited)

S. Kitaoka*, T. Matsudaira, M. Wada, M. Tanaka, T. Ogawa, Japan Fine Ceramics Center, Japan; Y. Kagawa, The University of Tokyo, Japan

The oxygen permeability of polycrystalline α-alumina wafers, which served as models for alumina scales on alumina-forming alloys in TBC systems, under steep oxygen potential gradients (ΔP_{O2}) was evaluated at high temperature. Oxygen permeation occurred by the grain boundary (GB) diffusion of oxygen from the higher-oxygen-partial-pressure (P_{O2}) surface to the lower-P_{O2} surface, along with the simultaneous GB diffusion of aluminum in the opposite direction. The fluxes of oxygen and aluminum at the outflow side of the wafer were significantly larger than at the inflow side. Furthermore, Lu and Hf segregation at the GBs selectively reduced the mobility of oxygen and aluminum, respectively. A wafer with a bilayer structure, in which a Lu-doped layer was exposed to a lower P_{O2} and an Hf-doped layer was exposed to a higher P_{O2}, effectively enhance the oxygen shielding capability. When the sign of ΔP_{O2} was reversed, however, the oxygen permeability of the wafer was comparable to that of a non-doped wafer. Co-doping with both Lu and Hf markedly increased the oxygen permeation, presumably because the Lu-stabilized HfO_2 particles that were segregated at the GBs acted as extremely fast diffusion paths for oxygen through the large number of oxygen vacancies introduced by the solid solution of Lu in the particles.

4:50 PM

(ICACC-PRECS-009-2014) Overview of Research on C/SiC Ceramic Matrix Composites in Shanghai Institute of Ceramics (Invited)

S. Dong*, J. Hu, Y. Kan, Z. Wang, X. Zhang, Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Shanghai Institute of Ceramics is a comprehensive research organization, whose study cover fundamental research, engineering research and production of inorganic non-metallic materials. As an important research orientation in the Institute, C/SiC composites have attracted much attention due to their excellent properties and wide applications. In recent years, a great progress has been made in C/SiC composites. To gain high performance C/SiC composites and realize their application, we conduct our study through interface and coating design, matrix modification, reinforcement decoration and applied behavior assessment. Based on the improvement of impulse chemical vapor deposition (CVD) technique, PyC, PyC/SiC, multilayer PyC/SiC interphases, and SiC coating with different morphology, multilayer SiC-UHTC coating have been prepared. C/SiC composites with different function have been developed by matrix modification. For example, ultra-high temperature ceramic (UHTC) matrix composites able to withstand temperature over 2000 DC are fabricated by introducing UHTC component into SiC matrix. Furthermore, multi-scale enhancements C/SiC composites with improved thermal conductivity and mechanical properties are obtained by reinforcement decoration, using carbon nanotubes as the second reinforcement.

5:10 PM

(ICACC-PRECS-010-2014) Research and Product Development Activities at Du-Co Ceramics: Current Status and Future Challenges (Invited)

L. Cooper Rothen*, Du-Co Ceramics Co., USA

Research and development activities conducted by a privately owned manufacturer of custom design ceramic component parts include material and process developments to achieve competitive manufacturability which are often customer driven for a wide array of specific applications as well as to generally enhance the material offerings of the Company. Du-Co Ceramic Company's advantages and challenges in the area of business development and growth will also be highlighted.

5:30 PM

(ICACC-PRECS-011-2014) Pseudobrookite-type Porous Ceramics: Synthesis, Pore structure and Applications (Invited)

Y. Suzuki*, University of Tsukuba, Japan

Recently, we have focused on porous ceramics with orthorhombic pseudobrookite-type structure (e.g., MgTi2O5 and Al2TiO5), which have relatively low bulk thermal expansion coefficients among oxides, attributable to microcracks which are formed by the anisotropic crystal structure. A particular pseudobrookite-type oxide, aluminum titanate (Al2TiO5, AT) has been most frequently studied as an excellent thermal shock resistant material. In this presentation, our recent activity on the pseudobrookite-type porous ceramics will be introduced, e.g. AT-based recyclable household-water-purification filters and so on.

3rd Global Young Investigator Forum

GYIF I

Room: Coquina Salon H
Session Chairs: Trilok Singh, Institute of Inorganic and Materials Chemistry; Thomas Fischer, University of Cologne

1:30 PM

(ICACC-GYIF-001-2014) Ln^{3+}-Doped Gd_2O_3 Nanostructures for NIR-NIR Bioimaging (Invited)

E. Hemmer*, INRS-EMT, Canada; T. Yamano, H. Kishimoto, Tokyo University of Science, Japan; F. Vetrone, F. Légaré, INRS-EMT, Canada; K. Soga, Tokyo University of Science, Japan

Bioimaging is an important tool allowing the visualization and understanding of biomedical processes. However, the main disadvantage of common organic dyes is color fading, auto-fluorescence, phototoxicity and scattering when UV light is used as the excitation source. Consequently, the penetration depth is limited. Yet, the use of NIR light reduces phototoxicity and scattering resulting in deeper penetration, and imaging of deeper tissue areas becomes possible. NIR absorbing and emitting compounds are promising candidates to overcome the disadvantages of common dyes. Facing the need of new, reliable NIR-NIR biomarkers, Gd_2O_3:Er^{3+},Yb^{3+} nanorods and particles were synthesized by hydrothermal and precipitation processes. Their suitability as biomarkers for 980-nm excited NIR emission was investigated. *In-vitro* tests revealed a cytotoxic effect in case of incubation of macrophages with bare nanostructures, which was deduced from the poor chemical stability of Gd_2O_3 under the acidic conditions found inside macrophages, but it could be overcome with surface modification with PEG-*b*-PAAc. The *in-vivo* biodistribution in mouse organs was investigated with an over-1000-nm NIR *in-vivo* fluorescence bioimaging system. This system allows the time-resolved observation of the distribution of the nanostructures in the mouse body. The use of Gd_2O_3 doped with Ho^{3+} besides Er^{3+} allows multicolor imaging based on their 1.2 and 1.5-μm emission.

2:00 PM

(ICACC-GYIF-002-2014) Three-dimentional printing of dense and porous materials for bio ceramics

S. Tasaki*, University of Cologne, Germany

Bio ceramics materials and biocompatibility structures have been manufactured for tissue engineering via 3D-printing in recent years. Computer aided design and manufacturing process can efficiently create customization and the small amount of products. For example, human teeth are all different shapes and high mechanical strength. Therefore, it is not possible to mass production. Two different methods are used for the dental implant to reproduce these properties; (1) hand-made manufacturing by dental technicians, which takes several hours, and (2) grinding the ceramic blocks using automatic milling equipment. However, these techniques are not efficient. In contrast, the 3D printing has attracted significant attention. I will present ceramics implant of dense and porous materials fabricate by stereolithography.

2:20 PM

(ICACC-GYIF-003-2014) Modification of TiO_2 nanotubes for various applications

S. Mathur, Y. Gönüllü*, University of Cologne, Germany; B. Saruhan, German Aerospace Centre (DLR), Germany

Relying on its unique properties, titanium dioxide is employed in a versatility of applications, gas sensors, photocatalysis and energy storage materilas being some of them. Low temperature synthesis of undoped and doped TiO_2-coatings and their nano-structuring enhance these properties. In this work, TiO_2 nanotubes (NTs) were synthesized through anodization of titanium substrate. As-prepared TiO_2 NTs were modified by doping method with various dopant elements such as Cr, Al, V, Pt or Li. Undoped and doped TiO_2 NTs were characterized for different applications such as gas sensor, energy storage material and photocatalytic applications. In conclusion, nano structured and modified TiO_2 layers showed better results than bulk TiO_2 layers in different application. The nano-structured TiO_2-gas sensor has faster and more stable response toward CO and NO_2 than the reference TiO_2 sensor. In addition, doping in to nano tubular TiO_2 layers makes the sensor layer more sensitive and selective towards NO_2. Undoped and doped TiO_2 NTs were also investigated for energy storage materials.Scaling down the morphology of TiO_2 layers from bulk to nano provided higher surfaces for lithium intercalation in energy storage applications. In summary, different kind of TiO_2 layers and doped TiO_2 NTs were synthesized with different methods and characterized their properties in each application area.

2:40 PM

(ICACC-GYIF-004-2014) Direct integration of metal oxide nanowires on sensor platforms

T. Fischer*, S. Mathur, University of Cologne, Germany

An optimized CVD technique is presented, allowing the direct deposition of nanowires onto multifunctional gas sensor substrates with embedded heaters and read-out electronics, thus facilitating the integration of nanostructures in devices. The deposition of different thin-films and/or nanowires on sensor arrays enables the facile production of electronic noses, capable of differentiating complex gas mixtures combining different sensor signals simultaneously. Using various promotors for the anistropic growth of nanowires, according the vapor-liquid-solid (VLS) growth model for metal-oxides on the same sensor platform, variably modified SnO_2, Fe_2O_3 or TiO_2 nanostructures can be synthesized in a one step process. This approach opens the way to a deeper understanding of the structure-property relation in metal-oxide nanowires, enabling a targeted synthesis of defined nanostructures for various applications.

GYIF II

Room: Coquina Salon H

Session Chairs: Yakup Gönüllü, Inorganic Chemistry; Satoko Tasaki, University of Cologne

3:20 PM

(ICACC-GYIF-005-2014) ALD of transparent and conducting doped ZnO thin films for TCO and Memristive applications

T. Singh*, S. Wang, A. Sasinska, T. Leuning, S. Mathur, Institute of Inorganic and Materials Chemistry, Germany

Suitable molecular precursors in thermal or plasma-enhanced atomic layer deposition techniques offers a viable solution for overcoming thermodynamic impediments involved in thin film growth. The use of atomic layer deposition enables the realization of various functional coatings whose application spectrum spans from transparent conductive coatings, scratch-proof films to anti-bacterial materials. Over the past decade, we have developed several new precursor systems in order to demonstrate the competitive edge of molecule-based plasma coatings. Our work on a large number of metal oxide systems and their characterization towards microstructure, compositional and functional properties supports the advantages of chemical design in simplifying deposition processes and optimizing functional behaviour. This talk will present ALD processed highly transparent (> 85%) and conducting thin films of ZnO, V2O5, Nb2O5 and transition metal doped ZnO thin films for TCO and memory applications.

3:40 PM

(ICACC-GYIF-006-2014) Luminous complex point-defect structure in cerium-doped cubic boron nitride

R. Ishikawa*, ORNL, USA; N. Shibata, University of Tokyo, Japan; F. Oba, Kyoto University, Japan; T. Taniguchi, NIMS, Japan; S. D. Findlay, Monash University, Australia; I. Tanaka, Kyoto University, Japan; Y. Ikuhara, University of Tokyo, Japan

Cubic boron nitride is a promising system for photonics and opto-electronic applications owing to the large band gap (6.2 eV). Because of the strong covalent bonding nature and their small atomic size, it has been extremely difficult to dope luminous elements such as large-size rare-earth atoms. Recently we have achieved stable rare-earth doping in cBN host lattice using high-pressure (5 GPa) and high temperature (1773 K) flux method, and the millimeter size single crystal exhibits blue-colored luminescence. In this study, we directly determine the atomic site and valence state of Ce dopants using sub-angstrom resolution scanning transmission electron microscope (STEM, JEM ARM-200CF at 200 kV) imaging and spectroscopy. Combining with the systematic first-principles calculations, we uncover the mechanism of how such a huge dopants are accommodated into the strong covalent cBN host lattice. We found the single Ce dopants are randomly distributed but substituted for the anion N anti-site. Moreover, the valence state is determined to be 3+ by single-atom sensitive spectroscopy. Combining with first-principles calculations, we conclude the most preferable defect structure is negatively charged (Ce-4VB)6-, surrounding four B vacancies (VB). Our findings indicate even dopants with large size mismatch can be stably incorporated into host lattice through the formation of complex point-defect structure.

4:00 PM

(ICACC-GYIF-007-2014) Properties of Yttria-Stabilized-Zirconia as Thermal Barrier Coating

C. Gergel*, Ohio State University, USA; L. Ghosn, NASA Glenn Research Center, USA

Thermal barrier coatings have the capability to produce more efficient engines and turbines. Understanding the varying modulus of ZrO2-8wt%-Y2O3 and knowing how CMAS alters the properties of EB-PVD 7YSZ and air plasma sprayed 8YSZ are important in applying modern coatings to their potential without risk of failure.

SiC/SiC ceramic matrix composites are applicable due to their high temperature capabilities but need to be coated with environmental barrier coatings. A Zirconia-multicomponent rare earth silicate top layer, alloyed ytterbium silicate mid layer, and a HfO2-Si bond coat layer is observed to understand how this coating can affect the stress concentration of the system. The elastic moduli of the three thermal barrier coatings are estimated as well as the modulus after CMAS infiltration on the latter two. A model has been designed for the CMC and EBC system which can be used to predict delamination and cracking.

4:20 PM

(ICACC-GYIF-009-2014) Fabrication and Properties of RE4Si2O7N2 (RE=Y, Lu) Ceramics A Systematic Theoretical-Experimental Study

L. Sun*, Institute of Metal Research, China; J. Wang, Institute of Metal Research, China

Ceramic materials with good high-temperature properties and low thermal conductivity remain one of the research focuses for both scientific significance and technological importance. Recently, density functional theory based computational method has developed as a major part of study along with the conventional methods of materials processing and characterization. In this work, equilibrium crystal structure, elastic stiffness parameters and temperature-dependent lattice thermal conductivity of RE4Si2O7N2 (RE=Y, Lu) are investigated by integrated theoretical and experimental methods. Our results indicate that Y4Si2O7N2 and Lu4Si2O7N2 exhibit excellent room temperature mechanical properties, such as high hardness, high bending strength, low shear modulus and moderate Young's modulus. Most significantly, both materials maintain high strength and stiffness up to high temperature. In addition, they exhibit very low thermal conductivity from room to high temperature. The effect of rare earth element on lattice thermal conductivity of RE4Si2O7N2 ceramics is finally discussed.

4:40 PM

(ICACC-GYIF-010-2014) Novel polymer/metal oxide nanocomposites for high-efficiency energy harvesting and transmission

R. Raccis*, L. Wortmann, S. Ilyas, A. Kaouk, S. Mathur, University of Cologne, Germany

In the research we present, nanocomposites were created from conjugated polymer blends and novel metal oxide nanoparticles. The aim was the enhancement of conductivity and water electrolysis efficiency through p-n junction geometry control. Composites of PEDOT-PSS and n-type nanoparticles were drop-cast and electrodeposited to test conductivity enhancement in conjugated polymers via nanoparticle inclusion below the percolation threshold, and studied via cyclic voltammetry. Composites of conjugated polymer blends and nanoparticles were created for enhanced solar-driven water electrolysis and studied via linear voltammetry. Concerning conductivity enhancement, the systems presented up to +540% conductivity in the dark and up to +900% gained conductivity under solar illumination compared to pure PEDOT-PSS, while keeping the nanostructures' weight fraction below 2%. Concerning water electrolysis, the systems showed photocurrent densities up to a factor 20 higher than state-of-the-art hematite layers and onset potentials below 0.2 V. We thus formulated a new and compact model for n-type-based conductivity enhancement of p-type systems, as well as developed novel polymer-based water-splitting systems, which open new avenues of research for cheap energy harvesting and transmission.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Growth

Room: Oceanview
Session Chair: Giovanni Fanchini, University of Western Ontario

1:30 PM

(ICACC-FS2-001-2014) 3D Atom-by-Atom Mapping of Electronic Materials and Nanostructures (Invited)

O. Moutanabbir*, Ecole Polytechnique Montreal, Canada

Harnessing nanoscale and quantum phenomena in semiconductors creates valuable opportunities to achieve novel or superior functionalities with actual or potential impacts on nanoelectronics, optoelectronics, photonics, carbon-free energy conversion, and bio-integrated technologies. A precise probe of the structure and composition of semiconductor nanostructures is of paramount importance to understand the basic properties on the nanoscale of these highly attractive systems. Developing this body of knowledge is a crucial step to implement the emerging nanotechnologies and control their performance. In this presentation, we will describe the use of laser-assisted atom probe tomography to achieve tri-dimensional atom-by-atom mapping of single semiconductor nanostructures. The successful application of this technique enables a precise and rigorous analysis of the composition of a nanostructure and provides unprecedented insights into its internal structure. Examples including metal-catalyzed nanowires, nanomembranes, and superlattices will be presented and discussed. Note: This work is an active collaboration with the group of David N. Seidman at Northwestern University

1:50 PM

(ICACC-FS2-002-2014) 3D Photonic Architectures by Self-Assembly and Directed Solidification of Eutectics (Invited)

P. Braun*, University of Illinois at Urbana-Champaign, USA

Nanoscale integration of phases with metallic and non-metallic character is critical for the realization of optical metamaterials. However, in the near-infrared and visible wavelength regime, the creation of useful metamaterials requires the ability to fabricate three-dimensional (3D) complex structures with high precision using techniques that ultimately enable large-scale manufacturing. A new paradigm for the design and fabrication of metamaterials is therefore needed. Our team is appling unique template-based and post-synthetic materials transformations in conjunction with powerful computational design tools to develop the scientific underpinnings of and to produce 3D metamaterials derived from directionally solidified eutectics. Our approach involves close interactions among computational design, photonic theory, eutectic materials development, template fabrication, materials chemistry, and optical characterization.

2:10 PM

(ICACC-FS2-003-2014) Controlling microstructure of semiconducting polymers through their precision synthesis (Invited)

C. Luscombe*, M. Durban, A. Rice, University of Washington, USA

Semiconducting polymers are actively under development for use in light-weight, flexible, disposable organic light-emitting diodes, and thin-film transistors. A key application which is currently attracting a lot of interest for semiconducting polymers is their use in organic photovoltaic devices (OPVs). The main drive for developing OPVs is the lower cost associated with their manufacturing, because of the fact that organic semiconducting polymers can be solution processed. Poly(3-hexylthiophene) (P3HT) remains one of the most commonly used polymers in organic photovoltaics due to its desirable electronic properties. Our group has been studying and developing techniques to grow semiconducting polymers using a living polymerization method. This has allowed us to synthesize polymer architectures that we haven't been able to access till now including polythiophene brushes, star-shaped P3HT, as well as hyperbranched P3HT. It also allows us to accurately control the molecular weights of P3HT and produce materials with a narrow molecular weight distribution. More recently, we have been used our polymers to obtain nanowires, and have looked at the effect of crystal coherence length on charge mobility. In this talk, I will talk about the synthetic strategies used, and the thin film morphologies these polymer architectures provide.

2:30 PM

(ICACC-FS2-004-2014) Rare Earth doped Yttrium Aluminum Garnet (YAG) Ceramics

C. Yilmaz*, R. Ergun, U. Unal, Koc University, Turkey

Interest in producing YAG as ceramic laser gain medium has been increasing continuously since first demonstration of reactively sintered, polycrystalline, transparent Nd:YAG that could operate with a performance comparable to single-crystal laser. The aim of this study is synthesis and characterization of rare earth doped polycrystalline ceramic YAG materials that can be used as a laser source via modified sol-gel processes. Different precursors of Ce(III), Pr(III), Eu(III) and Tm(III) doped YAG were synthesized via Citrate and Pechini methods. Nitrate salts of Y(III) and Al(III) were used as starting agents for YAG precursor and nitrate salts or oxides of rare earths (RE) for dopant element. Citric acid as chelating agent and ethylene glycol for faster polymerization were introduced into the medium. The formation process and structure of the phosphor powders were investigated by TG-DTA, XRD, SEM, XRF and XPS. Both methods yielded phase-pure YAG crystallites upon calcination at temperatures between 850-1200°C. However, YAG nanocrystals were obtained at lower calcination temperatures and with lower crystallite sizes by using Pechini system. Production of transparent ceramics from these powders via slip casting followed by vacuum sintering is under process. Transparent, polycrystalline RE:YAG materials will be tested for lasing activity.

3:20 PM

(ICACC-FS2-005-2014) Analysis on Functionally Graded AAO with a variation of Microstructure in Metal Matrix

H. Shin*, H. Lee, Korea institute of Industrial Technology(KITECH), Republic of Korea; S. Jung, Sungkyunkwan University, Republic of Korea

The anodic aluminum oxide(AAO) is the regular nano-porous structure of being grown from metal matrix through the anodic process in acid solution. The AAO has been generally applied in the nano template for the nano devices such as electronic components, sensor parts and so on. It has been recently focused on that the consumer needs various designs and ingenious functions in electronic component and sensor part, which can be obtained by forming the nano devices having functionally graded property. The AAO sheet with a gradient distribution of tens to hundreds nano pores is indispensible for manufacturing the nano device with functionally graded properties. In this study, the microstructure of the metal matrix was controlled through optimized heat-treatment processes, and the AAO was grown on the metal matrix. The relationship between the microstructure of metal matrix and the morphology of AAO was analyzed.

3:40 PM

(ICACC-FS2-006-2014) Effect of Substrate Temperature on Structural, Optical and Electrical properties of Ba0.95Sr0.05(Fe0.5Nb0.5)O3 thin film grown by Pulse Laser Deposition

P. K. Patel*, K. L. Yadav, Indian Institute of Technology Roorkee, India

The thin film of Ba0.95Sr0.05(Fe0.5Nb0.5)O3 (BSFN) ceramics on ITO coated glass substrate were prepared by Pulse Laser Deposition Technique (PLD). The thin films were deposited with a fixed energy density of 1.5 J/cm2 in oxygen pressure of 10 Pa at 500 °C, 550 °C and 600 °C substrate temperature. Deposited films were annealed at 500 °C for 1 hr in vacuum. Structural, electrical and optical properties were studied having different substrate temperature. Thin films were analyzed using low angle X-ray diffraction. All thin films have a single phase perovskite structure. AFM analysis showed the well developed uniform and nanosize grains of BSFN thin films in all the samples. Average grain size and surface roughness of the thin films were estimated by AFM analysis. The optical band gap, refractive index and extinction coefficient of thin films are studied which were synthesized at various temperature. The optical band gap was estimated using the reflectance and transmission data. The optical band gap was found to be 2.56 eV, 2.61 eV and 2.68 eV for 500 °C, 550 °C and 600 °C heated substrate temperature respectively. A comparative study of dielectric properties and I-V characteristics of thin films and BSFN bulk ceramics will be reported at the time of presentation.

Multiferroics

Room: Oceanview
Session Chair: Oussama Moutanabbir, Ecole Polytechnque de Montreal

4:00 PM

(ICACC-FS2-007-2014) Semiconducting ferroelectrics for photovoltaics (Invited)

R. Nechache*, INRS-EMT, Canada

Substantial and controllable bandgap tuning in functional perovskite oxides is becoming gradually important for design and development of highly efficient optoelectronic devices. In particular lowering the bandgap of ferroelectric without altering the physical properties is a promising way to achieve highly efficient photovoltaic solar cells. In addition to their in-built potential originating from their spontaneous polarization, which can be used to efficiently separate the photogenerated electron-hole pairs, low bandgap enables the increase of energy harvesting from the Sun's broad spectrum and the reduce of the charge carriers recombination. Based on research reports, recent unsuccessful attempts demonstrate difficulties to fabricate such materials which still remain a great challenge. Here we will present, the controlled growth and characterization of multiferroic (MF) Bi2FeCrO6 (BFCO) thin films and heterostructures via pulsed laser deposition. Our investigation demonstrated that BFCO bandgap can be lowered and tuned, down to 1.4 eV, by tailoring the Fe/Cr cation ordering and the ordered domain size in thin films. We demonstrate highly efficient single and multilayer MF solar cells, up to 8.1%, featuring a low bandgap BFCO layer which largely exceed the previously reported PZT-based PV device performance.

4:20 PM

(ICACC-FS2-008-2014) Enhanced surface-quality, magnetic and ferroelectric properties in epitaxial PZT/LSMO multiferroic heterostructures grown using dual-laser ablation

D. Mukherjee*, M. Hordagoda, H. Srikanth, S. Witanachchi, P. Mukherjee, University of South Florida, USA

Multiferroic heterostructures of ferroelectric $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) and ferromagnetic $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) are highly desired multifunctional materials for magnetoelectronic devices. Laser ablation of PZT/LSMO thin films is complicated by the non-congruent ablation of PZT and the Mn_3O_4 impurity phase precipitation during LSMO film growth. Here, we report on the epitaxial growth of PZT/LSMO thin films on $SrTiO_3$ and MgO (100) substrates using the dual-laser ablation (DLA) technique that combines the outputs of a KrF excimer and a CO_2 lasers. Emission spectroscopy of the DLA plumes showed higher excitation of the ablated species leading to better film morphology and crystallinity. ICCD plume-imaging revealed a broader angular distribution leading to particulate-free uniform films over large areas. XRD analysis demonstrated the single crystalline nature of the PZT/LSMO films. AFM scans revealed smoother surfaces with roughness values as low as 1 nm. Cross-sectional HRTEM images showed atomically sharp interfaces with no structural defects. Magnetic measurements showed higher saturation magnetization of 250-280 emu/cm^3 and in-plane magnetic anisotropy in the PZT/LSMO films. DLA deposited films showed enhanced remnant polarization of 70-90 μC/cm^2 as compared to 30-45 μC/cm^2 for single laser deposited films under the same conditions.

4:40 PM

(ICACC-FS2-009-2014) Controlled seed-layer assisted growth of hierarchically-ordered Pb(Zr0.52Ti0.48)O3 nanostructure arrays with improved ferroelectric properties

A. Datta*, D. Mukherjee, S. Witanachchi, P. Mukherjee, University of South Florida, USA

Tetragonal Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) exhibits the highest piezo and ferro-coefficients and is of great technological interest for piezoelectric transducers, pyroelectric sensors, high-dielectric capacitors and non-volatile memory devices. Recent research on PZT nanostructures have shown huge enhancement of properties useful for sustainable micro/nano-powering sources. In order to have exciting opportunities of fundamental research and innovative applications of PZT nanostructures, development of a facile, low-cost method is necessary for fabricating high quality nanostructures that may expand the outreach of probes for understanding the structure-property relations in PZT nanostructures. In the present work, we report on the optimized growth of hierarchically-ordered PZT nanostructure arrays by a seed-layer assisted method using an integrated pulsed laser deposition and hydrothermal process on STO:Nb substrates. These nanostructures show oriented-attachment and create a dense, non-porous thin-film. The improved nanostructuring density enables us to measure FE properties from the PZT nano-capacitor without using polymer fill layer. As an outstanding improvement, well saturated FE hysteresis loop with high degree of squareness and P$_r$ value (54 μC/cm^2 at coercive field (E$_c$) of 237 kV/cm) is realized at an applied driving voltage of 9 V.

5:00 PM

(ICACC-FS2-012-2014) Vanadium dioxide: a “smart” material for “smart” technological opportunities (Invited)

A. Hendouai*, M. Chaker, INRS-EMT, Canada

Vanadium dioxide (VO2) is a “smart” material that undergoes a reversible insulator-to-metal transition (IMT), characterized by a dramatic increase of both its conductivity and reflectivity in infrared and terahertz (THz) ranges of wavelengths when the temperature is increased above 68°C. In a series of studies, our group has demonstrated new application opportunities based on the IMT in VO2 thin films. For example, by incorporating VO2 films in an appropriate multilayer structure, we recently developed VO2-based smart coatings that are able to respond to the temperature by adapting its thermal emittance to radiate more heat at high temperature and less at low temperature. This behavior is quite interesting for application as smart radiator device (SRD) for the passive thermal control of spacecrafts. By choosing adequately the thickness of a SiO2 layer in a multilayer structure containing a VO2 film, we have been able to achieve an unprecedented temperature-dependent emittance variation in the 3 – 5 μm range of wavelengths, known as Mid-Wave Infrared (MWIR) range. This modulation offers the possibility to change dramatically the so-called IR signature of the coating. We also demonstrated that doping VO2 with a mixture of tungsten and titanium remarkably influences both optical and resistivity characteristics of the IMT in VO2 films toward applications in uncooled infrared and THz bolometers.

FS3: Rare Earth Oxides for Energy, Optics and Biomedical Applications

Rare Earth Oxides for Energy, Optics and Biomedical Applications

Room: Coquina Salon D
Session Chair: Sudipta Seal, UCF

1:30 PM

(ICACC-FS3-001-2014) Sol-gel derived active materials for diode-pumped Yb disk lasers

T. Ribeiro, L. Santos, M. Goncalves, R. M. Almeida*, Instituto Superior Tecnico, Portugal

Many industrial and scientific applications require high-power diode-pumped solid state lasers with good beam quality. The key challenge in designing a successful solid-state laser is how to best manage the generation of waste heat in the pumping process and the removal of that heat. The thin disk laser concept offers high optical efficiency, good output beam quality and good thermal management. Due to the small thickness of the disk, the absorption efficiency has to be increased by re-imaging the unabsorbed pump power onto the disk several times in a multi-pass scheme. For the fabrication of the active material, an alternative to Yb:YAG single crystal is being pursued using Sol-Gel (SG) processing. The SG method is a wet chemical technique to produce glassy and ceramic materials in both monolithic and film form at relatively low temperature, with the advantage of rather low cost. Yb-doped thick films have been prepared in glassy phospho-alumino-silicate (SiO2-Al2O3-P2O5) and crystalline YAG (3Y2O3.5Al2O3) matrices by both dip- and spin-coating and their photoluminescence (PL) has been measured as a function of the Yb concentration. Results of structural (XRD, FTIR and Raman spectroscopies) and optical characterization (SE and PL as a function of the Yb concentration) are presented and discussed. These results appear promising for the possible use of these SG derived materials in Yb disk lasers.

1:50 PM

(ICACC-FS3-002-2014) Solid-state Single Crystal Conversion for Sr5F(PO4)3 Ceramics

Y. Li*, Y. Wu, Alfred University, USA

Solid-state single crystal conversion (SSCC) has been applied to convert polycrystals to pore-free single crystals with no grain boundaries in order to obtain better performance for materials. In this study, as a recognized promising candidate of transparent ceramics for lasers applications, Sr5F(PO4)3 (S-FAP) polycrystalline ceramics have been fabricated, and more importantly, firstly shown the possibility for the conversion to single crystals by adopting the SSCC method. The polycrystals and single crystals (seed crystals) were heat treated at 1400 oCfor 24h in an air environment. The single crystals and polycrystals were measured with X-ray diffraction (XRD) and scanning electron microscopy (SEM). The movement of the boundary between single crystals and polycrystals were recorded through SEM. It reveals that the SSCC for the S-FAP can be achieved at a certain temperature for a certain time from the boundary mobility.

2:10 PM

(ICACC-FS3-003-2014) Why Lasers Need Ceramic Materials (Invited)

M. Bass*, University of Central Florida, USA

This paper presents the optical properties of solid state laser materials as they have been for the last 50 years, what the laser designer would prefer them to be to achieve better performance, and suggestions concerning how ceramic laser media can deliver on the desired properties. Conventional laser media are limited in size and are restricted to a single selection of doping concentration(s). A single doping concentration leads to non-uniform absorption of pump power, non-uniform heating and, often, severe stress. It also means very bad laser beam quality. A model for non-uniform doping density will be shown leading to uniform pump absorption and consequent improved laser performance. Experimental confirmation has been demonstrated and now it is time for non-uniformly doped ceramic laser media prepared according to this model. Laser media with un-doped regions are also important and will be described as opportunities for ceramic laser media. In addition, ceramic laser media make possible very large gain media for very high power systems and greatly lowered cost small laser media are possible when they are cut out of large ceramic pieces. In summary, this paper lays out the reasons why rare earth doped ceramic materials will play a major role in the future of solid state lasers.

2:40 PM

(ICACC-FS3-004-2014) Neuroprotective Effects of Nanoceria Formulations in a Murine Model of Multiple Sclerosis (Invited)

J. Erlichman*, K. Heckman, W. DeCoteau, M. Skeels, St. Lawrence University, USA

Evaluating the biological effects of nanoceria has been difficult due to significant differences in methods of synthesis, particle size, surface charge, stabilizing agents and the biological test beds used. We examined the effects of differing nanoceria in a murine model of multiple sclerosis (MS) by comparing the neuroprotective potential of several nanoceria formulations: Ce- citrate stabilized (Sigma-Aldrich), Ce-acetate stabilized (Alfa-Aesar), and custom-synthesized citrate-EDTA stabilized (CeNPs). The citrate-EDTA stabilized CeNPs reduced clinical symptoms and motor impairment in EAE animals, whereas the citrate/acetate nanoparticles provided no neuroprotection or worsened symptoms. Nanoceria brain deposition did not necessarily correlate with biological efficacy, suggesting that peripheral factors may influence their biological activity. For example, though Alfa-Aesar particles were present in the brain, they failed to improve EAE severity, whereas the CeNPs were detected at a three times higher level and did alleviate disease symptoms. Thus, the surface stabilizer appears to markedly impact the in vivo biodistribution patterns and biological efficacy of nanoceria, perhaps by influencing protein adsorption and initiation of additional biological cascades.

3:30 PM

(ICACC-FS3-005-2014) Multi-Modal Molecular Imaging to Study Radio-Protection by Cerium Oxide Nanoparticles (Invited)

P. R. McDonagh*, L. Yang, P. Jose, S. Gobalakrishnan, M. Sun, R. Mikkelsen, J. Zweit, Virginia Commonwealth University, USA

The efficacy of radiation therapy (RT) is tempered by the risk of induced side effects in normal tissues. Co-treatment with cerium oxide nanoparticles (CONPs) during RT may reduce this risk by preferentially protecting normal tissue over tumor tissue. The mechanisms of radio-protection are not well characterized, but may be related to differences in tissue microenvironment. One characteristic of the tumor microenvironment (TME) is lower than normal pH, which we have shown to slow CONPs' redox reactions. We have also demonstrated that lower than normal pH decreases CONPs' uptake in cancer cell culture. To study the effects of the TME on CONPs uptake and pharmacokinetics *in vivo*, a multi-functional nanoparticle platform was developed through intrinsic radiolabeling and extrinsic surface functionalization using various radionuclides (^{141}Ce, ^{111}In, ^{65}Zn, ^{89}Zr) and biocompatible polymer coatings. This labeling strategy enables in vivo SPECT or PET imaging. Based on the polymer coatings, blood circulation and renal/hepatic clearance of radiolabeled CONPs (rCONPs) can be manipulated. *Ex vivo* biodistribution results matched SPECT imaging of ^{141}Ce-rCONP, showing accumulation in the liver and spleen in a mouse over a one week period. These studies will open the door for future *in vivo* biomedical imaging examining CONPs' microenvironment dependent properties and helping their translation to the clinic.

4:00 PM

(ICACC-FS3-006-2014) Engineered optical ceramics for laser applications (Invited)

R. Gaume*, University of Central Florida, USA

The past decade has seen significant advancements in the fabrication and characterization of laser ceramics with, in particular, the ability to produce engineered gain media with unique spatial refractive index profiles and dopant profiles to enhance laser efficiency and brightness. The aim of the present paper is to review those advances and discuss some of the current challenges.

4:30 PM

(ICACC-FS3-007-2014) Effect of Cerium Nanomaterials on the Mechanical Property of Cell membrane

A. Ly*, S. Das, S. Barkam, S. Seal, University of Central Florida, USA

Cerium dioxide nanoparticles CNPs were reported in many studies to have therapeutic potential, specifically abnormalities associated with oxidative stress. However, to further research and development of the biomedical applications based on this material, one needs to understand the effect of CNPs on living organism. In this study, CNPs (size 3-5nm) and cell were selected. We analyzed mechanical property and the adhesion energy of cells' membranes with and without CNPs by using Atomic Force Microscopy (AFM). In particular, the Force-Distance spectroscopy mode was used to estimate elasticity of cells membrane. Different concentrations (0.1, 50, 125, and 250μM) of CNP were added to the cells and incubated for different time period (0, 15, 30 and 60 minutes). In those cells with 250μM of CNPs added, we noticed that there was a significant change in cell elasticity observed. The changing also increased significantly with the increasing of incubation time and at 1hr incubated the changing in cell elasticity is maximum. However, there was no significant change in cell elasticity was observed over 1hr time period for 0.1μM and 50μM of CNPs. This result indicates that nanoceria interaction/internalization to cell can change the cell membrane elasticity at high concentration but makes no effect to the mechanical property of cell at low concentration.

4:50 PM

(ICACC-FS3-008-2014) Role of dilute La-doping in enhancing the polarization in epitaxial $Pb_{1-x}La_xZr_{0.52}Ti_{0.48}O_3$ thin films

M. Hordagoda*, D. Mukherjee, University of South Florida, USA; D. Ghosh, J. L. Jones, University of Florida, USA; S. Witanachchi, P. Mukherjee, University of South Florida, USA

$PbZr_{0.52}Ti_{0.48}O_3$ (PZT) has remained the ferroelectric material of choice for its wide range of applications from non-volatile memories to sensors and actuators. La doping in bulk-PZT has shown to improve its properties, however, reports on La-doped PZT (PLZT) thin films show disparate results. Here, epitaxial PLZT thin films with atomic (at.) % of La varying as 0.1 %, 0.5 % and 1 % were deposited on $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/$SrTiO_3$ (100) substrates using pulsed laser deposition. XRD analysis confirmed the epitaxial relationship in the deposited films. AFM scans revealed their smooth surface morphologies with roughness of 10 nm. Cross-sectional HRTEM images showed atomically sharp interfaces with no structural defects. LSMO/PLZT/LSMO thin film capacitors showed enhanced remnant polarization (P_r) for all driving voltages from 1 V to 9 V as compared to those fabricated using undoped PZT films. The 0.1 at. % PLZT showed a 122 % enhancement in polarization with the highest P_r of 91 μC/cm^2 at 9 V as compared to the undoped PZT; with progressively decreasing P_r at higher doping levels. XRD strain analysis revealed in-plane compressive strains in the PLZT films leading to increased tetragonality of the PZT unit cell. The donor induced defect-dipole contribution coupled with a strain-compression relaxation mechanism was proposed to explain the enhanced properties in the PLZT thin films.

S4: Armor Ceramics

Special Topic Focus: Adhesive Bonding

Room: Coquina Salon E
Session Chair: Lionel Vargas-Gonzalez, U.S. Army Research Lab

1:30 PM

(ICACC-S4-001-2014) Surface treatment of alumina and silicon carbide for improved adhesive bond strength in armour (Invited)

A. Harris*, J. Yeomans, P. Smith, University of Surrey, United Kingdom; B. Vaughan, S. Burnage, Lockheed Martin UK, United Kingdom

Surface treatments of alumina and silicon carbide have been investigated to determine if a range of preparations can improve ballistic performance when using a toughened epoxy adhesive. Differing surface conditions for each ceramic have been characterised; as-fired and laser treated samples as well as grit blasted alumina and refired silicon carbide. Physical and chemical changes to the surface were investigated using scanning electron microscopy, profilometry, energy dispersive x-ray spectroscopy, x-ray photoelectron spectroscopy and sessile drop technique. It was found that laser treating alumina and silicon carbide altered the surface morphology and also affected the chemistry with the presence of a greater concentration of hydroxyl groups. These chemical changes were tentatively linked to the improved wettability and the increased polar component of the surface energy. Quasi-static testing was undertaken to measure the tensile and shear strength of these surface preparations using butt and double lap joint tests respectively. Laser treated surfaces demonstrated improvements in bond strength. The results from the ballistic tests were consistent with the predictions made on the basis of the results from the quasi-static testing. The damage arising from the laser treated tile arrays resulted in fewer disbonds and thus by inference improved multiple hit ballistic performance.

2:00 PM

(ICACC-S4-002-2014) Surface Modification of Ballistic Ceramic and Composite Materials by Use of Atmospheric Pressure Plasma

L. Vargas-Gonzalez*, V. Rodriguez-Santiago, A. Bujanda, U.S. Army Research Lab, USA

This work aims to explore the potential benefit for atmospheric pressure plasma as a treatment method for improving the adhesion between layers in ceramic/polymer structures. Silicon carbide ceramics and ultra-high molecular weight polyethylene surfaces were characterized after exposure to He–O2 dielectric barrier discharge. An increase in surface oxygen content, as SiOx compounds on the ceramic and oxygen-containing polar groups (carboxyl, carbonyl, and hydroxyl) on the UHMWPE composite, increased the hydrophilicity of the two constituent materials. Surface wetting and affinity to bonding with urethane-based adhesives increased significantly. While the surface roughness of SiC remained relatively unchanged, the preferential etching of the polyurethane-based composite matrix over the UHMWPE fiber by the plasma also contributed to the improvement in adhesion of the composite. Ballistic penetration and deformation of the treated SiC/UHMWPE will be explored to elucidate whether the modified surfaces enhance the high-rate mechanisms of the ceramic/composite system.

2:20 PM

(ICACC-S4-003-2014) The Application of Materials Analytics to Explore Adhesive Performance

M. S. Bratcher*, U.S. Army Research Laboratory, USA; M. C. Golt, Bowhead Science and Technology, LLC, USA; R. Jensen, W. Kosik, U.S. Army Research Laboratory, USA

Composite armor systems are multimaterial systems usually comprised of ceramics, composites and metals that are assembled and bonded together with adhesives. Given the widely varying properties of these components and the objective of meeting both structural and ballistic performance requirements, the criteria for adhesive selection plays a key role for development of new armor systems. To that end, the Army Research Laboratory has adopted a Materials Selection Analysis Tool (MSAT) to enable thorough data collection and analysis in adhesive development programs. MSAT is used to store, organize and mine cradle-to-grave data and descriptions to improve the adhesive selection process. Specifically, MSAT data mining helps identify alternative adhesives when new program requirements, such as performance, cost reduction or environmental compliance, are imposed. The adhesives data captured in MSAT is complex but by applying informatics tools, correlations between adhesive properties and performance can be recognized and models to predict performance can be augmented. In this paper we will report on a recent campaign of over 1000 lap-shear tests using two adhesives under a variety of test conditions as a demonstration of the utility of the MSAT database and analysis tools.

Glass and Transparent Ceramics

Room: Coquina Salon E
Session Chair: Jeffrey Swab, Army Research Laboratory

2:40 PM

(ICACC-S4-004-2014) Hardness and Crack Resistance of Oxide Network Glasses

M. M. Smedskjaer*, Aalborg University, Denmark

Predicting the properties of new glasses prior to manufacturing is a topic attracting great industrial and scientific interest, but the lack of long-range order and the long time scales for relaxation greatly complicate the traditional modeling efforts. Mechanical properties are currently of particular interest given the increasing demand for stronger, thinner, and more flexible glasses in recent years. Here we review our recent findings on predicting and understanding the indentation derived mechanical properties of oxide network glasses of industrial interest. For example, we have enabled quantitative calculations of glass hardness using temperature dependent constraint theory. We have also revealed the effects of different composition variables, thermal history, pressure history, and humidity on hardness and crack resistance of borosilicate and aluminosilicate glasses.

3:20 PM

(ICACC-S4-005-2014) Comparison of Starphire and BOROFLOAT Characteristics

A. Wereszczak*, Oak Ridge National Laboratory, USA

Starphire soda-lime silicate glass and BOROFLOAT borosilicate glass are used in transparent armor systems. To help support the interpretation of how these two glasses ballistically respond, a suite of test and material characterizations were completed so to describe and contrast their differences. Compositional, physical properties, elastic properties, flaw size distributions and concentrations, tensile/flexure strength, fracture toughness, spherical indentation and hardness, transmission electron microscopy, striae, high pressure responses via diamond anvil cell testing, and laser shock differences are described and interpreted. Comparisons of those two glasses are made with a reference fused or vitreous silica glass. Possible ramifications of these results in context to potential ballistic response are presented. Research sponsored by WFO sponsor Purdue University under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

3:40 PM

(ICACC-S4-006-2014) Investigation of failure mechanisms in glass under dynamic loading using high speed x-ray phase contrast imaging

N. Parab, M. C. Hudspeth, B. Claus, J. T. Black, Purdue University, USA; S. Luo, Sichuan University, China; K. Fezzaa, X. Xiao, Argonne National Laboratory, USA; W. W. Chen*, Purdue University, USA

Glass is a critical material for transparent armor applications because of high hardness, low weight, low cost and high transparency. However, failure mechanisms due to ballistic impact and penetration are still not well understood in different types of glasses. In this study, failure/damage mechanisms under dynamic loading in different types of glasses are investigated using high speed x-ray phase contrast imaging (PCI). High speed x-ray PCI offers an ideal technique to study the evolution of subsurface damage under dynamic loading. First, a modified Kolsky bar was synchronized with high speed x-ray phase contrast imaging at Advanced Photon Source in Argonne National Lab. Borosilicate and soda-lime glasses were investigated under a dynamic indentation loading using a knife edge indenter driven at a velocity of 8-10 m/s. It was observed that an angular crack develops in front of the indenter in borosilicate glass similar to Hertzian cone cracks commonly observed in penetration experiments in brittle materials. Straight line cracking was observed to initiate from the indenter in soda-lime glass. In post mortem analysis, soda-lime glass was observed to erode the indenter more than the borosilicate glass. It can be concluded that there are significant differences in the damage mechanisms in different types of glasses.

4:00 PM

(ICACC-S4-007-2014) Nucleation and Growth of Internal Cracks in Glass

D. Shockey*, T. Kobayashi, T. J. Holmquist, SRI International, USA; A. A. Wereszczak, Oak Ridge National Laboratory, USA

In most applications surface flaws control the strength and failure behavior of glass. Under shock wave loading, however, cracks can nucleate internally, providing an opportunity to pinpoint the inherent crack-initiating inhomogeneities and measure intrinsic strength. Controlled laser shock experiments on borosilicate and soda lime glass are described, damage observations are presented, and details of crack nucleation and growth are discussed. Damage on cross sections of specimens shocked at different magnitudes and durations is correlated with the stress-time environment, obtained from finite element simulations, in attempting to establish spall failure criteria.

4:20 PM

(ICACC-S4-008-2014) Detecting and Mapping Flaw Size Distributions on Glass Surfaces

A. Wereszczak*, M. Ferber, Oak Ridge National Laboratory, USA

Tensile or flexure strength of glass, and the critical stress associated with crack initiation on its surface, are dependent on flaw sizes and their locations. The introduction, sizes, concentrations, and distribution of those flaws at any moment of time are a cumulative consequence of the glass's manufacturing, packaging, and handling histories. The mechanical response is therefore always different, even for the same glass, because the likelihood is low that those histories are always repeated. A "High Resolution Defect Classification System" is under development that rapidly identifies and maps surface-located flaws on glass surfaces that are potentially strength-limiting. Surface discontinuities as small as 8 μm are detectable and many square centimeters per second can be scanned. The instrument and technique are described, and preliminary results of examinations of Starphire and BOROFLOAT glass surfaces, and their association with strength-limitation and crack initiation, are presented. Research sponsored by WFO sponsor US Army Tank-Automotive Research, Development and Engineering Center under contract DE-AC05-00OR22725 with UT-Battelle, LLC. As the authors are not Government employees, this document was only reviewed for export controls, and improper Army association or emblem usage considerations. All other legal considerations are the responsibility of the authors and their employer.

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(ICACC-S4-009-2014) Transparent Ceramics for Demanding Optical Applications

M. R. Pascucci*, M. V. Parish, N. D. Corbin, B. Boucher-Puputti, CeraNova Corporation, USA

Transparent ceramics are finding increasing use in demanding optical applications where glasses and halides/sulfides/selenides are limited, and single crystals are not practical. Polycrystalline ceramics offer a unique combination of mechanical, optical, and electrical properties that enable window and dome applications that previously were not possible. Transparent ceramics are being developed for use in a number of applications with each material possessing a distinctive set of properties that address a particular application. The current status of CeraNova's fine grain transparent ceramics for dome and window applications will be presented with emphasis on their exceptional properties for specific applications.

5:00 PM

(ICACC-S4-010-2014) Highly Transparent Alumina Ceramics Prepared by Combined SPS/HIP process

M. Trunec*, J. Kastyl, Brno University of Technology, Czech Republic; Z. J. Shen, Stockholm University, Sweden

Polycrystalline fine-grained alumina is one of the most suitable transparent ceramics for ballistic and high-temperature applications because of its excellent mechanical and thermal properties. Unfortunately, its transparency in the visible wavelength region is limited due to the birefringent crystal structure of alumina. The present work is aimed at grain size refinement of fully dense alumina ceramics towards the nanometer range in order to increase the transparency of birefringent alumina in the visible and near-infrared wavelength regions and also improve mechanical properties. Pressureless presintering followed by Hot Isostatic Pressing (HIP) and Spark Plasma Sintering (SPS) are the two most common densification processes for transparent polycrystalline alumina. An alternative sintering process combining the advantages of both methods was proposed and successfully applied. Green bodies consolidated by the gelcasting of alumina suspensions doped by zirconia and spinel nanoparticles were densified by a combined SPS/HIP process and compared with bodies sintered by either SPS or HIP methods. The combined SPS/HIP process proved its effectiveness and provided transparent alumina bodies with an average grain size of 270 nm and a real in-line transparency of over 70% (at 640 nm wavelength and 0.8 mm sample thickness). The principles and benefits of the combined method are explained and discussed.

5:20 PM

(ICACC-S4-011-2014) Optimization of the spark plasma sintering condition for transparent spinel

M. Vu*, R. Haber, Rutgers University, USA

Polycrystalline transparent spinel is a promising candidate for light weight transparent armor and infrared window applications. The spark plasma sintering (SPS) technique has been used to produce a fine-grain microstructure which potentially yields a high hardness value for spinel. By controlling the SPS heating rate at ≤ 2.5oC/min up to 1350oC with a 10 minute hold, an in-line transmittance ≥ 50% in the visible region can be attained for a 3mm-thick spinel sample. The current work demonstrates that, beside the nature of the starting powder, the heating rate during spark plasma sintering is the decisive factor in attaining a high transparency for polycrystalline spinel. Experimental data also show that a longer dwell time does not contribute to increasing the transmittance of the samples.

S6: Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage

Li-ion Battery Technology - Advanced Electrodes I

Room: Ponce De Leon
Session Chairs: Bradley Fahlman, Central Michigan University; Valerie Pralong, CNRS CRISMAT

1:30 PM

(ICACC-S6-001-2014) Strategies for the synthesis of new materials for Li ion batteries (Invited)

V. Pralong*, CNRS CRISMAT, France

Regarding the field of energy storage, the design of new materials that provide high energy densities and long cycle life together with being economic and environmental benign is crucial. Our research is focused on the synthesis by soft chemistry of new "metastable" frameworks with large tunnels or layered structures at low temperature, which is in perfect appropriateness with such a target. We will discuss on our strategies to generate original framework. The first approach is based on topotactic reactions starting from existing phases with a compact anionic framework. In this case, we will show that the lithium insertion leads to rock salt type structure. The second approach is related to polyanionic frameworks. In order to favor reactivity, we are using protonic materials, either as precursors or as matrix for intercalation, containing transition elements with adequate redox potential (Fe, Mn, V, Ti). Then, structure-properties relationships are studied and the possibility to use these materials as electrode materials for power generation systems is evaluated. We will discuss our recent results on iron, manganese and vanadium based materials (LixFeOHSO4, Li2Mn(SO4)2, Li2VO3, Li5W2O7).

2:00 PM

(ICACC-S6-002-2014) High performance Li7MnN4 as negative electrode material for lithium-ion batteries

J. Pereira-Ramos*, CNRS, France; E. Panabiere, CNRS, France; N. Emery, CNRS, France; S. Bach, CNRS, France; P. Willmann, CNRS, France

More competitive anode materials must be found allowing the benefits of a better rate capability and enhanced safety for advanced lithium and Li-ion batteries.. Our group is engaged in the investigation of the metallic nitrides which offer various structures with redox systems working at low potentials. In addition to layered structures, we demonstrate there is an interest in using 3D compounds. We show here that Li7MnN4 exhibiting an antifluorite structure, is a good candidate anode material with a rechargeable specific capacity of 240 mAh g-1 at about 1.2 V. With the aim of optimizing the rate performance of Li7MnN4 we demonstrate the promoting effect of an appropriate ball-milling process: an excellent capacity retention is obtained during cycling at 1C. Even at 5C the promoting effect of ball-milling results in a remarkable high and stable capacity vs. cycles of 120 mAh g-1, which compares very well with the behavior achieved for Li4Ti5O12 while the pristine material is practically inactive. In order to completely understand its electrochemical properties we highlight its structural response upon the first Li extraction-insertion cycle using in operando XRD experiments. A 3-phases mechanism is detailed for Li7-xMnN4 which explains its electrochemical fingerprint and the excellent cycle life of this promising negative electrode for Li-ion batteries.

2:20 PM

(ICACC-S6-003-2014) Hydrothermal Synthesis and Characterization of LiMnPO4 Cathode Material for Li-ion Battery

E. Camci*, K. Aydinol, Middle East Technical University, Turkey

Olivine structured LiMnPO4 was synthesized by hydrothermal method and the effect of the synthesis parameters were examined during studies. LiMnPO4 suffer from low electrical and ionic conductivity due to low lithium diffusion kinetics. There are different approaches to overcome these conductivity problems of LiMnPO4; minimizing the particle size, coating the particles with carbon and metal ion doping. All possible solutions including additional processes such as coating and ball milling were investigated to achieve better electrochemical characteristics of LiMnPO4. Lithium hydroxide, manganese (II) acetate and ammonium phosphate are precursors. Since an alkaline medium is required for the precipitation of LiMnPO4, ammonia solution was used to adjust pH. After hydrothermal reaction at 200°C, pure and crystalline LiMnPO4 were produced. In order to test the samples, LiMnPO4 powder was pressed into pellets and AC impedance and CV measurements were carried out. Also, the sample cells were charged and discharged on the multi channel battery tester. The cut-off voltage range in charge-discharge tests was 2.6-4.5 V vs. Li+/Li. The capacity of the carbon coated LiMnPO4 was 70 mAh/g. In conclusion, LiMnPO4 powders were synthesized by hydrothermal method followed by calcination and ball milling. The electrochemical test results also show the increase in the performance after additional processes.

2:40 PM

(ICACC-S6-004-2014) Capacity Enhancement of doped Li4Ti5O12 Anode for Li Battery Application

K. Fung*, S. Tsai, C. Ni, M. Chen, National Cheng Kung University, Taiwan; A. Orliukas, Vilnius University, Lithuania; G. Bajars, University of Latvia, Latvia

Lithium titanium oxide spinel Li4Ti5O12 has been reported to be a zero-strain lithium insertion host material because it exhibits extremely small variations of the lattice parameters during the charge and discharge processes. However, lithium titanium oxide spinel or lithium titanate exhibits rather low electrical conductivity. To improve the capacity and rate capability, coating the lithium titante particles with a conductive additive has been used. Since titanium ions show multi-valent states, the conductivity of lithium titanate may highly depend upon the addition of aliovalent dopant or surrounding atmosphere. In this study, the synthesis of lithium titanium spinel with or or without dopants will be conducted under different atmosphere. XRD will be used to investigate the high-temperature reaction between lithium oxide and titania under different atmosphere. Furthermore, sintered lithium titanium oxide spinel will be heat-treated under different atmosphere. The resistance of sintered lithium titanium oxide will be monitored as a function of annealing time. It is expected that the resistivity of lithium titanium oxide will be significantly reduced when exposed at low oxygen partial pressure and/or added with proper alio-valent dopants. As a result, the capacity of $Li_4Ti_5O_{12}$ is enhanced by the addition of dopant, especially with high-rate charge/discharge.

Li-ion Battery Technology - Advanced Electrodes II

Room: Ponce De Leon
Session Chairs: Bradley Fahlman, Central Michigan University; Valerie Pralong, CNRS CRISMAT

3:20 PM

(ICACC-S6-005-2014) Reversible Lithium Capacities of Partially Oxidized Graphene Nanostructures (Invited)

C. Uthaisar, A. Antic, P. A. Medina, D. Hicks, V. Barone, B. D. Fahlman*, Central Michigan University, USA

Graphene oxide (GO) was synthesized from expanded graphite (EG) and multi-walled carbon nanotubes (MWCNTs) by a modified Hummer's method, and was post-reduced under different temperatures and hydrazine conditions. GOs and partially/fully reduced GOs were characterized by a variety of techniques such as FT-IR, Raman spectroscopy, TGA, SEM, XRD, XPS, and elemental analysis. These characterization methods showed that temperature had a much more significant effect on the performance of reduced-GOs as anode materials than the choice of the environment. The electrochemical performance of reduced-GOs was greatest when the temperature of reduction was 250 °C regardless of the chemical environment. Within this temperature range, reduced-GOs show a high first-cycle specific capacity over 2000 mAh/g and 1000 mAh/g reversible and irreversible, respectively at a relatively large current density of 500 mA/g. For reduced-GOs at 250 °C and under vacuum, the reversible capacity was maintained at 500 mAh/g during 100 cycles. This performance points to reduced GOs as an attractive alternative to graphite; we will further delineate the effect of surface functionalization on the Li capacity in these materials. Overall, these nanomaterials are capable of further improving the capacity and lifetime of Li-ion batteries.

3:50 PM

(ICACC-S6-006-2014) Investigation of the electrode / electrolyte interphase in lithium-ion batteries using MAS NMR (Invited)

N. Dupré*, M. Cuisinier, Institut des Matériaux Jean Rouxel CNRS, France; M. Hirayama, R. Kanno, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Japan; D. Guyomard, Institut des Matériaux Jean Rouxel CNRS, France

Interfacial reactions and the growth of a passivation layer at the electrode surface upon cycling have been proven to factor into the overall battery behavior in terms of irreversible capacity loss, charge transfer kinetics, and storage properties. This work gives an overview of the NMR approach developed to extract and interpret information on the electrode/electrolyte interphase in Li battery materials. The use of quantitative 7Li, 19F and 31P MAS NMR is combined with XPS and EELS to study the interphase chemistry and to unravel its inhomogeneous architecture. To illustrate the technique capabilities as a diagnosis tool to probe evolution of electrochemical behavior and/or failure mechanisms along electrochemical cycling, it will be shown that the electrochemical behavior of LiFePO4 is strongly driven by its surface chemistry via parameters such as aging, coating or even crystalline orientation. Widely considered as chemically inert toward the electrolyte, LiFePO4 actually exhibits a complex, dynamic interaction with classical LiPF6 / EC:DMC solution. Solvents are degraded on LiFePO4 surface at high potentials and their decomposition products form a SPL type interphase that subsequently dissolves at lower potentials. For an air-aged LiFePO4, the chemisorbed/incorporated water or hydroxyl groups lead to the dissolution of the LiFePO4 upon contact with the electrolyte or cycling.

4:20 PM

(ICACC-S6-007-2014) Fabrication of all-solid-state rechargeable lithium batteries using a Li-rich solid solution cathode material

H. Munakata*, K. Ando, M. Shoji, K. Kanamura, Tokyo Metropolitan University, Japan

To achieve higher energy density than 300 Wh kg^{-1} is one of important targets in the development of rechargeable lithium batteries and requires high capacity cathode and anode materials. Li-rich solid solution materials, i.e. Li_2MnO_3-$LiMO_2$ (M = Co, Ni, Mn, etc.), have attracted much attention as promising new cathodes with the discharge capacity of over 300 mA h g^{-1}. However, the solid solution cathodes need to be charged at a high potential of 4.5 V vs. Li/Li$^+$ or more in the first charge cycle, resulting in the oxidative decomposition of conventional electrolyte solutions. Oxide-based Li-ion conducting ceramic electrolytes have wide electrochemical window whose upper limit is greater than 5.0 V vs. Li/Li$^+$. Therefore, their application instead of liquid electrolytes, namely, fabrication of all-solid-state rechargeable lithium batteries is a practical approach to achieve 300 Wh kg^{-1} using solid solution cathodes. In this study, the compatibility of ceramic electrolytes with Li-rich solid solution cathodes is investigated by preparing all-solid-state rechargeable lithium batteries.

4:40 PM

(ICACC-S6-008-2014) One-step approach of a Fe2O3/carbon composite for use in a high-performance lithium ion battery

Y. Li*, D. Zhang, Q. Liu, W. Zhang, J. Gu, S. Zhu, State Key Laboratory of Metal Matrix Composites, China

A simple approach was developed for the fabrication of a Fe2O3/carbon composite by impregnating activated carbon with a ferric nitrate solution and calcinating it. The composite contains graphitic layers and 10 wt.% Fe2O3 particles of 20–50 nm in diameter. The composite has a high specific surface area of ~828m2 g-1 and when used as the anode in a lithium ion battery (LIB), it showed a reversible capacity of ~623 mAh g-1 for the first 100 cycles at 50 mA g-1. A discharge capacity higher than ~450 mAh g-1 at 1000 mA g-1 was recorded in rate performance testing. This highly improved reversible capacity and rate performance is attributed to the combination of (i) the formation of graphitic layers in the composite, which possibly improves the matrix electrical conductivity, (ii) the interconnected porous channels whose diameters ranges from the macro- to meso- pore, which increases lithium-ion mobility, and (iii) the Fe2O3 nanoparticles that facilitate the transport of electrons and shorten the distance for Li+ diffusion. This study provides a cost-effective, highly efficient means to fabricate materials which combine conducting carbon with nanoparticles of metal or metal oxide for the development of a high-performance LIB.

5:00 PM

(ICACC-S6-009-2014) Preparation of cubic Li7La3Zr2O12 film by chemical vapor deposition

H. Katsui*, T. Goto, Tohoku University, Japan

Li7La3Zr2O12 (LLZ) is a promising material for the electrolyte in all all-solid-state lithium-ion batteries because of its high ionic conductivity and chemical stability. However, no fabrication of LLZ films with inherently high conductivity has been reported. In the study, we fabricated the cubic and tetragonal LLZ films on polycrystalline Al2O3 and SrRuO3 substrates by metal organic chemical vapor deposition (CVD), and the effect of the deposition temperature on the phase formation, morphology, deposition rate, and ionic conductivity were investigated. LLZ films were deposited on polycrystalline Al2O3 or SrRuO3 substrates in a vertical cold-wall type CVD chamber. Li(DPM), La(DPM)3 and Zr(DPM)4 were used as precursors. The deposition temperature was 923–1273 K. The phases and morphology of the LLZ films were investigated by X-ray diffraction and a scanning electron microscopy. Au paste was coated on the LLZ film/SrRuO3 substrate to examine the electrical conductivity by AC impedance analyzer at the frequency of 10–2–106 Hz and at 298–375 K. At the deposition temperature of 1023–1173 K, LLZ films with the tetragonal symmetry formed. The cubic LLZ films having fine granular surface morphology were obtained at the deposition temperature of 1173–1223 K. The deposition rates of these LLZ films were approximately 20 μm h–1. The ionic conductivity of the cubic LLZ film exhibited 1.40 10–5 Scm–1 at 298 K.

S7: 8th International Symposium on Nanostructured Materials and Nanocomposites

Nanomaterials for Energy I: Photovoltaics

Room: Coquina Salon B
Session Chair: Sanjay Mathur, University of Cologne

1:30 PM

(ICACC-S7-001-2014) Nanowire device concepts for thin film photovoltaics (Invited)

S. H. Christiansen*, Max Planck for the Science of Light, Germany

Aligned silicon nanowire (SiNW) arrays to aim for power conversation efficiencies >>15% are fabricated on multi-crystalline Si layers on glass substrates using reactive ion etching with prior lithographic patterning using densely packed polystyrene (PS) spheres. Diameter, length, density and shape of SiNWs can be controlled and tuned for highest absorptions (close to 90%). Cell concepts with SiNWs are realized: (i) a hybrid organic/inorganic cell using SiNWs as absorber and PEDOT:PSS as a hole conducting polymer; (ii) a semiconductor-insulator-semiconductor (SIS) cell with SiNWs as absorbers, oxide (few Å thick Al2O3 by atomic layer deposition-ALD)) tunneling barriers for charge carrier separation and a transparent conductive oxide (TCO – here: Al:ZnO, by ALD). Initial thin film solar cell prototypes reached open-circuit voltages of > 680 mV, short-circuit current densities of even > 35 mA/cm2 and efficiencies >13%. Advanced analytics to improve materials and cells are: (i) electron beam induced current (EBIC) to study charge carrier distributions; (ii) electron backscatter diffraction (EBSD) to study structural quality of the multi-crystalline Si layer; (iii) integrating sphere measurements to study optical properties and (iv) 4-point nano-probing to study electrical properties. Alternative electrodes such as graphene or silver nanowire webs are studied to even further improve the cells.

2:00 PM

(ICACC-S7-002-2014) Understanding and improving the performance of hybrid solar cells (Invited)

B. Conings*, L. Baeten, H. Boyen, M. Van Bael, J. Manca, Hasselt University - IMO division IMOMEC, Belgium

Hybrid (organic/inorganic) solar cells typically use a donor polymer to absorb light and a metal oxide as acceptor. The latter can be synthesized in various nano-patterns prior to the deposition of the donor polymer, which finally results in a rigid heterojunction, thus giving hybrid solar cells the edge regarding morphological stability compared to fully organic ones. Nanorod arrays of ZnO are deemed most suited for this purpose as they offer both continuous high mobility charge transport pathways and a large interfacial area with the polymer absorber. Unfortunately, the efficiency of such hybrid solar cells is still falling behind on fully organic solar cells, despite the favorable properties of ZnO acceptors as compared to the commonly used fullerene derivative acceptors in organic solar cells. In this contribution, systematic strategies are presented to improve the efficiency of hybrid solar cells built on ZnO nanorod arrays. Different aspects of the hybrid devices will be highlighted with a keen eye on optimization, both from a fundamental as well as an engineering point-of-view. Taking into account geometric and optical considerations together with charge transport properties and electronic structure, several tactics for efficiency enhancement will be discussed that might assist in raising the efficiency of hybrid solar cells to the level of organic solar cells or beyond.

2:30 PM

(ICACC-S7-003-2014) Electroceramic oxide films and composites by solution chemistry (Invited)

G. Westin*, Uppsala University, Sweden

Thin oxide films of complex composition such as perovskites and spinels are of immense importance for a wide range of applications and new possibilities in e.g. multi-ferroics, fuel-cells, batteries, photo-catalysts and solar cells makes the interest remain strong. There is an increased demand for control to achieve increasingly complex and often multi-phase materials with a great deal of precision down to a few nm in size. This puts great demands on the processing techniques, and for an industrial exploitation the materials also need to be prepared in large scale at a low cost. It seems that solution based processes have the greatest for this. Here all-alkoxide based routes to spinels and perovskite films-, ultra-thin films and coatings are described. The structures are also combined into composites of great potential for multi-ferroics and renewable energy. The conversion of the gel to oxide by heat-treatment is described in detail based on; TGA/DSC, TEM-EDS, SEM, XRD and IR spectroscopy. The influence of the precursors and heat-treatment on the target oxide will be discussed and correlated to key properties.

Nanomaterials for Energy II: Photoelectochemical and Photocatalytic Systems

Room: Coquina Salon B
Session Chairs: Gunnar Westin, Uppsala University; Michael Wark, Carl-von-Ossietzky University Oldenburg

3:20 PM

(ICACC-S7-004-2014) Doped and Core/shell Structured Hematite Nanorods for Efficient Solar Water Splitting (Invited)

S. Shen*, Xi'an Jiaotong University, China

In this study, a facile solution-based method was developed to fabricate hematite nanorods coated with ultrathin overlayer of TiO2 or AgxFe2-xO3, as well as doped with Ta5+. The core/shell nanorod structures of α-Fe2O3/TiO2 and α-Fe2O3/AgxFe2-xO3 were obtained by annealing solution-fabricated β-FeOOH nanorod arrays which were first ultrasonicated in TiO2 sol and Ag+ aqueous solution, respectively. In the α-Fe2O3/TiO2 nanorod structure, TiO2 overlayer could extract photogenerated holes from α-Fe2O3 core via the quantum-mechanical tunneling process, resulting in promoted charge carrier separation, and hence greatly improved photoelectrochemical performance for water splitting, with IPCE increased by a factor of 4.5 from ~2.0% to 9.0% at 400 nm. In the α-Fe2O3/AgxFe2-xO3 nanorod structure, the surface doping of Ag+ ions gave rise to increased electron donor density, which also led to the enhancement in photoelectrochemical performance with IPCE at 400 nm increased from ~2.0% to ~7.5%. Ta5+ doping was found to effectively enhance the PEC performace for water splitting, due to the improved conductivity, increased donor density and reduced charge recombination. However, excessive Ta doping will reduce the PEC acitivity, by forming insulating layer of Ta-rich oxide over the hematite surface.

3:50 PM

(ICACC-S7-005-2014) Photocatalytic hydrogen generation from pyrochlore and perovskite mixed metal oxides (Invited)

M. Wark*, Carl-von-Ossietzky University Oldenburg, Germany; J. Soldat, P. Wang, Ruhr-University Bochum, Germany; R. Marschall, Justus-Liebig-University Giessenhum, Germany

Mixed-oxide photocatalysts with pyrochlore or perovskite structure are active photocatalysts for H2 production from water splitting. We show that the synthesis of perovskite barium tantalate photocatalysts is possible by a new sol-gel technique employing complexing agents. Due to low temperature (873 K) and short time (4 h) calcination the powders consist of small highly crystalline particles. Compared to the pure phase enhanced photocatalytic H2 generation was found for samples consisting of nanocomposites of different Ba-tantalates. Ca-tantalates were formed by varying the ratio of Ta/Ca precursors in a molten salt synthesis route. Nanocomposites formed with a Ta/Ca ratio of about 1.5-1.8, consisting of two or three phases, produces > 1,2 mmol h-1 H2 by overall water splitting with 0.5 wt% of co-catalyst NiO whereas the single phases are almost inactive. In non-stoichiometric Y2-xTi2O7-1.5x pyrochlores reduced cationic lattice distortion due to Ti excess enhances photocatalytic H2 formation. Bismuth incorporation decreases the band gap energy to 3.1 eV. Maximum H2 production rates were achieved with samples possessing Ti-excesses of 10 - 50 %, depending on the Bi content. Large bismuth cations distort the TiO6-octahedral geometry; the formation of A,O`-site vacancies due to titanium excess reverses this effect, improving the charge carrier separation and thus, the photocatalytic activity.

4:20 PM

(ICACC-S7-006-2014) Hematite-nickel oxide hetero-junction thin film for solar hydrogen application via chemical vapor deposition

S. Tasaki*, T. Singh, S. Mathur, University of Cologne, Germany

Hydrogen energy attracts attention due to greenhouse gas reduction and next generation energy security. This uses fossil fuels and also emits carbon dioxide. So, there is a method of splitting water into hydrogen and oxygen with photocatalysts, to focus on the process of producing hydrogen without carbon dioxide. We propose the α-iron oxide (hematite) / nickel oxide multi layer thin film photocatalyst. This thin film was synthesized by a chemical vapor deposition (CVD). The deposited film morphology and thickness by cross section analysis were characterized by scanning electro microscopy and the crystalline phases were characterized by X-ray. The Ultraviolet–visible spectroscopy absorption spectra were recorded in the range 250–800 nm. The band gap was calculated by Tauc plot using absorption data. corresponding author: Prof. Dr. Sanjay Mathur (sanjay.mathur@uni-koeln.de)

4:40 PM

(ICACC-S7-059-2014) Template-Free Fabrication of Colloidal Grid Array by Convective Self-Assembly (Invited)

M. Miyahara*, Y. Mino, S. Watanabe, Kyoto University, Japan

The arrangement of colloidal nanoparticles into ordered structures is a fundamental technique for various applications. In a typical approach, topographically or chemically pre-modified substrates are utilized to assemble particles into a desired configuration, which, however, involves complicated and costly processes. The convective self-assembly is an attractive process, in which a hydrophilic substrate is immersed in a colloidal suspension, and the colloidal particles are carried into the contact line by convective flow of solvent induced by evaporation at the tip of the meniscus. We explore a simple method to arrange colloidal particles into a grid array by this technique. Through the first step, a highly ordered stripe colloidal array forms on a hydrophilic substrate. The key factor for the stripe pattern is the concentration in the suspension. Simply repeating this process with the substrate tilted by 90 degree as the second step, particles will assemble into a grid pattern, which however has never been accomplished without the plasma cleaning in between the two steps: The recovery of complete hydrophilicity is indispensable. We developed a simple model to predict the periodicity of the resultant colloidal stripes, and fabricated a large-size colloidal grid network pattern of gold nanoparticles to demonstrate the versatility of our method.

5:10 PM

(ICACC-S7-008-2014) Atomic Layer Deposition and Plasma-enhanced CVD of Metal Oxide Thin Films for Energy Applications

T. Singh*, A. Mettenbörger, T. Leuning, S. Wang, A. Sasinska, S. Mathur, Institute of Inorganic and Materialsersity of Cologne Chemistry, Univ, Germany

Application of tailor-made molecular precursors in low pressure or plasma-enhanced chemical vapor deposition techniques offers a viable solution for overcoming thermodynamic impediments involved in thin film growth. The use of atomic layer deposition and cold plasmas enables the realization of various functional coatings whose application spectrum spans from transparent conductive coatings, scratch-proof films to anti-bacterial materials. Over the past decade, we have developed several new precursor systems in order to demonstrate the competitive edge of molecule-based plasma coatings. Our work on a large number of metal oxide systems and their characterization towards microstructure, compositional and functional properties supports the advantages of chemical design in simplifying deposition processes and optimizing functional behaviour. This talk will present ALD and PECVD processed thin films of different metal oxides (WO3, TiO2 and Fe2O3) and functionalized thin films by chemically and physically grown nanoparticles. This 3D nanoparticle covering of metal Oxides (MOx) thin films open up new aspect of material properties, which can lead to advanced material technologies. The presentation will include application of MOx thin films of metal oxides and heterostructures for photoelectrochemical (PEC) applications.

5:30 PM

(ICACC-S7-010-2014) Titania Nanobowl Arrays used in Photoelectrocatalytic Degradation of Acid Orange 7

P. J. Arias*, F. Quintero, H. Zea, National University of Colombia, Colombia

We report the use of titania nanobowl arrays prepared by anodizing in photoelectrocatalytic degradation of acid orange 7 (AO7), a recalcitrant dye widely used in textile and food industries. Anodizing was performed using commercial grade reactants on Ti foils in ethylene glycol containing 0.1 wt.% NH_4F using two parallel Ti foils as cathodes and applying a square pulse DC voltage alternating between 20 V and 80 V. An opaque, loose layer was easily removed by washing afterwards. The foil was then annealed at 500 °C for 9 h. Photoelectrocatalytic degradation of AO7 was performed with this foil as anode in a photoreactor with two parallel Ti foils as cathodes. Effect of applied voltage, electrolyte and dye concentration were studied under UVA light in the ranges from 0 - 3 V, 0 - 0.2 M Na_2SO_4, 11.2 - 19.0 mg l^{-1}, respectively. The greatest color removal was 75 % after 3 hours at 1 V, 0.025 M Na_2SO_4 and 15.5 mg l^{-1} AO7, entirely due to the synergy of photoelectrocatalysis. SEM of the anode reveals a nanobowl array morphology that corresponds to the footprint of a titania bamboo-like nanotube array that composed the opaque layer removed after anodizing. Degradation performance is comparable to complete titania nanotube arrays, which is remarkable. Additionally, with this procedure titania nanotube arrays can be easily removed for other applications.

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

In Honor of Professor Stuart Hampshire I; Oxynitride & Related Materials

Room: Coquina Salon A
Session Chairs: M. Singh, OAI/NASA GRC; Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology (AIST)

1:30 PM

(ICACC-S8-001-2014) Oxynitride Glasses as Grain Boundary Phases in Silicon Nitride: Correlations of Chemistry and Properties (Invited)

S. Hampshire*, University of Limerick, Ireland

Silicon nitride is recognised as a high performance material for both wear resistant and high temperature structural applications. Oxide sintering additives, such as yttrium or rare earth oxides plus alumina or magnesia, are used in processing the ceramic to provide conditions for liquid phase sintering, during which the oxides react with surface silica on the Si3N4 particles and some of the nitride to form an oxynitride liquid which allows densification and transformation of alpha- to beta-Si3N4. On cooling, an oxynitride glass is formed at triple point junctions and as intergranular films between the elongated hexagonal silicon nitride grains. The properties of silicon nitride, especially fracture behaviour and creep resistance at high temperatures are influenced by the glass chemistry, particularly the concentration of modifier and the volume fraction within the ceramic. This paper provides an overview of liquid phase sintering of silicon nitride ceramics, grain boundary oxynitride glasses and the effects of chemistry and structure on properties. As nitrogen substitutes for oxygen in bulk oxynitride glasses, increases are observed in glass transition and softening temperatures, viscosities, elastic moduli and thermal expansion coefficient. These property changes are compared with known effects of grain boundary glass chemistry on properties of silicon nitride ceramics.

2:00 PM

(ICACC-S8-002-2014) Oxynitride Glasses: From SiALONs to Bio-Materials (Invited)

R. Brow*, Missouri S&T, USA

From their initial discovery as grain boundary phases in silicon nitride ceramics to more recent developments of nitrided bio-glasses, oxynitride glasses have garnered much attention from both glass scientists interested in the property changes that accompany the enhancement of structural cross-linking with the replacement of oxygen by nitrogen, and from materials engineers eager to exploit these interesting materials for many applications. Stuart Hampshire's many contributions to our understanding and appreciation of oxynitride glasses will be reviewed, with a particular emphasis on his important studies of structure-property relationships in the silicate oxynitride systems and his more recent studies of oxynitride glasses for biomedical applications.

2:30 PM

(ICACC-S8-003-2014) The Evolution of Toughened Ceramics (Invited)

P. F. Becher*, University of Tennessee, USA

The evolution of our understanding of the mechanisms to increase the fracture toughness of ceramics has been remarkable. One is tempted to suggest that the addition of straw to mud to improve dried bricks as one of the first toughening processes that has now evolved as fiber-reinforced ceramics for brake pads and aircraft engine components. Over the last four decades, ceramists have examined and utilized processes like micro-cracking and grain bridging induced by increased grain size and/or second phase additions to increase fracture toughness. The stress-induced phase transformation of tetragonal zirconia ceramics and composites yields substantial increases in toughness although these gains are temperature sensitive. Nonetheless, transformation toughened zirconia ceramics have wide application. In addition to fiber- reinforced ceramics, whisker-reinforced ceramics offer increased toughness and strength, which is retained over a considerable temperature range. Some the limits and benefits of these toughening mechanisms will be described.

3:20 PM

(ICACC-S8-004-2014) The properties of fine grained coatings using small-scale testing (Invited)

S. Liu, Singapore Institute of Manufacturing Technology, Singapore; J. M. Wheeler, EMPA - Materials Science & Technology, Switzerland; P. R. Howie, University of Cambridge, United Kingdom; X. Zeng, Singapore Institute of Manufacturing Technology, Singapore; J. Michler, EMPA - Materials Science & Technology, Switzerland; W. J. Clegg*, University of Cambridge, United Kingdom

This paper discusses the deformation behaviour of a hard coating of a fine-grained CrAlN with a Si_3N_4 grain boundary phase. The yield and flow behaviour of these materials is measured directly using micropillar compression. Using measurements of the hardness obtained by nanoindentation, it is shown that the variation of the yield stress with the hardness is similar to that in conventional materials. To investigate why such coatings might show improved properties, the resistance to cracking has been measured using a new small-scale toughness test. Using in-situ testing in the SEM, the toughness of the fine-grained coatings is measured to be almost twice that of a conventional CrN-based coating, and consistent with changes in the cracking behaviour that can be directly observed.

3:50 PM

(ICACC-S8-005-2014) Preparation and properties of aluminosilicate glasses containing N and F (Invited)

M. J. Pomeroy*, University of Limerick, Ireland

Sialon and silicon nitride ceramics contain intergranular glass as a result of the need for oxide sintering additives. This paper reviews factors affecting the properties of such glasses and indicates how composition variables can be used in additive equations to understand important predictors of property values. Such information can then be integrated into understanding how properties develop in sintered sialons and silicon nitride.

4:20 PM

(ICACC-S8-006-2014) Influence of dopant and N/O anion exchange on the electronic structure and luminescent properties of oxynitride based phosphors

Z. Lences*, I. Ibrahim, M. Hrabalova, L. Benco, P. Sajgalik, Institute of Inorganic Chemistry, Slovakia

Silicon nitride/oxynitride-based ceramics are well established as engineering materials in many industrial applications. In the last decade these materials have attracted a high attention due to their ability to serve as a host lattices for phosphors. In this study europium and cerium-doped MgSiN2 and LaSi3N5 have been synthesized from Si/Mg2Si/Si3N4 or LaSi/Si/Si3N4 mixtures doped with Eu2O3, Sm2O3 or CeO2 by direct nitridation. The emission band of LaSi3N5:Eu phosphor was in the green light region, while MgSiN2:Eu emitted red light. The influence of Ce addition on the luminescent properties of LaSi3N5:Eu and MgSiN2:Eu phosphors will be also discussed. First-principles density-functional theory (DFT) calculations were performed to enhance the understanding of the electronic structure of the stoichiometric LaSi3N5 and La/Eu (La/Sm or La/Ce) and N/O substituted ternary nitrides. The electronic structure and band gaps were calculated also using the hybrid functional (HSE) which gives results in reasonable agreement with experimental data. Silicon oxynitride-based phosphors were prepared also from polymer derived Si-O-C-(N) precursors and Al-alkoxide. Depending on the host lattice, i.e. O-sialon or beta-sialon, on the substitution level Si/Al and N/O, and on the doping Eu content green or yellow light emitting phosphors were prepared.

4:40 PM

(ICACC-S8-007-2014) Characterisation of Some Oxynitride Glass- Ceramics by TEM: Effect of Starting Composition and Heat- Treatment Temperature on Crystallisation Products

H. Yurdakul, Dumlupinar University, Turkey; E. Dolekcekic*, S. Turan, Anadolu University, Turkey; M. J. Pomeroy, S. Hampshire, University of Limerick, Ireland

One of the most interesting phases discovered in the Y-Si-Al-O-N system is termed B-phase, Y2SiAlO5N. YSiAlON glasses with compositions of Y:Si:Al = 3.45:3:2 and varying nitrogen contents (N=5, 8, 15, and 22 equivalent %) were produced by melting appropriate powder mixtures under nitrogen at 1715 °C. Glass-ceramics were obtained by heat treatment of the glasses for 10 hours under a nitrogen atmosphere in the range 950-1200°C. From previous investigations, these compositions are expected to produce either B-phase (Y2SiAlO5N) or Iw-phase (Y3Si2Al1(O,N10) (i.e. 10 equivalent % N) after heat treatment, depending on N content and temperature. Samples were characterised by SEM (JEOL JSM-840), TEM (JEOL 2100F) and XRD (Philips X'Pert) and the data obtained from XRD were further analysed to obtain unit cell parameters of some phases. PEELS analysis by TEM technique have been applied to get further information about B-phases formed from low nitrogen content glasses to compare with available unit cell parameters and XRD data. This observation proves that this phase is a low nitrogen containing configuration B-phase (a= 3.84 Å and c = 9.75 Å). Furthermore, the detailed lattice characteristics of B-phase were atomically carried out using different state-of-the-art aberration-corrected transmission electron microscopes.

5:00 PM

(ICACC-S8-008-2014) Pressureless Sintering of SiAlON Ceramics

F. Kara*, Anadolu University, Turkey; U. Akkasoglu, MDA Advanced Ceramics, Turkey; S. Turan, A. Kara, Anadolu University, Turkey; H. Mandal, Sabanci University, Turkey

SiAlONs are ceramic materials for a number of wear applications and the properties of SiAlONs can be tailored for specific applications. The main sintering method of SiAlON is gas pressure sintering. Gas pressure sintering is a rather costly method due to high investment and operation costs . Therefore, there is a need to to develop pressureless sintering method of SiAlON ceramics to reduce their production cost and enable wider scale applications. Main drawback of pressuless sintering of SiAlON ceramics is the limitation of sintering temperature below 1800 0C in order to avoid Si3N4 decomposition. Therefore, rather reactive additive combinations and good processing conditions need to be developed. In this study, dense SiAlON ceramics were attempted to be produced by pressureless sintering of dry pressed compacts . With this respect, additive composition and amount, granule character, sintering temperatures etc. have been investigated as a way to achieve sintered densities over 99% and resultant properties are discussed.

5:20 PM

(ICACC-S8-009-2014) SiAlON Phosphors from a Preceramic Polymer and Nano-sized Fillers

E. Bernardo*, G. Parcianello, S. Pilati, P. Colombo, University of Padova, Italy; A. C. Delsing, H. T. Hintzen, Eindhoven University of Technology, Netherlands

A commercial polysilazane, mixed with nano-sized fillers particles, has been used for the first time for the preparation of both β’- and α’-SiAlON-based phosphors, giving origin to yellow, green and blue luminescence under blue or near UV excitation, depending on processing conditions. β’-phase was obtained by mixing the preceramic polymer with both γ-Al2O3 and Si3N4 nanoparticles, whereas the Ca α-phase was achieved by adding γ-Al2O3 and CaCO3 nanoparticles. Luminescence in all samples was due to the addition of low amounts of Eu2O3 nano-particles. The reduction of Eu3+ into Eu2+ occurring in SiAlON was favoured by the presence of carbon derived from the pyrolysis of the preceramic polymers. The nanometric distribution of fillers and the high yield of the selected preceramic polymers in terms of Si and N atoms, led to the development of the desired phases at relatively low firing temperatures (e.g. 3 h at 1550-1600°C in pure nitrogen).

S10: Virtual Materials (Computational) Design and Ceramic Genome

Ceramic Genome and Modeling of Structure and Property I

Room: Coquina Salon G

Session Chair: Jingyang Wang, Institute of Metal Research

1:30 PM

(ICACC-S10-001-2014) Classification of CSH Crystals via a Quantum Mechanical Metric (Invited)

W. Ching*, C. C. Dharmawardhana, University of Missouri-Kansas City, USA; A. Misra, University of Kansas, USA

The calcium silicate hydrates (CSH) is the main binding phase of concrete comprised a mired phases of complex crystalline minerals that are poorly ordered. The traditional classifications metrics give little understanding of the chemical and mechanical behavior of these CSH crystals which prompts for new and more fundamental approach to understand the complex nature of the problem. We approach this problem with a comprehensive study of the mechanical and electronic structures of a large number of CSH crystals within a wide range of Ca/Si ratio ranging from 1.00 to 3.00. The phases considered include: Jennite [Ca9Si6O18(OH)6-8H2O], three phases of Toberomite (T9A [Ca5Si6O17-5H2O], T11A[Ca4Si6O15(OH)2-5H2O] and T14A[Ca5Si6O16(OH)2-7H2O]), Afwillite [Ca3 (SiO3OH)2-2H2O], α-C2SH [Ca2(HSiO4)(OH)], Killalaite [Ca6.4(H0.6Si2O7)2(OH)2], Suolunite [CaSiO2.5(OH)-0.5H2O], Xonotlite [Ca6Si6O17(OH)2] and Portlandite [Ca(OH)2], alite [3CaO SiO2] and belite [2CaO-SiO2]. We use the bond order density (BOD) as a theoretical metric to classify this class of material to gain the much needed insight to the structure of CSH gel.

2:00 PM

(ICACC-S10-002-2014) Experimental and Computational Studies of Damage Production and Recovery in Irradiated Ceramics (Invited)

W. J. Weber*, M. Backman, University of Tennessee, USA; O. H. Pakarinen, Oak Ridge National Laboratory, USA; F. Djurabekova, K. Nordlund, University of Helsinki, Finland; M. Toulemonde, University of Caen, France; A. Debelle, University Paris Sud, France; Y. Zhang, Oak Ridge National Laboratory, USA

The interaction of ions with solids results in energy loss to both atomic nuclei and electrons. We have integrated experimental and computational approaches to investigate the separate and combined effects of nuclear and electronic energy loss on the response of ceramics to ion irradiation over a range of energies. In amorphous SiO2, there is a synergy between nuclear and electronic energy loss on experimental damage evolution that is confirmed by large-scale molecular dynamics simulations. In SiC, the electronic energy loss can lead to reduced defect production, which depends on the ratio of electronic to nuclear energy loss. To understand and develop predictive models of this phenomenon, separate effects experiments were carried out on SiC. Pre-damaged states were created in single crystal SiC with ions in the high nuclear energy loss regime. The effect of electronic energy loss on these pre-damaged states was investigated by irradiation with ions at a high ratio of electronic to nuclear energy loss. The results reveal that electronic energy loss leads to defect recovery that is dependent on the electronic energy loss densities. Large-scale molecular dynamics simulations confirm that the electronic energy loss leads to recovery of irradiation defects via an inelastic thermal spike phenomenon in SiC. This work was support by U.S. DOE, BES, MSED.

2:30 PM

(ICACC-S10-003-2014) Impact of Interlayer Interaction on Thermal Conduction in Layered Thermoelectric Oxides (Invited)

M. Yoshiya*, Osaka University, Japan

Thermal conduction that determines thermoelectric conversion efficiency significantly deviates from macroscopic layered composites, in that interlayer interaction significantly alter phonons in each layer which are already confined within the layer to some extent. This deters consequent thermal conduction in each layer from being elucidated in terms of conventional theories for thermal conduction, most of which are proposed for bulk materials. Perturbed molecular dynamics simulations have been conducted to numerically examine the thermal conduction in classes of layered oxides. The numerical analyses involved in the perturbed molecular dynamics enable us to quantify each layer's contribution to overall thermal conduction. Extensive computational experiments have been carried out to numerically sort out what materials properties other than the one directly related to thermal conductivity govern the thermal conduction in each layer, in order to facilitate further materials design based on computation, with much emphasis on the layered materials where both point and planar detects coexist. Possible strategies to further supress thermal conductivity in the layered oxides without deteriorating electronic conterparts in order to optimize the efficiency of heat-to-electricity energy conversion.

Ceramic Genome and Modeling of Structure and Property II

Room: Coquina Salon G
Session Chairs: Wai-Yim Ching, University of Missouri-Kansas City; Liping Huang, Rensselaer Polytechnic Institute

3:20 PM

(ICACC-S10-004-2014) Integrated method to search low thermal conductivity ceramics (Invited)

J. Wang*, Institute of Metal Research, China

Searching for advanced ceramics with extremely low thermal conductivity is highly demanded for developing thermal insulation components or thermal-electric conversion devices. Unfortunately, experimental measurement is very difficult to deduce intrinsic lattice thermal conductivity without the influences of defects and radiation heat. Also, theoretical calculation does not always bring out reliable prediction on temperature dependence of thermal conductivity for complex ceramics. In this presentation, integrated method is used to investigate thermal conductivities of some complex ceramics, such as the rare-earth containing silicon oxynitrides, silicates and phosphates. Theoretical predictions clearly illustrate the predominant effects of crystal structure and chemical composition on temperature dependent thermal conductivities. Dense and bulk ceramics are synthesized and used for evaluating intrinsic lattice thermal conductivity in experiments. The theoretical and experimental thermal conductivities are in good consistence from room to high temperatures. This presentation highlights some advanced ceramics with extremely low thermal conductivities and provides reliable integrated method to determine lattice thermal conductivity.

3:50 PM

(ICACC-S10-005-2014) Electronic Structure and Optical Properties of Stable Phases in Calcium Aluminate System

W. Ching, University of Missouri-Kansas City, USA; A. Huassain*, The Islamia University of Bahawalpur, Pakistan; P. Rulis, University of Missouri-Kansas City, USA

First-principles calculation on the electronic structure, bonding and optical properties of five stable phases of binary calcium aluminate nCaO-mAl2O3 [C3A, C12A7, CA, CA2, and CA6 as well as the C12A7-electride phase] have been carried out using the ab initio orthogonalized linear combination of atomic orbitals (OLCAO) method. These crystals have very complex structures and different Ca/Al ratio. All the five phases are wide gap insulators. The C12A7-electride phase exhibits a region of metallic bands within a large gap in the range of -1.14 to 0.81 eV. Results on the band structure, density of states, effective charges, bond order values, etc. will be presented and discussed. The calculated optical properties in the form of frequency-dependent complex dielectric functions show that information that the C3A has the largest refractive index among these crystals.

4:10 PM

(ICACC-S10-006-2014) Variable-composition Structural Optimization and Experimental Verification of Manganese Borides

H. Niu*, X. Chen, D. Li, Y. Li, Institute of Metal Research, Chinese Academy of Sciences, China

In combination with the variable-composition evolutionary algorithm calculations and the first principles calculations, we have systematically searched the compounds (including their crystal structures) in the extensively investigated binary Mn-B system. Our results have uncovered four viable ground state compounds, with Mn2B, MnB, MnB4 and previously never reported MnB3 and two metastable compounds of MnB2 and Mn3B4 . Our calculations demonstrated that the early characterized mC10 structure of MnB4 showed dynamical instability with much imaginary phonon frequencies and instead, a new mP20 structure is predicted to be stable both dynamically and thermodynamically, with a considerable energy gain and no imaginary phonon frequencies. The new MnB3 compound crystallizes in the monoclinic mC16 structure which lies 3.2 meV/atom below the MnB (oP8) ↔ MnB4 (mP20) tie-line at T = 0 K. Furthermore, these proposed phases have been verified by our annealed samples after the arc-melting synthesis and the corresponding powder XRD measurements. This discovery of the MnB3 compound could help in the design of boron-based intermetallics with appealing electronic, magnetic and mechanical properties through the variable- composition evolutionary search without any input of structural and compositional parameters from experiment. Corresponding author: xingqiu.chen@imr.ac.cn

4:30 PM

(ICACC-S10-007-2014) Nanocrystalline Ceramic-Oxides: Microstructure Evolution and Materials Design (Invited)

D. Aidhy*, Y. Zhang, Oak Ridge National Laboratory, USA; W. Weber, University of Tennessee, USA

Nanostructured ceramic materials have generated tremendous interest in the past two decades due to their outstanding technological characteristics. However, nanocrystalline materials are prone to grain growth, and preserving their grain size during synthesis or under operating conditions has been found to be one of the biggest challenges primarily due to the unknown atomic level grain growth mechanisms. In this talk, we reveal that grain growth in nanocrystalline materials occurs via a novel 'disorder-driven' mechanism not observed in the decades of research on ceramic-oxide materials. This mechanism is found to operate kinetically much faster than the conventionally known mechanisms. The unraveling of this mechanism now explains fast grain growth observed experimentally under both irradiation and thermal annealing conditions for nanocrystalline materials synthesis. In addition, to prevent grain growth in nanocrystalline materials, we also elucidate a framework to design dopant-pinned grain boundaries where we propose a new criteria to selectively choose appropriate dopants in designing grain-growth resistant nanocrystalline ceramic-oxides.

5:00 PM

(ICACC-S10-008-2014) A theoretical study of oxygen permeation in α-alumina

T. Ogawa*, A. Kuwabara, C. Fisher, H. Moriwake, Japan Fine Ceramics Center, Japan; K. Matsunaga, Nagoya University, Japan; K. Tsuruta, Okayama University, Japan; S. Kitaoka, Japan Fine Ceramics Center, Japan

Recent oxygen permeation experiments of α-alumina have enabled the dependence of grain boundary (GB) diffusion coefficients on oxygen partial pressure to be measured. These measurements suggest that the dominant diffusion species, i.e., O and Al vacancies, alter depending on the partial pressure. In this study, we investigate the observed switchover of diffusion species based on density functional theory (DFT). Although the main terms of the formation energies of O and Al vacancies have been established in previous calculations, the Fermi level remains an unknown parameter. We calculated the Fermi level under conditions of charge neutrality between the charged O and Al vacancies and free electrons and holes. When the bulk band gap is used to determine the Fermi level, no switchover in the diffusing species is observed over a wide range of partial pressures. In this case, Al vacancies are always formed preferentially. To take GB effects into account, we also calculated the gaps of GBs. Our results show that the gaps of GBs are much smaller than those of the bulk, sometimes by as much as 60%. Using the smaller gaps of GBs, O vacancy formation is found to become preferable at low partial pressures, consistent with oxygen permeation measurements. Our results suggest that the GBs, particularly differences in band gap and ease of free electron creation, have a large influence on mass transport in this important ceramics.

5:20 PM

(ICACC-S10-009-2014) Energetics of Dopants and Oxygen Vacancies at Grain Boundaries in CeO2: Insights from Density Functional Theory

V. Cooper*, D. Aidhy, Oak Ridge National Laboratory, USA; H. Xiao, W. Weber, University of Tennessee, USA

Recent studies on ion conduction at interfaces/grain boundaries (GBs) has provided conflicting results in terms of whether nanocrystalline materials could be used to enhance ionic conductivity. Primarily the lack of understanding originates from the energetics of oxygen vacancy pinning at GBs by the segregated dopants. Using density functional theory calculations, we disentangle the effects of dopants and GBs on oxygen migration, and systematically illustrate the effect of the type of dopant segregation on oxygen conduction, dopant-oxygen vacancy binding energetics at GBs, and oxygen migration energy at GBs thereby developing a framework to predict new doped-materials particularly suited for enhancing oxygen conduction in nanocrystalline oxide materials.

5:40 PM

(ICACC-S10-010-2014) Developing Stability Diagrams for Interfaces and Nanostructured Materials in Support of the "Materials Genome" Project (Invited)

N. Zhou, J. Luo*, UCSD, USA

Bulk phase diagrams are one of the most useful tools for materials science. Materials researchers have long recognized that interfaces and nanostructured materials that have a large amount of interfaces can exhibit thermodynamic stability that drastically differs from bulk materials. A series of studies aim to extend the bulk CalPhaD methods to grain boundaries and to develop grain boundary "phase" (complexion) diagrams, which have been proven useful for predicting solid-state activated sintering behaviors; these recent efforts are documented in a recent review [J. Am. Ceram. Soc. 95: 2358 (2012)]. In a most recent study, we further extended bulk CalPhaD methods to model binary poly/nanocrystalline alloys and developed a new kind of stability diagram for poly/nanocrystalline alloys, in which lines of constant normalized grain boundary energies and "equilibrium" grain sizes are plotted in the bulk phase diagram. These stability diagrams (as extensions to bulk phase diagrams) can be used as general materials science tools to accelerate materials design in the spirit of the Materials Genome initiative.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

Material Design

Room: Coquina Salon F

Session Chair: Per Eklund, Linkoping University

1:30 PM

(ICACC-S12-001-2014) Magnetic MAX phases from first principles and thin film synthesis (Invited)

J. Rosen*, Thin Film Physics Division, Sweden

First-principles calculations have been used to study trends in phase stability for potential magnetic MAX phases. These self-organized atomic laminates are based on Cr_2GeC, Cr_2AlC, and Cr_2GaC, with Mn substituting Cr over a range 0 - 100 %. Theoretical results show stable MAX phase alloys, and examples of atomic compositions and atomic configurations being used to tune the magnetism between different states. This has been explored experimentally by thin film deposition through arc as well as sputtering methods. Predicted new MAX phases have been successfully synthesized, and the magnetic properties evaluated, in accordance with observations from theory. Selected films display a ferromagnetic signal well above room temperature.

2:00 PM

(ICACC-S12-002-2014) Materials Design From ab initio Calculations : Nanolayered MAX Phases

W. Luo, M. Ramzan, R. Ahuja*, Uppsala University, Sweden

The Mn+1AXn (n=1 to 3) phases referring to as MAX phases, wherein M is an early transition metal, A is an A-group element (mostly IIIA and IVA) and X is either C and/or N, possesses some fascinating properties usually associated with metals and ceramics. The MAX phases are layered hexagonal structures with two formula per unit cell, which can be described as close-packed layers of M6X octahedra interleaved with layers of A elements. In present work, we have theoretically investigated the mechanical and physical properties of the 211 (n=1), 312 (n=2) and 413 (n=3) MAX phases, and the relation with those of their counterpart binaries. Generally speaking, the MAX phases are consisted with strongly coupled M6X octahedra with weakly bonded A layers, which results in the special properties of MAX phases. The effect of A elements has also been discussed. The present work present a general overview on materials properties from a computational point of view

2:20 PM

(ICACC-S12-003-2014) Ab initio determination of the ionic channel of the thermal conductivity of select 211 MAX phases

G. A. Hug*, L. Andrea, ONERA-CNRS, France; L. Chaput, Université de Lorraine, France; A. Togo, Kyoto University, Japan

We have computed the ionic component of the thermal conductivity tensor from ab initio for a selected choice of MAX phases. Our method consists in solving the Boltzmann transport equation of the phonon density in a scheme where the lifetime is calculated from the phonon-phonon interactions. In order to obtain the energy and q-dependent lifetimes, the anharmonic phonon spectra are computed from a third order expansion of the electronic total energy with respect to atomic displacements. The electronic structure and hence the force constants are computed in the framework of the Density Functional Theory using the VASP code. The Phonopy code was used for preparing the necessary VASP-cases and post-processing to obtain the third order dynamical matrix. The anharmonicity can be viewed as a three phonons interaction. A Fermi golden rule is applied to compute the lifetime as the inverse of the self-energy. Our results show that the ionic channel of the thermal conductivity is highly anisotropic, with a higher component in the basal plane. We will discuss this behavior in connection with the so-called "rattling" effect of the A elements.

2:40 PM

(ICACC-S12-004-2014) MAX Phase's transport properties

W. Yu, V. Mauchamp, V. Brunet, T. Cabioch, Institut PPRIME, France; L. Piraux, L. Gence, Institute of Condensed Matter and Nanosciences, Belgium; A. Drevin-Bazin, M. Beaufort, J. Barbot, S. Dubois*, Institut PPRIME, France

The anisotropy of Ti2AlC transport properties are understood from the compared study of both a highly-oriented (000l) Ti2AlC thin film and a Ti2AlC polycrystalline bulk sample. The c-axis resistivity, extracted from the ones of the two latter samples using an effective medium approach, is found to be one order of magnitude higher than the basal-plane resistivity [1]. The basal plane and c-axis resistivities were measured on highly-oriented (000l) and (11-20) Ti3SiC2 thin films deposited respectively onto [0001] and [11-20] oriented SiC surfaces. The measured c-axis resistivity is shown to be four times and eight times higher than the basal plane resistivity at room temperature and at high temperature respectively. The basal plane resistivity of the highly-oriented (000l) Ti3SiC2 thin film is moreover shown to be in good agreement with the resistivity measured on a Ti3SiC2 single crystal. Transport measurements have also been performed on polycrystalline Ti2AlC(1-x)Nx MAX phase solid solutions. The modification of the resistivity versus the C content is discussed in terms of Mott's approximation and free electron model. Finally, transport properties of sub stoichiometric Ti2AlCx and Ti2AlNx MAX phases have been studied. It is demonstrated that vacancies are strong scatters of electrons. [1] V. Mauchamp et al., Phys. Rev. B 87, 235105

Methods for Improving Damage Tolerance, Oxidation and Thermal Shock Resistance I

Room: Coquina Salon F

Session Chair: William Fahrenholtz, Missouri University of Science and Technology

3:20 PM

(ICACC-S12-005-2014) Carbon Fiber Reinforced Ultra-high Temperature Ceramic Based Matrix Composites (Invited)

S. Dong*, Q. Li, Y. Kan, X. Zhang, L. Gao, Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Carbon fiber reinforced silicon carbide matrix (Cf/SiC) composites are widely used as thermal structural elements in aerospace area, such as rocket nozzles, nose tips and aeronautic jet engines, because of their unique physicochemical and mechanical properties. However, the applying temperature of Cf/SiC composites is limited at 1650°C, because of the active oxidation of silicon carbide at temperature above that. It is an effective way to improve the high-temperature performance of Cf/SiC composites via introducing ultra high temperature ceramic (UHTC) component to SiC matrix and coatings, namely, fabricating UHTC based composites. Such kind of materials have attracted great attentions for potential applications in the thermal protection systems of hypersonic flight vehicles. In present study, UHTC based composites and coatings are prepared by polymer infiltration and pyrolysis process and chemical vapor infiltration technique, respectively. The microstructures, phase assemblages, as well as mechanical and ablative properties of the materials are studied. Both microstructure and phase evolution during the oxidation and ablation process are investigated and the mechanism is analyzed. The result indicated that the oblation property of UHTC based composites are much better than that of Cf/SiC composites, mainly due to the formation of UHTC oxides on the material surface during testing.

3:50 PM

(ICACC-S12-006-2014) Microstructure, mechanical properties and oxidation behavior of short SiC fiber reinforced HfC- and TaC-based materials

L. Pienti*, L. Silvestroni, C. Melandri, D. Dalle Fabbriche, D. Sciti, CNR, Italy

Nearly fully dense HfC- and TaC-based composites containing 15 vol% short SiC fibers as reinforcing phase were produced by hot pressing at 1700-1750°C. Suitable sintering additives were selected in order to get a full densification at temperatures well-tolerated by SiC fibers. This work aims at studying the effect of SiC fibers on microstructure, thermo-mechanical properties and oxidation resistance. Microstructural characterization outlined a strong interaction between the carbide matrix and SiC fibers. The following properties were evaluated: Vickers hardness, fracture toughness by chevron notched beam, elastic modulus, 4-pt bending strength at room temperature and at 1200°C in Ar, linear CTE up to 1300°C in Ar, thermal conductivity up to 1900°C in Ar, thermal shock by water quenching method. Oxidation tests in air were carried out with thermogravimetric analysis up to 1500°C and at 1650°C in a bottom up loading furnace. TaC-based materials generally possessed higher thermo-mechanical properties compared to HfC but lower oxidation resistance. Properties of fiber-reinforced composites were compared to those of unreinforced ones.

4:10 PM

(ICACC-S12-007-2014) Development and Evaluation of ZrB_2-Graphite Fibrous Monolithic Ceramic Composites

J. Watts*, G. Hilmas, W. Fahrenholtz, Missouri University of Science and Technology, USA

The addition of SiC and other second phases to ZrB_2 has been shown to improve a number of properties including fracture toughness, thermal shock resistance, and strength. However, these composites generally still exhibit catastrophic failure. The goal of this research is to develop a ZrB_2 based composite which will exhibit graceful failure and still possess acceptable mechanical and oxidation properties. This was accomplished by producing a fibrous monolithic architecture consisting of a ZrB_2 based cell and a graphite based cell boundary. The core/shell architecture was formed through a co-extrusion process. Composites were produced with varying core to shell ratios in order to determine how much cell boundary is necessary to produce graceful failure and if there is an optimal ratio. The core material alone has a flexural strength of ~850 MPa while a composite having a core to shell ratio of 4.7:1 exhibited a strength of ~370 MPa. Oxidation testing has also been performed to determine how varying the core to shell ratio effects oxidation resistance.

4:30 PM

(ICACC-S12-008-2014) Self-protective C-C composites for high temperature oxidation resistance using reverse infiltrated ultra high temperature ceramic coatings

L. S. Walker*, E. L. Corral, The University of Arizona, USA

Carbon-Carbon (C-C) composites are ideal materials for structural components on aerospace vehicles however they lack necessary oxidation resistance for high heat flux oxidizing environments. Ultra high temperature ceramics (UHTCs) have excellent oxidation resistance at high temperature but lack fracture toughness for use in structural components. By forming ceramic coatings of UHTCs on and within C-C composites using liquid precursors a ceramic matrix composite can be formed with the mechanical properties of C-C and the oxidation resistance found in UHTCs. Coatings are processed by vacuum infiltration and heat treatment to 1500°C to fill internal voids, however they do not form surface coatings. The chemistry of the coatings are designed and optimized isothermally using dynamic non-equilibrium TGA at 1600°C then tested as larger scale parts using an oxy-acetylene ablation torch at >1600°C. Oxidation response of the coatings is a dynamic process with the oxide scale changing chemistry and viscosity as it develops a protective surface layer.

4:50 PM

(ICACC-S12-009-2014) Compositional design of ultra-refractory ZrB2-SiC ceramics for extreme environments (Invited)

F. Monteverde*, National Research Council of Italy, Italy

MB2 (M= Zr, Hf) with SiC additions in various amount and shape (particulate, whisker, short fiber) is a bright example of composition design of materials which has captured the attention of the UHTC community. This class of composites brings efficiently together the combination of excellent mechanical properties and resistance to oxidation at very high temperature. The drive is indeed the need of leading edges for future hypersonic vehicles with sharp profile. Such passive components are subject to very stressful heat fluxes in harsh plasmas from atmosphere, and temperatures above 2300K for several minutes may become a projected service condition. Methods for enhancing the resistance to oxidation when the protection of external glassy silica-based films begins to fail are currently under investigation. Refractory carbides like B4C or WC are of great interest in relation to the multiple favorable effects they induce on densification and properties once added to ZrB2-SiC composites. Microstructure and key properties of hot-pressed ZrB2-SiC materials processed with the addition of third phases such WC and/or B4C were analyzed, and compared to other ZrB2-SiC doped with (limited content of) Si-bearing third phases. Resistance to oxidation in oxidizing furnaces was also investigated and compared to that obtained by using an arc-jet testing facility.

5:10 PM

(ICACC-S12-010-2014) Evaluation of oxidation resistance of ZrB2-SiC-ZrC ceramics for application at above 2000 K

Y. Arai*, M. Ishikawa, Y. Kogo, Tokyo University of Science, Japan; S. Guo, National Institute for Material Science (NIMS), Japan; K. Goto, Institute of Space and Astronautical Science/Japan Aerospace Exploration Agency (ISAS/JAXA), Japan; H. Suzuki, Iwaki Meisei University, Japan; T. Yasuno, National Police Agency, Japan

The purpose of this study is to evaluate the oxidation resistance of ZrB2-SiC-ZrC (ZSZ) and to explore higher oxidation resistant materials than SiC. In this study, ZSZs were oxidized by three different methods. Firstly, ZSZ were oxidized up to 1773 K by using thermo gravimetric analyses. The result showed that ZSZs has oxidation resistance due to formation of oxide scale. Secondly, ZSZs were heated at 1973 K in airflow by IR image furnace. The result revealed that ZSZs containing more ZrC formed ZrO2 rich scale, whereas ZSZs containing more ZrB2 formed SiO2 rich scale. The highest oxidation resistance will be realized to form liquid SiO2 scale with ZrO2 skeleton. Therefore, it is important to adjust composition of ZSZ. Finally, in order to compare their oxidation resistance, ZSZ, ZrB2-SiC, and SiC were oxidized up to 2073 K by using ZrO2 furnace. The results showed that oxide scale remained on the surface of ZSZ and ZrB2-SiC even after the oxidation test. On the contrary, no oxide scale was found on the surface of SiC. By comparing with ZSZ and ZrB2-SiC, ZSZ formed oxide scale with ZrO2 skeleton. On the other hand, ZrB2-SiC formed oxide scale without ZrO2. It is essential to not only have SiO2 scale but also have rigid ZrO2 skeleton. Thus, it is implied that ZSZs are more attractive candidate as an advanced thermal protection system.

5:30 PM

(ICACC-S12-011-2014) Preparation,microstructure and ablation properties of C/C-Zr(Hf)B2-Zr(Hf)C-SiC composites derived from polymeric precursors (Invited)

W. Zhang*, X. Wei, J. Li, Institute of Process Engineering, CAS, China

C/C-Zr(Hf)B2-Zr(Hf)C-SiC composites were fabricated by chemical vapor infiltration of pyrolytic carbon as interphase and polymeric impregnation/pyrolysis (PIP) of SiC, Zr(Hf)C and Zr(Hf)B2 as ceramic matrix derived from a kind of hybrid polymeric precursors. The formed ultra-high temperature ceramic matrix of SiC-ZrC-ZrB2 and SiC-HfC-HfB2 were designed to improve the oxidation and ablation resistance of C/C composite at very high temperatures. Investigations on the pyrolysis process of the hybrid polymeric precursors showed a completely phase transformation into carbides and borides at temperatures above 1500 deg C. Multiscale structure of the prepared composites were characterized, which showed that carbon fibers were covered by pyrolytic carbon and the Zr(Hf)C and Zr(Hf)B2 nano-particles distributing homogeneously in a continuous SiC matrix. Ablation properties of the composite was investigated with a plasma torch and arc-heated wind tunnel tests at temperatures of 1800~2200deg C. The composite exhibits very low ablation rates of 0.18×10-3 mm/s at 1800 deg C and 0.37×10-3 mm/s at 2000 deg C in the plasma torch after 1000s testing, as compared to a similar rate of 0.30×10-3 mm/s in the wind tunnel at 1900 deg C after 600s testing.

Tuesday, January 28, 2014

2nd Pacific Rim Engineering Ceramics Summit

Pacific Rim Ceramic Technologies: Trends and Directions II

Room: Coquina Salon C
Session Chair: Min Wang, The University of Hong Kong

8:10 AM

(ICACC-PRECS-012-2014) Bioceramics and Nanocomposites for Human Hard Tissue Repair and Regeneration (Invited)

M. Wang*, The University of Hong Kong, Hong Kong

Contemporary bioceramics research started in the 1970s, which led to the phenomenal growth of bioceramics as viable materials for the repair and reconstruction of human hard tissues. Various bioceramics in different forms have since been developed for dental, orthopaedic and other applications. Rapid progresses in nanoscience and nanotechnology in recent years have greatly advanced bioceramics R & D. Apart from improved mechanical properties, nanostructured bioceramics may provide better biological performance. Furthermore, nano-scale features of bioceramics can influence cell behaviour and hence tissue formation. Using bioactive bioceramics to develop non-porous nanocomposites for hard tissue repair and porous nanocomposite scaffolds for hard tissue regeneration is a major research area. Many polymer-based composites containing micro- or nano-sized bioceramic particles such as hydroxyapatite have been produced and assessed for repairing bone in low load-bearing parts of the body. Multifunctional nanocomposite scaffolds incorporated with bioactive calcium phosphate nanoparticles can be made using various techniques and they exhibit high potential for bone tissue regeneration. In this paper, some of our research on bioceramics and porous and non-porous nanocomposites will be presented. A few critical issues in biomaterial design, fabrication and evaluation will be discussed.

8:40 AM

(ICACC-PRECS-013-2014) Two photon polymerization of inorganic-organic hybrid materials (Invited)

R. Narayan*, UNC/NCSU Joint Department of Biomedical Engineering, USA

Laser processing is finding growing use in fabricating devices for diagnosis and treatment of medical conditions. Two photon polymerization is an additive, layer-by-layer processing approach in which temporal and spatial overlap of photons is used for photopolymerization of photosensitive resins within highly-localized volumes. A medical device may be prepared by polymerizing the photosensitive resin along a laser trace that is moved in three dimensions with a micropositioning stage. Several classes of photosensitive resins, particularly inorganic-organic hybrid materials, may be processed by means of two photon polymerization. Two photon polymerization provides many advantages over conventional methods for scalable processing of medical devices with microscale or nanoscale features. Two photon polymerization can be performed in a conventional setting; no cleanroom facilities are required. In addition, two photon polymerization is a rapid, single-step process. We have used two photon polymerization to create tissue engineering scaffolds, microneedle arrays, and other medical devices. Use of novel photosensitive resins and characterization of two photon polymerization-processed medical devices will be discussed.

9:00 AM

(ICACC-PRECS-014-2014) Nanoscale structure and modification of Biomaterials (Invited)

F. Rosei*, INRS, Univ of Quebec, Canada

Modifying the nanostructure/chemistry of materials allows to optimize their properties [1]. Our strategy rests on creating nanopatterns that act as surface cues [2,3], affecting cell behavior. Chemical oxidation creates unique topographies [4], becoming a general strategy to improve biocompatibility. Our treatment selectively inhibits fibroblast growth while promoting osteogenic cell activity [5] in vitro. Enhancement of mechano-biocompatibility may occur by coating with spider silk [6, 7]. Improvement of antibacterial properties using laser and plasma strategies will also be discussed [8].

9:20 AM

(ICACC-PRECS-015-2014) Progress in Research and Development on MAX Phases and the Perspectives (Invited)

Z. Sun*, AIST, Japan

It has been some14 years since the term "MAX phase" came into view. The MAX phases are a group of layered ternary compounds with the general formula $M_{n+1}AX_n$ (M: early transition metal; A: group A element; X: C and/or N; n=1-3), which combine some properties of metals, such as good electrical and thermal conductivity, machinability, low hardness, thermal shock resistance and damage tolerance, with those of ceramics, such as high elastic moduli, high temperature strength, and oxidation and corrosion resistance. The publication of papers on the MAX phases has shown an almost exponential increase in the past decade. The unique properties made this family of compounds attractive to materials scientists and industries alike. MAX phases in the form of bulk, film, powder, as well as composite have been synthesized in the past years, totaled over 60 in the family, not including their solid solutions or those whose existence only predicted by theoretical studies. Physical and mechanical properties of these MAX phases, and the MAX-based materials, were extensively explored. This talk will cover the latest development on the synthesis, properties of MAX phases, and some perspectives of their applications.

10:00 AM

(ICACC-PRECS-016-2014) Development of Joining Process Technology of Silicon Carbide (Invited)

S. Suyama*, Toshiba Corporation, Japan

High-strength reaction-sintered silicon carbide (High-strength RS-SiC) with strengths in the 1000 MPa class has been developed, featuring a fully dense structure, small sintering shrinkage, and low sintering temperature. Applications of this material to large and/or complex-shaped components are expected, and a suitable joining process is thus needed for practical use. In this study, the newly joining process was developed in which selected reaction-sintering process to match the CTE of joining layer with the substrate, we achieved both good thermal stability and high joint strength in high-strength RS-SiC components joined with SiC and Si in which the size of the microstructure was controlled. The coefficients of thermal expansion of the high-strength RS-SiC substrate and the joint layer were almost identical because the compositions of the substrate and the joining layer were almost the same. Various components could be joined using newly developed process.

10:20 AM

(ICACC-PRECS-017-2014) Prospective and challenges of nanolaminated ternary carbides and nitrides (MAX phases) (Invited)

Y. Zhou*, Aerospace Research Institute of Material & Processing Technology, China

The nanolaminated ternary carbides and nitrides with a general formula of Mn+1AXn, where M is an early transition metal, A is a

IIIA or IVA element, X is C or N, combine the merits of both metals and ceramics. The salient properties of this family of materials include low density, high strength and modulus, damage tolerance, being machinable and resistant to thermal shock and oxidation. The unique combination of these properties make them promising for applications in extreme environment like aerospace vehicles, GIV nuclear reactors as well as in commercial products such as solid oxide fuel cell, automobile engine catalysts etc., in the form of either structural components or corrosion resistant coatings. However, the high fabrication cost, low high-temperature strength and poor high-temperatures stability are the main challenges to their more extensive applications. In this presentation, methods to reduce the fabrication cost like slip casting/pressureless sintering, electrophoretic deposition (EPD), and reaction/diffusion bonding to make large size components will be introduced. Novel methods to improve the high temperature properties such as solid solution strengthening, particulate strengthening, formation of protective layers at high temperatures will also be discussed. Finally, structural features and properties of recently discovered new materials will be outlined.

10:40 AM

(ICACC-PRECS-018-2014) Genome Approach for advanced ceramics (Invited)

J. Wang*, Institute of Metal Research, China

Recent progress in ceramic modeling has significantly enhanced the efficiency to understand fundamentals of properties, to optimize performances and to design new ceramics with tailored properties. In the last ten years, ceramic genome researches are very active in China and great progresses have been made both in modeling, simulation and design of advanced ceramics. In this presentation, I will at first briefly overview some genome research projects in China. Thereafter, two major projects of my research group will be focused. The first program is the genome approach of nano-laminated transition metal carbides and nitrides, which show tunable crystal structure and fascinating macroscopic properties. The second one refers to prediction and realization of novel ceramics with very low thermal conductivity. The results demonstrate that genome approach is an efficient integrated method to develop advanced ceramics with outstanding properties.

11:00 AM

(ICACC-PRECS-019-2014) High-precision process technology for ceramic ferrules (Invited)

S. Masaki*, S. Nakano, K. Ikegai, Adamant Kogyo Co., Ltd., Japan

In recent decades, a great deal of research efforts have been devoted to fabricate zirconia ferrules that have been generally utilized as optical connectors for the physical contact of optical fibers in the fields of ICT. The optical fibers with a diameter of 125 micrometer should be linearly inserted into zirconia ferrule and uniformly aligned without any bending and crashing. In addition, the fiber core must be physically and coaxially connected with that of another fiber, because the mismatched concentricity between optical fibers can easily cause large optical loss. Thus, (1) the dimensional tolerance at submicrometer level for the inner diameter in zirconia ferrules and (2) perfect concentricity have been required. To solve these problems, we developed high-precision ceramic process technology combined with injection molding and polishing technique. Mixing of organic binder and zirconia powder, various viscosities of compounds, injection pressure, injection rate, surface roughness of core pin and high-precision polishing technology have been systematically and comprehensively studied. In the zirconia ferrules obtained, the surface roughness of inner diameter was around 10nm and typical attenuation value was less than 0.2dB. The potential and issues in applying this high precision process technology to other industrial fields such as energy, environment, aerospace and medical will be also examined and discussed.

11:20 AM

(ICACC-PRECS-020-2014) Erosion Mechanism of Ceramics in the Fluorocarbon plasma and Development of a New Plasma Resistant Materials (Invited)

S. Lee*, Y. Oh, H. Kim, Korea Institute of Ceramic Engineering & Technology (KICET), Republic of Korea

Oxide ceramics are widely used as plasma-facing materials, typically in fluorocarbon plasma in the semiconductor industry. We investigated surface interaction of the oxides through X-ray photoelectron spectroscopy technique. After exposure to fluorocarbon plasma, the ceramic surfaces consisted of a top polymer layer as thin as 1 nm with a concomitant highly fluorinated ceramic layer underneath the polymer. So, the removal rate of this non-volatile fluorinated layer determined the etch rate of the oxide, which was physically sputtered by ions incident on the surface. The surface fluorination of the oxide ceramics appears to accelerate this erosion process compared to without the fluorination. In this talk, we will also mention a few possible cases about the generation of particulate contamination from the ceramics, which has been serious concern in the semiconductor industry. Finally, possible new plasma resistant materials will be shown with new compositions and structures.

11:40 AM

(ICACC-PRECS-021-2014) New functional ceramics in Taiwan (Invited)

J. Huang*, C. Lee, National Cheng Kung University, Taiwan

The research and development of new functional ceramics in Taiwan have played decisive roles in many fields, such as information and communication, electronic, energy, sensor, biomedical application, etc,. and educated many technicians and researchers from academy to industry. In this talk, some of the designing concepts and processing strategies of new functional ceramics and their future impacts will be illustrated, based on our long-term projects in Taiwan. At first, three dimensional ceramics with highly mechanical performance were designed, including Si3N4 and Al2O3 based nanocomposites; Secondly, two dimensional ceramic film with designing of crystal composition and interfaces are included, like superior piezoelectrical response of AlN on diamond, mechanical reliability of SiN/TiAlN multi-layered coating, low-cost MLCC, high capacitance in graphene-based rechargeable battery, and bionic eye implant; Following, one-dimensional ZnO nanowires and nano-array with better optoelectrical performance and zero-dimensional nano-hybridized ceramics for drug release agents were made through the bottom-up chemical approach. These novel nanostructures will have great impact in the near future. Lastly, the innovation of carbon based materials has great influence on electronic industry and semiconductor manufacturing in Taiwan. An overview of current new functional ceramics in Taiwan will be addressed.

3rd Global Young Investigator Forum

GYIF III

Room: Coquina Salon H
Session Chairs: Annika Leifert, TU Dresden; Craig Smith, Ohio Aerospace Institute

9:00 AM

(ICACC-GYIF-011-2014) Superplasticity in yttria-stabilized zirconia ceramics

M. Shirooyeh*, University of Southern California, USA

Superplastic deformation during high temperature tensile creep test was investigated in examples from both 3-mol% yttria-stabilized tetragonal zirconia (3YTZP) and 8-mol% yttria-stabilized cubic zirconia (8Y-CSZ) fine-grained ceramics. A zirconia–spinel (3Y-TZP – 30 vol% MgAl2O4) composite was consolidated via a Current-Activated Pressure-Assisted Densification (CAPAD) process to produce a dense nanostructured zirconia–spinel ceramic. Furthermore, a zirconia (8Y-CSZ) ceramic containing a small amount of amorphous silica phase was produced and the effect of the glassy intergranular phase on grain growth during plastic deformation was examined. The experimental data as well as microstructural observations suggest zirconia ceramics containing an appropriate second phase have a potential for exhibiting excellent superplastic behavior.

9:20 AM

(ICACC-GYIF-012-2014) Fabrication of Anode-Supported Micro-Tubular Solid Oxide Fuel Cells by Dip Coating

H. J. Avila-Paredes*, R. De la Torre García, Universidad Autónoma Metropolitana Unidad Iztapalapa, Mexico

Solid Oxide Fuel Cells (SOFCs) are clean, efficient and environmental-friendly devices that convert chemical into electrical energy. Tubular SOFCs offer many advantages over planar cells, such as better on/off capability, higher thermal shock and thermocycling resistances, and easier sealing. In addition, higher volumetric power density is achieved when the diameter of cells is scaled-down. In this contribution, we present results of a fabrication process based on a dip coating technique to produce anode-supported micro-tubular SOFCs with a diameter of about 3 mm. By using this technique it is possible to design a porosity gradient within the anode, so that the effect of the anode functional layer is increased. Cells were produced by sequentially depositing ceramic inks, based on commercial powders of $NiO\text{-}Ce_{0.8}Gd_{0.2}O_{2\text{-}x}$ (GDC) for the anode and GDC for the electrolyte on a polymer substrate (sacrificial core). After sintering of the half-cells, the cathode (commercial $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$) was deposited on the electrolyte and sintered. The active cathode length for the complete cells is around 10 mm.

GYIF IV

Room: Coquina Salon H
Session Chairs: Thomas Fischer, University of Cologne; Hugo Avila-Paredes, Universidad Autónoma Metropolitana Unidad Iztapalapa

10:00 AM

(ICACC-GYIF-013-2014) Processing and microstructure of Si3N4 based nanocomposites for highly wear-resistant application

C. A. Lee*, National Cheng Kung University, Taiwan; H. Lu, National Chin-Yi University of Technology, Taiwan; T. Goto, Tohoku University, Japan; H. Lin, Oak Ridge National Laboratory, USA; R. Tu, Wuhan University and Technology, China; P. K. Nayak, National Tsinghua University, Taiwan; C. Chen, National Cheng Kung University, Taiwan; J. Huang, National University of Kaohsiung, Taiwan

Si3N4 have received a great deal of attention in structural and wear applications at ambient and elevated temperatures. In order to achieve Si3N4 with better wear performance than before, we design the Si3N4 based nanocomposites by (i) incorporating nano-TiC and (ii) doping with Y2O3 as sintering aids. In the first part, the nanopowder mixture of β-Si3N4 and TiC were rapidly consolidation by spark plasma sintering. The synthesized Si3N4/TiC nano-nano composites with 20&30 wt% TiC content exhibit the lowest wear rate, probably attributing to lower asperity stresses and wear damage on the contact surfaces; Secondly, amorphous Si3N4 nanopowders doped with 6wt% Y2O3 was our interest owing to the potential having better mechanical properties at high temperatures. Because this nanopowder pre-existed large amount of surface oxygen, high energy ball milling of nanosized carbon black and Si3N4 powder and following carbothermal reduction treatment was applied, and thus monolithic Si3N4 nanoceramic free of Si2N2O was obtained, resulting in lower wear rate than that without removal of oxygen. For the two systems, their wear performances are mainly dominated by microstructures and chemical composition of sintering bulks, and therefore the relationship between processing parameters and microstructural evolution of Si3N4 nanoceramics and Si3N4/TiC based nanocomposites will be addressed.

10:20 AM

(ICACC-GYIF-014-2014) The Importance of Tribofilms on the Tribological Behavior of Layered Nanolaminates (MAX Phases)

S. Gupta*, University of North Dakota, USA

It is fairly well established that the layered hexagonal MAX phases are thermodynamically stable nanolaminates displaying unusual and sometimes unique properties. These phases are so-called because they possess a Mn + 1AXn chemistry, where n is 1, 2, or 3, M is an early transition metal element, A is an A-group element and X is C or N. They are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously soft for transition metal carbides and nitrides. Recently, first generation MAX Phase based composites shafts were successfully tested against Ni-based superalloy at 50,000 rpm. This study further demonstrates the potential of MAX Phases and their composites in different tribological applications. The main objective of this presentation is to present recent progress in understanding the tribological behavior of MAX Phases and their composites. I will also demonstrate a way of classifying the different tribofilms to understand the complex tribological behavior of these solids over a wide range of different experimental conditions.

10:40 AM

(ICACC-GYIF-015-2014) Mechanical Reinforcement of Copper Films with Ceramic Nanoparticles

A. Leifert*, B. Schumm, N. Mohamed-Noriega, A. Meier, TU Dresden, Germany; C. Nowka, Leibniz Institute for Solid State and Materials Research Dresden, Germany; G. Mondin, S. Doerfler, TU Dresden, Germany; S. Hampel, Leibniz Institute for Solid State and Materials Research Dresden, Germany; E. M. Lopez Cuellar, Universidad Autonoma de Nuevo Leon, Mexico; S. Kaskel, TU Dresden, Germany

The homogeneous distribution of different ceramic nanoparticles (NPs) into copper films by a wet chemical approach results in metal matrix composites with metallic electrical conductivity and enhanced hardness and wear resistance. Metal ion-containing polymeric precursor solutions were deposited by dip-coating and transformed to metal films by annealing and reduction. TiO_2, TiC and SiC NPs in different concentrations were dispersed in the precursor solution. The use of nanoparticulate ceramics permits the homogeneous distribution within the metallic film. The wet chemical approach enables simple variation of the desired NP material and concentration in the composite. Incorporation and distribution of the NPs were shown by X-ray diffractometry and energy-dispersive X-ray spectroscopy, respectively. Sheet resistance was determined by four-point measurements and was only marginally increased by the presence of NPs compared to pure copper films. The mechanical properties were investigated by a pencil hardness scratch test (ISO 15 184) and nanoindentation. All NPs tested increased the hardness and wear resistance of the composite copper films. TiO_2 showed the highest effect. By incorporation of various, finely dispersed ceramic NPs into copper films, metal matrix composites with metallic conductivities as well as enhanced hardness were prepared.

11:00 AM

(ICACC-GYIF-016-2014) Matrix cracking in 3D fiber-reinforced SiC/SiC

C. Smith*, R. Bhatt, Ohio Aerospace Institute, USA

SiC/SiC ceramic matrix composites with 3D fiber reinforcement are currently being explored by NASA as candidate materials for 2700°F applications. 2D fiber-reinforced CMCs suffer from deficiencies such as relatively low through-thickness thermal conductivity, impact resistance, and interlaminar tensile and shear strengths. These properties can be improved by using 3D architectures. In addition, modeling has shown that the through-thickness fibers may lead to better infiltration of the matrix. Samples with 2D and several different 3D architectures and were prepared with a hybrid CVI/PIP matrix. Room temperature tensile tests were conducted, along with acoustic emission and electrical resistance measurements, to determine the influence of fiber architecture on tensile properties and to quantify damage mechanisms and failure modes.

11:20 AM

(ICACC-GYIF-017-2014) Characterization of Matrix Materials for Additive Manufacturing of Silicon Carbide-Based Composites

S. X. Zhu*, The Ohio State University, USA; M. C. Halbig, NASA Glenn Research Center, USA; M. Singh, Ohio Aerospace Institute, USA

Silicon carbide-based ceramic matrix composites are enabling materials for a number of high-temperature and extreme environment applications. Current composite fabrication methods include chemical vapor infiltration (CVI), melt infiltration (MI), polymer infiltration and pyrolysis (PIP), or hybrid fabrication methods. These approaches are labor intensive, time and energy consuming, and often expensive. The development of cost-effective additive manufacturing approaches like Laminated Object Manufacturing (LOM) will further increase the viability of their implementation. However, in order to investigate fabrication of silicon carbide fiber reinforced silicon carbide matrix composites (SiC/SiC), a number of materials and process parameters have to be developed and optimized. In this study, polymer mixtures consisting of various types of SiC, Si, and C particulates along with other additives were used as fiber prepreg materials. The prepreg materials were characterized using Thermogravimetric Analysis (TGA) to observe characteristic decomposition patterns in air and nitrogen from room temperature up to 1000°C. X-ray diffraction (XRD) was used to identify phases in samples pyrolyzed at temperatures of 700°C, 1000°C, 1200°C, and 1450°C. Effect of filler particle size, temperature, and pyrolysis conditions on the weight loss behavior and final reaction products have been studied.

11:40 AM

(ICACC-GYIF-018-2014) Damage Characterization of EBC Coated SiC/SiC Ceramic Matrix Composites Under Imposed Thermal Gradient Testing

M. P. Appleby*, G. N. Morscher, The University of Akron, USA; D. Zhu, NASA Glenn Research Center, USA

Due to their high temperature capabilities, Ceramic Matrix Composite (CMC) components are being developed for use in hot-section aerospace engine applications. Harsh engine environments have led to the development of Environmental Barrier Coatings (EBCs) for silicon-based CMCs to increase thermal and environmental capabilities. This study aims at understanding the damage mechanisms associated with these materials under simulated operating conditions. A high heat-flux laser testing rig capable of imposing large through-thickness thermal gradients by means of controlled laser beam heating and back-side air cooling is used. Tests are performed on uncoated composites, as well as CMC substrates that have been coated with state-of-the-art ceramic EBC systems. Results show that the use of the EBCs may increase temperature capability and performance by reducing the effects of stressed oxidation and environmental degradation. The ability of electrical resistance (ER) and acoustic emission (AE) measurements to monitor damage state during high temperature testing is shown; suggesting their usefulness as a valuable health monitoring technique. Micromechanics models are used to describe the localized stress state of the composite system, which is utilized along with ER modeling concepts to develop an electromechanical model capable of characterizing material behavior.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Energy

Room: Oceanview
Session Chairs: Christine Luscombe, University of Washington; Isabella Concina, CNR-IDASC SENSOR Laboratory & Brescia University

8:00 AM

(ICACC-FS2-013-2014) Nanochemistry for Engineered Functional Materials for Light Harvesting and Energy Applications (Invited)

S. Mathur*, T. Fischer, University of Cologne, Germany

Chemical nanotechnologies have played, in the past few decades a major role in the convergence of life, physical and engineering sciences leading not only to simple collaboration among the disciplines but to a paradigm shift based on true disciplinary integration. The successful synthesis, modification and assembly of nanobuilding units such as nanocrystals and wires of different materials have demonstrated the importance of chemical influence in materials synthesis, and have generated great expectations for the future. Implications of chemistry as an innovation motor are now visible for knowledge leap forward in various sectors such as materials engineering for energy, health and security. Inorganic nanostructures inherit promises for substantial improvements in materials engineering mainly due to improved physical and mechanical properties resulting from the reduction of microstructural features by two to three orders of magnitude, when compared to current engineering materials. The examples will include chemically controlled production of heterostructures for sensing and light-harvesting application.

8:20 AM

(ICACC-FS2-014-2014) All solid hybrid thin film solar cells with perovskite materials (Invited)

S. Hayase*, Kyushu Institute of Technology, Japan

This report is on all-solid dye-sensitized solar cell (Hybrid thin film solar cells) consisting of a transparent conductive oxide layered glass/a dense TiO2 layer working as a hole blocking layer/a porous TiO2 layer/a metal oxide thin layer (surface passivation layer)/a perovskite layer (CH3NH3PbI3)/a hole collection layer/Ag/Au layers. It was found that surface traps of TiO2 at around 4.2 eV from vacuum level (trap density: 10(15)/cm3) disappeared by the surface passivation. Photovoltaic performance of all-solid dye sensitized solar cells without TiO2 surface passivation was 6.59%. The efficiency increased to 7.53 % when the porous TiO2 layer was passivated with the Y2O3 thin layer. The electron injection and charge recombination kinetics measured by transient spectroscopic methods are reported. Finally we report 10.2% all solid hybrid thin film solar cells.

8:40 AM

(ICACC-FS2-015-2014) Thermal conductivity of graphene laminates and nanocomposites for energy applications (Invited)

G. Fanchini*, University of Western Ontario, Canada

While the thermal conductivity of individual graphene flakes have been extensively studied during the last 5 years, investigations on graphene laminates for energy applications are still at an early stage. Here, we review our efforts in measuring and modeling the thermal properties of transparent-conducting graphene laminates by thermooptical techniques to link such properties to the optoelectronic properties of the films [1]. Thermal conductivity decreases with increasing electrical conductivity. For sufficiently large platelets, the influence factor in controlling the thermal conductivity is represented by junctions between neighboring graphene platelets. The thickness of such junctions is determined by the number of graphene layers (N) forming each platelet. Since both the thermal and electrical properties depend on N, a model that leads to a relation between thermal and electrical conductivity and is general enough to be applied to a large class of laminates, can be drawn. Finally, we describe the thermophysical properties of specific graphene-based thin film nanocomposites, including graphene-RNA mixtures [2] and graphene-poly(3,4-ethylene-dioxythiophene):polystyrene-sulfonate (PEDOT:PSS) electrodes for solar cells [3]. 1.Ahmed, Ezugwu, Divigalpitiya, Fanchini, Carbon 61 (2013) 595 2.Sharifi, Ahmed, Fanchini, subm (2013) 3.Ezugwu, Ahmed, Divigalpitiya, Fanchini, TSF 534 (2013) 520

9:00 AM

(ICACC-FS2-016-2014) Improving Photoresponse of Dye-Sensitized Solar Cell by Co-Sensitization (Invited)

L. Han*, National Institute for Materials Science, Japan

In recent years, wide interesting was attracted by using two or more dyes with complementary absorbance wavelength to enhance light harvesting in dye-sensitized solar cells (DSCs). In this presentation, the effort of developing co-sensitizers for Ru dye will be discussed. In the incident-photon-to-current efficiency (IPCE) spectrum of black dye based DSC, there is a dip induced by the absorption of triiodide at around 380 nm and the IPCE value at wavelength range from 450 to 550 nm is relatively lower than the high platform at = 600-700 nm. Thus we aimed to improve the lower photoresponse at these regions by developing complementary co-sensitizers for black dye. The ideal co-sensitizer should have high molar extinction coefficient than that of triiodide at the near UV region and have a moderate molecular size to co-adsorb with black dye on TiO2 surfaces, and in the meantime effectively suppress the electron from TiO2 recombination with I3 in the electrolyte as well as dyes aggregation. Accordingly, we developed a simple donor-π-acceptor (D-π-A) structured organic dyes Y1 and HC5 with dibutoxyphenyl or N,N-dioctylaminophenyl group as the donor moiety, thiophene as a π-spacer, and cyanoacetic acid as the acceptor/anchor, which successfully enhanced the IPCE of black dye at UV region in a cocktail DSC and helped achieve the highest certified conversion efficiency of 11.6%.

9:20 AM

(ICACC-FS2-017-2014) Excitonic Solar Cells: Engineering Materials And Processes To Boost Solar Energy Conversion (Invited)

I. Concina*, University of Brescia, Italy

Excitonic solar cells (XSCs) have been often presented as promising and green alternatives to traditional photovoltaics, thanks to the use of relatively non toxic materials together with simple processes that should bring together good photoconversion efficiencies while maintaining acceptable long term stability. XSCs are devices relying on optimized physico-chemical equilibria among all the components and whose functional performances are dependent on correct processing, too. Herein, we review the current status of research on XSCs, with a particular emphasis on dye- and quantum dots-sensitized solar cells (DSCs and QDSCs, respectively). We will present and discuss some critical issues, in particular: i) fabrication of efficient photoanodes based on nanostructured metal oxides (TiO2, ZnO and SnO2) through the engineering of structures and band gaps and the application of hybrid organic-inorganic networks; ii) use of mild processes for device fabrication, with a particular consideration for both a near future scale up and compatibility with plastic substrates for flexible photovoltaics; iii) fabrication of highly efficient QDSCs, based on the reproducible and straightforward preparation of efficient cathodes, which is at present one of the factors limiting the production of reproducible devices. The optimization of the harvesting layers will be as well discussed.

10:00 AM

(ICACC-FS2-018-2014) Designing Novel Nanostructured Materials for High-Performance and Low-Cost Fuel Cells (Invited)

S. Sun*, Institut National de la Recherche Scientifique, Canada; G. Zhang, Institut National de la Recherche Scientifique, Canada; M. Cai, General Motors Research & Development Center, USA; R. Li, the University of Western Ontario, Canada; J. Dodelet, Institut National de la Recherche Scientifique, Canada; X. Sun, the University of Western Ontario, Canada

PEM fuel cells (PEMFCs) are expected to play dominant role in future clean energy solutions for various applications. However, short life-time and high cost of Pt catalyst are the main obstacles for the commercialization of PEMFCs. It is well accepted that the catalytic activity and durability of Pt catalysts are highly dependent on their morphology, and therefore the exploration of novel Pt nanostructures has become an area of considerable interest. To date, most studies have mainly focused on zero-dimensional (0D) nanoparticles of Pt. Very recently, one-dimensional (1D) structures of Pt, such as nanowires (NWs), have emerged as a new type of promising fuel cell catalyst, exhibiting much enhanced performance compared to the commercially-used Pt/C nanoparticle catalysts. Here, we will systematically introduce our recent work on 1D Pt NWs for fuel cells, including: (i) A facile method to synthesize Pt NWs (4 nm in diameter), which exhibit 3-times better activity and 5-fold better durability than the state-of-the-art commercial catalyst made of Pt nanoparticles;1-3 (ii) PtNWs on Sn@CNT nanocable 3D electrode with much enhanced performance in ORR, MOR, and CO tolerance;4 (iii) Diameter control of Pt NWs grown on CNTs and N-doped CNTs.

10:20 AM

(ICACC-FS2-019-2014) Integrating 2D Materials in Electron emission and PEM fuel cells (Invited)

D. H. Chua*, National University of Singapore, Singapore

Today's 2D nanosheets, ranging from graphene and metal dichalcogenides, have attracted much attention due to their unique properties with low dimensional effects and chemically versatile. As such, this gives rise to many potential applications such as chemically active electrocatalyst in hydrogen evolution, electrically active materials in optoelectronics and unique morphology in electron emitters and energy storage devices. In this talk, I shall like to give short review on the application of these 2D composite materials in large area electron emitters and PEM fuel cells. We have shown that with careful design and engineering, 2D graphene films can be effective as electron emitters. Through modifying graphene and MoS2, the hybrid 2D composites can prove to be more effective. I shall further report on some of the approach used in obtaining electron emitters and how it can be translated for direct applications as highly efficient and corrosion-resistant electrodes in PEM fuel cells.

10:40 AM

(ICACC-FS2-020-2014) Development of quantum dot sensitized solar cells

Y. Tachibana*, RMIT University, Australia

Semiconductor quantum dots (QD) have recently received immense interest in regards to solar energy conversion devices, particularly for photovoltaic cells. The attractive property of these dots is known as "quantum size effect", where the band gap energy becomes larger by reducing QD size. By employing this concept, the light absorption wavelength range can be tuned by controlling the QD size. The potential energy levels of the QD conduction and valence bands can also be adjusted with the QD size. An appropriate size will be selected to optimize efficient photo-induced charge separation and retard charge recombination at the QD interfaces (Optimum Gibbs free energy difference), thereby facilitating performance improvement of their photovoltaic devices. In this presentation, we will discuss the relationship of the QD interfacial nanostructures with the photo-induced electron transfer rates, identified by time-resolved laser spectroscopies, and solar energy conversion efficiency. Synthetic strategies of semiconductor QDs, and interfacial interaction of QDs with metal oxide semiconductors and electrolytes will be shown. The relationship of interfacial dynamics with PV device functions, and the kinetic optimization to improve solar cell performance will be discussed. We acknowledge the JST PRESTO program and the University-Industry Collaboration Office, Osaka University, Japan for their financial support.

Optics I

Room: Oceanview
Session Chair: Fiorenzo Vetrone, INRS-EMT, Université du Québec

11:00 AM

(ICACC-FS2-021-2014) Detection of Plasmonic Induced Heating Using Terahertz Radiation (Invited)

R. Naccache, M. Clerici, L. Razzari, F. Vetrone, R. Morandotti*, INRS-EMT, Canada

The rapid ascent of nanoscience has garnered significant attention in recent years. Much of the interest generated has dealt with the use of nanoparticles in imaging and therapeutics. Of particular interest are the metal nanoparticles (MNPs), which show a surface plasmon resonance (SPR) following excitation with an appropriate irradiation source. An interesting by-product of the SPR is a localized temperature increase, which in an in vitro or in vivo setting can be used to heat the interstitial waters and induce hyperthermia in cells. This can be used differentiate healthy versus cancerous cells since the latter typically contain larger quantities of these interstitial waters. Detection and imaging are possible via the use of Terahertz (THz) waves, which possess absorption and refractive indices that are sensitive to temperature changes in the cell waters. Hence, heating, using SPR, is investigated and temperature changes in water are detected in a THz pump and probe setup.

11:20 AM

(ICACC-FS2-022-2014) Patterning of multicomponent oxides intended for photonic applications (Invited)

J. Margot*, Université de Montréal, Canada; M. Chaker, INRS-EMT, Canada

Despite its successful implementation in industry, etching has mainly evolved empirically rather than through scientific investigation, which considerably limits technology transfer. Therefore, except for a few classical materials like Si et SiO2, only a limited amount of publications is available for unconventional materials such as ferroelectric materials (PLZT, BST, SBT), electro-optic materials (SrTiO3, LiNbO3, CaBaNb2O6), metal-insulator transition materials (VO2), and unconventional conductors (Pt, IrO2, ITO, LaNiO3). However, such materials are central to a number of advanced applications and their patterning is one of the key elements towards their integration into devices. Developing reliable etching processes is challenging as most of them present a low reactivity with usual etching gases such as fluorinated and chlorinated gases. Their etching is mainly governed by ion sputtering and the reactive gases forming the plasma sometimes interact with materials surface to form compounds that inhibit etching. In this presentation, we will review the work performed by our group over the last decade on the etching of multicomponent oxides, with a particular focus on the etching of SrTiO3 and CaBaNb2O6. We will also show how simulation can provide information on the redeposition of sputtered species on patterned surfaces, taking as an example the case of an unconventional conductor.

11:40 AM

(ICACC-FS2-023-2014) Nanoantenna Arrays Resonating in the Terahertz Spectral Region (Invited)

L. Razzari*, INRS-EMT, Canada; A. Toma, Istituto Italiano di Tecnologia, Italy; M. Clerici, INRS-EMT, Canada; S. Tuccio, M. Chirumamilla, Istituto Italiano di Tecnologia, Italy; M. Shalaby, INRS-EMT, Canada; C. Liberale, R. Proietti Zaccaria, G. Das, F. De Angelis, Istituto Italiano di Tecnologia, Italy; M. Peccianti, R. Morandotti, INRS-EMT, Canada; E. Di Fabrizio, Istituto Italiano di Tecnologia, Italy

Optical nanoantennas are nano-fabricated devices able to convert free-space optical radiation into localized energy. Due to this, they can be used to enhance the electromagnetic field and to localize it on a scale well beyond the diffraction limit. Nanoantennas have thus become key elements for a variety of applications, including single-molecule spectroscopy, nano-imaging and extreme nonlinear optics. Notwithstanding this, most of the achievements have been so far limited to the visible and infrared spectral regions. Our aim is to extend these concepts to the terahertz region of the electromagnetic spectrum. In my talk, I will review our recent results regarding arrays of gold nanoantennas resonating at terahertz frequencies. These nanostructures have been designed to resonate in a range (~ 1-2 THz) that is particularly interesting for applications and covers the spectral band offered by standard zinc telluride sources. In addition, numerical simulations have shown that terahertz nanoantennas exhibit a field enhancement factor of a few hundreds in the near field, suggesting their use in terahertz few-molecule spectroscopy and localized terahertz nonlinear experiments.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanics & Characterizations I

Room: Coquina Salon D
Session Chairs: Jonathan Salem, NASA GRC; Rajan Tandon, Sandia National Lab

8:00 AM

(ICACC-S1-001-2014) Improving the Fracture Toughness from Atomic-Scale Modeling

M. Bauchy*, M. Abdolhosseini Qomi, H. Laubie, MIT, USA; C. Bichara, CINaM, France; R. Pellenq, MIT, USA; F. Ulm, CINaM, France

Rigidity theory has revealed to offer a practical scheme to study glasses while only relying on their topology. It has led to the recognition of a rigidity transition, which separates flexible glasses, showing internal degrees of freedom that allow local deformations, from stressed-rigid glasses. This transition occurs when the number of constraints (bond-stretching and bond-bending) equals the number of degrees of freedom. Recently, the existence of an intermediate phase (IP) characterized by a rigid but unstressed network was reported. Inside the IP, glasses show remarkable properties such as a maximal fracture toughness. The rigidity framework has been used to study C-S-H, the binding phase of cement, which is believed to be responsible of its mechanical properties and its durability. For the analysis, we rely of 150 C-S-H samples produced by molecular dynamics simulations. We report the existence of a composition-driven rigidity transition in C-S-H, the latter being flexible at high Ca/Si and stressed-rigid at low Ca/Si. Inspired by the many studies in glass science relying on the rigidity theory, this analysis makes it possible to make some prediction about the composition dependence of the mechanical properties. Predicted elastic moduli and hardness show a good agreement with experiments. We demonstrate that the isostatic cement, characterized by a Ca/Si of 1.5 show optimal fracture toughness.

8:20 AM

(ICACC-S1-002-2014) Evaluation of Fracture Mechanics Based Tools for Bi-Material Interface Design

P. M. Rao*, X. Wang, United Technologies Research Center, USA; R. G. Hutchinson, Pratt & Whitney, USA; G. V. Srinivasan, United Technologies Research Center, USA

The demand for sustaining continually higher temperatures in the hot sections of gas turbine engines is driving the application of Thermal Barrier Coatings (TBCs) in such harsh operating environments. In service, TBCs are subject to delamination and spallation, thereby rendering their adequate design a challenging task. Computational methods such as the J-integral method, the Virtual Crack Closure Technique (VCCT) and Cohesive Zone Modeling (CZM) are evaluated in a parametric framework to predict the interfacial crack driving force at the bi-material junction of a model TBC-substrate system. The crack-tip strain energy release rate G, computed either via the J-integral method or the VCCT, gives the interfacial crack driving force. Each of the above methods is evaluated against standard metrics: ease of problem setup, computing time and accuracy of the results as compared to published analytical solutions. The predicted G is supplied as input to the CZM framework, which is used to perform parametric investigations of mixed-mode crack propagation at the model TBC-substrate bi-material interface.

8:40 AM

(ICACC-S1-003-2014) In-plane shear response of continuous fiber ceramic matrix composites: modeling and experiment

V. P. Rajan*, F. W. Zok, University of California, Santa Barbara, USA

The in-plane shear response of continuous fiber ceramic matrix composites (CMCs) was investigated both experimentally and theoretically. Iosipescu shear tests were conducted on crossply laminates. Digital image correlation was used to capture the strain evolution of the composite under load, as well as to assess whether the Iosipescu test induces a uniform state of shear in the specimen ligament. In tandem with the experimental efforts, a micromechanics-based model for the shear response of a unidirectional CMC was developed. Representative volume elements were generated for both cracked and uncracked CMCs subject to shear loading, and were simulated in a commercial finite element package. Fibers were found to undergo local bending at matrix cracks: a mechanism that might limit shear ductility in these materials. Analytical expressions were developed that capture the dominant stress distributions (bending and tension) within the constituents. Using a fracture mechanics approach, the steady-state matrix cracking stress in shear was estimated in the limit of large slip lengths. The result is analogous to those of Aveston-Cooper-Kelly (1961) and Budiansky-Hutchinson-Evans (1986) for the matrix cracking stress of a unidirectional CMC in uniaxial tension.

9:00 AM

(ICACC-S1-004-2014) Degradation in mechanical performance due to weave defects in a 3D woven ceramic matrix composite

J. H. Shaw*, F. W. Zok, UC Santa Barbara, USA

Textile-based CMCs offer the ability to incorporate features such as cooling holes or attachment points directly into the fabric preform without the need for subsequent machining of the densified composite and without cutting any fibers. Other (undesirable) features, such as geometrical variability of the tow trajectories, may also be introduced during the weaving process or handling of the woven preform. Digital image correlation has been used to study the effects of such features on the tensile response of woven C/SiC composites. This talk will discuss the degradation in mechanical performance due to individual defects as well as differences observed in the local failure process.

9:20 AM

(ICACC-S1-005-2014) Electromechanical Modeling of SiC/SiSiC Composites Under Tension

C. R. Baker*, E. Maillet, G. N. Morscher, M. P. Appleby, University of Akron, USA

The implementation of Ceramic Matrix Composites (CMCs) in high temperature applications necessitates the acute understanding of stress-dependent damage evolution. Monitoring the damage state of CMCs via the use of electrical resistance (ER) has been shown to be effective, being exceptionally sensitive to transverse matrix cracking and subsequent damage accumulation. However, ER behavior is not only a function of the damaged state of the composite, but also its local stress state. Here, several earlier concepts in ER modeling are adopted, but extended to allow for more accurate assumptions, including interfacial wear, stochastic crack initiation and others. Comparison with experiment shows good agreement, indicating even more potential as an accurate damage and health monitoring technique.

10:00 AM

(ICACC-S1-006-2014) High Velocity Impact Resistance of SiC/SiC Composites

C. R. Baker*, University of Akron, USA; A. L. Gyekenyesi, Ohio Aerospace Institute, USA; G. N. Morscher, E. Maillet, University of Akron, USA

Foreign object damage costs the aviation industry over $10B annually. As the implementation of non-oxide ceramic matrix composites (CMCs) in aerospace applications approaches, the acute understanding of the impact resistance as well as the associated residual properties becomes increasingly necessary. To that end, high velocity impact resistance and post-impact mechanical performance of SiC/SiC composites were studied experimentally. In situ acoustic emission monitoring was utilized during the ballistic tests. In addition, post-impact nondestructive evaluation (NDE) techniques were performed revealing complicated damage morphology. Select specimens were also tested destructively to confirm the NDE observations. Correlations between NDE results and post-impact mechanical properties were made with the results being utilized for models that capture impact resistance and residual properties.

10:20 AM

(ICACC-S1-007-2014) Origin of "Tough Behavior" in Short Carbon Fiber-SiC Matrix Composites: Discussion Based on Micro-Fracture Process

R. Inoue*, H. Kakisawa, Y. Kagawa, The University of Tokyo, Japan; Y. Kagawa, National Institute for Materials Science, Japan

Short carbon fiber-SiC matrix (SCF/SiC) composite behaves as a very tough material and allows formation and existence of numerous numbers of micro-cracks. However, fracture toughness of SCF/SiC composite is in the range of monolithic ceramics: 2~3 MPam1/2. Tough mechanical behavior of SCF/SiC composite is difficult to explain from its fracture toughness. In the present study, SCF/SiC composite was cut into compact disk specimen and DCDC specimen, and mechanical tests are done at room temperature using these specimens. Micro-damage evolution process of SCF/SiC composite from stress concentration source is directly observed. The result shows that failure of SCF/SiC composite is completely independent of the existence of the source, but depends on local heterogeneous structure. Fracture model is made based on the observation and role of short carbon fiber bundle in the composite is discussed using the developed fracture model; especially in terms of energy fracture criterion.

10:40 AM

(ICACC-S1-008-2014) Effect of Specimen Geometry on Microstructural Fracture Behavior in Nano Composites under HVEM

H. Serizawa*, Osaka University, Japan; T. Shibayama, Hokkaido University, Japan; H. Murakawa, Osaka University, Japan

As a result of R&D efforts about microstructural evaluation techniques of advanced multifunctional material, an in-situ observation method of fracture behavior on nano structures by using high voltage electron microscope (HVEM) has been developed. By using this method, interfacial fracture behavior of a miniaturized double notch shear test (DNS) for SiC fiber reinforced SiC matrix composite was observed and the inter-laminar shear strength between SiC matrix and coated carbon layer on SiC fiber was also measured. In addition, by using the finite element method with the interface element, the fracture behavior of miniaturized DNS could be demonstrated. However, the influence of specimen geometry on fracture behavior has not been revealed. So, in this research, the finite element analyses with the interface element were conducted by changing the geometry of the miniaturized DNS to identify the appropriate condition for measuring the inter-laminar shear strength. As a result of serial computations, one of the most adequate specimen geometry was found to be 25 micro meter in length, 15 micro meter width and 0.15 micro meter in thickness, where the distance between double notches was 12 micro meter. Moreover, the influence of mechanical properties for SiC and the interface on the fracture behavior will be discussed in order to expand the applicability of this miniaturized test.

11:00 AM

(ICACC-S1-009-2014) Dimensioning and testing of ultra fast rotating composite structures made of carbon fiber reinforced carbon

H. Richter*, D. Weck, A. Langkamp, W. Hufenbach, Technische Universität Dresden, Germany

Textile reinforced ceramic matrix composites like carbon fiber reinforced carbons feature excellent specific strength and stiffness as well as high temperature stability. Furthermore, the textile reinforcing architecture allows the tailored adaptation of fibers according to the existing thermo-mechanical and thermo-physical load paths. Therefore textile reinforced ceramics are virtually predestined for applications in ultra fast rotating high performance components. The development of textile reinforcing architectures for fast rotating structures made of carbon-carbon composites results from extensive analyses via analytic and numerical calculating models. The rotating composite structures were optimized with regard to deformation behavior, strength and heat conduction in radial direction. Afterwards the developed disk-shaped composite structures were tested by dint of high speed centrifugation and burst tests. Thereby an improved knowledge was achieved for novel rotor design in terms of deformation behavior during centrifugal loading, limit of rotational speed and burst behavior. The analysis of burst behavior via high speed cinematography allows for documentation of burst sequences as well as classification of fragmentation patterns in burst case. This is an imperative prerequisite for the assessment of arrangements for burst protection.

11:20 AM

(ICACC-S1-010-2014) Improved Adhesive Characterization and Selection Using High Throughput Testing and Materials Informatics

M. S. Bratcher*, U.S. Army Research Laboratory, USA; M. C. Golt, Bowhead Science and Technology, LLC, USA; R. Jensen, W. Kosik, U.S. Army Research Laboratory, USA

Composite armor on Army ground vehicles requires adhesives to be selected based on multiple criteria. Much like aerospace applications, high strength adhesives are highly desirable, but at the same time, highly damage-tolerant adhesives efficiently absorb impact energy and perform well in ballistic events. Current work at the Army Research Laboratory addresses the challenge of adhesive selection through the development of a Material Selection Analysis Tool (MSAT) which is an interactive database for storing comprehensive sample attributes, raw test data, experimental procedures and test methods. Recent work includes an exhaustive study of over 1000 samples of two adhesives, an epoxy and an acrylate, using the single lap joint test with varied experimental parameters. Given the complexity of the entire data set, a materials informatics approach was required and developed to identify the adhesive properties and experimental conditions that correlate most directly to maximum strength and maximum elongation. This approach helps map the high-strength/damage-tolerance performance trade-space for these adhesives.

11:40 AM

(ICACC-S1-011-2014) Study on prediction model the stiffness of unidirectional composites

H. Zhang*, W. Wen, H. Cui, Nanjing University of Aeronautics and Astronautics, China

As known to all, the properties of composites are determined by the properties of the fibers, the matrix and the interface. In the meantime, there is no comprehensive model that can determine the stiffness as a function of the mechanical properties of their components. Most models are the functions of the properties of the fibers and the matrix. And the errors of these models come from neglect considering the properties of the interface. In this paper, a comprehensive model is developed by considering all the three components of unidirectional composites. And the predicted model is verified by experiments.

S4: Armor Ceramics

Special Topic Focus: Boron Carbide I

Room: Coquina Salon E

Session Chair: Jerry LaSalvia, U.S. Army Research Laboratory

8:30 AM

(ICACC-S4-012-2014) On microstructure and electronic properties of boron carbide (Invited)

H. Werheit*, University Duisburg-Essen, Germany

Boron carbide (homogeneity range B4.3C – B~11C) with ~ 15 atoms per elementary cell arranged in B12 or B11C icosahedra, CBC, CBB chains or B□B (□, vacancy)arrangements. Their contents depend on the actual chemical composition. They are statistically arranged, thus excluding x-ray diffraction and NMR as methods for structure analysis. This problem was solved by phonon spectroscopy on isotopically pure boron carbide. – Theoretical band structure calculations on hypothetical structures failed, concluding boron carbide to be metallic in contrast to its experimentally proved semiconducting character. The actual band scheme (gaps 2.09 and 2.41 eV) is consistent for numerous results by various experimental methods. – Seebeck coefficients of ~300 μV/K up to at least 2000 K make it a promising candidate for thermoelectric energy conversion. Theoretical speculations on superconductivity up to 28 K have been experimentally disproved.

9:00 AM

(ICACC-S4-013-2014) Synchrotron X-ray Diffraction and Raman Spectroscopy Studies of Elasticity and Structure of B4C to 70 GPa

M. H. Manghnani*, P. Dera, A. Hushur, University of Hawaii, USA

In this study synchrotron X-ray diffraction (XRD) and Raman spectroscopy measurements have been carried out on polycrystalline and single-crystal (nearly stoichiometric) B4C in a diamond-anvil cell to 70 GPa. The results, in conjunction with high-pressure ultrasonic, Brillouin measurements, are discussed in light of the shock wave data in order to understand the compression behavior, establish the equations of state, and explain the observed poor ballistic performance. Our powder XRD data show detectable discontinuous changes within the studied pressure range, and the Raman spectroscopy, electrical conductivity measurements, and shock wave data suggest a more complex behavior. Detailed strain/stress analysis based on the peak profile broadening reveals two regions of discontinuous strain change, which cannot be explained by the transformations of pressure transmitting medium. These changes can be tentatively associated with electronic transformations and changes in bonding. Preliminary results from the electrical resistivity and optical measurements support this interpretation. Single-crystal structure refinements clearly demonstrate that the sample does not exhibit inverse molecular behavior. At 60 GPa the compression of the icosahedral units is 6% smaller than the compression of the unit cell, in agreement with the spectroscopic results.

9:20 AM

(ICACC-S4-014-2014) Strain-Rate Sensitivity of the Amorphized Zone Surrounding Quasistatic and Dynamic Vickers Indentations in Boron Carbide

G. Parsard*, G. Subhash, University of Florida, USA

Whereas most structural ceramics exhibit strain-rate hardening, the reported weakening during high-velocity ballistic response of boron carbide has been attributed to a localized pressure-induced phase transformation, which results in localized loss of crystallinity. In this study, the strain-rate dependence of this localized amorphization is investigated using microVickers indentation testing at quasistatic (10-second duration) and dynamic (100 μs duration) strain rates. The resulting indentation imprints are then scanned using Raman spectroscopy to detect evidence of the phase transformation. Successive mechanical polishing steps are used to remove submicron depths of material from the indented surface of the specimens, providing access to subsurface material for further Raman probing. Our preliminary studies based on indentation hardness suggest that the intensity of amorphization beneath dynamic indentations is greater than that which is beneath quasistatic indentations of similar loads. By using Raman data to generate 3D representations of the transformed zones beneath quasistatic indentations and dynamic indentations at similar loads, comparisons will be made and conclusions will be drawn regarding the size and shape of the amorphous zone, the intensity of amorphization, and the dependence of those characteristics upon load and strain rate.

10:00 AM

(ICACC-S4-015-2014) Further Results on the Characterization of Knoop Indents in Boron Carbide

J. LaSalvia*, E. Shanholtz, K. Behler, U.S. Army Research Laboratory, USA; V. Domnich, Rutgers University, USA; K. Strawhecker, S. Walck, U.S. Army Research Laboratory, USA

An attempt to analyze the variation of Knoop hardness with indentation load in a commercial boron carbide was previously reported. No definitive conclusions were reached on the mechanisms governing the hardness-load curve despite observations of changes in microstructural features associated with stress-induced solid-state amorphization (SSA) with increasing load, or fitting the hardness-load data with the proportional specimen resistance (PSR) and multi-fractal scaling law (MFSL) phenomenological strength models. Examination of sub-surface deformation features did not provide sufficient insight due to less than ideally prepared cross-sections. In this study, examination of the variation in Knoop hardness with load in boron carbide is revisited. The hardness-load curves for commercial and research-grade boron carbides were determined. The hardness-load data was analyzed using the PSR and MFSL strength models. The surface indents were characterized by scanning electron, Raman, and atomic-force microscopies. Cross-sections, prepared by an improved method, were also examined in order to determine the distribution of SSA boron carbide beneath the indents at various loads. These results and others will be presented.

10:20 AM

(ICACC-S4-016-2014) Stability of Indentation-Induced Amorphous Boron Carbide: Effect of Annealing Treatments

V. Domnich*, Rutgers Univ, USA; J. C. LaSalvia, U.S. Army Research Laboratory, USA; R. A. Haber, Rutgers Univ, USA; E. R. Shanholtz, U.S. Army Research Laboratory, USA

Boron carbide is a material of choice for lightweight armor applications due to its exceptional mechanical and physical properties. It has been shown in the literature that boron carbide experiences structural instability under contact loading, such as indentation, scratching, and shock impact, resulting in the formation of amorphous phase. The effect of annealing treatments on the amorphous phase formed under Knoop indentation in an armor-grade boron carbide is reported in this work. Indented boron carbide specimens were annealed under high vacuum and controlled atmosphere conditions. Raman microspectroscopy was used to image the distribution of amorphous phase in the indentation contact zone as a function of annealing conditions. The impact that oxidation has on the spectral features of amorphized boron carbide and various carbon forms is demonstrated.

10:40 AM

(ICACC-S4-017-2014) Compressive Strength of Single-Crystal Boron Carbide Micropillars

J. Ligda*, Army Research Laboratory, USA; V. Domnich, Rutgers University, USA; T. Tanaka, National Institute for Materials Science, Japan; J. LaSalvia, B. Schuster, Army Research Laboratory, USA

Literature data on mechanical properties and deformation behavior of boron carbide single crystals is very limited. This is due to the difficulty in effectively producing single crystal boron carbide on the size scales needed for conventional testing. The elastic constants for a B5.6C single crystal were measured by ultrasound spectroscopy technique by McClellan et al. The nanoindentation hardness and elastic modulus for two different surface orientations of a B4.3C single crystal were measured by Domnich et al. To improve the understanding of anisotropy in the mechanical properties of boron carbide, a large single crystal B4.3C specimen obtained by a floating zone technique was obtained for this study. Additional specimens were large grains in polycrystalline boron carbide of nominal B4C stoichiometry, with crystallographic orientations identified by electron back scatter diffraction. Mechanical behavior was studied using small scale testing techniques such as nanoindentation and microcompression because the small sample volumes needed for such tests allow for sample inside the large grains. Following testing, analysis using Raman spectroscopy and electron microscopy was used to determine if a relationship exists between the amount of amorphization and either the crystallographic orientation or composition.

11:00 AM

(ICACC-S4-018-2014) Synthesis and Consolidation of Submicron-Grained Boron Carbide

K. C. Mills*, C. D. Haines, R. K. Sadangi, D. G. Martin, D. Kapoor, US ARMY, USA

K. Mills, C. Haines, D. Martin, R. Sadangi and D. Kapoor US-Army ARDEC, Picatinny Arsenal, NJ 07806 Dense, nanocrystalline ceramics offer a multitude of unique mechanical, optical, and electrical properties which have the potential to enhance or revolutionize current applications of ceramics. Most open literature reports, however, are of oxide ceramic systems. This fact is primarily a result of the commercial availability of oxide nanopowders. Carbide and nitride synthesis cannot typically be performed by the commercially amenable oxygen-fuel combustion methods used for nanocrystalline oxides. Efforts are currently underway to synthesized nanocrystalline Boron Carbide(B4C) via inductively coupled plasma

– inert gas condensation (ICP-IGC) and subsequently sintering using field-assisted sintering technology (FAST). XRD, SEM and BET surface area analysis has verified the nanocrystalline nature of the synthesized powder. Characterization of the sintered B4C verifies that sub-micron grain size is maintained after achieving high density. Microhardness, fracture toughness, and oxygen content are in line with commercially available conventional grain size ballistic B4C even at densities as low as 98%. For a baseline, conventional micron-scale powders were sintered under identical conditions and compared with the submicron materials and it is shown to compare favorably with hot pressed ceramic.

11:20 AM

(ICACC-S4-020-2014) Assessing the Carbon Concentration in Boron Carbide: A Combined X-Ray Diffraction and Chemical Analysis

K. A. Kuwelkar*, V. Domnich, R. A. Haber, Rutgers University- New Brunswick, USA

Boron carbide is an extremely hard ceramic and finds applications in the armor, abrasives and nuclear industries. With the single phase range extending from ~9 to 20 at.% C, boron carbide properties are dependent on its stoichiometry. This work focuses on the analyses of commercial boron carbide powders to determine the total carbon, free carbon and bound carbon concentrations which is important in calculating the stoichiometry for boron carbide that would affect its performance. X-Ray diffraction techniques were used to determine the free carbon content in the commercial powders using the spiking method. A relationship was established between the relative intensities of the carbon and boron carbide peaks to the percentage of added carbon, and the free-carbon content was obtained by extrapolation. The asymmetry of the carbon peak was modeled using curve fitting techniques based on the amorphous, disordered and ordered nature of carbon. The variations in the stoichiometry of various commercial boron carbide powders have also been reported in this work.

S6: Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage

Li-ion Battery Technology - Diagnostics and Characterization

Room: Ponce De Leon

Session Chairs: Dean Miller, Argonne National Laboratory; Dewei Chu, The University of New South Wales

8:00 AM

(ICACC-S6-010-2014) What can we learn from measurement and characterization of Li-ion battery single particles? (Invited)

D. J. Miller*, C. Proff, J. Wen, Z. Yang, L. Trahey, R. P. Winarski, B. Stripe, Argonne National Laboratory, USA

One of the challenges in correlating Li-ion battery performance with structure is the fact that most measurements provide average properties that are difficult to correlate with local microstructure. We approach this challenge by electrochemical cycling of single particles upon which detailed characterization can be carried out before and after various periods of cycling. The electrochemical cycling of single particles shows the same characteristic signatures as those observed in measurement of coin cells, confirming the validity of these measurements to global behavior. By using a measurement platform compatible with a variety of microstructural characterization approaches, we are able to characterize single particles at various points in cycling, providing an improved opportunity to correlate changes in structure with changes in electrochemical performance. This presentation will detail our approach and the insights gained from these correlated measurements. *Research sponsored by the U.S. DOE, Office of Science and by the U.S. DOE, EERE – Vehicle Technologies Program, under contract DE-AC02-06CH11357. The Electron Microscopy Center, Center for Nanoscale Materials, and Advanced Photon Source at Argonne are supported by the Office of Science.

8:30 AM

(ICACC-S6-011-2014) In SituTransmission Electron Microscopy of Anode Materials for Li ion Batteries (Invited)

R. Shahbzian-Yassar*, Michigan Technological University, USA

Nanostructured anode materials have received considerable attention in energy storage devices due to the enhanced electrochemical reactions at the surface and their unique electrical and mechanical properties. Among new anode materials, tin oxide, silicon, and titanate nanostructures are promising anode materials because of their energy capacity and safer performance for Li-ion batteries. The major obstacle for these new materials is the lack of scientific knowledge on the electrochemical reactions that happen inside a battery under charging and discharging conditions. Using real-time transmission electron microscopy (TEM) at atomic resolutions should shed light into some of the fundamental questions in this field. This presentation focuses on the in-situ observation of lithiation and delithiation inside an aberration-corrected STEM. The electrochemical testing of these low dimensional structures were conducted inside a transmission electron microscope equipped with a novel in-situ electrical probing holder. The intercalation of Li-ions in Si and SnO2 nanorods was monitored during charging and the fracture of nanorods was quantified in terms of size. In addition, the intercalation of crystalline anatase and amorphous TiO2 was studied and their fracture events were monitored in real time.

9:00 AM

(ICACC-S6-012-2014) Experimental Confirmation of Low Surface Energy in LiCoO2 and Implications for Lithium Battery Electrodes

P. Maram*, G. Costa, A. Navrotsky, University of California Davis, USA

Several authors showed that nanosized LiCoO2 has anisotropic surface properties affecting the surface electronic structures as a result the voltage profile of (de) intercalation is dramatically changed. Recent experimental studies confirm the surface electronic spin transition from low spin to high spin or intermediate spin states in nanophase LiCoO2 and also showed that surface energies computed using DFT were quite low (about 1.2 J/m2). We show, by direct oxide melt solution calorimetric measurements, that the surface energy of LiCoO2 is substantially lower than that of other simple rocksalt oxides such as CoO and NiO. The energetics of water adsorption to the surface of nanoscale LiCoO2, studied by water adsorption calorimetry, is found to be significantly less exothermic than on CoO, NiO and other binary transition metal oxides. This work suggests that the changes in coordination, valence, and spin state of cobalt near the surface of stoichiometric LiCoO2, strongly affects the surface energy thereby water binding energy. In seeking new electrode materials, one should consider low surface energy, which usually correlates with loosely bound surface water as a desirable attribute. Details will be presented.

9:20 AM

(ICACC-S6-013-2014) Electrochemical Performance of Large Area Graphene Films Prepared by Rapid Heating and Quenching at Ambient Pressures

L. David*, G. Singh, Kansas State University, USA

We study the process of graphene growth on Cu and Ni substrates subjected to rapid heating (approx. 8 °C/sec) and cooling cycles (approx. 10 °C/sec) in a modified atmospheric pressure chemical vapor deposition furnace. Electron microscopy followed by Raman spectroscopy demonstrated successful synthesis of large area few-layer graphene (FLG) films on both Cu and Ni substrates. The overall synthesis time was less than one hour. Further, the as-synthesized films were utilized as anode material and their electrochemical behavior was studied in a lithium half-cell configuration. FLG on Cu (Cu-G) showed reduced lithium-alloying capacity when compared with SLG, BLG and Bare-Cu suggesting its substrate protective nature (barrier to Li-ions). While FLG on Ni (Ni-G) showed better Li-cycling ability similar to that of other carbons suggesting that the presence of graphene edge planes (typical of Ni-G) is important in effective uptake and release of Li-ions in these materials.

Li-ion Battery Technology - Characterization and Design

Room: Ponce De Leon

Session Chairs: Dean Miller, Argonne National Laboratory; Dewei Chu, The University of New South Wales

10:00 AM

(ICACC-S6-014-2014) Synchrotron x-ray and neutron studies of nanocomposite materials for energy applications (Invited)

Y. Ren*, Argonne National Laboratory, USA

The increasing demands for alternative energy sources and energy storage systems have created a fast growing global market for renewable energy technologies. Among all research efforts, development of new materials, especially nanocomposites, is one of top priorities. Atomic level knowledge of nanocomposites is of vital importance for understanding their functionalities as well as for further improvements of material design and development. However, due to structural irregularity and complicated nanodomain intergrowth of multiple phases (for example, the Li and Mn rich composite cathode materials), fundamental characterization of their true structures becomes more and more challenging, and requires multi-scale approach using complementary techniques and computational calculations. Recently, we have applied synchrotron x-ray and neutron techniques, together with other experimental methods and computational modeling and simulation, to study the complex structural property of various nanomaterials and nanocomposites, which have great potential for energy conversion and storage technology. In this talk, we will present our recent results and discuss some challenging issues.

10:30 AM

(ICACC-S6-015-2014) Self-discharge phenomenon of a high voltage Li(MnNi)O spinel investigated by Raman spectroscopy

R. Baddour-Hadjean*, J. Pereira-Ramos, Y. Dridi, CNRS, France

High voltage Li(MnNi)O spinel oxides are known to be promising positive electrodes for Li-ion batteries. We have recently reported new data on the local structural changes induced in LiMn2O4 and LiNi0.4Mn1.6O4 during the lithium insertion reactions. In particular, the intermediate phases involved in both systems in a 3 phase structural mechanism have been evidenced through a rigorous RS study of electrochemically deintercalated-intercalated samples. Furthermore, we have shown the great sensitivity of the Raman probe to monitor the changes in the Ni redox state in LiNi0.4Mn1.6O4 from Ni2+ to Ni4+ during the charge-discharge processes, which makes this technique a powerful tool to evaluate the state of charge of this cathode material. This is the first successful application of RS to characterize redox species in an electrode material. We present here a novel application of RS devoted to the study of the self discharge phenomenon of LNMO. A detailed analysis of the Raman spectra of Li1-xNi0.4Mn1.6O4 electrodes versus time storage in LiPF6/EC/DMC electrolyte has allowed to depict quantitatively the mechanism involved at high voltage when the electrode material is kept at rest in the charged state. The kinetics and the reversibility of the self-discharge phenomenon of LNMO electrode can then be estimated.

10:50 AM

(ICACC-S6-016-2014) Material and Interface Characterization of Complete Li-ion Coin Cells Using Differential Scanning Calorimetry

P. J. Ralbovsky, B. Fidler*, Netzsch Instruments, USA

Characterization of Li-ion coin cell materials and their Interfaces is required to make increasingly better performing and inherently safer materials and cells. Traditional Differential Scanning Calorimetry (DSC) has been widely used to characterize single or in some cases multiple components. However, there are some certain drawbacks to the approach related to how the sample is configured in the instrument such as (1) reproducibility of inhomogeneous and multiphase samples; (2) sample preparation and transfer into DSC crucible; (3) inability to measure half or full cells; and (4) the inability to monitor voltage during testing. A new system has been developed were typical coin cell casings (i.e., CR2032) can be used as the sample and reference crucibles inside a high sensitivity DSC instrument. This allows the user to run complete coin cells, and pre-condition the cell prior to testing without need of any sample transfer. Voltages can be monitored during a typical scanning test or cells can be cycled in an isothermal environment to measure efficiencies directly. Interfaces developed through cell conditioning remain preserved during sample testing.

11:10 AM

(ICACC-S6-017-2014) Stable Electrochemical Performance of Graphene/SiBCN Layered Composite Electrode for Lithium Ion Battery Applications

L. David*, G. Singh, Kansas State University, USA

Exfoliated graphene oxide (GO) and boron modified poly(ureamethylvinyl)silazane were blended and pyrolyzed to synthesize freestanding SiBCN-graphene composite papers (~10 μm thick). The structural and chemical characterization of the composite prepared with varying polymer concentrations were carried out using electron microscopy, XRD, and FT-infrared spectroscopy. High resolution microscopy images shows layer by layer stacking of GO sheets with SiBCN particles between each layer. The SiBCN-graphene composite paper anodes showed stable charge capacity of approx. 180 mAh/g even at high current density of 2400 mA/g. The average columbic efficiency (second cycle onwards) was observed to be approx. 99%.Moreover, at current density of 1600 mA/g with symmetric cycling the anode exhibited stable charge capacity of 50 mAh/g even after 1000 cycles.

11:30 AM

(ICACC-S6-018-2014) Self-assembled Metal Oxide Nanomaterials for Energy Efficient Nanoelectronics and Future Energy Storage Nanodevices (Invited)

D. Chu*, A. Younis, The University of New South Wales, Australia

Metal oxide nanomaterials have important applications in energy efficient electronics and energy storage devices because of their unique semiconducting/dielectric properties. However, attempts to assemble these nanoscale objects into sophisticated structures, nanoelectronics, and nanodevices have been largely unsuccessful. In this work, we have developed effective approaches to well-organized metal oxide nanostructures and devices by using self-assembly technology. For example, self-assembled dielectric oxide nanocubes have been fabricated and their superior electrical properties for random access memories have been demonstrated. Besides, a novel type of supercapacitor devices has been proposed based on graphene paper/oxide semiconductor nanocrystals hybrid structure.

S7: 8th International Symposium on Nanostructured Materials and Nanocomposites

Nano-Bio Interactions

Room: Coquina Salon B
Session Chairs: Christina Graf, Freie Universitaet Berlin; Eva Hemmer, INRS-EMT

8:00 AM

(ICACC-S7-011-2014) Nanostructured Materials and Nanocomposites for OTN-NIR Small Animal Fluorescence Imaging (Invited)

K. Soga*, N. Venkatachalam, Tokyo Univ. of Science, Japan; E. Hemmer, INRS, Canada

Recent trends of the small animal fluorescence imaging are to elongate the observation wavelength for avoiding the optical loss and blur of the capturing images due to optical scattering. Current wavelength for the imaging is limited up to 1000 nm due to the limitation of the imaging device based on silicon semiconductor. Compared to the current imaging wavelength around 900 nm with the observation limit of several mm depth, much deeper, several cm, observation depth can be achieved by using the fluorescence at the wavelength over 1000 nm (OTN). The authors have developed both imaging systems by using InGaAs CCD for the OTN-near infrared (NIR) observation and OTN-NIR fluorescent probes. One of the candidate phosphors for the OTN-NIR fluorescence is the rare-earth doped ceramic nanoparticles (RED-CNP). To use the RED-CNP for the small animal imaging, size control of the CNP and mono dispersion in live bodies are required. For fulfilling the conditions, biocompatible polymers, such as polyethylene glycol (PEG) together with the ligand molecules must be conjugated on the surface of the probes. The conjugation can be achieved by using block copolymers or phospholipids. The formation of the nanosturctures and nanocomposites for the OTN-NIR bioimaging probes will be reviewed together with the demonstrative works of the OTN-NIR fluorescence small animal imaging.

8:30 AM

(ICACC-S7-012-2014) Silver and Silicon Nanostructures: From Plasmonics to Cancer Theranostics (Invited)

V. Sivakov*, Institute of Photonic Technology, Germany; V. Y. Timoshenko, M. V. Lomonosov Moscow State University, Russian Federation; S. Demyanov, National Academy of Science, Belarus

Creation of 1D nanostructures has opened up a new area for device applications in energy and life science. This paper has a two-fold objective: nanostructures formation and application for practical solar energy and bio-plasmonic/biomedicine. SiNWs with different morphologies and geometries with unique optical and electrical properties can be successfully and easily produced by top-down technology. We anticipate that the concepts presented here will also be highly relevant to the development of future, more efficient photovoltaic single- or multi-junction devices. Dendrite like or self-organized Ag-nanostructures grown by wet-chemical approach of Ag, can produce a significant enhancement of Raman scattered signals. Signal enhancement for a few or even just single Ag-dendrite is demonstrated by analyzing the enhanced Raman signature standard dye molecules, bio-molecules or drugs. Silicon nanostructures are to time intensely studied as the basis for the novel theranostic agents. Our interest to Si is explained by the natural properties of Si-nanostructures such like biocompatibility and biodegradation, and low toxicity that make them interesting for biomedical applications. In vitro effects on proliferation of stem and cancer cells, including combined effects of SiNPs and ultrasonic exposure for stimulation of the effect of nanoparticles was investigated and shown promising results in the cancer therapy.

9:00 AM

(ICACC-S7-013-2014) Selective and Highly Sensitive Iron Oxide Nanoparticles as Magnetic Resonance Imaging (MRI) Contrast Enhancers (Invited)

C. Graf*, D. Nordmeyer, P. Stumpf, C. Goroncy, D. Groeger, Freie Universitaet Berlin, Germany; C. Boeglin, Institut de Physique et de Chimie de Strasbourg Département Surfaces-Interfaces, France; S. B. Riese, J. Dernedde, Charité – Universitätsmedizin Berlin, Germany; R. Haag, E. Ruehl, Freie Universitaet Berlin, Germany

Iron oxide nanoparticles (FeOx NP) are applied as T2 contrast agents in MRI. The aim of the present study was to obtain NP with optimized magnetic properties as well as a high stability in biological media and selective targeting. Monodisperse, spherical iron oxide (Fe3O4/γ-Fe2O3) NP (10-20 nm diameter) are prepared using iron oleate as precursor and stabilizer. X-Ray Magnetic Circular Dichroism is used to investigate their local structural and electronic properties and shows that the magnetization and the γ-Fe2O3 to Fe3O4 ratio of the NP are strongly increased by post-synthesis tempering in an oxidative environment. This likely causes a rearrangement of their crystalline order. A functionalization of the NP with hydrophilic ligands can have a similar effect. Transfer of the NP into aqueous media intensifies these processes. For selective MRI, the FeOx NP are functionalized with dendritic polyglycerol (dPG) or dendritic polyglycerol sulfate (dPGS). The obtained NP are highly stable in physiological media and show low cytotoxicity. Surface plasmon resonance studies and a flow chamber assay with leukemia cells show that the dPGS functionalized FeOx NP inhibit L-selectin ligand binding whereas the NP containing only dPG do not show this effect. These results indicate that dPGS functionalized FeOx NP are a promising contrast agent for inflamed tissue probed by MRI.

9:30 AM

(ICACC-S7-014-2014) Lanthanide-doped NaGdF$_4$ Nanostructures: Synthesis, Characterization and their Potential for Nanothermometry

E. Hemmer*, F. Légaré, F. Vetrone, INRS-EMT, Canada

Lanthanide (Ln^{3+}) containing compounds are known for their optical properties including narrow absorption and emission bands, high emission efficiency and long lifetime of excited states. Biomedical applications require small nanoparticles, ideally in the range below 20nm. Efficient emission at such small size is provided by doping Ln^{3+}-ions into a fluoride matrix. Thus, upconverting NaGdF$_4$:Er^{3+}/Tm^{3+},Yb^{3+} nanoparticles are synthesized by thermal decomposition. The in-situ modification with oleic acid allows dispersion in hexane, while a simple ligand exchange reaction provides dispersability in aqueous media enabling biomedical applications. Luminescence nanothermometry is an approach based on the T-dependent photoluminescence allowing for the monitoring of the temperature (T) of a biosystem. As thermal singularities are often one of the first indicators of a disease, cellular nanothermometry has the potential as a nanoscopic diagnostic tool. Its application requires non-toxicity, water solubility, and a final temperature resolution in the order of 0.2°C, whereas Ln^{3+}-based probes are promising candidates. The T-dependent emission properties of NaGdF$_4$:Ln^{3+} will be presented and their potential as nanothermometers will be discussed.

Nanoscopic Films and Composites I

Room: Coquina Salon B
Session Chairs: Elena Timofeeva, Argonne National Laboratory; Susanne Hoffmann-Eifert, Forschungszentrum juelich

10:00 AM

(ICACC-S7-015-2014) Nanocomposite Magnetoersistive and Magnetoelectric Films (Invited)

M. Jain*, University of Connecticut, USA

Solution synthesis methods allow low-cost fabrication of high quality pure and nanocomposite films. In this talk, the results of two biphasic nanocomposite systems: (i) colossal magnetoresistive films with low-field magnetoresistive effect and (ii) magnetoelectric (ME) nanocomposite films with strain coupling between the two phases, will be presented. In biphasic nanocomposites, concentration and connectivity of the two phases play an important role in defining their physical properties. For magnetoresistive films, which are of great interest for various applications including magnetic field sensors and spintronic devices, two approaches were used to fabricate nanocomposite film with insulators ZnO and MgO. In such manganite:insulator nanocomposite films of ($La_{1-x}Sr_xMnO_3$:MgO and $La_{1-x}Sr_xMnO_3$:ZnO), low-field magnetoresistance effect was found to be enhanced at low temperatures. For magnetoelectric films, which are of great interest for memory and sensing applications, magnetic nanoparticles (NPs) were incorporated in the piezoelectric matrix in order to observed the ME coupling that is mediated through mechanical strain at their interfaces between the two phases. The detailed ferroelectric and ME properties of 3-0 type nanocomposite thin films with various concentrations of $CoFe_2O_4$ NPs dispersed in $PbZr_{0.52}Ti_{0.48}O_3$ matrix will be presented.

10:30 AM

(ICACC-S7-016-2014) Integration of sub-10nm functional metal oxide films with tailored compositions for application in nonvolatile resistive switching memory devices (Invited)

S. Hoffmann-Eifert*, Forschungszentrum Juelich, Germany

The market of portable electronics and Green IT solutions demands for non-volatile memory circuits with high speed data access, high reliability, and low power consumption. One promising concept is the resistive switching random access memory (ReRAM) which is built from transition metal oxide thin films sandwiched between metal electrodes. Decisive for a stable device operation are a homogeneous microstructure and a controlled defect density in the oxide films of a few nm in thickness. Atomic layer deposition (ALD) can fulfill these requirements by its unique surface-reaction controlled self-limiting growth. The talk will comprise recent results on ALD TiO2 layers with tailored nanostructures. The relevance of the film structure for the resistive switching (RS) properties was clearly demonstrated. Double layers of oxides, e.g. TiO2/Al2O3, are studied for their possibility for device tuning. Group V metal oxides, Ta2O5 and Nb2O5, are interesting due to high endurance and threshold switching. The effect of cation non-stoichiometry on RS properties was demonstrated for ALD SrTiO3 thin films. The examples highlight the importance of ALD for the concept of ReRAM devices, because ALD enables a control of the film defect structure even for thicknesses in the nm-regime and for low growth temperatures.

11:00 AM

(ICACC-S7-033-2014) High Power Density Primary and Secondary Micro and Large-Format Batteries Based on Three-Dimensionally Templated Nanostructured Current Collectors (Invited)

P. V. Braun*, University of Illinois at Urbana-Champaign, USA

High power density and high energy density primary and secondary (rechargeable) nanostructured batteries were fabricated using a template based synthesis. By efficient design of the ion and electron transport pathways within the anode and cathode, we and others have shown it is possible to improve the power-energy relationship by minimizing the ohmic and other losses that occur when a battery is cycled rapidly. We have found a particularly effective way to provide these pathways is to use a holographically-defined or colloidal-based template to defined the structure of a 3D current collector. The electrochemically active material is then deposited on this current collector. The combination of a high surface area and short solid-state diffusion lengths offers a number of unique opportunities for both high energy and high power chemistries. As examples, we have formed conventional form-factor and microbattery high power cells based on a lithiated manganese oxide cathode and either carbon or NiSn anodes, and high energy cells based on silicon anodes and a few other materials. The large format cells are assembled using traditional routes using conventional separators, while the microbatteries are consist of anodes and cathodes interdigitated on a substrate.

11:30 AM

(ICACC-S7-018-2014) Microwave Assisted Processing of Copper Nano Inks for Electronic Interconnect Applications

S. Qi*, B. Vaidhyanathan, D. Hutt, Loughborough University, United Kingdom

Metal nanoparticle inks are widely used in electronic packaging applications where they are seen as suitable candidates for preparing conductive traces in printed circuits. Copper is considered as a cost-effective alternative to silver with greater abundance for wider exploitation in low cost, high volume applications such as printed electronics. However, the typical sintering temperature of Cu is much higher than that of the substrates used. To increase the uptake of Cu nano inks, alternative methods of sintering are under investigation. Microwave heating involves direct energy deposition in the material. Lower sintering temperatures and shorter processing times are often associated with microwave heating. The application of this selective heating methodology for the sintering of Cu nanoparticles may allow the utilisation of temperature sensitive substrates such as polymers for the production of printed electronic circuits. In this work, use of conventional and microwave assisted heating methods for the sintering of Cu nanoparticles was investigated in detail. Results indicate that lower processing temperatures can be achieved during the microwave processing of nano materials which auger well for the fabrication of Cu tracks on low temperature substrates paving the way for plastic electronics.

11:50 AM

(ICACC-S7-019-2014) Physical/Chemical Combinatorial Strategy Towards Multi-dimensional Perovskite Nano- and Micro-structures with Enhanced Functionality (Invited)

A. Datta*, D. Mukherjee, S. Witanachchi, P. Mukherjee, University of South Florida, USA

Perovskite oxides continue to be an important class of materials due of their high dielectric and piezoelectric coefficients, switchable nonvolatile polarization properties and interesting electrical and electronic properties. Realization of functional devices based on classic perovskite oxides such as $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) and emerging non-toxic, Pb-free oxides such as $Zn(M)O_3$ (M = Sn, Ti) have reinforced the investigation of these materials in multiple dimensions and length scales. However large-scale synthesis and integration of these materials with ordered low-dimensional structures and controlled crystal orientations is a challenge, due to their complicated methodologies and high-cost. We developed a novel and facile physical-chemical combinatorial approach for growing size and shape selective nano- and micro-structures of these materials on large-area substrates without using templates. The approaches involve depositing nano-seed layers of the desired materials by Pulsed laser deposition/RF sputtering/Electroplating techniques followed by oriented growth of nano- and micro-structures by solution processes. Improved tunability of morphologies were examined by XRD, SEM, AFM, TEM and Raman spectroscopy.

In-depth analyses of the electronic (field-emission), electrical and ferroelectric properties of the prototype devices will be presented.

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

In Honor of Professor Stuart Hampshire II; Novel Processing

Room: Coquina Salon A
Session Chairs: Pavol Sajgalik, Institute of Inorganic Chemistry, Slovak Academy of Sciences; MIchael Pomeroy, University of Limerick

8:00 AM

(ICACC-S8-010-2014) Laser milling of ceramic oxide compacts: application to dentistry and jewelry (Invited)

F. J. Cambier*, X. Buttol, V. Lardot, F. Petit, Belgian Ceramics Research Center, Belgium

A main factor influencing the cost of an oxide part is milling, which includes the wear of diamond tools and the slow machining rates to avoid any degradation of the surface quality. As a non-contact process, laser milling appears as a challenging technique. Main advantages are the absence of cutting stresses, no machine vibration and no tool wear. However, a typical problem is the formation of a molten material recast layer on the machined surface and low material removal rates. Such low material removal rate in conventional laser machining can be partly overcome by laser machining at the green state. Further improvement can be achieved if the ceramic mix is adapted to absorb the laser beam at its wavelength. The Hainolase process relies on mixing highly laser absorbent additives with poorly absorbent ceramic particles. Green ceramics "blanks" are processed, for instance by isostatic pressing. During the laser milling, even with very low energy, the carbon based additives explode by interaction with the laser, expelling unaffected neighbour particles. Such a process allows obtaining high machining rates by comparison with both the diamond tool milling and the classical laser process. After milling, the parts are sintered in one step and experiments made up to now show their mechanical properties are equivalent to those obtained classically. Examples of applications in different fields will be shown.

8:30 AM

(ICACC-S8-011-2014) Comparison of conventional and microwaves sintering of bioceramics (Invited)

A. L. Leriche*, E. Savary, University of Valenciennes, France; A. Thuault, University of Caen, France; J. Hornez, M. Descamps, University of Valenciennes, France; S. Marinel, University of Caen, France

Hydroxyapatite (HA) and beta-tricalcium phosphate present excellent biocompatibility because of their chemical composition close to human bone. However, their low mechanical properties limit their structural uses. An interesting way to improve their mechanical resistance consists in obtaining dense samples with fine microstructure. In this aim, microwaves represent a promising method due to the very short thermal treatment times. In this study, the direct microwaves sintering in a single mode cavity was first investigated. In the case of HA, >99% dense samples with submicronic microstructures were obtained in less than 15 minutes of irradiation. The resulting mechanical properties are therefore improved: higher Young's modulus (> 140 GPa for HA), higher hardness (> 9 GPa for HA) than those classically reported with other sintering processes. The obtained results are discussed according to the microstructures and the experimental parameters such as powder grain size, sintering temperature, microwaves irradiation time. The second part of this work consists in scaling up the microwaves process to obtain dense larger sized parts (more than 40mm diameter). To achieve this goal, two microwaves devices: a 2.45GHz multimode furnace and a 915MHz single mode oven were tested. The resulting microstructures and mechanical properties are discussed regarding the respective characteristics of those two microwaves processes.

9:00 AM

(ICACC-S8-012-2014) Bead-Milling and Post-Milling Recrystallization: An Organic Template-Free Methodology for the Production of Nano-Zeolite Catalyst

T. Wakihara*, the university of tokyo, Japan; J. Tatami, S. Inagaki, Y. Kubota, Yokohama National University, Japan; T. Okubo, the university of tokyo, Japan

A new method for the production of nanosized zeolite powder by a top-down approach has been performed. [1,2] In this study, ZSM-5 (MFI type structure) was first milled to produce a nanopowder. This technique can destroy the outer portion of the zeolite framework, which lowers the micropore volume of ZSM-5 zeolite. To remedy this, the damaged part was recrystallized using a dilute aluminosilicate solution after bead milling. From the combined bead milling and post-milling recrystallization, nanosized ZSM-5 zeolite approximately 50 nm in size with high crystallinity was obtained successfully.

9:20 AM

(ICACC-S8-013-2014) Supercritical fluid-assisted processing of ceramics

S. O. Matthews*, J. Matthews, SCF Processing Ltd, Ireland

Injection molding and extrusion techniques have been used to manufacture ceramic components. For over a decade the authors have been combining these conventional processing techniques with supercritical fluid technology to manufacture complex components with near net shape and porosity on demand. Recent advances in supercritical fluid based processing have resulted in a hybrid debinding technique that has enabled the removal of binder systems, used to shape the ceramic material, at subcritical pressures. The advantages of these recent developments include significant reductions in the binder removal time, the improved quality of the debound component and in certain cases the ability to reuse the binder system. This paper will report the recent developments of the now complete supercritical fluid technology based process and how it has been used to produce complex ceramic shapes.

10:00 AM

(ICACC-S8-014-2014) Teaching and Learning Sustainable Ceramic Processing (Invited)

R. D. Sisson*, Worcester Polytechnic Institute, USA

Typically ceramic processing has been taught with the emphasis on the science and engineering of the processes. In addition, the fundamentals of statistical process control (SPC) and control systems may have been incorporated into the syllabus. Recently "green" or "environmentally benign" processing design and analysis needs to be addressed due to government regulations and consumer interest. To include each of these important topics a holistic view of the process must be used. A process overview using a process flow diagram and the "through process model" identifying each step in the process can be developed. Student project teams can be formed and assigned the development of the process flow diagram for a new or current process. The goal of these project teams is to provide the opportunity for "active learning". These teams can be asked to apply the science and engineering to specific steps in the process. In addition, the teams can be asked to determine what process parameters and properties should be measured, how to measure them and what to do to analyze the data. The teams can also be asked to address the energy consumption of the process and identify techniques to reduce the energy needs. The teams should also be asked to identify and reduce any toxic materials use and determine methods for reduction. Finally the student teams should answer these questions; Is the process robust? Is the process sustainable?

10:30 AM

(ICACC-S8-015-2014) Thin film electrodes for gas and force sensor applications (Invited)

B. Saruhan-Brings*, German Aerospace Center, Germany

Nowadays sensors are applied to monitor the processes and to control emission and to observe the performance of components subjected to chemical and mechanical loading. NOx is one of the green-house emission, produced during combustion processes and cannot be avoided by improving the fuel-quality. Gas sensors are extensively used for the precise determination of the quantity and chemistry of gas emissions for the control of combustion processes. Another example for in-situ monitoring is the real-time detection at ball-bearings by force sensors. This presentation reports the recent developments at DLR related to doped/undoped oxide gas sensing layers for detection of NO2, CO and H2 at temperatures above 400°C. The sensor devices are based on a simple design. Doping and nanostructuring of TiO2 layers produced by anodisation yields favorable properties regarding sensors selectivity and sensitivity. Use of sensor arrays and integration of sensing layers into the compounds allows the measurement of a broader gas concentration variation at a wide temperature range in atmosphere including moisture and reducing gases. Diamond-like Carbon (DLC) enables the manufacturing of component-integrated force sensors for the life-time monitoring of the components and the systems in aircraft engines, wind power generation, etc. The studies carried out on reactive sputtered, AlN-doped DLC films as force sensors will be reported.

11:00 AM

(ICACC-S8-016-2014) Particle & Powder Technology: The Foundation of Process and Product Reliability (Invited)

M. J. Murtagh*, Corning Incorporated, USA

Particle level correlations that guide product structure-property outcomes in advanced processing and manufacturing technologies for glass and ceramic processes are well established. The influences of bulk powder effects (powders as used) on structure-property functions, however, remain elusive. Bulk powder effects depend on the ensemble of particles packing and require a multi-scale evaluation, which includes the meso-scale (powder level) to bridge nano/micro particle scale characteristics and bulk powder macro-scale behavior. To enable the characterization of meso-structure linkages between the particle scale and powder scale properties for structure-property function, Corning Incorporated has integrated three areas: 1) static particle measurements, i.e. particle profiles (size, shape, surface area, hardness, elastic modulus, fracture toughness, etc.), 2) comminution and dynamic powder measurements (bulk powder rheology), and 3) forming (i.e. glass and ceramic processes). A review of powder scale challenges to advance powder based manufacturing technologies will be discussed, which includes: meso-scale (dynamic) particle characterization, powder flow mechanics of cohesive powders, quantifying segregation and electrostatic effects, milling utilization and predictability, and nanoparticle processing and handling.

11:30 AM

(ICACC-S8-017-2014) Low Temperature Processable Yttria Doped Mullite Precursors

J. J. Rocha-Jimenez*, University of Guanajuato, Mexico; S. Tanaka, Nagaoka University of Technology, Japan; S. Hampshire, University of Limerick, Ireland; S. Sugita, University of Guanajuato, Mexico; M. J. Pomeroy, Y. Guo, University of Limerick, Ireland

The precursor crystallizes into mullite at temperatures lower than 1100°C and reaches high densities at temperatures near 1400°C. The particles used in this study are microcomposites type core-shell fabricated via homogeneous precipitation. In this approach special attention was made to keep away from the surface the SiO2 and Y2O3 rich phases, so the external shell is the alumina rich region. The presence of Y2O3 increases the mass transport of Si4+ ions trough the alumina rich region, resulting in the reduction of mullite formation temperature in more than 100°C. These particles can be sintered in the range between 1400°C to 1500°C, varying Y2O3 concentrations. As conclusions, less energetic consuming mullite ceramics can be fabricated from this technology. The junction of mullite-yttria avoid further processing problems involved when 2 types of particles are handled.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Virtual Materials Design and Modeling I

Room: Coquina Salon G

Session Chairs: Gerard Vignoles, University Bordeaux; Paul Rulis, University of Missouri - Kansas City

10:00 AM

(ICACC-S10-015-2014) Towards an Accurate Model of Amorphous Hydrogenated Boron Carbide: A Study in Electronic Structure and Spectroscopic Properties (Invited)

P. Rulis*, R. Cramm Horn, University of Missouri - Kansas City, USA

Amorphous hydrogenated boron carbide (a-$B_xC:H_y$) grown as a thin film via plasma enhanced chemical vapor deposition has a number of potential practical applications in solid state neutron detection and as a low-κ dielectric. Achieving optimal performance in these applications requires fundamental understanding of the relationship between the growth parameters, the resultant atomic scale structure, and the material properties. The purpose of this work is to determine appropriate models for different varieties of a-$B_xC:H_y$ grown under different conditions by comparing calculated spectroscopic data to experimental data. Presently, a series of models of a-$B_xC:H_y$ have been created through a customized version of the LAMMPS molecular dynamics package and the ab initio VASP package taking into account structural rules determined by an NMR spectroscopy study. A "gas phase condensation" scheme has recently been refined to more accurately model the experimental technique by which the material was actually created. Subsequent to model creation, the electronic structure and x-ray absorption near edge structure (XANES) spectroscopic properties of the models were computed and compared to available experimental data. The resultant data show promise for differentiating between different structures obtained via different growth parameters.

10:30 AM

(ICACC-S10-016-2014) Prediction of temperature-dependant thermal conductivity of some RE-Si-O-N ceramics

S. Luchao*, Institute of Metal Research, China; W. Jingyang, Institute of Metal Research, China

Exploring on ceramics with low thermal conductivity and high-temperature stability is a focused topic of both scientific significance and technological importance. DFT-based material modeling has been developed so successfully that it serves as an indispensible tool toward the efficient development of advanced ceramic. The present work will involve in a theoretical method to calculate temperature-dependant thermal conductivity of complex ceramics via first-principles calculations based on Debye model. Thermal conductivities as well as the minimum lattice thermal conductivities of five Y-Si-O-N ceramics are calculated at first and Y4Si2O7N2 is focused for very low lattice thermal conductivity from room to high temperatures. Thereafter, isostructural RE4Si2O7N2 ceramics are investigated as representative system to study the effects of rare earth elements on thermal conductivity. Finally, theoretical calculations are validated by experimental estimations of intrinsic lattice thermal conductivity.

10:50 AM

(ICACC-S10-017-2014) Equilibrating Complex and Disordered Materials (Invited)

W. Kob*, University Montpellier 2, France

Computer simulations have been shown to be an excellent tool to investigate the structural and dynamical properties of disordered systems such as supercooled liquids, glasses, and disordered crystals. However, one of the main obstacles to obtain quantitatively reliable results is that these properties depend on the history of the sample. Since standard computer simulations of atomistic systems cannot access time scales beyond micro-seconds, one needs sophisticated algorithms to equilibrate disordered systems even at low temperatures, i.e. to prepare samples that are equivalent to the ones obtained by a real experimental production procedure. In this talk I will discuss two approaches that allow to equilibrate disordered systems even at low temperatures: Parallel tempering and genetic algorithms. I will show that these algorithms do indeed permit to access the properties of the materials at low temperatures and hence will allow us to improve our ability to perform simulations under experimentally relevant conditions.

11:20 AM

(ICACC-S10-018-2014) Prediction of Phase Stability in TiAlN Coatings: From First-Principles to CALPHAD

Y. Zhang*, P. Franke, Karlsruhe Institute of Technology, Germany; J. Wang, Institute of Metal Research, China; H. J. Seifert, Karlsruhe Institute of Technology, Germany

PVD deposited TiAlN coatings can result in metastable (Ti,Al) N solid solution phases with cubic or hexagonal structures. The metastable phase formability and separation can greatly influence properties and performances of the coatings. Since only limited information is experimentally known for metastable and unstable phases, we resorted to ab-inito thermodynamics for their thermodynamic data. Alternative expressions for the lattice stability of c-AlN were derived from ab-initio calculated heat capacity and high pressure phase diagram respectively. Ternary interaction parameters for various metastable (Ti,Al)N solid solutions in different structures were derived by combining ab-initio and CALPHAD techniques. Thermodynamic descriptions for ternary compounds $\tau_1(Ti_3AlN)$, $\tau_2(Ti_2AlN)$ and $\tau_3(Ti_4AlN_3)$, were reassessed according to the latest experimental and ab-initio results. Pseudo-binary AlN-TiN section and isothermal sections in Ti-Al-N system were calculated and compared with experimental reports. The formation ranges of various (Ti,Al)N solid solutions and their spinodal decomposition behaviors were discussed based on the attained PVD and pseudo-binary AlN-TiN phase diagram. In conclusion, the TiAlN dataset obtained by a hybrid approach to integrate the ab-initio results with CALPHAD formalism can provide an important basis for designing and developing new coating materials.

Ceramic Genome and Modeling of Structure and Property III

Room: Coquina Salon G
Session Chair: William Weber, University of Tennessee

8:00 AM

(ICACC-S10-011-2014) Theoretical investigation of low energy recoil events and point defects of $SrTiO_3$ (Invited)

B. Liu*, Oak Ridge National Laboratory, USA; H. Xiao, University of Tennessee, USA; Y. Zhang, Oak Ridge National Laboratory, USA; W. J. Weber, University of Tennessee, USA

Perovskite structures, such as $SrTiO_3$, are one of model materials proposed for the immobilization of high-level nuclear wastes because its structure allows incorporation of both fission products and actinides. In addition, $SrTiO_3$ thin-films are used as insulating layers in dynamic random-access memories, ferroelectric thin-film structures, and high-T_c superconductor devices, as well as potential gate oxide candidates. In many of these applications, knowledge of defect production, stable defect configurations, defect migration and their effects on properties is critical. In this work, ab initio molecular dynamics simulations are used to study the dynamics of low energy recoil events. The threshold displacement energies for each sub-lattice are determined, and electron transfer is found to play the predominant role on the dynamics of recoil events. First-principles calculations are also performed to study the stable defect configurations created by the dynamic recoil events. The dependence of defect stability on the chemical potential and charge states are clarified, which can provide insights into interpretation of experiments. Finally, the donor like electron recombination processes for the O vacancy and the Sr/Ti interstitials occur at 2.7 to 2.9 eV, which explains the blue light emission observed in Ar+-irradiated $SrTiO_3$.

8:30 AM

(ICACC-S10-012-2014) Thermodynamic modeling of copper and iron oxides used as conversion electrodes in lithium ion batteries

M. Lepple*, P. Franke, D. M. Cupid, H. J. Seifert, Karlsruhe Institute of Technology, Germany

Compounds in binary and ternary sub-systems of the Li-Cu-Fe-O system are promising electrode materials for lithium ion batteries which exhibit the conversion mechanism. Thermodynamic descriptions of the multi-component systems can be used to predict equilibrium open circuit voltages and plateau capacities. Experimentally determined thermochemical and thermodynamic data are key input data for the thermodynamic optimization. For the experimental investigations, samples were prepared using the mixed oxide and sol-gel self combustion methods and were characterized using XRD and ICP-OES. Enthalpies of formation of different compounds were determined using high temperature oxide drop solution calorimetry in molten 3Na2O.4MoO3 solvent at 700 °C. The phase stabilities were measured in argon and argon/oxygen mixtures using simultaneous thermal analysis. Additionally, the heat capacities of the materials were measured using differential scanning calorimetery. This data and evaluated literature values were used to obtain a consistent thermodynamic description of the sub-systems Li-Cu-O and Li-Fe-O. Subsequently, coulometric titration curves of different starting compounds were calculated, which give the open circuit voltage along a selected composition path.

8:50 AM

(ICACC-S10-013-2014) Tailoring the Mechanical Properties of Glass Guided by Computer Simulations (Invited)

L. Huang*, Rensselaer Polytechnic Institute, USA

Silica glass one of the most widely and well studied materials, not only as an archetypical amorphous material, but also because of its anomalous thermo-mechanical properties. The most pronounced elastic anomalies that appear in silica and silica-rich glasses are the positive temperature derivative and negative pressure derivative of bulk modulus, as compared with normal glasses, such as soda-lime-silica window glass. By using molecular dynamics simulations based on a charge-transfer three-body potential, our study showed that the elastic anomalies in silica glass can be tuned by adding network modifiers, pressure-quenching or He-stuffing. The behavior of silica glass changes from abnormal to normal with increasing the content of network modifier, the quenching pressure and the amount of He atoms stuffed in the glass matrix. In between, glass with temperature or pressure independent elastic moduli can be obtained. Such intermediate glass is of critical importance for applications under extreme conditions of high thermal/mechanical shock.

9:20 AM

(ICACC-S10-014-2014) Development of a Numerical Model on Radiation Induced Segregation and Surface Nano–Structuring in a Binary System

E. Hernandez*, University of Michigan, USA; V. Tikare, Sandia National Laboratory, USA; L. Wang, University of Michigan, USA

Irradiation of materials leads to the formation of very complexed systems, chemically and morphologically in nature. Therefore, ion irradiation is often used to generate materials with enhanced properties for advanced applications. This is especially true in the semiconductor field where engineered materials have lead to the advancement of many electronics systems. Furthermore, ion irradiation has also been observed to lead to the formation of surface and embedded nano–structures, e.g. quatum dots (QD). We developed a hybrid model that simulates the formation of these complex structures. The main challenge in modeling such a complex synergetic system is the multiple processes taking place. Our numerical hybrid model couples Monte Carlo (MC) algorithms to a deterministic model taking advantage of their respective strengths. Our model shows that differential diffusion of radiation–induced defect is sufficient to drive depletion/enrichment of chemical components in a binary system. This chemical segregation leads to phase transformations by nucleation, coalescence and growth of the new phases. Sandia National Laboratories is a multi–program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE–AC04–94AL85000.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

Methods for Improving Damage Tolerance, Oxidation and Thermal Shock Resistance II

Room: Coquina Salon F
Session Chair: Yanchun Zhou, Aerospace Research Institute of Material & Processing Technology

8:00 AM

(ICACC-S12-012-2014) Oxygen incorporation in MAX phases (Invited)

M. to Baben*, L. Shang, J. Emmerlich, J. M. Schneider, Materials Chemistry RWTH Aachen University, Germany

As high stiffness, good oxidation resistance and self-healing behavior qualify certain MAX phases for high temperature applications, interaction with oxygen -especially incorporation of oxygen during the initial stages of oxidation- is essential for understanding and improving performance of these materials. Yet, systematic studies on oxygen incorporation in MAX phases are missing in literature. Oxygen incorporation in Ti2AlC, V2AlC and Cr2AlC was studied by ab initio calculations. Comparing calculated energies of formation for oxygen incorporation indicates that oxygen substitutes carbon in Ti2AlC and V2AlC, but is incorporated interstitially in the Al layer of Cr2AlC even for carbon deficient Cr2AlC. To evaluate these predictions, combinatorial DC sputtering was used to deposit thin films with different oxygen concentrations. Two phase-regions of Cr2AlC and Cr2Al were investigated in order to study oxygen incorporation in carbon deficient Cr2AlC. X-ray strain analysis data indicate that the a and c lattice parameters increase with oxygen content. These trends are in good agreement with the change of lattice parameters predicted by ab initio calculations and therefore corroborate the notion of interstitial oxygen incorporation in Cr2AlC. A metastable solubility limit for oxygen of 3.5 at.% was determined experimentally. These data may be of relevance during the initial stages of oxidation. [to Baben et al., Acta Mater. 60 (2012) 4810]

8:20 AM

(ICACC-S12-013-2014) A Critical Review of the Oxidation of Ti2AlC, Ti3AlC2 and Cr2AlC in Air

D. J. Tallman*, B. Anasori, M. W. Barsoum, Drexel University, USA

Of all the MAX phases, the most resistant to oxidation in air in the 900-1400 °C temperature range are Ti2AlC, Ti3AlC2 and Cr2AlC. A literature review, however, shows that while some claim the oxidation kinetics to be parabolic, others claim them to be cubic. Whether the kinetics are parabolic or better is of vital practical importance. By carefully re-plotting the results of others and carrying out one oxidation run for ≈3000 h at 1200 °C on a Ti2AlC sample, we conclude that the oxidation kinetics are better described by cubic kinetics and that even that conclusion is an approximation.

8:40 AM

(ICACC-S12-014-2014) Formation of a Nonstoichiometric Zirconium Oxide Interface during Oxidation of ZrB_2

M. Kazemzadeh Dehdashti, W. G. Fahrenholtz*, G. E. Hilmas, Missouri University of S & T, USA

A nonstoichiometric zirconium oxide layer has been observed during oxidation of ZrB_2 ceramics. A similar layer has been reported to affect the oxidation of zirconium, which occurs in two distinctive stages. During the first stage, oxidation kinetics are quasi-parabolic and the oxide scale formed is a black and dense nonstoichiometric zirconium oxide. During the second stage, the rate of oxidation is linear and the oxide scale is stoichiometric ZrO_2 with a bright appearance and tendency to spall. The formation of the nonstoichiometric zirconium oxide has not been reported for oxidation of ZrB_2. Although formation of a black scale has been observed between the ZrB_2 matrix and the outer scale, this layer was assumed to be zirconia with some retained boria. After oxidation at 1600°C for 6 hours, both nominally pure ZrB_2 and $(Zr,W)B_2$ contained the black layer, having a lower oxygen content than the bright layers. X-ray photoelectron spectroscopy showed that the black oxide scale contained nonstoichiometric zirconium oxide. Despite the same total oxide scale thicknesses for pure ZrB_2 and $(Zr,W)B_2$, the ratio of thickness of the black to white scale was higher for $(Zr,W)B_2$. This was attributed to a higher stability of the protective boria-metal oxide liquid phase, resulting in a delay in the transition from the black to white phase of zirconia and improved oxidation resistance for $(Zr,W)B_2$.

9:00 AM

(ICACC-S12-015-2014) Comparing Oxyacetylene Torch Testing and Furnace Facilities for Oxidation of Aerospace Materials

M. Miller-Oana*, L. Walker, M. Packard, P. Neff, E. Corral, University of Arizona, USA

We are interested in evaluating test facilities used for screening materials for oxidation behavior. The oxyacetylene torch and thermal gravimetric analyzer (TGA) furnace are commonly used for understanding oxidation behavior of materials such as carbon and ultra-high temperature ceramics (UHTCs). However, oxidation behavior is dependent on its environment. The environments of the torch and TGA vary in heating rates, temperatures, and gas species; therefore, we are comparing the oxidation behavior of carbon and UHTCs in both facilities. The torch facility is capable of fast heating rates (>500°C/min), high temperatures (>2000°C), high gas velocities (~200 m/s), and oxygen rich environments (<12 kPa O2). The TGA is capable of temperatures up to 1600°C, oxygen rich environments (~19 kPa O2), and in situ mass measurements. Carbon and UHTC oxidation rates are obtained from torch and TGA facilities. Carbon materials can be used as a model system, which can then be applied to more complex materials such as UHTCs.

9:20 AM

(ICACC-S12-016-2014) Oxide phase stabilization and high temperature oxidation resistance of Zr and Ta alloyed $Ti_{1-x}Al_xN$ coatings

R. Hollerweger*, H. Riedl, M. Arndt, Vienna University of Technology, Austria; R. Rachbauer, OC Oerlikon Balzers AG, Liechtenstein;
P. Polcik, Plansee Composite Materials GmbH, Germany; J. Paulitsch,
P. H. Mayrhofer, Vienna University of Technology, Austria

Oxidation resistance of $Ti_{1-x}Al_xN$ hard coatings is a key issue for cutting, drilling and machining applications. However, the formation of porous oxide scales at temperatures > 800 °C is limiting the coating lifetime. Alloying Zr or Ta to $Ti_{1-x}Al_xN$ has proven to significantly retard the oxidation processes. Nevertheless, detailed investigations on the structure-property-relations of these alloying elements and their influence on the oxidation resistance and phase formation are still missing. Therefore, Zr and Ta alloyed $Ti_{1-x}Al_xN$ coatings were deposited by cathodic arc evaporation and isothermally annealed at 850 and 950 °C in synthetic air for 5 h. For investigating the oxidation kinetics differential scanning calorimetry and thermo gravimetric analysis were used. X-ray diffraction of the oxidized films indicates that Zr favors the formation of a dense anatase dominated oxide scale, whereas Ta favors the formation rutile dominated oxide scale. Remarkably, both oxide scales result in a significant increase of the oxidation resistance as compared to multi-phased oxide scales like typically obtained for $Ti_{1-x}Al_xN$.

Structure-Property Relationships I

Room: Coquina Salon F
Session Chair: Greg Hilmas, Missouri University of Science and Technology

10:00 AM

(ICACC-S12-033-2014) Dopant effects on the preparation and performance of ultra high temperature ceramics (Invited)

G. Zhang*, Shanghai Institute of Ceramics, China

Ultra high temperature ceramics (UHTCs) with chemical and physical stability at high temperatures (e.g., above 2000 degree C) and in reactive atmospheres (e.g., monatomic oxygen) are key materials for applications in thermal protective systems of hypersonic flights (nose cones, leading edges and engine parts) and liquid/solid rocket engines. The UHTC family mainly includes compounds with melting temperatures of above 3000 degree C, such as borides, carbides and nitrides of transition metals and their composites. The sintering behaviors and material performances of UHTCs are closely related to the sintering additives (dopants), which will improve densification processes, optimize the microstructures, and improve the mechanical properties and oxidation resistances. In this presentation we will report our recent results on the dopant effects on the densification processing, solid solution formation, microstructure tailoring and material properties in the UHTC systems including ZrB2, HfB2, ZrC, HfC based ceramic materials.

10:20 AM

(ICACC-S12-018-2014) Processing and Thermal Conductivity of ZrB_2-ZrC Ceramics

G. J. Harrington*, G. E. Hilmas, W. G. Fahrenholtz, Missouri University of Science and Technology, USA

Solid state sintering of ZrB_2 is difficult due to its strong ionic and covalent bonding characteristics which limit the necessary diffusional processes. Densification has been improved by various researchers by attrition milling with WC to reduce particle sizes. One drawback from WC milling is W contamination, via the formation of $(Zr,W)B_2$, which leads to a significant decrease (~60% @ RT and ~12% @ 1300°C) in thermal conductivity (k). Previous research has shown that the presence of ZrC within ZrB_2, preferentially forms a (Zr,W)C solid solution instead of $(Zr,W)B_2$, resulting in an increase in k. In addition, ZrC has been shown to be an effective sintering aid for ZrB_2 by promoting solid state sintering. Therefore, the interaction between ZrC additions and WC contamination to ZrB_2 has been studied to evaluate the densification and k of the system. As-received commercial ZrB_2 and attrition milled powders were hot pressed with varying additions of ZrC (0-10 vol%). Hot pressing was performed between 1900 and 2100°C, depending on the milling procedure and ZrC content, to produce fully dense material, while minimizing processing temperatures. XRD was used to evaluate the formation of the (Zr,W)C solid solution. Heat treatments after densification were performed to study how the W content can be optimized by processing. The resulting k of the as processed and heat treated materials were then evaluated up to 2000°C.

10:40 AM

(ICACC-S12-019-2014) Microstructure and mechanical properties of (Ta,Hf)C ultra-high temperature ceramics

O. Cedillos*, D. D. Jayaseelan, W. E. Lee, Imperial College London, United Kingdom

Compounds of the TaC-HfC system have extremely high melting points (e.g. 4TaC-1HfC: 3990°C), making them candidates for thermal protection structures in hypersonic space vehicles. Compounds of 4TaC-1HfC were synthesised and sintered using various methods. Commercial powders of TaC and HfC were mixed with 0.5 wt% C and B_4C as sintering aids and sintered at 2100°C using hot pressing (HP) and spark plasma sintering (SPS). The effect of additives on sintering behaviour was evaluated using SEM, XRD and TEM. Isolated regions of Hf-B-C phase were found in samples with B_4C (~97% relative density) whereas a single phase material with 92% relative density was produced with 0.5 wt% C. An SPS furnace was used to produce TaC-HfC ceramics by self-propagating high-temperature synthesis (SHS) followed by sintering at 2100°C. Reactive processing routes included reactive spark plasma sintering (RSPS) and a two-step SHS and then SPS method. Reactant powders were prepared from Ta, Hf and carbon black. Core/rim structures of HfO_2/HfC in a matrix of (Ta,Hf)C were found in samples produced by reactive routes. The two-step processing route was found to be more effective than RSPS in producing dense TaC-HfC ceramics (~98%). Mechanical properties were measured (Hv_1: 17.96 ± 1.38 GPa, K_{Ic}: 2.53 ± 0.49 $kgMPam^{½}$) by nano and Vickers indentation. XRD analysis showed that solid solutions are formed during sintering.

11:00 AM

(ICACC-S12-020-2014) Effect of ZrB_2 particle size and $MoSi_2$ volume fraction on the mechanical properties of ZrB_2-$MoSi_2$ composite ceramics

R. J. Grohsmeyer*, Missouri University of Science and Technology, USA; A. D'Angio, National Research Council of Italy, Italy; G. Hilmas, W. Fahrenholtz, Missouri University of Science and Technology, USA; F. Monteverde, National Research Council of Italy, Italy; L. Silvestroni, National Research Council of Italy, Italy; D. Sciti, National Research Council of Italy, Italy

Mechanical properties of hot pressed zirconium diboride-molybdenum disilicide (ZrB_2-$MoSi_2$) composites were tested at room temperature and at elevated temperatures. ZrB_2 with starting particle sizes ranging from 1 to 8 microns was mixed with 5 to 35 vol% $MoSi_2$ additions and hot pressed to full density. Hot pressed billets were machined into test bars. Flexure strength was measured in four-point bending at room and elevated temperature (up to 1500 °C), and thermal expansion coefficient was measured from room temperature up to 1500 °C. In addition, room temperature properties such as Young's modulus, Vickers and nano-indentation hardness, chevron notch fracture toughness, and Poisson's ratio were measured and will be reported. Final phase content and microstructure were characterized using scanning electron microscopy, energy dispersive spectroscopy, optical microscopy and X-ray diffraction. The effects of varying ZrB_2 particle size and $MoSi_2$ volume fraction on the processing, densification behavior, and microstructure of ZrB_2- $MoSi_2$ composites will be discussed in a separate presentation.

11:20 AM

(ICACC-S12-021-2014) Densification mechanisms and microstructural characteristics of ZrB_2-$MoSi_2$ ceramics varying starting ZrB_2 particle size and $MoSi_2$ content

A. D'Angiò, National Research Council, Italy; W. Fahrenholtz, R. Grohsmeyer, G. Hilmas, Missouri University of Science and Technolgy, USA; F. Monteverde*, National Research Council, Italy; D. Sciti, National Research Council, Italy; L. Silvestroni, National Research Council, Italy

Zirconium diboride-based composites containing 5 to 35 vol% $MoSi_2$ were fully densified by hot pressing sintering with an applied uniaxial pressure of 30 MPa. The densification behavior was investigated through the analysis of the shrinkage vs. temperature curves and correlated to $MoSi_2$ volume fraction and ZrB_2 starting particle size (varying from 1 to 8 microns). The microstructural features were investigated by means of imaging with a FEG scanning electron microscope–energy dispersive spectroscopy, X-ray diffraction and depth sensing nano-indentation measurements. Formation of solid solution $(Zr,Mo)B_2$ shell structures around ZrB_2 core grains were commonly observed. Silicon carbide and other oxide species such as ZrO_2 and SiO_2, as well as Mo-B-O were also detected. The effect of the ZrB_2 mean grain size and amounts of $MoSi_2$ on densification and final microstructures were discussed and correlated to the final content of secondary phases.

11:40 AM

(ICACC-S12-022-2014) Densification and Mechanical properties of ZrB_2-TiB_2 Ultra High Temperature Ceramic Composites

K. Sengottaian*, B. S. Murty, S. Bakshi, Indian Institute of Technology Madras, India

Re-entry vehicles experience extreme high temperatures during the entry into earth's atmosphere. Thermal protection system of these types of vehicles should possess structural stability at high temperatures. Ultra high temperature ceramics (UHTCs) are candidate materials for thermal insulation components of atmospheric re-entry vehicles, mainly characterised by high melting point of above 3000 °C. ZrB_2 and TiB_2 possess high melting points above 3000 °C along with high thermal and electrical conductivity and high hardness. A composite of ZrB_2 and TiB_2 has advantage of being lighter and less expensive than 100% ZrB_2. In this present study,25ZrB_2-75TiB_2,50ZrB_2-50TiB_2, 75ZrB_2-25TiB_2 composites by vol.% have been investigated. Powder mixtures of ZrB_2 and TiB_2 were milled for 4h followed by spark plasma sintering at 1500 °C. Microstructure and phase analysis have been determined using SEM and XRD and the mechanical properties (hardness and indentation fracture toughness) of the composites are evaluated using nanoindentation and micro-hardness testing and compared with ZrB_2 and TiB_2.

2nd Pacific Rim Engineering Ceramics Summit

Pacific Rim Ceramic Technologies: Trends and Directions III

Room: Coquina Salon C
Session Chairs: M. Singh, OAI/NASA GRC; Do Kyung Kim, KAIST

1:30 PM

(ICACC-PRECS-022-2014) Material Challenges and Opportunities for Commercial Electric Aircraft (Invited)

A. K. Misra*, NASA-Glenn Research Center, USA

Significant reduction in carbon dioxide emission for future air transportation system will require adoption of electric propulsion system and more electric architectures. Various options for aircraft electric propulsion include hybrid electric, turboelectric, and full electric system. Realization of electric propulsion system for commercial aircraft applications will require significant increases in power density of electric motors and energy density of energy storage system, such as the batteries and fuel cells. In addition, transmission of MW of power in the aircraft will require high voltage power transmission system to reduce the weight of the power transmission system. Finally, there will be significant thermal management challenges. Significant advances in material technologies will be required to meet these challenges. Technologies of interest include materials with higher electrical conductivity than Cu, high thermal conductivity materials, and lightweight electrically insulating materials with high breakdown voltage, high temperature magnets, advanced battery and fuel cell materials, and multifunctional materials. The presentation will include various challenges for commercial electric aircraft and provide an overview of material improvements that will be required to meet these challenges.

2:00 PM

(ICACC-PRECS-023-2014) Nanostructured Dielectrics for High Energy Density Capacitors (Invited)

F. Dogan*, Missouri University of Science and Technology, USA

Recent research efforts at Missouri S&T on nanostructured dielectric ceramics for high energy density capacitor applications will be reviewed. Titanium dioxide ceramics with various grain sizes were investigated by impedance spectroscopy techniques. Dielectric loss peak identified in coarse grain TiO2 was attributed to space charge polarization occurring at the grain boundaries. Electric modulus representation of the impedance data showed two types of relaxation processes in coarse grain dielectric, whereas only one type was observed in fine grain dielectric. Long-range migration of oxygen vacancies was found to be the dominant conduction mechanism for fine grain TiO2, while electron hopping between localized states was attributed to dielectric relaxation in coarse grain TiO2. Effects of donor and acceptor type dopants on the sintering and dielectric properties of nanostructured titanium oxide ceramics will be discussed.

2:30 PM

(ICACC-PRECS-024-2014) The Research Trend for the Next-Generation Rechargeable Batteries in Korea: A Perspective for Materials Design Approaches (Invited)

D. Kim*, KAIST, Republic of Korea

Lithium-ion batteries (LIBs) have been deeply investigated due to their high energy density and a long lifetime as the power supply of mobile devices. Although LIBs can provide higher energy density than other rechargeable battery types, they still have limitations on energy density and high cost to apply electric vehicles (EVs) and large energy storage systems (ESSs). Therefore, alternative rechargeable battery systems which can go beyond current LIBs have been extensively pursued. In order to achieve high performance next-generation batteries, several research projects for the development of rechargeable Li-air batteries, Li-S batteries, and Na-ion batteries are currently underway at R&D institutes of Korea. In this presentation, recent research progress for beyond LIBs in Korea will be briefly introduced. In particular, the necessary approaches as well as the future direction of research from a perspective for materials design will be discussed.

3:20 PM

(ICACC-PRECS-025-2014) Introduction of industrial root technology: A bridge between R&D philosophy and its practical embodiment (Invited)

S. Lee*, Korea Institute of Industrial Technology, Republic of Korea

SME (Small and Medium-sized Enterprise) supporting policy focusing on the innovative technology development followed by subsequent profit making has been systematically pursued in every nation. Under this circumstance, it is very natural that national R&D budget reaches 4-5% of total annual budget of each OECD country. Unfortunately, however, the ratio of the practical industrialization supported by the governmental R&D scheme is reported to be only 10-30% of the total numbers of research projects. Through tremendous efforts to overcome this phenomena, a strong bridge between R&D philosophy and its practical embodiment for the industrialization has been suggested, namely, the industrial root technology. The industrial root technology consists of 6 technology fields, such as casting, molding, welding/joining, heat treatment, surface modification, and forming. In this report, the development case study of each technological category is attempted to explain in order to grasp the main idea and its function of the industrial root technology for the related industry. Future mega trend of its development shall be also mentioned.

3:50 PM

(ICACC-PRECS-026-2014) The Role of Regional Institutes in Technology Development, Transfer and Education: The Ohio Aerospace Institute Model (Invited)

M. Heil*, Ohio Aerospace Institute, USA

This presentation will discuss how the non-profit Ohio Aerospace Institute (OAI) works with industry, academia, US federal laboratories, and government organizations to develop and transfer technologies, educate and train the workforce and help organizations succeed in the growing global aerospace marketplace. Examples will be shared of technologies developed and transferred by OAI and of partnerships developed and managed by OAI.

4:10 PM

(ICACC-PRECS-027-2014) UBE's Future Activity on Ceramics (Invited)

T. Ishikawa*, Ube Industries, Ltd., Japan

Ube Industries have many types of ceramics, whose main resources are bountiful elements in the earth, that is to say, Mg, Ca, and Si. Of these, silicon nitride powder (E10) with very high purity and SiC-based fibers (Tyranno) with high heat-resistance are well-known all over the world. The productivity of both materials will be increased in near future accompanied by the improved characteristics for many types of applications (structural materials, aerospace applications, and so on). Besides, Ube Industries have produced fine spherical silica powder with sharp mono-dispersion using precursor method. This type of spherical silica is expected for the wide application in the fields of electronics devices. Furthermore, making the best use of the production process of the aforementioned Tyranno, we have developed unique photo-catalytic fiber with very high quantum efficiency. In addition to these materials, Ube Industries is one of the big companies manufacturing Mg-based ceramic powders and Ca-based ceramic powders. Especially, Ube's MgO shows very high thermal-conductivity and excellent moisture-stability. In this presentation, wide information of these functional ceramics will appear along with comparative information.

4:30 PM

(ICACC-PRECS-028-2014) Development of electro-optical single crystals for energy saving (Invited)

K. Shimamura*, E. Garcia Villora, National Institute for Materials Science, Japan

Optical technology progress in a wide range of applications, and still demands the further development. Since conventional crystal materials face some of the limitations, these issues require new optical single crystals. Here, novel single crystals with advantageous characteristics will be introduced. β-Ga_2O_3 exhibits the largest band gap (Eg = 4.8 eV) among TCOs. 1 and 2 inch size β-Ga_2O_3 single crystals were grown by the FZ and EFG techniques, respectively. Epitaxial growth of InGaN-MQW on β-Ga_2O_3 was realized by the MOCVD technique. Vertical structured blue LEDs on β-Ga_2O_3 with different packaging styles were demonstrated. A new concept of high-brightness white LEDs based on Ce:YAG single crystal phosphor plates (SCPPs), which can overcome the conventional temperature- and photo-degradation problems, is proposed. SCPPs demonstrated excellent thermal stability with no temperature quenching, high values of luminous efficacy and increased quantum efficiency. $Tb_3(Sc_{1-x}Lu_x)_2Al_3O_{12}$ (TSLAG) single crystals with 1 inch in diameter have been designed and grown for high-power laser machinery. TSLAG showed a higher visible transparency and a larger Faraday rotation than $Tb_3Ga_5O_{12}$. TSLAG is therefore very promising material in particular for new magneto-optical isolator applications in the VIS-NIR wavelength. Authors would like to thank to Koha Co., Ltd., and Fujikura Ltd., for the collaboration.

4:50 PM

(ICACC-PRECS-029-2014) Three Dimensional Printing of Ceramics Dendrites to Modulate Energy and Material Flows (Invited)

S. Kirihara*, Osaka University, Japan

Ceramics dendrites with spatially ordered micro cavities were successfully fabricated by three dimensional printing of stereolithography. Micro lattices pattern were propagated spatially in computer graphic space. Ceramics nanoparticles were dispersed in to photo sensitive liquid resins to obtain thixotropic slurries. The paste material was spread on a grass substrate by using a mechanical knife edge, and an ultra violet micro pattern was exposed by a digital micro-mirror device to create cross sectional solid layer. The ceramics dendrites were obtained by layer stacking. The composite precursor was dewaxed and sintered in an air atmosphere. Through this process, solid electrolyte dendrites of yttria stabilized zirconia were fabricated for fuel cell miniaturizations Gaseous fluid profiles and pressure distributions in the formed ceramic lattices were visualized and analyzed by a finite element method. Subsequently, alumina photonic crystals with a diamond lattice structure were fabricated. Electromagnetic wave properties were measured by using a terahertz time domain spectroscopy. A complete photonic band gap was exhibited, and a localized mode to select the wavelength was obtained by introducing a defect cavity. Moreover, artificial bones of hydroxyapatite scaffolds were modeled to realize excellent biological compatibilities. Graded porous structures in the artificial bones were processed.

5:10 PM

(ICACC-PRECS-030-2014) Development of High-Thermal-Conductivity Silicon Nitride Ceramics for Power Module Applications (Invited)

Y. Zhou*, H. Hyuga, Y. Yoshizawa, T. Ohji, N. Murayama, K. Hirao, National Institute of Advanced Industrial Science and Technology (AIST), Japan

With increasing power supply and packing density, requirements for ceramic substrates used for power modules are getting higher. Ceramic substrates with both high thermal conductivity and good mechanical properties are needed. In the past few years, we have carried out studies of preparing silicon nitride ceramics via a route of sintering of reaction-bonded silicon nitride (SRBSN) process, where green compacts composed of a high purity silicon powder doped with sintering additives were firstly nitrided in a nitrogen atmosphere and then sintered at higher temperatures to attain full densification. The silicon nitride ceramics prepared by this SRBSN method showed obviously higher thermal conductivity compared to the silicon nitride ceramics prepared by the conventional gas pressure sintering of silicon nitride powder. The improvement of thermal conductivity was attributed to the lower content of oxygen impurity dissolved in the lattice of Si3N4 grains. Moreover, the SRBSN silicon nitride ceramics showed high fracture toughness. By minimizing the lattice oxygen content and appropriately enhancing grain growth through optimizing the nitridation and sintering conditions, silicon nitride ceramics possessing thermal conductivity as high as 177 W/(mK) and fracture toughness around 11 MPa m1/2 could be fabricated. (Part of the research work was supported by NEDO, Japan)

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Optics II

Room: Oceanview
Session Chair: Mauro Epifani, CNR-IMM

1:30 PM

(ICACC-FS2-024-2014) Solutions for synthesis of complex photo-active materials (Invited)

G. Westin*, Uppsala University, Sweden

Solar energy harvesting for fuel or electricity generation requires versatile and cost efficient synthesis routes capable of producing very complex functional nano-materials at low cost. The wide spectrum of solution based processes probably provide the most promising routes for this purpose, but the complexity and diversity of the reactions taking the precursor molecules in solution to gels or nano-particles and their further processing into ceramic purpose designed structures require much understanding. Therefore knowledge about the entire route from precursor to target oxide is needed to produce well controlled high quality materials and make choices of suitable techniques. The synthesis of complex materials systems from metal-organic precursors will be described with an emphasis on doped and non-doped semi-conductor nano-particles and wires and core-shell structures including oxides of Fe, Co, Ti and Zn. Properties will be correlated with the detailed structures of the materials.

1:50 PM

(ICACC-FS2-025-2014) Highly Photosensitive Fiber Fabricated from Photo-Thermo-Refractive Glass (Invited)

P. Hofmann, University of Central Florida, USA; K. Al Yahyaei, University of Arizona, USA; C. Jollivet, A. Van Newkirk, R. Amezcua-Correa, E. Antonio-Lopez, D. Ott, M. SeGall, I. Divliansky, L. Glebova, L. Glebov, A. Schulzgen*, University of Central Florida, USA

With the goal to extend applications of highly photosensitive photo-thermo-refractive (PTR) glass from bulk glass components to the fiber optic platform, we have successfully fabricated single material fibers and step index fibers from PTR type glasses. The fibers were drawn from rod-in-tube preforms which have been prepared using specialty diamond tools for shaping and polishing of the glass materials. We measured attenuations of less than 0.1 dB/cm in our PTR glass fibers. Strong fiber Bragg gratings were inscribed into the novel fibers demonstrating the fibers photosensitivity. High grating strength of up to 20 dB were reached and maintained even at 12 hour exposure to temperatures above 400 °C. Our results open exciting new avenues for the development of holographic PTR glass fiber optic components which may be applied in fiber optic devices that require high temperature stability and high optical power levels.

2:10 PM

(ICACC-FS2-026-2014) Advanced Photonics based on Infrared Glass and Glass Ceramic Solutions (Invited)

K. Richardson*, University of Central Florida, USA; J. Musgraves, IRradiance Glass, Inc., USA; P. Wachtel, Clemson University, USA; T. Mayer, D. Werner, Pennsylvania State University, USA

Advanced photonic devices require novel optical materials that serve specified optical function but also possess attributes which can be tailored to accommodate specific optical design, manufacturing or component/device integration constraints. Multi-component chalcogenide glass (ChG) materials have been developed which exhibit broad spectral transparency with a range of compositionally tunable physical properties that be tuned to vary with composition, material microstructure and form. The opportunities to exploit these materials in multiple forms (i.e., bulk optics, coatings) for a diverse range of applications extending from planar chem-bio sensing, to bulk MWIR imaging systems, is discussed. Key findings on optimization of material thermal mechanical stability, CMOS fabrication compatibility and overall component manufacturability, are presented.

2:30 PM

(ICACC-FS2-027-2014) Full Color Up-conversion Fluorescence as Full Color Display

H. N. Luitel*, Saga University, Japan; H. Gotou, Shinwa Bisho Kabushiki Khaisa, Japan; T. Watari, Saga University, Japan

Up-conversion (UC) phosphors are materials which convert long wavelength photons to short wavelength photons. These UC luminescence materials with strong luminescence in the visible region has enormous applications like in displays, spectral convertors for solar modulus, high density optical storage, infrared detection and sensors, bio medical diagnosis etc. These UC phosphors were synthesized by conventional solid state reaction method. A 980 nm cw laser was used as excitation source and fluorescence was measured using Ocean Optics USB 4000 instrument. Phase evolution and morphology was measured by Shimadzu XRD 6300 and Hitachi SEM 4000, respectively. Bright up-conversion phosphors of full color in visible range viz. blue, green, orange and red were successfully fabricated. The CaMoO3:Tm3+/Yb3+/Li+, ZnO. TiO2:Er3+/Yb3+, CaZrO3:Er3+/Yb3+, Y2O3:Er3+/Yb3+/Li+/Zn2+ phosphors exhibited Blue, Green, Orange and Red UC luminescence, respectively, pumped by 980 nm cw laser. The UC emission brightness dependency according to the host compositions, rare ions concentrations (Er3+,Yb3+,Tm3+) or charge compensator (Li+,Zn2+ etc.) were studied and discussed extensively. The underlined mechanisms of UC fluorescence was studied by laser pump powder dependency of emission taking into consideration of orange emitting ZnO.TiO2:Er3+/Yb3+ phosphor.

3:20 PM

(ICACC-FS2-028-2014) Effect of non-stoichiometry on the terahertz properties of YAG optical ceramics

R. Gaume*, University of Central Florida, USA; D. Steere, S. K. Sundaram, Alfred University, USA

We have investigated the effect of non-stoichiometry in fully dense optical ceramics of Y3Al5O12 on their dielectric response between 0.5 and 4THz, and compared to that of a single-crystal. A set of twenty ceramic samples was prepared by solid-state sintering of Y2O3 and Al2O3 mixtures with compositions ranging from -0.62 mol% to +0.96 mol% of Y2O3 on either side of the central garnet composition. After sintering, all samples were highly translucent in the visible, with attenuations better than 2 cm-1. In this study, the samples were characterized using time-domain THz spectroscopy. Contrary to single-crystals, all ceramic samples exhibit multiple weak resonances below 3.6 THz with amplitudes that depend on their composition. In addition, our experimental results show that the static permittivity goes through a minimum at the stoichiometric composition (ε0 = 10.83) and varies by more than 1% in this composition range. This trend is well reproduced by a simple resonance model.

Advanced Applications

Room: Oceanview
Session Chair: Luca Razzari, INRS-EMT

3:40 PM

(ICACC-FS2-029-2014) Modified metal oxide nanomaterials for gas sensing: from doping to surface coating and beyond (Invited)

M. Epifani*, CNR-IMM, Italy

A relationship exists between chemoresistive gas sensors and heterogeneous catalysis. In catalysis, the focus is on the chemical transformation of a known gas-phase. In gas-sensors, the gas-phase is expected to be of unknown composition and in very low concentrations (ppm or even ppb). It is necessary to amplify and translate into a readable signal the outcome of the chemical reactions at the sensor-gas interface. For this reason the focus is on the electrical behavior of the oxide sensing layer. It is then not surprising that the same concepts of catalysis can be useful in gas-sensors. Well-known application of catalysis background is the addition of noble metals to metal oxides for improving the gas-response. In this work, first the synthesis Pd/SnO_2 and Pt/TiO_2 nanocomposite systems by colloidal techniques will be reviewed for sensing applications. Moreover, since in the TiO_2-V_2O_5 catalyst vanadia usually modifies the surface of titania, it can be expected that such system may also be a powerful sensing material. Here the synthesis of TiO_2-V_2O_5 colloidal nanocrystals will be discussed. Comparison of the sensing properties of the TiO_2 and TiO_2-V_2O_5 nanocrystals will show the beneficial effect of the surface V deposition, opening the way to similar material architectures for improved gas-sensors. Hence, extension to the TiO_2-WO_3 system will be the last example to be discussed.

4:00 PM

(ICACC-FS2-030-2014) Multiphoton Excited Nanoparticles as Multi-Modal Bioimaging Probes (Invited)

F. Vetrone*, Institut National de la Recherche Scientifique - Énergie, Matériaux et Télécommunications, Université du Québec, Canada

Multiphoton excited luminescent nanomaterials are emerging as useful tools in diagnostic medicine and therapeutics. These nanomaterials are excited with near-infrared (NIR) light, which is silent to tissues thus minimizing autofluorescence and possesses greater tissue penetration capabilities. Well-known multiphoton excited nanomaterials include semiconductor quantum dots and gold nanorods, which require femtosecond (fs) excitation light to induce the luminescence resulting in increased spatial resolution, as the excitation will only occur at the focal point. An alternative to these multiphoton excited nanomaterials is lanthanide (Ln^{3+})-doped upconverting nanoparticles, which have the ability to (up) convert NIR light to higher energies spanning the UV to the NIR. This occurs via the process of upconversion and results from the multitude of Ln^{3+} electronic energy states, many of which are equally spaced leading to the sequential absorption of multiple NIR photons. These real energy states are long-lived and thus, upconversion can be observed following excitation with low energy cw NIR diode lasers. In contrast, other multiphoton excited nanomaterials require the simultaneous absorption of photons from ultrafast fs lasers. Here, we present various types of multiphoton excited nanoparticles and show how they could be used as multi-modal bioprobes for imaging as well as the diagnostics and therapeutics of cells.

4:20 PM

(ICACC-FS2-031-2014) Design and Mass Transport in Hexaboride Nanomaterials for Hydrogen Storage Applications (Invited)

O. A. Graeve*, University of California, San Diego, USA; V. R. Vasquez, University of Nevada, Reno, USA

This project focuses on two novel and complementary processing techniques for the continuous and scaled nanomanufacturing of boride materials (solution combustion synthesis for production of the boride powders and spark plasma sintering for consolidation of the powders), as well as on fundamental studies that can eliminate critical roadblocks during scale-up. We present two compounds, CaB_6 and LaB_6, as model materials for representing the effectiveness of the process for the preparation of borides. The technique results in high-purity powders with unique cubic morphologies, where the surfaces correspond to the {001} faces of the crystals. Characterization of these structures will be discussed. In addition, we use molecular dynamics with representative potentials to describe the interactions and diffusion of gases in the hexaboride cages. Molecular dynamics calculations provide significant insight on the type of gases that could be stable in these cages and how the hexaboride structure affect their mobility and stability in the system. We also describe how the effect of external fields such as electric, pressure gradients, and heat flow affect the relative positions of the atoms in the structures and their mass transport behavior. The diffusion process is characterized using mean square displacement of atoms and the Einstein relation to evaluate diffusion coefficients.

4:40 PM

(ICACC-FS2-032-2014) Chalcogenide glass ceramics based on GeSe2-Sb2Se3 for photo-catalysis (Invited)

X. Zhang*, Y. Xu, B. Fan, L. Calvez, H. Ma, University of Rennes I, France; X. Fan, Q. Shen, X. Qiao, Q. Luo, Zhejiang University, China; A. Lafond, CNRS, France

This presentation deals with the fist results concerning the preparation and properties of chalcogenide glass ceramics with outstanding photoelectric properties. The precursor chalcogenide glasses have been prepared by using the conventional technique employing vacuum sealed silica tube. The glass ceramics have been obtained by heat treating the precursor glasses at appropriate temperatures for different durations. The photoelectrical properties of these new materials have been particularly studied. It has been demonstrated that intense photocurrent can be obtained. P-type and n-type as well as simultaneously p- and n-type glass ceramics can be obtained with the same composition just by adjusting the heat treatment process. These glass ceramics have strong visible absorption and have been tested for photo catalysis through photodecomposition of orange methyl. Compared to the commercially available P25 TiO2, a much higher efficiency has been obtained with these new glass ceramics under visible illumination.

5:00 PM

(ICACC-FS2-033-2014) Eu2+-doped Alumina Scintillator produced by Gel-casting and Vacuum Sintering

Y. Wu*, Y. Yang, Alfred University, USA

Eu2+-doped alumina scintillator was prepared by gelcasting using a water soluble gelling agent followed by vacuum sintering. The suspension of Eu doped alumina was made by Eu2O3, Al2O3, water and a gelling agent mixed by the ball-milling method. The viscosity and gelling process were tested. The Eu2+ was produced by reduction of Eu3+ ions without reducing additives. The microstructure of the sintered ceramic was tested by Scanning Electron Microscopy (SEM) and the transmittance of the sintered bodies was characterized by Fourie Transform Infrared Spectrometry (FTIR). The influence of Eu2+ concentration on the 5d-4f luminescence properties under UV lamp excitation was investigated.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanics & Characterizations II

Room: Coquina Salon D
Session Chairs: Greg Morscher, University of Akron; Jiageng Su, Tsinghua University

1:30 PM

(ICACC-S1-012-2014) Advancements in Acoustic Micro Imaging for the Non-Destructive Inspection of Ceramic Components and Devices

J. H. Richtsmeier*, T. McClenahan, Sonoscan, Inc., USA

Acoustic Micro Imaging is an established non-destructive inspection technique that applies high frequency ultrasound for the inspection of materials, components and devices. The technology has been used for bond assessment, defect and flaw detection as well as overall materials characterization. Recent advancements and new developments have allowed more applications to be developed within the ceramics and composites marketplace including the following: * Higher Frequency Transducers * Rotational staging for bearings, tubes and cylinders * 3-D Virtual Rescan Mode (VRM) * Frequency Domain Imaging (FDI) * Acoustic Surface Flatness (ASF) Profilometry * Sonosimulator (multi-level analysis) * Integral Mode * Sonolytics (micro-slicing) This paper will cover recent advancements in Acoustic Micro Imaging as they pertain to various case studies and applications within the ceramic components and device marketplace.

1:50 PM

(ICACC-S1-013-2014) Acoustic Emission and Electrical Resistivity During Tensile Testing of Different Volume Fraction SiC/SiC Composites

A. Almansour*, E. Maillet, G. Morscher, The University of Akron, USA

Ceramic Matrix Composites (CMCs) are candidates for high-temperature applications such as the new generations of aircraft engines and hypersonic vehicles. In severe conditions, durability of CMCs is controlled by fiber exposure to environment, which depends on the damage state in the matrix. Matrix cracking is a stochastic phenomenon controlled by the initial population of flaws, interfacial properties and thermal residual stresses. The ability to model the stress-dependent matrix cracking in CMCs for various fiber types and fiber volume fractions is crucial for lifetime assessment in service conditions. Hi Nicalon, Hi Nicalon Type S and Tyranno ZMI reinforced minicomposites with BN interphases were tested with different fiber volume fractions. Tensile tests, acoustic emission and electrical resistivity monitoring were performed to assess damage development during the test. Microstructural analysis was performed to measure the actual crack density and spacing at failure. Crack density and spacing were analyzed to determine the exact crack formation, crack evolution and crack location. Finally, the mechanical behavior was modeled based on damage progression from health monitoring techniques.

2:10 PM

(ICACC-S1-014-2014) Health monitoring of Ceramic Matrix Composites using waveform-based analysis of Acoustic Emission

E. Maillet*, G. N. Morscher, The University of Akron, USA

The implementation of Ceramic Matrix Composites (CMCs) in the hot section of aircraft engines requires the understanding of the various damage modes that are involved and their relation to life expectancy. Acoustic Emission (AE) has been shown to be an efficient technique for monitoring damage evolution in CMCs. However, only a waveform-based analysis of AE can offer the possibility to validate and precisely examine the recorded AE data with a view to damage localization and identification. The present work fully integrates wave initiation, propagation and acquisition in the analysis of AE waveforms recorded at various sensors, therefore providing more reliable information to assess the relation between Acoustic Emission and damage modes. The procedure allows selecting AE events originating from damage, accurate determination of their location as well as their association to a source damage mode. The procedure was developed using AE data recorded during tensile tests on carbon/carbon composites and it was then applied to SiC/SiC composite systems in various testing conditions.

2:30 PM

(ICACC-S1-015-2014) Indicators for the damage evolution at high temperature under air of a SiC/[Si-B-C] composite subjected to cyclic and static loading

E. Racle*, N. Godin, P. Reynaud, M. R'Mili, G. Fantozzi, INSA Lyon, France; L. Marcin, Snecma Groupe Safran, France; F. Bouillon, Herakles Groupe Safran, France; M. Kaminski, Onera, France

The Low density and the high tensile strength of Ceramic Matrix Composites (CMC) make them a good technical solution to design aeronautical structural components. For a civil application, SiC/[Si-B-C] composites with self-healing matrix seems to be one of the best alternatives. To fully understand damage mechanisms and be able to design components, its behaviour has to be analysed during fatigue tests. The aim of the present study is to compare behaviour of this composite under static and cyclic loading. Tests are realised under the same conditions of temperature and maximal load levels in order to determine the effects of cycles on the sequence of damage mechanisms. Hence the evolution of mechanical parameters is analysed. Nevertheless the complexity of mechanisms and duration of tests make the use of complementary damage indicators necessary. Here different approaches based on acoustic emission are taken into consideration in order to quantify damage along the tests. First the analysis of acoustical energy enables to point out different levels of damage. Otherwise clustering is used to get the characteristics of each mechanism. It enables then the real-time detection of different phenomena and the formulation damage scenarii.

3:10 PM

(ICACC-S1-016-2014) Characterization of Thermal Expansion and Phase Transformations in the Ln2TiO5 System via in situ Synchrotron X-ray Diffraction (Ln= Dy, Y, Ho, Er) up to 1500 °C

K. C. Seymour*, R. W. Hughes, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Variations in processing and characterization methods have led to conflicting information regarding the number and types of phases present in the rare-earth titanate family. Conventional solid-state processing prevents the stable room temperature phase from developing, and quenching of high temperature phases for characterization proves to be problematic in providing an accurate description of the structure in the high temperature regime. In this study, stable room temperature phases were produced using an inorganic-organic entrapment process. Subsequently, synchrotron X-ray diffraction was employed in conjunction with a high temperature apparatus (a quadrupole lamp furnace) to study the evolution of the phases and characterize the thermal expansion behavior in selected rare-earth titanates in situ, in air. Relationships between rare-earth cation size and structural parameters up to 1500 °C have been investigated to bring clarity to this materials system.

3:30 PM

(ICACC-S1-017-2014) High Energy X-rays Characterizing the Material Behavior of High Temperature Thermal Barrier Coatings

K. Knipe*, S. Sofronsky, S. Siddiqui, A. Manero, University of Central Florida, USA; C. Meid, J. Wischek, German Aerospace Center, Germany; J. Okasinski, J. Almer, Argonne National Laboratory, USA; A. Karlsson, Cleveland State University, USA; M. Bartsch, German Aerospace Center, Germany; S. Raghavan, University of Central Florida, USA

This study monitors the material behavior of Thermal Barrier Coatings (TBC) used on turbine blades. Samples tested consisted of 7-8 wt% YSZ applied by EB-PVD with a NiCrCaAlY bond coat. Monitoring of the phases in each layer and their material, mechanical and thermal characteristics under thermal gradient and mechanical loads gives insight into the behavior of these coatings at high temperature. High-energy synchrotron x-rays were used to provide measurements with depth resolution through the bond coat and YSZ layers of 30 to 50 μm. X-ray diffraction patterns were taken using a 2D detector, giving accurate 360° lattice parameter measurement. The necessary information for the separation of lattice parameter changes between thermal expansion and residual mechanical strain was obtained by varying mechanical loading at high temperature. Monitoring lattice parameters such as c/a for the t' YSZ phase gives insight into stabilizer concentration over cycling and corresponding load bearing capabilities. Additionally, these measurements give the susceptibility to phase transformations of the bond coat and its load bearing capability at high temperature under various loading conditions. Results from this study provide knowledge of how these coatings behave at high temperature and its dependence on phase and lattice parameters under variable real life thermal gradient and mechanical loads.

3:50 PM

(ICACC-S1-018-2014) Piezospectroscopy Measurements of Thermal Barrier Coating Systems

A. Manero*, S. Siddiqui, S. Sofronsky, K. Knipe, University of Central Florida, USA; C. Lacdao, M. Smith, Cleveland State University, USA; J. Wischek, C. Meid, German Aerospace Center, Germany; A. Karlsson, Cleveland State University, USA; M. Bartsch, German Aerospace Center, Germany; S. Raghavan, University of Central Florida, USA

This research presents results for spectroscopy studies on thermal barrier coating layered systems. The primary study was conducted on a nickel superalloy cylindrical sample, with a multi-layer system deposited via electron beam physical vapor deposition (EB-PVD) including a thermally grown oxide (TGO) and partially stabilized zirconium oxide (YSZ) top coat. Selected spectroscopy studies were investigated via Raman Spectroscopy and Photo-Luminescence Spectroscopy with a 532 nm diode laser and Renishaw Ramascope via a 10x fiber optic probe. Readings were collected around the circumference in 10 degree increments, and yielded the variation of the materials' characteristic peaks from which a residual stress profile was determined around the circumference for multiple layers. The findings uniquely show the stress profile of the YSZ and TGO during early cycling, and present variations around the circumference for varying locations in the testing area. Results showcase the degree of uniformity during this stage of development. The outcomes of these studies will advance the understanding of TBC residual stress during early cycling for cylindrical specimens, and provide valuable material response information for system modeling.

4:10 PM

(ICACC-S1-019-2014) Coefficient of Thermal Expansion and Pressure-Induced Phase Transformation Measurement of β-eucryptite Doped with Mg

Y. Chen*, S. Ramalingam, I. E. Reimanis, Colorado School of Mines, USA

Lithium aluminum silicates such as β-eucryptite ($LiAlSiO4$) are well-suited for thermal shock resistant structures, precision optics platforms, and various other applications where low or negative coefficient of thermal expansion (CTE) is required. Particularly, β-eucryptite has potential use in many of these applications because it exhibits an average negative CTE. β-eucryptite is also known to undergo a reversible pressure-induced phase transformation at ~0.8 GPa to ε-eucryptite. Previous result shows that when β-eucryptite is doped with small amounts of Zn (as low as 0.1 molar percent), the CTE increases significantly, and the tendency of microcracking decreases greatly compared with pure β-eucryptite. The present study extends the work to Mg doped β-eucryptite on both CTE and pressure-induced phase transformation. Since Mg and Li have similar ionic radius, it is likely that Mg substitutes for Li in the β-eucryptite structure and changes structural ordering along the c-axis. Dilatometry is used to measure the CTE of doped and un-doped β-eucryptite synthesized from chemical precursors while in situ DAC-Raman spectroscopy is used to investigate pressure induced phase transformations in both.

4:30 PM

(ICACC-S1-020-2014) Optical Dilatometry

C. Linseis*, Linseis Messgerate GmbH, Germany

Dilatometry has been used to characterize ceramic materials, for many decades. (i.e. the coefficient of thermal expansion and the sintering processes.) The classical push rod dilatometers are widely used due to high resolution and a comparably low cost. However, during the measurement the sample needs to be pressed with a certain force, which may affect sintering investigations, negatively. New Optical Dilatometers have been developed for more precise measurements, in recent years. These systems provide measurements without external loads on the sample. The working principle of the new innovative Optical Dilatometers provides many essential benefits. The new Optical Dilatometer measures both the linear and volumetric Coefficient of Thermal Expansion (CTE). These parameters can be measured in any surrounding atmosphere or in high vacuum. The instrument also enables very accurate studies of the sintering process. The instrument can also be used as a Heating Microscope to determine the surface tension from the measured sample contact angles.

S3: 11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Status and Prospectives of SOFC and SOEC

Room: Coquina Salon H

Session Chairs: Mihails Kusnezoff, Fraunhofer IKTS; Jeffry Stevenson, Pacific Northwest National Lab; Alexander Michaelis, Fraunhofer Inst. for Ceramic Technology & Systems; Narottam Bansal, NASA Glenn Research Center

1:30 PM

(ICACC-S3-001-2014) SOFC as the central control and essentials supply of plant factory aka vertical farming

L. Tseng*, Electric Energy Express, Taiwan

An SOFC unit in operation will generate electricity and heat, plus carbon dioxide and water. Those come out from SOFC are the essentials for plants to grow through the photosynthesis reaction. The electricity will light up LED with adjustable output spectrum; while the heat will provide a growing environment for plants especially in the long winter regions. Higher CO2 concentration and moisture will facilitate the process of photosynthesis. The un-wanted CO2 and extra heat in some regions will become the necessary growing elements for plants, plus the use of controllable light sources, the harvest can be double-folded. The most attractive is the operational cost saved for running a plant factory.

1:50 PM

(ICACC-S3-002-2014) High-Temperature Direct Fuel Cell Material Experience

C. Yuh*, M. Farooque, FuelCell Energy, Inc., USA

Worldwide demand for fuel cells for green and high efficiency power generation is growing to conserve fossil fuels, efficiently utilize renewable biogases, and reduce emissions of greenhouse and acid-rain precursors. FuelCell Energy (FCE) is meeting this growing demand for green power with its Direct Fuel Cell products (DFC®). It is based on high-temperature internal-reforming carbonate fuel cell technology, operated at approximately 550-650°C, capable of achieving an electric simple-cycle efficiency approaching 50% (LHV). FCE has been engaged in DFC development since the mid-1970s and has advanced the technology by developing an in-depth understanding of the life and performance controlling factors, practical and low-cost solutions, and verification in multi-year field operations. The stack service life has been advanced to 5 years for the current generation, and improvements continue. In developing the DFC, extensive high-temperature material experiences such as oxidation and Cr effect, dual-atmosphere corrosion, redox stability, use of protective or conductive coatings, thermo-mechanical stress effect, etc. have been gathered. There are many similarities between DFC and SOFC in terms of operating conditions, performance, materials stability, cost and manufacturing. In this paper, DFC materials design considerations and experience will be discussed, explaining how the DFC experience could be applicable to the SOFC.

2:10 PM

(ICACC-S3-003-2014) Biomass gasification and catalytic reforming for SOFC

U. Cheong*, national taiwan university, Taiwan; W. J. Wei, national taiwan university, Taiwan

Biomass is one of the promising renewable energy sources. However, thermal processing produces tar and sulfur which will make catalyst or anode coking and poisoning during gasification. Molten salt catalysts for tar reforming have the potential to prevent the shortages, and greatly reduce the char formation. In this paper, four bio-masses have been gasified, including palm fiber (PF), municipal solid waste (MSW), cryptomeria waste (CW) and waste sawdust (WS). Gasification without and with catalysts at 673 K or 1073 K, produces about 26 % char, 26 % tar and 48 % fuel gas, which analyzed by gas chromatography (GC) consists of about 25 % methane, 25 % hydrogen and 50% carbon monoxide. Through dry reforming of the gas and tar decomposition, the syngas is used for self assembled SOFC. The feasibility of using those four bio-masses will be discussed and compared.

2:50 PM

(ICACC-S3-004-2014) Stacks on basis of CFY interconnects: status and prospects

M. Kusnezoff*, S. Megel, N. Trofimenko, A. Michaelis, Fraunhofer IKTS, Germany

Present-day Solid Oxide Fuel Cell based systems address different markets and utilize various stack technologies. Stacks on basis of CFY interconnects manufactured by Plansee SE have been continuously developed since 1992 and now are emerging into stationary CHP market in USA. The development of core stack components was originally started in Europe by Siemens, Plansee SE and Sulzer Hexis. In the last three years it has been succeeded to establish lab scale production of CFY stacks with commercial component suppliers. CFY stack addresses primarily the stationary applications in the power range 300 W to 100 kW. By continuous development and optimization of stack components (cells, interconnects, functional layers and seals) following promising results has been achieved: broad stack temperature operation window (air inlet temperature reduced up to 550°C by keeping air outlet temperature constant at 820°C), enhanced long-term stability (degradation rates <0,7 % / kh), degradation free thermal and load cycling as well as good tolerance to system start/stop cycles (degradation <4% per 40 cycles). CFY stacks developed at IKTS have been tested in various systems with power output between 300 W and 6 kW by external partners. System tests show good trasferability of laboratory results into prototype and field systems.

3:10 PM

(ICACC-S3-005-2014) SOECs: Prospects and Problems (Invited)

P. V. Hendriksen*, R. Kiebach, M. Chen, X. Sun, J. V. Høgh, K. Agersted, J. J. Bentzen, Y. Liu, S. Molin, S. Ebbesen, C. Graves, A. Hauch, P. Hjalmarsson, J. R. Bowen, M. B. Mogensen, Technical University of Denmark, Denmark; C. G. Greisen, Topsoe Fuel Cell, Denmark; B. V. Mathiesen, Aalborg University, Denmark

Concerns to reduce future adverse effects on the global climate have led to increased focus on means to reduce anthropogenic CO2 emissions. The amount of electricity generated from renewable and intermittent energy sources (e.g. wind and sun) is thus likely to increase globally in the coming decades. Solid oxide electrolysis cells (SOECs) have the potential to become a key technology in enabling this providing an energy efficient way to “store” electricity from periods of sur-plus production and for transferring this energy to the transport sector in the form of gaseous or liquid hydro-carbon fuels. State of the art SOFCs have been shown to be fully reversible. However, there are important differences between SOFC and SOEC operation specifically in terms of degradation phenomena. In this presentation we discuss the prospects of the technology for enabling larger shares of intermittent production in the system and provide examples from scenario analyses of its role in a future energy system based on 100 % renewable energy. Highlights from the technical SOEC R&D at DTU Energy Conversion and TOFC will further be given. Finally, potential problems in terms of life time limiting degradation phenomena in SOEC operation will be discussed in detail, based on own findings as well as literature. This will cover both microstructural degrada-tion at electrode and cell level and degradation phenomena with stack components like interconnects.

3:40 PM

(ICACC-S3-006-2014) SOEC developments status at sunfire GmbH (Invited)

D. Klemm*, T. Strohbach, sunfire GmbH, Germany; A. Glauche, KERAFOL Keramische Folien GmbH, Germany; J. Schefold, EIFER Institut, Germany; D. Schimanke, C. Geipel, C. von Olshausen, sunfire GmbH, Germany

Since 2012 the company sunfire GmbH (Germany) - former staxera GmbH - is coordinating the 3 year lasting German public funded project “SunFire” and is working together with 7 German industrial and scientific partners. The project deals with: - development of solid oxide electrolysis cells, stacks and system components, - electrolysis system modules under pressure (first prototype 10 kW at 15 bars; parameters chosen according to industrial requirements), - power-to-liquid process based on Fischer Tropsch synthesis (first test plant for one barrel FT-product/day). The steam electrolyser development has already shown significant progress with respect to a lowering degradation to values approaching the conditions for practical applications. Results of long-term testing over up to 3000 h of electrolyte supported cells (6Sc1Ce and 10Sc1Ce doped Zirconia) with LSCF oxygen electrode and Ni-GDC hydrogen electrode will be presented as well as the development goals for our first pre-industrial prototype.

4:10 PM

(ICACC-S3-007-2014) Development of a cost-efficient and performing High Temperature Steam Electrolysis stack

J. Mougin*, M. Reytier, J. Cren, M. Petitjean, CEA/LITEN, France

The main challenges for High Temperature Steam Electrolysis (HTSE) to become competitive towards other hydrogen production technologies are the increase of performance and durability and the decrease of cost. For that purpose, a "low-weight" stack has been designed, including advanced cells and stack components. A performance of -1.9 A/cm2 at the thermoneutral voltage of 1.3 V has been obtained at 800°C at the scale of a 3-cells stack and its robustness upon thermal cycling has been validated. The upscaling of the technology has been checked with a stack of 10 cells that allowed producing 0.9 Nm3/h of hydrogen. Techno-economical analysis showed that this low-weight design led to a considerable decrease of the stack cost and makes possible a decrease of the hydrogen price down to 2.5 €/kg for big production plants (500 t/d). HTSE technology also enables to co-electrolyze steam and CO2 which is emphasized in the present work.

4:30 PM

(ICACC-S3-008-2014) Stability Testing Beyond 1000 Hours of Solid Oxide Cells under Steam Electrolysis Operation

J. Schefold*, A. Brisse, European Institute for Energy Research, Germany

Solid Oxide Cells operated in the steam-electrolysis mode are capable to reach high electrical-to-chemical energy-conversion efficiency for hydrogen production. Efficiency can exceed 100 %, provided that additional thermal energy is supplied for evaporation and/or cell heating. In that case, cell voltages of 1.0 to 1.1 V are reached, largely below those of low-temperature electrolysers (PEM or Alkaline). At EIFER, extensive long-term SOC testing is done from single cells to stacks in a power range from around 20 W to 2 kW and operation periods above 1000 h to - so far - up to 9000 h. Both electrolyte and H2-electrode supported cells are tested. The cells are state-of-the-art SOFC, in cases with modified electrodes. Voltage-degradation rates of 1 to 2 % per 1000 h are achieved at current densities of 0.7 to 1.0 Acm-2 and steam conversion rates of 30 to 50 %. This extrapolates to operation times of 2 to 4 years, sufficient for demonstration in a larger scale and even for practical application. Impedance spectroscopy is applied as in-situ tool for degradation analysis without interrupting the nominal DC current flow. Degradation is found to come from (ohmic) resistance increase as well as from electrode deactivation. Degradation seems only moderately increased compared to the fuel-cell (SOFC) mode, where, moreover, current densities under long-term operation are usually smaller.

S4: Armor Ceramics

Special Topic Focus: Boron Carbide II

Room: Coquina Salon E
Session Chair: Vladislav Domnich, Rutgers Univ

1:20 PM

(ICACC-S4-021-2014) Densification of Commercial and Rapid Carbothermal Synthesized Boron Carbide

M. F. Toksoy*, W. Rafaniello, R. A. Haber, Rutgers University, USA

Commercial and Rapid Carbothermal Reduced (RCR) powders have been used to evaluate sintering of boron carbide by Spark Plasma Sintering (SPS). Powder properties and sintering parameter are varied to establish better understanding on sintering of boron carbide powder. Particle size and its distribution, homogeneity and XRD patterns are determined and evaluated. Boron carbide powders are processed by Spark Plasma Sintering process. Sintering variables such as, temperature, pressure and dwell time, are changed and densification procedures for boron-carbide are determined.

1:40 PM

(ICACC-S4-022-2014) Effect of SiO_2 and B_2O_3 Additives on the Microstructure and Hardness of Hot-Pressed Boron Carbide

K. D. Behler*, E. R. Shanholtz, U.S. Army Research Laboratory, USA; K. Xie, Johns Hopkins University, USA; J. C. LaSalvia, U.S. Army Research Laboratory, USA

Boron carbide (B_4C) is an attractive material for armor applications due to its low density and high hardness. Unfortunately, because of its atomic bonding, crystal structure, and microstructure, B_4C is not only very brittle, but also has been shown to be susceptible to stress-induced solid-state amorphization (SSA) and shear localization. Low fracture resistance, stress-induced SSA, shear localization, and perhaps melting are believed to be responsible for B_4C's loss in shear strength above its Hugoniot Elastic Limit (HEL) and its poor performance against certain ballistic threats. Consequently, there is strong interest in improving B_4C's resistances to fracture and shear localization. Limited work on other armor ceramics has shown that those with engineered grain boundaries not only possess higher fracture toughness values, but are also resistant to shear localization. In this investigation, initial attempts to engineer the grain boundaries of B_4C are reported. Precursors for SiO_2 and B_2O_3 were added to B4C powders and ultrasonically mixed. The SiO2/B2O3 ratio was varied and the total additive content was chosen to be 5 and 10 vol.%. The resulting powders were consolidated by hot-pressing. The effect of the additives on resulting densities, phases, microstructures, elastic properties, Knoop hardness values were determined. Experimental procedures and results will be presented.

2:00 PM

(ICACC-S4-023-2014) Improving the Hardness and Toughness of Boron Carbide Using Alumina as a Sintering Aid

K. Xie*, Johns Hopkins University, USA; F. Toksoy, Rutgers University, USA; J. LaSalvia, The Army Research Lab, USA; R. Haber, Rutgers University, USA; K. Hemker, Johns Hopkins University, USA

Boron carbide is an attractive engineering material due to its low density and super hardness, making it a suitable potential material for body armor applications. However, consolidated pure boron carbide processed by spark plasma sintering generally exhibits heterogeneous microstructure and relatively high porosity, which are detrimental to the overall mechanical properties. Use of appropriate sintering aids offers the possibility of increasing toughness through changes in grain boundary cohesion, microstructural homogenization, and reduced porosity. In this study, the effect of adding 5% alumina as a sintering aid and the role of sintering temperature (1600, 1700 and 1800oC) on the microstructure and mechanical properties of the consolidated boron carbide were investigated. The addition of alumina and sintering at 1700 and 1800oC homogenized the microstructure and reduced the porosity by filling the nano-pores with Al-rich phases. This resulted in harder and tougher consolidated boron carbide as compared to its pure counterpart.

2:20 PM

(ICACC-S4-024-2014) Novel Synthesis and Densification of Ultra-Hard Boron Suboxide

R. Pavlacka*, G. Gilde, K. Xie, K. Hemker, U.S. Army Research Laboratory, USA

A novel method for synthesizing boron suboxide had been developed. Whereas previous synthesis methods have prevented further exploration due to cost and extensive post-synthesis processing, this inexpensive and scalable procedure produces sub-micron sinterable powder with minimal post-synthesis processing. Details of the powder synthesis method will be described. Characterization of the synthesized powders and densified ceramics will be discussed.

2:40 PM

(ICACC-S4-025-2014) Application of mechanism-based, defect-distribution-driven analytical model for dynamic brittle failure to boron carbide

N. Daphalapurkar*, Johns Hopkins University, USA

The dynamic failure of ceramics in a Kolsky bar has been demonstrated to be dominated by the presence of defect distributions within the material. The dominant failure mechanism in ceramics under high strain rate compression is fracture. Prior work has demonstrated presence of other mechanisms of deformation and fracture, such as slip, amorphization and perhaps micro-twinning. For boron carbide subjected to high strain rates in a Kolsky bar, however, dynamic deformation and dynamic failure mechanisms have not been fully characterized. In this study, we focus on the possible competition between the mechanisms of fracture and slip. We use Hu-Ramesh mechanism-based, defect-distribution-driven analytical model to estimate the relative importance of fracture and slip in boron carbide over a range of strain rates and confinements. Results from this study might assist in providing guidance for design of experiments to characterize the relative importance of fracture and slip in boron carbide.

3:20 PM

(ICACC-S4-026-2014) Mechanical properties of icosahedral boron carbide explained from first principles (Invited)

N. Vast*, Ecole Polytechnique, France

When stressed by an impact beyond its Hugoniot elastic limit, B4C shows a gradual loss of strength, which had not been understood for a long time: was it mechanical in nature, or due to a phase transition? We have shown that none of these hypotheses is valid, and have instead illustrated the role of point defects. By a density-functional-theory study of neutral defects, vacancies have been found to be boron vacancies in the C–B–C chains, and to yield a discontinuous variation of crystal volume upon increasing pressure, caused by the formation of carbon-carbon bonds in the chains. The dynamical failure of B4C is attributed to the formation of these C–C bonds. Consequences of this understanding on the from-first-principled design of new materials for shielding will be discussed, as part of an ongoing work being performed with Antoine Jay, Jelena Sjakste and Olivier Hardouin Duparc (LSI).

3:50 PM

(ICACC-S4-027-2014) First Principles Based Multiscale Multiparadigm Simulations on Boron Carbide (B4C), boron, and Related icosahedral materials aimed of developing improved performance (Invited)

W. A. Goddard*, A. Jaramillo-Botero, Q. An, H. Xiao, S. Zybin, California Institute of Technology, USA

We report First Principles based Atomistic simulations aimed at characterizing and understanding the mechanical and dynamic properties of B4C and Boron icosahedral solids and at improving these properties by selective alloying or processing. First we use QM and QM/MD (DFT) to elucidate the relationships between bonding and mechanical properties for various distributions of Carbon in B4C and in various phases of Boron and to explore effects of alloying on ductility. Then we develop the ReaxFF reactive force field to fit accurately the QM description for large scale deformations. This enables reactive molecular dynamics studies on atomistic models with millions of atoms. We will report the Garffield genetic algorithm for optimizing the fit to QM and the aARRDyn adaptive accelerated ReaxFF reactive dynamics methodology extending time scales from 100ns to milliseconds. These results will be used to for realistic simulations of the failure properties of the new materials alloys.

4:20 PM

(ICACC-S4-028-2014) Modeling Nonlinear Elasticity, Intrinsic Instability, and Failure of Boron Carbide (Invited)

J. Clayton*, US ARL, USA

A number of crystalline solids demonstrate amorphization or structure collapse associated with loss of shear stiffness at high pressure, including quartz, berlinite, garnet, and boron carbide. Loss of intrinsic stability can be associated with various forms of the so-called Born criteria. In this work, a third-order anisotropic elastic model for trigonal boron carbide crystals is then developed using experimental and DFT data. This model reproduces observed behaviors under hydrostatic and uniaxial (shock) compression, including the onset of instability at around 4% compression in the latter. A primitive continuum amorphization model is implemented in mesoscale simulations, wherein transformation is triggered upon attainment of stress-induced intrinsic instability. Polycrystal simulations demonstrate effects of impact stress, grain geometry, and crystal polytype in dynamic/shock compression. Directions for further research are outlined that could resolve ambiguities in the present approach. Phase-field models for structural transformation and failure in boron carbide that predict mininum-energy configurations with a minimum number of free parameters are suggested.

4:50 PM

(ICACC-S4-029-2014) Quantum Mechanical Study of Fracture in Boron Carbide

T. D. Beaudet*, Army Research Laboratory, USA; J. R. Smith, University of Michigan, USA

Due to its low density and high hardness, boron carbide is of interest as a potential armor material. However, a low fracture toughness could limit ballistic performance and associated armor applications. Knowledge of the fracture toughness and traction-displacement relations for transgranular and intergranular fracture processes would provide guidance to developing tougher materials. Results from first-principles density functional computations of these quantities will be presented. Atomistic level fracture processes for boron carbide will also be shown. Finally, comparison with available experimental results will be made.

S6: Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage

Li-ion Battery Technology - Applications

Room: Ponce De Leon
Session Chairs: Charles Sorrell, University of New South Wales; Shoji Mao, Tokyo Metropolitan University

1:30 PM

(ICACC-S6-019-2014) Micro Battery Development: from Fundamental Research to Manufacturing (Invited)

J. Xiao*, H. Chen, S. S. Cartmell, Q. Wang, T. Lozano, T. Carlson, Z. Deng, Pacific Northwest National Laboratory, USA

The Juvenile Salmon Acoustic Telemetry System (JSATS) project supported by the U.S. Army Corps of Engineers, Portland District, has yielded the smallest micro-acoustic transmitter commercially available to date. To study smaller fish and permit implantation by injection using a needle, the JSATS micro-acoustic transmitter was reduced in weight and volume. This study focuses on the development of micro-battery design based on lithium/ carbon monofluoride (Li/CFx with x = 1) chemistry. A steady high-rate pulse current with required lifetime was achieved while the weight and volume of the battery was significantly reduced. The newly designed micro-batteries have intrinsically lower impedance than the batteries currently used in JSATS transmitters, leading to significantly improved electrochemical performances within a wide operating temperature range from -5°C to 25°C. The fundamental science related with fluorination chemistry will also be discussed to tune the power/energy ratio for various requirements for practical applications.

2:00 PM

(ICACC-S6-020-2014) Nanocrystalline TiO2 Thin Films on Poly(Ethylene Terephthalate) at ≤130°C (Invited)

C. Pham, D. Hanor, J. Cox, C. Sorrell*, University of New South Wales, Australia

Photocatalytic thin films of TiO2 were deposited onto PET substrates at atmospheric pressure using low-temperature and low-cost processes. The route involved the preparation of stable aqueous sols of TiO2 at ~95°C, film deposition by dip-coating, and post-deposition drying at ~130°C. The resultant coatings were characterised by HRSEM, HRTEM, FIB, XRD, XPS, AFM, laser Raman microspectroscopy, UV-VIS spectrophotometry, and tape pull-off. The films were observed by HRSEM, HRTEM, and AFM to be comprised of nanocrystallites of 5-10 nm diameter and nanoagglomerates of 15-25 nm size. The films were determined by XRD and laser Raman microspectroscopy to consist of anatase, with a trace of brookite. Under UV irradiation, all films exhibited photocatalytic activity, as measured by the photo-oxidation of methylene blue. Tape pull-off results demonstrated that the films were well adhered.

2:30 PM

(ICACC-S6-021-2014) Properties of the Solid Ionic Conductor: Li7La3Zr2O12

J. Wolfenstine*, J. Allen, J. Read, Army Research Laboratory, USA;
T. Thompson, I. David, J. Sakamoto, Michigan State University, USA

High Li-ion conductivity (>10-4 S/cm) solid state electrolytes based on Li7La3Zr2O12 (LLZO) are under consideration for use in Li/S, Aqueous Li/Air, Li batteries (solid/liquid). In order to be used in these applications several requirements must be met. These include; high ionic conductivity, chemical stability, electrochemical stability and mechanical integrity. As a result, this presentation will discuss the following: 1] methods to achieve high ionic conductivity, 2] the chemical stability of LLZO with Li, S, water and various anode and high voltage cathode materials, 3] cycling of cells containing a LLZO electrolyte at room and elevated temperature, and 4] mechanical properties such as; modulus and fracture toughness.

2:50 PM

(ICACC-S6-022-2014) The Effect of Processing and Microstructural Variables on the Li-ion Conductivity of Li0.29La0.57TiO3

J. Wolfenstine*, C. Cooper, C. Brennan, A. Sutorik, Army Research Laboratory-APG, USA

Aqueous Li-Air batteries offer the potential for higher energy compared to current battery technologies. One of the main technical issues with aqueous Li-Air batteries is that they require a solid Li-ion conducting membrane. One membrane material under consideration is Li0.29La0.57TiO3 (LLTO). As a consequence it is important to prepare dense LLTO and investigate the variables which influence the Li-ion conductivity of LLTO. Li0.29La0.57TiO3 powders were prepared by a solid-state method, calcined, cold isostatically pressed and sintered at 1200C for various times. The ionic conductivity and electronic conductivity of the dense LLTO samples was measured. The effect of phase content and Li-ion composition on lattice conductivity and the effects of bulk density and grain size on the total conductivity will presented.

Li-ion Battery Technology - Design and Solar Application

Room: Ponce De Leon
Session Chairs: Charles Sorrell, University of New South Wales; Shoji Mao, Tokyo Metropolitan University

3:30 PM

(ICACC-S6-025-2014) Photovoltaic Properties of (Bi, Na) TiO3-BaTiO3 Ferroelectric Ceramics Prepared by Spark Plasma Sintering (Invited)

D. Wang*, L. Chen, The University of New South Wales, Australia; N. Chan, The Hong Kong Polytechnic University, Hong Kong; B. Luo, The University of New South Wales, Australia; J. Dai, The Hong Kong Polytechnic University, Hong Kong

Photovoltaic (PV) effect in ferroelectrics shows many unique features such as large above bandgap photovoltage and the ability to tune the photovoltaic response by controlling the polarization etc. In this study, photovoltaic properties of lead-free (Bi0.5Na0.5) TiO3-xBaTiO3 (BNBT) ferroelectric ceramics prepared by spark plasma sintering (SPS) were investigated under UV and white light illumination, and compared with their counterparts fabricated by conventional sintering (CS). Larger photovoltaic responses were found in SPSed BNBT, owing to their more homogeneous microstructures with smaller grain size. In addition, the donor doping effect was studied in order to further enhance the PV responses and get a better understanding of the underlying mechanisms of ferroelectric photovoltaic effect with respect to the charge carrier behavior. A typical above bandgap photovoltage of ~55 V was obtained in SPSed Nb-doped BNBT ceramics with a thickness of 1 mm, demonstrating the potential of the BNBT lead-free ferroelectrics for the applications in future solar energy technology.

4:00 PM

(ICACC-S6-024-2014) Broadband Dielectric Spectroscopy of Materials for Lithium Batteries: From Low Frequencies to Microwaves (Invited)

J. Badot*, Chimie ParisTech, CNRS, France; K. Seid, Adama Science and Technology University, Ethiopia; O. Dubrunfaut, SUPELEC, UPMC Univ Paris 06, Univ Paris-Sud, CNRS, France; P. Soudan, B. Lestriez, Université de Nantes, CNRS, France

The improvement of battery performance requires the rationale optimization of the composite electrode. The developments of new experimental techniques as well as methodologies are needed to understand the relationships between the composition, the architecture and the performance of composite electrodes. The “ex-situ” broadband dielectric spectroscopy (“ex-situ” BDS) technique (40 Hz to 10 GHz) is used here to measure the electronic transport across all observed size scales of the composite materials for lithium batteries containing each an active material (e.g. LiFePO4, LiNi1/3Mn1/3Co1/3O2, etc.), carbon black and a polymeric binder. An innovative device (measurement cell) has been developed to make synchronized BDS measurements and electrochemical cycling (“operando” BDS). The frequency range is about 1 kHz – 5 GHz. In this work, data acquisitions were made on dry electrode and then on an electrode wetted with an electrolyte, before and after the first charge, the first discharge, and several cycles. The new device opens thus important prospects to determine the evolutions of the multi-scales electrical properties during electrochemical cycling. The results demonstrate that the broadband dielectric spectroscopy technique is very sensitive to the interactions between lithium ions and electronic species across size scales within the electrode architecture.

4:30 PM

(ICACC-S6-023-2014) Design and fabrication of all-solid-state rechargeable lithium batteries for future applications (Invited)

M. Shoji*, J. Wakasugi, R. Osone, T. Nishioka, H. Munakata, K. Kanamura, Tokyo Metropolitan University, Japan

The replacement of organic liquid electrolytes with inorganic solid electrolytes is a challenge to extend the versatility of rechargeable lithium batteries. The safety and operating temperature of batteries are surely enhanced by the thermal stability of solid electrolyte. However, the most desirable feature of solid electrolytes is high mechanical strength. Up to now, almost all the rechargeable batteries have been constructed in a layer-by-layer fashion (2D structures), in which a trade-off relationship exists between the energy density and power density. For future energy storage/use applications such as electric vehicles and renewable energy systems, this trade-off relationship should be removed by 3D battery configurations, for example, in which rod-like anodes and cathodes are alternately located. The self-standing characteristic of solid electrolytes makes it easy to construct 3D structures. So far, we have focused on oxide-based solid electrolytes such as $Li_{0.35}La_{0.55}TiO_3$ (LLT) and $Li_7La_3Zr_2O_{12}$ (LLZ) due to high lithium-ion conductivity as well as high mechanical strength, and formed their hole-array structures. In the presentation, fabrication of those hole-array structures and evaluation of the all-solid-state batteries using the structured solid electrolytes will be reported.

5:00 PM

(ICACC-S6-026-2014) Towards the Conversion of a Solid Oxide Cell into a High Temperature Battery

C. M. Berger*, O. A. Tokariev, P. Orzessek, A. Hospach, N. H. Menzler, M. Bram, W. J. Quadakkers, H. P. Buchkremer, Forschungszentrum Juelich, Germany

This work is a contribution towards converting a high temperature solid oxide cell (SOC) into a Rechargeable Oxide Battery (ROB). In this battery, a SOC works alternately in fuel cell and electrolyzer mode. Instead of externally storing the electrolytic hydrogen, a stagnant atmosphere composed of hydrogen and steam is used directly as an oxidizing and reducing agent for a metal-metal oxide material, which serves as integrated energy storage. As a consequence, all the expenses related to pumping losses, heat losses and further components can be avoided. Storage components are manufactured by means of tape casting or extrusion using iron oxide (Fe_2O_3) based slurries or pastes. Several material mixtures have been studied and analyzed to assess their suitability as storage material in the battery. To prevent storage degradation, “inert” oxides (8YSZ, Al_2O_3, ZrO_2) as well as “reactive” oxides (Mn_2O_3, Y_2O_3, CeO_2, TiO_2, CuO, MgO, CaO) were used as functional additives. These oxides were then classified with respect to their ability to promote reaction and/or to inhibit sintering and other ageing phenomena. Redox cycling, thermogravimetric studies, stack tests and microstructural analyses of storage components by XRD and SEM have shown that especially the use of 8-40 wt.% CaO provides promising redox cycle performance due to the reversible formation of mixed oxide phases ($Ca_2Fe_2O_5$, $CaFe_5O_7$, $CaFe_3O_5$).

5:20 PM

(ICACC-S6-027-2014) Electrospray Deposition of CuAlO2 Thin Film and Possibility of Y Doping

Y. Liu*, Y. Wu, Alfred University, USA

The growth of p-type transparent conducting oxide (TCO) thin film has gained much attention for its potential in making functional windows for solar energy harvesting. In this work, p-type transparent conducting CuAlO2 thin films have been deposited on quartz glass by a cost-effective electrospray technique. Copper nitrate and aluminum nitrate were examined as metal sources in the precursor solutions for deposition. By modifying the precursor concentration and electrospray parameters, dense and uniform coatings were obtained. The as-sprayed thin film was in the amorphous phase and by post annealing in argon atmosphere, a pure delafossite phase of CuAlO2 was formed. In order to further improve the electrical conductivity of p-type CuAlO2, Y was doped for the first time as substitution of trivalent Al3+ cation. The attempt is based on the theory that modulation of M3+ radius in Copper-based Cu1+M3+O2 could increase O interstitials, thus decreasing the sheet resistance. CuAl1-xYxO2 (x=0.01,0.03,0.05) thin films were prepared and the effects of Y3+ occupation on Al3+ sites on the surface microstructure, visible transmittance and electrical properties were investigated. Finally, enhancements in electrical conductivity were observed in Y-doped CuAlO2 prepared by electrospray, which would be promising in practical applications.

5:40 PM

(ICACC-S6-028-2014) Modelling and Simulation of Lithium Bromide-Water solar-powered absorption cooling system for Riyadh

E. D. Kerme*, King Saud University, Saudi Arabia

The use of solar energy in the application of cooling and air conditioning is getting more attention especially in Saudi Arabia. This is due to the fact that solar energy is most available when cooling is most needed. In other words, the variation in the supply of energy during the day is closely in phase with the cooling demand. In this paper modeling and simulation of Water-lithium bromide solar-powered absorption cooling system using flat plate collector is done. The simulation work has been done by using EES program in order to simulate the various cycle configurations and solar energy parameters for Riyadh, Saudi Arabia. In this regard, effect of hot water inlet temperature on coefficient of performance, flow ratio and cooling capacity, heat transfer rate and temperature of condenser, absorber and evaporator has been studied. In addition, the effect of absorber, condenser and evaporator temperature on coefficient of performance and flow ratio has been investigated.Eventually, by using the solar radiation of Riyadh, the influence of collector types on collector efficiency and the useful heat gain has been studied.

S7: 8th International Symposium on Nanostructured Materials and Nanocomposites

Nanoscopic Films and Composites II

Room: Coquina Salon B

Session Chairs: Vladimir Sivakov, Institute of Photonic Technology; Steffen Teichert, University of Applied Sciences Jena

1:30 PM

(ICACC-S7-021-2014) Electrochemical Routes for the Production of Free Standing Nanowire Structures and Nano Functional Surfaces (Invited)

M. Ürgen*, Istanbul Technical University, Turkey

Electrochemical methods are widely used in nanotechnology for templating and nanofunctionaliaztion of surfaces. The best known examples of these applications’ are aluminum and titanium anodic oxides. Aluminum and titanium metals when anodized in suitable solutions are capable of producing nanoporous structures. The regularity, size and thickness of these structures can be tuned easily by playing with the metal structure and also by adjusting the electrochemical parameters during the anodization process. Moreover applicability of this method on large surface areas brings a big advantage when compared to other techniques such as lithography. In this presentation after a brief introduction of aluminum and titanium anodization, application examples will be given concentrating on the studies conducted in our research group. The first examples of application will be on utilization of aluminum anodic oxides for production of free standing nanowire structures that can be used as super capacitors and substrates for surface enhanced Raman spectroscopy. The second group of examples will be on the usage of titanium anodic oxides as gas sensors. These oxides with their controllable nanostructures have a high potential for gas sensing applications. The example will be on the improvement of gas sensing properties titanium oxide nanostructures by doping them with aluminum.

2:00 PM

(ICACC-S7-057-2014) Sol Gel synthesis of Indium doped ZnO TCO films for PV cells

O. Dinner, G. E. Shter, G. S. Grader*, Technion, Israel

Transparent conductive oxide layers (TCO) play significant role in the PV cells. Typical requirements for electrical and optical properties are: conductivity>$1x10^3[(\Omega cm)^{-1}]$and a transparency>80% in the VIS-NIR. Currently, the most common TCO is ITO. However, its manufacturing cost is high due to the increasing scarcity of indium. We present initial results on preparation of Indium doped ZnO (IZO) TCO films for PV cells via the sol gel spin coating. The effect of the precursor synthesis method was investigated to improve the stability of the IZO structure during treatment at elevated temperature (> 350°C). The direct spin coating of transparent liquid of IZO precursor and, alternatively, spinning of the opaque IZO nano-suspension (sol) prepared by solvothermal synthesis were used as basic methods. The dopant and stabilizer concentrations were varied in the ranges of 0-5% mol and 0-10% wt. respectively. The thermal behavior of the precursors was studied by TGA/DTA/MS. Ways to control the particle size in suspension were found and tested. Films thickness was varied by increasing the number of deposited layers to control the porosity of the TCO. Final thickness ranged from 200nm up to 2μm while maintaining high transparency in the visible and NIR spectrum and low resistivity. The different profiles of thermal treatment were tested and a minimal resistance of 60 Ohm/square was achieved for the TCO mentioned above.

2:20 PM

(ICACC-S7-024-2014) Montmorillonite-based nanocomposites: modular compounds for electrorheological fluids

C. S. Peyratout*, ENSCI, France; M. Geist, University of Wuerzburg, Germany; K. Boussois, A. Smith, ENSCI, France; D. G. Kurth, University of Wuerzburg, Germany

Nanocomposites prepared from Na-montmorillonite and metallo-supramolecular polyelectrolytes (MEPE) based on nickel and bis-terpyridine ligands are prepared by an aqueous synthesis. Intercalation is confirmed by IR-spectroscopy, thermogravimetric analysis and X-ray powder diffraction. The rheological response in the presence of an electric field of the dispersed nanocomposites in silicone oil is measured with a rheometer. The nanocomposites show a distinct electrorheological effect depending on the concentration and the kind of intercalated species. The effect occurs with a low content of active materials while only very small currents are observed.

2:40 PM

(ICACC-S7-026-2014) Synthesis of Coaxial WO2.9/Al Thermite Nanocomposite

J. Al-Sharab*, New York University of Polytechnic Institute (NYU-Poly), USA; Z. Dong, S. D. Tse, B. H. Kear, Rutgers University, USA

Al-coated WO2.9 nanowires, forming a thermite nanocomposite, are fabricated using a combined flame and solution synthesis method. Such geometry not only presents an avenue to tailor heat-release characteristics due to anisotropic arrangement of fuel and oxidizer, but also possibly eliminates or at least minimizes the presence of an Al2O3 passivation film between the aluminum and metal oxide. This paper describes characterization of the co-axial WO2.9/Al nanocomposite, where the Al layer thickness is ~16 nm, covering WO2.9 nanowires of diameters from 20-50 nm and lengths ~10 μm. Ignition and combustion of the thermite composite material has been demonstrated.

Materials Integration and Gas Sensors

Room: Coquina Salon B

Session Chairs: Mustafa Ürgen, Istanbul Technical University; Bilge Saruhan-Brings, German Aerospace Center

3:20 PM

(ICACC-S7-020-2014) Nanomaterials and Nanoanalysis for Microelectronics (Invited)

S. Teichert*, University of Applied Sciences Jena, Germany

The current development of microelectronics is still driven mainly by the extension of common device concepts to smaller sizes. One of the keys on this way is the introduction of new materials on the nanoscale into the classical silicon production technology. The report is focused on materials and analytical challenges of the further development of DRAM nonvolatile memories. After a brief introduction to the basics of a DRAM cell the parameters of the cell capacitor are discussed with special emphasis on materials requirements. The preparation of corresponding dielectric materials by atomic layer deposition and its analysis by different methods will be presented in more details. A further part of the presentation is dedicated to analytical challenges of vertical transistor structures needed in future DRAM generations.

3:50 PM

(ICACC-S7-023-2014) Nanostructured ZnO: Synthesis and Gas Sensing Properties

V. Galstyan*, E. Comini, C. Baratto, A. Ponzoni, University of Brescia and CNR INO, Italy; E. Bontempi, M. Brisotto, University of Brescia, Italy; G. Faglia, G. Sberveglieri, University of Brescia and CNR INO, Italy

ZnO has been considered a promising material for gas sensors, solar cells, UV light-emitting diodes, piezoelectric nanogenerators, and nanopiezotronics. During the last years, advancements in preparation methods improved the electrochemical and electrophysical parameters of ZnO. Investigations have shown that the variations of shape and size of nanostructured ZnO enlarged its application. Therefore it is very important to control the size and the shape formation of nanostructured ZnO during the growth. We have developed a new chemical route for ZnO nanostructures preparation that combines electrochemical anodization and thermal annealing in a very convenient technique to obtain crystalline nanostructures on stiff and flexile substrates. The preparation parameters like the type and the concentration of electrolyte, the anodization voltage and the current have been tailored to obtain the nanosized ZnO structure. Obtained structures have been characterized by SEM, AFM, micro-Raman spectroscopy and XRD. The structures are composed by nanoparticles forming elongated aggregates with chain-like morphology. The chemical sensing characteristics of the structures have been tested towards ethanol, acetone, CO and NO2. The preliminary results have shown that obtained ZnO nanostructures are interesting for chemical sensing. The low temperature processes allow preparation on many types of substrates, even flexible ones.

4:10 PM

(ICACC-S7-025-2014) Mesoporous transparent bulk SiOC processed via hydrogen decarbonization as optical gas sensor

G. D. Soraru*, A. Quaranta, S. Dirè, V. Nguyen, University of Trento, Italy; M. Narisawa, Osaka Prefecture University, Japan

Bulk aerogel samples obtained from bis(triethoxysilyl)methane, have been pyrolyzed at high temperature in flowing hydrogen. The materials treated at 800°C are bulk, micro/mesoporous, transparent and colorless silicon oxycarbide glasses while those pyrolyzed at higher temperature, 1100°C, turn pale brown keeping all the other features.

Structural characterization performed by FT-IR and 29Si MAS NMR confirmed the formation of the silicon oxycarbide network showing the presence of mixed O-Si-C units. Specific surface area above 600 m2/g with pore sizes lower than 5 nm were measured by N2 adsorption for the 800°C samples. Moreover, samples pyrolyzed at 800°C show an intense blue photoluminescence feature when excited with UV light. We'll show that these new SiOC materials can be used as optical gas sensor for O2 and mixed organic vapour (MOC) owing to the interaction of the gas species with the luminescent centers.

4:30 PM

(ICACC-S7-027-2014) CdS Quanty Dots Sensitized WO3 Thin Film as Chemical Gas Sensors

I. Concina*, E. Comini, CNR-IDASC SENSOR Laboratory & Brescia University, Italy; S. Kaciulis, CNR-ISMN, Institute for the study of nanostructured materials, Italy; G. Sberveglieri, CNR-IDASC SENSOR Laboratory & Brescia University, Italy

The present work explores the properties of a WO3 thin film sensitized with CdS quantum dots (QDs) as gas sensor. CdS QDs have been generated and grown in situ by means of SILAR (successive ionic layer absorption and reaction) technique, which delivers naked nanocrystals directly on the oxide surface. Absence of any capping ligand preserves the permeability toward gases of the active composite layer and allows QD to mediate the interaction between the analytes and the metal oxide surface. WO3 surface coverage is modulated by applying different precursor concentration as well as different number of SILAR cycles and the properties as gas sensor of the composite materials tested towards several gases at different temperatures and under dark/illumination conditions. Composite materials were found to be Cd-enriched in all cases, this feature suggesting the presence of Cd2+ ions free on the nanocrystal surface with an uncomplete coordination sphere capable to interact with external chemicals. CdS QDs were found to significantly increase the conductivity of WO3 (up to two orders of magnitude). An optimal equilibrium between precursor concentration and number of SILAR cycles was found allowing for an increased sensitivity and selectivity towards some compounds, being this latter feature determined by the affinity of Cd2+ ions on the surface with the analyte.

4:50 PM

(ICACC-S7-028-2014) Gas sensing mechanism of undoped and doped TiO_2 nanotubes (NTs) at intermediate operating temperatures

S. Mathur, Y. Gönüllü*, University of Cologne, Germany; B. Saruhan, German Aerospace Centre (DLR), Germany

The increasing concern in the detection of combustion gases calls for the development of highly sensitive sensor devices as well as for the understanding and determination of simplified models of sensor operation mechanisms. Bulk undoped and doped TiO_2 layers have been used as gas sensors for years. However, TiO_2 based systems require improvements in order to increase the stability of sensing layer, increase of selectivity and decrease of response times at intermediate operating temperatures (300°C-600°C). Although there are reports in literature demonstrating the achieved improvements by nano-structuring in the case of TiO_2, nevertheless, the reasons for the effect of morphology and doping of TiO_2 NTs on gas sensing have been rarely investigated. This work describes the fabrication of TiO_2 NTs sensor layers through anodization of titanium as well as an effective doping process for Cr doped TiO_2 NTs. Moreover, it reports the effect of microstructural parameters on sensor behaviour using the impedance response and equivalent circuit models at various temperatures. The results show that, sensing mechanism develops in dependency of thickness, temperature or dopant elements. The thickness of the NTs has an influence on sensing mechanism until a certain thickness is reached. However, after this critical point, the thickness does not affect the sensing properties.

5:10 PM

(ICACC-S7-029-2014) Novel carbon nanotube gas sensors functionalized by Si(O)CN

A. Karakuscu*, A. Ponzoni, Sensor lab, CNR-IDASC and University of Brescia, Italy; L. Hu, University of Colorado, USA; C. Baratto, Sensor lab, CNR-IDASC and University of Brescia, Italy; R. Cecato, University of Trento, Italy; R. Raj, University of Colorado, USA; G. Faglia, G. Sberveglieri, Sensor lab, CNR-IDASC and University of Brescia, Italy

CNTs are one of the excellent candidates for gas sensing application owing to its high specific surface areas, providing a large number of active surface sites. However, there are still limitations against their commercial usage of CNTs as gas sensors such as long recovery time, detection of limited gases, and strong influence of humidity and other gases. In this work, novel polymer derived ceramic (PDC) functionalization is proposed for stable, reproducible and enhanced gas sensing properties in CNT gas sensors. PDC functionalization is very simple process: liquid precursor completely coats the surfaces of the CNTs without requiring any surface modification. After heat treatment, a monolayer of PDC, which is a semiconductor ceramic, is created on CNT. The stability of the CNT/PDC sensor is verified up to 520°C, while the CNT sensor without PDC coating loses the conductance after 250°C due to structural modification. Certainly, the high temperature and creep resistance nature of PDC gives high temperature stability (≥250°C) but it also improves the gas sensing performance. PDC coating changes the recovery from irreversible to reversible. Moreover, due to self limiting thickness it gives a great advantage to prepare the reproducible sensors. It is demonstrated that even after repeating the measurements several times, the CNT/PDC sensor gives the same gas responses.

5:30 PM

(ICACC-S7-030-2014) Inorganic Surface Modification of Titania Nanocrystals for Enhanced Chemical Gas Sensors

M. Epifani*, CNR-IMM, Italy; E. Comini, SENSOR Lab, Department of Information Engineering, Brescia University and CNR-IDASC, Italy; R. Díaz, Electrochemical Processes Unit, IMDEA Energy Institute, Spain; C. Force, NMR Unit,Centro de Apoyo Tecnológico, Universidad Rey Juan Carlos, Spain; R. R. Zamani, Institut de Recerca en Energia de Catalunya (IREC), Barcelona, Spain; J. Arbiol, Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Spain; T. Andreu, Institut de Recerca en Energia de Catalunya (IREC), Barcelona, Spain; P. Siciliano, CNR-IMM, Italy; G. Faglia, SENSOR Lab, Department of Information Engineering, Brescia University and CNR-IDASC, Italy; J. R. Morante, Institut de Recerca en Energia de Catalunya (IREC), Barcelona, Spain

The addition of noble metal nanoparticles to metal oxides is a well-known procedure for enhancing the response of chemoresistive gas sensors. This modification of the base metal oxide material is suggested by catalysis field, where spillover by supported noble metals has been deeply exploited. Heterogeneous catalysis and gas sensors have several points of contact, and trying to get new suggestions from catalysis can only be expected to be fruitful and stimulating. Pushed by this fact, we observed that the titania-supported vanadium pentoxide is a well known oxidation catalyst of organic compounds, making it an ideal candidate for sensing volatile organic compounds. Using this material architecture for processing gas-sensing devices required the development of suitable colloidal synthesis techniques. In the present work we will show the successful deposition of vanadium oxide onto the surface of colloidal titania nanocrystals. The presence of a surface layer of vanadium oxide, together with core doping of the titania support, was ensured by detailed crossed characterization techniques. We will show that the surface modification of anatase effectively enhances the anatase sensing properties. Ethanol sensing will be an example of such properties. We conclude that this material typology enlarges the concept of additives, by introducing a whole new range of possible material architectures.

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

In Honor of Professor Stuart Hampshire III; Silicon Nitride

Room: Coquina Salon A
Session Chairs: Francis Cambier, Belgian Ceramics Research Center; Anne Leriche, University of Valenciennes

1:30 PM

(ICACC-S8-018-2014) GB chemistry of silicon nitride based nano-composites – implications to fracture behavior - experimental and theoretical study

P. Sajgalik*, M. Hnatko, Z. Lences, M. Gall, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia; Z. Chlup, Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Czech Republic

Six different sintering aids (Lu2O3, Yb2O3, Y2O3, Sm2O3, Nd2O3 and La2O3) were used for the processing of dense Si3N4/SiC micro/nano composites. Formation of SiC nano–inclusions was achieved by in situ carbothermal reduction of SiO2 by C during the sintering process. Room temperature fracture toughness, hardness and strength showed increasing tendency when the used rare-earth element in the oxide additive changes from a large to a small rare-earth cation (i.e. from La3+ to Lu3+). Besides the highest hardness and reasonably high fracture toughness and strength of composite material with Lu2O3 sintering additive. The first principle calculations were used for the explanation of the fracture behaviour of the composites depending on the rare earth additive. The energy of fracture was calculated with respect to the chemical composition of GB. The experimental and theoretical results will be discussed.

2:00 PM

(ICACC-S8-019-2014) Local mechanical properties of Si_3N_4 ceramics measured using very small cantilever specimens (Invited)

J. Tatami*, M. Katayama, Yokohama National University, Japan; T. Takahashi, T. Yahagi, Kanagawa Academy of Science and Technology, Japan; T. Horiuchi, M. Yokouchi, Kanagawa Industrial Technology Center, Japan; K. Yasuda, Tokyo Institute of Technology, Japan

Knowledge of local mechanical properties is important to understand the nature of the bulk mechanical properties of ceramics. In this study, the local mechanical properties, such as strength and grain boundary fracture toughness of Si_3N_4 ceramics, were measured using using very small cantilever specimens prepared by focused ion beam technique. The sample size for strength measurement was 2.5x2x15mm. Average of the bending strength of the very small cantilever specimens was 4.7GPa, which was 4 times as high as that of JIS type specimens (3x4x40mm). Such high strength resulted from reduction in flaw size of the very small specimens. Grain boundary fracture toughness of Si_3N_4 ceramics prepared by adding different kinds of rare earth oxides was measured using very small cantilever specimens, in which a sharp single edge notch was also machined along a grain boundary. The grain boundary fracture toughness depends on the added rare earth oxide as a sintering aid. It was higher than the fracture toughness of SiAlON glass usually existing as the intergranular glassy film, which suggested that the IGF structure should be different from the bulk SiAlON glass.

2:30 PM

(ICACC-S8-020-2014) Old and New in SRBSN (Sintered Reaction Bonded Silicon Nitride) (Invited)

H. Kim*, KIMS, Republic of Korea

Silicon nitride is one of the best ceramic materials with many useful properties, however, actual application is limited mostly due to its high production cost. Use of silicon powder instead of expensive silicon nitride powder is, therefore, attractive. The development history of RBSN and SRBSN as well as the pros and cons of SRBSN will be reviewed. Dense SRBSN(sintered reaction bonded silicon nitride) ceramics with high strength and toughness was obtained by modifying the structure of RBSN followed by the high temperature gas pressure sintering. A fraction of fine silicon powder was added to modify the structure of RBSN after nitridation. Addition of fine silicon powder to coarse silicon powder leads to the early onset of phase transformation and sintering, which lowers the post sintering temperature to give full densification. The conditions to give porous microstructure with acicular grains was investigated in sintered RBSN in order to modify the pore structures. SRBSN DPF filter shows better trapping efficiency of PM compared to commercial cordierite filter. Future works to be done in SRBSN will be explained and future possibilities and directions will be discussed.

3:20 PM

(ICACC-S8-021-2014) Si3N4 Based Materials for Structural Applications, What is Next? (Challenges and Potentials) (Invited)

H. M. Mandal*, Sabanci University, Turkey; F. Kara, S. Turan, A. Kara, Anadolu University, Turkey

Si3N4 based ceramics have wide range of applications due to their favourable properties. Although, recently, these types of materials are also getting an interest for the functional applications especially on optical, their main commercial usage is still limited to the structural applications where key properties are mechanical and thermal not only for high temperatures but also room to moderate temperature applications. The wider spread use of Si3N4 and SiAlON are limited due to the high cost of good quality Si3N4 powders and high processing cost. Therefore, there is a need to develop new compositions and processing schemes that will enable to further optimize the properties and also reduce the cost. In this study, Si3N4 based compositions were designed with different type of cations. The precise understanding of the roles of cations in both Si3N4 and also SiAlON host lattices are the key parameters for the design. The effect of cations on the composition, the type of intergranular phase, the development of the resultant microstructures and further heat treatment will be presented. The atomic scale observations on Si3N4 and SiAlON lattices will be presented and discussed in terms of impact on properties and applications. Particular emphasis will be given to the possible routes of overcoming the obstacles to wide spread use of these materials and consequent research needs.

3:50 PM

(ICACC-S8-022-2014) Developments of Silicon nitride based composite materials (Invited)

C. Balazsi*, Bay Zoltan Nonprofit Ltd. for Applied Research, Hungary

Silicon nitride (Si3N4) materials present good thermo-mechanical and tribological properties. These properties enable them to sustain the wearing conditions enduring some engineering parts. Several structural applications for silicon nitride ceramics are known on the basis of combination of these properties. Carbon nanotubes (CNTs) showed to possess exceptional mechanical and electrical properties It is expected the addition of CNTs will radically improve the quality of ceramic matrices. Silicon nitride ceramics have been fabricated by a number of techniques, gas pressure sintering, hot pressing, pressure-less sintering and hot isostatic pressing. Comparison of conventional sintering techniques (gass pressure sintering (GPS), hot pressing (HP) or hot isostatic pressing (HIP)), and SPS process was studied. The structural, mechanica changes during different sintering will be presented.

4:20 PM

(ICACC-S8-023-2014) Medium Pressure PIM of Silicon Nitride using a Novel Binder System Concept for Improved Dispersability and Removal by Thermal Evaporation

R. Pompe*, GOCERAM AB, Sweden; D. Yan, W. Zhang, Beijing SINOMA Synthetic Crystals Co., Ltd., China

The binder system performance is a key feature of all viable PIM technologies. Goceram has invented and commercialized Medium Pressure PIM with a back-bone polymer/paraffin wax as a baseline binder. Responding to the most recent trends, a conceptually novel binder system has been developed featuring introduction of a secondary main, multi-functional binder. This secondary component delivers multiple functionalities such as: extractability by water and additional function as a dispersant/surfactant and viscosity modifier. Furthermore, it is thermally evaporable, allowing optional recovery. Using this binder concept, silicon nitride powder pre-mixed with sintering additives could be worked into a feedstock with a considerably increased solid loading, by 5 – 9 vol% over the baseline system. Initial evaluation confirmed excellent moulding response and the parts could be debinded as stand-alone without any powder embedment support. Investigation by SEM of the GPS-sintered material showed fully densified microstructure. These initial results indicate a great potential of this technology for mass-production of many silicon nitride components.

4:40 PM

(ICACC-S8-024-2014) Fabrication of c-axis oriented Si3N4 ceramics by highly magnetic field

T. Takahashi*, Kanagawa Academy of Science and Technology, Japan; J. Tatami, Yokohama National University, Japan; S. Tanaka, Nagaoka University of Technology, Japan

Silicon nitride (Si3N4) has intrinsic promising good thermal and mechanical properties. Especially, the high thermal conductivity appears to the c-axis direction due to crystal anisotropy. In this work, c-axis oriented silicon nitride ceramics were fabricated by orientation of coarser β-Si3N4 seed crystals through a magnetic field orientation process and subsequent sintering. Two kinds of β-silicon nitride powders and an α-silicon nitride powder were used as raw materials. Yttrium oxide, hafnium oxide and silicon oxide were also added as sintering aids. The slurry of these powders in water was prepared by stirrer mixing and ultrasonic radiation using polyethyleneimine as a dispersant. It was placed in a rotating magnetic field at 10 T followed by drying to prepare particle oriented green compacts. They were sintered at 1900°C for 6h in 0.9MPa N2. The relative density of the Si3N4 ceramics was over 99%. The Lotgering factor of (002) plane in β-Si3N4 achieved over 0.70 (random orientation: 0, perfect orientation: 1.0) after sintering in the Si3N4 ceramics prepared at 10T. The reason for successful fabrication of highy c-axis orientated Si3N4 ceramics is orientation of the coarser β-Si3N4 seed crystals and significant grain growth of elongated β-Si3N4 during sintering.

5:00 PM

(ICACC-S8-025-2014) Study on thermal conductivity of epoxy resin/silicon nitride composites

A. Shimamura*, H. Hyuga, Y. Hotta, K. Hirao, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Epoxy resin is one of the most widely used thermosetting polymers and commonly applied in electrical engineering material. The thermal conductive property of epoxy resin has been improved by the introduction of inorganic filler such as SiO2, BN and AlN. Although silicon nitride (Si3N4) is high thermal conductive and chemically stable non-oxide ceramic, there has been few reports on addition of Si3N4 as inorganic filler. In this study, synthetic silicon nitride filler was incorporated into epoxy resin to improve its thermal conductivity. The volume fraction of the Si3N4 filler was changed from 0.0 vol% to 70 vol%. The microstructure of the composites was examined using scanning electron microscopy (SEM). Thermal conductivities of the composites were measured by laser-flash method. SEM imaging showed homogeneously dispersed Si3N4 filler particles in the composite with filler loading content less than about 55vol%. The thermal conductivity was enhanced with increasing of the Si3N4 content, but it was dropped down after certain content of Si3N4 filler due to shortage of epoxy resin in the composite. The thermal conductive property was compared with the composites adding commercially available Si3N4 powders. Our composite added with the synthesized Si3N4 showed higher thermal conductivity than those commercial Si3N4 powder/epoxy resin composites.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Virtual Materials Design and Modeling II

Room: Coquina Salon G

Session Chair: Magnus Rohde, Karlsruhe Institute for Technology (KIT)

1:30 PM

(ICACC-S10-020-2014) Image-Based Computation of Thermo-Elasticity for C/C Composite Bundles (Invited)

G. L. Vignoles*, P. Engerand, A. Gillard, G. Couégnat, O. Caty, University Bordeaux, France

In the frame of a virtual material approach on thermo-elasticity of C/C composite materials, a bundle-scale study has been carried out, on the basis of image analysis. Samples of C/C composites with needled woven layers of carbon fibers and gas-processed carbon matrix were imaged, and the images cut into sub-images containing 10 to 50 fibers. Fiber/matrix/pore segmentation was made prior to a finite element analysis with appropriate boundary conditions on all sub-images. Tendencies correlating the elastic modulus and thermo-elastic tensor coefficients to sub-image properties, such as relative phase amounts and directional morphological indicators were drawn and can be inserted in a change-of-scale procedure from bundle scale to composite scale through a “handbook homogenization” technique.

2:00 PM

(ICACC-S10-021-2014) Homogenization and sensitivity analysis for optimal thermoelastic design of metal-ceramic composites

R. Piat*, Y. Sinchuk, Karlsruhe Inst of Technology, Germany

The minimal compliance thermoelastic design of the 2D local orthotropic structures under thermo-mechanical loading is investigated. The local distribution of the material orientation (i.e. distribution of the anisotropy) is the design variable. Two kinds of thermoelstic problems are considered: in the first one, the temperature field is independent from the design variable and in the second one, the temperature field is dependent from the design variable. The optimal material orientation is calculated as solution of local optimization problem in terms of stresses. The local thermo-mechanical properties are calculated as solution local optimization problem in term of stresses. Numerical examples illustrating the optimization methodology are presented for metal-ceramic composite with lamellar microstructure consisting of the alumina and aluminum-silicon phases.

2:20 PM

(ICACC-S10-022-2014) Multi-scale modeling of shape distortions during sintering of bi-layered porous structures

T. T. Molla*, R. Bjork, H. L. Frandsen, N. Pryds, Technical University of Denmark, Denmark

Models that describe the densification and viscous behaviors of porous bodies during sintering are often based on assumptions of simplified or ideal microstructures. Considering realistic microstructures can improve the prediction capabilities of the already established theories like the continuum theory of sintering. A new multi-scale numerical approach for modeling distortions during sintering of macroscopically inhomogeneous structures is developed. The microstructures of the porous bodies are described by unit cells based on the Kinetic Monte Carlo (KMC) model. During the sintering process both the densification rate and the viscosity are calculated from a KMC model coupled with finite element methods. Computational homogenization is used to extract the effective viscosities from a boundary value problem defined on the micrographs of unit cells simulated by the KMC model. Example of simulation of sintering of a bi-layer is presented to justify the multiscale model. The approach can be considered as an extension to the continuum theory of sintering combined with the meso-scale kinetic Monte Carlo model.

2:40 PM

(ICACC-S10-023-2014) Generation and Calibration of Stochastic Virtual Textile Composite Specimens for Analyzing Local Strain Variations

M. Blacklock, J. H. Shaw, F. W. Zok, University of California, USA;
B. N. Cox*, Teledyne Scientific Company, USA

Virtual Tests are an emerging engineering tool to aid materials design. A widely recognized feature is the need for a Virtual Test system to effectively incorporate both simulations and experiments to gain a sufficient level of insight. The overall aim of the National Hypersonic Science Center's Virtual Test development program is to develop a process that is capable of reproducing stochastic woven textile specimens by employing computational models that use as an input experimentally derived geometrical information and the mechanical and thermal properties for tow-scale domains. Models are presented that outline the generation of stochastic virtual specimens of woven ceramic composites where geometrical information is gathered from experimentally obtained micro-computed tomography images of a test specimen and used to calibrate a Geometry Generator that employs a Markov Chain algorithm to rapidly reproduce statistically representative virtual specimens. Anisotropic elastic tow-scale properties are derived and calibrated from micro-mechanical models and manufacturer's data. Validation of the calibration stages is obtained by evaluation of local fiber tow behavior calculated from finite element simulations with topographical and load-displacement data obtained via digital image correlation for a carbon fiber/SiC matrix composite.

Virtual Materials Design and Modeling III

Room: Coquina Salon G
Session Chairs: Walter Kob, University Montpellier 2; Masato Yoshiya, Osaka University

3:20 PM

(ICACC-S10-024-2014) Modelling of laser surface alloying and dispersing of technical ceramics (Invited)

M. Rohde*, Karlsruhe Institute for Technology (KIT), Germany

Laser surface melting and alloying are important techniques to improve the properties of a material locally without affecting the bulk. In ceramic components these methods can be used to optimise the fracture toughness, friction and wear but also the thermal and electrical conductivity. The objective the model development was to enable the prediction of the heat flow, the temperature and the velocity field at the ceramic surface and also the distribution of the second phase particles which determines the modified properties. Model calculations have been performed on the basis of a finite element model (FEM) in order to get more insight in the heat and particle transport during melting and solidification. The results of the model calculations give quantitative information about the temperature and the velocity field during the laser process in the ceramic substrate. Detailed numerical studies have been performed to calculate the extension of the melt pool and the volume fraction of the particles for a wide range of process parameters. It could be shown that the extension of the melt pool and the dispersion zone, as well as the particle distribution depend not only on the laser process parameters process parameters but also on the thermodynamic properties of the ceramic.

3:50 PM

(ICACC-S10-025-2014) Microstructure optimization for the two dimensional problem of heat conduction in fiber reinforced composites

R. Piat*, G. Stasiuk, V. V. Deshpande, Karlsruhe Inst of Technology, Germany

Use of composite materials for high temperature applications is a major area of research. These applications demand the components to sustain high temperatures and protect the electronic equipment in their vicinity from the extreme heat. The paper deals with development of a computational methodology to optimize the microstructure of the fiber reinforced composites such that the temperatures generated in the components made from these composites be minimised. The fiber orientation of a two dimensional fiber reinforced composite subjected to thermal loading is optimised for two optimization problems. First problem deals with minimization of maximum (hot spot) temperature of the material and the second problem deals with minimization of temperature of a specified region of the material. Mori-Tanaka scheme for unidirectional fiber reinforced composites is used as a micromechanical model to determine the effective thermal conductivity of the material. For both the optimization problems, the criterion for the fiber orientation is derived analytically and the obtained formulation is implemented on sample problems.

4:20 PM

(ICACC-S10-026-2014) Simulation of C/C Composite Ablation under Fluid Flow

G. L. Vignoles*, M. Besnier, University Bordeaux, France; G. Couégnat, CNRS, France; L. Duquesne, G. Perrot, University Bordeaux, France; J. Epherre, CEA, France

Surface recession simulations have been developed for the description of the morphological evolution of C/C composite under ablative conditions. So far, interesting results on roughness morphology and on recession kinetics had been produced when considering only diffusion of the etching gases combined to heterogeneous reaction and to solid gasification. However, the flow of the etching gas over the surface had not been fully taken into account. In the present work, this has been carried out, by coupling two pieces of software: a computational fluid mechanics code, and the home-made diffusion/advection/reaction/surface recession software AMA. The CFD code exports velocities, which are read by AMA and used to modify the gas transfer; in the other way, AMA exports a mesh of the gas-phase above the surface in which velocities can be computed. Some preliminary results on the influence of the "wind" on the morphology and kinetics of surface ablation are presented and discussed.

4:40 PM

(ICACC-S10-028-2014) First Principles Calculations of Boron Suboxide

J. S. Dunn*, Army Research Laboratory, USA; V. Kumar, Vijay Kumar Institute, India

Single crystal B6O is the third hardest naturally occurring material after diamond and boron nitride, making it a competitive material for armor, abrasive, and nuclear applications. However, like many structural ceramics, its inherent fracture toughness is low (~4.5MPa*m^0.5). This limitation has been partially resolved in the Si3N4 material system by using an intergranular glassy film (IGF) in combination with a self-reinforced microstructure to maximize energy dissipation during fracture. The Army initiated a program to apply these principles to B4C with limited success. Imperfect glass wetting, high glass viscosity, and strong B4C/glass adhesion resulted in incomplete densification (90% of theoretical). Since B6O and B4C have similar chemistries and crystal structures, these problems are also expected for the B6O material system. The compositional design space for doped-glass systems is very extensive; therefore a method is needed to identify promising regions in order to reduce the number of processing experiments. First principles models based on Density Functional Theory (DFT) offer a promising way to explore the wettability, thermodynamic stability, and the adhesion strength of grain boundary interfaces. In this poster, we present the most recent results for our DFT model of defect-free and doped bulk B6O.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

Novel Processing I

Room: Coquina Salon F

Session Chair: Sylvain Dubois, Institute PPRIME

1:30 PM

(ICACC-S12-023-2014) A current overview of the MAX phases and thin film processing (Invited)

P. Eklund*, Linkoping University, Sweden

This invited talk reviews recent developments in the MAX-phase field with focus on thin-film physics and engineering. A brief overview of thin-film processing methods (sputtering, arc deposition, CVD) will be given, with an emphasis on the characteristic attributes of each method and especially how they relate specifically to processing of MAX phases. New approaches such as spraying techniques and aerosol deposition will also be discussed. The thin film research in the area of MAX phases will also be discussed in correlation to the rapidly emerging field of two-dimensional MXene materials derived from bulk MAX phases. Properties of thin film MAX phases are discussed with an emphasis on features where thin-film processing can contribute to understanding the complex materials science problems involved; in particular transport properties such as conductivity and thermopower.

2:00 PM

(ICACC-S12-024-2014) Elevated Temperature Tribological Behavior of MAX Phase Coating Deposited by High Velocity Oxyfuel Spraying

C. Zhang, S. Rengifo, A. Nieto, A. Agarwal*, Florida International University, USA

Ternary carbide based MAX phase(s) has been extensively studied for their unique combination of properties like metals and ceramics. Due to these properties, MAX phase has been proposed as an excellent high temperature coating for applications such as jet engines, automobiles, aircrafts, and petrochemical installations. However, there are few studies on use of MAX phase as a coating. This study reports on Ti2AlC based MAX phase coating deposited by High Velocity Oxyfuel Spraying (HVOF) technique. A 60 μm thick coating was deposited on Inconel 625 alloy substrate. The coating is characterized for microstructure, phase and nano-scale hardness and elastic modulus by nanoindentation. High temperature wear tests were conducted on MAX phase coating and Inconel 625 alloy using a ball-on-disk tribometer at 600 oC at a high load of 20 N. The coefficient of friction for MAX phase coating was 0.65 and 0.36 at room temperature (RT) and 600 oC, respectively. Coating displayed improved wear resistance at room temperature (RT) and 600 oC as compared to Inconel 625 alloy substrate. Wear tracks were analyzed via SEM and EDS to understand the wear mechanism.

2:20 PM

(ICACC-S12-025-2014) Synthesis and densification of Cr2AlC powder using Spark Plasma Sintering apparatus

S. Lee*, H. Oh, KIMS, Republic of Korea; S. Choi, Hanyang University, Republic of Korea

Spark plasma sintering (SPS) apparatus was used for the fabrication of Cr2AlC powder at low temperature. The mold for the synthesis was specially designed in order to prevent the application of pressure during SPS process for powder synthesis. The synthesis of nearly X-ray pure Cr2AlC powder was achieved at 1000oC by using the SPS synthesis technique. The size of the synthesized Cr2AlC powder ranged at 1 - 10 μm. Lamellar structure, which is one of the characteristics of MAX phases, was identified in the powder. The size of the Cr2AlC powder did not efficiently decrease when using a planetary mill. Instead, the powder became more roundish after the milling. High energy ball mill (Spex mill) was more efficient for the comminution of the MAX powder. The average particle size decreased to 1.5 μm after the high energy ball milling for 10 min. The densification of the synthesized powder was performed using the SPS apparatus with changing the holding time at the temperature range of 900 - 1100oC. The densification more strongly depended on the sintering temperature than the holding time. The relative densities of samples sintered at 900 and 1100oC under 30MPa pressure were 87 and 98%, respectively. The formation of secondary phases was suppressed in the specimens sintered at 1100oC. The elastic modulus, hardness, flexural strength and fracture toughness of the sintered specimens were evaluated.

2:40 PM

(ICACC-S12-026-2014) Densification and Phase Evolution of SHS Derived Ti_3AlC_2 Powders in Pressureless Sintering and Hot Pressing Processes

L. R. Chlubny*, J. Lis, AGH University of Science and Techniology, Poland

Ti_3AlC_2 belongs to the interesting group of ternary nanolaminate materials called MAX phases. These compounds are characterised by heterodesmic chemical bonding and thanks to that they possess unique set of properties which locating them between metals and ceramics. One of the best methods of synthesizing of sinterable, fine precursors of this materials is Self-propagating High-temperature Synthesis (SHS), which is effective, fast and efficient. Utilization of exothermal effect of the chemical reaction for initiation of the self-sustaining process as well as adiabatic conditions is the basis of this method. As a result of the SHS synthesis of various substrates in different stoichiometric proportions, powder containing mostly Ti_3AlC_2, TiC and Ti_2AlC were obtained. Selected powders were examined for potential sintering possibilities both with pressurless sintering and hot-pressing techniques in various conditions. Changes in the phase compositions of the materials were observer and optimal sintering conditions were established.

Novel Processing II

Room: Coquina Salon F
Session Chair: Carmen Carney, UES, Inc

3:20 PM

(ICACC-S12-027-2014) Nanostructured HfC-SiC composite prepared using reactive spark plasma sintering

S. Lee*, F. Lun, KIMS, Republic of Korea; H. Lee, Pusan National University, Republic of Korea

HfC-SiC composites has recently attracted attention due to its excellent thermal and chemical stability as well as nice mechanical properties such as high strength, elastic modulus and hardness. In the present work, dense (98%) and nano-structured HfC-SiC composites were fabricated. For that purpose, reactive spark plasma sintering (R-SPS) was applied at 1750oC under 80MPa pressure using HfSi2 and C powders as the source materials. Ultra-fine (~150nm) and homogeneously distributed HfC and SiC grains were obtained in the dense composites due to the high energy milling of raw powders, molecular-level homogeneity of Si and Hf in HfSi2, and low sintering temperature by R-SPS. HfSi2, which may strongly decrease the high temperature properties of the composites, was nearly completely consumed during the densification process. The peaks of HfSi2 were not detected by XRD in the sintered specimens. The Vickers hardness, Young's modulus and fracture toughness of the composites were measured.

3:40 PM

(ICACC-S12-028-2014) Reaction Spark Plasma Sintering and Mechanical Properties of Monolithic Titanium Boride

K. Sengottaian*, B. S. Murty, S. Bakshi, Indian Institute of Technology Madras, India

Titanium borides have wide applications in the areas of such as ultra high temperature applications, cutting tools, armour, reinforcements in MMCs, etc. It presents high temperature structural stability, extreme hardness, and low density along with good electrical and thermal conductivity. However, owing to the predominantly covalent bonding, very high temperature is needed to achieve full densification. This study reports the synthesis and densification of TiB_2 by reactive spark plasma sintering. Elemental Ti and B powders were taken in a stoichiometric ratio and mechanically milled for 4h and 8h. The mechanically activated powders were reaction spark plasma sintered to more than 99% density at temperatures of 800 °C and 1400 °C. The sintered compact was studied using XRD and SEM. XRD confirmed the formation of TiB_2 with small amounts of TiB phase. Nanoindentation results revealed the nanohardness of (>26GPa) and elastic modulus (>570GPa) values. Indentation fracture toughness of above 3.3 MPa.$m^{1/2}$ is achieved in all the samples.

4:00 PM

(ICACC-S12-029-2014) Producing Zirconium Diboride Components with Complex, Near-Net Shape Geometries by Room-Temperature Injection Molding of Aqueous Ceramic-Polyvinylpyrrolidone Suspensions

V. L. Wiesner*, J. P. Youngblood, R. W. Trice, Purdue University, USA

Room-temperature injection molding is proposed as a novel, low-cost and more energy efficient manufacturing process capable of forming complex-shaped zirconium diboride (ZrB_2) parts. This innovative processing method utilized aqueous suspensions with high powder loading and a minimal amount (<5 vol.%) of water-soluble polyvinylpyrrolidone (PVP), which was used as a viscosity modifier. Rheological characterization was performed to evaluate the room-temperature flow properties of ZrB_2-PVP suspensions. ZrB_2 specimens were fabricated with high green body strength and were machinable prior to binder removal despite their low polymer content. After binder burnout and pressureless sintering, the bulk density and microstructure of specimens were characterized using Archimedes technique and scanning electron microscopy. X-Ray Diffraction was used to determine the phase compositions present in sintered specimens. Ultimate strength of sintered specimens will be determined using ASTM C1323-10 compressive C-ring test.

4:20 PM

(ICACC-S12-030-2014) Densification and Scaleup Mechanical Properties of Direct Current Sintered High Purity ZrB2 Ultrahigh Temperature Ceramics

D. Pham*, L. S. Walker, W. Pinc, E. L. Corral, University of Arizona, USA

Zirconium diboride (ZrB2) is an ultra-high temperature ceramic (UHTC) with properties that make it ideal for use as thermal protection system (TPS) materials. Direct current sintering (DCS) of UHTCs is advantageous as it allows densification at lower temperatures with total densification times under 30 minutes. Various processing methods and sintering additives are used to make fully dense ZrB2, however, the effects on the mechanical behavior of highly pure ZrB2 using (DCS) needs further investigation. This study focuses on understanding the mechanical properties of ZrB2 after DCS as a function of powder processing and oxygen reducing agents to produce full density and low oxygen impurity ZrB2. Powder is processed with minor additions of carbon or boron carbide (<1wt%) to produce high purity ceramics with smaller grain size and higher Vicker's hardness and flexural strength compared to nominally processed ZrB2. High purity laboratory scale ZrB2 (~2cm discs) has exceptional flexural strength (~630MPa) and processing techniques are translated to large scale processing. Using a large scale DCS furnace at The University of Arizona, large scale UHTC parts >10cm are produced for mechanical testing to determine the feasibility of DCS scaleup.

4:40 PM

(ICACC-S12-031-2014) Carbothermal reduction synthesis of nanocrystalline refractory carbides powders using sucrose as carbon source

Y. Zhao*, Y. Zhou, H. Liu, J. Li, Z. Feng, Aerospace Research Institute of Materials and Processing Technology, China

Ultra-fine carbides (ZrC, HfC, TaC, NbC, and WC) powders were produced by carbothermal reduction reactions, using sucrose as the carbon source and the corresponding transition metal oxides as metal sources. The changes of the Gibbs′ free energy of reactions with temperature were calculated under the standard state and CO partial pressure using thermodynamic data. The reaction paths of carbothermal reduction were monitored by differential thermal analysis (TG-DTA) in flowing argon atmosphere. And phase evolutions during the reduction reaction at different temperature were investigated by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Based on above analysis and observation, different reaction mechanisms were studied. The synthesized carbides powders had a small average crystallite size (≤100nm) with oxygen content less than 1.0 wt%.

5:00 PM

(ICACC-S12-032-2014) Tough ceramics by microwave sintering of nanocrystalline titanium diboride ceramics

D. Demirskyi*, National Institute for Materials Science (NIMS), Japan; D. Agrawal, The Pennsylvania State University, USA; A. Ragulya, Frantsevich Institute for Problems in Material Science, Ukraine; Y. Sakka, National Institute for Materials Science (NIMS), Japan

Dense composites of TiB2 with additions of TiN have been produced by microwave sintering. Microwave sintering was conducted at 1200-1700°C under controlled atmosphere. The effects of composition, sintering temperature, on densification, microstructure, and mechanical properties were investigated. Microwave sintering resulted in uniform crack-free uniform microstructure, as well as maximum relative density of 99% and bending strength of 368±15 MPa, Young's modulus of 440±11 GPa, electric resistivity of 2x10-5

Ω cm, Vickers hardness of 26.2 ±0.4 GPa, and a fracture toughness of 6.2±0.34 MPa m1/2 were obtained using 36 wt.% TiB2, and sintering for 10 min at 1650°C.

Poster Session A

Room: Ocean Center Arena

(ICACC-S1-P001-2014) Comparison of Thermo Mechanical Properties in Alumina and Alumina-Carbon Nano Composite Sintered by SPS

H. Gheisari Dehsheikh*, F. Zilabi, Shahreza University, Islamic Republic of Iran

Spark plasma sintering method (SPS) is more than a decade to be an interesting alternative to classical densification processes for ceramic materials. On the other hand, SPS has recently been paid attention as an alternative method to obtain dense and fine-grained ceramics at low temperatures. SPS, also known as plasma activated sintering, is a method applicable for rapid sintering of metals and ceramics. Owing to the advantage of rapid heating, the alumina ceramics obtained by SPS have a grain size and density comparable to those of HPed ones. In fact, if there is alteration in those transport characteristics, there may be some difference in all subsequent diffusion related to the processes such as grain growth, creep and high temperature deformation of SPS densified materials. This study describes hot deformation and deformation mechanisms of alumina based materials densified by SPS (AP/SPS), and somewhat comparison with alumina-carbon nano composite (AC/SPS). Starting materials,pure alumina and carbon particles nano sized, were densified by SPS at 65 MPa (1200 °C). The grain size of the alumina SPSed was 50% coarser than the grain size of alumina-carbon nano composite sample (455 nm versus 310 nm). Generally, the fineness of SPS materials microstructure shall speed up all processes related to diffusion.

(ICACC-S1-P002-2014) Advanced insulation properties for environmental and economic ceramic product

M. A. Melhem*, Civil Engineering Faculty, Syrian Arab Republic

Recently, there are many researches have concerned with the developing of the residential and industrial buildings conditions in order to save energy as much as could. Heating insulation plays an important role in minimizing the required energy for the buildings. On the other hand, ceramic products are modern building materials and it is used widely in many types of buildings. So, we try in this research to develop a ceramic product within two aspects: economic and environmental. Our ceramic product contains some types of industrial wastes like: husk dusts, wood dusts, which are burning totally during the firing stage and leave voids and pores in the body of ceramic product. These pores cause a reducing of the unit weight up to 20% and consequently, it causes an increasing in the insulation properties up to 30%. It means a saving of the energy by using these ceramic products in the buildings. We also try to reach to a lower unit weight and lower thermal conductivity by increasing wastes percentage more, but in this situation it should be used a special alkali solution. We depend on experimental and analytical methods. We apply the required tests on the raw materials and the ceramic samples. Then we analyze the results by using known mathematical formulation.

(ICACC-S1-P003-2014) Evaluation of ceramic/ceramic (SiC/SiC & Al2O3/Al2O3) joint interface prepared via brazing

A. Ghazi Daryani*, A. Nemati, Sharif University, Islamic Republic of Iran

The purpose of this paper was joining 2 ceramics by metal fillers to investigate the interface of SiC/SiC & Al2O3/Al2O3 with the same metal interlayer (Ag-Cu-Ti).joints are performed by brazing method under certain conditions in a furnace with controlled atmosphere,using the filler metal.The properties has been studied by using mechanical test (shear strength) & microscopic examination(SEM) & phase analysis(XRD) & elemental distribution was conducted by EDAX.Heat treatment was performed according to phase diagram to gain the desirable joint.the proper joining was obtained applying a metal layer of Ag-Cu as well as an active metal of Ti-6Al-4V to increase wetability & proper strength. Microscopic investigations revealed penetration & activation of elements from interface to the bulk of ceramic body and this “in turn” was the major reaction in the joints.Both joints showed the deepest penetration of Ti from interface to ceramics.XRD results showed TiC & Ti5Si3 were the most important phases in the SiC/SiC interface &TiO &V2O5 for Al2O3/Al2O3.The strength of both joints was increased till optimum time & temperature condition and diminished after forming of some phases as TiC in (SiC/ SiC)&TiO in (Al2O3/Al2O3) which inhibit the formation of more strong interface.the optimum time & temperature were suggested to be 900°C & 90’ for SiC/SiC & 900°C & 60’ for Al2O3/Al2O3. Keywords:SEM,XRD,EDAX

(ICACC-S1-P004-2014) Fabrication of Highly Dense Pure SiC Ceramics via the HTPVT Method Using Nano SiC powders

L. Bobo*, Y. Jianfeng, Xi’an Jiaotong University, China

The dense SiC were prepared by high-temperature physical vapor transport (HTPVT) method using nano SiC powders (500nm) as raw material. The effects of temperature and holding time upon the grain size, growth rate, thickness and orientation of silicon carbide were explored, and the concentration gradient, random nuclei of SiC on polycrystalline phase growth during SiC PVT growth were studied. The growth mechanism was explained from the perspective of thermodynamics and kinetics. The result shows grain size of the SiC nucle increased with the growth temperature lower than 2200 degrees Celsius, and decreased with the growth temperature higher than 2200 degrees . The XRD shows the majority of silicon carbide crystal β-SiC (3C-SiC) with the growth temperature lower at 2000 degrees, above 2200 degrees of silicon carbide is 6H-SiC, From 2000 to 2200 degrees temperature range, 3C-SiC is less and less, and 6H-SiC is more, that this temperature range is the 3C-SiC the transition to the 6H-SiC phase. Microstructure shows that the growth of silicon carbide is hexagonal columnar silicon carbide grains above 2200 degrees, the average grain size of SiC material is 100um, while the characteristics of α-SiC grains is abvious.

(ICACC-S1-P005-2014) Effect of thermal cycling on thermal conductivity of diamond particle reinforced copper composites

M. J. Kruszewski*, L. Ciupinski, M. Rosinski, K. J. Kurzydlowski,
A. Michalski, Warsaw University of Technology, Poland

Copper-diamond composites are prospective thermal management materials because they posses high thermal conductivity as well as relatively low coefficient of thermal expansion which is mandatory from the viewpoint of possible application as a heat sink for electronics. This application requires high reliability of components, and in this respect the thermal fatigue of the material and its influence on thermal conductivity of the composites is of special interest. In this study copper matrix composites with different volume fraction of diamond particle reinforcement (50, 55 and 60 %) were fabricated by a powder metallurgy method, namely Pulse Plasma Sintering. The thermal cycling tests in the temperature range of -50 to 200 °C and total number of 2000 cycles were conducted. To evaluate an influence of thermal fatigue on thermal conductivity of the composites thermal properties measurements were performed in as-fabricated state and after 100, 200, 500, 1000 and 2000 thermal cycles. It was shown that a degree of thermal conductivity degradation is related to the amount of the matrix in the composite where the highest degradation was observed for composites with 55 % of diamond. Significant spread of thermal conductivities measured for composites with the highest diamond content may be attributed to their structure inhomogeneity

(ICACC-S1-P006-2014) Image reconstruction of defects 100 mm deep by probe array using TSVD

Y. Nishimura*, T. Suzuki, National Institute of Advanced Industrial Science and Technology, Japan

The possibility of inspecting defects in ceramic materials using UT probe array methods was studied to investigate the reliability of ceramic products. In making large structural product of many small blocks, such products are likely to include fatal defects inside, particularly in joints, and their fractural response are much faster and more drastic than those of metal materials. Therefore, it is necessary to detect internal defects by non-destructive testing (NDT). UT probe array is easy to reconstruct the image of internal defects and it is convenient for non-UT-specialists to identify internal defects as well. Electrically scanning the inside of the sample enables reconstructing 3D image of internal defect in a much shorter time. However, it is not short enough to scan a large ceramic products, yet. D.Braconnier and S.Hirose proposed methods using aperture synthesis or inverse problem solving to reconstruct a image of internal defects effectively for each and applied them to metal materials. Inverse problem solving produces better images than aperture synthesis. However, their response function matrix is likely to be singular. In this study, internal defects image were reconstructed by Truncated Singular Value Decomposition. It was investigated how sampling frequency and number of elements affects and truncation index affect on the reconstructed defect images.

(ICACC-S1-P007-2014) Compressive Strength and Durability of Concrete Utilizing Recycled Concrete Aggregate

E. D. Magdaluyo*, L. Atterado, J. Paz, University of the Philippines, Philippines

Concrete mixtures can be tailored to provide a wide range of mechanical and durability properties to meet the design specifications of a structure. The effects of recycled concrete aggregate and other processing parameters such as aggregate replacement ratio, type of admixture and slump height on the early and late compressive strength as well as the initial and secondary water absorption rate of different concrete mixes were investigated. The study utilized Taguchi design of experiment in the production of high strength concrete and response surface methodology was employed in the analysis of the relationship between the processing parameters with respect to the response variables. Using 10% of recycled fine aggregate with Mira P99 admixture, and slump height of 4-6 inches showed an optimum condition and yielded a predicted maximum compressive strength at around 8400 psi. The failure mode observed was generally a shear fracture type. For the water absorption rate, only the admixture had a significant effect. Using natural aggregates with Mira P99 admixture and slump height of 6-8 inches showed the optimum condition that will yield the minimum water absorption rate. Scanning electron microscopy images revealed that utilizing recycled concrete aggregate resulted to a porous surface morphology of the concrete compared to the natural aggregates.

(ICACC-S1-P008-2014) Standard Property Measurements of Advanced Ceramics

J. D. Helfinstine*, Corning Inc., USA; J. Salem, NASA GRC, USA; G. Quinn, American Dental Association Foundation, NIST, USA; S. Gonczy, Gateway Materials Technology, Inc., USA

Mechanical and physical properties of ceramic bodies can be difficult to measure correctly unless the proper techniques are used. The Advanced Ceramics Committee of ASTM, C-28, has developed dozens of consensus test standards and practices to measure various properties of a ceramic monolith or composite or coating. Measured properties that give the “what, how, how not, and why” for many mechanical, physical, thermal, and performance properties. Using these standards will provide accurate, reliable, and complete data for rigorous comparisons with other test results from your test lab, or from somewhere else. The C-28 Committee has involved academics, and producers, and users of ceramics to write and continually update more than 45 standards since the committee’s inception in 1986. Included in this poster will be a pictogram of the C-28 standards and how to obtain individual copies with full details or the complete collection of all of them in one volume. A listing of other committees that might be of interest will be included.

(ICACC-S1-P010-2014) Microstructure and Mechanical Properties of Silicon Carbide (SiC) with MgO-Y2O3 Oxide System as Sintering Agent

H. Gocmez*, M. Tuncer, S. Altun, Dumlupinar University, Turkey

The scope of this study covers the sintering of nanocrystalline SiC powders prepared via citrate gel method. SiC samples were pressureless sintered at 1700 - 1800 oC using magnesia-yittria oxide (1-10 v %) addition. The powder properties were characterized by weight change (TG-DTA), x-ray diffraction (XRD), laser diffraction and SEM/EDS methods. The effects of different content of MgO-Y2O3 and various sintering temperature on the densities, microstructure and mechanical properties (hardness and fracture toughness) of SiC ceramics were investigated.

(ICACC-S1-P011-2014) Crack Generation in TiC-316L Steel Cermets Using Vickers Indentation

C. Jin*, K. Plucknett, Dalhousie University, Canada

Cermets are composite materials that combine hard, brittle ceramics with a ductile metal phase. Compared with conventional hardmetals such as WC/Co, cermets are lighter in weight while maintaining high strength, toughness, good wear and corrosion resistance. Due to its high melting point and low density, TiC is used in a variety of applications, such as bearings, drawing dies, etc. In the present work, stainless steel binders (grade 316L) have been utilised for the preparation of TiC-based cermets, with the steel content varied from 5 to 30 vol. %. Samples were fabricated using a simple vacuum melt-infiltration procedure, at temperatures between 1475°C and 1550°C, held for up to 240 minutes. It is demonstrated that a core-rim structure arose for the cermets when sintered at 1550°C for 240 minutes, with accommodation of selected steel constituents into the rim of the TiC grains. The Vickers indentation response of these materials has been assessed. Two primary indentation-cracking patterns may arise, namely median cracks or Palmqvist cracks, which relates to the volume fraction of ductile metal binder present. In particular, this work assesses the influence of the steel binder content and grain size on the Vickers indentation response, using sequential polishing to determine the sub-surface crack patterns. Preliminary use of a focused ion beam microscope for evaluation of the crack path will also be discussed.

(ICACC-S1-P012-2014) Effects on Mechanical and Thermal Properties by Varying the Interconntectivity of SiC in a Si:SiC Composite System

A. L. Marshall*, M Cubed Technologies, Inc., USA

This study expands upon a previous effort and examines the effects of firing temperature on mechanical and thermal properties of Reaction Bonded SiC (RBSC). RBSC lends itself to many potential applications including: thermal applications due to the high thermal conductivity, low tailorable thermal expansion, and high specific stiffness; armor applications due to the high hardness, high Young’s modulus, and low density; and also high-temperature wear applications due to the high hardness and stability at elevated temperatures. Composites of silicon carbide particles (SiCp) and silicon (Si) are fabricated by the reactive infiltration of molten Si into preforms of said particles and carbon. Through heat treatment methods, necking of the SiCp is promoted in the pre-infiltration state which will allow further tailoring of material properties. Correlations are drawn between the firing temperature and the resultant mechanical and thermal properties.

(ICACC-S1-P013-2014) Microstructure-Property Relationships in SiC/Diamond Composites as a Function of Diamond Content

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The addition of diamond reinforcement to silicon carbide (SiC) results in significant improvement in properties such as stiffness, hardness, wear resistance, thermal conductivity, and thermal stability. At very high diamond content, some properties can approach those of monolithic diamond, while maintaining the manufacturability of SiC. However, properties prediction is difficult, with the response often non-linear with respect to the SiC to diamond ratio. The present work creates a systematic set of reaction bonded diamond-reinforced SiC composites where diamond content is varied, but other microstructural parameters, such as grain size, are maintained constant. Physical, mechanical, and thermal properties are measured, and correlations with diamond content are generated.

(ICACC-S1-P014-2014) Effect of SiC:B_4C Ratio on the Properties of Si-Cu/SiC/B_4C Composites

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A series of Si-(Cu)/SiC/B_4C composites with varying SiC:B_4C ratios were fabricated using the reaction bonding technique with an alloyed melt infiltration containing 10 and 20 wt% copper. Changing the SiC:B_4C ratio can have a dramatic effect because of the density difference between SiC (3.21g/cc) and B_4C (2.51g/cc). This property becomes important in lightweight, high stiffness applications. The addition of copper is interesting because of its high corrosion resistance and high conductivity as well as the low processing temperature. The composites were characterized using microstructural imaging, physical properties and mechanical behavior. The influence of copper additions and compositional changes on density, Young's modulus, hardness and strength are discussed. A comparison to standard Si/SiC reaction bonded materials is also presented.

(ICACC-S1-P015-2014) Tensile Creep Testing of Different Volume Fraction SiC/SiC Composites

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Ceramic Matrix Composites (CMCs) are promising candidates for high-temperature applications such as hot section and exhaust components of advanced turbine and hypersonic engines. Therefore, the tensile creep behavior of precracked and as-received Hi Nicalon, Hi Nicalon Type S and Tyranno ZMI reinforced minicomposites with BN interphases was determined with different fiber volume fractions. Precracked samples were tested in air at 800 C and fiber stress of 1000MPa. As-received samples were tested in air at 1200 C and fiber stress of 1000MPa. Strain was measured using LVDT and electrical resistivity monitoring was performed to assess damage development during the test. Finally, the results were compared to previous high temperature fiber creep data to understand load sharing effects and creep associated with regions around matrix cracks.

(ICACC-S1-P016-2014) Damage Monitoring of Silicon Carbide Matrix Composites by Digital Image Correlation

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A silicon carbide matrix (SiC/SiC) composite is a promising candidate material for various engineering applications. For the practical design of composite components, the detailed failure mechanism need to be clarified since composites exhibit unique quasi-ductility in fracture. Composites' failure generally initiate from inherent internal/surface flaws as potential failure origins. Focusing on the surface flaw issue, identifying notch sensitivity is essential to judge damage tolerance of composite materials. To date, many extensive work evaluated notch sensitivity of various types of composites and it is convinced that composites with moderate fiber/matrix interface are generally notch insensitive. However, recent work by the authors claimed indicative notch sensitivity of advanced SiC/SiC composites by the off-axial tensile loading case. This study aims to identify the detailed damage accumulation behavior of this class of composites to fully understand their notch sensitivity. For that purpose, the digital image correlation (DIC) technique, which becomes a potential powerful tool to understand the detailed failure mechanism of composites, is specifically adopted to get a local strain distribution profile near the notch tip.

(ICACC-S1-P017-2014) The study on processing conditions for pressureless sintered SiC starting from solarcell wafer sludge

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This study is designed to investigate effects of processing conditions on physical properties of pressureless sintered SiC starting from solar cell wafer sludge. The main components of the sludge are SiC and Si powders. This sludgs were heat treated with carbon-black in vacuum in order to transform Si to SiC. These powders were milled to sub-micrometer level. After the treatment, the α/β ratio was determined by XRD. Granules for sintering experiments were made by spray dry process with sintering aids of B4C and carbon resin. Then they are pressed with CIP at 200MPa to make formed bodies. The formed bodies were sintered at over 2100C for 1hr in Ar atmosphere. To investigate the effects of the compositions and processing conditions on physical properties of sintered SiC, α/β ratio of starting materials, sintering temperate and contents of B4C and carbon resin were controlled. Flexural strength, hardness and toughness were measured and compared with microstructures of sintered specimen.

(ICACC-S1-P018-2014) Durability Results from Ceramic Matrix Composite with Differing Porosity Levels

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With ever increasing interest in ceramic matrix composites for high temperature applications, the effect of defects needs to be understood. One of the key defects is porosity that is inherently present from the manufacturing approaches that are available. While porosity effects are clearly noted for elastic properties based on a rudimentary view from a rule of mixtures approach, the effect on durability is not as clear. This is due to the dominance of fibers on the in-plane mechanical properties. A series of samples were fabricated to different levels of porosity. Tensile and durability testing will be conducted. As appropriate, non-destructive screening will be performed before and after durability testing of select samples. The results from these tests will be presented and trends noted based on mechanical and micro-structural analysis. Insight into such behavior will be a key in setting future non-destructive rejection levels.

(ICACC-S1-P019-2014) Ultra-fine WC Cemented Carbides Prepared by a Novel Nitride Conversion Method

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WC based cemented carbides have attracted considerable attentions for use as cutting tools, rock drill tips and other wear-resistant components because of their excellent wear resistance, high hardness and toughness. It has been found that ultra-fine grained WC exhibit superior mechanical properties and abrasion-resistance in comparison with traditional WC with grain size larger than 0.5 μm. However, limited by the quality of WC nano-powder and the sintering technique, it is difficult to prepare ultra-fine WC cemented carbides. This poses an obstacle for further improvement of the properties of the materials. In this study, WC nano-powder is synthesized through an innovative nitride conversion method and the powder is compacted by spark plasma sintering (SPS). The characteristics of synthesized powder, sintering behavior, mechanical properties and microstructure of the bulk cemented carbides are investigated. WC powder obtained by the nitride conversion method showed a high specific surface area of 24.6 m^2/g and the grain size is about 30nm. The powder shows good sintering ability. Dense WC cemented carbides can be obtained by SPS at a sintering temperature of 1420°C, which is lower than the reported data.

(ICACC-S1-P020-2014) A high-temperature neutron diffraction study of Nb2AlC and (Ti0.45Nb0.55)2AlC

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The temperature-dependent crystal structures of Nb2AlC and (Ti0.45,Nb0.55)2AlC, determined using Reitveld analysis of high temperature neutron diffraction time-of-flight data, is reported here for the first time for temperatures ranging between 295-1273K. The compositions are 87.5 wt% Nb2AlC, 7.6(3) wt% Nb4AlC3, 2.5(1) wt% Al2O3, and 2.4(2) wt% Nb2O5 for the sample with no Ti, and 81.6 wt% (Ti0.45,Nb0.55)2AlC, 11.0(6) wt% (Ti0.5,Nb0.5)5AlC4, 2.1(2) wt% (Ti0.5,Nb0.5)C, 2.1(2) wt% Al2O3, and 3.1(2) wt% Nb2O5 for the solid solution with Ti. Samples were tested at the Spallation Neutron Source located at Oakridge National Laboratory using the Engineering Materials Diffractometer beam line (VULCAN). In addition to these samples, an Nb2AlC sample created with a different procedure was tested at the Lujan Neutron Scattering Center located at Los Alamos National Laboratory using the HIgh-Pressure-Preferred Orientation beam line (HIPPO). The composition of this material was determined to be 94.25 wt% Nb2AlC, 4.41(10) wt% Nb4AlC3, and 1.34(6) wt% Al2O3. The average linear thermal expansion in the a and c directions are, respectively, 7.1(1) x 10-6 K-1 and 7.00(8) x 10-6 K-1 for Nb2AlC, and 7.86(9) x 10-6 K-1 and 6.86(10) 10-6 K-1 for the (Ti0.45,Nb0.55)2AlC. The CTE's determined from both HIPPO and VULCAN are within the uncertainty of each other and are relatively comparable to other MAX phases.

(ICACC-S1-P021-2014) Effects of Stress Concentrators on Damage Evolution in SiC/SiC Composites

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Non-oxide ceramic matrix composites are currently being investigated for high temperature applications. Geometric induced redistribution of stress is an important factor in determining the mechanical performance quality of engineered materials, and understanding of it is necessary for their ultimate implementation as components. Towards this understanding, several melt infiltrated SiC/SiC coupons of different notch configurations were tested in tension with modal acoustic emission and electrical resistance monitoring. Accurate stress-dependent damage locations were determined and compared with destructive fractography, revealing complicated damage morphology and allowing for comparison of traditional un-notched coupons.

(ICACC-S1-P022-2014) Effect of MgO and CaO doping on the superplasticity of silicon nitride ceramics with Al_2O_3-Y_2O_3 additives

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The flow behavior of superplastic silicon nitride (Si_3N_4) materials is significantly influenced by the microstructural changes as grain growth, elongation and alignment along tensile axis. Such microstructural changes inevitably inhibit meanwhile viscous flow of individual grains by grain-boundary sliding. These could consequently induce strain hardening and degrade the superplastic maximum elongation. Such compositional change of glassy phase is expected to occur due to the vaporization of glassy phase during process. Thus, the microstructural development and the change of glass composition must be sufficiently considered in order to reveal the deformation mechanism and improve the superplastic ability in Si_3N_4 nanoceramics. In this work, the superplastic deformation behavior of Si_3N_4 polycrystals containing Y_2O_3-Al_2O_3-MgO (SN-YAM) and Y_2O_3-Al_2O_3-CaO (SN-YAC) was investigated at 1650 °C with an initial strain rate of $5x10^{-4}$ s^{-1} under tension. The SN-YAM and SN-YAC samples deformed up to the tensile elongation of ~300% and ~170%, respectively. The extensive grain growth and elongation in addition to the weight loss were observed during deformation. The change of the microstructure and the localized chemistries of glassy phase at grain boundaries and triple pockets during deformation were analyzed, and its effect on the superplastic behavior was discussed.

(ICACC-S1-P023-2014) Processing and Characterization of Basalt Fiber Reinforced Ceramic Composites for High Temperature Applications Using Polymer Precursors

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The development of high temperature structural composite materials has been very limited due to the high cost of the materials and the processing needed. Ceramics can take much higher temperatures, but they are difficult to produce and form in bulk volumes. Polymer Derived Ceramics (PDCs) begin as a polymer matrix, allowing a shape to be formed, to be cured and be pyrolized in order to obtain a ceramic with associated thermal and mechanical properties. The two PDCs used in this development are polysiloxane and polycarbosilane. Polysiloxanes contain a silicon oxycarbide backbone when pyrolized up to 1000°C. Polycarbosilane, an organosilicon polymer, contain a silicon-carbon backbone; around 1200°C, β-SiC begins to crystallize. The use of basalt in structural and high temperature applications has been under development for over 50 years, yet there has been little published research on the incorporation of basalt fibers as a reinforcement in composites. Basalt is a naturally occurring material found in volcanic rock.Continuous basalt fiber reinforced PDCs have been fabricated and tested for the applicability of this composite system as a high temperature structural composite material. Testing for this included thermal and mechanical testing per ASTM standard tests.

(ICACC-S3-P024-2014) Effect of Anelastic Relaxation and Phase Transformations on the Elastic Properties of Stabilized Zirconias

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Stabilized zirconias with high ionic conductivity are currently essential electrolyte material for solid oxide fuel cells (SOFCs) and batteries. In this paper, we report on the temperature dependent elastic properties of two stabilized zirconias, namely Yttria Stabilized Zirconia (YSZ) and Scandia-Ceria Stabilized Zirconia (SCZ). The elastic properties were studied using Resonant Ultrasound Spectroscopy (RUS), Dynamic Mechanical Analysis (DMA) and Cyclic Compression Testing. It was found that elastic moduli change with temperature in non-linear manner with large peaks in the mechanical loss coefficients (or mechanical damping) at different temperatures. A strong mechanical damping or attenuation is related to the either reversible phase transformations or to the stress induced anelastic relaxation due to hopping of the oxygen vacancies in dopant-vacancy defect complexes. Effects of applied stress, temperature and stress frequency on the changes of elastic moduli with temperature are discussed in more details in this paper.

(ICACC-S3-P025-2014) Eu2Zr2O7 carbonate composite as an electrolyte used in the low temperature SOFC

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An Eu2Zr2O7 carbonate composite (abbreviated as EZO-C) was prepared by immersing porous EZO with a relative density of approximately 65-70% into a molten mixture of carbonates containing 1:1 molar ratio of Li2CO3 and Na2CO3 at 500°C. The relative density of the composite was close to 100%. Electrical conductivity of EZO-C reached 1.18(2) x 10-1 Scm-1 at 500°C. After about 3 weeks (500 h) measurement at 490°C, which is slightly lower than the melting temperature of the carbonate mixtures, it dropped and leveled off at about 5.65(3) x 10-2 Scm-1. For the pure EZO oxide with a relative density of 95.3(2)% prepared at 1600°C, electrical conductivity and ionic transference number (ti) were 7.09(2) x 10-5 Scm-1 and 1.00(2), respectively at 500°C. Electrical conductivity of the EZO-C is more than 3 orders of magnitude larger than the pure oxide. EZO-C is a potential electrolyte in the solid oxide fuel cells (SOFCs) at low temperature.

(ICACC-S3-P026-2014) Effect of CeO2 Addition on the Ionic Conductivity of 8 mol. % Y2O3 – ZrO2

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Solid oxide fuel cells (SOFCs) based on 8 mol.% Y2O3 – ZrO2 (8YSZ) electrolyte requires high working temperatures (800-1000°C) to render a reasonable power density. Most of the research and development work on SOFCs worldwide has been devoted on lowering its high operational temperature to intermediate temperature range (500-700°C). In the present work, the novel CeO2-8YSZ nano-composites were synthesized and tested with the aim to develop higher ionic conductive electrolyte materials for SOFCs. Spark plasma sintering (SPS) method was utilized to synthesize nano-composites of 8YSZ with different CeO2 contents (0, 5, 10, and 15 wt. %). The SPS was performed on the powder mixtures of 8YSZ and CeO2 under 30 MPa at 1200°C and with the soaking time of 5 min. Densities of all the sintered samples were estimated to be 96% of theoretical density or above. The XRD profiles collected at room temperature suggest dissolution of CeO2 in 8YSZ matrix, whereas TEM investigation shows isolated CeO2 rich regions indicating the formation of composite. The ionic conductivity measurement was performed using AC impedance spectroscopy in air from 300°C to 700°C. The effect of CeO2 addition on the structure and ionic conductivity of 8YSZ will be discussed.

(ICACC-S3-P027-2014) Performance and microstructural stability of fibrous composite cathodes for solid oxide fuel cells

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We propose the MIEC fiber with ionic conducting particles embedded within fiber instead of simple external composite method. This structure is devised to strengthen the advantages of 1D cathode. When the 1D structure composed of nano-grains MIEC materials is applied to the cathode, it is expected to not only maximize the number of reaction sites which is comparable to that of the nanoparticles, but also minimize the interfacial resistance due to longer continuous grain-boundary/interface which ensures much faster transport of both electrons and oxygen ions compared to nanoparticles. The Sm0.2Ce0.8O1.9 (SDC) particles were embedded in the Sm0.5Sr0.5CoO3–δ (SSC) fiber matrix as the composite cathode for SOFCs application by electrospinning. The single cell with the fiber composite cathode shows much higher performances compared to the cell with the powder composite cathode operating at measuring temperatures, which is ascribed to the microstructural contribution originating from fibrous structure. In order to prove the feasibility of the SSC fibers with embedded SDC nanoparticles as a practical cathode, the long-term stability test was examined under operating conditions since the fibers are prone to lose their structures.

(ICACC-S3-P028-2014) Recoverable Performance of Plasma-Sprayed Metal-Supported Solid Oxide Fuel Cell

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The LSGM (La0.8Sr0.2Ga0.8Mg0.2O3) based Ni-MoFe metal-supported solid oxide fuel cell with a nano-structured anode LDC (Ce0.55La0.45O2)-Ni is prepared using an atmospheric plasma spraying coating process and a post heat-treatment process with a pressure of 0.8 kg cm-2 at 850 °C for 4 h. The measured open circuit voltage is greater than 1 V at temperatures ranging from 600 to 750 °C and the measured maximum output power densities are 788, 666, 497 and 317 mW cm-2 at 750, 700, 650 and 600 °C respectively, using H2 as fuel and air as oxidant. In the 280 h durability test at 400 mA cm−2 constant current density and 650 °C, the measured voltages starting from 0.822 V and ending at 0.775 V show a degradation rate of about 20% kh−1, but after the tested cell is heat treated at the 800 °C and OCV condition for 4 h, the measured voltage at 400 mA cm−2 constant current density load and 650°C is back to 0.825 V which is greater than the initial cell voltage of 0.822V. All of the measured I-V and I-P curves, AC impedances and the voltages before and after the durability test show the tested cell is recovered and demonstrate the heat treated process at the 800°C and OCV condition for 4 h is effective to recover the performance of the prepared metal supported cell. The phenomenon of the recoverable cell performance is also observed in the experimental data of another prepared metal supported cell.

(ICACC-S3-P029-2014) Changes of Elastic Properties of Pure and Doped Cerias with Temperature as Determined by Resonant Ultrasound Spectroscopy

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Cerias doped with aliovalent cations, such as gadolinia doped ceria (GDC) are excellent ionic conductors that are commonly used as electrolyte materials for Solid Oxide Fuel Cells. In this paper, we report on the effect of the type of doping cation (gadolinia, lanthana, scandia, yttria, and zirconia) and their concentration on elastic properties of ceria. Young's and Shear moduli of pure and different doped cerias were determined using Resonant Ultrasound Spectroscopy (RUS) in the 25 – 900 ºC temperature range. In addition, the ultrasonic attenuation (or mechanical loss, Q^{-1}) was determined as a full with at the half maximum of the resonant peak at different frequencies and temperatures. It was found that although elastic moduli decrease almost linearly with temperature, Q^{-1} shows frequency dependent maximum at different temperatures for different doped cerias. This phenomenon is discussed in more detail in the paper in the light of the anelastic relaxation of oxygen vacancy-dopant associates by oxygen vacancy hopping.

(ICACC-S3-P030-2014) Effects of TiO2 Addition on Microstructure and Ionic Conductivity of Gadolinia-doped Ceria Solid Electrolyte

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Ceria containing trivalent rare earth ions is a solid electrolyte with higher ionic conductivity than yttria fully-stabilized zirconia. Consequently, these ceria-based ionic conductors are considered promising materials for application in solid oxide fuel cells operating at intermediate temperatures (500-700C). One of the most utilized approaches to optimize the electrical conductivity and other properties of these solid electrolytes is the introduction of a second additive in the structure. In this work, ceria-20 mol% gadolinia with additions of TiO2 was prepared by solid state reaction. The main purpose was to investigate the effects of the additive on densification, microstructure and electrical conductivity of the solid electrolyte. Sintered pellets were characterized by evaluation of apparent density, X-ray diffraction, Raman spectroscopy, scanning electron microscopy and electrical conductivity by impedance spectroscopy. The additive was found to influence all studied properties. Besides the increase on densification, TiO2 addition influences the blocking of charge carriers at the grain boundaries due to solute exsolution. Moreover, the Gd2Ti2O7 pyrochlore phase was detected at grain boundaries for contents in excess of the solubility limit.

(ICACC-S3-P031-2014) Ceramic Deposition of Electrolyte Layer for Large Area SOFC

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Solid Oxide Fuel Cells are promising devices for electricity generation for their high efficiency, fuel flexibility and modularity. Shaping processes able to considerably reduce the manufacturing costs are however required to bring the SOFC technology to the market. The overall processing of these devices has to become as simple and cost effective as possible in order to reduce the cost connected to the production of both the single layer and the entire device. Although the supporting elements are commonly produced by tape casting, several different techniques have been explored for the production of the thin electrolyte layer. The production of a dense electrolyte is the key point to assure high electrochemical performances to the entire cell. The work addresses the main issues connected to the production of a dense YSZ electrolyte layer onto a NiO-YSZ supporting anode with three of the most common and easy scalable ceramic deposition processes: tape casting, screen printing and wet powder spray. The influence of the nature of the deposition process on the tape formulation and thermal treatments of the green bilayer are studied and compared. The requirements needed to obtain a camber-free large area half-cell are examined and deeply described. A careful optimization of the process parameters and sintering set-up allows the production of flat cells with well sintered electrolyte with all the techniques proposed.

(ICACC-S3-P032-2014) Manufacturing of Sn-LaCrO$_3$ by solution combustion for SOFC

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Doped lanthanum chromite was investigated as ceramic interconnect materials to be used in high-temperature solid oxide fuel cells (SOFCs). In this work, a doped Sn-LaCrO$_3$ powder was produced in continuous synthesis by solution combustion. The doped lanthanum chromite powders were characterized in terms of crystalline phases, thermal analyses and transmission electron microscopy (TEM). X-ray diffraction pattern have identified the presence of Cr$_2$O$_3$ only for the no doped sample. The processing technique used in this work show the presence of LaCrO$_3$ for all investigated materials. No addition thermal treatment was necessary to produce this phase in the solution combustion process.The thermal analyses have shown that the mass loss is associated to the Sn and Cr volatilization. The LaCrO$_3$ particles observed by TEM show a round morphology and a homogeneous particle distribution. The TEM analyses show anaverage particle size of 42 nm.

(ICACC-S3-P033-2014) Fabrication and characterization of anode supported thin film IT-SOFCs by pulsed laser deposition

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Decreasing the operating temperature in solid oxide fuel cells (SOFCs) will aid in increasing their portability and durability. However, the resistance of electrolyte and overpotential of electrode increase significantly at lower temperatures. Pulsed Laser deposition (PLD) is a promising method to prepare thin films, thus reducing the ohmic resistance of the electrolyte and maximizing electrode electrochemical performance with microstructural and morphological control depending on deposition conditions. In this research, SOFC cells consisting an electrolyte, functional layers, and cathode thin film layers grown by PLD on electrically conductive porous supports were fabricated and tested. The control of microstructure of cathode and anode functional layers in different deposition conditions and its relationship with the performance are discussed.

(ICACC-S3-P034-2014) Proton exchange resistance of a zirconate proton conductor

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Proton conducting solid oxide fuel cells (P-SOFCs) offer an attractive means to generate electricity directly from hydrogen (a renewable energy resource) with high energy conversion efficiency and high power. The slow transfer kinetics of hydrogen into and out of the electrolyte at the electrodes is a key barrier towards increasing the cell performance and lowering operation temperature. In this presentation, the resistance to proton transport at the electrodes of a proton conducting zirconate material will be examined using impedance spectroscopy. Porous metal and thin film electrodes deposited on the bulk specimens are studied. The origins of the resistance and capacitance observed in impedance spectra will be discussed. The dependence of resistance on temperature and water, hydrogen, and oxygen partial pressures from which rate limiting mechanisms can be inferred will also be discussed.

(ICACC-S3-P035-2014) Synthesis and Characterization of Yttrium-doped Barium Cerate BaCe1-xYxO3-δ via Modified Sol-gel Pechini Method

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Yttrium-doped barium cerate has been investigated due to its excellent proton conductivity and considered promising electrolyte material for solid oxide fuel cell (SOFC) application. In this study, the yttrium-doped barium cerate BaCe1-xYxO3-δ (x = 0.15, 0.20) was synthesized via modified sol-gel Pechini method. The resulting powder was sintered at 1000 C to remove the excess organic components and obtain the final product. X-ray diffraction analysis showed the formation of perovskite structure. However, extended exposure to sintering time at high temperature resulted to the formation of secondary phase yttrium-doped ceria mainly due to barium vaporization. Increasing the dopant and longer soaking time resulted to the formation of larger grain crystal habit. The presence of endothermic peak at around 900 C from thermogravimetric analysis suggests the change from amorphous state to crystalline phase of yttrium-doped barium cerate ceramic material.

(ICACC-S3-P036-2014) Decreasing the Chemical Expansion of SOFC Electrodes: The Role of Charge Localization

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Expansion of non-stoichiometric oxides upon reduction, largely owing to an increase in cation size, can cause significant mechanical stresses in solid oxide fuel cell components and lead to early device failure. Factors controlling this chemical expansion, particularly in perovskite-structured oxides, need to be investigated in order to design highly durable electrodes. In this work the role of charge localization was studied for the first time by experimental and theoretical approaches. Density functional theory calculations showed that delocalization of charge on the multivalent cations contributing to expansion should decrease the chemical expansion coefficient. Experimentally, localization of charge on Ni ions was tailored in the mixed conductor La$_{0.9}$Sr$_{0.1}$Ga$_{1-x}$Ni$_x$O$_{3-\delta}$ by changing the Ni content. In a prior study, low values of x (e.g., 0.1) resulted in semiconductor-like activated conductivity, suggesting localized charge, whereas large values of x (0.5) produced metallic conductivity, consistent with delocalized charge (Long *et al., J. Electroceram.*, 1999). Chemical expansion was studied by *in situ* X-ray diffraction, dilatometry, and thermogravimetric analysis of bulk samples, using N$_2$/O$_2$ mixtures from 600 to 900°C. Increasing charge delocalization correlated with a significant decrease in chemical expansion coefficient (13% for x=0.1 to 0.5), in agreement with theoretical predictions.

(ICACC-S3-P037-2014) Combinatorial pulsed laser deposition of La0.8Sr0.2MnxCo1-xO3±δ for SOFC cathode applications

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Combinatorial screening of materials is the emerging synthesis technique to acquire entire multi-component system in one experiment. In this work, we propose a new methodology, where combinatorial approach is implemented to study the mass transport properties of La0.8Sr0.2MnxCo1-xO3±δ perovskite family of thin films to be used as cathodes in Low Temperature SOFCs (below 700°C). Combinatorial samples are prepared using composition spread technique by combinatorial Pulsed Laser Deposition (PLD). Plume maps of La0.8Sr0.2CoO3 (LSC), La0.8Sr0.2MnO3

(LSM) are firstly obtained. Then, spatial distribution of thickness and composition gradient are studied through simulation by mixing and changing the plume positions of LSC and LSM. Structural and compositional analysis of the sample are made by X-Ray diffraction (XRD), Micro-Raman analysis, Energy dispersive spectroscopy (EDAX). Secondary Ion Mass Spectroscopy (SIMS) and Impedance spectroscopy are being measured at different points on the combinatorial sample in order to find D* and k* and to study the electrochemical properties of this La0.8Sr0.2MnxCo1-xO3±δ family of thin films. A novel methodology of screening cathodes by combinatorial PLD and SIMS analysis is presented as a powerful technique to search for new materials for LT-SOFCs

(ICACC-S3-P038-2014) Finite-elements simulation study of the feasibility of micro solid oxide fuel cells systems for portable applications

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The widespread use of portable electronic applications has led an increasing demand for more efficient, durable and versatile power supply. Currently, μSOFCs are presented as a promising alternative to Li-ion batteries. Although μSOFCs have been gaining attention as power generator, SOFC technology has not yet burst on portable market because of high operation temperatures and slow start-up. In this work, a computational fluid dynamics model has been constructed in order to balance properly between a rapid start-up and a thermally self-sustaining operation of a μSOFC device with 1Wel output. Several design requirements have been adjusted to study the temperatures distribution within the system based on the effect of non-adiabatic heat losses (conduction, natural convection mixed with radiation). For example the effectiveness of the insulator, the presence of post-combustions or the influence of grid silicon nerves on SOFC's membranes have been discussed. The results of the thermal simulations show the feasibility of a μSOFC system as a power generator with a self-thermally operation at about 750°C while ensuring a sufficiently low external temperature (<35°C) in steady state, and with a reduced times (<2min) and low consumed energy (<750J) for start-up.

(ICACC-S3-P039-2014) Oxidation Suppression of Metallic Interconnects using Thermal-Sprayed Protective Coating

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Metallic interconnects are less expensive, more conductive and capable of forming complex shapes than ceramic interconnects for SOFC applications. Most metallic interconnects use alloys containing chromium. At elevated temperatures, chromia scales from the interconnect react with cathode and degrade its performance. Manganese cobalt oxide ($(Mn,Co)_3O_4$, MCO) with spinel structure is found to be a good material to form a protective coating for metallic interconnects. In this study, the high-temperature ferritic stainless steel Crofer 22H and nickel-chromium alloy Inconel 625 were thermally sprayed with MCO. The oxidation, scale structure, and resistance of these metallic substrates are investigated using XRD, TEM, SEM, and microanalysis.

(ICACC-S3-P040-2014) Effect of Cation Mixing on Structural and Electrical Properties of Mixed Conducting $LaFeO_3$ Perovskite in Reducing Atmosphere

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$LaFeO_3$ perovskite is a mixed ionic/electronic conductor with good stability at various oxygen partial pressure. However, its low conductivity prohibits its uses in practical applications. To enhance the conductivity of perovskite oxides, the addition of aliovalent dopants is an effective way through so-called charge compensation mechanism. The objective of this work is to enhance the conductivity of $LaFeO_3$ by using the addition of double dopants in the cation sublattices of $LaFeO_3$ perovskite. For instance, some of La ions in the A-site sublattice are replaced by Ca^{2+} ions. Some of Fe ions in the B-site sublattice are replaced by Co ions. The samples are fabricated by solid state reaction method at 1300°C based on the formula of $La_{0.8}Ca_{0.2}Fe_{1-x}Co_xO_3$(x=0~0.4). All the samples show typical p-type semiconducting behavior. The addition of Co tends to enhance the conductivity of $La_{0.8}Ca_{0.2}FeO_3$. When 40% of B-site cation sublattice was replaced by Co ions, the conductivity of $La_{0.8}Ca_{0.2}Fe_{1-x}Co_xO_3$ was enhanced from 90 S/cm to 255 S/cm. However, the stability of $La_{0.8}Ca_{0.2}Fe_{1-x}Co_xO_3$ tends to decrease with increasing amount of Co addition. The enhancement in conductivity and instability in reducing atmosphere will be rationalized in light of defect chemistry and bond strength between the transition metal ions and oxygen ions.

(ICACC-S3-P041-2014) Lattice structure, electrical and electrochemical properties of Co-doped SrTiO3 as electrode material for SOFC

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SrTiO3 is a potential material for electrode of solid oxide fuel cells (SOFCs) because of its good structural stability in wide range of oxygen partial pressures. Doped SrTiO3 shows good mixed ionic and electronic conducting feature. La-doped SrTiO3 (LST) have been investigated extensively as anode material for SOFCs. It displays high electrical conductivity, good structural stability but unsatisfied electrochemical properties. Co-doping at B-site can improve the oxygen ionic conductivity and electrocatalytic activity of LST. However, more Co-doping makes LST change from n-type to p-type conductor. As cathode materials, the highly Co-doped LST exhibits high electrical conductivity, lower ASR, high output power density and good chemical compatibility with LSGM electrolyte. The La, Co-doped SrTiO3 should be a good candidate for electrode material of symmetric cells.

(ICACC-S3-P042-2014) Investigation of carbon deposition behavior on ferritic alloys in low S/C ratio using direct heating method

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Prevention of carbon deposition is one of the challenges for highly–efficient operations of solid oxide fuel cells (SOFCs) systems in low steam/carbon (S/C) environments. Ferritic Cr2O3- and Al2O3-forming alloys are utilized for constituent materials of SOFCs and systems. When humidified methane with a steam to carbon ratio (S/C) of less than 1 is used as a fuel, carbon deposition would easily occur on the alloy surface. The prevention of carbon deposition on the alloy surface with the low S/C should make it possible to develop robust SOFCs having a high fuel to electricity conversion efficiency. In this study, carbon deposition behavior of oxide scales formed on the alloys, which were heated directly, was investigated to reveal the mechanism of carbon deposition on alloy surface. ZMG232L and NCA-1 foils were directly heated up to 1173 K in the steam of CH4-H2O gas mixture (S/C=0.02) to evaluate carbon deposition on alloy surface. The results show the Al2O3 scale on NCA-1 was better tolerated to carbon deposition than Cr2O3 scale on ZMG232L. It is suggested that optimized oxide scale on the alloy surface can be tolerated to carbon deposition in low S/C environments.

(ICACC-S4-P043-2014) Electrical Properties of Silicon Carbide Identified Through Scanning Probe Microscopy

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Polycrystalline Silicon Carbide (SiC) has been identified as a very capable structural ceramic due to its high strength, high hardness, and low density. Conductive Atomic Force Microscopy (C-AFM) is a powerful current-sensing technique that is able to measure the conductivity variations across samples. This study details a method of performing C-AFM on SiC samples as a way to understand the electrical properties which are governed by the presence of crystallographic defects within and between the grains, such as dopants, vacancies, dislocations, and stacking faults. Conductivity maps generated by this technique provide a visualization of the distribution of these defects across the polycrystalline sample. These maps clearly show each grain having a core-rim structure with the highest conductivities localized at the grain boundaries and at the interface between the rim and the core. The core, being intrinsic SiC has a low conductivity compared to the defect containing rim which has an elevated conductivity. By applying an external bias to the sample, current-voltage (I-V) curves have been generated that confirm the non-ohmic nature of SiC. This behavior is attributed to an electrostatic barrier at the grain boundaries. Application of this method can provide insight into how the starting materials and processing conditions influence both the electrical and mechanical properties.

(ICACC-S4-P044-2014) X-ray Computed Tomography (XCT) of Ceramics

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In order to better quantify the damage and failure of ceramics in ballistic events, simplified experiments are conducted to induce macroscale cracking and damage in confined ceramic targets. Spherical and cylindrical penetrators at various striking velocities are used to impact the confined cylindrical targets. Only the damage and cracking that occurs on the free surface is traditionally observed. Although destructive cross-sectioning and polishing techniques are occasionally accomplished, they are often difficult and time-consuming. To better understand the mechanisms driving the target response, an X-ray computed tomography (XCT) technique is used to map out the three-dimensional macroscale damage and cracking that occurs in the ceramic after a ballistic event. Time-dependent crack propagation and damage evolution in silicon carbide (SiC) ceramics are predicted using the Kayenta macroscopic constitutive model. Comparisons are made between the current ballistic simulations, and the experimental non-destructive analysis. The XCT technique allows for non-destructive verification and validation of the computational models.

(ICACC-S4-P045-2014) Orientation Dependence of Indentation Crack Length for Single-Crystal SiC

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Single-crystal SiC has a modulus of elasticity and hardness comparable to traditionally manufactured SiC with the additional benefit of transparency. It also displays anisotropy, where mechanical properties vary with crystal orientation. The variation of hardness with orientation is well-known, but crack propagation has not been as thoroughly investigated. Thus, Vickers and Knoop static indentations were carefully placed on 4H-SiC and 6H-SiC so that the indent diagonals were aligned along a specific crystal orientation. It was found that the crack lengths in the <110> directions were generally greater than those in the <010> directions, as would be expected for single-crystal SiC. Secondary cracks originating from the edges of the indents were also observed. This data confirms the activation of the {001}<110> system. The crack behavior is significant for the use of single-crystal SiC for transparent armor.

(ICACC-S4-P046-2014) Transparent AlON Pressurelessly Sintered from Powder Synthesized by a Novel Solid-state Reaction Method

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Transparent aluminum oxynitride (i.e. AlON) ceramics possesses many interesting properties, such as robust mechanical strength, good chemical attack resistance and good transparency from ultraviolent to mid-infrared rang, which make it an ideal candidate for transparent armor, missile dome and optoelectronic window, etc. However, pressureless sintering of transparent AlON is a great challenge. In order to solve the problem, fine AlON powder of high sinterbility is desired. In this work, AlON powder was prepared through solid-state reaction between carbon coated Al2O3and AlN in nitrogen. It was found that the carbon coating layer on Al2O3 and AlN particle surfaces could strongly retard the coalescence and growth of the particles during the AlON synthesis process. As a result, fine AlON powder with a particle size about 0.5μm was obtained at a relatively low temperature of 1700°C. This powder showed a spherical particle morphology and was well dispersed, which endowed it with high sinterbility. Under the aid of proper sintering additive, transparent AlON with an average in-line transmittance above 80% at ultraviolet to infrared range were obtained through pressureless sintering.

(ICACC-S4-P047-2014) The Effects of Testing Methods on the Strength of Glass

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Ballistic performance is an important parameter for Army armor systems. The weakness of one single component could be the Achilles heel resulting in complete failure. For transparent armor applications, glass plays an important role, however determining the actual strength of glass is problematic. Typical glass strength numbers are presented in the literature as ranges. Variations of mechanical properties in glass occur to minor changes in composition, test method employed, and processing. A standardized method needs to be utilized to ensure that strength data can be compared universally. The use of a standard methodology becomes more important when reporting strength increases in coated or treated glasses. In order to attribute any real strength increase to the coating or treatment, one must be able to eliminate all the other possible variables within the test method itself. Testing methodology effects on equibiaxial flexure strength testing from ring size ratio and glass specimen dimensions will be studied following the procedure outlined in ASTM C1499. The goal of this study is to formalize a test method that can be used universally and determine more accurately the strength of glass.

(ICACC-S4-P048-2014) Synthesis of Boron-rich Boron Carbide by Rapid Carbothermal Reduction

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Rapid carbothermal reduction has been proven to produce submicron, homogeneous boron carbide powders in the carbon rich region of the phase diagram. The problem with these powders is that they often time contain free carbon which inhibits some of the mechanical properties of the dense material. The purpose of this study is to find the parameters (feed composition, temperature, run time, etc.) needed to produce boron rich boron carbide powders and dense samples, as well as examine the resulting properties of these materials.

(ICACC-S4-P049-2014) Specimen Preparation Methodologies for Revealing Deformation Features Beneath Knoop Hardness Indents in Boron Carbide

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Contact loading using sharp indenters of different geometries has been a traditional method for measuring hardness properties of metals and ceramics. Because of its relative simplicity, this technique has also been extensively utilized in studies examining various characteristics of material inelasticity including deformation mechanisms. In addition to surface characteristics, sub-surface inelastic deformation features provide additional information on the material's physical response to contact loading and unloading. Revealing these deformation features beneath indents has a number of challenges, the most important being the minimization of artifacts introduced by the preparation method. In this work, several different methodologies for preparing boron carbide cross-sections to reveal deformation features beneath Knoop hardness indents are reported. These methodologies include a mix of both mechanical and ion-beam techniques. SEM and Raman microscopy are used to characterize the cross-sections. Advantages and disadvantages of mechanical and ion-beam techniques are discussed.

(ICACC-S6-P050-2014) Effect of F and C on the charge-discharge behavior of TiO2 nanotube anodes

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Carbon-coated and F-ion doped TiO2 nanotubes are prepared using the hydrothermal method and characterized by electrochemical measurement. TiF4 and glucose are added in the starting materials as the F and C sources. The prepared TiO2 nanotubes has anatase phase only, and XPS analysis shows the presence of F and C. Carbon coating effectively suppresses the severe growth and agglomeration of individual nanotubes, and in turn, results more open-structured nanotube clusters, leading to high Li-ion capacity. On the other hand, F-ion doping stabilizes the interface between the nanotube surface and electrolyte, which leads to the high capacity and excellent rate capability. At 1C, the highest capacity of titania nanotube is about 196 mAh/g after 100 cycles, and even at 20C, the capacity is still about 166 mAh/g.

(ICACC-S6-P051-2014) Synthesis and characterization of LiMnBO3/C as a potential cathode material

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Pristine and carbon-incorporated LiMnBO3 is synthesized at various temperatures, and their lithium electrochemical performance is investigated. The crystal structure is changed from monoclinic to hexagonal, with an increase of the calcination temperature. Pristine LiMnBO3 shows very limited capacity with large polarization; however, the capacity is hugely increased with carbon-incorporation by ketjen black or sucrose, which not only increases the electronic conductivity, but also suppresses severe particle growth. LiMnBO3 calcined at 600°C shows the best electrochemical performance, with the capacity of 108.2 mAh/g after 50 cycles. Based on these results, further improvements can be made, by the reduction of particles size, and the optimization of the mixed phase.

(ICACC-S6-P052-2014) Toward achieving long term performance stability of Li ion batteries: can evaluation of trace and ultra-trace level contaminants help?

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While it is easy to realize the significance of major elements on the performance of electrode materials, the impact of trace contaminants is often hard to foresee, particularly in the discovery phase of new electrode materials. The detrimental impacts of “un-wanted” components often emerge during the long term performance assessment of Li ion batteries under conditions simulating real life experience, to the extent to dictate the economic viability. The “solid sampling” glow discharge (sector field) mass spectrometry (GDMS) is a highly sensitive trace analysis technique, with the ability to provide quantitative measurements on all elements and isotopes in the periodic table, from mg/kg to ug/kg, in complex solids. Due to its exceptional long term repeatability and reproducibility, it has become an indispensable supply chain QC/QA tool for electronic, photovoltaic, LED, nuclear energy and aerospace industries which rely on 4N+ purity advanced materials. In this study, we will demonstrate that GDMS can be effectively used for purity QC/QA of advanced electrode material manufacturing.

(ICACC-S6-P053-2014) Synthesis and Battery Performance of Spinel-Type Lithium Iron Manganese Silicate Crystals

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Lithium ion battery (LIB) has many problems. Those problems are caused by using LiCoO2 as a cathode material of LIBs. Therefore, it is of importance to develop new cathode materials without rare elements. Recently, Honma et al. developed a new spinel-type lithium iron silicate LiFeSiO4 through the quenching of a melt with the composition of 25Li2O-25Fe2O3-50SiO2 (mol %), and proposed that LiFeSiO4 has a potential for the new cathode materials in LIBs. This research was investigated to improve the cell performance by substitution of Mn in the crystals. Quenched samples for the composition of LiFexMn1-xSiO4 (LFMS) were prepared by a melt-quenching method on x=0-1.0. The quenched samples were examined by XRD, AC impedance, TEM, cell performance test to clear the information of samples. A fabrication of Spinel-type LFMS crystals were succeeded during the quenching of melts with composition of LFMS at x=0-0.3. And the XRD peaks of position for the formed crystal were sifted according to Vegard’s law. Adobe x=0.3, the melt was vitrified by splat quenching. The conductivity was decreased from with increasing the quantity of Mn substituted. The cause of conductivity decreasing was concluded by increasing the conduction inhibition with the increase of Mn. It is found that the cell performance was improved by Mn substitution.

(ICACC-S6-P054-2014) Ultrahigh temperature ceramics as novel solar absorbers for CSP systems

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Ultra high temperature ceramics include borides and carbides of early transition metals and are presently considered a class of promising materials for several applications, the most appealing ones being in the aerospace and energy sectors. In the aerospace ultra-refractory diborides are currently studied mainly as thermal protection materials for leading edges and nose cones. Ultra refractory carbides are instead studied as new rocket nozzles for novel propulsion systems. A novel potential application for UHTCs is in the field of solar thermal power, as solar absorbers. UHTCs possess favourable properties (very high melting points and good thermo-mechanical properties at high temperatures) that can be advantageously exploited to increase the operating temperature of thermodynamic solar plants in concentrating solar power systems. This has the advantage to potentially increase the efficiency of the overall system. This work reports on the thermal, mechanical and optical characterization of several hafnium and zirconium diborides and carbides, pure or containing secondary phases to evaluate their potential as novel solar absorbers. A review of the most important requirements that a material should possess as solar absorbers is given and in this perspective properties of UHTCs are compared to those of silicon carbide.

(ICACC-S4-P055-2014) Characterization of Knoop Indents in Several Boron-Icosahedral Based Ceramics by SEM and Raman Spectroscopy

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The effect of load on Knoop hardness values for boron suboxide, aluminum dodecaboride, and aluminum magnesium boride is examined. Another more well-known boron-icosahedral based ceramic, boron carbide, has been shown to undergo stress-induced solid-state amorphization (SSA) when subjected to Knoop indentation. Stress-induced SSA occurs when the crystal lattice becomes mechanically unstable during loading, losing shear rigidity, and having no inelastic deformation mechanisms or thermodynamic phase transitions available to limit the increase in strain energy. The critical load at which this occurs depends on crystal symmetry, elastic constants, and the state of stress. Because of their similarities to boron carbide (rhombohedral), it is natural to consider whether boron suboxide (rhombohedral), aluminum dodecaboride (tetragonal), and aluminum magnesium boride (orthorhombic) are also prone to undergo stress-induced SSA. Surface indentation features were examined by electron and Raman microscopy, and the indentation-size effect characterized using phenomenological models. Experimental procedures and results will be presented and discussed.

(ICACC-S6-P056-2014) Silicon Oxycarbides: Novel High Reliability, Safe and High C-rate Materials for Li+ Anodes

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Polymer derived silicon oxycarbide (SiCO) amorphous ceramics represent a new material for the reversible storage of lithium due to their high capacity (~800mAhg-1) and cyclic stability at high C-rates [1]. However, the lithium insertion voltages are much lower (~500mV) than the lithium extraction voltages yielding a hysteresis in the voltage versus capacity plot [2]. This conventional battery architecture coats SiCO with carbon black as a conducting agent. My project alters this architecture, coating carbon with the active SiCO, yielding smaller lithium extraction voltages. My project seeks to shed light on the mechanisms responsible for the lower lithium extraction voltages present in the SiCO coated carbon structures. [1] D. Ahn, R. Raj, Journal of Power Sources 196 (2011) 2179 - 2186 [2] D. Ahn, R. Raj, Journal of Power Sources 195 (2010) 3900-33906

(ICACC-S4-P057-2014) Operational Equations of State with Arbitrary Heat Capacity

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Operational Equations of State (EoS) can be defined as the EoS which have the form of different operators. For the shock-wave community, the classical example of the operational EoS is the famous Mie-Gruneisen equation. This EoS converts the experimentally determined Hugoniot adiabata data into the EoS. This EoS, by definition, is automatically fully compatible with those Hugoniot experimental data. After the conversion the resulting EoS can be used also for a variety of other high-rate problems. With all its valuable features, the Mie-Gruneisen EoS suffers serious weaknesses as well. In particular, it is thermodynamically inconsistent unless its heat capacity depends solely on the specific entropy. In many applications the heat capacity is assumed to be as a constant. This assumption makes the Mie-Gruneisen EoS thermodynamically consistent but it does not always provide sufficient flexibility in modeling physical phenomena, especially, dynamic ones. In the paper, we discuss operational EoS allowing to model materials with arbitrary heat capacity. The suggested EoS are thermodynamical complete and consistent and can be recommended for modeling shock and blast phenomena.

(ICACC-S6-P058-2014) Nanostructured $LiCoO_2$ Cathode by Hydrothermal Process

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The development of a high performance Li-ion thin film battery is essential for nano/micro electronics that require micro power source. In this study, the main objective was to fabricate a nano-size $LiCoO_2$ film as the cathode of the Li-ion thin film battery. The hydrothermal process was adopted for the thin film deposition of $LiCoO_2$. The solutions were prepared from the lithium nitrate and cobalt acetate in deionized water. $LiCoO_2$ thin film was precipitated on a substrate during hydrothermal process and followed by annealing at desired temperatures up to 4h in air. The crystallization of $LiCoO_2$ film was analyzed by DTA/TG and XRD. A well crystallized hexagonal $LiCoO_2$ and cubic Co_3O_4 film were obtained. The surface morphology of as deposited $LiCoO_2$ film was examined by SEM. Finally, CV test and charge/discharge tests were conducted on an assembled Li battery using the deposited $LiCoO_2$ film by hydrothermal process.

(ICACC-S4-P059-2014) Evaluation of Flaws in Composite Materials Using a Microwave Interference Scanning System

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Microwave frequency scanning is a relatively new NDE method that has undergone significant basic development and technical advancement over recent years. It has significant advantages of ease of use, one sided inspection, compactness, modularity, portability, applicability in varied environments, non-ionizing radiation, and lack of need of transferring medium between probe and specimen. A series of microwave scans using a probe with a 24.6 GHz emitter were performed on a polymer composite panel with engineered flaws both before and after being bonded to an aluminum plate. Engineered flaws included simulated delaminations of different sizes in the top, middle, and bottom of the composite panel, as well as bond line delaminations between the panel and plate. Microwave scans of the panel pre- and post bonding of the aluminum back plate will be shown. The quality and characteristics of the scans will be discussed, including the detectable feature size in the scan data.

(ICACC-S6-P060-2014) Lead-Free Epitaxial $Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$ Thin Films for Piezoelectric Energy Harvesting

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$(1\text{-}x)BaZr_{0.2}Ti_{0.8}O_3\text{-}xBa_{0.7}Ca_{0.3}TiO_3$ (BZT-xBCT) has been recently recognized as a promising lead-free piezoelectric material because of their high piezoelectric coefficient in bulk form with a morphotropic phase boundary (MPB) near x=0.5. However, studies on epitaxial BZT-BCT thin films are still insufficient. In this work, BZT-xBCT thin films with x = 0.3 - 0.7 were deposited on $SrRuO_3$ electroded $SrTiO_3$ (001) single crystal substrates using pulsed laser deposition. X-ray diffraction and high resolution transmission electron microscope confirmed a highly epitaxial growth of all the as-deposited films. The optimal ferroelectric and piezoelectric responses were attained in the BZT-0.5BCT thin films with a remanent polarization $P_r = 14.5\ \mu C/cm^2$ and an effective piezoelectric coefficient $d_{33,eff} > 100$ pm/V. It should be noted that the observed piezoelectric coefficients of our BZT-BCT thin films are comparable to those reported in PZT thin films, suggesting the BZT-BCT thin films are promising lead-free alternative to serve as high-performance piezoelectric energy harvesting devices. In addition, vertical strain enhanced piezoelectric activity in BZT-BCT/Sm_2O_3 nanocomposite films is also reported in this paper.

(ICACC-S4-P061-2014) Robust Hand-Held Microwave Interferometry System

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A hand-held microwave interferometry system has been developed to complement the portable automated system for rapid examination of localized regions of dielectric components, including ceramic composite armor. The Hand-Held Tool incorporates a simplified operator interface and unique, self-aware position tracking capability to permit ease of use in field environments. It utilizes the EvisiveScan microwave interference scanning technique, which has been used to image composite ceramic armor and ceramic matrix composite components, and other complex dielectric materials.. Validation included artificial and in-service damage of ceramic armor, surrogates and ceramic matrix composite samples. Validation included correlation to Portable Automated EvisiveScan images. The technique has demonstrated detection of cracks, interior laminar features and variations in material properties such as density. The image yields depth information through phase angle manipulation, and shows extent of feature and relative dielectric property information. It requires access to only one surface, and no coupling medium. Data are not affected by separation of layers of dielectric material, such as outer over-wrap. This work is supported by the US Army Tank-Automotive Research, Development and Engineering Center (TARDEC) and the US Army Research Laboratory who provided test panels.

(ICACC-S6-P062-2014) Mn doped ZnO Nanopowders by Direct Chemical Synthesis Method

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Over the past few decades, diluted magnetic semiconductor has drawn wide attention due to its potential application in spin-based electronics. In 2001, Dietl et al. [Dietl et al. Science, 2000] theoretically predicated that ZnO is one of possible host materials to achieve room temperature ferromagnetism. After that, room temperature ferromagnetic characteristics of Mn:ZnO material has been reported extensively. Most of them were fabricated using physical method, such as pulsed laser deposition or molecular beam epitaxy. Chemical synthesis was also widely employed for the fabrication of Mn:ZnO nanostructures due to its simple process, low cost and effective dopant doping. However, room temperature ferromagnetism is usually observed when the fabricated nanostructures is performed post annealing. In order to understand the mechanism of the ferromagnetism, we synthesized Mn:ZnO nanostructures using hydrothermal method. In this report, we studied the magnetic properties and microstructure of Mn:ZnO nanoparticles using electron spin resonance, superconducting quantum interference devices and transmission electron microscopy (TEM) with and without post annealing. We found that the as-prepared sample has ferromagnetic ordering, antiferromagnetic ordering and paramagnetism. High doping concentration may induce amorphous structure since for Mn concentration higher than 9.3%, impurities could be observed after post annealing.

(ICACC-S4-P063-2014) Limits of accelerating numerical analysis study of the failure mechanism of ceramics during low velocity impact used in protective systems

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The rapid advancement of computing power and recent advances in numerical techniques and material models have resulted in accurate simulation of ballistic impacts into multi-layer armor configurations. For both transparent and opaque protective systems, low velocity impact damage can compromise structural integrity. Modeling and simulation of material impact by various threat types has proven to be a significant analysis tool in the identification of damage mechanisms and the failure process. Drop-tower experimentation is used to assess the damage of low velocity impact of ceramics. However, numerical simulations at impact velocities between 2 and 5 m/s take long to produce results. Our effort examines various ways of accelerating the numerical study, by (a) increasing the impact velocity of the current impactor; and (b) by keeping the impact kinetic energy constant while decreasing the impactor mass. The failure mechanisms of laminate targets were studied by numerical analysis and the results were compared to available experimental data from various nondestructive techniques. Successful output of this modeling effort will provide useful information of damage propagation through targets used in protective systems by establishing acceptance criteria for any future material prior to its fielding.

(ICACC-S6-P064-2014) Processing and Electrical Characterization of Mn-doped Lead-free Ferroelectric (Bi0.5Na0.5)TiO3-BaTiO3 Thin Films

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Having the increasing environmental concerns in manufacturing and disposal of lead-based piezoelectric materials, lead-free products are developed and investigated in many fields around the world. In this study, manganese doped 0.94(Bi0.5Na0.5)TiO3-0.06BaTiO3 (MnBNBT) thin films were epitaxially grown on SrRuO3-coated SrTiO3(001) single crystal substrates by pulsed laser deposition. The effects of deposition temperature and oxygen partial pressure on the ferroelectric, dielectric and local piezoelectric properties of the films were studied. The optimal ferroelectric and piezoelectric properties were found in thin films deposited at T = 700 °C and PO2 = 200 mTorr with remnant polarization Pr = 32.7 μC/cm2 and the effective piezoelectric coefficient d33 over 100 pm/V. Our results indicate that the MnBNBT thin films are promising candidates for use in ferroelectric memory and piezoelectric micro-actuators.

(ICACC-S6-P065-2014) Polymer-derived Siliconoxycarbide Intercalated Graphene Composite Papers for Li-ion Battery Anode

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Exfoliated graphene oxide (GO) and polysiloxane were blended and pyrolyzed to synthesize freestanding SiOC-graphene composite papers (~10 μm thick). The structural and chemical characterization of the composite prepared with varying polymer concentrations were carried out using electron microscopy, XRD, and FT-infrared spectroscopy. High resolution microscopy images shows layer by layer stacking of GO sheets and an increase in interlayer spacing was observed by X-ray analysis. FTIR peaks at 3400 cm-1 (O-H), 1720 cm-1 (C=O), 1600 cm-1 (graphene), 3056 cm-1 (Si-CH=CH2) and 1034 cm-1 (Si-O-Si) confirmed the successful functionalization of SiOC with GO. Thermo-gravimetric analysis showed enhanced thermodynamic stability of the composite paper up to at least 700 °C in flowing air. The SiOC/Graphene composite paper anodes showed stable electrochemical capacity of approx. 500 mAh/g which was twice that of free standing graphene anodes. The average columbic efficiency (second cycle onwards) was observed to be approx. 97%.

(ICACC-S6-P066-2014) Free-Standing Polymer Derived SiCN/MoS2 Composite Paper Anode for Li-Ion Battery

L. David*, G. Singh, Kansas State University, USA

We study synthesis of free-standing polymer derived SiCN/ MoS2 composite paper anode for Li-ion battery application. This was achieved following a two-step approach: First, polysilazane was interfaced with exfoliated MoS2 nanosheets which upon pyrolysis resulted in SiCN/MoS¬2 composite. Second, dispersion of SiCN/MoS2 in isopropanol was vacuum filtered resulting in formation of a self-standing composite paper. Physical and chemical characterization of the composite was carried out by use of electron microscopy, Fourier transform infrared spectroscopy (FT-IR) and Thermo-gravimetric analysis (TGA). FT-IR data indicated complete conversion of polysilazane precursor to SiCN ceramic, while electron microscopy confirmed layered structure of the paper. Thermo-gravimetric analysis showed enhanced thermodynamic stability of the composite paper up to 800°C. Electrochemical analysis of SiCN/MoS2 composite paper anodes showed that Li-ion can reversible intercalate in the voltage range of 0-2.5 V with a first cycle discharge capacity of 770 mAh/g at a current density of 100 mA/g.

(ICACC-S7-P067-2014) Synthesis of multi-compositional nanoparticles using RF thermal plasma method

S. Sohn*, S. M. Song, S. M. Cho, NuriVista Co. Ltd., Republic of Korea

As the current trend in the electronic devices has been towards miniaturization and high-fuctionalization, their ceramic components are also required to be down-sized. Accordingly, nano particles are increasingly used as a raw matials. In general, the particles are getting smaller, it becomes more difficult to mix and disperse them thoroughly. This problem may cause the deterioration of microstructural homogeity and resultant electrical property. In order to solve this problem, we synthesized multi-compositional and nano particles which are individually composed of several kinds of elements (e.g. Si-Mg-Ba-Mn-V-O) using RF thermal plasma technique. As raw materials, we used commercial powders (1~10 micron), such as SiO2, MgCO3, BaCO3 Mn3O4 and V2O5. The synthesized particles were characterized by FE-SEM, TEM with EDS, XRF and BET. As results, it was found that the synthesized particles showed approximately 30nm in average, spherical shape and amorphous phase. They were also confirmed to be compositionally homogeneous, and have a same ratio with the corresponding mixture of starting materials, within the margin of ± 10%.

(ICACC-S12-P068-2014) Simultaneous Synthesis and Densification of ZrB_2 Ultra High Temperature Ceramic Composites reinforced with Carbon Nanotubes

K. Sengottaian*, B. S. Murty, S. Bakshi, Indian Institute of Technology Madras, India

Zirconium boride is an Ultra High Temperature ceramics (UHTCs) displaying several unique properties such as high melting point of above 3000 °C combined with high electrical and thermal conductivity. Low density, extreme hardness and low volatility in corrosive environments makes this material suitable for ultra high temperature applications like thermal protection systems of atmospheric re-entry vehicle, hypersonic flight, rocket propulsion, etc. However, the fracture toughness and oxidation resistance of ZrB_2 needs to be improved. Present study aims to improve fracture toughness by addition of multi-walled carbon nanotubes (CNTs). Elemental Zr and B powders were taken in stoichiometric ratio and ball milled for 8hr with 10:1 ball to powder ratio. Dispersed CNTs were added to the Zr-B powder and milled for 30 more minutes. The milled powder was reaction spark plasma sintered at 1500 °C to produce ZrB_2 composites containing 0, 1, 2 and 4 vol.%. CNTs. To confirm the phase formation XRD was carried. Microstructural studies were performed by TEM and HRSEM/EDX. Hardness and elastic modulus were obtained by nanoindentation and the indentation fracture toughness was also measured. The effects of CNTs on grain size, densification kinetics, and mechanical properties are discussed.

(ICACC-S12-P070-2014) Oxidation of β–SiC–SiC_f/BN/SiC_m Composite in Static Air and Combustion Environments

A. Mohan*, Indian Institute of Technology (I.I.T) Madras, India; U. Kumar, National Aerospace Laboratories (Council of Scientific and Industrial Research), India; A. S. Gandhi, Indian Institute of Technology (I.I.T) Madras, India

The oxidation resistance of Silicon carbide fiber reinforced silicon carbide (SiC_f/SiC_m)composites is not adequate at temperatures exceeding 1200°C, especially when exposed to moisture-laden high velocity gases due to the formation of the volatile $Si(OH)_4$. In the present study, composites with 40 vol.% of fibers with boron nitride (BN) interfacial coatings were prepared by isothermal isobaric chemical vapor infiltration (ICVI) process. A silicon carbide seal coating was applied to the composites by chemical vapor deposition (CVD) process. The oxidation studies of composites were carried out at 1200°C, 1300°C and 1400°C for various time periods up to 100 h, in static air and in a combustion environment. Oxidation in combustion environment were performed using an oxy-acetylene flame. The change in the specimen weight due to oxidation was plotted against the time of exposure to determine the oxidation kinetics. Combustion experiments were carried out to study the composite recession and to analyze the paralinear kinetics. The phase constitution of the specimens were investigated by X-Ray diffraction (XRD) studies. The microstructure and degradation of the composite after oxidation were analyzed by scanning electron microscopy (SEM). It was found that the degradation of the top surface, the fiber and the matrix exhibit different features.

(ICACC-S12-P071-2014) Optimization of Fusion Welding Parameters for ZrB_2-20vol.% ZrC

D. King*, G. Hilmas, W. Fahrenholtz, Missouri University of Science and Technology, USA

Plasma arc welding was used to join ZrB_2 containing 20 vol.% ZrC (ZrB_2-20ZrC). The billets were prepared by ball milling ZrB_2 and ZrC powders in acetone with phenolic resin as a sintering aid. Billets nominally 64 mm by 64 mm by 5 mm were hot-pressed to near theoretical density, diamond machined, and diced into coupons. Welding current, plasma flow rate, and welding speed were optimized using a 3^3 factorial experiment. Completed welds were evaluated for penetration depth and porosity, and assigned a figure of merit to determine effectiveness of the parameter combination. Pre-heats of the coupons, prior to welding, were used to aid in the resistance to thermal shock. In order to reduce pre-heat temperatures, parameters from the 3^3 factorial that produced effective welds were then subjected to a 3^2 factorial in which current ramp rate and temperature were studied. Hardness and penetration measurements were used to determine the effectiveness of the current ramp rate and pre-heat combinations in order to optimize the welding parameters of ZrB_2-20ZrC based on welding current, plasma flow rate, welding speed, current ramp rate, and pre-heat temperature.

(ICACC-S12-P072-2014) Experimental methods for ZrB_2-$MoSi_2$ composite powder granule production for dual architectural toughening of UHTC composites

A. D'Angiò, National Research Council of Italy, Italy; R. Grohsmeyer*, W. Fahrenholtz, G. Hilmas, Missouri University of Science and Technolgy, USA; F. Monteverde, D. Sciti, L. Silvestroni, National Research Council of Italy, Italy

Dual composite (DC) architectures have been shown to increase fracture toughness while maintaining hardness in cemented carbides designed for room temperature applications. The goal of this research is to study fundamental microstructure-processing-property relationships in DC ceramics composed of zirconium diboride (ZrB_2) sintered with molybdenum disilicide ($MoSi_2$) additions. An example DC ceramic architecture might consist of granules (mm sized regions) of ZrB_2 with an engineered quantity of $MoSi_2$, uniformly dispersed in a ZrB_2 matrix containing a different volume fraction of $MoSi_2$. Further, the ZrB_2 in these distinct microstructural regions might also be engineered to have different particle sizes. To date, the research has focused on the development of the ZrB_2-$MoSi_2$ granules using freeze-casting of powder mixtures and co-extrusion of high-solids-loaded thermoplastic polymer preforms. Attainable granule size ranges and morphologies will be discussed with respect to particle size and composition, as well as the mechanical properties of the same composites in bulk form. Finally, the possible advantageous use of the resulting granules in planned DC architectures will be discussed.

(ICACC-S12-P073-2014) Oxidation Protection of Carbon/carbon Composites above 2000 K

Y. Song*, Z. Feng, Aerospace Research Institute of Material & Processing Technology, China

A SiC/MoSi2/ZrO2 multi-layer coating was fabricated on the carbon/carbon composites by using the pack cementation, slurry and plasma spraying process. Phase composing and elements were analyzed by XRD/EDS. Intensity and Roughness testing demonstrates that the coating has a compact interfacial bonding strength. To simulate the environmental conditions, coating system is tested by high-frequency plasma wind tunnel. The results show that under 2100 K and the loss rate of weight of the composite is 3.15×10-6g/s after 600 seconds of the test. With a stable and reliable antioxidant capacity, the composite show good oxidation resistance over 2000 K.

(ICACC-S12-P074-2014) Heat transfer through phenolic resin/ EPDM rubber blended composites

S. Sagar*, N. Iqbal, A. Maqsood, National University of Sciences and Technology (NUST), Pakistan

In order to enhance the thermal endurance/resistance and mechanical strength of ethylene diene monomer (EPDM) rubber composites, variant concentrations of phenolic resin (PR) were introduced into the polymer matrix. Heat transfer properties of the blended composites were investigated according to the established ASTM standards. It is observed from the heat transport and thermal decomposition data that thermal insulation/stability character of the rubber composite specimens was augmented with increasing the thermoset resin blending concentration in the host matrix. The ultimate tensile strength and hardness were remarkably elevated with the progressive addition of PR in the EPDM matrix. Scanning electron microscopy coupled with energy dispersive spectroscopy was performed to observe the fractured morphology, and to scrutinize the effect of PR concentration to retain the surface morphology of the composite specimens in the high temperature environment during the thermal transport study.

(ICACC-FS2-P075-2014) Phosphate double cladding optical fibers for short cavity pulsed lasers

D. Milanese*, E. Mura, J. Lousteau, N. G. Boetti, G. C. Scarpignato, L. Scaltrito, M. Rondinelli, Politecnico di Torino, Italy

Phosphate glasses are interesting materials for the fabrication of double cladding optical fibers suitable for pulsed lasers in the near infrared wavelength region. The fabrication of Nd, Yb and Yb/Er doped phosphate glasses will be reported together with the characterization of their thermal and optical properties. Suitable passive glasses for 1st and 2nd cladding were manufactured with the aim of obtaining the designed numerical apertures while maintaining well-matched physical properties for stress-free configurations. Preform fabrication by means of rotational casting will be discussed and compared to traditional rod in tube technique in particular regarding the interfaces between core and 1st cladding and between 1st and 2nd cladding. Double cladding optical fibers will be presented and characterized in terms of attenuation loss via cutback method. The demonstration of laser emission will follow by employing fiber pigtailed laser diodes for the excitation of the rare earth ions.

(ICACC-FS2-P076-2014) Pr-doped As_2Se_3-based glasses for biosensing

Y. Shpotyuk*, B. Bureau, C. Boussard-Pledel, V. Nazabal, University of Rennes 1, France

The IR spectroscopy is known to be very important tool for biosensing, due to a set of vibrational fingerprints of molecules in the mid- and far-IR. That is why the investigation of chalcogenide fibres possessing wide IR optical window is an actual task having a great practical importance. The Se-based chalcogenide glasses such as As_2Se_3 belong to such class of materials. Being performed as optical fibre doped with rear-earth ions, these glasses significantly extend their functionality due to numerous transitions appeared in the range up to 10 μm. In this work, we studied the network-forming ability of Ga-doped As_2Se_3-based glasses within two important cut-sections, the first being $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ (x = 0, 1, 2, 3, 4, 5) and second being $Ga_2(As_{0.4}Se_{0.6})_{98-y}Te_y$ (y = 0, 10, 15, 20, 30). Addition of Te should increase the quantum efficiency of rare-earth elements incorporated in a glassy matrix. Within conventional melt-quenching technology, it was possible to introduce up to 3 at. % of Ga into As_2Se_3 matrix. The synthesized $Ga_x(As_{0.4}Se_{0.6})_{100-x}$ alloys with 4 and 5 at. % of Ga occurred to be partly crystallized due to appearance of Ga_2Se_3 crystallites. For further introduction of Te, the $Ga_2(As_{0.4}Se_{0.6})_{98}$ specimen was selected as host matrix. The most stable glass $Ga_2(As_{0.4}Se_{0.6})_{88}Te_{10}$ containing maximum amount of Ga and Te was chosen for further doping by Pr and fibre drawing.

(ICACC-FS2-P077-2014) Photoluminescence properties of red emitting ZrO2:Eu3+,M3+ (M=Sm, Ce, Dy, Bi, Al) phosphors for white-light emitting diodes

S. J. Yoon, K. Park*, Sejong University, Republic of Korea

White light-emitting diodes (w-LEDs) have received a significant attention in solid-state lighting area because of their high energy efficiency, good reliability, long lifetime, and environmental friendliness. Thus, w-LEDs show high potential for replacement of incandescent and fluorescent lamps. We studied the microstructure and photoluminescence properties of Zr0.89-xO2:0.11Eu3+,xM3+ (M=Sm, Ce, Dy, Bi, Al) phosphors synthesized by solution combustion method. The Zr0.89-xO2:0.11Eu3+,xM3+ phosphor powders showed spherical morphology and smooth surface. The emission of the electric dipole 5D0→7F2 transition for the phosphors was much stronger than that of the magnetic 5D0→7F1 transition, indicating high-purity red color emission. The addition of Al3+ for Zr4+ substantially improved the photoluminescence properties of Zr0.89O2:0.11Eu3+. On the other hand, the addition of Sm3+, Ce3+, Dy3+, and Bi3+ for Zr4+ degraded the photoluminescence properties of Zr0.89O2:0.11Eu3+. We believe that Eu3+ and Al3+ co-doped ZrO2 could be a promising candidate as a red phosphor for w-LEDs.

(ICACC-FS2-P078-2014) Comparative study of ZnSe powders synthesized by two different methods and sintered by Hot-Pressing

G. Zhou*, L. Calvez, University of Rennes, France; G. Delaizir, Universite de Limoges, France; X. Zhang, J. Rocherulle, University of Rennes, France

ZnSe is an important infrared optical material. In this work, ZnSe powders have been synthesized using two different methods: hydrothermal route and high energy ball milling. The obtained powders have been dispersed and separated through the ultrasonic process. A comparison has been made between the powders by means of X-Ray powder Diffraction (XRD) and Scanning Electron Microscopy (SEM). The as-prepared ZnSe powders and the fine powders obtained after ultrasonic separation have been sintered by conventional uniaxial Hot-Pressing (HP) technique in order to prepare ZnSe bulk ceramics respectively. The optical properties of the ceramics sintering with different powders have been characterized and compared. As a result, the sintering of the fine hydrothermal powder presents the best transparency in the visible and infrared range. The transmission exceeds 60% in the range from 11 to 19 μm.

(ICACC-FS3-P079-2014) Synthesis and sintering of ceria, praseodymia and samaria nanorods

K. Castkova*, A. Matousek, E. Bartonickova, J. Cihlar jr., J. Cihlar, Brno University of Technology, CEITEC - Central European Institute of Technology, Czech Republic

In order to control the size and shape, various reaction conditions of synthesis of ceria, praseodymia and samaria particles were studied. The particles were synthesized by precipitation of cerium (Ce), praseodymium (Pr) or samarium (Sm) salts in aqueous ammonia under different conditions. The powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmition electron microscopy (TEM), infrared spectroscopy (IR) and thermogravimetric analysis (TGA). High temperature behavior and sintering of particles were studied. Different particle shapes of ceria were prepared by precipitation synthesis starting from Ce nitrate. Whilst spherical nanoparticles were formed at pH=7-10, nanorods were obtained in the strong basic medium. On the other hand only nanorods were formed from Pr and Sm salts independently on pH. According to XRD as-synthesized powders were crystalline. Formation of Ce3+ hydroxide and its oxidation to Ce4+ hydroxide/oxide was crucial for the morphology dissimilarity of the particles. Ceria nanorods were not stable at calcination temperatures higher than 500°C and broke up into separated spherical nanoparticles, therefore the ceramics made from nanorods had microstructure similar to that prepared from spherical nanoparticles. The nanorods of Sm and Pr oxides were stable and therefore the elongated grains were find in the sintered praseodymia and samaria ceramics.

(ICACC-FS3-P080-2014) Investigation of the influence of CuO and SnO doping on the luminescence of Dy^{3+} ions in phosphate glass

J. A. Jimenez, L. Haney*, University of North Florida, USA

The search for luminescence enhancements of rare-earth ions in dielectrics via co-doping with sensitizers continues to be an active area of research given the significance of these optical materials for modern technologies. In this work, Dy^{3+}-doped phosphate glasses prepared by the melting technique were doped with CuO and SnO, or merely SnO, with the purpose of investigating on the sensitizing effect of ionic copper and tin species on the luminescence of Dy^{3+} ions in the matrix. The spectroscopic properties of the melt-quenched glasses were assessed by optical absorption and photoluminescence spectroscopy. Dysprosium ions luminescence was observed under non-resonant UV excitation in the copper and tin co-doped glass in connection with an excitation band appearing around 290 nm not observed in a purely Dy^{3+}-doped reference. The data suggests the presence of twofold-coordinated tin centers and single Cu^+ ions at the origin of energy transfer processes which result in populating the $^4F_{9/2}$ emitting state in Dy^{3+}. A significant role of the tin centers is suggested by the data obtained for the Dy^{3+}-doped glass containing SnO only.

(ICACC-FS3-P081-2014) Anti-cancer activity of cerium oxide nanoparticles depends on its surface chemistry

S. Barkam*, S. Das, V. Perez, S. Seal, UCF, USA

Malignant melanoma is one of the most common cancers diagnosed and techniques such as surgery, chemotherapy and radiation are used to kill tumor cells. The down side in these techniques is that it cannot distinguish tumor cells from the healthy once which unintentionally get exposed to chemical agent/radiation. In our previous work, we have shown that dextran coated cerium oxide nanoparticles (Dex-CNPs) is selectively toxic to cancer cells without effecting the normal cells. However, the mechanism involved in the selective bifunctionality of Dex-CNPs is still unknown. In this study we have exposed the dextran coated ceria nanoparticles (Dex- CNPs) to light leading to photoreduction thereby effecting the surface oxidation state ratio of Ce4+/Ce3+ with similar shape and size. The exposure to light initiates a color change from dark to pale yellow indicating the reduction of Ce4+ to Ce3+. Dex-CNPs exposed to light have reduced cytotoxicity towards squamous cell carcinoma cells and decreased Ce4+/Ce3+ ratio. It has been observed that, higher Ce4+/Ce3+ ratio is more efficient in hindering tumor growth by effectively hindering the tumor-stoma interaction. In conclusion this study provides an in depth understanding of the key chemical and physical properties of the system along with storage and handling that can improve its efficacy.

(ICACC-FS3-P082-2014) Understanding the Material Aspects of Cerium Oxide Nanoparticle's Reactive Oxygen Species

A. Gupta*, S. Das, S. Seal, University of Central Florida, USA

Cerium oxide nanoparticles (CNPs) are known for its superoxide radical and hydrogen peroxide scavenging capabilities in the biological environment. Redox reaction between Ce+3 and Ce+4 and/or oxygen vacancies are considered to be the main mechanisms behind this scavenging activity. However, no concrete evidence is available to understand the main mechanism behind the scavenging activity of CNPs. In this attempt, Lanthanum (La) and Samarium (Sm) doped CNPs were prepared in controlled atmosphere of dextran polymer. Doped CNPs were characterized using X-ray diffraction, FT-IR spectroscopy, HRTEM and UV-vis. Raman spectroscopy was utilized to calculate the oxygen vacancies. Superoxide dismutase and catalase activity of doped CNPs were accessed using SOD and Amplex Red assays. In this study we will sketch the mechanism of cerium oxide catalytic activity in respect to its surface chemistry.

(ICACC-GYIF-P083-2014) Influence of the anionic stabilization of alumina particles by anions of chloroacetic acids in 2-propanol dispersions on physico-mechanical properties of alumina ceramics prepared by electrophoretic deposition

D. Drdlik*, CEITEC BUT - Central European Institute of Technology, Brno University of Technology, Czech Republic; H. Hadraba, CEITEC IPM - Central European Institute of Technology, Academy of Sciences of the Czech Republic, Czech Republic; J. Cihlar, CEITEC BUT - Central European Institute of Technology, Brno University of Technology, Czech Republic

The influence of anionic stabilization of alumina particles in acidic 2-propanol dispersions on physical properties of deposits prepared by electrophoretic deposition (EPD) was studied. Dispersions contained 0.85, 1.70, 4.25, 12.75 or 21.25 wt.% of monochloracetic, dichloracetic or trichoracetic acid, 15 wt.% alumina and 2-propanol. It was found that the surface of alumina particles were stabilized by small amount anions of acids presented in dispersion and chemisorbed on particle surfaces. The rest of ions of acidic stabilizers increased the electrical conductivity of dispersion medium. The influence of electrical conductivity of dispersions on EPD yields, density, roughness and hardness of prepared deposits was described. Maximum yields of EPD of the electrical conductivity in the range of γ=2.5 to 5.5x10-4 S/m were achieved. Maximum relative densities of sintered alumina deposits in the range of γ=2.5 to 22.0x10-4 S/m were reached. On the other hand smooth surfaces of alumina deposits with low roughness were obtained from dispersions with relatively high electrical conductivity (γ=7.0 to 80.0x10-4 S/m), and these values were different for each stabilizer. Based on these results the physical and mechanical properties of alumina deposits were discussed.

Wednesday, January 29, 2014

2nd Pacific Rim Engineering Ceramics Summit

Pacific Rim Ceramic Technologies: Trends and Directions IV

Room: Coquina Salon C

Session Chairs: Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology (AIST); Swapan Das, CSIR-Central Glass & Ceramic Research Institute

8:10 AM

(ICACC-PRECS-031-2014) Energy Efficiency Challenges Addressed Through the Use of Advanced Refractory Ceramic Materials (Invited)

J. G. Hemrick*, Oak Ridge National Laboratory, USA

Refractory ceramics can play a critical role in improving the energy efficiency of traditional industrial processes through increased furnace efficiency brought about by the employment of novel refractory systems and techniques. Examples of advances in refractory materials for furnace applications related to aluminum, gasification, glass, and lime will be highlighted, along with how these advances can be applied to other processes. The energy savings strategies discussed will focus on reduction of chemical reactions, elimination of mechanical degradation caused by the service environment, reduction of temperature limitations of materials, and elimination of costly installation and repair needs. Key results of several case studies resulting from US Department of Energy (DOE) funded research programs will be discussed with emphasis on applicability of these results to high temperature furnace applications and needed research directions for the future.

8:40 AM

(ICACC-PRECS-032-2014) Research & Developmental activities in the field of Refractory Ceramics in India: An overview (Invited)

S. K. Das*, CSIR-Central Glass & Ceramic Research Institute, India

With the present budget giving thrust on infrastructure projects, India will observe a phenomenal growth in steel and cement sectors despite of current economic melt down. Per capita steel consumption in India is mere 48-50 kg/annum against global average of 198-200 kg/annum, while that of cement is 158-160 kg/annum against Chinese average of around 1000 kg/annum. These facts strengthen one's belief that the potential ahead for India is enormous and that justify the good fortunes of refectory industry in India. It is now accepted that refractory industry is increasingly becoming a knowledge base industry and this calls for scientific and technological need assessment, judicious investment on human resource development and innovative research in refractory science and application engineering by establishing in depth knowledge on product-performance relationship. This article reviews some of the refractory related issues such as raw materials, production and research in India. Since refractory raw material crisis is a burning issue worldwide and India has a huge wealth of industrial mineral assets, its problem and prospects through value creation are discussed in detail. The paper also reviews some of the innovative research work being pursued in India at academic and industry perspective along with the futuristic research needed to cope up with the changing industrial scenario.

9:00 AM

(ICACC-PRECS-033-2014) R&Ds on Energy-Saving Manufacturing Process of Silicon Nitrides (Invited)

T. Ohji*, H. Hyuga, Y. Zhou, N. Kondo, M. Hotta, K. Hirao, National Institute of Advanced Industrial Science and Technology (AIST), Japan

In order to improve productivity of silicon nitride ceramics and composites, a great deal of research efforts have been devoted in these years in AIST, Japan. Reaction bonding processing has some advantages, such as low sintering shrinkage and low raw material cost. We intended to develop rapid nitridation process for reaction-bonded Si3N4 based ceramics using optimal sintering additives. Thermo-gravimetric analysis revealed that the addition of ZrO2 substantially reduced the starting temperature and time required for the main nitridation reaction. The obtained samples show almost full densities and relatively good mechanical properties which are comparable to those of conventional materials produced from fine silicon nitride powders. Another important approach is the low-temperature sintering with atmospheric-pressure. We investigated sintering behavior of α- and β-phase powders at low temperatures below 1600°C under atmospheric-pressure nitrogen. The silicon nitride samples fabricated from β powder were almost completely densified, while those from α-powder were not densified. The sintered body with additives of yttria and spinel from low-cost β-powder showed relatively good mechanical properties, indicating a potential to manufacture energy/cost-saved silicon nitrides.

9:20 AM

(ICACC-PRECS-034-2014) Convalescing Energy Efficiency of Firing Process in Whiteware Cluster in India (Invited)

L. K. Sharma*, D. Karmakar, C. Prasad, Central Glass & Ceramic Research Institute, India

Khurja is more than 600 years old historic ceramic whiteware cluster in north India. It has more than 200 oil fired kilns. Pottery manufacturing started in coal fired downdraft kilns. With the growing technological changes worldwide, this cluster too switched over its firing process from coal fired DD kilns to oil fired intermittent & continuous kilns during 90's. Later, formulations were developed to suit the firing with LPG fuel in roller hearth kilns for the fast firing period of 180 and 240 mins. Effects of various technological interventions like reduction in firing cycle hours, reduction in dead kiln furniture mass, reduction in refractory weight of the Kiln Cars base, improvements in products loading density and analysis as well as modifications in flue gases ratio were studied to improve energy efficiency. Impact of change in kiln furniture material as well as design engineering resulted the energy saving in the range of 15-30% based on product range. Modifications in the ratio of the flue gases in firing zone of the kilns resulted the saving of energy in the range of 1 -7%. The effect of all the technological interventions in ceramic white-wares firing process have been discussed in this paper ultimately resulting the energy savings through different techniques and contributing to the improvements in air quality of the cluster by reducing SO2 and NO2 levels by 45% and 62% subsequently.

10:00 AM

(ICACC-PRECS-035-2014) Hybrid-interface based Future Materials (Invited)

K. Kim*, Pusan National University, Republic of Korea

New R&D Center for Hybrid Interface Materials (HIM) at Pusan National University granted via Global Frontier program by Ministry of Science, ICT and Future Planning (MSIP) conducts intensive researches on the future materials utilizing the hybrid interface to resolve challenging issues of advanced materials for future society. Hybrid interface technology is to form the connection in electronic, atomic, molecular and structural level among different kind of materials so that new function of materials and/or components can be revealed, and it is to create the future materials of high-performance, hybrid-function and a new feature through design-syntheses-evaluation of interface volume and composition. In this research, we make attempts for new structure (or composite) of the design, implementation, and evaluation of the hybrid-interface volume materials with convergence of various techniques of materials computation field. In this talk, the idea and some examples of our new research will be discussed.

10:30 AM

(ICACC-PRECS-036-2014) Polymer-Derived Ceramics: Fundamentals and Applications (Invited)

L. An*, university of central florida, USA

Polymer-derived ceramics (PDCs) are a new class of materials synthesized by thermal decomposition of polymeric precursors. Compared to "traditional" polycrystalline ceramics made by powder metallurgy processing, PDCs exhibit a unique, complex amorphous structure with nano-scaled heterogeneity and a set of unique and superior structural and functional properties. Therefore, PDCs are not only an ideal material system for understanding fundamental issues, but also promising for many applications. In this talk, I will give a brief summary on the progress of PDCs in structural models, property mechanisms and applications.

10:50 AM

(ICACC-PRECS-037-2014) Ceramic fillers as the key for high performance polymers

J. Eichler*, ESK - a 3M company, Germany

3M and ESK provide a wide variety of fillers to various industries. In this talk a review will be given on some of the most exciting recent applications. Due to its combination of properties hexagonal boron nitride is the ideal material for use as filler in polymers to increase thermal conductivity and maintaining electrical insulation. Electrification of cars is just one example where these fillers might be a key to fullfill the market needs of the future. Silicon carbide as a filler for polymers in tribological applications has started to gather more interest since energy efficiency standards were raised for pumps in recent years. The high abrasion resistance and clever design enables low friction seals and bearings. Nextel fibers is a well established source for high quality ceramic fibers. Multiple applications are known in this field. The trend of developing not just a ceramic solution, but a materials solution independent of material is very well visible in this application. The barriers between materials and application fields are thinning and todays solutions can only be achieved in teams with multiple backgrounds.

11:10 AM

(ICACC-PRECS-038-2014) High Performance SRBSN (Sintered Reaction Bonded Silicon Nitride) (Invited)

H. Kim*, KIMS, Republic of Korea

Silicon nitride is one of the best ceramic materials with many useful properties, however, actual application is limited mostly due to its high production cost. Use of silicon powder instead of expensive silicon nitride powder is, therefore, attractive. Dense

SRBSN(sintered reaction bonded silicon nitride) ceramics with high strength and toughness was obtained by modifying the structure of RBSN followed by the high temperature gas pressure sintering. The conditions to give porous microstructure with acicular grains was investigated in sintered RBSN in order to modify the pore structures. The efforts were made to enlarge the average pore size of porous SRBSN to reduce the pressure drop of the SRBSN filter. SRBSN DPF filter shows better trapping efficiency of PM compared to cordierite filter. Especially SRBSN filter shows better trapping efficiency for nanosized PM possibly due to the smaller pore size with minimum pressure drop compared to the conventional cordierite filter. Future works to be done in SRBSN will be explained and future possibilities and directions will be discussed.

11:30 AM

(ICACC-PRECS-039-2014) Addressing Water Mark Problem in Porcelain Tile Industries in India (Invited)

C. Agarwal*, Imerys ceramics India, India

Water mark after laying tiles in bathroom or floor is a very serious challenge for ceramic tiles manufacturers all over. Porcelain tiles commonly used for wall and floor application have an apparent porosity up to 5% causing water absorption. This is due to micro pinholes in porcelain tiles not fully covered by the engobe layer. Water seepage takes place through the engobe layer by capillarity, resulting in a dark patch on the glaze surface. The only solution lies in the quality of ball clay for engobe. Imerys Ceramics India has designed a new blend Certiwhite F2T that works very well to arrest water and not allowing any water mark on Porcelain glaze tile surface. The main characteristics of the ball clay were optimized through blending of different quality ball clay's. Experiments on large scale gave interesting results for the tiles having water absorption up to 15%. This paper deals with mineral solutions addressing water marks and glaze issues for Indian porcelain tile manufacturers.

11:50 AM

(ICACC-PRECS-040-2014) Microstructure Development and Properties of SnO_2-TiO_2 Binary Composites via Spinodal Phase Separation (Invited)

T. Sekino*, Tohoku University, Japan; T. Kusunose, Kagawa University, Japan; S. Tanaka, Tohoku University, Japan

SnO_2-TiO_2 binary system is well known to exhibit a solid solution over 1430°C and to form a spinodal phase separation by annealing within its immiscibility region, which exhibits characteristic lamellar structure. Such self-organized composite structure has a large hetero-interface area within its bulk form, which might act as "functional interface" in ceramic materials. In this research, we have challenged multidisciplinary controls of spinodal-originated composite and materials functions of the binary oxide system. Fe^{3+} was doped to the binary oxides via solid-state reaction sintering. Sintering below 1330°C, it was mainly composed from SnO_2 and TiO_2 rich grains, whereas above 1360°C, typical lamellar structure started to form even after the sintering, which phenomenon could not be observed for the non-doped system. It was considered that the lamellar was formed by the Ti diffusion to the SnO_2 grains at low-temperature and then mutual-diffusion of the Ti and Sn started to complete the lamellar formation at higher sintering temperature. Electrical resistivity of the composite depended on the phase development. Detailed microstructural development and electrical properties of the self-organized SnO_2-TiO_2 ceramic composites will be discussed.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanical Behavior

Room: Coquina Salon D

Session Chairs: Monica Ferraris, Politecnico di Torino; Andrew Gyekenyesi, OAI/NASA GRC

8:00 AM

(ICACC-S1-021-2014) Mechanical Behavior of SiC Coated, High Conductivity Graphite Foam (Invited)

A. Gyekenyesi*, C. Smith, M. Singh, Ohio Aerospace Institute, USA

High conductivity graphite foam offers great potential regarding heat exchangers, thermal energy storage devices, and thermal protection systems due to the material's inherent high specific conductivity, open cell structure and associated large surface area. As such, the foam may prove to be an enabling technology in many relevant aerospace and energy production domains. Prior to full scale implementation, the mechanical behavior needs to be well understood. Furthermore, uniform coatings need to be explored in order to enhance the strength as well as offer protection from aggressive environments (e.g., oxidative and corrosive applications). Here, mechanical test procedures were developed to obtain and compare the compressive and tensile properties of uncoated and CVR (chemical vapor reaction) SiC coated graphite foams. Multiple densities of the graphitic carbon foam were tested. Lastly, the thermal diffusivities and conductivities were assessed to assure that the SiC coating did not negatively affect the thermal properties.

8:30 AM

(ICACC-S1-022-2014) Fracture Mechanics Properties of Fused Silicas used in the International Space Station

J. Salem*, NASA GRC, USA

The fracture toughness and slow crack growth of two silicas were measured as part of a program to review the reliability of the International Space Station windows. The materials exhibit the same fracture toughness, with the quartz-based silica exhibiting a higher power law crack growth exponent. A limited review of the literature on fused silica indicates excellent agreement of fracture toughness, but a very wide range of slow crack growth parameters, even from the same institution, with strength based methods usually yielding lower power law exponents than direct crack velocity measurements. The difference relates to the non-linearity of the v-KI curve and the tendency of the measurements to emphasize one end of the velocity curve. Use of the exponential function captures the nonlinearity and leads to better agreement between results; however, the results also imply that similitude is needed in terms of velocity range and specimen preparation.

8:50 AM

(ICACC-S1-023-2014) Effect of microstructure and grain boundary chemistry on slow crack growth in silicon carbide

N. Al Nasiri*, E. Saiz, Imperial College London, United Kingdom; J. Chevalier, National Institute for applied Science, INSA de Lyon, France; L. J. Vandeperre, F. Giuliani, Imperial College London, United Kingdom

Due to the covalent nature of bonding in Silicon carbide, it is expected to have excellent resistance to environmental assisted failure. Therefore, SiC ceramics are being considered for a wide range of applications where water may be present. However, SiC cannot be densified without sintering aids and these could induce sensitivity to environmental assisted failure. Although many studies have been performed on the effect of these additives on strength and toughness, less is known about the way they influence the resistance to environmentally assisted failure. Hence a range of SiC materials have been prepared with different chemistries and microstructures. In terms of chemistry, solid state sintering with B and C as additives is contrasted with liquid phase sintering using Al2O3 and Y2O3. In terms of microstructures, homogeneous fine grained microstructures are contrasted with elongated grains. Slow crack growth was analysed using double torsion tests at room temperature in water with crack speeds ranging between 10-7 to 10-4 m/s as well as using constant stress rate tests with loading rates varying between 20 MPa s-1 and 0.02 MPa s-1. The results of both test methods are discussed to show the influence of both microstructure and chemical composition on environmental degradation. Case studies will be presented to illustrate the significance of these effects in different applications.

9:10 AM

(ICACC-S1-024-2014) Plastic Deformation and Cracking Resistance of SiC Ceramics Measured by Indentation

J. M. Wade*, S. Ghosh, P. Claydon, H. Wu, Loughborough University, United Kingdom

Hardness is deemed as a measurement of resistance to plastic deformation of materials, but cracking accompanying the deformation of ceramics has recently been reasonably interpreted as one of the essential contributors to the widely-known size effect of hardness, commonly termed the indentation size effect (ISE). On the basis of the physical activities behind the ISE, we intend to have the ISE measurement adapted as a means of quantitatively assessing the plastic deformation and the cracking resistance of ceramics. We studied three types of silicon carbide ceramics that were manufactured from same chemical formulation and processing route, but dwelled for different times at high temperature to give distinctive microstructures; from homogeneous, equiaxed grains to highly heterogeneous, elongated grains. By fitting the ISE data with proportional specimen resistance model (PSR), the a1 and a2 parameters are extracted with good enough confidence. The a2 value is interpreted as the "true hardness" and the a1 the fracture surface energy. To reinforce the physical meaning of a1, cracking initiation resistances were measured with Hertzian Indentation and the cracking damage response to Vickers Indentation under variable loads was examined with SEM. Discussion is provided for the points to be made from this study.

9:30 AM

(ICACC-S1-025-2014) Hardess of Composite Oxide Ceramics for Infrared Transparent Systems

J. A. Miller*, I. E. Reimanis, Colorado School of Mines, USA

The hardness of several MgO-Y_2O_3 composites was measured at various length scales to study deformation mechanisms as a function of microstructure with the intent to better understand strengthening mechanisms in transparent ceramic composites. Pure Y_2O_3, 25-75 vol.%, and 50-50 vol.% MgO-Y_2O_3 composites were synthesized via thermal decomposition synthesis, and the hardnesses, densities, and microstructures of these specimens were compared to a commercially available 50-50 vol.% MgO-Y_2O_3 powder. XRD was used to confirm MgO and Y_2O_3 phases were present, SEM was used to evaluate the microstructure, and hardness measurements were performed. It was found that the Y_2O_3, 25-75 vol.% MgO-Y_2O_3, 50-50 vol.% MgO-Y_2O_3, and the commercial specimen had macro hardnesses of 6.3, 7.9, 6.0, and 10.4 GPa and densities of 96.2%, 96.2%, 92.0%, and 96.3%, respectively. The hardness of the 50-50 vol.% composite was nearly half that of the composite made with commercial powder even though the density was only slightly lower. The relations between the microstructure, infrared transmission and hardness are discussed.

10:10 AM

(ICACC-S1-026-2014) High Failure Resistance Behavior in Alumina-Based Multilayer Microstructure Composites With Highly Textured Compressive Layers

Y. Chang, G. L. Messing*, Penn State University, USA; R. Pavlacka, Army Research Laboratory, USA; R. Bermejo, Montanuniversitaet Leoben, Austria

A new class of laminar microstructure composites with both equiaxed and textured Al_2O_3 layers at different thickness ratios was fabricated, with the aim of obtaining flaw-tolerant materials. Residual stresses were tailored in the microstructure composites by control of the volume ratio between equiaxed and textured material. Internal compressive stresses as high as –650 MPa were developed in the textured layers. The effects of equiaxed/textured layer thickness ratio and thickness of the internal textured layers on the magnitude of residual stresses, threshold strength, fracture toughness, work of fracture, and fracture behavior of the composites were investigated. Experimental findings, supported by a fracture mechanics model, showed that optimizing the equiaxed to textured volume ratio in the first layers to around 6:1 and increasing template loading to 10% to obtain 5% porosity in the textured layers yielded a significant increase in the threshold strength (up to 300 MPa) and apparent fracture toughness (up to 11 $MPa.m^{1/2}$). The crack arrest/flaw tolerance behavior was attributed to compressive stresses generated by thermal strain mismatch between the adjacent layers. Work of fracture was also enhanced due to crack bifurcation/deflection in the textured layers associated with the anisotropic fracture energy of the oriented microstructures.

10:30 AM

(ICACC-S1-027-2014) Torsion tests on joined materials

M. Ferraris*, M. Salvo, A. Ventrella, F. Smeacetto, S. Rizzo, V. Casalegno, Politecnico di Torino, Italy; D. Gross, Darmstadt University, Germany; Y. Katoh, ORNL, USA

Results of an experimental investigation on glass ceramic joined SiC and steel tested in torsion will be presented. Torsion tests are proposed in ASTM F734-95 (2006) and ASTM F1362-09, but none of them is directly applicable to joined ceramics; one recent standard (ISO 13124) has been proposed for testing the shear bond strength of ceramic-ceramic, ceramic-metal, and ceramic-glass joining at ambient temperature by compression tests on cross-bonded test pieces. Advantages and disadvantages of each test are discussed and compared, with particular focus on the measurement of pure or apparent shear strength. Torsion test was found suitable to measure the pure shear strength of joined samples, provided that the fracture occurs in the joined area.

10:50 AM

(ICACC-S1-028-2014) A New Analysis of the Edge Chipping Resistance of Brittle Materials

G. D. Quinn*, J. B. Quinn, American Dental Association Foundation, USA

Edge chipping is a common problem with brittle materials such as ceramics used for dental restorations, consumer wares, substrates and wafers, and advanced ceramic structural applications. Concentrated contact forces applied near an edge can cause a flake to pop off. Although knappers have used this methodology to make lithic tools for thousands of years, edge chipping is a nuisance in many cases and can cause unwanted failures. Early analyses devised by the National Physical Laboratory in London and elsewhere emphasized linear force versus distance trend analysis, but more extensive recent testing has revealed nonlinear trends. Dr. Janet Quinn first applied and refined the edge chipping test to dental materials which are susceptible to chip fracture. In this presentation, a new model for edge chipping resistance is presented. It is based on energy balances between indenter work, and material deformation and fracture responses.

11:10 AM

(ICACC-S1-029-2014) Strength characterization of tubular ceramic materials by flexure of sectored specimens

K. Kwok, H. L. Frandsen, M. Søgaard, P. V. Hendriksen*, Technical University of Denmark, Denmark

Several sustainable energy technologies under development such as oxygen transport membranes and solid oxide fuel cells make use of tubular functional ceramic components. The development of suitable materials requires the mechanical strength at operating temperatures and atmospheres to be characterized efficiently. However, typical characterization process is time-consuming due to the large number of tests required for a reliable statistical strength description. A highly efficient experimental facility capable of testing multiple planar specimens under flexure in controlled environments has recently been reported. This paper extends the application of such test facility to tubular ceramic materials. Flexure of sectored specimens is proposed as the strength test for this purpose. The stress field, effect of dimensions, and Weibull parameters are analyzed with finite element analyses. The strengths of Zr-doped-$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFZ) and MgO ceramics are measured with the proposed methodology at room temperature and at T = 850 °C. Observed fracture paths of tested specimens are consistent with predicted stress distributions, and the validity of the characterization method is hence established. The strength reductions with temperature are 18% and 41% for porous and dense BSCFZ respectively.

11:30 AM

(ICACC-S1-030-2014) Experimental analyses to the mechanical behavior of carbon-carbon composite under compressive loading in through-thickness direction

H. Richter*, M. Andrich, W. Hufenbach, Technische Universität Dresden, Germany

The dimensioning of complex-stressed structures made of textile reinforced ceramics based on analytical and/or numerical calculating models requires knowledge of a complete material dataset with the mechanical properties during tensile, compressive and shear loading in the in-plane as well as the through-thickness direction. Currently, the material properties in the in-plane direction are able to be measured sufficiently well with standardised test procedures. Particularly with regard to dimensioning of thick-walled or three-dimensionally stressed structures the knowledge of material properties in through-thickness direction, and in this case especially during compressive loading, is of vital importance. The outcome of this is a demand of a suitable test methodology to determine the required specific material values for composite dimensioning experimentally. With the exception of a few publications in the field of fiber reinforced plastics there is no proven test routine particularly for ceramic matrix composites. Therefore, within the scope of the hereby realised experimental analyses the influence of geometrical and material-inherent parameters like the shape of specimen, the cross-section area in test range or the open porosity on the material properties during uniaxial compressive loading in through-thickness direction was investigated.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Advanced Thermal Barrier Coatings: Failure Mechanisms and Process Modeling

Room: Coquina Salon G

Session Chair: Dongming Zhu, NASA Glenn Research Center; Robert Vassen, Forschungszentrum Juelich, GmbH

8:00 AM

(ICACC-S2-001-2014) Attack of Thermal Barrier Coatings in Gas-Turbine Engines by Molten Silicate Deposits (Sand, Ash) and its Mitigation (Invited)

N. P. Padture*, Brown University, USA

Ceramic thermal barrier coatings (TBCs) are used to insulate and protect hot-section metallic components in gas-turbine engines for aircraft propulsion and electricity generation. However, the higher temperatures and extreme conditions in high-efficiency engines are making TBCs prone to deposition of undesirable silicates ingested by the engines, engendering new materials issues. The undesirable silicates (calcium-magnesium-alumino-silicate glass or CMAS) can be in the form of sand and volcanic ash in the case of aircraft engines, and coal fly ash in the case of syngas-fired engines used for electricity generation. The understanding of mechanisms by which these types of deposits damage conventional yttria-stabilized zirconia TBCs will be presented. Demonstration and understanding of approaches to mitigate this type of damage in new TBCs will also be presented, together with a discussion of guidelines for the development of TBCs for future gas-turbine engines.

8:30 AM

(ICACC-S2-002-2014) Thermal stability and CMAS resistance of ZrO2-Y2O3 and Gd2Zr2O7 thermal barrier coatings deposited by a novel low power plasma process (Invited)

F. Rousseau*, Ecole Nationale Supérieure de Chimie de Paris, France; O. Lavigne, M. Vidal-Sétif, ONERA, France; D. Morvan, Ecole Nationale Supérieure de Chimie de Paris, France

The elaboration of thermal barrier coatings with a simple, efficient and cheap process is a technological and economical issue for both civilian and military engine end users. In this context, a new plasma process has been developed at a laboratory scale, the LPPR (Low Power Plasma Reactor) process. The LPPR permits to elaborate micro/nanostructured TBCs from aqueous precursors. The precursors consist of nitrates which are sprayed in a plasma discharge at low power. Thus it has been possible to obtain highly porous 8YpSZ coatings exhibiting a thermal diffusivity 2-3 times lower as compared with standard industrial TBCs. The present work aims to evaluate the thermal stability of two types of LPPR deposited coatings, the standard 8YpSZ and the CMAS resistant Gd2Zr2O7 compositions. It will focus on the evolution of their morphology, structure and porosity. Characterization will be performed in the as sprayed state and after ageing at various temperatures/durations by means of scanning electron microscopy (coupled with EDS analysis), X-ray diffraction and water porosimetry. Furthermore the interaction between Gd2Zr2O7 and a model synthetic CAS (23.5 CaO, 15 Al2O3, 61.5 SiO2, wt%) will be studied at several temperatures/durations in order to test the efficiency of such LPPR deposited Gd-zirconate as a resistant coating to molten deposit.

9:00 AM

(ICACC-S2-003-2014) Solubility of oxides from ZrO2-Y2O3 and ZrO2-Nd2O3 systems in a molten CAS: Selection of a thermal barrier composition resistant to CAS infiltration

M. Vidal-Setif*, N. Chellah, C. Rio, O. Lavigne, ONERA, France; M. Vilasi, C. Rapin, C. Petitjean, P. Panteix, Institut Jean Lamour, France

Thermal barrier coatings (TBCs) are routinely used in the hot section of gas turbines. However, with the increase of the operating temperatures, new TBC degradation mechanisms has emerged such as the attack by molten calcium- magnesium alumino silicate (CMAS) resulting from the ingestion of siliceous minerals by the engine. It consists in infiltration by molten particles of the porous microstructure of the TBC associated with chemical interaction between CMAS and TBC based on a dissolution-reprecipitation process. This work presents the thermodynamic and kinetic study related to the dissolution into a synthetic CAS of different oxides from the ZrO2-Y2O3 and ZrO2-Nd2O3 systems. The chosen oxides, in powder form, are ZrO2, Y2O3, Nd2O3, ZrO2-4%mol Y2O3, ZrO2-10%mol Y2O3, ZrO2-12%mol Nd2O3 and the pyrochlore Zr2Nd2O7. Solubility tests were performed at three temperatures 1200°C, 1300°C and 1400°C at durations varying from 5 min to 4h. In a second time, 5 compositions of zirconia- based dense ceramics are tested as regards to CAS infiltration: three with increasing amount of yttria and the two previous neodymia doped zirconia. It is observed that the infiltration of CAS in the ceramic grain boundaries is stopped in the case of neodymia doped zirconia and with the zirconia allied with the higher amount of yttria.

9:20 AM

(ICACC-S2-004-2014) Limitations of Rare Earth Reactive Crystallization for CMAS Mitigation in T/EBCs

D. L. Poerschke*, C. G. Levi, University of California Santa Barbara, USA

Thermal barrier coatings (TBC) based on rare earth (RE) zirconates, notably $Gd_2Zr_2O_7$ (GZO), offer potential for mitigating molten silicate (CMAS) attack compared to RE-lean compositions such as yttria stabilized zirconia (YSZ). This behavior has been attributed to reactive crystallization whereby the dissolution of the coating into the melt causes rapid precipitation of a RE/Ca apatite silicate within the TBC porosity, limiting melt penetration and loss of compliance. In principle, this behavior is characteristic of the entire class of RE zirconate and hafnate materials, which would permit substitution of cations based on other coating design requirements. Recent studies on CMAS resistance of Yb-based multilayer thermal/environmental barrier coatings (T/EBC) for SiC-based composites, however, showed diminished effectiveness compared to GZO. To better understand the nuances of reactive crystallization in this family of materials the effect of RE and Zr/Hf cation substitution has been systematically studied at 1300°C, relevant to advanced TBC systems, and 1500°C, the purported coating temperature for emerging T/EBC systems. The results reveal significant dependence of this CMAS mitigation strategy on the TBC composition that pose challenges and provide guidance for the design of future coating systems.

10:00 AM

(ICACC-S2-005-2014) Advanced thermal spray methods for thermal barrier coatings (Invited)

R. Vassen*, N. Schlegel, S. Rezanka, G. Mauer, D. Mack, Forschungszentrum Jülich GmbH, Germany

Several new thermal spray methods have been developed which allow the manufacture of columnar, highly strain tolerant thermal barrier coatings. One of the methods is the suspension plasma spraying, in which suspensions of fine, submicron meter powders are injected into the plasma plume. Under specific processing conditions columnar, finely structured coatings develop. Another method is the plasma spray - physical vapour deposition (PS-PVD) process in which powders are not only molten but even evaporated leading to a PVD-like columnar structure. In addition, a microstructure with segmentation cracks is discussed. Such coatings can be manufactured by applying hot spraying conditions. All these three type of coatings are compared with the conventional micro-cracked thermal barrier coatings with respect to microstructure, physical properties ad performance.

10:30 AM

(ICACC-S2-006-2014) Emerging Issues in Hot-Section Materials Development for Gas Turbine Systems and Use of Alternative Fuels (Invited)

M. H. Sullivan, T. J. Montalbano, J. P. Horwath, D. R. Mumm*, University of California, Irvine, USA

This talk will provide an overview of emerging issues in the development of hot-section materials for advanced turbine systems with improved performance and higher turbine inlet temperatures – and efforts to power these systems on alternative fuels. Tests of turbine systems fueled with syngas or bio-derived fuels have shown that the chemical composition, growth kinetics and microstructures of protective thermally grown oxides may be altered relative to those obtained with combustion of conventional fuels. With components protected by thermal barrier coatings, several additional concerns arise in utilizing alternative fues. In many cases, the hot section flow path materials are exposed to substantially higher water vapor levels and unique non-combustibles in the hot-section flow path, leading to unique and severe degradation modes. Current efforts to characterize surface deposition, molten phase infiltration, and the role of TBC coating microstructure on the associated corrosive/thermo-chemical attack, and thermo-mechanical responses, will be described.

11:00 AM

(ICACC-S2-007-2014) Solid particle erosion of TBCs: jet tester modelling and erosion forecasts

F. Cernuschi*, L. Augello, RSE, Italy

Thermal barrier coatings (TBC) are used to protect hot path components of gas turbines from hot combustion gases. Depending on the operating conditions, solid particle erosion can be an issue for TBCs, as a matter of fact sand, volcanic ashes could enter into the turbine promoting erosion.. Electron beam physical vapour deposition (EB-PVD) coatings exhibit better solid particle erosion than PS TBCs.. Nowadays segmented APS coatings and PS - PVD™ have been developed to improve solid particle erosion of plasma sprayed TBCs. At RSE solid particle erosion tests have been performed on TBC with different microstructures for comparison purposes. As a first step to forecast erosion in gas turbine, the laboratory jet tester has been simulated by a simple analytical model describing the speed of erodent particles as a function of their size and shape. By this way, for each TBC type, the volume eroded by a single particle is estimated and a rough evaluation of the overall erosion rate can obtained, after preliminary calibration of the model starting from experimental data. Forecasts of erosion rate for four type of TBCs (standard porous APS, EB-PVD, PS-PVD™ and highly segmented APS) depending on test conditions are discussed.

11:20 AM

(ICACC-S2-008-2014) Lifetime Modeling of Plasma Sprayed Thermal Barrier Coatings

C. Nordhorn*, R. Muecke, R. Vassen, Forschungszentrum Juelich GmbH, Germany

Plasma sprayed thermal barrier coatings are frequently used in land-based gas turbines to increase the heat resistance of the metallic turbine components. The protective coating systems typically consist of a NiCoCrAlY bond coat and an YSZ topcoat. Spallation of the top coat is the predominant failure mechanism. In order to assess the durability of plasma sprayed thermal barrier coatings under different operating conditions, a numerical lifetime model has been developed, which is based on the analysis of the mechanical system response under extreme thermo-cyclic loads. The thermally induced stress fields in the topcoat are calculated by finite element analyses including the effects of topcoat sintering and bond coat microstructure. The surface texture of the bond coat is approximated by a cosine function, whose parameters are derived from measured roughness parameters. In addition, the thermally induced growth of an oxide layer and the relaxation processes in the top coat are taken into account. In consequence of the cyclic loading, cracks propagate within the topcoat close to the bond coat interface. For life prediction, the transient energy release rate is compared to its critical, crack-length dependent value. The modeling results comprise statistical evaluations of the crack and energy release rate evolutions and are contrasted to experimental lifetime results, which are obtained by cyclic burner rig tests.

11:40 AM

(ICACC-S2-009-2014) Investigation of bond coat rumpling under the TBC and on a bare bond coat using computed X-ray tomography and 3D SEM-Photogrammetry

S. Shahbazmohamadi*, N. Asadizanjani, E. H. Jordan, University of Connecticut, USA

Bond coat surface geometry change known as rumpling can be a contributing factor to the failure of TBC systems. The methods previously used to quantify the rumpling under the TBC involved serial sectioning were destructive and lacked the 3D information. In this work, Computed X-ray Tomography (CT scan) has been used as a tool to record the 3D surface geometry of the bond coat underneath the TBC. Several challenges involving the use of X-ray CT on thermal barrier coatings have been addressed and remedies have been proposed to optimize the quality of the 3D images. In addition, the image processing procedures needed to extract quantified surface information of the bond coats are explained in detail. The bare bond coat samples with no TBC on are also imaged using the optimized SEM-based 3D imaging technique already developed and published by the authors. The two results have been compared to investigate the effect of the TBC on the behavior of bond coat rumpling in Thermal barrier coatings.

S3: 11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Cell Manufacturing

Room: Coquina Salon H

Session Chairs: Toshio Suzuki, National Institute of Advanced Industrial Science and Technology; Enrico Traversa, King Abdullah University of Science and Technology

8:00 AM

(ICACC-S3-009-2014) Progress and Challenges of Metal supported SOFC (Invited)

N. Christiansen*, Topsoe Fuel Cell A/S, Denmark

Attention to reliability and robustness of SOFC cells and stacks is increasing as the technology moves from laboratory and pilot scale to demonstration at real operation conditions. Metal supported cells are expected to offer several potential advantages due higher tolerance toward internal temperature gradients and temperature shock. Furthermore the metal supported SOFC concept is expected to yield improvements in cell material cost, component handling and stack assembling and offers several new perspectives regarding novel cell and stack designs. For stack interconnects materials featuring low Cr evaporation and improved corrosion resistance has been provided by thin film coating Fe-22Cr strip steels with Co and Co/Ce. Cells and stacks exhibit ASR of 0.5 Ωcm2 at 650 oC. Stable anodes and improvement of corrosion resistance of the metallic backbone structure by oxide infiltration. Chemical and physical properties of the cells and stack developed in the consortium of TOFC and DTU are modelled and simulated by European R&D partners in the EU project METSAPP. The paper will discuss resent progress and challenges in the metal supported SOFC concept and draw comparisons to the worldwide status within this

8:30 AM

(ICACC-S3-010-2014) mT-SOFC: Fabrication and performance under fuel cell and electrolysis operation modes (Invited)

V. M. Orera*, M. A. Laguna-Bercero, A. Larrea, H. Monzón, C.S.I.C., Spain

Higher energetic density, better resistance to thermal stresses and smaller starting times as compared with conventional planar stacks, make the microtubular SOFC, (mT-SOFC) devices suitable for portable applications. Fabrication of mT-SOFC is a challenging process where several ceramic layers of different compositions and microstructures have to be put together in a final device with cylindrical geometry. Several co-sintering processes at different temperatures and using distinct atmospheres have to be implemented to complete the required functional behavior. Results concerning fabrication and cell performance will be presented. Cells with the following composition and operation temperaturewill be described: (anode/electrolyte/cathode) YSZ-Ni/YSZ/LSM, YSZ-Ni/YSZ/YSZ-LSM/LSM working around 800 C both in FC andHT-SOE mode, YSZ-Ni/YSZ/GDC/LSCF, YSZ-Ni/YSZ/GDC/GDC-LSCF/LSCF, YSZ-Ni/YSZ/GDC/Pr2NiO4+δ, YSZ-Ni/YSZ/Pr2NiO4+δ operating at 700 C, GDC-Ni/GDC/LSCF at 600 C and GDC-Ni/GDC/Nd2NiO4+δ at 600 C. Some very recent results concerning the use of mT-SOFC for CO2-H2O co-electrolysis will be finally presented. Critical aspects for the incorporation of SOFC to the market are duration and price. Some estimations of costs and results of durability experiments will be also given.

9:00 AM

(ICACC-S3-011-2014) Doping NiO and 8YSZ, and optimisation of tape cast multilayer design for production of Metal Supported Solid Oxide Fuel Cell by co-sintering

P. Satardekar*, University of Trento, Italy; D. Montinaro, Viale Trento, Italy; V. M. Sglavo, University of Trento, Italy

The cost-effective route of co-sintering tape cast multilayers for the production of metal supported Solid Oxide Fuel Cell encounters major issues. These include metal support–anode interaction, coarsening of electrocatalyst, delamination of multilayers, and limited densification of the electrolyte. In this work, ferritic stainless steel, Ni-YSZ cermet and 8YSZ were considered as support, anode and electrolyte, respectively. The co-sinteribility of multilayers was enhanced by properly doping the anode and the electrolyte. The RedOx kinetics of NiO could be modified with Al dopant, thereby preventing the steel-induced reduction of NiO and also inhibiting Ni coarsening. Moreover, the use of Al-doped NiO for the anode resulted in finer and more porous microstructure. The electrolyte was doped with Fe this being proved to be a good sintering aid. For 2 and 4 mol% Fe-doped 8YSZ the onset of sintering shifted from 1190°C (for pure 8YSZ) to 1050°C . The optimised green multilayer consisting of Fe-8YSZ/Al-NiO-YSZ/intermediate layer/steel was co-sintered at 1350°C in Ar - 3% H_2.GDC-steel composite was shown to be the most effective intermediate layer in avoiding delamination and interdiffusion. Sintering profiles and Fe loads were optimized for obtaining electrolyte densification.

9:20 AM

(ICACC-S3-012-2014) Single Step Production of Cathode Supported SOFC

A. Gondolini*, E. Mercadelli, P. Pinasco, A. Sanson, ISTEC-CNR, Italy

Cathode-supported solid oxide fuel cells (SOFCs) offer several advantages over anode-supported ones. In terms of structural stability, for example, they do not suffer from the volume contraction and expansion typical of the redox cycle of Ni-based supported cells. For the production of the half-cell a thin film electrolyte is screen printed on the green tape substrate and co-sintered to form the electrolyte/cathode bilayer. The anode is commonly deposited on the as-sintered half-cell. An additional thermal treatment at lower temperatures is necessary to obtain a complete cell. In this study the possibility to obtain a SOFC constituted by a porous LSM-GDC supporting cathode with GDC dense electrolyte and a NiO-GDC anode in a single thermal step that includes also the formation of the perovskitic cathodic phase was investigated. The so-called reactive sintering was in fact considered to exploit the porosity induced by the precursor decomposition during the thermal treatment for the formation of the La0.8Sr0.2MnO3 (LSM) phase. To obtain dense electrolyte and porous electrode a sintering aid and a pore former were added respectively to the GDC and NiO-GDC starting powders. The effect of the reactive sintering approach on the single step production of the entire cell was investigated. Cathode supported cell with dimension 5x5cm^2 has been successful fabricated by cost-effective technologies in a single-step.

Joining Technology

Room: Coquina Salon H

Session Chairs: Prabhakar Singh, University of Connecticut; Niels Christiansen, Topsoe Fuel Cell A/S

10:00 AM

(ICACC-S3-013-2014) Novel glass-ceramic compositions for application as sealants for Solid Oxide Cells (Invited)

F. Smeacetto*, A. De Miranda, M. Salvo, M. Ferraris, P. Leone, A. Lanzini, M. Santarelli, Politecnico di Torino, Italy

The development of sealants for solid oxide fuel cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs) is a significant challenge as they must meet very restrictive requirements; they must withstand the severe environment of the SOFC and SOEC devices (high oxygen partial pressures and reducing gas environments) and be thermo-chemically and thermo-mechanically compatible at 750-800°C with the materials to which they are in contact with . This study focuses on the preparation and characterization of new glass compositions with self-healing behaviour based on the Ca-Al-Na-Si-O system. Glass-based sealants were characterized by heating stage microscopy, differential thermal analysis, dilatometer, X-ray diffraction, and Vickers micro hardness. Sintering and crystallization behaviour for new glass-ceramic compositions are reviewed and discussed. Both new glass-ceramic sealant composition showed excellent compatibility with Crofer22APU coated with Mn1.5Co1.5O4 and the YSZ electrolyte, as revealed by SEM and EDS measurements. The performance of the sealants was also tested in short stack configuration. Post mortem examinations are reported and discussed.

10:30 AM

(ICACC-S3-014-2014) Microstructure and thermal cycling properties of reactive air brazed joints (Invited)

E. Skiera*, C. Li, B. Kuhn, T. Beck, L. Singheiser, Forschungszentrum Jülich, Germany

High temperature solid oxide fuel cell technology poses harsh requirements for seals. For secure operation, the seals have to be reliable under isothermal high temperature and thermal cycling conditions. Reactive air brazing (RAB) gained increasing interest as a technique potentially offering superior joint ductility and thus robustness. To imitate real-life operating conditions, high temperature (550°C, 675°C and 800°C) double-shear testing was applied to characterize RAB metal/ceramic joints. Shear and creep properties were obtained by constant deformation rate and stress relaxation experiments. The resistance of the joints to rapid temperature changes was examined by cycling samples between 250°C and 800°C for more than 4000 times. The thermal cycling capability was evaluated by ambient temperature delamination testing after thermal cycling. Three different brazes (pure Ag, Ag4mol%Cu and Ag0.5mol%Al) were compared in terms of high and ambient temperature mechanical behavior. The influence of joint microstructure and microstructural changes during isothermal aging / thermal cycling will be addressed in detail.

11:00 AM

(ICACC-S3-015-2014) Compliant sealing glass for SOFC applications: effect of fillers on thermal cycling and validation in a generic stack fixture test

Y. Chou*, J. Choi, J. W. Stevenson, Pacific Northwest National Lab, USA; V. Garcia-Negron, R. Trejo, B. Armstrong, E. Lara-Curzio, Oak Ridge National Lab, USA

A commercial silicate based sealing glass (SCN-1) is currently evaluated as a candidate sealing glass for solid oxide fuel applications. The glass contains about 17% alkalis and remains vitreous during heat treatment, unlike the conventional sealing glass which turns into a rigid glass-ceramics after heat treatment. Inert ZrO2 fillers (short fiber and hollow balls) were used to minimize pore coarsening and were first screened with thermal cycle stability test. Glass with fillers was used to seal a ceramic bilayer to an aluminized AISI441 substrate. High temperature leak rate was measured. In addition candidate glass was validated in a stack fixture test for ~1500h and 3 thermal cycles. Cell performance will be reported and compared to refractory glass. Post-mortem and SEM analysis will be conducted to address the contaminant issues.

11:20 AM

(ICACC-S3-016-2014) High-Temperature Viscous Sealing Glasses for Solid Oxide Fuel Cells

C. Kim*, J. Szabo, R. Crouch, R. Baird, MO-SCI Corporation, USA; R. K. Brow, J. Hsu, C. Townsend, R. Reis, Missouri University of Science and Technology, USA

Solid oxide fuel cells (SOFCs) require robust seals that can prevent intermixing of air and fuel, remain inert in reducing and oxidizing environments while in contact with SOFC materials, and maintain their effectiveness through repeated thermal cycles. One potential technology that can meet these constraints uses viscous seals that are capable of healing themselves if they fracture during a thermal cycle. Alkali-free, alkaline earth borosilicate glass compositions have been developed as viscous sealants for SOFCs. These glasses possess desirable thermo-mechanical properties and thermo-chemical characteristics, and exhibit promising hermetic sealing and healing behavior under SOFC operational conditions. The dilatometric softening points (Ts) and the glass transition temperatures (Tg) of the glasses are generally under 650°C, the lower bound of the SOFC operating temperature. To date, glass seals between a NiO/YSZ bi-layer and aluminized 441 stainless steel have survived hundreds of thermal cycles (750°C to RT) under wet forming gas or in dry air at a differential pressure of 0.5 psi (26 torr) without failure. Healing of glass seals that were cracked by thermal shock was observed upon reheating.

11:40 AM

(ICACC-S3-017-2014) Characterization and Performance of a High-temperature Glass Sealant for Solid Oxide Fuel Cell

C. Liu*, R. Lee, K. Tsai, S. Wu, K. Lin, Institute of Nuclear Energy Research, Taiwan

The crystalline properties and thermal stabilities of a novel borosilicate glass (GC9) developed at INER, have been investigated for use as high-temperature seals in solid oxide fuel cell (SOFC). The kinetics of isothermal and non-isothermal crystallization of the GC9 glass were examined by TG/DTA and XRD at various crystallization temperatures of 700~900°C and heating rates of 2.5~50°C/min, respectively. A sandwich specimen of metallic interconnect and MEA jointed by the GC9 glass was aged at 800°C for

1,000 hours to examine the compatibility and interfacial stability. High-temperature leak rate measurements of the GC9 glass were performed under the condition of aging (800°C) and thermal cycling (RT~800°C). The glass transition temperature, softening temperature, and coefficient of thermal expansion of the GC9 glass are 652°C, 745°C, and 11.0 ppm/°C, respectively. In the study, there was about 50% of fine ceramic phases, mainly Ba3La6(SiO4)6, embedded in the GC9 glass matrix and thus resulted in a superior mechanical strength at elevated temperatures. No obvious interfacial interaction or diffusion between the GC9 seals and the adjacent plates was found after long-term aging. Additionally, the average leakage rates were 2.25×10−5 and 5.58×10−5 mbarl/s/cm corresponding to the aging and thermal cycling tests.

S4: Armor Ceramics

Modeling

Room: Coquina Salon E
Session Chair: Costas Fountzoulas, U.S.Army Research Laboratory

8:00 AM

(ICACC-S4-030-2014) Using Micromechanics-based Models to Inform the Design of Advanced Ceramic Materials

A. L. Tonge*, The Johns Hopkins University, USA; K. T. Ramesh, The Johns Hopkins University, USA

Due to the large parameter space available in terms of processing paths and raw materials, it is difficult and costly to use experimental methods alone to develop promising paths towards improved performance of advanced ceramics for impact applications. Computational models that link the material failure processes to the material microstructure and the macroscopic loading under relevant impact conditions can provide guidance for materials design and reduce the number of ceramic processing paths that require investigation. We have developed a micromechanics based material model where each energy dissipation pathway in the model is linked to a set of microstructural parameters. These dissipation pathways include viscous heating through shock formation, elastic softening as a result of micro-crack growth, granular flow of the fully damaged material, and plasticity. Using this model we can examine the relative importance of each energy dissipation pathway for a variety of loading conditions such as dynamic uniaxial compression, and edge on impact. Insights from this investigation suggest promising directions for future effort in the development of improved advanced ceramics.

8:20 AM

(ICACC-S4-031-2014) Numerical study of stress and fracture propagation in glass during ring-on-ring testing

C. G. Fountzoulas*, J. J. Swab, P. J. Patel, U.S.Army Research Laboratory, USA

Glasses are the primary striking ply materials used in transparent armor due to availability, cost, and existing mature manufacturing. Glass fracture patterns are unique in nature and they reflect the nature of the glass. Moreover, glass fracture examination provides information as to the direction of the breaking force. The density of cracks in fractured glass is highly correlated with the fracture pressure, with a higher fracture pressure resulting in a higher crack density that is anticipated to the increase stored energy with increasing pressure. During a ring-on-ring testing a slowly moving compressive load is applied on the glass which results in the failure of it. Initial 3D modeling and simulation of the cracking propagation throughout the compressed glass substrate has shown that the presence of the supporting ring accelerates the failure towards the edges of the rectangular glass substrate. The objective of the current numerical study is to delineate the mechanism and shed light to the physics of the stress wave propagation in the glass during the ring-on-ring testing. The simulated cracking pattern of the glass will also be compared to available experimental data for model validation. In addition, the effect of the relative position of the upper and lower rings to the failure of the glass will also be studied by 3D modeling and simulation using commercial software.

8:40 AM

(ICACC-S4-032-2014) Prediction of roughness in transverse crack surfaces from impact on a glass-polycarbonate two-layer system

F. Bobaru*, Y. Wang, University of Nebraska-Lincoln, USA; J. Yu, C. Yen, ARL, USA

We present a peridynamic model for the damage and fracture evolution in a glass-polycarbonate thin-plate system from impact with a small rigid projectile at velocities ranging from 60m/s to 150m/s. The computational results show how and why certain damage patterns form in the glass plate and the origin of various crack systems that develop in the plate. A careful analysis of the corresponding experimental results indicate intriguing roughness on the surface of a circumferential transverse crack with ridges in the order of tens of micrometers or less, that extend to a diameter of about 4 cm from the impact center. The peridynamic solution, while using a much coarser discretization than the size of this roughness, is nevertheless capable of showing a similar roughness, albeit in an average sense. The results further validate the peridynamic computational model and clarify the meaning of the peridynamic horizon size used in this work.

Testing and Evaluation / Materials Characterization / Quasi-Static and Dynamic Behavior I

Room: Coquina Salon E
Session Chair: Sikhanda Satapathy, U.S. Army Research Lab

9:00 AM

(ICACC-S4-033-2014) Characterization of Silicon Carbide Microstructure Using Nondestructive Ultrasound Techniques

V. DeLucca*, R. A. Haber, Rutgers University, USA

Ultrasonic nondestructive evaluation has conventionally been used to measure elastic properties and locate large flaws in many types of materials used for a number of different applications. Recent advances in acoustic spectroscopy have enabled ultrasound techniques that can be used to examine the microstructure of dense ceramic bodies. In this study, methodology is developed for nondestructively characterizing the microstructure of spark plasma sintered (SPS) silicon carbide using high frequency ultrasound acoustic spectroscopy. Several silicon carbide samples with varying microstructures were produced by varying the processing and sintering conditions. Comparison of the acoustic attenuation spectra of the silicon carbide samples with microstructural information from field emission scanning electron microscopy (FESEM) is used to determine a relationship between microstructural properties and ultrasound response.

9:20 AM

(ICACC-S4-034-2014) The Effect of Microstructure on the Static and Dynamic Mechanical Response of Reaction Bonded B4C-SiC-Si Ceramics

P. Jannotti*, G. Subhash, University of Florida, USA

Static and dynamic indentation and compression experiments were performed on reaction bonded ceramics which contained varied boron carbide, silicon carbide and silicon content. Static indentation experiments revealed that ceramics containing minimal residual silicon yielded the highest hardness, increasing almost linearly with decreasing silicon content by up to 14%. Dynamic indentation experiments showed that the rate sensitivity of hardness ranged from -21% to +27%, largely due to the localized amorphization of the boron carbide phase. Interestingly, despite high boron carbide content, the reaction bonded ceramic with diamond particle additions showed a slight increase in dynamic hardness. Raman mapping of the residual indents showed that varied processing led to reduced amorphization (i.e., effected volume and maximum intensity). Static and dynamic uniaxial compression experiments revealed that reduced silicon content increased the compressive strength almost linearly by up to 10% and 24%, respectively. Reduced silicon content also led to increased rate-sensitivity, increasing from 22% to 38%. Raman mapping will be used to investigate the influence of thermal mismatch between boron carbide, silicon carbide and silicon during processing (e.g., residual microstresses and defect density) on the deformation behavior and the resulting mechanical properties.

10:00 AM

(ICACC-S4-035-2014) Shock experiments to study source of inelasticity in ceramics

S. Satapathy*, C. Williams, D. Dandekar, U.S. Army Research Lab, USA

Rosenberg (1994) had proposed that Griffith's failure criteria should be more applicable for brittle materials in their post-elastic behavior as compared to von Mises plasticity behavior. He supported his proposition with plate impact experiment data for various ceramic materials. Grady (1995) observed that most ceramics agree with Griffith's prediction that the compressive strength should be an order of magnitude higher than the tensile strength, even though the ratio is not a constant for all ceramics. The loading conditions in these Rosenberg's experiments are "radial loading" in that the principal stresses increased in constant proportion to each other. Kanel and Zaretsky (2002) carried out a confined plate impact experiment by radially confining the sample, where the stress state doesn't evolve radially, and found mixed results. We extend the above investigation by carrying out radially confined plate impact experiments with at least three different levels of lateral confinement. With three data points, we would be able to identify the source of inelasticity in a more robust manner than either investigating a "radial loading" path where no confinement pressure is applied, or with only two data points as was reported by Kanel and Zaretsky. The experimental result and analysis of such confined plate impact experiments will be presented in this paper.

10:20 AM

(ICACC-S4-036-2014) Direct and Reverse Electromechanical Response of Piezoelectric Ceramics under Impact

L. Shannahan, L. E. Lamberson*, Drexel University, USA

Experimental measurements of the in-situ stress-strain-charge response of single crystal X-cut alpha-quartz and SiC (6H) and (4H) specimens are used to examine the electromechanical inelastic constitutive relations under dynamic conditions. Uniaxial stress states in the crystals at strain rates of 10(E)3 1/s on a Kolsky bar apparatus are examined at various levels of initial charge across the samples to probe the effect of polarity, and the influence of reverse piezoelectric response on damage failure mechanisms. While the quartz exhibits a slight increase in the piezoelectric response during unloading with no initial charge present, potentially due to the dielectric breakdown of air; silicon carbide tends to exhibit leakage current and complete dielectric breakdown at a threshold compressive stress. These effects are further probed under non-uniform loading conditions with a single-stage gas gun at strain rates of 10(E)4 1/s and higher.

10:40 AM

(ICACC-S4-037-2014) High-Rate Three-Point Flexure of Ceramic Materials using a Three-Bar Kolsky Method

D. Casem*, J. Swab, A. Dwivedi, J. Wright, U.S. Army Research Lab, USA

An analysis of a three-Bar Kolsky bar for performing high-rate three-point flexure on brittle ceramic materials is presented. A three-bar arrangement is used (one input bar and two output bars) to provide measurements of force at each loading point and the verification of specimen equilibrium. To improve the accuracy of these measurements, thin (3 - 6 mm diameter) aluminum bars are used. The use of thin bars requires unusually precise pulse-shaping, which is accomplished by the use of tapered striker bars in conjunction with deformable pulse shapers. Different sample geometries are investigated both numerically and experimentally, and it is shown that non-standard short/non-slender beams can be used to improve equilibrium and can still be adequately described by elementary beam theory. Experiments are presented on the high-rate flexure of alpha-SiC.

11:00 AM

(ICACC-S4-038-2014) Static and dynamic fracture toughness of Sintered and Reaction Bonded SiC and B_4C composites

J. J. Pittari*, G. Subhash, University of Florida, USA

The static and dynamic fracture toughness (K_{Ic}) of several sintered and reaction bonded ceramics was investigated by four-point bend chevron-notch testing method. Static bend tests were conducted using an electro-mechanical universal testing machine, while the dynamic experiments are being performed using a Hopkinson Pressure Bar and anvil setup. Six types of silicon carbide (SiC) and/or boron carbide (B_4C) ceramic composites with varying compositions and microstructures manufactured through pressureless sintering (PS) and reaction bonding (RB) processes were tested. The sample geometry is in accordance with Configuration A of the ASTM C1421 testing standard. The Digital Image Correlation (DIC) measurement technique was used to record crack mouth opening displacement (CMOD) and verify stable crack nucleation and growth. Measurements made using this technique are to be confirmed through Moiré interferometry analysis. All the RB composites displayed higher K_{Ic} values than the sintered ceramics. RB boron carbides exhibited higher K_{Ic} values than RB silicon carbides. It is anticipated that strain rate sensitivity will be observed in the K_{Ic} values of all materials. The fracture surfaces are being investigated utilizing scanning electron microscopy (SEM) to determine the influence of strain rate on the mode of fracture due to differing microstructures.

11:20 AM

(ICACC-S4-039-2014) Analysis of Interacting Cracks Due to Sequential Indentations on Single Crystal SiC

A. Trachet, G. Subhash*, University of Florida, USA

Single-crystal SiC, though not typically associated with armor applications, is transparent with high hardness and elastic modulus. The investigation of single-crystal SiC as a transparent armor requires evaluating its multi-impact behavior because visibility, in addition to ballistic performance, is crucial. Sequential indentation is an appropriate representation of how a material behaves under a multi impact type situation. Two α-SiC polytypes, 4H- and 6H-SiC, were subjected to 100-g Vickers and Knoop static indentations on the (001) face. The indentations were carefully placed so that the indent diagonals were aligned along a specific crystal orientation. Indents were initially located far apart and gradually brought closer together in order to observe the changes in crack pattern. At small distances (less than 20 μm apart), crack joining behavior was seen when the indents were aligned along the major directions of the crystal, and pass-by behavior was noted for directions 15° from the major directions. This observation confirms the anisotropic behavior of the material, which has ramifications for how single-crystal SiC is employed as transparent armor.

11:40 AM

(ICACC-S4-040-2014) An Innovative Transmission Electron Microscopy Sample Preparation Technique for Heavily Deformed Ceramic Materials

C. V. (Weiss) Brennan*, US Army Research Lab, USA; S. D. Walck, Bowhead Science & Technology, USA; J. J. Swab, US Army Research Lab, USA

A new technique for the preparation of heavily deformed and cracked ceramic materials for examination in a transmission electron microscope (TEM) is described in detail. TEM is a very powerful technique for studying deformed ceramic armor materials, since microstructure, crystal structure, and defect information can be obtained and used to understand the deformation mechanisms. However, preparing a thin (<200nm) TEM samples of heavily stressed and cracked materials is a challenge. In this study, TEM samples are prepared underneath indentation sites in SiC (ranging from 300g-2kg), although the technique could also be applied to the TEM sample preparation of other brittle ceramic materials, such as B_4C. The cracked regions underneath the indents must first be infiltrated with a specialized low-viscosity epoxy under vacuum, and then the sample can be mechanically polished and thinned to electron transparency using the focused ion beam (FIB) or low-energy ion milling. TEM studies on these samples demonstrate the success of this sample preparation technique in producing "true" TEM specimens with little contamination or artifacts. This sample preparation technique was applied to SiC, and some preliminary results on the deformation mechanisms in quasi-statically indented SiC are described.

S6: Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage

Energy Storage Technology (Sodium Battery and Beyond)

Room: Ponce De Leon
Session Chairs: Do Kyung Kim, KAIST; Sean Li, The University of New South Wales

8:00 AM

(ICACC-S6-029-2014) Ultrahigh performance of Sulfur Nanowire array for Lithium Sulfur battery (Invited)

S. Moon, Y. Jung, W. Jung, D. Kim*, KAIST, Republic of Korea

Alternative rechargeable battery systems whose energy densities can go beyond those of LIBs have been extensively pursued.Elemental sulfur is a promising cathode material for a number of desirable properties. Sulfur cathodes have a theoretical specific capacity of 1675 mAh g-1. Moreover, using sulfur as the cathode material for batteries has many other advantages such as low cost, abundant, environmental benignity and widespread availability Despite the considerable promises, a number of significant challenges need to be solved for the commercialization; intrinsic poor electrical conductivity of sulfur, dissolution of high-order polysulfides in electrolyte and large volumetric expansion of sulfur. In the present investigation, we developed a sulfur electrode focusing on electrode design. In the electrode design perspective, sulfur was completely covered by minimal amount of carbon, and the carbon coated sulfur nanowire was highly aligned. The electrode design address all of the aforementioned issues at once and result in excellent electrical performance

8:30 AM

(ICACC-S6-030-2014) Organic Electrode Materials for Sodium Ion Batteries (Invited)

A. Abouimrane*, W. Weng, Y. Cui, K. Amine, Argonne National Laboratory, USA

Organic electrode materials have recently attracted great attention as active materials for rechargeable batteries due to their enviormental friendly characteristics. With the successful application of organic anodes in the Li ion batteries, sodium ion batteries using organic electrode material become popular in the past year. Sodium ion battery is one of the most attractive rechargeable batteries which utilizes cheaper and more abundant sodium material but affords nearly the same power as lithium battery. We found that the sodium derivative disodium terephthalate (C8H4Na2O4) can accommodate the sodium ion insertion /de-insertion reversibly. Moreover we investigated possible sodium insertion in other sodium based carboxylate molecules, such as monosodium terephthalate (C8H5NaO4), terephthlaic acid (C8H6O4), disodium tetrafluorather-phthalate (C8Na2F4O4), 1,2,4,5-tetrasodium terephthalate (C10H2Na4O8), 1,4,5,8-naphthalene-tetracarboxylic dianhydride (C14H4O6) and tetrasodium 1,4,5,8-naphthalenetetracarboxylate (C14H4Na4O8). Detailed mechanistic studies have been conducted through X-ray, FTIR and EPR techniques. In addition, a 3.6 V Na-ion full cell coupling these organic anodes with Na0.75Mn0.7Ni0.23O2 cathodes delivered more than 268 mA h g–1 discharge capacity after 50 cycles. This represents the first example of a sodium ion full cell incorporating an organic based anode material.

9:00 AM

(ICACC-S6-031-2014) Sodium insertion properties of titanates and related materials as negative electrodes for sodium ion batteries (Invited)

A. Kuhn*, Universidad San Pablo-CEU, Spain; J. Pérez-Flores, Universidad San Pablo-CEU, Spain; M. Hoelzel, TU München, Germany; C. Baehtz, Helmholtz-Zentrum Dresden-Rossendorf, Germany; F. García-Alvarado, Universidad San Pablo-CEU, Spain

Sodium ion batteries are actually turning into an attractive alternative to lithium ion batteries, challenging lower cost and sustainability for large scale applications. In contrast to numerous studies on cathode materials for sodium ion batteries, only few metal oxides, useful as anode materials with low operating voltages, are known to date to insert sodium ions in a reversible way. Sodium hexatitanate, $Na_2Ti_6O_{13}$, has been very recently evaluated as anode host for sodium ion batteries. In this work we have investigated the sodium insertion properties of several hexatitanates $A_2Ti_6O_{13}$ having different A channel ions, as well as related materials. Structural evolution during electrochemical sodium insertion and de-insertion has been monitored in depth by using in situ synchrotron X-ray diffraction operated in commercial CR2032 coin cells.

9:30 AM

(ICACC-S6-032-2014) Crystallization behavior of sodium iron phosphate glass-ceramic cathode for sodium ion batteries

T. Honma*, A. Sato, N. Ito, T. Togashi, T. Komatsu, Nagaoka Univeristy of Technology, Japan

Triclinic $Na_{2-x}Fe_{1+x/2}P_2O_7$/C composite was prepared by glass-ceramics method. We found that $Na_{2-x}Fe_{1+x/2}P_2O_7$/C composite can be used as cathode active materials for Sodium ion battery with high current density rate performance over 10C (2mA/cm2) condition and stable electrochemical cycle performance. A 2μm glass precursor powder in composition of $Na_{2-x}Fe_{1+x/2}P_2O_7$/C (x=0 to 0.44) was crystallized in tubular furnace around 600-650° C with carbon source to reduce iron valence state and to coat grain surface with carbon. In cathode properties $Na_{2-x}Fe_{1+x/2}P_2O_7$/C composite exhibits 86mAh/g (253Wh/kg) as reversible discharge energy density that is half amount of that for $LiFePO_4$, however in 10C condition they kept

45mAh/g (110Wh/kg) even in 2μm grain size. We also confirmed that the glass-ceramics exhibits good water durability.

Advanced Materials for Energy Harvesting and Storage

Room: Ponce De Leon
Session Chairs: Do Kyung Kim, KAIST; Sean Li, The University of New South Wales

10:10 AM

(ICACC-S6-033-2014) Enhancement of Thermoelectric Properties of Ca3Co4O9 based Oxides (Invited)

S. Li*, The University of New South Wales, Australia

The transition metal oxide Ca3Co4O9 is one of the most promising high-temperature thermoelectric materials owing to its inherent layered structure that provides a unique approach to enhance the thermoelectric properties by manipulating the dopant in the crystal lattice. In addition, porosity is another key feature to be used for reducing the thermal conductivity. In this work, the figure of merit of polycrystalline Ca3Co4O9 has been enhanced to ~0.72 at 966 K through the co-doping technique with porosity control. These new findings may provide fundamental principles to optimise the performance of this cobaltite system for various applications.

10:30 AM

(ICACC-S6-034-2014) Comparative study on thermoelectric properties of polycrystalline Ca0.9Yb0.1MnO3: effects of processing method and sintered density

R. Kabir*, T. S. Zhang, The University of New South Wales, Australia; R. Donelson, CSIRO, Australia; S. Li, The University of New South Wales, Australia

This paper reports high temperature thermoelectric properties of ytterbium doped manganite, Ca0.9Yb0.1MnO3, synthesized by using different methods and processed at different conditions. The powders synthesized by using solid state reaction (SSR) were micron-sized particles, from which samples with relative density of 68-98% could be prepared after milling for different time durations and sintering at 1250oC for 10 h. Nano-size powders were synthesized by using co-precipitation (CP). Samples with different densities could be obtained after sintering for 10 h at different temperatures from 950-1150oC. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to study microstructures of the sintered samples. It is found that samples with relative density of 86% had highest power factor. A maximum dimensionless figure of merit (ZT = 0.16 at 973K) was observed for the sample with 86% relative dense from the CP-processed powder. The effects of synthesis method and processing condition can be explained by considering grain size and density of the samples.

10:50 AM

(ICACC-S6-035-2014) Electrical and Thermal Transport Properties of Hf doped In2O3

B. Zhu*, T. Zhang, University of New South Wales, Australia; R. Donelson, Commonwealth Scientific and Industrial Research Organisation, Australia; S. Li, University of New South Wales, Australia

Hf doping in Indium oxide was carried out to investigate its effect on its electrical and thermal transport properties. Bulk In2O3 were synthesized by co-precipitation and conventional sintering. The solubility of Hf in In2O3 is higher than 3 at. % with the co-precipitation sintering technique. The results show that the abrupt decrease in electric resistivity at lower doping levels enhances Power Factor(PF) although Seebeck coefficient decrease. This may be correlated with the evolution of carrier concentration caused by the change of doping level. It is indicated that the doping element plays important role in electrical transport properties of these materials. Thermal conductivity increase is due to the decrease in the electric resistivity. The thermoelectric performances are improved at low doping level where high PF is obtained with low thermal conductivity. ZT value with 0.24 is attained in doped samples.

11:10 AM

(ICACC-S6-036-2014) Thermal Stability and Evolved Gas Analysis of Selected Semiconductor Materials by a Simultaneous Thermal Analysis Instrument with Mass Spectrometer Skimmer System

E. Post*, NETZSCH Geraetebau GmbH, Germany; B. Fidler, NETZSCH Instruments, USA

Compound semiconductors of the families II-VI, I-III-VI2, etc. are excellent candidates for thin film solar cells, thermoelectric modules etc. due to the variable band gaps. Limitations in the application and production are often the relative low thermal stability of these compounds. During decomposition additionally more or less toxic gas species are evolved. With a STA-MS Skimmer system were the thermal stability and the evolved gases of selected semiconductors investigated. This STA mass spectrometer coupling system allows also the detection of heavier gas species as Se, PbSe, PbTe etc. The analysis of the fragment distribution and intensity with theoretical abundance values show a very good accordance

11:30 AM

(ICACC-S6-037-2014) Hierarchical Nanostructured Porous Carbons for Energy-related Applications

K. Chae, L. Huang*, Rensselaer Polytechnic Institute, USA

Hierarchical nanostructured porous carbons (HNPCs) have unique porous structure, namely, mesopores (2 nm<pore size<50 nm) in combination with micropores (<2 nm). The bimodal pore size distribution provides a good balance between mesopores for rapid diffusion and micropores for highly active sites for reactions, both are important for energy-related applications such as electrode materials for super-capacitors and for lithium ion batteries. Here we developed a unique computational approach to mimic the synthetic route of HNPCs in molecular dynamics simulations. By tuning the atom-template interaction, template radius, template spacing, initial carbon number density, various properties such as topological defect concentration, pore size distribution, mesopore wall thickness, etc, can be tailored. We further investigated the influence of the porous structures on transport properties of HNPCs. A selective reflection wall in the middle of a vacuum chamber was used to generate HNPCs in slab geometry and to impose a pressure gradient for promoting a steady-state flow on the either side of the membrane. A systematic study was carried out to enhance the transport properties of HNPCs by optimizing the porous structures through synthesis parameters. Findings from this study will provide guidelines for rational design of porous materials for various energy-related applications.

11:50 AM

(ICACC-S6-038-2014) Overview of High Energy Solid State Capacitor (HESSCAP) Development at Marshall Space Flight Center

L. Allen*, C. Hill, T. Rolin, M. Strickland, NASA MSFC, USA

Past and present efforts by the authors to develop High Energy Solid State Capacitors (HESSCAPs) will be presented. As space missions require more power from battery systems for longer and more complex missions, there is a significant challenge to the battery power system to meet these demands. As a result, NASA Marshall Space Flight Center (MSFC) has been leading agency research and development of enhanced energy storage technologies. The primary beneficiary of the technology would be the Space Launch System (SLS) Upper Stage, which can always take advantage of mass reduction and design simplicity for improved launch capability; however, nanosatellites, avionics subsystems, and many public-sector industries would be able to make similar use. Information will be presented on the treatment of coated & uncoated barium titanate powders; thick-film, thin-film, and novel deposition techniques; and densification improvements through various alternate approaches. Scanning electron microscopy, capacitive assessments, and life-cycle testing will also be discussed.

S7: 8th International Symposium on Nanostructured Materials and Nanocomposites

Nanomaterials for Energy III: Batteries I

Room: Coquina Salon B
Session Chairs: Gurpreet Singh, Kansas State University; Bala Vaidhyanathan, Loughborough University

8:00 AM

(ICACC-S7-017-2014) Bottom-up approach to epitaxial complex oxide nanostructures and nanocomposite thin films with outstanding magnetic, superconducting and electronic properties (Invited)

X. Obradors*, T. Puig, N. Mestres, M. Coll, J. Gázquez, A. Palau, S. Ricart, J. Arbiol, A. Queraltó, P. Cayado, V. Rouco, R. Guzmán, J. González, M. de la Mata, P. Garcés, L. Soler, M. Gibert, J. Zabaleta, A. Llordés, ICMAB - CSIC, Spain

Generation of large area arrays of self-organized oxide nanostructures (nanodots, nanowires) and thin films or nanocomposites provides unique opportunities for the development of novel functionalities with a wide range of potential applications (magnetic, superconducting, electronic, etc.). Bottom-up approach based on chemical solution deposition (CSD) offers a high throughput and cost-efficient route for the generation of complex oxides. In recent years we have widely investigated the unique microstructural and physical properties of different sorts of CSD and ALD grown functional oxide nanostructures and thin films, including CeO2, ferromagnetic La1-xSrxMnO3 (LSMO) and YBa2Cu3O7 (YBCO) - derived nanocomposite superconductors. A few outstanding properties of these complex oxides where internal strain and the electronic properties are controlled at the nanoscale will be reviewed. We will stress that bottom-up approaches have a strong potential to create novel complex functional materials with outstanding performances.

8:30 AM

(ICACC-S7-031-2014) One-pot mechanical process to make nanocomposite structure for advanced materials (Invited)

M. Naito*, T. Kozawa, A. Kondo, H. Abe, Osaka University, Japan

One-pot mechanical process is a green and sustainable powder processing technique that creates advanced materials with minimal energy consumption and environmental impacts. This process achieves bonding between nanoparticles to make various kinds of composite particles using the particle surface activation given by mechanical energy. It can also be applied to synthesize nanoparticles without extra heat assistance. By the combinations of both nanoparticle synthesis and its bonding, unique nanocomposite structures including nanocomposite granules are favorably created. They are promising materials for the electrodes of lithium ion batteries. Furthermore, the assembling of these composite particles and granules leads to the control of nano/microstructure of advanced materials. On the other hand, this bonding principle can be also applied to bond nanoparticles with substrate to form mechanically deposited porous films. They have porous and unique network structure, which are used for many purposes such as electrodes of fuel cells. In this presentation, the one-pot mechanical process will be introduced, and its applications for making advanced materials will be explained.

9:00 AM

(ICACC-S7-032-2014) Design of Self-supported Metal Oxide Heterostructures and Hybrids for Energy Storage Applications

R. Fiz*, M. Bueyuekyazi, University of Cologne, Germany; A. Gutierrez-Pardo, University of Seville, Spain; S. Mathur, University of Cologne, Germany

Electrochemical energy storage systems (i.e. batteries and supercapacitors) are the focus of intensive present-day research due to their use in a wide range of applications, from small portable devices to large stationary plants. The requirements for their use vary in terms of cost, specific power and energy, charging/discharging rates, safety issues and cycle life. The design and development of novel electrode materials is crucial to improve their performance in a specific application. In this work, new concepts for the design of novel hybrid anode nanoarchitectures are applied and tested, combining carbonaceous materials with different metal oxide systems in the search of materials with enhanced properties. SnO2 nanowires are directly grown by chemical vapor deposition on different current collectors, and modified leading to heterostructures with different morphologies and compositions. In contrast to the traditional electrode preparation, the self-supported configuration allows the direct integration of the active material in the current collector without the need of external conductive agents or binders simplifying the fabrication process. Also, the nanostructuctured morphology and the proper combination of the heterostructure constituents lead to an improvement of both capacity and stability of the electrode material when compared to using SnO2 nanowires alone.

9:20 AM

(ICACC-S7-034-2014) Nanoparticles and carbon nanomaterial coated fine particles for various applications prepared through colloidal and CVD combined process (Invited)

H. Kamiya*, Y. Nomura, A. Kurumiya, Tokyo University of Agriculture and Technology, Japan; M. Iijima, Yokohama National University, Japan; I. Anoshkin, A. Nasibulin, E. Kauppinen, Aalto University School of Science, Finland

Functional inorganic oxide, metal nanoparticles and carbon nanomaterials are well known to have various functional properties. However, hard aggregates of nanoparticles and CNT during wet and dry preparation process were formed in gas and liquid phase. In this research, new processing protocols to prepare composite particles which carbon nanomaterials and nanoparticles has uniformly and densely attached on the surface of different species of fine core particles with several micron meter in diameter were developed. Firstly, surface modified oxide nanoparticles were prepared in liquid phase and adsorbed on fine particles. By the selection of optimum surface organic molecular structure and organic solvent, high coverage of metal oxide nanoparticles on fine particles was achieved. Surface interaction control between oxide nanoparticles and fine core particle was useful to increase the number density of adsorbed nanoparticles on fine particles. Secondly, for the composites with carbon nanomaterials, we applied the above method to prepare carbon nanofiber coated graphite particles. After CoO nanoparticles preparation and their adsorption on graphite fine particles in toluene, the reduction of CoO and the formation of dense layers of carbon nanofibers were successfully conducted on the surface of graphite particles by CVD process.

Nanomaterials for Energy IV: Batteries II

Room: Coquina Salon B
Session Chairs: Gurpreet Singh, Kansas State University; Bala Vaidhyanathan, Loughborough University

10:00 AM

(ICACC-S7-035-2014) Robust Li-ion battery anodes prepared from nanostructured polymer-derived ceramics (Invited)

G. Singh*, Kansas State University, USA

Polymer-derived ceramics (such as SiOC and SiBCN) prepared from controlled thermal degradation of certain silicon based polymers have emerged as promising anode materials for Li-ion battery applications. Here, we demonstrate synthesis and electrochemical performance of nanostructured silicon oxycarbide/carbon nanotube (SiOC/CNT) and SiOC/graphene composites. The composite synthesis was achieved through controlled thermal decomposition of Tetramethyl-tetravinyl cyclosiloxane precursor on carbon nanotubes or graphene surfaces. Thick Li-ion battery anode (prepared at a loading of~ 1.0 mg/cm^2) showed stable charge capacity of 686 mAh/g even after 40 cycles. The average coulombic efficiency (excluding the first cycle loss) was 99.6 %. Further, the post electrochemical imaging of the dissembled cells showed no apparent damage to the anode surface, highlighting improved chemical and mechanical stability of these ceramic composites.

10:30 AM

(ICACC-S7-036-2014) Graphene-based Nanomaterials as Next Generation Lithium-ion Battery Anodes

R. Mueller*, S. Mathur, R. Raccis, R. von Hagen, University of Cologne, Germany

Graphene-based nanomaterials occupy the center stage of current research with respect to the investigation of new and advanced anode materials for Lithium-ion batteries. Whether as phase pure material or as nanocomposites along with various metal oxides, graphene has already been proven of bearing the capabilities to play a key role in the development of next generation rechargeable batteries. In this work, we would like to present a facile microwave assisted reaction for the fabrication of functional graphene/metal oxide nanocomposites. The reduction of graphene oxide (GO) with M2+ ions (M = Sn, Fe, Co) in aqueous media is shown to offer distinct advantages such as effective separation of single and few layered graphene by in situ formed metal oxide nanoparticles as well as stabilization of the oxide phase during electrochemical cycling, leading to anode materials exhibiting high capacities and stable cycling performances. Additionally, the incorporation of different nitrogen-sites (i.e. graphitic, pyrrolic and pyridinic) was shown to further improve the performance of graphene-based nanomaterials. Due to defects in the pyridinic and pyrrolic environments an electron-accepting tendency arises, thus leading to higher binding energies as well as an increased amount of binding sites for Li atoms.

10:50 AM

(ICACC-S7-037-2014) One-Pot Mechanical Synthesis of Cathode Materials for Lithium Ion Batteries

T. Kozawa*, A. Kondo, E. Nakamura, H. Abe, M. Naito, Osaka University, Japan

Lithium ion batteries (LIBs) have widely contributed to a miniaturization of portable electronic devices because of the high operating voltage and energy density compared with traditional lead-acid, Ni-Cd, and Ni-MH batteries. Currently, commercial cathode materials for LIBs are mainly three type structures; layered, olivine, and spinel structures. These cathode materials are generally synthesized by conventional solid-state reaction and liquid reactions including hydrothermal, sol-gel, and co-precipitation reactions. However, these synthetic methods involve repeated heating process and multistep process. From a viewpoint of an energy saving, more simplified synthetic method is necessary for the processing of cathode materials. In this presentation, mechanical synthetic method utilized frictional and shearing forces acting on particles is proposed for preparation of cathode materials. Mechanical synthesis of various cathode materials is achieved by one-pot process without external heating. Additionally, the mechanically synthesized powder consists of the porous granules packed with nano-sized primary particles and is suitable structure for the cathode design.

11:10 AM

(ICACC-S7-038-2014) Random and aligned nano-structured metal oxides for energy storage devices (Invited)

B. Saruhan-Brings*, C. G. Mondragón Rodríguez, German Aerospace Center, Germany; Y. -. Gönüllü, University to Cologne, Germany

Batteries require long time to charge but store greater charges, while capacitors can be charged very rapidly within seconds, but suffer from lower energy densities. With new electrodes which introduce pseudo-capacitance and higher surface area, super-capacitors charge rapidly and also have higher electrical energy densities and supply this longer. These features are desirable for a variety of applications such as storage of energy from renewable energy supplies and for start-up and acceleration of electrical vehicles. Addition of pseudo-capacitance combines features of both rechargeable battery and standard capacitor for mobile technologies. Our research focuses on development of electrode materials based on mixed oxides aiming the increase of specific capacitance and energy density through faradaic pseudo-capacitive reactions. This work demonstrates the fabrication of pseudo-capacitive single and mixed oxide films grown by sputter technique on graphite and anodic oxidation of titanium. Electrochemical methods are used to tailor the materials properties for energy storage. The results indicate that the optimum combination of redox oxides with the electrolytes play an important role in the enhancement of the capacitance and storage capabilities. Capacitive charge-storage tests of aligned nanostructured coatings in core+shell architecture indicate the occurrence of cation intercalation supported storage.

11:40 AM

(ICACC-S7-039-2014) Chemical Synthesis and Functionalization of Inorganic Nanowires and Nano-Heterostructures

S. Mathur*, T. Fischer, A. Lepcha, T. Singh, R. Müller, I. Giebelhaus, A. Gad, R. Raccis, R. Fiz, University of Cologne, Germany

One dimensional (1D) inorganic materials are gaining increasing attention because of their unique structural features and interesting functional properties. Given the structural stability, they show promising application potential in vacuum as well as in oxidizing atmospheres, which provides them a competitive edge over their carbon-based counterparts. We have developed a generic approach for the size-selective and site-specific growth of nanowires by combining vapor-liquid-solid (VLS) approach with the chemical influence of molecular precursors. A novel sensing concept was developed based on the integration and correlation of complementary functionalities originating from multiple junctions in a singular nanostructure to palliate the current issues in gas sensor technologies such as low power consumption, low operating temperature and cost effective production. In this work, the gas sensing and solar energy harvesting abilities of metal oxide semiconductors were utilized to deliver a self-sustained gas sensing signal without any external power sources. In particular, the synthesis and structural characterization of SiCN@Ge, SnO_2@Sn, ZnO@Si, and CdS@TiO_2@SnO_2 will be presented and their application potential will be discussed. In addition, hyperbranched structures grown by sequential CVD processes will be presented.

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

Novel Sintering & Forming I; Flash Sintering, etc

Room: Coquina Salon A
Session Chairs: Rishi Raj, University of Colorado, Boulder; Eugene Medvedovski, Endurance Technologies Inc.

8:10 AM

(ICACC-S8-026-2014) Field Assisted Viscous Flow and Crystallization in a Sodium Aluminosilicate Glass at Elevated Temperature

R. Tessarollo, University of Trento, Italy; R. Raj*, University of Colorado at Boulder, USA; V. M. Sglavo, University of Trento, Italy

The effect of electric fields (DC and AC) on the onset of viscous flow in Na2O.Al2O3.2SiO2 is investigated in this project. A remarkable reduction in the softening temperature, far below the normal glass-transition/softening temperature, is shown and ascribed to the nucleation of defects in the glass under the electric field. The proposed mechanism is that these defects produce electron-hole pairs leading to a highly non-linear increase in the electrical conductivity of the glass causing, in addition, viscous flow. Isothermal experiments showed the presence of an incubation time for the onset of viscous flow that can be divided into two different contributions: (i) a first time lapse from the moment in which the field is applied to the onset of conductivity increase, depending on the strength of the field applied and the temperature; and (ii) a second time lapse from the onset of conductivity increase to the onset of viscous flow, depending on the specific electric power dissipating through the glass. Crystallization (Carnegieite and Mullite crystals) has also been observed in experiments with DC electric field applied, especially in the surface in contact with the positive electrode.

8:40 AM

(ICACC-S8-027-2014) Photoemission measurements during flash sintering

J. Lebrun*, J. S. Francis, R. Raj, University of Colorado at Boulder, USA

During flash sintering of ceramics, electric fields are responsible for a non-linear increase in self-diffusivity which accounts for a large enhancement of sintering and densification kinetics. Several hypothesis have been proposed to explain this unusual behavior. Among them, the nucleation of neutral Frenkel pairs of cations and anions, along with the generation of electron and hole pairs, would explain the concomitant increase in self-diffusivity and conductivity observed. In this paper, combined photoemission and pyrometer temperature measurements have been carried out during flash of already sintered materials. Photoemission is indeed observed and is shown to be a result of both thermoemission and electroemission that respectively account for sample Joule heating and generation and recombination of electron hole pairs, confirming that the flash event is fundamental to defect generation.

9:00 AM

(ICACC-S8-028-2014) Effect of flash sintering on Monoporosa tiles

F. Trombin*, University of Trento, Italy; J. Francis, R. Raj, University of Colorado at Boulder, USA; V. M. Sglavo, University of Trento, Italy

This is a preliminary study of the possibility of transitioning the flash sintering technology into manufacturing of Monoporosa tiles. The material under study is a mixture of clays which makes its behavior under an applied electric field difficult to predict. The sintering of cylindrical samples is possible at the temperature of 950 °C under a DC electric field of 2 kV/cm, in few seconds compared to 1150 °C for over 1 hour in case of conventional method. The possibility to conduct the process further lower temperatures is now under investigation. The main obstacles are the arcing between the positive electrode and the sample's surface and the dielectric breakdown. These two phenomena bring to the local formation of mullite which results in aberration of the original geometry and microstructure. New types of electrode are now under testing in order to avoid these problems and allow the usage of a higher current density. The incubation time under different applied field at different temperature have also been studied and the effect of AC is being considered.

9:20 AM

(ICACC-S8-029-2014) Flash Sintering of Electronic Ceramics

B. Vaidhyanathan*, S. Ghosh, K. Annapoorani, J. Binner, P. Ramanujam, Loughborough University, United Kingdom

Electroceramic devices such as varistors and capacitors are used in most of the modern day electronic appliances and constitute a multi-billion$ market. Conventional fabrication of these devices involves high sintering temperatures and long processing time. Since sintering controls the electrical properties, it is necessary to develop simpler and less demanding processing methods. In a report on 'flash sintering' (FS) it was demonstrated that full sintering of dog-bone shaped zirconia ceramics can be achieved at 850oC in just 5 seconds rather than normally used 1450oC for few hours. This opens up the possibility of achieving significant energy savings during manufacture and the ability to produce fine grained ceramics. However the exact mechanisms by which this phenomena occur is not yet clear and the methodology is untested for the sintering of other complex functional materials. At Lboro' we investigated the feasibility of sintering nanocrystalline ZnO-varistors, BaTiO3-capacitors and CCTO dielectrics using this method along with simultaneous measurements of shrinkage, online thermal distribution mapping and atmospheric control. This allowed the fabrication of disc-shaped electroceramics using a controlled flash sintering approach and the properties of the devices are compared with conventionally sintered components. A phenomenological model is proposed to explain the flash sintering behaviour.

10:00 AM

(ICACC-S8-030-2014) Spark plasma sintering and mechanical properties of magnesia-yttria (50:50 vol.%) nanocomposite

L. Huang, W. Yao, J. Liu, A. K. Mukherjee, J. M. Schoenung*, UC Davis, USA

It has been demonstrated that decreasing grain size in polycrystalline ceramics is an effective approach to improve mechanical properties, which can be realized by either introducing a second phase to develop a duplex-phase or composite structure or applying advanced processing techniques such as spark plasma sintering. Fully dense magnesia-yttria (50:50 vol.%) nanocomposites with average grain sizes ranging from 125 to 223 nm have been prepared by spark plasma sintering, and grain growth is mainly dominated by grain boundary diffusion. A coarser grained sample prepared by post-sinter annealing was also studied for comparison. Samples with finer grain sizes exhibit higher microhardness. Fracture toughness, 1.52 MPa m1/2 on average, is independent of average grain size of the samples.

10:20 AM

(ICACC-S8-031-2014) Flash sintering and electrolytic breakdown 8YSZ

J. Downs*, V. Sglavo, University of Trento, Italy

The flash sintering phenomenon has been demonstrated in a variety of ceramic materials, resulting in dramatically lowered sintering temperatures and times. These flash sintering events are

accompanied by an unstable resistive breakdown in the material resulting in a current runaway that somehow is responsible for accelerated diffusion rates and joule heating. In order to understand the mechanisms that describe the electrical behaviors observed during flash sintering in 8YSZ, the breakdown behavior in fully dense specimens of varying grain size and in single crystals has been investigated using four-point measurements at constant temperatures up to 800°C. Fully dense samples showed similar, unstable electrical and heating behavior similar to what is observed in green samples. The I-V measurements have shown that the onset of electrical conductivity runaway is accompanied by the onset of mixed conduction. In single crystals, I-V behavior showed a transition at electric fields similar to those observed in dense samples and occurred at the onset of electrolytic reduction in the crystal but was not accompanied by joule heating. These results suggest that the mechanism responsible for the electrical behavior observed during flash sintering is related to the electrolytic reduction of the material. This reduction results in the creation of several different defects that can be related to the increased diffusion rates.

10:40 AM

(ICACC-S8-032-2014) Flash Sintering of $MnCo_2O_4$ composite with Ceria

A. Gaur*, V. M. Sglavo, University of Trento, Italy

Electric field assisted 'flash sintering' is an emerging technique for rapid and low temperature consolidation of ceramic materials. It has been applied to electrically conductive $MnCo_2O_4$ spinel (MC) and sintered at temperatures of 200-400 °C in 1-2 min under electric field of 10-15 V/cm. In the present work, flash sintering of $MnCo_2O_4$ containing variable amount of non-conductive CeO_2 is studied. The purpose is to understand the flash sintering behavior of the composite materials for a better control of the consolidation process. Flash effect in composite is observed to occur under higher electrical field and temperature in comparison to pure MC; conversely, the processing parameters are significantly lower than those required for ceria. From SEM analysis, composite containing 50 vol% ceria shows a residual porosity even when relatively high electrical field is used. For lower ceria content denser microstructure is obtained. The flash effect in the composites, which starts with an abrupt increase in conductivity and results in very quick sintering, seems to be dominated always by the spinel. The addition of ceria is shown to stabilize (through an initial stable increase of the temperature) and homogenize the flash effect in the composite.

11:00 AM

(ICACC-S8-033-2014) Direct Current Sintering (DCS) for rapid, large scale densification of silicon nitride ceramics

W. Pinc*, L. S. Walker, E. L. Corral, University of Arizona, USA

Electric assisted sintering techniques utilize joule heating to achieve rapid heating rates, resulting in short processing times and microstructures not obtainable with traditional sintering technologies. A critical limitation of the technology, however, has been insufficient demonstration of scale up beyond the small (<30 mm) parts typically produced. The University of Arizona uses a large scale Direct Current Sintering (DCS) furnace to address the challenges of producing large parts (> 10 cm) via electrical based sintering. Silicon nitride (Si_3N_4) is of interest to a number of industries due to its high fracture toughness and high temperature stability. The DCS furnace is used to investigate the production of large scale, uniform Si_3N_4 parts. A model is developed relating Si_3N_4 part size and total current required to achieve temperature via DCS processing.

11:20 AM

(ICACC-S8-034-2014) Direct Current Sintering (DCS) for rapid, large-scale densification of ZrB_2 ultra high temperature ceramics

L. S. Walker*, D. Pham, W. R. Pinc, E. L. Corral, The University of Arizona, USA

Electrical based sintering techniques utilizing direct current joule heating have become the preferred densification technique for advanced materials due to the ability to reach high density, limit grain growth and retain metastable phases. The state of the art technologies, however, have very limited sample size due to power and load limitations making them unfeasible for large scale manufacturing. By using a high power large scale DCS furnace facility at The University of Arizona samples >10cm diameter can be sintered to high temperature enabling processing of unique materials to industrially relevant sizes. Zirconium diboride (ZrB_2) is an Ultra High Temperature Ceramic (UHTC) of great interest for its high temperature properties, but sintering parts to high density is challenging. By using DCS large samples of high quality ZrB_2 can be produced to investigate the uniformity, microstructure and mechanical properties of large scale UHTC parts. An experimentally based model of the large scale DCS process for conductive materials has been developed to understand the ZrB_2 material response to DCS processing.

11:40 AM

(ICACC-S8-035-2014) An Industrial Microwave (Hybrid) System for In-line Processing of High Temperature Ceramics

R. Peelamedu*, D. Seccombe, BTU International, USA

It is well known that the interaction of microwave energy with materials can result in direct volumetric heating that brings down the operational costs compared to a conventional heating system. The difficulty in controlling field uniformity has limited this technology from becoming successful. Most industrial processes desire a continuous mode of processing due to the high volume requirements. In addition to high temperatures, such processes need a continuous mechanism to move specimens in and out of the high temperature zone. Such furnaces are nonexistent in the marketplace due to cumbersome scale-up and cost issues. In this paper, we report an in-line hybrid microwave system that is capable of processing large samples at uniform temperatures. The system has the capability to operate between 100 deg C to 1200 deg C in a continuous manner.A unique feature of this system is very high degree of uniformity at elevated temperatures. For example, at 1200 deg C, we have measured the temperature uniformity across a process width to be ± 3 deg C. The system is also configured with appropriate multistep high power chokes that were internally designed and installed to prevent any leakage of microwave power at the entrance and exit points. The details of design, operation and data analysis will be presented in this talk.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

Structure-Property Relationships II

Room: Coquina Salon F
Session Chair: Johanna Rosen, Thin Film Physics Division

8:00 AM

(ICACC-S12-017-2014) An overview of high temperature deformation behaviour of candidate high temperature materials (Invited)

L. J. Vandeperre*, Imperial College London, United Kingdom

Ultra-high temperature ceramics are a class of ceramic materials with melting points in excess of 3000 °C, which could be useful in a range of applications where refractory properties are important such as glass making, nuclear fuels, and thermal protection systems of airplanes and spacecraft. In this paper examples will be given to illustrate how the different types of behaviour can be accessed experimentally and the deformation behaviour of a range of high temperature ceramics will be compared and contrasted to illustrate how in some materials deformation by diffusion dominates whereas in others power law creep is more important. The consequences for the design of microstructures with good resistance to high temperature deformation will also be discussed.

8:20 AM

(ICACC-S12-034-2014) Processing and Thermal Properties of ZrB$_2$ with Varying Boron Isotope Ratios

J. Lonergan*, W. G. Fahrenholtz, G. E. Hilmas, Missouri University of Science and Technology, USA

The effect of varying the ratio of boron isotopes on the thermal properties of ZrB$_2$ was studied. Reactive hot pressing of ZrH$_2$ and varying amounts of isotopically pure ^{10}B and ^{11}B powders were used to synthesize nominally phase-pure ZrB$_2$. Compositions ranging from 100% Zr^{10}B$_2$ to 100% Zr^{11}B$_2$ were synthesized and tested. Microstructures and compositions of both processed powders and dense billets were characterized. Thermal conductivity was calculated from the values of heat capacity, thermal diffusivity, and density for temperatures ranging from 25°C to 2000°C. Enrichment of ZrB$_2$ with either the ^{10}B or ^{11}B isotope was found to increase thermal conductivity compared to ZrB$_2$ prepared with natural boron. Electrical resistivity was tested using the van der Pauw method. When ZrB$_2$ was synthesized with 100% ^{10}B, the room temperature thermal conductivity was more than 120 W/m•K compared to around 105 W/m•K for conventional ZrB$_2$. Enrichment with the lighter ^{10}B isotope increases both the thermal diffusivity and heat capacity of ZrB$_2$. Measured electrical resistivity at room temperature for conventional ZrB$_2$ was 6.535 μΩ•cm and increased linearly with temperature. The reasons for increasing thermal conductivity with boron isotope enrichment will be discussed.

8:40 AM

(ICACC-S12-035-2014) Modelling Environmental degradation at elevated temperatures

F. Biglari, Imperial College, United Kingdom; F. Abdi, Alphastar Corp, USA; K. Nikbin*, Imperial College, United Kingdom

ABSTRACT A micro-scale finite element mesh consisting of multiple elements encased in micron sized grains with replicated shapes and dimensions derived from an isotropic metallic grain structure has been developed. In this type of mesh the crack path for intergranular and transgranular cracking conditions is allowed. Using representative random sized grain shapes repeated in sequence ahead of the crack tip the effects of crack angle ahead of the main crack tip could be considered in a more realistic manner. The stress distribution and the values of fracture mechanics parameters obtained from FE simulations ahead of the crack tip tension specimen which was allowed to deviate at random angles to within a grain size have been found to be consistent with theoretical solutions. It is shown that the mechanism for creep cracking using a uniaxial ductility constraint-based model coupled with a functionally distributed time-dependent environmentally assisted corrosion/oxidation surface attack can be realistically modeled using this technique. Prediction of crack paths as wells as surface or sometime internal damage, using normal distribution probabilistic method to allow for statistically varied random damage and crack growth development, are presented and discussed for a sample CT and a rectangular models of a steel under tension.

9:00 AM

(ICACC-S12-036-2014) Electronic structure and elastic properties of transition metal diborides TMB2 (TM= Y, Zr, Hf, Nb, and Ta)

Y. Zhou*, Aerospace Research Institute of Material & Processing Technology, China; J. Wang, J. Wang, Institute of Metal Research, CAS, China

The electronic structure and elastic properties of several TMBs including YB2, ZrB2, HfB2, NbB2 and TaB2 were investigated using first-principles calculations based on density functional theory. The lattice constants, bond lengths, and compressibility decrease when the number of valence electrons increases from 3 for Y to 4 for Zr and Hf, and then to 5 for Nb and Ta. Covalent, ionic and metallic bonds all contribute to the bonding in these materials, i.e., the B-B bonding is strong covalent, the TM-B bonding is ionic-covalent, and the TM-TM bonding is metallic. The mechanical properties are anisotropic due to the anisotropic chemical bonding nature, e.g., the Young's modulus in x and y directions are much higher than in z direction. The bulk modulus increases when TM changes from Y to Zr and Hf, and then to Nb and Ta; the shear modulus, however, increases from 145 GPa for YB2 to 228 GPa for ZrB2, reaches a maximum value of 230 GPa for HfB2, and decreases to 209 GPa for NbB2 and 189 GPa for TaB2. The Young's modulus is in the order of HfB2>ZB2>NbB2>TaB2>YB2. As a result of these calculations, YB2 is predicted to have the best thermal shock resistance since it has the lowest Young's modulus. The brittleness, based on the calculated solidity index S=0.75G/B, is estimated in the order of TaB2<NbB2<YB2<HfB2<ZrB2, and TaB2 is a potential damage tolerant UHTC.

9:20 AM

(ICACC-S12-037-2014) On the Atomic Displacement Parameters of the MAX Phases: Theory versus Experiment

N. Lane, Drexel university, USA; S. C. Vogel, Los Alamos National Laboratory, USA; G. Hug, ONERA-CNRS, France; A. Togo, Kyoto University, Japan; L. Chaput, Universite de Nancy, France; L. Hultman, Linkoping University, Sweden; M. W. Barsoum*, Drexel university, USA

The aim of this talk is to report on the atomic displacement parameters of select MAX phases obtained through first-principles phonon calculations in order to provide a foundation for modeling their high temperature properties. The calculations are compared to those determined from Rietveld analysis of high temperature neutron diffraction patterns. Out of the 20 MAX phases studied, the Al-containing phases showed the best agreement between theory and experiment. Given that the Al containing phases are also some of the most promising MAX phases for industrialization because of their high oxidation resistance and the low cost of their starting materials our work suggests that the MAX phases that are most desirable commercially may also be the most reasonable to model at high temperatures. This work provides a basis for understanding important phenomena associated with phonons, interatomic bonding, and thermal vibrations in periodic systems, which is not only relevant to the fundamental properties of the MAX phases but can be extended to other crystals in the solid state.

Enviromental Stability

Room: Coquina Salon F
Session Chair: Yanchun Zhou, Aerospace Research Institute of Material & Processing Technology

10:00 AM

(ICACC-S12-038-2014) Ultra High Temperature Mechanical Testing of ZrB_2 Based Ceramics (Invited)

G. Hilmas*, W. Fahrenholtz, E. Neuman, Missouri University of Science and Technology, USA

Zirconium diboride (ZrB_2) based ceramics are being proposed for future air and aerospace applications. Potential applications include the leading and trailing edges of hypersonic vehicles where thermo-mechanical loads would need to be supported for extended time periods at temperatures exceeding 2000°C. In this study, the mechanical properties of hot pressed ZrB_2 based ceramics were tested from room temperature to >2000°C. ZrB_2 with 0.5 wt% C, ZrB_2 with 30 vol% SiC and ZrB_2 with 10 vol% ZrC were hot pressed to full density at temperatures ranging from 1950 to 2150°C at an applied pressure of 32 MPa. The hot pressed billets were machined to produce ASTM standard flexure bars. Flexural strength was measured in four-point bending from room temperature to 1600°C in air and from 1600°C to 2300°C in a flowing argon atmosphere. Fracture toughness was measured for each composition using the chevron notched beam method and were also performed from room temperature to 1600°C in air and up to 2200°C in a flowing argon atmosphere. The flexure strength of these ZrB_2 based ceramics ranged from 380 to 680 MPa at room temperature and from 170 to 300 MPa at 2300°C. The fracture toughness ranged from 3 to 5 $\mathrm{MPa{\bullet}m}^{1/2}$ at room temperature and from 3.3 to 5.7 $\mathrm{MPa{\bullet}m}^{1/2}$ at temperatures exceeding 2000°C. The influence of microstructure, and testing environment, on the mechanical properties will be discussed.

10:30 AM

(ICACC-S12-039-2014) Modelling Damage and Creep Crack Growth in Ultra-High Temperature Ceramics

M. Pettina'*, K. Nikbin, Imperial College London, United Kingdom

Damage and failure assessment of ultra-high temperature structural ceramics is an area that needs substantial development. In order to develop a robust tool for predictive modelling it is important to assess what material and mechanical properties can be reasonably derived to input in the models. The paper reviews the state of art in both testing and modelling and identifies the material variables that need to derived for modelling ultra high temperature ceramics structural failure. It focuses on monolithic HfB2 and ZrB2 ultra-high temperature ceramics which seem to be the most attractive candidates for aerospace applications in extreme environments. Relevant properties of these materials together with the most effective manufacturing processes are considered. Particular attention is given to oxidation resistance at ultra-high temperatures and how it can be improved. Finally, other aspects of ultra-high temperature ceramics modelling are covered and the practicalities of deriving relevant data are discussed. In this way the essential properties required to develop predictive damage simulations are investigated, underlining the importance of having accurate materials test data.

10:50 AM

(ICACC-S12-040-2014) Effect of Neutron Irradiation on Select Mn+1AXn Phases

D. J. Tallman*, Drexel University, USA; E. Hoffman, Savannah River National Lab, USA; E. Caspi, Drexel University, USA; G. Kohse, Massachusetts's institute of Technology, USA; R. L. Sindelar, Savannah River National Lab, USA; M. W. Barsoum, Drexel University, USA

Gen IV nuclear reactor designs require materials that can endure long term operation in extreme environments of elevated temperatures, corrosive media, and fast neutron fluences (E>1MeV) with up to 100 displacements per atom (dpa). Full understanding of irradiation response is paramount to long-term, reliable service. The Mn+1AXn phases have shown potential for use in such extreme environments because of their unique combination of high fracture toughness values and thermal conductivities, machinability, oxidation resistance, and ion irradiation damage tolerance. Herein we report on the effect of neutron irradiation of up to 0.5 dpa at 70°C and 700 °C on Ti3AlC2, Ti2AlC, Ti3SiC2, and Ti2AlN. Evidence for irradiation induced dislocation loops and their effect on electrical resistivity is also presented. X-ray diffraction refinement of the resultant microstructures is provided, revealing the partial dissociation of Ti3AlC2 into TiC. Based on the totality of our results, it is reasonable to assume that the MAX phases, especially, Ti2AlC, are promising materials for high temperature nuclear applications.

11:10 AM

(ICACC-S12-041-2014) Processing and Testing of Ultrahigh Temperature Fiber-reinforced Ceramics

J. J. Stiglich*, B. E. Williams, Ultramet, USA

Ultramet has developed innovative processing for ultrahigh temperature fiber-reinforced ceramics. Using a rapid melt infiltration process, Ultramet fabricates high strength fiber-reinforced ceramic matrix composite structures that can operate in various hot-gas environments at temperatures in excess of 2800°C. A low temperature process has also been developed to apply fiber interface coatings to protect the fibers during processing and to maximize composite mechanical properties during use. The processing is applicable to ceramic matrices with extremely high melting points including zirconium carbide, hafnium carbide, tantalum carbide, and ceramic alloys. Hot-gas testing of melt infiltrated ceramic matrix composite structures in oxidizing environments has been performed at various facilities, and the components survived with low or no erosion. Processing and testing of ceramic composite materials will be discussed.

11:30 AM

(ICACC-S12-042-2014) Oxidation of HfB_2-SiC and HfB_2-$MoSi_2$ above 1700°C

C. Carney*, T. Parthasarathy, UES, Inc, USA; M. Cinibulk, Air Force Research Laboratory, USA

Oxidation resistance tests were conducted on HfB_2-SiC and HfB_2-$MoSi_2$ samples using direct electrical resistance heating above 1700°C. Analysis of the formed oxide scales shows a distinct difference between the two silicon bearing additives to HfB_2. SiC forms a layered oxide scale of HfO_2 and SiO_2 offering oxidation protection at 1750°C with an observed scale non-adherence at 1950°C. $MoSi_2$ promotes a mixed scale of SiO_2, HfO_2, and molybdenum oxides at all temperatures that remains adherent to the bulk up to 2500°C. For comparison, samples were heated in a high temperature zirconia furnace and by an oxyacetylene torch. Characteristics of the oxide scales will be presented and a discussion of possible mechanisms towards enhanced adhesion will be presented.

11:50 AM

(ICACC-S12-043-2014) Dynamic Non-Equilibrium Thermal Gravimetric Analysis of Ultra-high Temperature Ceramics

M. Miller-Oana*, L. Walker, E. Corral, University of Arizona, USA

We are interested in investigating true isothermal rate measurements for ultra-high temperature ceramics (UHTCs) that are candidates for thermal protection systems (TPS) on hypersonic flight vehicles. We oxidize UHTCs using Dynamic Non-Equilibrium Thermal Gravimetric Analysis (DNE TGA) up to 1600°C from 0.29 to 19 kPa oxygen partial pressure in order to obtain true isothermal oxidation behaviors. DNE TGA consists of heating up under inert atmosphere and switching to oxidizing environments once the isothermal period is reach. Once the isothermal hold period is completed, the gases are switched back to an inert environment until room temperature is reached. Dynamic non-equilibrium oxidation rate measurements yield results that increase with increasing temperature. We characterize the specimens after oxidation testing using scanning electron microscopy to determine oxide scale lengths and examine morphology.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Materials Science in Nuclear Waste Management

Room: Oceanview
Session Chair: Josef Matyas, PNNL

8:00 AM

(ICACC-S13-001-2014) Ceramic Waste Forms: Present status and perspectives (Invited)

S. Neumeier*, F. Brandt, A. A. Bukaemskiy, S. Finkeldei, Y. Arinicheva, J. Heuser, E. Ebert, C. Schreinemachers, A. Wilden, G. Modolo, D. Bosbach, Institute of Energy and Climate Research - IEK-6: Nuclear Waste Management, Germany

With respect to long-term safety aspects of geological disposal, the minor actinides and long-lived fission and activation products are of particular concern due to long half-lifes, high radiotoxicity and mobility in a repository system, respectively. Ceramic waste forms for the immobilisation of these radionuclides have been investigated extensively in the last decades since they exhibit certain advantages compared to other waste forms (incl. borosilicate glasses and spent fuel) such as high loadings and chemical durability. Various aspects with the focus on single phase waste forms, such as monazite and zirconates with pyrochlore structure will be discussed: (1) Powder synthesis suitable for the handling of radionuclides as well as ceramic production using cold pressing/sintering, hot isostatic pressing; (2) structural and microstructural characterisation using state of the art spectroscopic/diffraction (TRLFS, Raman, XRD) and microscopic techniques (SEM); (3) thermodynamic stability and reactivity under repository conditions in particular with respect to leaching/corrosion in aqueous environments (static and dynamic dissolution experiments on powders and pellets). The final goal is to provide a refined understanding on a molecular level of ceramic materials with respect to long-term stability under conditions relevant to deep geological disposal.

8:30 AM

(ICACC-S13-002-2014) Encapsulation of HLW in SiC for long-term immobilization (Invited)

J. Knorr*, GWT-TUD GmbH, Germany; A. Kerber, SiCeram GmbH, Germany

The use of silicon carbide as a supplementary barrier is described to improve the retention capability of waste packages thus contributing to the long-term immobilization of HLW in a repository. Most waste management programs discuss metallic canisters for waste packages. The experience has shown that such canisters corrode faster than assumed. The redundancy of the multi-barrier concept – technical plus natural barrier – is thus lost quite soon leading to the risk of a non-acceptable pollution of the environment. Prototypes and material samples are presented for the SiC encapsulation of spent fuel elements and vitrified waste from reprocessing in form of monolithic canisters, monolithic or segmented in-liners or overpacks. An extra layer at the inner wall preferably glassy-carbon-like protects the SiC against aggressive fission products and increases the retention capability additionally. Potting of SF canisters with a special cast composite gaining ceramic-like properties under heat and radiation improves important safety features (heat conductivity, sub-criticality, mechanical stability) to a great extent.The proposed supplementary ceramic barrier can be implemented in most existing waste package concepts. Encapsulation in SiC is more than just increasing redundancy of multiple barrier concepts - a new quality of robust and long-term stable encapsulation of HLW can be achieved.

9:00 AM

(ICACC-S13-003-2014) Silver-functionalized silica aerogel: An experimental platform for 129I remediation

J. Matyas*, Pacific Northwest National Lab, USA

The current reference material for removing radiodine from reprocessing plant off-gases is a silver-loaded zeolite (AgZ). However, recent studies indicate limitations in the sorption performance and long-term stability of AgZ. Also, immobilizing trapped radioiodine in AgZ requires addition of other materials, e.g., low-temperature glass. Therefore, we are developing silver-functionalized silica aerogel, an advanced material with high selectivity and sorption capacity for radioiodine that, after being loaded with iodine, can be consolidated into a durable high-iodine-loaded waste form. The presentation will discuss the results from sorption studies, the development of an engineered form of silver-functionalized silica aerogel as well as methods and techniques to consolidate iodine-loaded aerogel into a dense silica-based waste form, including the iodine retention during consolidation.

9:20 AM

(ICACC-S13-004-2014) The Impact of O/M and Dopants on the Sinterability of Actinide and Rare-earth Oxides

J. B. Henderson*, Netzsch Instruments North America LLC, USA

Actinide and rare-earth oxides are used in applications ranging from burnable poisons in nuclear fuel to fuel cells, catalyst components, etc. Many of these materials are sintered in off-stoichiometric conditions, which impacts the quality of the oxide. Sintering is controlled by the defect structure and concentration which, in turn are controlled in part by stoichiometry, i.e. oxygen-to-metal ratio (O/M). The purpose of this work was to quantify the interrelationship between O/M, defects and diffusion. The materials investigated were UO_2, CeO_2, $GdO_{1.5}$ and CeO_2-$GdO_{1.5}$ blends. The measured thermal expansion and O/M data demonstrate the impact of stoichiometry on sinterability. For the more complex powder blends, the data show that stoichiometry plays an even more important role, because both sintering of the solutionized system and diffusion of the gadolinia dopant into the fluorite structure are affected. This can create a blocking mechanism which compromises final density. The results of this work will be presented.

Materials Science and Technologies for Advanced Reactors I

Room: Oceanview

Session Chairs: Kurt Terrani, Oak Ridge National Laboratory; Theodore Besmann, Oak Ridge National Laboratory; Yutai Katoh, Oak Ridge National Laboratory

10:00 AM

(ICACC-S13-005-2014) Silicon Carbide Composite for Boiling Water Reactor Channel Application (Invited)

K. Yueh*, Electric Power Research Institute, USA

Recent severe boiling water reactor (BWR) channel bow issues and the desire to replace in-core zirconium fuel materials for accident tolerance is fueling a renewed interest in the use of none traditional nuclear materials. Silicon carbide has been identified as a potential candidate material. A comprehensive feasibility evaluation was performed. Initial irradiation induced volumetric swelling, impact and thermal shock fragmentation resistance, and silica release into the coolant has been identified as issues. An assessment based on fuel design and published SiC properties suggest a flux gradient of up to 25% is acceptable for irradiation swelling. Impact and LOCA quench thermal shock testing indicate SiC composite has acceptable fragmentation resistance. Irradiation of test coupons in both axial and transverse orientations are planned in the Oak Ridge National Laboratory High Flux Isotope Reactor to quantify irradiation induced volumetric swelling at 260 and 280°C at multiple fluence levels. The MIT research reactor, with a pressurized water loop, will be used to evaluate silica release at 280°C. Test samples from the MIT research reactor will also generate volumetric swelling and creep data.

10:30 AM

(ICACC-S13-006-2014) Silicon Carbide Oxidation in Steam (Invited)

K. Terrani*, B. Pint, L. Snead, Y. Katoh, Oak Ridge National Laboratory, USA

Silicon carbide (SiC) materials have a long history in nuclear applications, particularly in high temperature gas reactor systems and fusion platforms. Emerging in recent years are proposals for extension of their application to light water reactor (LWR) systems. For all these applications and particularly for the latter, the mechanism and magnitude of SiC oxidation in steam is of great importance. To address this need, a series of complementary experiments spanning a temperature range of 1200-1700 °C, pressure range of 0.1-2 MPa, and a gas flow velocity range of 1-150 cm/s have been carried out on monolithic and composite SiC materials in pure steam environments. In this manner the details of the oxidation kinetics and degradation mechanisms for SiC materials in these environments have been captured. This information can be utilized in system level analysis tools to examine the viability and response of nuclear systems under severe accident scenarios.

11:00 AM

(ICACC-S13-007-2014) Fabrication and Corrosion Resistance of Joined SiC and SiC Composite Structures Required in Advanced Nuclear Reactor Design

C. Lewinsohn*, J. Fellows, M. Wilson, H. Anderson, Ceramatec, Inc., USA

Silicon carbide (SiC) exhibits excellent thermal and radiation stability which make it attractive for application in high temperature, gas-cooled advanced reactor designs operating at high neutron flux conditions that push or exceed the limits of conventional materials. Some SiC composite structures also may be utilized in existing and anticipated reactors with lower operating temperatures and fluxes where the slower oxidation rates of SiC compared to most metals may be advantageous (for example, accident tolerant fuel structures for LWRs). Fabrication of complex shapes or sizes of SiC and SiC-composite components requires joining subassemblies, such as three dimensional solids (fuel elements, reflector, core support blocks), two dimensional plates (heat exchangers), and cylindrical pipes (control rod guides, hot ducts), all using robust and reliable joining methods. The reliable joint needs to have high strength and corrosion resistance, the ability to thermally cycle and retain its properties, and to withstand neutron irradiation. This research discusses a new joining method (whose joint has shown strengths equivalent to monolithic SiC), applied to SiC and composite SiC structures, with associated corrosion resistance of the joint in various conditions.

11:20 AM

(ICACC-S13-008-2014) Fabrication and Properties of SiC Composite Tubes for Fuel Cladding Application

W. Kim*, D. Kim, J. Park, J. Park, Y. Jung, Korea Atomic Energy Research Institute, Republic of Korea

SiCf/SiC composites have extensively been studied for fusion and advanced fission energy systems due to their excellent high temperature properties, irradiation tolerance, inherent low activation and other superior physical/chemical properties. Owing to these superior physical/chemical properties, there have also been efforts for applying the SiCf/SiC composites to fuel claddings for various types of advanced reactors including light water reactors (LWR). For the application of LWR fuel cladding, the kinetics of the SiC corrosion under a LWR condition needs to be clarified and the fabrication of composite tubes with well-controlled properties should be preceded. The development of a robust joining technology for the end-plug and the matrix microcracking susceptibility are also significant challenges for the application of SiC composite cladding. In this study, we have investigated the effect of CVD process parameters on various properties of SiC tubes such as microstructure, stoichiometry, and mechanical properties. We have also studied the corrosion behavior of chemically vapor deposited (CVD) SiC under various LWR water simulating conditions. In addition, preliminary results on joining studies using diffusion bonding and laser joining techniques will be presented.

11:40 AM

(ICACC-S13-009-2014) Diffusion Bonding of Zircaloy-4 and Select Mn+1AXn Phases

D. J. Tallman*, B. Anasori, M. W. Barsoum, Drexel University, USA

Zircaloy-4 (Zr-4) is the current fuel cladding of choice for light water reactors (LWR), mainly due to its high strength, corrosion resistance and low neutron cross section. However, limitations on maximum operating temperature and catastrophic failure in case of loss of coolant accidents are some of its limitations. Recently, the Mn+1AXn, MAX phases, have been proposed as candidate materials to be used as supplemental protective barriers on Zircaloy. Before such an application can be realized however, the interactions between Zr-4 and select MAX phases must be understood. In this talk we report for the first time on the interactions between Zr-4 and 3 different MAX phases i.e. Ti3SiC2, Ti3AlC2 and Ti2AlC in the 1100-1300 °C range. In all cases, the A-group element (i.e. Al or Si) diffused out of the MAX phase and formed intermetallics with the Zr-4. Interestingly the Al from the Al-containing MAX phases penetrated deeper into the Zr-4 than the Si forms Ti3SiC2.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Fibers, Matrices, Coatings and Interfaces

Room: Coquina Salon D
Session Chairs: Randall Hay, AFRL/RXCC; Jacques Lamon, CNRS

1:30 PM

(ICACC-S1-031-2014) Size effects on the fracture strength of CMCs

J. Lamon*, CNRS, France; M. R'Mili, INSA Lyon/University of Lyon, France

The investigation of size effects on the strength of CMCs, is a prerequisite to the prediction of component fracture from laboratory test data. However, the experimental investigation of these effects is limited by practical difficulties related to manufacturing and cost of specimens. Furthermore, lack of reproducibility in the microstructure may favor the contribution of extrinsic factors. A sound approach seems to be to take advantage of the important feature that fracture is dictated by the multifilament tows. The present paper examines size effects on the tensile behavior of multifilament tows. In a first step, the model of tow behavior was validated on glass and Nicalon SiC fibers. Then, a relation for tow strength dependence on pertinent dimension was derived from predictions of tow behavior. Results were compared with experimental data obtained on minicomposites and 2D woven SiC/SiC. Trends in dimension dependence were anticipated.

1:50 PM

(ICACC-S1-033-2014) Glass fiber tow: a model specimen for the investigation of the post fatigue behavior of SiC fibers

J. Lamon*, CNRS/ENS, France; M. R'Mili, INSA Lyon/University of Lyon, France

The fracture of CMCs is dictated by the fibers and the tows. Therefore, the determination of behavior of filaments and tows is useful to infer the behavior of composites. This approach produced interesting results for the investigation of static fatigue by subcritical crack growth at elevated temperatures. However, an experimental approach requires a huge amount of tests at high temperatures. Models provide a powerful alternative which allows predictions of the behavior in many situations. Like SiC fibers, glass fibers are sensitive to subcritical crack growth, as a result of a reaction with environment. This reaction occurs at room temperature in water. In the present paper, a model of residual behavior of tows after static fatigue is validated using the experimental behavior determined on glass fiber tows. For this purpose, glass fiber tows containing 2000 filaments were tested in static fatigue at room temperature in water. Then, the residual behavior of tows was measured using tensile test. This behavior was predicted using the slow crack growth parameters extracted from the fatigue test. Comparison assessed the models of delayed failure and residual behavior which were then applied to predict the residual behavior of Hi Nicalon fibers, for which the slow crack growth parameters have been determined in a previous work.

2:10 PM

(ICACC-S1-034-2014) Creep Mechanisms and Microstructure Evolution of Nextel™ 610 Fiber in Air and Steam

R. Hay*, AFRL/RXCC, USA; C. Armani, M. Ruggles-Wrenn, AFIT, USA; G. Fair, AFRL/RXCC, USA

Creep rates of Nextel™ 610 alumina fibers were measured at 1100°C and 100 - 500 MPa in air and in steam. Steam increased creep rates and reduced fiber lifetimes. Fiber microstructures were characterized by TEM. Grain growth, fiber-axis grain elongation, and pore growth were quantified. Grain growth and elongation were also quantified for Nextel™ 610 fibers heat-treated for 1 to 100 hours in air at 1100° - 1500°C, and in a ceramic composite heat-treated for 10,000 hours at 1200°C. Grain growth laws that account for texture and shape anisotropy were determined. The contributions of pore growth and fiber-axis grain elongation to creep strain were quantified for creep in air and in steam. Pore growth was more pronounced in steam and grain elongation more pronounced in air. Creep and failure mechanisms consistent with observed microstructural changes are discussed.

2:30 PM

(ICACC-S1-035-2014) Foreign Object Impact Damage in Ceramic Matrix Composites

R. S. Kumar*, M. Mordasky, G. Ojard, United Technologies Research Center, USA

Ceramic matrix composite (CMC) components in a gas turbine engine environment can be subjected to accidental particle impact conditions that can cause surface and sub-surface damage in the material. Such damage, which is often referred as foreign object damage (FOD), can lead to severe performance degradation of the component. It is therefore essential to develop and validate models that can predict FOD damage in complex CMC components. Such models can then be used for 1) effective design of CMC components for FOD resistance and 2) as input to models that can predict the post-FOD performance of CMC structures. The present work is focused on Finite Element (FE) modeling of the impact process in a layered two-dimensional CMC material and its validation using impact experiments. The model considers ply damage mechanisms using a continuum damage approach, whereas the delamination mechanism is modeled explicitly using cohesive-zone FE method. The validation experiments are conducted on clamped-clamped CMC beams using a gas-gun impact apparatus. Post-test analyses of the specimen are conducted to discern the extent of surface and sub-surface damage and the results are compared against corresponding FE analysis.

2:50 PM

(ICACC-S1-036-2014) Boria Fluxing of SiC in Ceramic Matrix Composite Aeropropulsion Applications

B. McFarland*, E. J. Opila, University of Virginia, USA

Ceramic matrix composites comprised of SiC fibers, a BN interphase, and a SiC matrix form borosilicate glasses under high-temperature oxidizing conditions. The mechanisms responsible for excessive oxidation leading to composite degradation are being investigated. Glass coatings of known boria/silica composition were applied onto CVD-SiC and SiC/ iBN fibers. The glasses were synthesized from sol-gel precursors and converted to glass by heat treatment. Glass compositions ranged from 0 – 40 wt% boria with the remainder silica. The glasses were characterized by ICP-OES, FTIR, and XRD to confirm the composition and borosilicate glass structure since boron leaching can occur during sol-gel synthesis and drying. The coated coupons, fibers, and monolithic glasses were exposed in dry oxygen at 1200 or 1300 °C for 100 hours and weight change was continuously monitored by thermogravimetric analysis. Preliminary oxidation results show 1) silica glass layer slows oxidation; 2) low boria concentrations increase oxidation rate, but 3) higher boria concentrations show rapid oxidation at early times and slower oxidation rates at longer times due to enhanced oxygen transport and boria volatility occurring concurrently. SiC oxidation results as a function of glass coating composition, temperature, time, and gas environment will lead to the development of a life-prediction model for SiC fiber consumption.

3:30 PM

(ICACC-S1-037-2014) The role of water vapor on the intermediate temperature oxidation of SiC-fiber composites and volatilization of BN fiber coatings

M. N. Rossol*, F. W. Zok, University of California Santa Barbara, USA

BN is used as a debond-layer in SiC-fiber ceramic matrix composites due to its thermal stability relative to graphite and its ability to form a condensed phase, B2O3, when exposed to oxidizing environments. However, BN fiber coatings are still susceptible to degradation when exposed to water vapor, as is the case in a combustion environment. We investigate this phenomenon by performing a sequential oxidation study of commercially available SiC-fiber composites in water vapor-containing environments. Optical profilometry is used to quantify changes in fiber height caused by the relaxation of residual stresses upon recession of the BN fiber coating, and an environmental scanning electron microscope is used to characterize morphological changes at the fiber matrix interface. Finally, we also investigate the mechanical response of SiC-fiber composites at intermediate temperatures in air and in water vapor.

3:50 PM

(ICACC-S1-038-2014) Processing and testing of Re2Si2O7 as a weak interface for SiC/SiC composites

E. Boakye*, P. Mogilevsky, T. A. Parthasarathy, K. A. Keller, T. Key, UES Inc., USA; H. S. Randall, M. K. Cinibulk, AFRL, USA

Rare-earth disilicates (RE2Si2O7) may serve as a potential oxidation-resistant coating alternative to carbon or BN for CMC fiber-matrix interphases. In our prior work, the formation of α, β and γ-Y2Si2O7 and γ-Ho2Si2O7 powders at different temperatures and processing environments were investigated. Silica - yttrium hydroxide and silica - holmium hydroxide dispersions were made and heat-treated at 1000° - 1400°C for 8 h in air to form, α, β and γ-Y2Si2O7. In this work, dense α, β, γ-Y2Si2O7 and γ-Ho2Si2O7 monoliths were formed using field assisted sintering technique (FAST) at a pressure of 20 kN and at temperatures of 1050° - 1200°C/ 1h. Subsequently, their Vickers hardness was measured. Further, SCS-0 fibers were incorporated into α-, β- and γ-Re2Si2O7 matrixes and densified at 1050°C - 1200°C using FAST. Fiber push-out experiments were conducted, and the average sliding stress values were determined. TEM investigations for possible deformation of Re2Si2O7 in indented pellets and pushed out fiber/matrixes interfaces are also reported. Preliminary results of Y2Si2O7 coatings on Tyranno-SA fiber tows are also reported.

4:10 PM

(ICACC-S1-039-2014) Mechanical behavior of alumina based wound highly porous CMCs

S. Hackemann*, DLR - German Aerospace Center, Germany

All-oxide ceramic matrix composites have been developed for long term applications at high temperature and oxidizing environmental conditions such as combustor walls of gas turbines. The good toughness and thermoshock resistance of the investigated WHIPOX-CMCs (Wound Highly Porous Oxide) relies on the interaction of ceramic fibers and a porous, weak matrix with a low modulus. The winding technique enables variable fiber architecture, but makes the experimental investigations of the mechanical behavior and modeling of the material quite complex. Unidirectional material was tested under uniaxial tension, shear and compression. Additionally, off-axis tests and torsion tests combined with tensile and compression loads were conducted to determine in-plane failure under multiaxial loading. The investigations of inter-fiber fracture revealed, that the assumption of an isotropic cross section perpendicular to the fiber direction with respect to strength is not true. The transformation of elastic constants from unidirectional material to wound material with variable fiber orientations cannot be carried out straightforward, as the influence of the cross-over lines and the evolution of shrinking cracks and their crack density for different fiber orientations have to be taken into account. Depending on the fiber orientation, cross-over lines play a major role with respect to fiber dominated failure.

4:30 PM

(ICACC-S1-040-2014) Characterization of fiber matrix interface in CMCs using single fiber push out tests

C. Steinborn*, H. Klemm, A. Michaelis, FhG IKTS Dresden, Germany

Model composites with different matrices and silicon carbide SCS-6 fibers have been fabricated. Matrix formation by reactive sintering of Si3N4 (zero shrinkage technique) and hot pressing of rare earth disilicates has been used to adjust different porosity and matrix strength. To generate a wide range of interfacial strength, fiber surface has been activated by oxidation the outer carbon fiber coating and the deposition of different coating materials. The character of the fiber-matrix interface was found to be different when parameters for matrix formation have been changed. By this means a damage tolerant behavior of the CMC can be obtained by adjustment of the load transfer rate and the ability of the interface to deflect cracks. Single fiber push-out tests by micro-indentation technique have been applied as an effective tool to investigate the interaction between fiber and matrix. Force-displacement curves have been used to indicate characteristic points like crack initiation (push in) or complete debonding (push out) of the fiber. Finally correlations between microstructure, fiber surface condition and interfacial shear strength will be discussed.

4:50 PM

(ICACC-S1-041-2014) Characterization of Advanced SiC/SiC Composite Tubes Under Monotonic Axial Tensile Loading at Ambient Temperature

J. Su*, Tsinghua University, China; J. Hemrick, Oak Ridge National Laboratory, USA; S. Yu, Tsinghua University, China; C. Shih, Oak Ridge National Laboratory, USA; R. J. Shinavski, Rolls-Royce High Temperature Composites, USA; S. Gonczy, Gateway Materials Technology, Inc, USA; Y. Katoh, Oak Ridge National Laboratory, USA

SiC/SiC composites are promising candidate materials for future nuclear systems, e.g. control rod sheath for very-high temperature gas-cooled reactors, advanced cladding in light water reactor systems and core structure materials in fusion reactors. Some of the applications require SiC/SiC composites in a tubular form. Understanding the mechanical behavior and the development of test methods are needed for SiC/SiC composite tubes because of their markedly different geometries compared to flat plates. In this study the axial tensile properties of continuous fiber-reinforced SiC/SiC composite tubes were evaluated at ambient temperature according to the newly developed ASTM Standard C 1773. The test articles were small diameter tubes of biaxially braided Hi-Nicalon -reinforced CVI SiC matrix composite and tri-axially braided Hi-Nicalon Type S, CVI SiC matrix composite both with multilayer PyC/SiC interphase. Preliminary results indicate excellent tensile fracture behaviors of the composites studied. The results will be compared with the tensile properties of similar materials tested with flat coupon specimens and hoop tensile properties of similar tubes and discussed for the effects of fiber orientations and the open edge.

5:10 PM

(ICACC-S1-042-2014) Carbon and Boron Nitride Interphase Coatings for SiC_f/SiC Composites by Electrophoretic Deposition Method

K. Yoshida*, H. Akimoto, A. Yamauchi, T. Yano, Tokyo Institute of Technology, Japan; M. Kotani, T. Ogasawara, Japan Aerospace Exploration Agency (JAXA), Japan

Continuous silicon carbide fiber-reinforced silicon carbide matrix composites (SiC_f/SiC) are one of the key materials for high-temperature gas turbine, spacecrafts and future nuclear and fusion power reactors. It is important to form the optimum fiber/matrix interface to obtain high performance SiC_f/SiC composites. Fabrication process of high-performance SiC_f/SiC composites that is simple, environmentally benign and low-cost has been strongly requested. Present authors proposed the novel process of interphase coatings for SiC_f/

SiC composites based on electrophoretic deposition (EPD). In this study, EPD process was applied for the formation of the carbon- and boron nitride (BN)-interphase coatings for uni-directional SiC_f/SiC composites, and their mechanical properties were investigated. Relatively homogeneous carbon-interphase was formed on SiC fibers by EPD method. The uni-directional SiC_f/SiC composites using SiC fibers with carbon interphase fractured in pseudo-ductile manner with large amount of fiber pull-out. However, the SiC_f/SiC composites using SiC fibers with BN-interphase fractured in pseudo-ductile manner with very small amount of fiber pullout. The reason was considered that sintering additives would react with BN-interphase and the interpahse did not act effectively.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Advanced Thermal Barrier Coatings I: New Compositions, Processing, Testing Development

Room: Coquina Salon G

Session Chair: Rodney Trice, Purdue University; Yutaka Kagawa, University of Tokyo

1:30 PM

(ICACC-S2-010-2014) Processing and Properties of Yttrium Aluminum Garnet Thermal Barrier Coatings Made By the Solution Precursor Plasma Spray Process (Invited)

M. Gell*, E. Jordan, J. Roth, C. Jiang, University of Connecticut, USA; B. Nair, J. Wang, HiFunda LLC, USA

YSZ is used extensively as a TBC because of its favorable combination of physical and mechanical properties. One of the key properties is a very high thermal expansion coefficient which provides a low thermal expansion mismatch with the underlying metal and good thermal cycling durability. The starting point for this research was to select an oxide ceramic with potentially higher use temperature and other favorable properties, but with higher thermal expansion mismatch than YSZ to determine whether the greater thermal expansion mismatch strains could be overcome using the strain-tolerant microstructure that is produced by the solution precursor plasma spray (SPPS) process. The precursors used were yttrium and aluminum nitrates dissolved in water or ethanol. A wide range of precursor and plasma spray parameters were investigated and will be described. These experiments showed that 250 micron thick YAG TBCs could be deposited by the SPPS process. SPPS YAG TBCs with two candidate microstructures were selected for cyclic furnace testing at 1182o and 1121oC. It was found that the cyclic lives of the SPPS YAG TBCs were greater than baseline APS YSZ TBCs run in the same test. Additional properties of the SPPS YAG TBCs were measured and will be reported.

2:00 PM

(ICACC-S2-011-2014) Performance of advanced thermal barrier coating systems in a thermal gradient test rig

R. Vassen*, V. Kochubey, Forschungszentrum Jülich GmbH, Germany; T. Wobst, Rolls-Royce Deutschland LtdCo, Germany; B. Rittmeister, GfE Fremat GmbH, Germany; F. Brückner, Fraunhofer IWS, Germany

Within a national funded project advanced atmospherically plasma-sprayed thermal barrier coating (TBC) systems have been developed. As substrate material the Nickelbase superalloy Mar-M 247 and as bond coat a CoNiCrAlY was used. The investigation of the TBC systems include differently thermal sprayed bond coats, samples with and without an advanced interface structure applied by a laser cladding process as well as different TBC materials. The baseline was a standard yttria stabilized zirconia coating applied as a single layer on top of the bond coat. After a first phase of optimization of microstructure and performance in isothermal and gas burner rig testing, promising systems have been selected for further evaluation. In this paper especially the results of gradient testing with surface temperature up to 1500°C will be discussed. Also the influence of the interface structure on the performance will be described and the failure mode for these systems analyzed in detail.

2:20 PM

(ICACC-S2-012-2014) The influence of process parameters on the microstructure evolution of ZrO2-CeO2-TiO2 thermal barrier coatings

C. Macauley*, University of California Santa Barbara, USA; D. Lipkin, GE Global Research, USA; S. Sampath, Stony Brook University, USA; C. Levi, University of California Santa Barbara, USA

The higher operating temperatures required to increase gas turbine efficiency exacerbate some mechanisms that shorten the working life of TBCs. The phase stability of the current industry-standard TBC composition, yttria stabilized zirconia (YSZ) inherently limits the use of YSZ at higher operating temperatures, motivating the search for new compositions with improved capabilities. CeO2 and TiO2 co-doped zirconia has shown promise as a potential 'next generation' TBC. A relatively large, non-transformable, single-phase tetragonal field stabilized at 1350°C has been reported. Compositions within this phase field have been manufactured into coatings by air-plasma spray. It is shown that segregation during thermal spraying may lead to undesirable microstructure and phase evolution. To elucidate the influence of process parameters such as plasma gun power, coatings were produced using different spray conditions. Raman, XRD and TEM analyses provide insight into the underlying mechanisms governing segregation and highlight the importance of understanding the influence of processing on coating performance. This material is based upon work supported by the NSF under Award # DMR-1105672 and the Department of Energy under Cooperative Agreement DE-FC26-05NT42643.

2:40 PM

(ICACC-S2-013-2014) Thermal Conductivity and Phase Stability in the Y2O3-Ta2O5-ZrO2 System

S. Shian*, A. M. Limarga, Harvard University, USA; R. M. Leckie, C. G. Levi, University of California, USA; D. R. Clarke, Harvard University, USA

Having low thermal conductivity, high temperature stability, and fracture resistance, multicomponent Y2O3-Ta2O5-ZrO2 system has been a subject of interests for the next generation thermal barrier coatings (TBC). We investigate the thermal properties of single, two-phase, and three-phase materials within the system and discover, despite large variations in compositions, most materials share common characteristics; their thermal conductivity are similar and are relatively temperature independent. Such behaviors can be attributed to the extensive mass disorder in the crystal lattices that significantly decreases the phonon mean free path. In comparison, the Kapitza resistance is relatively small, which minimize the effect of thermal interface resistance stemming from phases and/or grain boundaries. Long term structural stability study at high-temperature in air indicate while certain phases evolve, few distinct compositions remain unchanged, indicating that the latter may be suitable for further exploration as TBC system.

3:20 PM

(ICACC-S2-014-2014) Performance and Stability of Unique Multiphase Thermal Barrier Coatings (TBCs) (Invited)

D. E. Wolfe*, M. P. Schmitt, The Pennsylvania State University, USA; A. K. Rai, UES Inc, USA; R. Bhattacharya, D. Zhu, NASA Glenn Research Center, USA

Novel multiphase Electron Beam-Physical Vapor Deposition (EB-PVD) and Air Plasma Spray (APS) thermal barrier coatings (TBCs) have been investigated. Two phase composites and two phase multilayer microstructures composed of rare earth doped zirconia were deposited onto a variety of substrate materials and compared to baseline 7 wt% yttria stabilized zirconia (7YSZ) coatings. The TBCs are tested in terms of erosion and thermal conductivity along with a full microstructure characterization. It is shown that tailoring the total rare earth concentration via multiple phases can allow for increased erosion resistance with respect to a cubic type phase while maintaining sufficiently low thermal conductivity. The stability of these multilayer and composite TBCs is then investigated through a combination of heat treatments, x-ray diffraction and electron microscopy. Transmission electron microscopy along with energy dispersive spectroscopy and selected area diffraction are performed on select samples to investigate interfacial reactions and phase transformations.

3:50 PM

(ICACC-S2-015-2014) Optimum wavy multilayer structure for high efficiency thermal radiation energy reflection coatings

M. Yamazoe*, H. Kakisawa, Y. Kagawa, University of Tokyo, Japan;
S. Kitaoka, M. Tanaka, Japan Fine Ceramics Center, Japan

Control of thermal radiation energy is efficient way to reduce flow of heat energy from high temperature use environment, thus possible to reduce cooling loss. Oxide ceramics multilayer coatings can reflect thermal radiation energy by interference effects. To obtain higher efficiency, multilayer structure with wavy morphology is applied, the design procedure is not well developed, however. In the present study, effects of thickness ratio of layers, number of layers, and materials properties of the layers on the reflection efficiency are simulated using Finite Element Time Domain (FETD) method. The simulation is focused on Mie scattering range and practically planned materials combinations: e.g., Al_2O_3 and $Y_2Ti_2O_7$ layers, total 5~15 layers. Arbitrary interfaces or surface shape, and multilayer coating with different thickness are assumed in the analytical model. Radiation source is set to 2000°C and the coating temperature is set to 1300°C. Assuming black body radiation from the source, optimum multilayer coating allows reflection efficiency of thermal radiation energy above ~50%. Discussions are made on the wavy effect using interference behavior inside the coating layer.

4:10 PM

(ICACC-S2-016-2014) Temperature Measurements of Thermal Barrier Coating Surfaces Using a Cr-Doped $GdAlO_3$ Thermographic Phosphor

J. I. Eldridge*, T. J. Bencic, D. Zhu, NASA Glenn Research Center, USA;
M. D. Cuy, Vantage Partners, USA; D. E. Wolfe, Penn State University, USA;
T. P. Jenkins, MetroLaser, Inc., USA; S. W. Allison, D. L. Beshears, Emerging Measurements, USA; B. Heeg, Lumium, Netherlands

It has been recently shown that Cr-doped $GdAlO_3$ (Cr:$GdAlO_3$) is a thermographic phosphor that produces remarkably high-intensity broadband luminescence with sufficiently long decay times to make effective luminescence-decay-time-based temperature measurements above 1000°C. The retention of intense luminescence produced by Cr:$GdAlO_3$ at high temperatures offers substantial benefits for implementing luminescence-based temperature measurements of thermal barrier coating (TBC) surfaces in a turbine engine environment. The strong luminescence intensity of this thermographic phosphor at elevated temperatures provides substantial benefits for testing in turbine engine environments compared to previously used rare-earth doped oxide phosphors. In particular, high intensity luminescence is required to overcome the very restricted solid angle of light collection associated with engine probe designs. The higher luminescence intensity also opens up the possibility performing fast non-rastered 2D temperature mapping of TBC-coated surfaces. Lastly, highly efficient excitation of luminescence at high temperature allows adoption of lower-intensity, but much more compact and inexpensive, excitation sources compatible with on-wing testing. Examples will be presented that highlight these advantages.

4:30 PM

(ICACC-S2-017-2014) Stress in NiCoCrAlY Bond Coat Induced by Phase Transformation

Y. Chen*, University of Manchester, United Kingdom; X. Zhao, Shanghai Jiao Tong University, China; P. Xiao, University of Manchester, United Kingdom; N. Curry, N. Markocsan, P. Nylen, University West, Sweden

The evolution of residual stress in NiCoCrAlY bond coat after cyclic oxidation at 1150 °C was investigated using X-ray method. Bond coat samples were deposited on a superalloy substrate using high velocity oxygen fuel (HVOF). The stress is tensile, and gradually builds up as oxidation proceeds. In addition, the stress is higher in a thinner bond coat for a given oxidation time. To understand this phenomenon, factors such as bond coat/substrate thermal expansion mismatch, martensitic transformation of the bond coat were examined. It is concluded that the stress is related to the beta-gamma phase transformation in the bond coat driven by selective oxidation of Al and bond coat /substrate interdiffusion. Following this, surface rumpling of the same material after cyclic oxidation at 1150 °C was further investigated. The initially flat surface of the bond coat rumples after 50 cycles. The undulation magnitude, characterized by root mean square roughness (Rq), is higher on a thinner bond coat after 50 cycles. Rumpling also occurs on the coating thermally cycled in vacuum, but does not on NiCoCrAlY alloy after cyclic oxidation. The results demonstrate that the substrate plays a decisive role in the evolution of rumpling. It is concluded that, apart from bond coat/substrate CTEs misfit, stress induced by beta-gamma phase transformation through interdiffusion is another major contribution to surface rumpling.

4:50 PM

(ICACC-S2-018-2014) Contribution of in situ high temperature Raman spectroscopy to the fundamental understanding of CAS/8YPSZ interaction

S. Margueron*, S. Ropers, University of Lorraine, France; M. Vidal-Sétif, C. Rio, O. Lavigne, Onera, The French Aerospace Lab, France

The use of thermal barrier coatings in the hot sections of gas turbine engines has allowed higher engine operating temperatures leading to temperatures of the order of 1200°C. At such temperatures, thermal barrier coatings are susceptible to corrosion by molten CMAS. Studying this corrosion using a synthetic model CMAS allows a better understanding of the CAS/TBC interaction. The 1170°C eutectic CAS composition (61,5SiO2-15Al2O3-23,5CaO wt.%) has been selected because, at 1200°C, CAS viscosity is low enough to infiltrate the porous TBC microstructure. A chemical reaction takes place between CAS and TBC, resulting in new phases formation. The Raman scattering experiments are performed using 8YPSZ with initial CAS deposition and treated at several time and temperatures. After identification, at room temperature, using visible laser excitation, of the Raman signatures of the different reaction phases and initial constituents, in-situ monitoring has been followed during thermal cycles by ultraviolet Raman spectroscopy at high temperature and room temperature.

5:10 PM

(ICACC-S2-019-2014) Effects of deposition rate and temperature gradient on the damage mechanisms of thermal barrier coatings subjected to corrosion by glassy deposits

A. Harris*, E. Jordan, University of Connecticut, USA

As thermal barrier coatings (TBCs) have become standard in the manufacture of gas turbine engines, understanding factors that can greatly limit TBC life has become a critical part of the design process. Attack by molten glass deposits of ingested debris (dust, sand, ash, etc.) composed primarily of calcium-magnesium-aluminosilicates (CMAS) can drastically reduce coating life. While fine debris is ubiquitous in the atmosphere, its composition and concentration can vary significantly based on geography, which can have a strong effect on its threat to TBCs. Bi-layer TBCs - an air plasma sprayed yttria-stabilized zirconia inner layer and a solution precursor plasma sprayed gadolinium zirconate outer layer - were deposited on bond coated superalloy substrates. TBC samples were thermally cycled using a custom-designed thermal gradient rig while an aqueous CMAS precursor solution was intermittently applied. Samples were cycled to failure and to "half-life" using different CMAS dose rates and at different front side temperatures. The effect of these two variables on the CMAS-TBC reaction was studied using X-ray diffraction and electron microscopy with energy dispersive X-ray spectroscopy.

5:30 PM

(ICACC-S2-020-2014) In situ measurement of modulus of elasticity for 7 wt. % YSZ Electron Beam-Physical Vapor Deposition Thermal Barrier Coating for small strains

S. Ahmadian*, E. H. Jordan, University of Connecticut, USA

Modulus of elasticity for an in situ 7 wt. % yttria stabilized zirconia (YSZ) electron beam-physical vapor deposition (EB-PVD) on Low Pressure Plasma Sprayed (LPPS) NiCoCrAlY bond coat thermal barrier coating (TBC) is determined by a four-point-bend test rig for small strains at two different strain rates. In addition the effect of heat treatment on modulus of elasticity is investigated. A complete set of measurement uncertainty analysis with statistical analysis is performed to quantify the overall error in measuring the modulus of elasticity. It is found that EB-PVD coating has low in-plane modulus of elasticity and also the assumption of linear elastic is not valid for strains above 0.1%. Note that thermal expansion mismatch strain between the EB-PVD and the underlying metal is about 0.75%. Therefore it is suggested that a more profound constitutive model be used for strains beyond 0.1% for meaningful and more accurate stress-strain relationship for modeling purposes. On the other hand having such a low modulus of elasticity (~30GPa compressive) hinders upon justification of using single crack fracture mechanics for investigating failure mechanism.

S3: 11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Micro-SOFCs

Room: Coquina Salon H

Session Chairs: Vincenzo Esposito, Technical University of Denmark; Sascha Kuehn, eZelleron GmbH; Ling-yuan Tseng, Electric Energy Express

1:30 PM

(ICACC-S3-018-2014) Full Metal Fuel Cells (FMFCs) with Solid Oxide Thin Films allow start-up from room temperature to 850 °C in 10 Seconds (Invited)

S. Kuehn*, K. Paciejewska, A. Stoeck, S. Mnich, L. Winkler, eZelleron, Germany

One Drawback in the commercialization of Solid Oxide Fuel Cells (SOFCs), especially concerning mobile applications, is their long start-up time of typically several hours and the low thermo-cycling stability. A fuel cells ability to start-up in a few seconds and to resist more than one thousand full thermo-cycles demands high requirements to the fuel cells ability to withstand thermo-mechanical stress. Thermo-gradients of several hundred degrees Celsius and heat-up-ramps of more than 6.000 K/min can be demonstrated by omitting brittle materials like glasses or thick ceramic films. Metallic substrates, interconnects, cathode current collectors and metallic sealing's combined with thin ceramic films (<10 μm, sub-micro- or nano-crystalline texture) lead to a high thermo-mechanical shock resistance. A full metal fuel cell (FMFC) was developed and combined with thin ceramic functional layers. Low-cost high-throughput manufacturing steps like powder injection molding and aqueous electrophoretic deposition were used to create the complex microstructure matched to the high requirements of a quick-startable fuel cell with very high-power densities.

2:00 PM

(ICACC-S3-019-2014) WATT Fuel Cell & Parker Hannifin Target RV & Marine CHP Markets (Invited)

C. Finnerty*, S. DeWald, WATT Fuel Cell, USA

WATT Fuel Cell (WATT) has developed the most marketable and cost-effective solid oxide fuel cell (SOFC) technology for portable and potentially small stationary applications. WATT has partnered with Parker Hannifin (Parker) to integrate its next generation fuel cell technology into their combined heat and power (CHP) modular platform. This results in a quiet, reliable and cost effective alternative to generators. WATT's advanced tubular SOFC platform allows for wider operating tolerances which in turn permit the use of inexpensive, yet reliable supporting components to be integrated into the complete system. WATT's fuel cell systems are designed based on ease of manufacture, simplicity and cost. These parameters drive decisions on form factor, material choices, reforming chemistry and production processes. WATT's production focused designs provide competitive power densities and overall fuel efficiency. A combined heat and power (CHP) system unit using WATT's fuel cell technology will provide customers with new levels of fuel to energy conversion efficiency in the portable energy market creating more value to the customer and a shorter return on investment. WATT's partnership with Parker is expected to bring this fuel efficient and affordable CHP system to the RV and Marine markets commencing in 2014. WATT is leading a new era for fuel cell technology focused on cost-optimization of manufacturing fuel cells.

2:30 PM

(ICACC-S3-020-2014) All-ceramic μSOFC fully integrated in Si for a new generation of reliable micropower generators (Invited)

I. Garbayo, IMB-CNM, CSIC, Spain; D. Pla, A. Morata, IREC, Spain; L. Fonseca, IMB-CNM, CSIC, Spain; S. Sanna, V. Esposito, DTU RISO, Denmark; N. Sabaté, IMB-CNM, CSIC, Spain; A. Tarancón*, IREC, Spain

The huge number of portable devices with increasing energy demand is reactivating the research in the field of portable power. The recent integration of SOFCs in Si have shown a promising alternative to current Li-ion batteries. By reducing the electrolyte thickness and smart integration into low thermal mass structures, the SOFC technology has overcome the major drawbacks for application in portable devices,i.e., high operating T and long startup times with high energy consumption. This paper shows the fabrication and performance of an all-ceramic μSOFC fully integrated in Si, for the first time. The use of ceramics as electrodes greatly improves the reliability of metal-based devices strongly affected by dewetting processes. The device is fabricated by using Si microtechnology and large-area pulsed laser deposition of active thin films (anode, electrolyte and cathode). The scalability is proved by wafer-level batch mode processing. A comprehensive microstructural and electrochemical analysis of the anode, cathode and electrolyte is also presented. Area specific resistances below 0.3 Ωcm2 for the individual components is achieved at T<700°C. A power density of ca. 100 mW/cm2 with an open circuit voltage of 1.05V is obtained at 750°C based on a CGO/YSZ/LSC μSOFC. A new generation of fully-ceramic μSOFC is presented as a promising alternative to current micropower generators.

3:20 PM

(ICACC-S3-021-2014) Thin-film and nanostructure-based anode-supported solid oxide fuels cells by multi-scale architecture: Low-temperature performance and thermomechanical stability (Invited)

J. Son*, Korea Institute of Science and Technology (KIST), Republic of Korea

Recently, extensive research efforts have been put to lower the operation temperature of the SOFC. Especially, the low-temperature operation of SOFCs is essential to realized micro-SOFCs for high-performance portable power sources. Hence, thin-film electrolytes and nanostructure electrodes are implemented at an ever increasing rate to decrease the operation temperature of the SOFC. Nonetheless, the reliable implementation of thin-film and nanostructure components has been largely unsuccessful due the frail nature of the components and the cell platform. On the other hand, realization of thin-film electrolytes and nanostructure electrodes over a realistic SOFC platform like a porous anode-support (anode-supported TF-SOFC) has been extremely difficult, thus only a few successful cases have been reported. In this talk, the successful realization of anode-supported TF-SOFC by means of multi-scale architecture will be introduced. The multi-scale architecture of the TF-SOFC not only enables to reliably implement thin-film electrolytes and nanostructure electrodes to SOFCs; but also secures the thermomechanical stability of TF-SOFC. The ultimate level of the low-temperature performance and significantly improved thermomechanical stability of the multi-scale architectured anode-supported TF-SOFC will be presented.

3:50 PM

(ICACC-S3-022-2014) The Eneramic® Power Generator – A Reliable Fuel Cell Battery Hybrid System for Off-grid Power Supply

A. Poenicke*, S. Reuber, C. Wunderlich, A. Michaelis, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

Off-grid power generation is considered as an attractive market for fuel cells. For this purpose, a compact SOFC battery hybrid system was developed that operates on commercially available fuels. Due to its progressive thermal packaging, the mobile prototype achieves a net efficiency of 22 % using commercial balance of plant components. By direct preheating of the SOFC stack with start burner off-gas it was possible to reduce the cold start time of the system. Thus, this SOFC system is designed for frequent start-up and cycling capability. In consequence the planar SOFC stack was tested with rapid heating rates up to 20 K/min in furnace and hotbox environment. The power degradation caused by system cycling is less than 0.1 % per cycle. Finally, the optimization of stack temperature conditions has improved the lifetime of the SOFC stack significantly.

4:10 PM

(ICACC-S3-023-2014) Portable solid oxide fuel cells (SOFCs) and holder operated with biofuel

M. Chen*, U. Cheong, W. J. Wei, National Taiwan University, Taiwan

Solid oxide cell stacks sealed with glass consist of channels for air and fuel, and sufficiently supply a power (ca. 60 W) sustainable for the heating of Intermediate Temperature (IT)-SOFC by using various hydrocarbon biofuels. The insulation materials, including high alumina and SiC castables, ceramic blanket were chosen due to their moldability, thermal resistance, and low pollution. Their thermal conductivities and early fracture strength have been measured in the range of 0.2 to 0.51 W/mK and about 3 MPa, respectively, between 373 K and 973 K. The heated cells and cell holder are also analyzed by thermal imager, and comparing to the simulated results of temperature distributions and thermal stress by ANSYS©13.0 software.

4:30 PM

(ICACC-S3-024-2014) Fabrication and characterization of a micro-reformer unit fully integrated in silicon for ethanol conversion

D. Pla, IREC, Spain; N. Jiménez, INTE-UPC, Spain; M. Salleras, IMB-CNM, CSIC, Spain; I. Garbayo, G. Gadea-Diez, A. Morata, IREC, Spain; N. Sabaté, IMB-CNM, CSIC, Spain; J. Llorca, INTE-UPC, Spain; A. Tarancón*, IREC, Spain

This work reports the design, manufacturing and experimental results of a micro-reformer for hydrogen-rich gas generation from ethanol liquid for portable-solid oxide fuel cell (SOFC) feeding. The reformer has been designed as a silicon micro monolithic substrate compatible with the mainstream microelectronics fabrication technologies (photolithography, wet etching, chemical vapor deposition and reactive ion etching). Design and geometry of the system have been optimized for minimizing heat losses in order to satisfy the high temperature requirements of the reforming process. The current design has dimensions of 15x15 mm2 in area, 500µm in thickness and an effective reactive area of more than 36 cm2 which consists of an array of more than 4.6x104 vertical micro channels perfectly aligned (50µm diameter) and an integrated serpentine tungsten (W) heater. These micro channels have been coated with a noble metal-based catalyst for the reforming. The micro-reformer has been successfully tested under diluted feed conditions at the 600-800°C temperature range – optimal operation temperatures for SOFCs - achieving high specific hydrogen production rates, high ethanol conversions (>80%) and adequate selectivity profiles. This functional converter is the basis for a complete gas processing unit as a subsystem of an entire micro-SOFC system.

4:50 PM

(ICACC-S3-025-2014) Performance of Ni-based Anode Supported SOFCs with Doped Ceria Electrolyte at Low Temperatures (300~550°C)

T. Suzuki*, B. Liang, T. Yamaguchi, H. Sumi, K. Hamamoto, Y. Fujishiro, National Institute of Advanced Industrial Science and Technology, Japan; N. Sammes, POSTECH, Republic of Korea

The performance of a conventional anode supported micro-tubular SOFC using doped ceria as an electrolyte and Ni-based cermet as an anode is evaluated at low operating temperatures between 294-544 °C. OCVs of over 0.9V are obtained at all measured operating temperatures, and power generation is observed as low as 294°C. The power density of the cell is 0.6 $\mathrm{Wcm^{-2}}$ at 544 °C operating temperature with 47 % fuel utilization, and is 5 mW $\mathrm{cm^{-2}}$ at 294°C operating temperature with an open circuit voltage of 0.95 V. According to impedance spectroscopy, stronger influence of gas flow rates on the cell performance is observed at higher operating temperature.

5:10 PM

(ICACC-S3-026-2014) Adjustment of process parameters for attaining a dense gadolinium-doped ceria layer for production of microtubular SOFC cells

K. M. Paciejewska*, S. Kuehn, S. Mnich, eZelleron GmbH, Germany

Target of the experimental investigations presented here was the development of a dense barrier layer for microtubular SOFC from a commercially available gadolinium-doped ceria (GDC20) powder. The preparation of suspensions as well as the process of sintering was adjusted. The results show that, besides the colloidal stability, the width of the particle size distribution (PSD) plays a key role. Two methods were applied: grinding and centrifugation for achieving a narrow PSD width. As a result, the particles could be sintered together at 1400°C. In contrast, the powder only dispersed by ultrasonic dissolver revealed a porous layer even at 1600°C. Furthermore, experiments at the sintering process were performed, which show that not only temperature and sinter time, but also temperature gradient and partial steps of sintering are of big importance for a consistent consolidation and small grain size.

5:30 PM

(ICACC-S3-027-2014) Extrusion and optimization of carbon resistant tubular IT-SOFCs

A. Azzolini*, V. M. Sglavo, Università di Trento, Italy

Extrusion is a fast and reliable way to shape moldable pastes into long tubes with constant cross section. This technique is applied to the fabrication of the anode layer of small tubular SOFC. In this work the composition and preparation of pastes for the extrusion, the deposition via dip-coating of electrolytic layer and co-sintering of the anode supported half cell have been optimized. Considering that the cell is to be operated at IT (700°C) and to be fed with methane or light hydrocarbons, 10mol% gadolinia doped ceria ceramic powder (CGO10) was employed as ionic conductive phase in both layers. To avoid carbon deposition, copper was chosen as the electronic conductive phase in the anode. To match the firing treatments for the co-extruded half-cell, and to avoid the phase separation of copper oxide, lithium and cobalt oxides were added to the electrolyte as a sintering aids. The anode was extruded in tubular shape through a ram extruder connected to a Material Testing System to optimize paste properties. The electrolytic layer was deposited on the tubes surface via dip-coating in a slurry containing CGO10 powder and an organic vehicle. The half cells were then sintered for 3 hours at 1100°C obtaining tubes measuring 4mm of external diameter, constant wall thickness of 300um and dense electrolytic layers of 15um. The anode showed tailored porosity and evidence of a well connected and extended triple phase .

S4: Armor Ceramics

Testing and Evaluation / Materials Characterization / Quasi-Static and Dynamic Behavior II

Room: Coquina Salon E

Session Chair: Matthew Bratcher, U.S. Army Research Laboratory

1:20 PM

(ICACC-S4-041-2014) Design of Ballistic Resistance Nano Ceramic-Plastic Composites

N. R. Bose*, D. Sanyal, Central Glass & Ceramic Research Institute, India

Researchers all over the world are developing various ballistic resistance armor for the protection of human lives and vehicles. The weight and stiffness of rifle armor is a major technical challenge. The density, hardness and impact toughness are among the materials properties that are to be balanced in the design systems. In this paper the authors have highlighted the design of ballistic resistance multilayers advanced fibre reinforced nano ceramic-plastic composite by adopting novel sol-gel derived method and calendaring fabrication techniques. The total system is based on four layers of advanced level different composite panels. The first layer (bullet striking plate) of 6 mm thick was made by sol-gel derived nano ceramic composite (zirconia nano fibre reinforced silicon carbide) using zirconium oxychloride, phenolic resin, and tetraethyl orthosilicate. The second layer of 12 mm thick was made with multiple ply of glass cloth reinforced epoxy composite. The third layer of 8 mm thick was made with nylon fabric reinforced geopolymer based composite embedded in elastomeric hot melt compound. The fourth layer of 10 mm thick was made with polycarbonate sheet. This multilayered advanced nano ceramic-plastic composite panels of 36 mm thick have been specially made for testing against high velocity bullet.

1:40 PM

(ICACC-S4-042-2014) Effect of novel geometric designs on the performance of ceramics against projectile impact

P. Karandikar*, M. Aghajanian, B. Givens, A. Liszkiewicz, S. Wong, M Cubed Technologies, Inc., USA

Standard armor tiles have smooth or solid front and back surfaces. One key shortcoming of ceramics used in armor is their low toughness, resultant damage after first impact, and the effect of this damage on performance against subsequent impacts (multi-hit capability). The poor multi-hit capability of ceramics has limited their use in armor to a mosaic of small tiles. In metallic armor, e.g. steel-based P-900, it has been shown that incorporating perforations and angled perforations enhances performance on projectile impact. Such geometric designs or features could have different effects on the ballistic performance of ceramics under single and multiple impacts. The key objective of this study was to assess how such geometric features affect ballistic performance of ceramics under the first impact. To this end, systematic sets of ceramic tiles (100 x 100 mm) were made with various geometric features such as perforations, blind perforations, knobs, and cones on the front and the back. These tiles were backed with ultrahigh molecular weight polyethylene. These were subsequently impacted with an armor piercing projectile to measure V50 per the MIL Standard 662. The normalized V50s were compared to assess the effect of these geometric features on the performance during the first impact.

2:00 PM

(ICACC-S4-043-2014) Ceramic Matrix Composite Enhanced Armor Structures

A. Fortini, J. Stiglich*, Ultramet, USA

This presentation will describe prototype ballistic testing of ceramic matrix composites (CMC's) as an important component of a ballistic protection structure. The carbon fiber reinforcements are available in 2D and 3D structures developed for high temperature aerospace applications. Matrix examples include SiC, ZrC,TiB2, and alloys of these compounds. Both flat and curved shapes have been developed. The SiC matrix CMC's have been tested with SiC strike plates against 0.30 cal/7.62 mm APM2 projectiles at 2800 to 2900fps in prototype ballistic experiments. Initial results showed projectile defeat at areal densities between pure SiC and pure B4C. Ballistic tests and data will be presented. Extensions of this technology could include a B4C strike face and/or a B4C matrix to lower the areal density to below that of pure B4C.

2:20 PM

(ICACC-S4-044-2014) Testing method for ceramic armor and bare ceramic tiles

E. Carton*, G. Roebroeks, TNO, Netherlands

TNO has developed an alternative, more accurate and more configuration independent ceramic test method compared to the standard DoP-test method. In this new method ceramic tiles and ceramic based armor are tested as target without a semi-infinite backing layer. An energy approach is chosen to evaluate and rank the target materials penetration resistance. By measuring the armor materials energy absorption, by subtracting the residual projectile energy after penetration from the projectile energy before impact, an independent performance parameter for the ceramic or ceramic based armor has been obtained. This parameter is still related to the specific projectile used in the test. The presented alternative testing method for ceramic based armor uses a high speed camera technique to determine residual velocity of target material fragments and of projectile remains. The residual mass of the projectile is determined, capturing the penetrated projectile (and ceramic fragments) in a water basin. Investigation of the projectile remains after the impact event, provides valuable information on the two projectile to target interaction stages; dwell and penetration. The test method and analysis method is described in this paper. Results on bare ceramic and ceramic based armor samples are presented and discussed.

2:40 PM

(ICACC-S4-045-2014) Flash X-ray cinematography analysis of the interaction of small caliber projectiles with different types of SiC ceramics

E. Strassburger*, S. Bauer, Fraunhofer EMI, Germany; S. Weber, DLR Institute of Structures and Design, Germany

In order to improve the performance of ceramic composite armor it is essential to know the mechanisms during each phase of the projectile/target interaction and their influence on the penetration resistance. A flash X-ray imaging method has been developed at EMI, which provides up to eight flash radiographs in one experiment. A multi-anode flash X-ray tube is utilized with this method, and the fluorescent image of the transmitted radiation is photographed by means of a high-speed digital camera. This technique has been applied to visualize and analyze the penetration of 7.62 mm AP projectiles into three different types of SiC ceramics. Two commercial SiC grades and one type of C-SiSiC ceramics, developed by DLR, have been studied. The influences, not only of the ceramic but also the backing material, on dwell time and projectile erosion have been studied. Penetration curves have been determined and their relevance to the ballistic resistance is being discussed.

3:20 PM

(ICACC-S4-046-2014) Surface constraint effects on ceramic ballistic performance

J. McDonald, S. Satapathy*, U.S. Army Research Lab, USA

Ceramics used for ballistic applications possess low tensile strength that leads to extensive cracking, which in turn leads to lower penetration resistance. The tensile stress state results from the radially expanding stress wave from projectile tip that causes tension in the hoop direction, and also arises from interaction of reflected compressive waves from free surfaces or interfaces with lower impedance. Another source of tensile stress is the surface wave expanding radially from the point of impact. By applying various surface constraints that may or may not introduce prestress in the ceramic, these cracks can be suppressed or delayed. We are exploring the effects of surface pressure and surface impedance change on wave propagation and crack-suppression in ceramics. Analytical and numerical treatment of surface constraint effects will be presented. New computational techniques to represent crack induced anisotropy and to represent surface constraint induced wave propagation will be discussed.

3:40 PM

(ICACC-S4-047-2014) Properties and Performance of Cubic-Boron Nitride

J. Swab*, E. Wilson, L. Vargas, E. Warner, Army Research Laboratory, USA

Cubic-Boron Nitride (CBN) is a lightweight ($\rho = 3.45$ g/cm3) ceramic material that is harder than all materials except diamond. Since harder ceramics tend to perform better as armor this material is of interest to the military community. C-BN is synthetically produced and is primarily used as an abrasive and in cutting tool applications. It is difficult to make in large sizes needed for armor applications or even sizes sufficient to determine basic mechanical properties. However, disks of CBN nominally 97 mm in diameter with thicknesses between 2.3 and 6.4 mm have recently been obtained. The properties (elastic modulus, strength, toughness, hardness, etc) and ballistic performance of this material were determined and compared to a commercially-available armor-grade boron carbide (B4C).

4:00 PM

(ICACC-S4-048-2014) Influence of the Crystal Structure on the Performance of Single Crystalline Transparent Armor

A. Krell*, Fraunhofer IKTS, Germany; E. Strassburger, Fraunhofer EMI, Germany

The surprising ballistic weakness of sapphire in all investigated orientations compared not only to sub-μm Al2O3 but also with reference to transparent spinel ceramics (with lower Young's modulus, hardness, and strength) was recently explained by records of the different dynamic fragmentation of these materials, and it was speculated that the reason of this difference could be the extreme fracture anisotropy of sapphire. This hypothesis was confirmed now by tests with single crystalline magnesium aluminate spinel which was investigated as an example of a cubic and, therefore, more isotropic material: In depth-of-penetration tests with different backings these cubic single crystals outperformed not only sapphire but exhibited an even higher ballistic stability (a smaller depth-of-penetration in the backing behind front-tiles of equal areal weight) than all investigated polycrystalline spinel ceramics with different grain sizes (ranging from 0.35 to ~75 μm). In fact, the mass efficiency of the spinel single crystals was on the same level as that of corundum ceramics with grain sizes < 10 μm. Therefore, the beneficial performance of cubic crystals provide experimental evidence that the lower ballistic strength of sapphire is a consequence of the fracture anisotropy of its lattice and does not represent a general shortcoming of single crystals vs polycrystalline ceramics.

4:20 PM

(ICACC-S4-049-2014) Analysis of the Fragmentation of AlON and Three MgAl2O4 Spinels under Ballistic Impact

E. Strassburger, M. Hunzinger, U.S. Army Research Laboratory, USA;
P. Patel, Fraunhofer Institute for High-Speed Dynamics, Germany;
J. W. McCauley*, U.S. Army Research Laboratory, USA

Systematic ceramic studies have shown that the fragmentation mode is one of the key factors influencing their ballistic resistance. In this study, the fragmentation of AlON and three types of spinels were analyzed: spinels with average grain sizes 0.6 μm and 1.6 μm and a bi-modal grain size spinel with 250 μm grains in a fine grain (5-20 μm) matrix. Test plates of the fine grain spinels (90 x 90 x 5.7 mm) and bi-modal spinel and AlON (100 x100 x 6 mm) were impacted with armor piercing 7.62 mm projectiles at 850 m/s and 1100 m/s velocities. The targets were integrated into a target box, which allowed for an almost complete recovery and analysis of the ceramic fragments. High-speed cameras were applied in order to visualize the different phases of impact and fragment formation. A significant difference in the fragment size distributions of bi-modal spinel and AlON was observed.

4:40 PM

(ICACC-S4-050-2014) Ballistic damage of alumina ceramics – learning from fragments

H. Wu*, S. Ghosh, Loughborough University, United Kingdom; C. Dancer, University of Warwick, United Kingdom; R. Todd, University of Oxford, United Kingdom

We have used transmission electron microscopy (TEM), optical luminescence spectroscopy (OLS) and scanning electron microscopy (SEM) to study the characteristics of the surfaces of alumina ceramic fragments generated by ballistic impact. The identified characteristics - transgranular fracture, intergranular fracture, plastic deformation and microcracking – showed a strong association with the sizes of fragments. Collected fragments with different sizes were quantitatively mapped against these characteristics, and transition points can be distinguished from such mapping. To understand the experimental results, a cavity model is adapted to describe the ballistic impact, and the estimated transient stresses and strain rates around a cavity are used to quantitatively predict the contribution of the observed fracture characteristics on the size of fragments, based on Grandy's model for fragmentation. This study demonstrates that information on fragments at different length scales can be informative for understanding the ballistic damage of ceramics.

5:00 PM

(ICACC-S4-051-2014) Evaluating the Rock Strike Resistance of Transparent Armor Materials

B. S. Aldinger*, Ibis Tek, LLC, USA

An alarmingly large percentage of historical transparent armor replacements were due to damage from rock strike impacts. Consequently, rock strike resistance (RSR) has become an increasingly common feature of transparent armor designs and is required for many programs. In order to assess the factors contributing to RSR, three test methods were first evaluated: ballistic aluminum projectile, ballistic ceramic ball, and dropped aluminum indenter, with the latter method being the most reproducible. A standard laminate was then designed and various strike face materials were used to create test samples. By varying the impact energy, an "E50" could be calculated at which 50% of test samples were damaged. Strike face thickness, material, and overall laminate thickness each affected the E50 and the observed failure modes. Some of the best properties for increased RSR were found to be contrary to common design practices for transparent armor laminates.

S7: 8th International Symposium on Nanostructured Materials and Nanocomposites

Nanodevices and Application of Nanomaterials

Room: Coquina Salon B

Session Chair: Hidehiro Kamiya, Tokyo University of Agriculture and Technology

1:30 PM

(ICACC-S7-040-2014) Sol-Gel and Transfer Technique for Preparing Ceramic Thin Films on Plastics (Invited)

H. Kozuka*, T. Fukui, M. Takahashi, H. Uchiyama, S. Tuboi, Kansai University, Japan

Techniques for preparing ceramic thin films on plastics are strongly demanded by those who target flexible electronic devices or aim at replacing glass substrates by lightweight plastic substrates. Performances of ceramic thin films emerge, in general, in their highly crystalline states with low porosities. However, crystallization and densification are driven at high temperatures where plastics cannot survive. This is why great efforts have been made so far on low-temperature processing. We have proposed a totally different technique, where a "firing" step guarantees the crystallization and densification of films. The technique comprises (i) the deposition of a gel film on a release layer on a silicon substrate, and (ii) the transfer of the fired film onto plastics. The transfer is conducted by melting the plastics surface, which can be realized by heating the plastics/ceramic-film/release-layer/silicon stack from the silicon substrate side. Ceramic thin films thus fabricated on plastics are crack-free and transparent. Anatase thin films with high reflectivity, ITO thin films with electrical conductivity, and ZnO thin films with (002) orientation were realized on plastics. Patterned ITO thin films could also be prepared on plastics simply by using a mother silicon substrate with periodic trenches. Dual patterning with alternating ITO and ZnO ribbons was also possible.

2:00 PM

(ICACC-S7-041-2014) Chemical Processing of Barium Titanate Thin Films by Hybrid-Integration (Invited)

H. Suzuki*, N. Sakamoto, N. Wakiya, Shizuoka University, Japan; T. Ohno, T. Matsuda, Kitami Institute of Technology, Japan

Barium titanate (BT) is a typical ferroelectric material and exhibits many excellent electrical properties. Barium titanate thin film is also used as a dielectric thin film for MLCC. However, BT thin films show relatively low dielectric and piezoelectric properties as well as a low Curie temperature. In this study, we deposited BT thin films with different orientations from molecular-designed precursor solutions on different substrates. As a result, electrical properties of the resulting ferroelectric BT thin films dramatically changed by the substrates and molecular-design, to show high dielectricity of about 1000 and Curie temperature by the film orientation and residual stress.

2:30 PM

(ICACC-S7-042-2014) Processing of nanostructured zirconia based ceramics: The art of the possible

K. Annapoorani*, S. Saremi, S. Huang, B. Vaidhyanathan, J. Binner, Loughborough University, United Kingdom

The processing of nanocrystalline ceramic powders into engineering components has been investigated via a series of research projects each focusing on a different stage of the manufacturing route viz., (i) the ability to control the agglomerates present in the powder resulting in the production of a free-flowing and crushable powder for die pressing, (ii) the formation of a low viscosity but high solids content suspensions suitable for slip casting & screen printing and (iii) the use of pressureless microwave-hybrid processing techniques. This holistic approach helped to transfer the developments achieved in each stage of the manufacturing process to the next and resulted in the ability to form fully dense ceramic components whilst restricting the grain growth to a minimum. The methodology has been employed to develop nanostructured zirconia based ceramic components exhibiting vastly superior hydrothermal ageing resistance suitable for use in petro-chemical valves, bio-medical implants and SOFC systems as well as for ballistic armour applications. These novel advancements are covered by a series of patents and papers and this talk will provide an overview of some of these developments.

2:50 PM

(ICACC-S7-043-2014) Dependence of NiO Dissolution in Yttria-Stabilized Zirconia on Particle Growth During Calcination

A. Morrissey*, J. Tong, B. P. Gorman, I. E. Reimanis, Colorado School of Mines, USA

It is critical to understand the distribution of Ni^{2+} ions in NiO-doped 10YSZ powders as it determines the subsequent microstructure evolution, and ultimately, the electrical and mechanical properties for a variety of applications. The distribution of Ni^{2+} ions in NiO-doped 10YSZ powder is examined with SQUID magnetometry, a technique that is highly sensitive to distinguish between randomly distributed Ni^{2+} ions in solid solution and ordered Ni^{2+} ions within NiO. High purity powders containing 0.01, 0.1, 0.5, and 1.0 molar percent NiO in 10YSZ (all concentrations below the solid solubility limit of NiO in 10YSZ) were made by a novel technique in which acetate precursors were used in a modified EDTA (ethylenediaminetetraacetic acid)-citrate synthesis method. The powders were calcined in air at either 873 K or 1273 K. The 873 K calcination leads to single phase nanoscale 10YSZ particles with NiO existing in complete solid solution. The 1273 K calcination produces a larger particle size, and leads to the formation of NiO particles; the amount of NiO depends upon the length of calcination time. Upon sintering the powders in air at 1773 K, the NiO dissolves back into 10YSZ. The results demonstrate that particle growth during calcination leads to the exsolution of Ni^{2+} ions to form NiO. This has important implications for the synthesis of NiO-doped 10YSZ from chemical precursors.

Synthesis and Application of Nanomaterials

Room: Coquina Salon B
Session Chairs: Johan ten Elshof, University of Twente; Xavier Obradors, ICMAB - CSIC

3:20 PM

(ICACC-S7-044-2014) Langmuir-Blodgett Films of 2D Oxide Nanosheets as Seed Layer for Oriented Growth of Functional Oxides on Si (Invited)

J. E. ten Elshof*, University of Twente, Netherlands

Oxide nanosheets are the oxide equivalents of graphene. They have a thickness of ~1 nm and can have lateral sizes up to tens of micrometers. They are made by exfoliation of layered oxides in aqueous solution using an ion exchange process. The resulting colloidal nanosheets are single-crystalline. Langmuir-Blodgett films of nanosheets can be used as textured crystalline templates onto which epitaxial oxides can be grown. We studied the mechanism of exfoliation and restacking of lepidocrocite-type titanates into Ti0.87O2 nanosheets in solution by small angle x-ray scattering, and developed a new method to monitor the kinetics of exfoliation by differential scanning calorimetry. The conditions for Langmuir-Blodgett (LB) deposition of nanosheets to >99% monolayer coverage on glass and silicon were optimized. SrRuO3 films were grown on Ca2Nb3O10 and Ti0.87O2 nanosheet films by pulsed laser deposition. SrRuO3 is ferromagnetic below 160 K and shows strong magnetic anisotropy. Depending on nature of the seed layer, [001] oriented films grew on Ca2Nb3O10, and [110] oriented films on Ti0.87O2. The influence of the seed layer on magnetization and Curie temperature is discussed.

3:50 PM

(ICACC-S7-045-2014) Chemical solution based synthesis and deposition of nano metal oxides (Invited)

A. Hardy*, M. Van Bael, Hasselt University, Institute for Materials Research, Inorganic and Physical Chemistry, Belgium

Metal oxides find applications in various fields including oxide electronics, energy generation and storage, health care etc. Often nanosizing of the oxide, has been found to lead to improved functionality. For nanometal oxides, a vast amount of synthesis routes are reported. Among these, wet chemical routes, have several advantages e.g. low cost apparatus, short synthesis times and compositional flexibility. Here, recent results are presented concerning wet chemical synthesis of metal oxide nanoparticles and thin films by means of sol-gel, hydro/solvothermal and thermal decomposition syntheses. In depth understanding of the precursor and synthesis mechanisms, as well as their effects on the final nano oxide's properties, is obtained by applying a wide range of characterizations including XRD, SEM, AFM, FTIR, Raman, UV/Vis and NMR spectroscopy, high resolution TEM, as well as physical characterization. This will be exemplified by studies of (doped) mono-metal oxides (e.g. ZnO, TiO2, VOx) and multi-metal oxides (high-k oxides, multiferroics, ferroelectrics, electrodes and electrolytes for LIB etc.) with possible applications in solar cells, data storage devices, lithium ion batteries etc. Based on these fundamental studies, insights are obtained that allow selection of process-material combinations with high potential towards industrial upscaling and final applications.

4:20 PM

(ICACC-S7-046-2014) Optimization of Aerogels for Use at High Temperatures

F. Hurwitz*, NASA Glenn Research Center, USA

Aerogels are highly insulating due to their mesoporous structure and high surface area, which inhibit gas convection and provide a tortuous path for solid conduction. Widely used silica aerogels are excellent thermal insulators to temperatures of up to 700C. At higher temperatures, silica aerogels begin to densify, and their thermal conductivity increases. Work at NASA Glenn Research Center has led to the development of a family of alumina, Aluminosilicate and titania aerogels which maintain a mesoporous structure to temperatures up to 1200C. The work includes a comparison of synthesis methods and compositions optimized to inhibit sintering to high temperatures, and reports thermal performace of composites utilizing these high temperature aerogels.

4:40 PM

(ICACC-S7-047-2014) BMT, a UHT Oxide Ceramic for Hypersonic Applications

S. Venugopal*, S. Hammouche, B. Vaidhyanathan, J. Binner, Loughborough university, United Kingdom

Current state of the art TPS systems are composed of diboride materials used either as monoliths or as reinforcements with C or SiC matrix can withstand very high temperatures of over 2500oC. However any non-oxide material is prone to oxidation. Whilst a material gets oxidised, due to the direct factors such as atmosphere and temperature, the repercussions including CTE mismatch and phase transformations and the associated volume changes result in porous oxide scales and contribute to severe stresses, loss of structures and further oxidation. The use of oxide materials as TPS also possess some challenge due to the phase transformation at higher temperatures, low fracture toughness, poor thermal shock resistance and low thermal conductivity. However, an oxide ceramic, barium magnesium tantalate (BMT, Ba3MgTa2O9) with a melting point of ~3000°C, has been identified as a promising oxide UHTC for aerospace applications. Nanostructured barium magnesium tantalate (BMT) has been prepared by sol-gel route and sintered. The high-temperature ablation resistance of the sintered pellets was studied using a purpose built oxyacetylene test facility at temperatures above 2500°C in neutral, reducing and oxidising environment, achieved by varying the gas flow rate. The thermal and mechanical properties of BMT have also been investigated for the first time with a view to evaluating the material for UHT applications.

5:00 PM

(ICACC-S7-048-2014) Synthesis, characterization and catalytic effect of zinc oxide nanoparticles

M. Öner*, B. Akin, Yildiz Technical University, Turkey

The synthesis of ZnO nanocrystals have attracted much attention due to the their morphology dependent properties and potential applications in many areas including transparent electronics, piezoelectric devices, chemical sensors, catalysts, pigments, varistors, solar cells and gas sensors. Numerous chemical strategies have been reported to synthesize ZnO crystals including controlled precipitation, hydrothermal and solvothermal methods, sol–gel, thermal decomposition of precursors, laser ablation, spray pyrolysis and microemulsion. However, precise control of over ZnO crystal synthesis remains a big challenge. Here, we report results of the synthesis and catalytic properties of various ZnO crystals. A solution chemistry based method was used to obtain ZnO nanocrystals. Effect of various parameters, including the temperature, solution composition and the concentration of water-soluble biopolymer carboxymethyl inulin (CMI) on the morphology, surface area, particle size and size distribution of zinc oxide were studied. The mean crystal sizes and other structural properties were investigated using by X-ray diffraction (XRD), FTIR, TGA/DTA, BET, SEM and particle sizer. The catalytic effect of the obtained ZnO crystals is elucidated in order to get suitable catalyst for 2-propanol dehydrogenation. It was found that the ZnO particles exhibited selectivity and activity for 2-propanol dehydrogenation.

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

Novel Sintering & Forming II; Additive Manufacturing, etc

Room: Coquina Salon A
Session Chairs: M. Singh, OAI/NASA GRC; Hai-Doo Kim, KIMS

1:30 PM

(ICACC-S8-036-2014) Additive Manufacturing of Ceramic Matrix Composites: Technical Challenges and Opportunities (Invited)

M. Singh*, Ohio Aerospace Institute, USA; M. Halbig, NASA Glenn Research Center, USA

Ceramic matrix composites are currently being developed and tested for a number of high temperature applications. Majority of these composites are being fabricated using processes which require extensive manual labor in various manufacturing steps (cutting and hand lay-up of preforms, composite fabrication, machining, etc) leading to high cost. Additive manufacturing (AM) approaches could provide cost-effective route and further speed-up their implementation. However, additive manufacturing, while well developed for polymers and metallic systems, is still in infancy for ceramic systems. In this study, we tried to develop materials and optimize parameters for Laminated Object Manufacturing of silicon carbide matrix composites (SiC/SiC). The carbonaceous polymer mixtures consisting of various SiC, Si, and C particulates along with additives were evaluated as prepreg materials. These materials were characterized using thermogravimetric analysis (TGA) and furnace heat treatments up to 1450°C. Laser cutting parameters were investigated for cutting SiC fibers and fiber prepregs at varying laser speeds and power and with the use of an Argon purge. Analysis of the heat affected zone was conducted through Scanning Electron Microscopy (SEM) to optimize cutting parameters. Various technical challenges and opportunities in additive manufacturing for ceramic matrix composites are presented.

2:00 PM

(ICACC-S8-037-2014) Manufacture of Functional Ceramic Nanopowders by Thermal Decomposition of Metal-Alginate Gel Structures (Invited)

G. M. Kale*, Z. Wang, M. Ghadiri, University of Leeds, United Kingdom

A novel and generic sol-gel method has been developed for manufacturing of a wide variety of high-purity metal oxide nanopowders and their solid state solutions, such as NiO, CoO, CuO, Fe2O3, CeO2(Gd2O3), ZrO2, Y2O3 and Y2O3-stabilised ZrO2. Sodium alginate or alginic acid is firstly used to produce a gel by ion exchange with an aqueous solution of a soluble metal salt, following which the gel is dried and thermally decomposed to produce nanopowders of the relevant metal oxides. By the virtue of the gel structure, the metal ions become immobile and cannot readily move close to each other, hence the possibility of producing nano-particles. Particle sizes of approximately 10-50 nm can be produced after calcination at a temperature range that is much lower than the conventional methods (i.e. 400-700 °C instead of well above 1500 °C). Powder X-ray diffraction (XRD) indicates perfect structures with no trace of impurity, and the calcination temperature controls the particle size.

2:30 PM

(ICACC-S8-038-2014) Fabrication of Bioceramics Implants by Stereolithography of Three Dimensional Printing

S. Kirihara*, Osaka University, Japan

Artificial bones of hydroxyapatite (HAP) and beta-tricalcium phosphate (β-TCP) scaffolds with dendritic lattice structures were modeled successfully to realize excellent biological compatibilities. Ordered porous structures were processed by stereolithography of a three dimensional printing system. The ceramics rods from 200 to 300 μm in diameters were arranged periodically to create lattice arrangements with four coordination number, and these aspect ratios were modulated continuously to realize biomimetic graded structures. The HAP and β-TCP particles of 10 μm in average diameter were dispersed into photo sensitive acrylic resins at 50 volume %, and the slurry were spread on a metal substrate with 50 μm in layer thickness by a mechanical knife edge. An ultraviolet laser beam of 355 nm in wavelength was scanned on the slurry surface to create cross sectional images. The solid micro structures were built by stacking the cross sections, and the formed objects were dewaxed and sintered at 600 and 1250 °C for 2 hs in the air atmosphere. The fine HAP and β-TCP microstructures of 98 % in relative density without cracks or pores were observed by a scanning electron microscopy. These successfully manufactured artificial bones and strictly designed bioscaffold structures can be expect to realize appropriate biochemical reactions and living fluid circulations in the near future tissue engineering.

3:10 PM

(ICACC-S8-039-2014) Additive Manufacturing: Interaction of Laser Light with Ceramic Powders

T. Muehler*, J. Günster, J. G. Heinrich, TU Clausthal, Germany

For selective laser sintering of ceramic powders a clear understanding of the coupling between laser light and ceramic powder is mandatory. For applications, such as additive manufacturing, laser energy should be equally distributed in a certain volume of the powder to initiate sintering. In a systematic study the interaction between light and ceramic powders as a function of the particle size (50nm – 10μm) has been investigated. As a model material high purity amorphous silica has been chosen. The measured wavelength range is 190 nm - 2500 nm, the main focused wavelengths are 1,07 μm and 1,95 μm, which are the wavelengths that common fiber lasers are emitting. For selective laser sintering, ideally the light penetrates into the powder compact, is absorbed in a defined volume element and can initiate local sintering. Powder compacts prepared with particle sizes significantly larger than the wavelengths do reflect almost 100% of the laser light, even though the individual particles are transparent. Thus, the laser light does not couple to such powder compacts and no energy is transferred into the powder volume. For particle sizes much less then the laser wavelength the powder compact becomes transparent. By addition of light absorbing materials the absorption and reflection capacity of powder compacts can by tuned and generates a homogenous heat introduction into the volume.

3:30 PM

(ICACC-S8-040-2014) A Novel Additive Manufacturing Technology for High-Performance Ceramics

J. Homa*, M. Schwentenwein, Lithoz GmbH, Austria

While Additive Manufacturing (AM)-technologies are already state-of-the-art in plastics processing or metalworking, the ceramic industry has been reluctant to implement this kind of technology due to insufficient quality of the parts produced by this means. Additive manufactured ceramics used to lack essential material properties such as density or strength, which hindered the application of such parts as technical ceramics. In this paper a new AM-technology, the Lithography-based Ceramic Manufacturing (LCM)-process, is presented. This technique is based on the selective curing of a photosensitive slurry by a mask exposure process. During the structuring, a photopolymer matrix is generated, which temporarily acts as scaffold and binder for the ceramic particles and is later on removed at elevated temperatures. Due to this approach, this novel technique achieves high green densities and thus, enables the production of strong, dense and accurate ceramic parts without any geometrical limitations. The parts produced using this technology have very similar mechanical properties as classical formed ceramic parts; for alumina a theoretical density of over 99.3 % and biaxial strength of over 500 MPa has already been realized. These characteristics render the LCM-process an innovative and capable production method, especially in the case of complex shaped structures, customized parts or small series production.

3:50 PM

(ICACC-S8-041-2014) Powder bed stabilization for powder-based additive manufacturing

A. Zocca*, C. M. Gomes, J. Guenster, BAM, Federal Institute for Materials Research and Testing, Germany

Many of the most successful and precise additive manufacturing technologies, such as the "powder-based three-dimensional printing" and the "selective laser sintering/melting (SLS/SLM)" are based on the deposition layer-by-layer of a flowable powder. The deposition of new layers is usually carried out by means of a roller or of a doctor blade, which causes a lateral force often resulting in the displacement of the part. Therefore, support structures are normally built along with the part to prevent this shifting. The buildup of these support structures consumes processing time and material, while their removal requires an additional process step. Especially in the case of SLS/SLM, the tight fixation by a support structure causes also internal stresses that potentially can deform the component. Furthermore the layer deposition strictly requires a flowable powder, which in turn restricts its particle size to a certain minimum processable size. A novel, easy and economic approach for the stabilization of the powder bed will be presented, which allows the production of ceramic and metallic parts without the use of a support structure. The preliminary results based on this set-up will be discussed, together with some case studies on different well-flowable and non-flowable powders. Indications of possible further advantages and drawbacks will be also given.

4:10 PM

(ICACC-S8-042-2014) Characterization of defects in 3D Inkjet Printed ceramic structures by high-resolution X-ray tomography

Y. Liu*, T. Wang, R. Bradley, B. Derby, University of Manchester, United Kingdom

The aim of this study is to understand and control the formation of defects in 3D inkjet printed ceramic structures by investigating the relationship among the defects generated in the ceramic structures, the printing parameters and ink composition. ZrO_2 inks have been printed using a laboratory scale MPP1000 Inkjet printer. Surface defects in a range of length scales from the powder size (20nm) to the inkjet drop diameter (100μm) have been studied through optical phase contrast microscopy (PCM) and scanning electron microscopy (SEM). The internal defects and 3D structure of the printed ceramics were characterised using high-resolution X-ray micro-tomography. Coffee staining phenomenon, which appears during the drying process of the printed drops, has been observed and can be controlled through using different solvents and solvent mixtures for the ink. It is clear that missing drops and overlaps between printed lines during printing mainly cause the surface defects. Internal defects of 1μm-10μm size and cracks have been observed in the printed ceramic volumes. Finally, the influences of solvents, droplet spacing and other printing parameters on the final defects have been studied.

4:30 PM

(ICACC-S8-043-2014) Implementing spiral architectures in TiB_2-SiC ceramics for the evaluation of mechanical properties

A. Els*, J. Watts, G. Hilmas, W. Fahrenholtz, Missouri University of Science & Technology, USA

Titanium diboride (TiB_2) is a ceramic with good chemical stability, high hardness and high fracture toughness, but is subject to microcracking from residual stresses which can greatly reduce its mechanical properties. Silicon carbide (SiC) is a common second phase addition to TiB_2 used to control grain growth and improve the mechanical properties. In the current study thermoplastics mixed with 56 vol% TiB_2 and 55 vol% SiC, individually, using a high shear mixer, were pressed into sheets and rolled to form spirals of 25 vol% SiC in a TiB_2 matrix. Spiral architectures have become of interest due to the predicted reduction of residual stresses and an increase in fracture toughness compared to simple particulate additions. Co-extrusion of the thermoplastics was used to reduce the spiral size to ~110 μm; below which, particle size becomes a limiting factor. Fracture toughness, hardness, and modulus of elasticity were determined for TiB_2-SiC composites containing both randomly and unidirectionally oriented spirals and compared with SiC particulate reinforced TiB_2 as a standard. The hardness in the TiB_2 matrix decreased with an increase in SiC hardness with respect to the standard. The flexural strength increased with decreasing spiral size, due to the decrease in macrocracking; though reduced in strength compared to the standard.

S9: Porous Ceramics: Novel Developments and Applications

Processing Methods for Porous Ceramics I

Room: Coquina Salon C
Session Chair: Paolo Colombo

1:30 PM

(ICACC-S9-001-2014) Ice templating porous materials: parameters multiplication goes (Invited)

S. Deville*, CNRS, France

Ice templating is able to do much more than macroporous, cellular materials. The underlying phenomenon –the freezing of colloids– is ubiquitous, at a unique intersection of a variety of fields and domains, from materials science to physics, chemistry, biology, food engineering, and mathematics, providing countless parameters that can be adjusted to control the phenomenon. I will discuss the latest advances on ice templating for porous materials and the benefits of using ice growth as a driving force for the self-assembly of elementary building blocks, leading to novel, porous or dense, structural or functional materials.

2:00 PM

(ICACC-S9-002-2014) Directionally Aligned Porous SiOC by Freeze-Casting of Polysiloxane

M. Naviroj*, Northwestern University, USA; P. Colombo, Università di Padova, Italy; K. Faber, Northwestern University, USA

This study aims to explore additional capabilities of freeze casting as a method to fabricate porous ceramics. The use of preceramic polymers introduces new considerations to the processing step as compared to typical freeze-casting processes where ceramic slurries are used. The type of preceramic polymer, solvent, catalyst, and degree of crosslinking all determine the processing behavior. In this study, highly porous SiOC samples with 70% porosity and directionally aligned pores were obtained by using commercial polysiloxane as the solute and t-butyl alcohol (TBA) as the solvent. Pore size ranges from ~5 to 20 microns. Camphene has also been used as the solvent for polysiloxane, however unfavorable solute-solvent interactions prevented successful fabrication of porous ceramics. It is shown that by judicious choice of solvent, preceramic polymers can be used in conjunction with the freeze-casting process to create highly porous ceramics.

2:20 PM

(ICACC-S9-003-2014) Fabrication of highly porous ceramic thermal insulators via novel gelation freezing route

M. Fukushima*, T. Ohji, Y. Yoshizawa, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Highly porous silica thermal insulators were produced using the gelation of silica particles dispersed gelatin solution followed by freeze drying and subsequently sintering. The relationship between the ice-template morphology and the parameters involved in gelation freezing processing was investigated, and the effect of microstructures on the thermal conductivities of silica insulators was investigated. Porosity of silica insulators ranged from 88 to 98vol%, and the thermal conductivity ranged from 0.05 to 0.16W/mK; these values could be modulated by changing the silica content in the gel stage. Gelation freezing route was proved to be feasible and potential processing route for the production of very highly porous insulators possessing machinability and very low thermal conductivity.

2:40 PM

(ICACC-S9-004-2014) Mechanical Properties of Directionally Porous Ceramics

A. Lichtner*, University of Washington, USA; D. Roussel, D. Jauffrès, M. Christophe, SIMAP/GPM2, France; B. Rajendra, University of Washington, USA

For many applications, ceramics with a high volume fraction of connected porosity is required (e.g. membranes, electrodes for fuel cells). However, the high porosity leads to reduced mechanical robustness. Designing ceramics using directional porosity is a promising way of tailoring microstructures to optimize various attributes without necessarily compromising mechanical properties. In this study, the elastic modulus and strength of directionally porous freeze-cast ceramics are explored. The freeze-casting process produces vertical pores with thicknesses ranging from 5 – 40 microns that run the length of the ceramic. Partial sintering results in an additional level of small pores which are found between the sintered particles that make up the walls of the large pores. We have studied the mechanical properties in compression in two directions: parallel and perpendicular to the directional pores and the results are directly compared with isotropically porous ceramics with similar pore volumes and pore sizes. The results provide insight into the mechanical properties of these designed anisotropic porous ceramics.

Membranes and High SSA Ceramics

Room: Coquina Salon C
Session Chair: Sylvain Deville, CNRS

3:20 PM

(ICACC-S9-005-2014) Development of Silica-based Membranes for Application to Energy Carrier Systems (Invited)

T. Tsuru*, Hiroshima University, Japan

Recently, NH_3 and methylcyclohexane (MCH) have been proposed as a H_2 carrier. NH_3 decomposes to H_2 and N_2; NH_3 is a CO_x-free H_2 carrier. MCH decomposes to H_2 and toluene (TOL) which will be re-hydrogenated and reused. In NH_3 and MCH systems, the hydrothermal stability of separation membranes is not required. More importantly, silica-based membranes should be designed by considering the molecular sizes of H_2 (0.289nm), NH_3 (0.326), N_2 (0.364), and MCH-TOL (>0.55), and the reaction temperatures (NH_3: 400-500C, MCH: 200-300C). In this presentation, our strategy of silica network engineering based on sol-gel processing will be introduced. For pore size tuning, we recently proposed “spacer” technique using a bridged alkoxide which consists of an organic linking group between two silicon atoms. For example, bis(tri-ethoxysilyl) ethane (BTESE), consisting of ethane group between 2 silicon atoms (-Si-CH_2-CH_2-Si-) as the minimum unit in hydrolysis and condensation reaction, was found to lead to loose silica networks, and showed approximately one order magnitude high H_2 permeance, and a high H_2 to SF_6 permeance ratio with a low H_2 to N_2 selectivity. Other types of bridges alkoxides, including methane, hexane, octane and benzene as the liking unit, will be also discussed. In addition, pure silica membranes derived from polyhedral oligometric silsequioxane (POSS) for NH_3 will be also introduced.

3:50 PM

(ICACC-S9-006-2014) Silver Nanoparticle-doped Ceramic Capillary Membranes for Enhanced Bacterial Filtration

S. Kroll*, J. Wehling, J. Köser, University of Bremen, Germany; P. Lindner, C. Lüder, S. Beutel, Leibniz University of Hanover, Germany; K. Rezwan, University of Bremen, Germany

In this study, we present a straightforward immobilization method based on silver nanoparticles to generate antibacterial-functionalized ceramic membranes for water purification. Excellent material properties of yttria-stabilized zirconia capillary membranes featuring an open porosity of 51 % with pore sizes ≤ 0.2 µm, a specific surface area of 8 m^2/g and a bending strength of 50 MPa offer promising filtration performances including high bacterial retention capacities of ≥ 99.9999 % and water permeate fluxes of nearly 600 L/hm^2. A highly bactericide membrane surface was created by a simple two-step process where silver ions were directly reduced on the membrane surface. By this immobilization strategy considerable high silver nanoparticle loadings up to 1700 particles/μm^2 were obtained. Filtrated bacteria were directly killed on the membrane surface and therefore, the secretion of extrapolymeric substances was avoided and the development of biofilms was repressed. To remove dead bacteria and to prevent pore clogging, back-flushing was used for membrane regeneration without affecting the surface properties. Leaching of immobilized silver nanoparticles was monitored and silver contaminant levels were determined. Even after incubation under aqueous conditions for two weeks, silver-doped ceramic capillary membranes were efficient in killing bacteria.

4:10 PM

(ICACC-S9-007-2014) New nanostructured SiOC aerogels for gas sensing applications

A. Karakuscu*, A. Ponzoni, Sensor lab, CNR-IDASC and University of Brescia, Italy; A. Parakkulam R., Deutsches Zentrum fur Luft- und Raumfahrt (DLR), Germany; G. Sberveglieri, Sensor lab, CNR-IDASC and University of Brescia, Italy; G. Soraru, D. Ayana, University of Trento, Italy; G. Faglia, Sensor lab, CNR-IDASC and University of Brescia, Italy

Due to their unique nanostructure in which silica nanosized clusters are encased into a graphene network, polymer-derived SiCO ceramics combine very high temperature stability with un-usual functional properties such as semiconductivity, piezoresistivity and luminescence. Accordingly, SiCO ceramics have been proposed as anode for Li-ion batteries, as white light LEDs and high temperature pressure sensors for operation in harsh environments. Here we show, for the first time, that that highly porous SiCO aerogels obtained through a pyrolysis process from ambient-dried hybrid silica aerogels, can be used as gas sensors for H_2 and NO_2. Our results show that sensors responded to H_2 with highest magnitude at temperatures above 500°C. On the other hand, the fastest response and recovery times occurred at lower temperatures (≤300°C) for NO_2.

4:30 PM

(ICACC-S9-008-2014) Proton conductivity of mesoporous silicas functionalized with sulfonic acid groups

M. Wark*, C. F. Seidler, Carl-von-Ossietzky University Oldenburg, Germany; R. Marschall, Justus-Liebig-University Giessen, Germany

In recent years our group demonstrated that Si-MCM-41 materials functionalized with SO3H or imidazole groups are promising additives in polymer electrolyte membranes for fuel cells enhancing the proton conduction and the water storage capacity. Benzene-PMO materials offer the further advantage that the presence of organic bridges allows a multiplicity of reactions and the crystalline pore walls enable more regular distribution of anchored groups. SO3H-functionalized ordered mesoporous benzene-PMOs were obtained via two grafting pathways: a) at the silica (silanol) groups with 3-mercaptopropyl-trimethoxysilane (MPMS) and subsequent oxidation with H2O2, b) at the benzene groups by heating in a 25% SO3/H2SO4 solution. Ion exchange capacities up to 1.7 mmol H+ g-1 and proton conductivites up to 0.01 S/cm at 140 °C and 50 % rel. humidity are realized. As shown neutron scattering (SANS) during N2 adsorption, functionalization at the aromatic rings is very homogeneous, but the distance between benzene rings is not optimum bridged. Thus, the SO3H-groups with flexible propyl linkers at silanol groups support the proton propagation further. Recent work shows that by co-condensation of tetraethylorthosilicate (TEOS) and MPMS to the mesoporous KIT-6 system, in-situ functionalization reaching ion exchange capacities > 2 mmol H+ g-1 are obtained. Thus, further improved proton conductivity is expected.

4:50 PM

(ICACC-S9-009-2014) Synthesis and Characterization of Aerogel Glass Materials for Window Glazing Applications

T. Gao*, Norwegian University of Science and Technology (NTNU), Norway; B. Jelle, Department of Materials and Structures, SINTEF Building and Infrastructure / Department of Civil and Transport Engineering, Norwegian University of Science and Technology (NTNU), Norway; A. Gustavsen, Norwegian University of Science and Technology (NTNU), Norway

Windows with improved energy efficiency have a huge potential to provide large energy savings in the building sector. Several advanced window technologies, such as vacuum windows, aerogel glazings, and electrochromic smart windows, are currently under substantial research. Among these, aerogel glazings represent an interesting and promising technology due to the fact that aerogel, which is essentially a porous silica material with a low thermal conductivity of about 0.015 W/(mK), can be prepared with controlled optical properties (e.g. transparent in visible range). However, aerogels are very brittle and therefore a difficult challenge for incorporation into window frames. In this contribution, we discuss the possibility of improving the mechanical strength of aerogel glazings while maintaining their optical transparency and thermal insulation properties. Initial characterization on a synthesized aerogel glass sample has shown promising results with respect to low mass density, low thermal conductivity, high optical transparency, and improved mechanical strength.

S11: Advanced Materials and Innovative Processing Ideas for the Industrial Root Technology

Low Friction Coating I

Room: Ponce De Leon

Session Chairs: Sangmok Lee, Korea Institute of Industrial Technology; Ali Erdemir, Argonne National Lab

1:30 PM

(ICACC-S11-001-2014) Ultra-fast Synthesis and Tribological Characterization of Hard Boride Layers on Metals and Alloys (Invited)

A. Erdemir*, Argonne Anational Laboratory, USA

Increasingly more demanding and very stringent operating conditions of next-generation tribological systems will require much stronger and harder materials that can last for the duration of intended applications. Accordingly, there is an urgent need for the development of more robust surface engineering technologies that can meet such requirements for future tribological systems. In this study, we report an ultra-fast boriding technique that can results in very hard and thick boride layers in minutes. Specifically, the new technique produces 80-100 μm-thick boride layers on steel substrates in about 30 min., depending on the type of steel. Compared to conventional surface treatment methods (e.g., nitriding, carburizing, and pack-boriding which are used extensively by industry to achieve superior hardness and tribological properties in all types of steel components), novel ultra-fast boriding provides great advantages in terms of productivity, versatility, and environmental cleanliness. It is done in a molten salt electrolyte consisting of a mixture of natural borax and sodium carbonate at elevated temperatures. Work pieces to be borided are attached to a cathode, while the crucible that holds the electrolyte acts as an anode. The hardness of borided steel surfaces may range from 17 GPa to more than 20 GPa (depending on the steel type).

2:00 PM

(ICACC-S11-002-2014) Customized Surface Technology - A modern Design Element to Increase Energy Efficiency by Friction Reduction (Invited)

T. Hosenfeldt*, Y. Musayev, E. Schulz, Schaeffler Technologies AG & Co., Germany

Coatings are increasingly applied to reduce the friction losses of car components, improve fuel efficiency and reduce CO2-emissions. This article describes how to use surface technology as a modern design element for components and systems to enable the demanding requirements on market leading automotive and industrial products. Therefore Schaeffler has developed and established a coating tool box for customized surfaces to deliver the right solutions for all that needs and requests with the corresponding coating system enabled by PVD-/ PACVD-, spraying or electrochemical technology. For innovative products it is extremely important that coatings are considered as design element and integrated in the product development process at a very early stage. The high complexity of lubricated tribological systems like valve trains and the large experimental effort needed for coating development show the need for a specific prediction of the friction behavior. Since an analytical prediction in such complex systems is not possible, always empirical studies are needed to determine the tribological behavior. This article presents the development and optimization of different multilayer artificial neural networks (ANNs) to predict the friction behavior on basis of tribological test data.

*Denotes Presenter

2:30 PM

(ICACC-S11-003-2014) Plasma Technologies: Functional Coatings for Automotive Applications (Invited)

W. Diehl*, Fraunhofer Institute, Germany

Thin functional coatings are the key to new and superior products in almost all industrial branches. The most flexible and widely used technology for deposition of thin films are plasma processes. These technologies are the first choice for an enormous bandwidth of materials and functions to be realized. A well-established class of hard coatings for automotive applications, mechanical engineering and tools are Diamond Like Carbon Coatings (DLC) and their metal containing derivatives. They are prepared by plasma processes such as PACVD, DC magnetron sputtering, and plasma activated evaporation. A new approach for the production of multilayer hard coatings for the protection against erosion under severe conditions is the hollow cathode gas flow sputtering technique (GFS). A sensor technology based on carbon films with high wear resistance and piezoresisitive properties has been developed for applications in force and load measurements and can be performed by PACVD. The application can be realised either as strain gauges on parts experiencing mechanical deformation or as direct contact in force closure. Hence, force and load measurement without significantly modifying the dimensions of technical parts are accessible as additional information.

Low Friction Coating II

Room: Ponce De Leon

Session Chairs: Tim Hosenfeldt, Schaeffler Technologies AG & Co.; Wolfgang Diehl, Fraunhofer Institute

3:20 PM

(ICACC-S11-004-2014) Innovative approach to the design and production of new functional hard coatings with low friction and corrosion protection

S. Shin*, J. Sun, C. Lee, S. Noh, K. Moon, KITECH, Republic of Korea

Significant research has been devoted to the preparation of nano-composite films to synthesize hard and super-hard thin films composed of ceramic/ceramic and ceramic/MeN nano composite. However, both hardness and elastic modulus tend to be high, and high elastic modulus of the films can cause intrinsic mismatch between substrate and thin films. It is also known that a high ratio of hardness to elastic modulus (H/E) is indicative of good wear resistance. Therefore, new nc-MeN/metal matrix films with high H/E index which can enhance durability have been suggested. This study reports on the structure and properties of nc-Zr(Al)N/Cu films synthesized by DC magnetron sputtering process with alloyed single target composed of Zr-Al-M-Cu metallic glass alloys. We also investigated the effect of the contents between nitride forming element such as Zr and/or Al and non-nitride forming elements such as Cu and /or Ni. The changes of hardness and elastic modulus with increasing the nitride forming elements were carefully investigated. Sputtering rates of the nano-composite films were in the range of 0.07~0.1 um/min with sputtering power range of 4.4~8.8 W/cm2. Both hardness and elastic modulus were increased with increasing the contents of nitride forming elements and the H/E index kept similar values in the range of 0.9~0.1.

3:40 PM

(ICACC-S11-005-2014) Carbon based PVD/PECVD coatings for high volume components production (Invited)

R. Tietema*, R. Jacobs, D. Doerwald, T. Krug, IHI Hauzer Techno Coating B.V., Netherlands

PVD coatings play an important role in the automotive industry. The majority of today's coatings are diamond-like carbon coatings, produced by different technologies and resulting in different coating properties. These coatings provide durable wear protection, but combine this with the potential to reduce friction. After being at first introduced in high pressure fuel injection systems of diesel engines, the increased engine power as a consequence of the HP injection gave an avalanche effect leading within a few years to the replacement of engine parts in both the valve train and power train by engine parts, designed with coatings for wear resistance. These coatings were mainly carbon based, but also non-carbon based coatings have found their way to automotive parts. Today coatings most commonly used are DLC coatings. Some nitride based coatings are applied as well in bearing systems and on piston rings. In the beginning of this century new regulations were introduced for the reduction of CO2 emission and a boost was given to the growth of DLC coatings on engine components because of their low friction properties. For CO2 emission reduction several measures are introduced to improve engine efficiency (weight reduction, engine downsizing, start stop engines, hybrid engines and partial cylinder shut off). As a consequence, components were more severely loaded and submitted to higher tribological wear.

4:00 PM

(ICACC-S11-006-2014) Wear and High Temperature Oxidation Behavior of Electroless Ni-P, Ni-B and Ni-W-B Coatings

S. Eraslan*, M. Urgen, Istanbul Technical University, Turkey

Carbon steels are widely used as structural material in various engineering applications. However, they are easy to suffer attack in aggressive solutions and atmospheres because of the high wear and oxidation rate. The protection of a base material from the reaction with the counter body and with ambient oxygen is usually ensured either by alloying with relevant elements or by deposition of a protective coating. The development of metal deposition processes based on electroless nickel on various surfaces has witnessed a surge in interest among researchers due to many excellent properties such as wear and corrosion resistance. It was reported several times in literature that codeposition of transition metal elements such as Mo, W, Nb, Ta and Re in binary electroless deposit improves the coating characteristics. However the number of the studies, which are related to high temperature oxidation behavior of electroless coatings and W incorporation are very limited. In this work, Ni-P, Ni-B and Ni-W-B coatings were deposited on mild steel substrates by means of electroless method. Wear and high temperature oxidation behaviors of the coatings were investigated. SEM, EDS, XRD and GDO-ES analysis were carried out to determine the structure and composition. It was seen that W incorporation in the structure has resulted in improvements on the wear and oxidation resistance of the coatings.

Energy Solution

Room: Ponce De Leon

Session Chairs: Tadachika Nakayama, Nagaoka University of Technology; Taejin Hwang, Korea Institute of Industrial Technology

4:20 PM

(ICACC-S11-007-2014) Luminescence Properties of Red Phosphors (Gd1-x, Mx)WO3 : Eu3+ (M = Ca, Al) Synthesized by Solution Chemistry Process

B. Kim*, Korea Institute of Industrial Technology (KITECH), Republic of Korea; G. Lee, J. Kim, Incheon University, Republic of Korea; T. Kim, Korea Institute of Industrial Technology (KITECH), Republic of Korea

The conversion phosphors are fabricated by solid state reaction methods, but these processes have complex oxide powder treatment processes to realize high performance red phosphors. In this study, the solution chemistry processes were applied to understand an optimum sensitizer condition of Gd-WO3 : Eu3+ red phosphors. The Gd-WO3 : Eu3+ red phosphors using sensitizers (Al or Ca) were prepared by mentioned process. The Gd-, Eu-, Ca-(or Al-) nitrate were dissolved in ethyl-alcohol, and WO3 powder was mixed into solution. The slurry was dried, calcined, and heat-treated at 1000 ~ 1200 °C for 10 h in air. All the samples were characterized by powder X-ray diffraction (XRD) using X-ray diffractometer. The optical properties were measured by photoluminescence. The (Gd1-x, Cax):Eu3+ doped tungsten oxide phosphors at various Ca2+ contents were excited at 463 nm. The dominant dipole transition was 612 nm. As increasing Ca2+ contents, the luminescent peaks are shifted from 612 nm to 609 nm without intensity changing. However, the (Gd1-x, Alx):Eu3+ doped tungsten oxide phosphors were shown the 613nm of luminescent peaks. When the Al contents were increased, the luminescent intensity increased until Al0.5 and then decreased more contents of Al. The experimental results revealed that x=0.5 of Al sensitizer as the highest phosphor intensity.

4:40 PM

(ICACC-S11-008-2014) Exfoliation and Functionalization of BN nanosheets for the Enhancement of Thermal Conducting Properties of Polymer-nanocomposites

H. Cho*, T. Nakayama, H. Suematsu, T. Suzuki, W. Jiang, K. Niihara, Nagaoka University of Technology, Japan

Exfoliation and functionalization of hexagonal BN nanosheets (BNs) with graphite-like layered structure was performed to fabricate high thermal conducting polymer-nanocomposite films. The redistribution of these nanofillers into linear assembly are controlled induced-by coordination of electrophoresis, Coulombic attraction, di-polarization, and static electricity under application of electric field. The h-BN is famous for its thermal anisotropy; when the h-BN are aligned perpendicular to the c-axis, their thermal conductivity increases by 20 times to 600 W/mK, compared to 30 W/mK that aligned parallel to the c-axis. The incorporation this 2-D nanofillers with thermal anisotropy and wide band gap (~5.5 eV) properties shows its potential as polymer-based nanocomposites as thermal interface materials in semiconductor, automobile, and aerospace industries. In this research, we try to overcome the limitation of the lower thermal conductivity of polymer by inducing filler-to-filler gaps in matrix as following; the surface of BN will be modified by chemical functionalization and the fillers will be exfoliated, and the resulting fillers will be incorporated into polymer by controlled application electric field-inducement.

5:00 PM

(ICACC-S11-009-2014) Reusing and recycling hazardous Sulfur byproduct waste for outdoor tiles

M. Binhussain*, M. El-Tonsy, KACST, Saudi Arabia

In this study, reusing and recycling hazardous sulfur byproduct waste materials was capsulated in a polymer matrix composition. Two main materials were used in developing composite sulfur byproduct tiles, namely; sulfur byproduct waste and polyvinyl chloride (PVC). The optimum mix composition of 60% PVC and 40% sulfur by weight was defined and presented. The density and the water absorption of sulfur-PVC composite tiles is about 67% and 15% less, respectively, than that of the clay ceramic tiles. The production process and cost of sulfur-PVC composite tiles was found to be competitive to the conventional clay ceramic tiles. It was evident that sulfur byproduct waste can be utilized in producing sulfur-polymer composite tiles for out-door application as well as a safe storage method for sulfur byproduct waste produced from oil and gas process. It was also evident that this novel method of reusing and recycling hazardous sulfur byproduct waste can be a useful process to limit its emission to the environment. Further investigation is recommended to improve the quality and the properties of the sulfur byproduct composite tiles.

5:20 PM

(ICACC-S11-010-2014) Production ROOT Technologies for Materials with Advanced Dye-Sensitized Solar Cell Properties

H. Kim*, T. Hwang, KITECH, Republic of Korea

As one of the key players in the Korean industrial production technologies, KITECH has put decent part of its resources (both financial and human) in finding the sustainable alternative energy solutions for the last decades. The developed production technologies are to be transferred to the small- and medium-sized enterprises (SMEs), and KITECH has filed number of patents and published papers, both disclosing effective methods of producing energy-harvesting materials and devices of advanced properties and functions. Among those, the production ROOT technologies for materials with advanced dye-sensitized solar cell (DSSC) properties has recently been developed in our group. Localized surface plasmonic resonance effect from the TiO2 photo anode was successfully induced by the addition of metal nano-dots. Silica-based binder was specially prepared and added to the low-temperature curable TiO2 paste, and it increased the energy conversion efficiency significantly. These developed techniques were integrated into a single production technology, which is now under way of industrial implementation in form of the in-line continuous production method of flexible DSSC panels. In this presentation the whole line-up of material processing technologies will be summarized.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

Novel Joining & Processing

Room: Coquina Salon F

Session Chair: Luke Walker, The University of Arizona

1:30 PM

(ICACC-S12-044-2014) Rapid joining of UHTCs, carbides, and nitrides by spark plasma joining (Invited)

W. Pinc*, L. S. Walker, E. L. Corral, University of Arizona, USA

Extreme environment materials, including ultra high temperature ceramics (UHTCs), carbides, and nitrides; are being investigated for use in thermal protection systems, nuclear fuel cladding, etc. all of which require complex shapes. In order to produce these complex shapes, a rapid ceramic joining method is needed which retains the properties of the substrates at the joint. Brazing and diffusion bonding can take hours to complete and use filler materials at the joint that exhibit properties insufficient for extreme environments. We have developed a rapid joining method, referred to as spark plasma joining, that takes ~20 minutes and produces joints with microstructures and properties identical to the substrates. UHTCs (ZrB_2, HfB_2), carbides (SiC, B_4C), and nitrides (Si_3N_4) have been successfully joined without any reduction in strengths.

2:00 PM

(ICACC-S12-045-2014) Thermal Properties of Zirconium Diboride With Transition Metal Boride Additions

D. McClane*, W. G. Fahrenholtz, G. E. Hilmas, Missouri University of Science and Technology, USA

The thermal properties were investigated for hot pressed zirconium diboride with additions of various transition metals. The equivalent of 3 mol% of each metal was added to the starting zirconium diboride as hafnium diboride, niobium diboride, ditungsten pentaboride, titanium diboride, yttrium diboride, tantalum diboride, molybdenum diboride, rhenium diboride, chromium diboride or vanadium diboride. In addition, 0.5 wt% carbon was added as a densification aid. Powders were hot pressed to nearly full density at 2150°C. Thermal diffusivity was measured using the laser flash method. Thermal conductivity was calculated from the thermal diffusivity results using temperature-dependent values for density and heat capacity. Electrical resistivity measurements were used to calculate the electron and phonon contribution to the thermal conductivity. X-ray diffraction analysis was used to determine the lattice parameters of the densified ceramics, verifying that the transition metal additives formed (Zr,TM)B2 solid solutions. The relationships among the location of the additive on the periodic table, the lattice parameters of the solid solutions, and the conductivities were compared for all of the compositions.

2:20 PM

(ICACC-S12-046-2014) Reaction Spark Plasma Sintering of Ti_2AlC from Ti, Al and TiC powders

H. Gao*, M. O'Neil, M. Radovic, Texas A&M, USA; M. Radovic, Texas A&M University, USA

Ti_2AlC was successfully synthesized by reaction Spark Plasma Sintering (SPS) of powder mixture of Titanium, Aluminum and Titanium carbide. The synthesis mechanism of Ti_2AlC was investigated through XRD characterization on samples sinteredi n a 700°C to 1500°C. Both Ti_2AlC and Ti_3AlC_2 were initially formed by reaction between TiAl and TiC in 1200 - 1400°C temperature range. With increasing temperatureto 1450°C, single-phase Ti_2AlC was continuously formed by reaction between TiAl and Ti_3AlC_2. However, Ti_2AlC would decompose to Ti_3AlC_2 above 1500°C. To compare with commercial Ti_2AlC, Vickers hardness and compressive strength were measured to be 4.2±0.3GPa and 1200±50MPa, respectively. The fracture surfaces were analyzed by scanning electron microscopy (SEM) and the relationship between microstructure and mechanical properties of the SPSed Ti_2AlC is discussed in this paper.

2:40 PM

(ICACC-S12-047-2014) Effect of Processing Route on the Mechanical Properties of Ti_2AlC

R. Benitez*, H. Gao, I. Karaman, M. Radovic, Texas A&M University, USA

Ti_2AlC belongs to a new class of materials referred to as MAX phases whose unique combination of metallic and ceramic properties makes them ideal candidates for high temperature applications. In this work, Ti_2AlC processed using different techniques (Pressureless sintering, Spark Plasma Sintering and Hot Isotactic Pressing) have been tested under quasistatic and cyclic compression loading at room temperature. The structure of the sintered samples was studied using X-ray Diffraction and Scanning Electron Microscopy with Energy-Dispersion Spectroscopy. In addition, Resonant Ultrasound Spectroscopy has been used to supplement mechanical compression testing to determine the elastic properties at room temperature, before and after mechanical cycling up to different loads. It was found that processing method in general, and amount of impurities (mostly $TiAl_x$) in particular, together with the grain size affect significantly the ultimate compression strength, (UCS), the stress at which the first cracks appears in compression, the strain to failure, as well as the hysteretic behavior of the composite.

New Composition / Composites

Room: Coquina Salon F
Session Chair: Thierry Ouisse, Grenoble INP

3:20 PM

(ICACC-S12-048-2014) $(Cr_xV_{1-x})_{n+1}AlC_n$ MAX phases solid solutions

T. Basyuk, P. Chartier, T. Prikhna, T. Cabioch*, University of Poitiers, France

The synthesis of $(Cr_xV_{1-x})_{n+1}AlC_n$ MAX phases solid solutions with n = 1,2,3 and x=0;0.25;0.5;0.75;1 was achieved by annealing cold compacted mixtures of Cr, V, Al and C powders at high temperature (1400°C to 1600°C) with or without isostatic pressure. $(Cr_xV_{1-x})_2AlC$ solid solutions were obtained for all the x values whereas the synthesis of $(Cr_xV_{1-x})_3AlC_2$ was achieved only for x=0.25,0.5 and 0.75 and that of the $(Cr_xV_{1-x})_4AlC_3$ phase for x=0, 0.25 and 0.5. Cr_2AlC samples are very stable up to 1600°C but a decomposition (Al loss) of the other phases occurred at 1500°C and 1600°C. Single phased and dense $(Cr_xV_{1-x})_2AlC$ solid solution samples were synthesized by HIP and indentation tests reveal that a solid solution hardening effect acts in this system. Structural parameters (lattice parameters, free positions (z) of the atoms in the unit cell) were deduced from Rietveld refinements of the X-Ray diffractograms. a and c lattice parameters decrease linearly between x= 0 to 1 for n=1,2,3 whereas the z-values remain almost constant. The interlayer distance between M atoms(Cr and:or V) and A atoms (Al) appears to be poorly sensitive to x and n, on the contrary of the interlayer distance between M atoms.

3:40 PM

(ICACC-S12-049-2014) Shape Memory Alloy (SMA)/MAX Phase Composites: High-Temperature Thermal and Mechanical Properties

L. Hu*, A. Kothalkar, R. Benitez, Texas A&M University, USA; E. Hoffman, Savannah River National Laboratory, USA; I. Karaman, M. Radovic, Texas A&M University, USA

NiTi/Ti3SiC2 composites that combine two unique material systems, a shape memory alloy (SMA) and a MAX phase, demonstrating two different pseudoelastic mechanisms, were processed using spark plasma sintering. Equal volume fractions of equiatomic NiTi and Ti3SiC2 were used. Microstructural characterization was conducted using scanning electron microscopy to study the distribution of NiTi, Ti3SiC2 and remnant porosity in the composite. Thermo-mechanical testing in the form of thermal cycles under constant stress levels was performed in order to characterize shape memory behavior and thereby introducing residual stresses in the composites. Evolution of two-way shape memory effect was studied and related to the presence of residual stresses in the composites. Damping behavior, implying the energy dissipation per loading-unloading cycle under increasing compressive stresses, of pure NiTi, pure Ti3SiC2, as-sintered and thermo-mechanically cycled NiTi/Ti3SiC2 composites, was investigated and compared with the literature data. The specific heat was measured in 300~600 K temperature range using a differential scanning calorimeter (DSC). Thermal conductivity was then calculated from the thermal diffusivity, specific heat, and density.

4:00 PM

(ICACC-S12-050-2014) Tribology of Novel MAX-Al Composites

R. Johnson*, T. Hammann, M. F. Riyad, S. Gupta, University of North Dakota, USA

MAX Phase-based composites have the potential to be used as shafts against SA (Super Alloys) foils for different foil bearing applications at 50,000 rpm from RT till 550 oC during thermal cycling. Earlier, despite several years of research there were no structural materials which could be used as a solid lubricant in the temperature range of RT to 550 oC. By making composites with hexagonal metals, it is also possible to enhance the damping behavior of these materials. Recently, readily machinable, relatively stiff, strong and light MAX-Mg composites with ultra high damping, for example, ~30% of the mechanical energy is dissipated at 250 MPa. In this presentation, authors will present tribological study of MAX-Al composites against different substrates, for example, alumina and Inconel. Detailed fundamental study about the origin and nature of tribofilms will be presented.

4:20 PM

(ICACC-S12-051-2014) Clicked-polymer-derived ceramics (cPDC): an efficient way to synthesize multielement composites SiC/ZrC

F. Bouzat*, R. Lucas, S. Foucaud, Y. Leconte, A. Maitre, SPCTS - CNRS UMR 7315, France

In the race for high performance materials, the non-oxide ceramics have a special place. Particularly, zirconium carbide (ZrC) and silicon carbide (SiC) are known as high refractory ceramics with good thermomechanical properties. ZrC has a high melting point (3400°C), hardness and strength. Moreover, SiC reacts in an oxidizing atmosphere to form a protective layer of silica. These composites should be interesting in advanced technology, especially for nuclear and aeronautic applications. Polymer derived ceramic (PDC) route, may be a promising route to avoid chemical heterogeneity and obtain high-performance composites with a homogeneous microstructure. Herein, an original click polymeric precursor route is described in order to generate SiC and ZrC ceramics thanks to the Copper(I)-Catalyzed Azide-Alkyne Cycloaddition (CuAAC). First, the method consisted in synthesizing and studying a polymer precursor of SiC hyperbranched. Secondly, the incorporation of the zirconium element in the structure is described, to obtain high-performance composites. Then, the thermal behaviors of the organic materials were investigated until 1400 °C. Thanks to XRD analysis, an α-SiC was unusually observed for materials obtained from the first polymer. The pyrolysis of the second polymer led to a composite α-SiC–ZrC.

4:40 PM

(ICACC-S12-052-2014) Synthesis of Boron-Containing Ceramic Precursors

C. Xu*, Institute of Chemistry, Chinese Academy of Sciences, China

Polymer-derived Boron-containing ceramics, such as BCN and SiBCN, have attracted particular interest owing to their unique excellent properties. Design and synthesis of new precursors for the ceramics have been an active research topic. In the present work, a series of new precursors were prepared, and their pyrolysis properties were investigated. Thus, the reaction of B-trichloroborazine with the primary amines containing unsaturated groups produced B-triaminoborazines, and the use of acetylenic lithium salts instead of amines resulted B-triacetylenicborazines. The molecules containing reactive ethynyl or vinyl groups were easily crosslinked via thermal polymerization. BCN ceramics were formed upon pyrolysis of these single source molecules under an inert atmosphere. Polyborosilazanes with different B/Si ratio were synthesized by co-ammonolysis of B-trichloroborazine and dichloromethylsilane. The ratio of Si/B affected the high temperature behavior of the precursor derived ceramics.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Materials Science and Technologies for Advanced Reactors II

Room: Oceanview

Session Chairs: Kurt Terrani, Oak Ridge National Laboratory; Theodore Besmann, Oak Ridge National Laboratory; Yutai Katoh, Oak Ridge National Laboratory

1:30 PM

(ICACC-S13-010-2014) Accident Tolerant Nuclear Fuel: Processing and Irradiation Behavior of UN TRISO Particles

T. M. Besmann*, Oak Ridge National Laboratory, USA; C. Silva, University of Tennessee, USA; T. B. Lindemer, Harbach Engineering and Solutions, USA; R. D. Hunt, S. L. Voit, H. Lin, M. K. Ferber, Oak Ridge National Laboratory, USA

Accident tolerant nuclear fuel consisting of UN kernels in TRistructual ISOtropic (TRISO) particles dispersed in a ceramic (SiC) matrix is being considered for LWR applications. The advantage of UN over UO2 is the higher fissile density which is needed to overcome the dilute fuel that results from use of TRISO particles. UN kernels were prepared by carbothermic reduction and nitridation. Analysis of fission product behavior was generated using thermochemical assessment of fuel-fission product equilibria and fission product release via recoil. Weibull statistics were used to obtain probability of failure as a function of burnup and coating layer thickness. Results of fuel particle fabrication and analysis of potential in-reactor behavior will be presented and potential stable particle configurations discussed. This work was supported by the US Department of Energy Office of Nuclear Energy, Fuel Cycle Research and Development Program.

1:50 PM

(ICACC-S13-011-2014) Irradiation creep of silicon carbide beyond the initial transient

Y. Katoh*, T. Koyanagi, C. Shih, Oak Ridge National Laboratory, USA; T. Hinoki, Kyoto University, Japan; L. L. Snead, Oak Ridge National Laboratory, USA

Irradiation creep is an important irradiation-induced phenomenon for nuclear materials. However, the irradiation creep of SiC, as well as all ceramics and ceramic composites, is only now becoming understood and studied. Recently, the authors reported on the creep behavior of SiC ceramics in the initial transient regime. As part of that work it was found that a linear stress dependency and a linear swelling-creep coupling existed for high purity CVD SiC, due likely to the stress-induced re-orientation of ultra-fine multi-dimensional defect clusters. That work is now extended to higher dose in an experimentally identical fashion beyond the transient regime, in the dose range of 1 dpa to ~ 10 dpa. The materials studied included grades of polycrystalline beta-phase CVD SiC and a monocrystalline 4H-SiC. Thin strip samples of these materials were irradiated in the High Flux Isotope Reactor in a temperature range ~300 to ~1200°C in the bend stress relaxation (BSR) irradiation creep capsules. The initial bending stress levels ranged from ~100 to ~300 MPa. The irradiation creep compliances will be analyzed and discussed based on the measurement of residual stress and permanent strain.

2:10 PM

(ICACC-S13-012-2014) Microstructural Stability of Neutron Irradiated Nano-Powder-Derived SiC

L. L. Snead*, Y. Katoh, K. Terrani, A. Perez-Bergquest, K. Leonard, Oak Ridge National Laboratory, USA

Silicon carbide (SiC) has been used in nuclear applications for decades in part due to its exceptional high-temperature properties and in part due to its irradiation stability. However, of the myriad types of SiC ceramics, there are few which can be considered radiation stable. The purpose of this paper is to discuss and contrast the irradiation stability of the SiC-based nano-powder ceramic material with chemically vapor deposited (CVD) SiC for which there is broad understanding. Nano-powder SIC ceramic has been irradiated into the saturation swelling range with mixed spectrum fission neutron and post-irradiation examination carried out including thermophysical and microstructural characterization. While the non-powder SiC ceramic evolves in a similar manner under irradiation as he model CVD SiC material thermophysical properties such as swelling and thermal conductivity are somewhat greater. Causes for these differences will be discussed in terms of the evolving microstructure and contrasted with less stable forms of SiC.

2:30 PM

(ICACC-S13-013-2014) Hot water corrosion at ion-irradiated surface of SiC

S. Kondo*, M. Lee, T. Hinoki, Kyoto University, Japan

SiC and SiC/SiC are attracting attention as alternative materials for fuel cladding because of the conceivable better chemical stability and strength under LOCA or beyond design basis conditions. The use of SiC may also allow uprated operation and/or long cycle operation with larger safety margin comparing to Zr based alloys. Although the excellent corrosion resistance in a hot water environment have been reported by many authors for high purity SiC, impurities, such as sintering aids and free Si, were reported to enhance the corrosion rates primarily by the selective corrosion at the grain boundaries. Furthermore, irradiation effects on the corrosion rates or the process is not clear even under LWR relevant normal operating conditions. In this study, the corrosion behavior after ion irradiation was studied for high purity CVD SiC and LPS SiC containing 3-12 wt% sintering aids. Samples were irradiated with Si ions up to 3 dpa at 300 °C in DuET facility, Kyoto University. The irradiated surface subjected to hot water was studied by scanning and transmission electron microscopy and the results will be compared with the unirradiated cases. This work was performed under contract with Toshiba Corporation in "Research and Development of Innovative Technologies for Nuclear Reactor Core Material with Enhanced Safety" entrusted to Toshiba by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

2:50 PM

(ICACC-S13-014-2014) Effect of Helium Irradiation on Ti3AlC2 at 500 °C

M. K. Patel, University of Tennessee, USA; D. Tallman*, J. A. Valdez, J. Aguiar, M. Tang, J. Griggs, E. Fu, Y. Wang, M. W. Barsoum, Drexel University, USA

We report for the first time on the effects of high (2x1017 ions/cm2; 14 at.%), fluence helium, He, irradiation of polycrystalline Ti3AlC2 samples at 500 °C. XRD confirmed that, despite a swelling along the c-axis and a shrinkage along the a-axis, the basic building block, viz. the Ti3C2 layers remained intact after the irradiation. The XRD results also suggest that the Al layers are disordered during the He implantation. Despite the high dose at a temperature of 500 °C, no evidence for bubbles was found; an important conclusion if this material is to be used in light water or other fission reactors in the future.

3:30 PM

(ICACC-S13-015-2014) Application of Advanced XRD techniques to the Study of Irradiation Effects in Ceramics (Invited)

A. Debelle*, Univ. Paris-Sud, France; A. Boulle, J. Channagiri, CNRS, France; T. Nguyen, Univ. Paris-Sud, France; S. Pellegrino, CEA-INSTN, France; F. Garrido, L. Thomé, Univ. Paris-Sud, France

Nuclear materials are inherently subjected to various sources of irradiation, from neutrons to fission fragments through alpha particles and recoil atoms. Irradiation most frequently leads to damage formation and in the particular case of crystalline materials, strain and stress develop and may play a role on the overall behaviour of the material. In the present work, the contribution of X-ray diffraction (XRD) to the study of ion-irradiated model, single-crystalline materials is highlighted. High-resolution experiments have been conducted (in a laboratory) to investigate single-crystals and the corresponding patterns have been fitted using a dedicated computer-code. This methodology allows having access to strain, stress and disorder depth profiles. Also, it is possible to get some additional quantitative information on the irradiation defects such as relaxation volume (which is related to the defect size) and concentration. To support these statements results regarding ceramic oxides (namely MgO and ZrO2) and carbides (namely SiC, TiC and ZrC) irradiated under different conditions are presented. Strain and disordered kinetics have been established and comparison between the different materials is presented.

4:00 PM

(ICACC-S13-016-2014) Ceramic Matrix Composites in Ti-B-Cr and Ti-B-Nb Systems Fabricated "in situ" by Self-propagating High-temperature Synthesis

M. Ziemnicka-Sylwester*, Hokkaido University, Japan

Ceramic matrix composites (CMCs) with predominant concentration of TiB_2 are recently the object of intensive studies due to their potential application in nuclear industry, or other high temperature devices. Therefore, the purpose of this investigation was to fabricate "in situ" non-porous composites consisting of borides from elemental powders in one stage process. The self-propagating high temperature synthesis (SHS) combined with pseudo-hot isostatic pressing (P-HIP) was proposed to utilize for densification the heat of highly exothermic reaction related to synthesis of TiB_2 and NbB_2 or CrB_2, respectively. The intended volume fraction of TiB_2 was 70% in both cases. The XRD patterns revealed that TiB_2 was predominant phase of each composite while the ceramic matrix consisted of ternary compounds $NbTiB_4$ or $Cr_{0.5}Ti_{0.5}B_2$, respectively. No unreacted elements were detected. However, the TiB_2-30vol.%CrB_2 composite exhibited better homogeneity and higher relative density. The Vickers hardness of 20.83+/-0.26 GPa for this composite, was also higher than that of 16.67+/-0.28 GPa for the composite containing Nb. Therefore, the SHS process can be applicable in order to fabricate "in situ" the CMCs, especially when sufficient amount of liquid phase can be ensured during densification.

4:20 PM

(ICACC-S13-018-2014) Processing of High Thermal Conductivity UO2-Composites using Spark Plasma Sintering (SPS)

G. Subhash*, University of Florida, USA

In recent years, spark plasma sintering (SPS) has emerged as a promising sintering technique to process difficult-to-sinter materials at significantly lower temperatures and shorter hold times. The merits of SPS include rapid processing, lower processing temperatures and low energy consumption. We have embarked on a comprehensive research program to fabricate UO2 pellets with different 2nd phase particles of SiC, diamond and carbon nanotubes (CNT). We have consolidated UO2 powders to 96% theoretical density at temperatures as low as 1050oC and processing time of only 30 seconds. On the contrary, the conventional sintering process requires a temperature of 1700oC and hold time of up to 24 hours to achieve the same result. SPS also offers additional benefits of being able to produce pellets of desired shape and size with controlled grain size. An in-depth study of the relationship between processing parameters and microstructure development has been conducted. In the next step we have developed high thermal conductivity UO2-SiC, UO2-Diamond and UO2-CNT composite pellets. The influence of particle size, volume fraction of 2nd phase, and the resulting thermomechanical properties will be discussed . Finally, a comparison between SPS processing and conventional processing as well as challenges faced during this research will be presented.

Poster Session B

Room: Ocean Center Arena

(ICACC-S2-P084-2014) Nanostructure of Ba (1-x)Co(x)TiO3 Thin Films Synthesized via Sol-Gel Method for Patch Antenna Application

H. Abdullah*, N. Abdullah, M. Zulfakar, W. Wan Jalal, Universiti Kebangsaan Malaysia, Malaysia

Barium cobalt titanate patch antenna has been successfully fabricated using sol-gel method with spin coating technique. The compositions of Ba (1-x)Co(x)TiO3 thin films are x = 0.00, 0.05, 0.10, 0.15 and 0.20. All the samples were annealed at 550 °C for 1h. X-ray diffraction (XRD) and atomic force microscopy (AFM) were used to characterize the microstructure of the thin films. Based on XRD patterns, the dominant peak were at 24° (2θ) with miller index (100) and 30.8° (2θ) with miller index (110). Based on the results, it is shown that grain sizes of the thin films are almost similar. The roughness of the thin films increased as the doping concentration increased. The thickness of the film also decreases when cobalt doping increased. The average dielectric constant of Ba (1-x)Co(x) TiO3 was ~15.24. The highest return loss obtained was 31.4 dB with dielectric constant of 15.28. The antenna return loss decreased with dielectric constant. The bandwidth obtained was sufficient for patch antenna application. The purposed of this compound was expected to be good with the performance of patch antenna application due to the unique properties of dielectric permittivity.

(ICACC-S2-P085-2014) Microstructure and high-strength glass-ceramic coatings

M. Gajek*, J. Lis, J. Partyka, AGH – University of Science and Technology, Poland

This paper presents the results of research on frits and glass-ceramic coatings for improving surface abrasion resistance. Tested materials based on compositions located in the primary crystallization field of diopside within the system MgO-CaO-Al2O3-SiO2. The results comprise investigations on the frits crystallization abilities, stability of the crystallizing phase under conditions of single-stage a fast firing cycle depending on their chemical composition. The effect of grinding starting material for nano-sized particles on the phase composition of crystalline layers as well mictrostructure and mechanical properties has been examined. Obtained layers are characterized by high microhardness in range 6~8 GPa and high wear resistance measured by the loss of weight below 100 mg / 55cm2 (PN-EN ISO 10545-7). Glass-ceramics layers of the ternary system MgO-CaO-Al2O3-SiO2, were examined with use of DSC, XRD, FTIR and SEM methods.

(ICACC-S2-P086-2014) Low Thermal Conductivity Yttria Stabilized Zirconia Thermal Barrier Coatings with Enhanced CMAS Resistance

C. Jiang*, E. H. Jordan, M. Gell, J. Roth, University of Connecticut, USA

Thermal barrier coatings (TBCs) are ceramic insulation layers applied to gas turbine engines to protect components from high gas temperatures, thus enabling higher firing temperatures and better durability. Lowering thermal conductivity of the coating is a fundamental development goal for achieving further improvements in gas turbine performance and durability. Yttria-stabilized-zirconia (YSZ) is currently the most popular material for TBCs, yet it is susceptible to attacks of a calcium–magnesium–aluminosilicate (CMAS) glassy deposit when in service, resulting in early-life failures. In the present work, a solution precursor plasma spray (SPPS) process has been used to produce YSZ TBCs with thermal conductivity as low as 0.6 W/m-K, while maintaining erosion resistance and durability. Various approaches have been taken to make the coating withstand CMAS attacks, such as doping with Al/Ti, applying gadolinium zirconate surface protective layers and blocking CMAS pathways by infiltration of calcium sulfate. CMAS resistance has been characterized in a specially-made thermal gradient rig, which largely mimics real engine environments.

(ICACC-S2-P087-2014) Hot Corrosion of La2Zr2O7 Plasma Sprayed Coatings by Volcanic ash

W. Lee, Korea University, Republic of Korea; B. Jang*, H. Araki, S. Kuroda, National Institute for Materials Science (NIMS), Japan; S. Kim, Y. Oh, H. Kim, Korea Institute of Ceramic Engineering and Technology, Republic of Korea

Thermal barrier coatings (TBCs) manufactured by plasma spray coating or electron beam–physical vapor deposition (EB-PVD) have been favored because their unique microstructures offer the advantage of superior tolerance to mechanical strain and thermal shock at the high temperatures at which gas turbines are operated. The high temperature capability of a TBCs used in a gas turbine is often degraded by deposits of calcium-magnesium-alumino-silicate (CMAS). The CMAS melts are produced when siliceous minerals (volcanic ash, dust and sand) are ingested with the intake air and deposited on the hot surface of TBCs. In the present work, we examine the properties of hot corrosion of La2Zr2O7 plasma sprayed coatings by volcanic ash. Samples of La2Zr2O7 coatings with thicknesses in the range of 30~500 μm were deposited by plasma spray coating. Hot corrosion between La2Zr2O7 coatings and volcanic ash was examined by heating samples to 1200C in air for time ranges between 10 min and 100hrs. Reaction layers between coatings and volcanic ash were found to increase with increasing oxidation time.

(ICACC-S2-P088-2014) Investigation on the Failure Mechanisms of Thermal Barrier Coatings

Y. Chen*, University of Manchester, United Kingdom; X. Zhao, Shanghai Jiao Tong University, China; P. Xiao, University of Manchester, United Kingdom; Z. Xu, Beijing Institute of Aeronautical Materials, China; L. He, Beijing Institute of Aeronautical Materials, China

Degradation behavior of thermal barrier coatings (TBCs) with a nickel aluminide bond coat produced by electron beam physical vapour deposition (EBPVD) technique was investigated. The yttria stabilised zirconia (YSZ) top coat consists of super fine columns compared with conventional TBCs. Segmentation cracks induced by sintering of YSZ were observed and the separations between adjacent cracks can be up to millimetres. Failure of TBCs occurs from the edge, and then extended to the inner part through buckling and spallation of the YSZ. Martensitic transformation of the bond coat, bond coat/substrate interdiffusion, and growth of spinel during oxidation were responsible for nucleation and propagation of separations at the YSZ/bond coat interface.

(ICACC-S2-P089-2014) Direct observation and strain measurement during cyclic heating/cooling process in oxide environmental barrier coatings on SiC/SiC substrate

T. Kuribara*, H. Kakisawa, Y. Kagawa, The University of Tokyo, Japan

Cracking behavior of oxide ceramic environmental coating accelerates degradation of SiC/SiC substrate components, such as oxygen diffusion path and stress concentration source for cracking of SiC/SiC component etc. In the present study, the effects of thermal stress caused by thermal expansion mismatch and sintering behavior of the oxide coating layer on cracking behavior of oxide environmental barrier coatings have been studied. Al2O3, mullite, and/or Al2O3-mullite mixture layers, in which thickness range from 50 to 200μm, are coated on monolithic SiC and SiC/SiC composite. Coated materials are subjected to thermal cyclic loading from room temperature to 1200°C. Direct observation and strain measurement of the coating layer surface is done during whole heating/cooling stage. Cracking behavior and cracking pattern of the coating layer are discussed with temperature and applied cycle dependence of thermal/residual stress state in the coating layer: temperature dependence of thermal expansion coefficient and modulus change by sintering are incorporated in discussion of strain distribution before and after cracking.

(ICACC-S2-P090-2014) Damage recovery behavior of Abalone shell: effects of mechanical states

J. Takehira*, H. Kakisawa, Y. Kagawa, The University of Tokyo, Japan

The repair behavior in Abalone shell after various kinds of mechanical damages damage has been studied. Dent damages are introduced to abalone shell by sharp or dull indenter, and drilling to understand the effect of mechanically identified damage on the repair process. Free cutting edge damage is also introduced by mechanical drilling process to understand the effect of stress free condition on the repair process. These damages are observed under various levels of length scales using adequate methods, such as optical microscopy and scanning electron microscopy etc. Various length scale stress and strain distributions of the dent damage area and near free edge region are also obtained analytically. After indentation, some of the Abalone shell is returned to seawater and keep its natural state in order to recover the introduced damages. After selected period, the damage areas of the abalone shell are re-observed and changes of the damage are compared. The observed change are modeled and discussed in terms of stress/strain state after initial damage, also discussed the effects of introduced stress/strain condition on the recovery process of Abalone shell.

(ICACC-S2-P091-2014) Environmental and Mechanical Stability of Environmental Barrier coated SA Tyrannohex SiC Composites under Simulated Turbine Engine Environments

D. Zhu*, M. Halbig, M. Singh, NASA Glenn Research Center, USA

The environmental stability and thermal gradient cyclic durability performance of SA Tyrannohex composites were investigated for potential turbine engine component applications. The work has been focused on investigating the combustion rig recession, cyclic thermal stress resistance and thermomechanical low cycle fatigue of uncoated and environmental barrier coated Tyrannohex SiC SA composites in simulated turbine engine combustion water vapor, thermal gradients, and mechanical loading conditions. Flexural strength degradations have been evaluated, and the upper limits of operating temperature conditions for the SA composite material systems are discussed based on the experimental results.

(ICACC-S2-P092-2014) Calcium-Magnesium-Aluminosilicate (CMAS) Infiltration and Cyclic Degradations of Thermal and Environmental Barrier Coatings in Thermal Gradients

D. Zhu*, B. Harder, J. L. Smialek, R. A. Miller, NASA Glenn Research Center, USA

In a continuing effort to develop higher temperature capable turbine thermal barrier and environmental barrier coating systems, Calcium-Magnesium-Aluminosilicate (CMAS) resistance of the advanced coating systems needs to be evaluated and improved. This paper highlights some of NASA past high heat flux testing approaches for turbine thermal and environmental barrier coatings assessments in CMAS environments. One of our current emphases has been focused on the thermal barrier - environmental barrier coating composition and testing developments. The effort has included the CMAS infiltrations in high temperature and high heat flux turbine engine like conditions using advanced laser high heat flux rigs, and subsequently degradation studies in laser heat flux thermal gradient cyclic and isothermal furnace cyclic testing conditions. These heat flux CMAS infiltration and related coating durability tests are essential where appropriate CMAS melting, infiltration and coating-substrate temperature exposure temperature controls can be achieved, thus helping quantify the CMAS-coating interaction and degradation mechanisms. The CMAS work is also playing a critical role in advanced coating developments, by developing laboratory coating durability assessment methodologies in simulated turbine engine conditions.

(ICACC-S5-P093-2014) Alpha-tricalcium phosphate-calcium sulfate hybrid bone cement blend:Hydration kinetics and mechanical properties

G. Alkan*, C. Durucan, METU, Turkey

The need for materials in irregularly-shaped bone defect filling operations induced the development of self-setting HAp cements which can be applied as injectable and/or moldable substitutes. The only calcium phosphate that converts to monolithic HAp from a single-solid precursor by hydration is α-tricalcium phosphate (α-TCP). Here, solid state synthesis of α-TCP has been performed, which is a metastable polymorph of TCP. A comparative/parametric study was carried out in determining hydraulic reactivity of α-TCP in forming HAp with various amount of (CaSO4).½H2O (CS) additions by isothermal calorimetry studies at 37 °C. It was found that calcium sulfate addition slows down the reaction kinetics and delays the cement-type conversion to HAp. However, it improves mechanical integrity/strength of the HAp cement product. An increase in tensile strength of HAp cement products from 4.5±0.1 MPa to 9.18± 0.1 MPa were achieved by proper amount of CS addition.

(ICACC-S5-P094-2014) Grade-1 titanium soaked in a DMEM solution at 37 C

A. Tas*, University of Illinois, USA

DMEM solutions are used in performing the in vitro cell culture studies. Hepes-buffered, phenol red- and sodium pyruvate-free DMEM solutions were used for the first time in testing the soaking of alkali-treated grade-1 Ti coupons at 37 C. Such DMEM solutions were depositing x-ray amorphous calcium phosphate (ACP) in one or two weeks on the soaked grade-1 Ti substrates. A limited number of previous studies focusing on the biomimetic coating of alkali-treated Ti6Al4V coupons in DMEM solutions have used different DMEM solutions, namely, the DMEM solutions of the previous studies were not Hepes-buffered and they contained phenol red and sodium pyruvate. The previous studies observed the formation of cryptocrystalline apatitic calcium phosphate (Ap-CaP) precipitates on the substrates. An inorganic solution (free of amino acids, vitamins, glucose, sodium pyruvate and phenol red), simulating the ion concentrations of the DMEM solutions, was used for the first time in forming ACP deposits on grade-1 Ti substrates upon soaking at 37 C for only 24 h. The scraped deposits were analyzed by ICP-AES, FTIR and XRD. The previous studies were attempting to analyze the calcium phosphate deposits while they were still on the Ti6Al4V substrates.

(ICACC-S5-P095-2014) The Effect of Mycobacterium Species and Mutation on Silver Nanoparticle Resistance in the Planktonic and Biofilm State

C. Larimer, M. S. Islam, A. Ojha, I. Nettleship*, University of Pittsburgh, USA

Opportunistic human pathogens in the mycobacterium genus are concentrated in biofilms in the "human environment" in ways that can promote infection. For example, there is a correlation between an increasing incidence of infections and the use of domestic showers, especially for immunocompromised individuals. This has demonstrated the need for durable surface protection strategies for domestic appliances and medical instruments that use water. Antibacterial nanoparticles have been proposed for such applications. This presentation will describe the effect of silver nanoparticles on the viability of three species of mycobacteria in their planktonic state. Considerable variation in the resistance was discovered with the pathogenic species being more resistant. Furthermore, silver resistant mutants of M. Smegmatis were easily cultured and found to be more resistant to a common antibiotic, isoniazid. The effect of the silver exposure on co-resistance to other metals will also be described. Additionally, the effect of silver nanoparticles on the growth of mycobacteria biofilm on ultrafiltration membranes was also evaluated using a newly developed membrane toxicity assay. Again, the effect of silver nanoparticles on biofilm growth was found to be dependent on the mycobacteria species. The consequences for nanoparticle surface protection will be discussed.

(ICACC-S5-P096-2014) In Vitro and In Vivo Evaluation of Scaffolds Composed of a Mixture of Silicate (13-93) and Borate (13-93B3) Bioactive Glass

M. N. Rahaman*, Y. Gu, W. Huang, Missouri University of Science and Technology, USA

Porous scaffolds composed of a single bioactive glass have been created and evaluated in previous studies. In the present study, scaffolds composed of a mixture of two different bioactive glasses (silicate 13-93 and borate 13-93B3) were created and evaluated for their response to osteogenic MLO-A5 cells in vitro and their capacity to regenerate bone in rat calvarial defects in vivo. Scaffolds with a fibrous microstructure, containing 0, 25, 50, and 100 wt% 13-93B3 glass, were fabricated by thermally bonding randomly oriented short fibers. Scaffolds with a grid-like microstructure, composed of 13-93 glass with an outer layer of 13-93B3 glass were prepared by robocasting. Scaffolds composed of 13-93 glass alone showed a better capacity to support cell proliferation and alkaline phosphatase activity than the scaffolds containing 13-93B3 glass. The amount of new bone in the defects implanted for 12 weeks with the scaffolds composed of 13-93 glass was higher than that in the defects implanted with the scaffolds containing 13-93B3 glass. While the 13-93 glass was only partially converted to hydroxyapatite at 12 weeks, the 13-93B3 fibers were fully converted and formed a tubular morphology. The consequences of the results for designing optimal bioactive glass scaffolds for bone regeneration are discussed.

(ICACC-S5-P097-2014) Animal study of Ti-7.5 Mo alloy co-implanted with calcium-based bone substitute as implant-bone gap filler

J. C. Lin*, J. Lee, Y. Lee, C. Chen, C. Ju, National Cheng-Kung University, Taiwan

The present study investigates the osteoconductive behavior of low modulus, biocompatible Ti-7.5Mo alloy rods co-implanted with calcium-based granules as a bone-implant gap filling material. To conduct the animal study, cylindrical-shaped (2 mm in diameter and 7 mm in height) Ti-7.5Mo alloy rods were implanted in the femur condyle of New Zealand white rabbits. The cavity for implantation was designed to comprise two cylindrical-shaped openings with the upper opening wider than the lower opening by about 3 mm. During implantation, a 2 mm dia. Ti-7.5Mo rod was first inserted into the lower opening, leaving a gap about 1.5 mm in thickness surrounding the implant in the upper opening. One side of the gap was filled with the bioresorbable calcium-based bone substitute (Ezechbone○R), while the gap on the other side was left open for comparison. Histological results indicate that, at 12 weeks post-implantation, new bone was observed all around the Ti-7.5Mo implant surface in the lower portion. In the upper portion, majority of the bone substitute material was replaced with new bone, indicating that the present Ca-based product may be used as a bone-implant gap filler. As a comparison, little new bone was observed on the other side of the gap. The research is supported by the National Science Council of Taiwan, Republic of China under the research grant NSC101-2622-E-006-030-CC2.

(ICACC-S5-P098-2014) Tribological behavior of biomedical friction couples: bioceramics Al2O3/100C6 and titanium /100C6

F. Mamoun*, L. Mohammed, Surface Engineering and Tribology Group, Laboratory of Metallurgy and Engineering Materials, Algeria

The purpose of this study is to evaluate and compared the friction and wear behavior of bioceramics Al2O3 and a high-strength titanium alloys Ti–6Al–4V for biomedical application sliding a gainst100C6. Tribological behavior was investigated by wear tests, using tribometers ball on disc and sphere on plane. These tests consisted of measuring the volumetric wear and the friction coefficient. Tribological tests have been carried out in ambient air with oscillating tribotester in accord with standards ISO 7148, ASTM G99-95a and ASTM G133-95 under different conditions of loads (3, 6 and 10N) and sliding speed (1, 15 and 25mm.s-1). As counter pairs, a 100Cr6 ball was used. Results show that the two alloys had similar friction and wear performance, although their grain structures and compositions are different. Large frictional fluctuations occurred, probably caused by formation and periodic, localized fracture of a transfer layer. Higher friction coefficient with larger fluctuation and high wear rate were observed at the higher sidings speed. The wear mechanism transforms from ploughing and peeling off wear at low sliding speed to plastic deformation and adhesive wear at elevated speed.

(ICACC-S5-P099-2014) Improving Pore Size and Porosity of Electrospun Nanofibrous Scaffolds for Enhancing Cell Infiltration

Q. Zhao, M. Wang*, The University of Hong Kong, Hong Kong

Electrospun tissue engineering scaffolds possess nanofibrous structures which are beneficial for cell attachment. But small pore sizes and low porosity in electrospun scaffolds impede cell infiltration and restrict the construction of cell-laden structures for regenerating complex body tissues. It is thus critical to develop methods to improve the pore size and porosity of electrospun scaffolds without changing their nanofibrous feature. In this investigation, adopting the sacrificial fiber strategy, dual-source dual-power electrospinning (DSDP-ES) was employed to make bicomponent scaffolds, with a post-electrospinning treatment to remove sacrificial fibers for enlarging pores and improving porosity. In DSDP-ES, PLGA and gelatin were spun out concurrently to make bicomponent scaffolds with intermeshed fibers. Multiple polymer jets were used for controlling the fiber ratio (2:1, 1:1 and 1:2) in scaffolds. The post-electrospinning treatment involved immersing bicomponent scaffolds in de-ionized water to remove gelatin fibers to obtain pure PLGA scaffolds. After the treatment, the average pore size could be increased by 176 to 518%. In vitro biological studies were conducted using endothelial cells. Cell viability, cell proliferation and cell infiltration were assessed for different scaffolds. Scaffolds with improved pore size and porosity exhibited better biological performance.

(ICACC-S5-P100-2014) Processing of Biomimetic TiO_2 Scaffolds for Bone Regeneration in Alveolar Defects

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Aim of the study The aim of the study was to create a cortical bone-like structure by processing a ceramic scaffold with a pore size gradient in order to prevent soft tissue invasion into the scaffold interior and thus the defect volume. Experimental design and methods Polymer sponge method was used to produce porous titanium dioxide (TiO_2) scaffolds. A dip-coating with a powder mixture (TiO_2, 10 wt% PE) followed by a thin slurry coating was applied to create the cortical bone-like structure. Sintering removed the as porogen acting PE to generate micro-porosity within the scaffold surface. Microstructure, architecture and mechanical properties were assessed with SEM, μCT and compressive tests. An in-vitro study culturing normal human osteoblasts on different surfaces (n=3/group) was performed. Confocal microscopy and SEM was used to assess the influence of surface texture on cell morphology and attachment after 1, 3 and 7 days of culture. Results A 2-step coating process with a water-TiO_2-PE ratio of 10:9:1 were most promising with regard to surface morphology. After 7 days of culture SEM and confocal microscopy results indicate that osteoblasts favour a dense surface structure with small voids. Conclusion A double-layer coating procedure showed most promising osteoblast morphology since osteoblasts were able to bridge structural flaws.

(ICACC-S5-P101-2014) Effect of Anodization Voltage on the Surface Characteristic of Titanium Oxide/porcine Bone-derived Hydroxyapatite Composite

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Titanium oxide was considered as bio-inert material but less bioactive. The incorporation of hydroxyapatite on titanium oxide would improve the bioactivity of this material. In this study, surface modification of the titanium substrate via anodization was employed for effective bonding of porcine bone derived hydroxyapatite. The effect of varying voltage on the pore diameter of the anodized titanium as well as the surface roughness and the wettability of the TiO2/HAp composite was investigated. It was observed that the average roughness and wetting angle of the TiO2/HAp composite increased as the voltage also increased from 40V to 80V. This could be attributed to the change in pore diameter of anodized titanium when subjected to varying voltage. An average pore diameter ranged from 36 to 90 nm.

(ICACC-S5-P102-2014) Influence of Magnetic Field on Fe3+-doped HAP Fabricated by Hydrothermal Method

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The doped ions can change the electron shell of HAP grain and finally affect the properties of the HAP. And it is known that the magnetic field affects the microstructure and properties of the ion-doped material. In order to study the effect of the magnetic field on the performance of HAP, the Fe3+-doped HAP was prepared using hydrothermal method in a magnetic field with different magnetic intensity. The influences of magnetic field intensity and doped ion amount on the properties of HAP particles were studied. XRD results indicated that the diffraction peaks of doped-HAP shifted to higher angle and there were more amorphous materials in comparison with un-doped HAP. With increasing the amount of doped Fe3+, the crystallinity of HAP and size of HAP grain at the direction of c-axis decreased. Magnetic field causes the doped-HAP to preferentially direct grow along the c-axis.

(ICACC-S5-P103-2014) The influence on heat treatment on the phase development of titania and its ability to nucleate apatite

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The main aim is to study the effect of heat treatment on the phase development of titania surface films on Ti. A second aim is to investigate the potential apatite formation on the formed titania film after soaking in simulated body fluids at 60°C. Ti plates(1cm×1cm×1mm) were heat treated at different temperatures from 200°C to 800°C with or without sodium hydroxide (NaOH) treatment. The different surface treatments are used to induce a more negatively charged Ti surface. The substrates were then soaked in PBS (containing Ca and Mg) solution at 60°C for 1d, 3d and 7d. The surfaces were analyzed using SEM, XRD and FTIR. Heat treatment (HT) increases the crystallinity of the Ti oxide surface. Treatment with NaOH produced a sodium titanate layer on Ti. A combination of HT and NaOH treatment produced a surface with high specific surface area. The results showed that apatite formed on all of the surfaces irrespectively of surface treatment after already 1d soaking in PBS solution. This could indicate that the HA formation could be dependent on the stability of saturated phosphate buffer solutions, not the surface chemistry, which could induce faster apatite nucleation and growth in the solutions under high temperature.

(ICACC-S5-P104-2014) Processing and Characterization of Alumina Flake Reinforced Bioinspired Nacre-Like Bulk Lamellar Composites

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Alumina flake reinforced epoxy matrix bulk composites that possess microstructural architecture inspired from that of natural nacre were fabricated by a hybrid conventional method called Hot Press Assisted Slip Casting (HASC). The alignment of alumina flakes in a brick and mortar structure was achieved by forcing the liquid epoxy resin to flow out from the flake-resin mixture through a porous filter. Correlation between processing parameters, flake content, flake orientation and mechanical property enhancement of the fabricated composites was investigated. Effect of interfacial compatibility on the mechanical properties of the bioinspired composites was investigated by modifying flake surfaces with different organofunctional silane coupling agents. Functionalized flake surfaces were studied by X-Ray Photoelectron Spectroscopy to confirm the success of surface modification. Results indicated that with an optimum amount of alumina flake content and brick-and-mortar like arrangement of the alumina flakes, nacre-like bulk lamellar composites reveal substantial improvement in strength and stiffness with respect to neat epoxy. Functionalization of alumina flake surfaces with silane improves the compatibility and interfacial bonding between the flakes and the matrix leading to further enhancement in the mechanical properties of bioinspired bulk inorganic-organic composites.

(ICACC-S5-P105-2014) Synthesis, Densification and Characterization of α-Al2O3-Hydroxyapatite Composites

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The synthesis and densification of Al2O3-(0-100 wt %) Hydroxyapatite (HA) composites is undertaken to determine whether hydroxyapatite improves the bioactivity of alumina on one hand, and whether alumina improves the mechanical properties of HA on the other hand. The Al2O3 powder is synthesized by a sol gel method that produces nanometric bohemite particles. The hydroxyapatite is synthesized by a precipitation method that produces nanometric HA particles. The two powders are mixed in a high energy mill, varying the HA content from 0 to 100%. The mixtures are densified by Spark Plasma Sintering at 1100°C/12 kN without holding time. The samples are characterized by FT-IR, XRD and SEM. The characterization shows that the hydroxyapatite does not transform in any of the sintered samples. On the other hand, the bohemite transformation depends on the composites composition. The pure alumina samples consist of α-Al2O3 round particles. The Al2O3-(5 to 20) HA samples are composed by a mixture of hexagonal platelets of α-Al2O3 and HA; the platelets width increases with the HA content. The Al2O3-(30 to 90) HA samples are composed by a mixture of δ-Al2O3, θ-Al2O3 and HA. The pure HA sintered samples are composed by equiaxial grains. It is obvious that the presence of HA has a deep influence on the sintering and transformation of the composites.

(ICACC-S7-P106-2014) The Functional Properties of ZnO Nanoparticles Composited Bamboo Pulp Fabric

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Monodispersed ZnO nanoparticles were synthetized in the Zn(NO3)2 and HSDA aqueous solution under hydrothermal condition, then the Bamboo Pulp Fabric was treated by immersion method in ZnO nanoparticles solution. The reaction mechanism was investigated. The Monodispersed ZnO was characterized by transmission electron microscope (TEM), X-ray diffraction (XRD) and ultraviolet/ visible light spectrophotometer. The functional properties of bamboo pulp fabric were characterized. The results indicated that the Bamboo Pulp Fabric treated with ZnO nanoparticles showed good UV protective properties and its UPF value can reach to 90.38. The UPF value of treated fabric drops to 70.42 after washing for 20 times, but also keep good UV protective properties. The ZnO nanoparticles treated fabric showed 99.91 % bacterial reduction of Staphylococcus aureus and 99.97 % bacterial reduction of Escherichia coli. The fabric was maintained at over 98.93 % reduction level even after being exposed to 20 consecutive home laundering conditions. In addition, the results of scanning electron microscopy (SEM) and X-ray spectroscopy (EDS) confirmed that ZnO nanoparticles have been fixed and well dispersed on bamboo pulp fabrics.

(ICACC-S7-P107-2014) Influence of Ti4+ on the energetics and microstructure of SnO2 nanoparticles

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Nanocrystalline Sn1-xTixO2 rutile-structured solid solutions have shown promise as gas sensors and photocatalysts. A fuller understanding of their microstructure and thermodynamics is necessary to improve the performance of the device. In this work, Sn1-xTixO2 (0.00 ≤ x ≤ 0.50) rutile-structured nanoparticles were synthesized by Pechini method at 500 °C for 15 h. Upon increasing the Ti4+ content, both crystallite size determined by XRD and particle size determined by N2 adsorption decrease. Surface energies and solid-solid interface energies were calculated by combining water adsorption calorimetry and high temperature oxide melt solution calorimetry. Both surface energy and solid-solid interface energy decreases with the addition of Ti4+. It is proposed that the stabilization of the particle and the crystallite size are a consequence of the decrease in the surface and interface energies caused by the Ti4+ surface segregation, which is supported by EELS. Given that the surface energy of pure TiO2 rutile reported in the literature is higher than the surface energy of pure SnO2, one may expect that the segregation of Ti4+ in the surface would increase the surface energy contradicting the results. However, it is suggested that the surface of the nanocrystalline Sn1-xTixO2 has a similar structure to TiO2 anatase, which has a lower surface energy compared to both SnO2 and TiO2 rutile.

(ICACC-S7-P108-2014) Preparation and spectroscopic assessment of copper nanocomposite glasses obtained via CuO and SnO co-doping

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Future applications of plasmonic nanocomposites in photonic devices demand for innovative means of material syntheses as well as a thorough understanding of the influence of material composition and processing on resulting optical properties. This work shows that a phosphate glass matrix prepared with stoichiometric amounts of CuO and SnO dopants by the melting technique can effectively precipitate Cu nanoparticles upon heat treatment. Optical absorption and photoluminescence spectroscopy, including emission decay dynamics, are employed in the characterization of the melt-quenched glass, and for investigating on the influence of thermal processing on material optical properties. The as-prepared material appeared highly luminescent producing blue-white and orange emissions in connection to contributions from twofold-coordinated tin centers and monovalent copper ions, respectively. Thermal processing results in the chemical reduction of ionic copper via tin ultimately producing Cu nanoparticles in the matrix as evidenced by the appearance of the surface plasmon resonance around 574 nm. As a result, copper ions luminescence decreases and the emission band shows a dip due to reabsorption by Cu nanoparticles in resonance.

(ICACC-S7-P109-2014) Nano ceramic Ba1-xSrxZrO3 (0 ≤ x ≤ 1) developed by Citrate Precursor route, Structural Characterization and Dielectric properties

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Few decades ago some smart materials (Dielectric, Magnetic, Piezoelectric, and Multiferroics Materials) were synthesized by the researchers who changed the era and attract the attention of the scientific community. Ceramics plays an important role not only in advance technology but also in household's wares. Dielectric materials are highly useful for Multilayer ceramic capacitors, DRAMS, sensors electrochemical devices, hydrogen separation and in fuel cells. We have successfully synthesized Barium Strontium Zirconate nanoparticles of the general formula Ba1-xSrxZrO3 over the composition range of (x= 0.0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.50, 0.75 and 1.0). These solid solutions were investigated by means of powder X-ray diffraction, transmission electron microscopy, scanning electron microscopy and BET surface area studies. XRD studies revealed the monophasic nature of the powders after heating the precursor at 1000°C. Smallest particle size with highest surface area was achieved for the composition x = 0.25 and comes out to be 17 nm and 94 m2g-1 respectively. Dielectric constant and loss factor were investigated as a function of frequency and temperature. The room temperature dielectric constant for x = 0.20 shows maximum value of 105 with very small dielectric loss of 0.0429.

(ICACC-S7-P110-2014) Effect of TiO2 and K2O additions toward nano-crystalline Cr4+:MgSiO4 in silica for broadband applications

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Chromium (Cr3+ and Cr4+) has broadband emissions in both Vis and NIR regions (700 - 1450 nm) upon its existence in trivalent or tetravalent states in host, respectively. The broadband emissions are attractive to many photonics applications, such as tunable laser source, low coherence source for Optical coherence tomography, ultra short pulse laser, etc. However, as known it is rarely to demonstrate lasing from Cr-doped glasses because of the high non-radiative rate in glass hosts. In contrast, it has been successfully demonstrated that Cr-doped crystals have better lasing properties. However, their crystal sizes have to be well controlled below submicron in order to avoid significant scattering loss in optical waveguides. In this study, the role of TiO2 and K2O additions in the Chromium-doped glasses and glass-ceramics is carefully investigated against Mg2SiO4 phase, Ti/K mapping, Cr4+ and Cr3+ fluorescence, and crystalline size and morphology. The results within our studied compositional ranges show that TiO2 alone has major effect on the crystalline size and K2O plays an important role on the formation of Cr4+:Mg2SiO4 phase. In sum, the right combination of both, such as 50.4%SiO2-16%Al2O3-16.9%MgO-1.65%TiO2-14.8%K2O-0.25%Cr2O3 is demonstrated successfully toward the formation of right Cr4+:Mg2SiO4 phase with nano- crystalline size and broadband emission.

(ICACC-S7-P111-2014) Facile Synthesis of Undoped and Non-metals Doped TiO2 for Visible Light Induced Destruction of Microcystin-LR

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Nano-titania has proven to be an excellent candidate for use in low cost photocatalysis and solar energy conversion. However, its large semiconductor band gap of 3.2 eV allows absorption of only the UV region of the solar spectrum resulting in low conversion efficiency. Visible-light-driven photocatalysts have attracted much attention because visible light is an important clean energy. Here, visible-light-induced degradation of microcystin-LR (MC-LR) using undoped and C, N and S doped titania anatase-brookite photocatalysts were investigated. These heterostructures were prepared via two methods i) sol gel ; ii) sol gel assisted with hydrothermal. The produced (B/A TiO2) catalysts were characterized by XRD, Raman spectroscopy, transmission electron microscopy (TEM), UV–Vis diffuse reflectance spectroscopy and N2 adsorption–desorption isotherms. The results indicated that XRD and Raman spectra revealed the formation of anatase and brookite mixed phases. The results show that the samples have a high surface area about 226 m2g-1 with a mesoporous structure. The nano-heterojunction were systematically evaluated as photocatalysts for the degradation of highly toxic microcystin-LR under visible light irradiation. The photocatalytic efficiency of the anatase-brookite photocatalysts under visible light was found to be increased by doping with the non-metals.

(ICACC-S7-P112-2014) Annealing treatment effect on the structure and photovoltaic properties of ZnO-CNTs nanocomposite thin film

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Polycrystalline ZnO-CNTs thin films were prepared by chemical bath deposition (CBD) method. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and electrochemical impedance spectroscopy (EIS) were employed to analyze the influence of annealing effects on the structures and photovoltaic properties of the ZnO-CNTs thin films. XRD measurement indicated that the crystallite size of ZnO-CNTs hexagonal wurtzite structure varies from 22 nm to 29.1 nm. FESEM image shows porous structures of ZnO-CNTs thin film annealed at 250 °C. The diameter of the CNTs like fiber in the nanocomposite thin film was measured about 70.01 nm. Photovoltaic performance measured by the power conversion efficiency (η), photocurrent density (Jsc), open-circuit voltage (Voc) and fill factor (FF) of the ZnO-CNTs photoanodes annealed at different annealing temperature of 200 °C, 250 °C and 300 °C. The highest power conversion efficiency of 0.53 % was achieved for the photoanode annealed at 250 °C. The annealing temperature of 250 °C was proposed as a suitable heat treatment effect to obtain the proper structure for the good photovoltaic properties of ZnO-CNTs photoanode.

(ICACC-S7-P113-2014) Structural and Morphology of Zn1-XCuxS films as anti-reflecting coating (ARC) affected the cell performance

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Thin films of Cu doped with ZnS were synthesized using sol-gel method to be applies as anti-reflective coating. This research involving three different Cu concentrations which being doped to the ZnS and then the thin film were heated at 550 oC for 1 hour. Anti-reflecting coating is prepared by doping Cu to ZnS with the equation Zn1-xCu xS where x = 0.00, 0.05, 0.10, 0.15 and 2.0. The effect of Cu doping on structural, microstructural and the cell performance. The structural of ZnS:Cu thin films was characterized by X-ray diffractometer (XRD). The patterns show two consistent peaks of monoclinic structure at (2 0 0) and (1 2 2). Microstructure images of anti-reflecting layer have been observed using Scanning Electron Microscope (SEM). The images show the formation of flakes morphology. The Efficiency of the silicon solar cell has been measured using Electrochemical Impedance Spectroscopy (EIS). The efficiency of the silicon solar cell without anti-reflecting coating gave the value of 0.000008%, while efficiency of silicon solar cell with anti-reflecting coating gave the value of 0.00011%. It is clear that the result obtained has been proven, that anti-reflecting coating helps the enhancement of light absorption.

(ICACC-S7-P114-2014) Effects of Mg contents on ZnAl2O4 thin films by sol gel method and its application

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A sol-gel method was used to prepare Zn(1-x)MgxAl2O4 thin films and GPS patch antenna. The structural, optical, chemical property and dielectric properties of (Mg/Zn)Al2O4 - based microwave dielectric ceramics have been investigated. The XRD patterns displayed the standard face-centered cubic of (Mg/Zn)Al2O4. The prominent peak can be observed at (311) for all samples. The addition of Mg was decreased the crystallite size and lattice parameter, while the apparent density was increase linearly. The FTIR spectrum shows the bonding of (Mg/Zn)Al2O4 occurred at 674 cm-1. By using ultra-violet (UV-Vis) spectrophotometer, the band gap (Eg) energy of undoped was observed slightly lower than the (Mg/Zn)Al2O4. The Atomic Force Microscopy (AFM) data shows the Root Mean Square (RMS) roughness was decreased due to the increment of Mg concentration. The decreases of the crystallite size and roughness tend to increase the ceramics density. The material with a higher density is associated with high dielectric constant (Er), which is suitable for GPS patch antenna application. The dielectric constant (Er) of Zn(1-x)MgxAl2O4 thin films was characterized using LCR spectrometer. As Mg content increases, the Er value is higher than undoped. The GPS patch antenna was fabricate using the Zn(1-x)MgxAl2O4. Finally, the measured magnitude of return loss at 1.5754 GHz meets the requirements of GPS application.

(ICACC-S7-P115-2014) Investigation of magnetic properties of $NiCo_{2-x}Fe_xO_4$ ($0 \le x \le 1.5$) spinel oxides

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It is well known that the magnetic properties of spinel oxides are widely determined by the distribution of cations between the tetrahedral and octahedral sites of their structure. In this paper, $NiCo_{2-x}Fe_xO_4$ (x= 0; 0.5; 1 and 1.5) spinel oxides were prepared by microwave assisted combustion method. The properties of powders were investigated by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electronic microscopy (SEM). Magnetic measurements were performed at room temperature using vibrating sample magnetometer (VSM). The thermogravimetric curves showed similar behavior where it was observed weight losses related the decomposition of nitrates and pyrolysis process of the materials. Besides, it can also be seen that the formation of oxide occurs at lower temperature for the samples containing iron. The XRD patterns of the samples showed features peaks of $NiCo_2O_4$, $NiFe_2O_4$ and NiO phases. With increasing iron content, there is a change in main peak that it becomes wider and moves to lower angular region. The average crystallite size is in the range of 10-20 nm. The morphology of samples revealed the presence of pores and agglomerates. The hysteresis curves exhibited paramagnetic behavior for the all samples. However, a weak ferromagnetic component was also observed for the doped samples. This weak ferromagnetic component becomes more evident with increasing iron content.

(ICACC-S7-P116-2014) Investigation of Multilayer Superhard Ti-Hf-Si-N/NbN/Al2O3 Coatings for High Performance Protection

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In this work we first obtained multilayered solid micro-and nanostructured coatings produced by several deposition techniques based on Ti-Hf-Si-N/NbN/Al_2O_3 on the steel substrate. It was found that the investigated coatings, along with high hardness (H) from 47 to 56 GPa and modulus of elasticity (E) from 435 to 570 GPa, the plasticity index We = (0.08-0.11), have a fairly low coefficient of friction (μ) which varies from 0.02 to 0.001 for a given mode of deposition. It is also shown that these multilayered coatings have high thermal stability (above 1000C). The annealing temperature up to 1070C in a vacuum about 10^{-2} Pa showed that the coating in the upper layers consisting of Ti-Hf-Si-N/NbN the size of nanograins increases from 25 to 56 nm (for the Ti-Hf-Si-N) and from 14 -15 to 35-37 nm for

NbN. The increase of steel microhardness at the "coating - substrate" interface, is due to the presence of the hardening near the border with coating formed as a result of impact during abrasive blasting and deposition of coating.

(ICACC-S7-P117-2014) Influence of deposition parameters on structure, elemental distribution, physical and mechanical properties of (Ti-Zr-Hf-V-Nb)N nitride high entropy alloys

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In current study nitride high-entropy alloys (Ti-Zr-Hf-V-Nb)N, obtained by the cathode vacuum-arc evaporation, were investigated using different complementary methods. Scanning electron microscopy with energy-dispersive analysis (SEM with EDS) and proton microbeam (μ-PIXE) were used to perform elemental structural analysis; X-ray diffraction analysis with "α-sin$^2\psi$" measurement of a stress-strain state was used for investigation of phase and structural state. Microhardness and tribological tests were used for perform mechanical and tribological analysis of nitride high-entropy alloys. It has been found, that investigated coatings have single-phase state with fcc-lattice. Also, coatings (Ti-Zr-Hf-V-Nb)N demonstrate high hardness (up to 44.34 GPa) and good wear resistance. The influence of deposition parameters (substrate voltage bias and working gas pressure) on elemental distribution, phase structure, hardness and Young modulus have been shown.

(ICACC-S7-P118-2014) Influence of sintering conditions on the electrical properties of sub-micrometric TiO2 ceramics

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The effects of the sintering on the electrical properties of submicron TiO2 have been examined by impedance spectroscopy in conjunction with SEM. TiO2 nanoparticles (~ 9 nm), synthesized by nonaqueous sol-gel route using TiCl4 as precursor and Theratane as solvent, were obtained. Conventional Sintering (CS) and Two Step Sintering (TSS) are used to prepared ceramics with different microstructures by means of thermal treatment at temperatures between 1000 and 1400°C and different soaking time. A final microstructure not fully dense (sintering at 1400 °C for 4 h yielded only 94% relative density) and a wide grain size distribution were observed. These facts may be due to the pre-sintering agglomeration state. TiO2 pellets tested by impedance spectroscopy showed that: (i) for CS, the increase of sintering temperature leads in a decreased resistance due to the increase of the conduction route after the pores closure; (ii) for TSS, the sintering setting practically does not affect intragranular conductivity. Notwithstanding, intergranular conductivity was strongly influenced by microstructure. The behavior of the electrical conductivity versus temperature and electrical parameters, such as: activation energy, blocking factors; were studied for different sintering conditions and conveniently related to the microstructure.

(ICACC-S7-P119-2014) Wood derived carbon as a scaffold for metal oxide deposition in hybrid energy storage materials

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Design and fabrication of porous carbons with appropriate properties has recently generated interest due to their application in energy storage devices (i.e. batteries and supercapacitors). In this work, we study porous graphitic carbons materials as a scaffold for metal oxide nanostructures with the aim of creating hybrid electrodes for use in electrochemical capacitors. The carbon scaffolds are obtained by pyrolysis of wood materials impregnated with either Fe or Ni as a graphitization catalyst. Once this catalyst is removed, a material which combines the open and interconnected porosity and high pore volume with the properties of graphitic material is obtained. This material exhibits a high surface area with mesoporosity in the 1-5 nm range, as well as higher electrical and thermal conductivity than wood derived pyrolytic carbons. Semiconducting metal oxides exhibiting pseudocapacitance can be then deposited in the macropores of these carbon scaffolds using CVD techniques to obtain hybrid electrodes with higher capacities and energy densities, as well as excellent cyclic stability.

(ICACC-S7-P120-2014) Copper modified layered cesium titanates for photocatalytic hydrogen production

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Solar driven photocatalysis with semiconductors is a promising solution to meet the increasing demand for hydrogen as alternative fuel. However, most oxide semiconductors possess large band gaps (> 3 eV) being only able to run the reaction with ultraviolet light. The cesium titanate Cs0.68Ti1.83O4 is a well suitable start-up material for band gap engineering to create visible light activity by cation doping (metal ions like Zn(II), Cu(II), Fe(III) or Ga(III) on Ti position) due to its open layered structure. Compared to the classic solid state reaction (SSR) a sol-gel process employing complexing agents leads to highly pure cesium titanates of small crystalline particles and high dispersion of incorporated metal ions. In photocatalytic H2 production with UV light the pure Cs0.68Ti1.83O4 generates about 3.1 mmol/h H2 after stepwise deposition of 0.075 wt.-% Rh as a co-catalyst. The SSR reference material generates only 0.6 mmol/h. Homogeneous incorporation of small amounts of copper decreases the band gap energy from 3.4 eV (Cs0.68Ti1.83O4) to 2.8 eV (Cs0.7Ti1.9Cu0.1O4). During the first stages of photocatalytic H2 evolution the incorporated copper ions in Cs0.7Ti1.9Cu0.1O4 are reduced to metallic Cu inducing vis-light absorption by surface plasmonic resonance. The formed metal Cu clusters act as co-catalyst and lead to a steady increase of the H2 rate exceeding the activity achieved with Rh.

(ICACC-S7-P121-2014) Photocatalytic activity of TiO2 nanoparticles prepared from dye wastewater treated sludge by using TiCl4

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For industrial wastewater treatment, the adsorption and precipitation methods of organic pollutants in wastewater by flocculants, such as Al2SO4, FeCl3 etc., have been used extensively. Precipitated sludge produced in this process are generally incinerated or dumped in disposal facilities. However, new construction of incinerator plant and landfill facility will generally be faced to trouble because of the difficulty in the formation of neighborhood consensus. In this study, we focused on TiCl4 as an alternative coagulant of Al2SO4, FeCl3 for effluent purification. In order to prepare high performance photocatalytic TiO2 nanoparticles from generated TiCl4 sludge after real dye wastewater treatment. First, TiCl4 aqueous solution was added into real dye house effluent after pH control by H2SO4. After adsorption of organic pollutants in wastewater, the precipitation of TiCl4 sludge were accelerated by NH3OH addition. By using above process, TiCl4 has become to possess almost same the performance as other commercial flocculants. Next, TiO2 anatase nanoparticles were obtained by heat treatment of the prepared sludge at ranging from 973 to 1073 K. The maximum specific surface area of TiO2 nanoparticles prepared from the sludge was 53.6 m2/g and their photocatalytic activity was almost equivalent to that of commercial photocatalyst, P25.

(ICACC-S7-P122-2014) Vertically Aligned Carbon Nanotube Based Ceramic Nanocomposites with Anisotropic

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One of the technical challenges to develop high temperature CMC coating material is that it can bond well with a metal substrate while having the necessary high-temperature mechanical and chemical properties to survive in the operating environment. Some major technical barriers in the development of CMC coating materials include: a) fabrication of high temperature coating CMC material with highly anisotropic thermal performance such as thermal conductivity, and b) good durability of the CMC coating-metal substrate bond line. In this study, we have developed high anisotropic thermal conductivity CMC nanocomposites coating based on vertically aligned carbon nanotubes (VACNT). CNTs are vertically grown on the Si substrate. The VACNT is cut into specific length using microtome and further tilted to specific orientation. The VACNT is biaxially stretched or compressed to yield particular volume fraction of CNTs in the nanocomposite. The VACNT is impregnated with polymer derived ceramic resin through the capillary flow. The VACNT/PDC resin mixture is cured and pyrolyzed into ceramic nanocomposites.

(ICACC-S7-P123-2014) Ablative Properties of Nanoparticle-Enhanced Carbon Phenolic Composites upon Oxyacetylene Torch Exposure

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During thermal loading of carbon-phenolic composites, carbon char layers form which definitively influence the thermal effectiveness of the composite material. The resulting chars are structurally weak and susceptible to mechanical erosion; reducing spallation or erosion of the char can enable use of less material thereby reducing the total weight. Finding a method to induce a thermomechanically stable and ordered carbon structure vastly improves the properties of composite materials. The addition of preexisting carbon within the laminate encourages a stable carbon structure. By means of a structural carbon char layer, the continued deposition of carbon residue from the thermal mechanisms of carbon-phenolic usage will complement the continued growth of stable char. Additionally, the existence of carbon nanoparticles within the matrix augments the interlaminar bonding of carbon layers while negligibly affecting the resin content of the total laminate. Innovative processing techniques and oxyacetylene torch testing are employed to properly evaluate the ablative properties of the nanoparticle-enhance carbon phenolic composites.

(ICACC-S8-P124-2014) ANN Modeling of WEDM Process Using Aluminum Oxide Based Ceramics

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The recent advancements in mechanical and chemical properties of ceramics have led to the development of high-strength and high-toughness ceramic composites. The machining of these ceramic composites is very cumbersome and expensive by using conventional techniques, specially when complex parts are manufactured. The wire electrical discharge machining (WEDM) is an alternative machining technique for electrically conductive ceramic materials, which are difficult to cut. In this study, the mathematical models of material removal rate (MRR) and surface roughness (SR) used for the machinability evaluation in the WEDM process of aluminum oxide-based ceramic material (Al2O3 + TiC) have been carried out. The experimental plan adopts the face centered central composite design (CCD). The mathematical models using Artificial Neural Network (ANN) are developed so as to investigate the influences of four machining parameters, including the peak current, pulse on time, duty factor, and wire speed, on the performance characteristics of MRR and SR. It has been proved that the proposed mathematical models in this study would fit and predict values of the performance characteristics, which would be close to the readings recorded in experiment with a 95% confidence level.

(ICACC-S8-P125-2014) Comparison of Microwave Processed and Conventionally Processed YSZ Electrolyte

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In the present study YSZ electrolyte has been fabricated by conventional processing and microwave processing and their effect on microstructure as well as electrical properties have been compared. The precursor of YSZ ($Zr_{1-x}Y_xO_{2-x/2}$) of composition x= 0.06, 0.08, 0.10, 0.12, 0.14 were prepared co-precipitation method. The co-precipitated hydroxides were decomposed into their corresponding oxides $Zr_{1-x}Y_xO_{2-x/2}$ by heating them at 500ºC for 4 hrs. All the oxides were characterized by XRD and the crystallite size of each composition were determined using Scherer Equation. The crystallite size was found to be in the nano range and was decreasing as the concentration of dopant YO1.5 was increasing. The decomposed $Zr_{1-x}Y_xO_{2-x/2}$ were sintered by microwave processing as well as conventional processing at 1400°C for 20 minutes and 4 hours respectively. The densities of the products obtained by microwave processing were comparable to the products obtained by conventional processing. The electrical conductivities of the YSZ obtained from microwave as well as conventionally processing were measured using complex impedance spectroscopy in the frequency range 100Hz to 5 MHz using LCR meter. It had been observed that they had almost equal bulk conductivities. This suggests that application of microwave in processing of YSZ can save time and energy without compromising on quality.

(ICACC-S8-P126-2014) Transparent Polycrystalline ZnAl2O4 ceramics fabricated by Spark Plasma Sintering

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Transparent polycrystalline ZnAl2O4 ceramics could enlarge the group of transparent ceramics. High purity ZnAl2O4 powder was synthesized by a simple high-temperature calcination method. ZnAl2O4 powders have spherical shape and the mean particle size was about 200 nm. ZnAl2O4 ceramics with the in-line transmission of 40% at the wavelengths of 550 nm were fabricated by spark plasma sintering (SPS) technique sintered at 1260 °C for 15 min, while the in-line transmission could be increased to 65% with 0.5 wt%tetraethyl orthosilicate (TEOS) as sintering aids. The morphologies and microstructure of ZnAl2O4 transparent ceramics were investigated. The results showed that the appropriate addition of sintering aids remarkably improved the densification of ZnAl2O4 transparent ceramics. The microwave dielectric properties of ZnAl2O4 ceramics fabricated by SPS were investigated at first. The dielectric constant εr varied from 8.14 to 8.62 with the increase of the sintering temperature from 1250 °C to 1400 °C, however, the Q×f value increased significantly up to a maximal value of 59 000 GHz at 1300 °C, which was slightly higher than the Q×f value of ZnAl2O4 ceramics sintered by the traditional oxide route (56300 GHz).

(ICACC-S8-P127-2014) Elaboration of sol-gel derived TiC-CNTs composites

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Due to the remarkable physical and mechanical properties of carbon nanotubes (CNTs), they are considered to be one of the promising reinforcements for structural ceramics. Sol-gel processing method provides a route to creating a uniform dispersion of CNTs in inorganic matrices; here, the combination of sol – gel with a conventional carbothermal reduction was used for synthesis of the CNTs reinforced TiC ceramic. This routine offers some advantages over the conventional powder processing associated with the lower reaction temperatures and shorter reaction times due to an intimate contact between the reactants. The materials were produced by pyrolysis at 800 0C and carbothermal reduction of metal alkoxide – CNT polymer blend at 1350 0C in an argon atmosphere. The concentration of the CNT was 0.35 and 0.5 wt%. The resulting product represents nanocrystalline TiC (particle size of about 90 nm) covered with CNTs. The powder was consolidated by spark plasma sintering technique. The short sintering time (5 min) and low temperatures (1500 – 1600 0C) help to minimise grain growth and CNT loss, leading to a dense eventual CNT/ceramic bulk. The structure of TiC/CNT composites was characterized by SEM, X-ray diffraction analysis and energy dispersive X-ray spectroscopy methods. The mechanism of the carbothermal reduction of the pyrolysed TiC/CNT precursors was studied by the rate of CO generation in effluent gas.

(ICACC-S8-P128-2014) Ultrahigh aspect ratio alumina nanofibers as reinforcements

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The phase conversions and morphological changes of commercial alumina nanofibers (ANF) with 7 nm and 40 nm in diameter during heat treatment were investigated. This super-high aspect ratio (length-to-diameter ratio is ~107) fibers are mostly composed of partially hydrated (2-6% wt.) gamma-alumina phase. The transformations of the ANF during heating up to 1480°C were studied simultaneous coupled thermal analysis (TG-DSC-FTIR) supported by XRD and SEM examinations. It was found that for ANF gamma-phase starts to transform into stable α-alumina from ~1250°C, but the water releases during most of the heating time at least in two stages. The behaviour of the material and observed changes are discussed and compared with literature date for different alumina materials. To produce nanocomposites, doping of the ANFs was attempted to obtain either ceramic (Al2O3 or ZrO2) or metallic (Cu) nano-particles on the surface of the nanofibers. As the major benefit of ANFs would be in their application in the ceramic-matrix composites, the sinterability of the single fibers is not relevant but rather the sintering process of the whole composite.

(ICACC-S8-P129-2014) Novel alumina–nanocarbon hybrids

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Carbon nanotubes and graphene are promising components for next-generation high-performance structural and multifunctional composites. Recently developed technology of alumina nanofibers (ANFs) production allows creating brand new hybrid carbon-ceramic nanomaterials. It was found that morphology, quality and quantity of CNTs/graphene on the ANF surface essentially depends on the pyrolysis of carbon source conditions such as gas flow, duration, temperature and the composition of the gas mixture. After ferrocene vapour pre-treatment and carbonization at 900 – 1100 oC (in the ethylene-hydrogen system), formation carbon nanostructures was confirmed by transmission electron microscopy and Raman spectroscopy. Thickness of graphene layer on ANF surface was found to depend on pyrolysis time. Optimum for the CNT formation ratio of total hydrogen [H] to the total carbon [C] in the range [H]/[C] = 20-45. Electrical conductivity of ANFs/nanocarbon hybrids increases up to 106 times. Nonconductive ANFs in combination with CNTs can be utilized for monitoring the conductivity change under certain conditions. Moreover, sintered ANF/nanocarbon material is expected to possess enhanced mechanical properties. The orientation of CNTs is of particular interest, such materials can have anisotropic heating and electrical conductivity and can be used as heating elements in highly loaded constructions.

(ICACC-S8-P130-2014) Measurements of Biaxial Flexural Strength of Ceramic Substrates for Power Modules

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The rapidly growing market of electric vehicle and hybrid electric vehicle demands high power density of the circuit in the power device. The heat dissipating board for the power modules usually consists of a ceramic substrate such as aluminum nitrides or silicon nitrides sandwiched by cupper plates. The mechanical sustainability of the substrate after sever heat cycles becomes more of a concern since thermal stress due to thermal expansion mismatch between Cu and ceramic plates damages the substrate. The fracture strength of the thin ceramic plate is one of the main factors which govern the thermal fatigue of the heat dissipating board. In this study, the biaxial flexural strength of both thin aluminum nitrides and silicon nitrides was measured by both ring-on-ring test and boll-on-three balls method. Two types of thin plate specimens were used for both jigs. The first one possess perfect flat and parallel surfaces, which was cut from a sintered bulk ceramics and was ground with a diamond wheel. The other type was as-sintered thin plate with a slight warpage, which was commercially available as the electronic ceramic substrates with high thermal conductivity. The effects wrapage of the disk specimens on the strength were compared between the two jigs to judge which type of the fixture is preferable. Part of the research work was supported by NEDO, Japan.

(ICACC-S7-P131-2014) Kevlar Fabric Supported PVDF Microfiltration membranes

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The novel research reports the fabrication and characterization of Kevlar supported micro-filtration (MF) membranes. Thermally induced phase separation technique was opted to generation microporosity within the PVDF film. The effect of variant polymer concentrations on the morphology and permeation of diverse solvents through the fabricated membranes was scrutinized. It is observed that with increasing the polymer concentration, the pore density and size within the membranes were diminished accordingly. The permeation data reveal that the flux through the MF membranes is directly dependent on the type of solvent and the polymer concentration used to fabricate the MF membrane.

(ICACC-S8-P132-2014) Advanced Measurements of Indentation Fracture Resistance of Alumina by the Powerful Optical Microscopy for Small Ceramic Products

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The indentation fracture (IF) method is one of the most effective solutions for the request of evaluating the fracture resistance of tiny ceramic components such as bearing balls since the conventional toughness testing are difficult to apply. However, the method has been regarded as a substandard method since the international round-robin tests on the IF method demonstrated that the between-laboratory consistency was terrible, which were reported about twenty years ago. Our previous studies on the errors of the IF method using both silicon carbides and silicon nitrides clarified that the operators' subjectivity in measuring crack length was the major cause of the wide scatter of fracture resistance, K_{IFR} between the laboratories. In this study, reproducibility of indentation fracture resistance, K_{IFR}, of alumina ceramics was evaluated by a domestic round robin with twelve laboratories. It was found that the variations in the fracture resistance among the participants were notably reduced as compared to those reported in the previous round-robin tests when the crack length was measured with a powerful microscope equipped with the traveling stage. The crack lengths of the returned samples were also measured by the authors and compared with the reported values from each participant to estimate the origin of measuring errors.

(ICACC-S8-P133-2014) Morphology Control of YAG Phosphor Powders by Alumina Seed Application

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Ce dopped YAG phosphor powders were synthesized using alumina powders for control of the powder morphology and size. Several kinds of alumina powders, which have different size and morphology, were used as the seeds. PVA solution were added to the sol precursors consisting of the seed powders and metal nitrate salts (yttrium nitrate and cerium nitrate) for atomic-scale homogeneous mixing. All precursor gels were calcined at 500°C and then heated at 1400°C ~ 1500°C in nitrogen-hydrogen atmosphere. The characterizations of the final synthesized powders were conducted by using XRD, SEM, PSA, PL and PKG test. All synthesized powders were crystallized to YAG phase without intermediate phase of YAM or YAP. The phosphor property and morphology of the synthesized powders were strongly dependant on the alumian seed type and the PVA content. Finally, the size was controlled from sub-micron to 30 μm and the morphology was varied from spherical to angular form. The phosphor properties, such as photo luminescence and luminous intensity were also varied according to the seed type and PVA content. The synthesized phosphor powder, which has a spherical powder morphology and an average particle size of 10 ~ 20 μm, showed an excellent phosphor properties in comparison with a commercial phosphor powder.

(ICACC-S8-P134-2014) The Microstructure and Dielectric Properties of Sm2O3 Doped Ba0.6Sr0.4TiO3-MgO Compound for Phase Shifters

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The structural, surface morphological, tunable and dielectric properties of Sm2O3 doped Ba0.6Sr0.4TiO3-MgO ceramics were investigated. Sm2O3 dopant effectively decreases the dielectric loss of BST-MgO ceramics. 0.2wt% Sm2O3 additives dramatically weaken the uniform of grains distribution and deteriorated the tunable ability. More uniform grains were observed with higher Sm2O3 concentration. The (ε(0)/ε(v))3-E2 characteristic is an indicator of the uniformity of grains in BST-MgO composite. For 1.2wt% Sm2O3 doped samples, the microwave loss at 2.5GHz is 0.00478 and the tunability is 6.52%, it basically meets the requirements of phase shifters.

(ICACC-S8-P135-2014) Fabrication of reaction bonded silicon carbide using gel-casted preform

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Reaction bonded silicon carbide (RB-SiC) is fabricated by infiltration of Si into a preform consisting of SiC and C, accompanying reaction between Si and C to form SiC. A gel-casted preform seemed suitable for RB-SiC from the following reasons. 1) Near-net shape preform can be made by gel-casting. 2) The preform is porous and has a infiltration pass for Si. 3) Residual carbon from the gel can be used for carbon source. Therefore, in this work, a preform is fabricated by gel-casting, and is provided for reaction bonding. Shape, infiltration and reaction, microstructure, and mechanical properties are investigated, and potential of gel-casted preform is examined.

(ICACC-S8-P136-2014) Fabrication of high-porosity mullite ceramic membrane supports with addition of vanadium pentoxide and aluminum fluoride

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In order to effectively improve porosity without degradation of mechanical strength, V2O5 and AlF3 were used as additives to cause the growth of mullite crystals with various morphologies during the fabrication of porous mullite membrane supports from industrial waste (fly ash) and natural bauxite. The sintering shrinkage, open porosity, pore size distribution, microstructure, thermal and mechanical property were characterized under various sintering temperatures and additive contents. The results indicate that with 3,wt% V2O5 and 4,wt% AlF3 additions the open porosity at 1400°C is significantly improved as high as ~50% without any pore-former. Phase composition and micro-morphology of the inter-locked mullite whiskers embedded in membrane supports were characterized by XRD and SEM-EDS. It is revealed that V2O5 and AlF3 can effectively lower mullitization temperature and cause the formation of fine mullite whiskers with high aspect ratio (for example, ~17 at 1300°C) via a vapor-solid reaction mechanism. The fabricated highly porous membrane supports, featuring a structure of inter-locked mullite whiskers, are expected to show some potential applications in filtration of dust-containing hot gas, as well as as supports for MF/UF membrane and catalysts.

(ICACC-S8-P137-2014) Effect of Molten Salt Synthesis Parameters on the Formation Kinetics, Morphology and Magnetic Properties of Barium Hexaferrite Ceramics

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In this study micron size barium hexaferrite (BaHF, BaFe12O19) platelets were prepared by molten-salt synthesis method in various weight proportions of NaCl-KCl salt mixtures as the liquid medium. The effects of calcination temperature and molten salt composition –x wt% NaCl and (100-x) wt% KCl-on the formation kinetics and amount of BaHF phase formation as well as on the morphology and magnetic properties of BaHF ceramics have been discussed. Inductively coupled plasma-mass spectroscopy was used to determine the solubility of the starting materials in the salts to understand the formation mechanism of BaHF. X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) and vibrating sample magnetometer (VSM) were used to identify the characteristics of the synthesized BaHF platelets. Quantitative XRD results showed that calcination in molten salt containing 100 wt% NaCl at 900 °C for 2 hours resulted in the highest production of BaHF. SEM results showed that KCl- rich molten salt led to the formation of sharper faceted platelet morphology, whereas NaCl-rich ones resulted in more round platelets. Flux compositions containing 70 to 90 wt% NaCl have led to the largest average platelet size. As the content of NaCl in the molten salt increases, hysteresis loss and hard magnetic behavior of the synthesized BaHF ceramics become pronounced.

(ICACC-S8-P138-2014) Porous mullite ceramic membrane supports prepared from coal gangue waste

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In this study, porous mullite (3:2 mullite) ceramics supports for filtration membrane were successfully fabricated from recycled coal gangue and bauxite at the sintering temperature from 1100 to 1500°C with corn starch as pore-forming agent. The effects of sintering temperature on sintering behaviors, phase evolution, mechanical strength and microstructure were studied in detail. The XRD results indicate that secondary mullitization reaction occurred from 1200 °C. In the dilatometric study, a unique volume-expansion stage was observed from 1282 to 1390 °C, causing an increase in porosity even at elevated temperature. Various amounts of corn starch were added to optimize open porosity and mechanical strength. Furthermore, the microstructural variations of the fabricated porous mullite ceramics were verified by SEM, coupled with EDS analysis. The results show that during secondary mullitization reaction, the mullite crystals were observed as rod-like morphology at 1350 °C and grew thick when sintering temperature increased to 1500 °C. The fabricated porous mullite ceramics have various pore-structures and mechanical properties with different corn starch additions, endowing its different functions as membrane supports.

(ICACC-S8-P139-2014) Ferroelectric Properties of Rare earth Doped $BaTiO_3$ Ceramics

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Doped barium-titanate ceramic is attracting much interest for its application as resistors with a positive temperature coefficient of resistivity (PTCR), multilayer ceramic capacitors (MLCC), thermal sensors etc. In those article $BaTiO_3$-ceramics doped with 0.01 up to 0.5 wt. % of rare earth (Ho, Er, and Yb) were prepared by conventional solid state procedure and sintered up to 1350 ºC for four hours. The microstructure investigations were done with SEM-JEOL 5300 equipped with energy dispersive spectrometer (EDS) system. SEM analysis of Er/$BaTiO_3$, Ho/$BaTiO_3$ and Yb/$BaTiO_3$ doped ceramics showed that in samples doped with a low level of rare-earth ions, the grain size ranged from 10-60 μm, while with the higher dopant concentration the abnormal grain growth is inhibited and the grain size ranged between 2-10 μm. In order to correlate the microstructure and dielectric properties of doped $BaTiO_3$-ceramics, the hysteresis loop and the capacitance and dielectric losses of the samples have been determined. Present results enabled establishing parameters for the prognosis of ferroelectric properties of $BaTiO_3$-ceramics according to the triad synthesis (technology) - structure - property

(ICACC-S9-P140-2014) Geopolymer Foams by Gelcasting

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Highly porous geopolymers, with homogeneous microstructure, open cells and porosity up to 90 vol%, were fabricated by gel-casting, a process commonly used to produce ceramic foams. Geopolymer foams were prepared by stirring an activated blend of metakaolin and fly ash with a mixture of potassium hydroxide and potassium silicate with Si/K = 1.66. The cell size and size distribution of the geopolymer foams could be efficiently adjusted by the control of some parameters such as solid content, surfactant type and content and mixing speed. The influence of each parameter on the porosity and other characteristics of the geopolymer foams was investigated. The foams were evaluated only after heat treatment at 80°C, which was conducted in order to complete the geopolymerization reactions. The produced components could be heat treated up to 1200°C in air without melting, if desired. The characteristics (morphology, strength, chemical and thermal resistance) of the geopolymer foams suggest that they could be employed as low cost replacement of porous ceramics in applications such as catalysis supports, adsorption and separation, filtration of hot gases and refractory insulation of furnaces. In addition, these components could be considered sustainable, as they reach their final properties after processing at temperatures not exceeding 100°C and part of the raw materials employed are industrial waste.

(ICACC-S9-P141-2014) Preparation of Intergranular Phase Replacement Techniques Porous Silicon Nitride Ceramic

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Silicon nitride ceramics are widely used as filtering and wave-transmitting materials within a wide range of temperature, primarily due to its high strength, thermol shock resistance and other advantages. Porous Si3N4 with grain glass phase free are fabricated by using liquid phase sintering at high temperature. Porous Si3N4 prepared by liquid phase sintering with optimal propeties was used as the matrix, after removing the grain boundry, then infiltrating phenolic resin and silicasol, the porous Si3N4 ceramics with grain glass phase free were synthesized. Porous Si3N4 ceramics sintered at 1650 degree for 2h in the atmosphere of pure N2 in six atmospheric pressure, samples consisted a lot of rod-like β-Si3N4 and small amount of SiO2 and α-Si3N4. Samples has bending strength 150MPa which is high than corroded samples. Ceramics with intergranular phase subsituted is fabricated successfully.

(ICACC-S9-P142-2014) Ceramic Filtering Elements Impregnated with Silver Nanoparticles for the Inactivation of Escherichia coli

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Brazil has vast amounts of hydric resources, whose quality has been deteriorating due to pollutant dumping. Conventional water disinfection methods are a solution, but they lead to the formation byproducts hazardous to human health. In this study, aiming to develop antibactericidal filters for water disinfection, silver nanoparticles were deposited on alumina foams through three routes: sputtering DC, dip coating and in situ chemical reduction of silver nitrate. The depositions were characterized through X-ray diffraction, scanning electron microscopy and EDS element mapping. The influence of the depositions on the properties of the ceramic foams was assessed and a preliminary antibacterial efficiency analysis was carried out. Characterization results indicate that the chemical reduction routes were efficient in depositing homogeneously distributed silver particles and that the molar concentration of the metallic precursor salt affects size and morphology of the particles: molar concentration of 0,4 mol/L resulted in spherical particles and 0,8 mol/L resulted in cubic particles. Incorporation of the polymeric film caused growth of the foam's mechanical resistance. The antibacterial efficiency analysis indicated that the chemical reduction filtering elements show potential for inactivation of Escheríchia coli in water for human consumption.

(ICACC-S9-P143-2014) Effects of sintering temperature on microstructure and properties of porous anorthite ceramics

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In this paper, porous anorthite ceramics with high porosity and ultra-low thermal conductivity have been fabricated using γ-Al2O3, CaCO3 and SiO2 as raw materials by foam gelcasting method, and effects of sintering temperature on microstructure and properties have been studied. Linear shrinkage of samples was determined by, where S is linear shrinkage, Hg and Hs are the heights of green body and sintered sample respectively. Bulk density and apparent porosity were measured by Archimedes method in distilled water. Thermal conductivity at room temperature was measured on 5×5×3 mm3 machined specimens, using the Thermal Transport Option (TTO) of Physical Properties Measurement System. Microstructure was observed using a scanning electron microscope. As sintering temperature increased from 1300 to 1450 centigrade, linear shrinkage increased from 10 to 17 %, apparent porosity decreased from 91 to 83 %, bulk density increased from 0.24 to 0.46 g/cm3, and thermal conductivity increased from 0.018 to 0.065 W/(mK). From microstructure observation, as sintering temperature increased, pore size became smaller, but grain size became bigger and grain shape became obviously. The results indicate that sintering temperature has significant effects on microstructure and properties. Thus, it is possible to adjust sintering temperature to control properties for potential applications.

(ICACC-S9-P144-2014) ZrB2-SiC foams from direct foaming methods

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ZrB2-SiC ceramics show good thermo-mechanical properties (UHTCs) that make them of interest for very demanding applications in different fields. Zirconium diboride-graphite foams were produced from direct foaming methods containing proteins as stabilizers and polysaccharides as gelling agent, and carbon was then converted to SiC, taking advantage of the reactive Si-infiltration technique. The highly porous microstructure of the samples was comprised of cells with a size ranging from a few microns to a few tens of microns, and the cells possessed intercommunicating windows. This processing approach enables to fabricate components with a homogeneous microstructure, suitable for several engineering applications.

(ICACC-S9-P145-2014) Processing and Properties of Low-Cost Ceramic Microfiltration Membranes

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Ceramic microfiltration membranes have been fabricated from inexpensive raw materials such as diatomite, kaolin, bentonite, and some sintering additives by a simple pressing route. Flat disk filters have been obtained by sintering the mixed materials with carbon black as an optional template. The prepared ceramic microfiltration membranes were sintered at different temperatures range from 950 to 1100ºC. The effects of sintering temperature, diatomite content, and additive composition on the porosity, pore size distribution, microstructure, flexural strength, permeability, and oil rejection rate of the ceramic microfiltration membranes were investigated. Flexural strength of the ceramic membranes was strongly dependent on the additive chemistry. Permeability of the ceramic membranes was primarily dependent on pore size rather than porosity. The oil rejection rate decreased with an increase in the applied pressure and the carbon black content. This was due to the fact that the high pressure enhanced the wetting and coalescence of oil droplets and this would enforce the oil droplet to pass through the small pores of membranes along the permeate. A maximum oil rejection rate of 97% was obtained in a ceramic membrane (porosity 32 %, flexural strength 30 MPa, average pore size 0.3 μm) sintered at 1000ºC.

(ICACC-S9-P146-2014) Cellular Ceramic Structures: Design, Optimization and Applications

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Silicon infiltrated silicon carbide ceramics are commonly employed because of their excellent chemical, oxidation, and thermal shock resistance. Si-SiC cellular ceramics are industrially employed in applications with high thermal loads, high temperatures and harsh environments. They are namely: porous burners, catalytic supports, heat exchangers, structural ceramic sandwiches, concentrated solar receivers and electric heaters. The poster presents some of the applications in which Si-SiC cellular structures are currently employed because of their higher performances, showing the design and optimization processes to increase product performance.

(ICACC-S9-P147-2014) Development of Ceramic Water Filter (CWF) for Point-of-Use Household Water Filtration Systems

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In this study, candle type ceramic water filter for point–of–use household filtration system was developed to significantly improve the anti- microbial quality of household water thereby reducing the risk of different waterborne diseases. Grog and ceramic support formulation, firing temperature and time were determined to give maximum desirability. From the porosity tests conducted, the 70% rice hull ash and 30% terracotta was considered the best grog formulation and the 55% grog and 45% terracotta clay was the chosen formulation for the final ceramic support. The molder for the candle type CWF was also developed. From the three mesh sizes of ceramic water filter raw materials prepared in this study that were subjected into three firing temperatures it was found out that 600 μm of both clay and grog and firing temperature of 10000C resulted to a desirable pore size distribution and porosity of 0.896 (Design Expert v.8).

(ICACC-S11-P148-2014) Optimum Selective Dissolution Process of Porous Metallic Glass Granules

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Porous metals can apply in various fields such as filters, catalyst supports and electrode material, when they have enough mechanical properties and chemical stabilities. To realize these unique porous metal structures, it is important to select mechano-chemically stable material system and reliable manufacturing process. In this study, the selective dissolution process was applied to fabricate porous Ni-based metallic glass(MG) granules. The brass powders have applied as a base-metal to optimize selective dissolution process, when the Ni-based MG remained as a relative novel-metals. The MG/brass composite granules (MG /40 vol. % brass) were fabricated by conventional ball-milling process under Ar atmosphere for 20 hours. The composite granules were selective dissolved in two kinds of acid solutions (H2SO4 or HNO3) to understand optimum process condition. When the H2SO4 solutions (10~30%) were applied in present process, the brass phases were remained in composite granules due to relative low reactivity. However, the HNO3 solutions could decide concentrations of acid and reaction times as unique process parameters. As increasing the concentration (10, 20% of HNO3) and time (1~24 hrs.), the reduction of brass phases in granules were accelerated remarkably. The optimum condition in maintaining initial granule structure was selected at 10% HNO3, 1 h condition, which had the highest specific surface area.

(ICACC-S11-P149-2014) Different in pyrocarbon matrices made by FB-CVI with vegetable precursors

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Carbon/carbon composites are useful in thermal and mechanical equipment. This composite is usually made by pyrolysis of polymers or CVD technique, both techniques are time consuming. This work shows some results of the use of film boiling chemical vapor infiltration, FB-CVI, a fast densification method to made carbon/carbon composite with different precursors. Carbon matrices were made using three different carbon precursors, hexane, ethanol and vegetable oil. All densification experiments were done in four different temperatures, 1173K, 1273K, 1373K and 1473K. Hexane showed the greatest deposition rate, and vegetable oil showed the smallest. Archimedes densities were different for all, and vegetable oil is the most porous samples. Samples were characterized by DRX, MEV, RAMAN and polarized optical microscopy. The pyrocarbon type deposited were also different for the three precursors, vegetable oil deposited an isotropic carbon while ethanol and hexane deposited laminar ones. The conclusion is that different types of precursors results in different pyrocarbon and different structures of matrix.

(ICACC-S11-P150-2014) Nono-sized quartz for glass-ceramic coatings – influence on coating structure and chemical resistance

J. Partyka*, J. Lis, M. Gajek, AGH University of Science and Technology, Poland

Glass-ceramic materials consist of multiple oxide systems, in whose most common are: SiO2, Al2O3, CaO, MgO, ZnO, K2O, and Na2O. Depending on oxide composition it's possible to recognize a few crystalline phases such as: anorthite, diopsyte, gehlenite, ghanite, willemite, cordierite, quartz, mulite etc. Phase which disperse crystalline phases is alumina-silicate glass, modified by cations of monovalent alkaline metals and/or bivalent alkaline earth metals. The results presented research shows major impact of quartz grain size on the structure of glass matrix, occurrence of crystalline phases, formation of nonbridging oxygen and as final a results differences in surface parameters like characteristic temperature, smoothness and chemical resistance.

(ICACC-S11-P151-2014) Low-temperature synthesis of BaTiO3 electroceramics through electric field-assisted sintering: microstructures and dielectric properties

J. M'Peko*, J. Francis, R. Raj, University of Colorado at Boulder, USA

BaTiO3 ferroelectric ceramics have been prepared in this work following both conventional and electric field-assisted flash sintering procedures. The conditions (of field, current and power density) under which the flash regime manifests without causing destructive breakdown in these materials are established. While the conventional sintering method, achieved at temperatures T>=1300 oC, leads to synthesizing high-density and coarse-grained ceramics, the flash sintering procedure shows to be strongly effective in producing highly-dense and fine-grained ceramics, at temperatures and times appreciably below the conventional ones. The combination of impedance spectroscopy and current-voltage (I-V) measurements allows to discuss on the effect of flash sintering at the microstructural level (at bulk and grain boundaries), as well as to explore the underlying mechanism, which most likely involves the nucleation of defects under electric field application. The dielectric permittivity and Curie temperature of these materials exhibit a clear dependence on the average grain size, a result of which is discussed in light of an extensive literature on size effects in BaTiO3 electroceramics.

(ICACC-S11-P152-2014) Surface oxidation behavior of porous Ni-based amorphous alloy under hydrothermal condition

M. Lee*, KITECH, Republic of Korea

The change of the specific surface area in porous Ni59Zr20Ti16Si2Sn3 metallic glass upon partial crystallization was investigated. The observed increase of the surface area of the annealed Ni-based metallic glass foams is due to the formation of homogeneously distributed Ni10(Zr,Ti)7 rod-shape intermetallic phases with nominal diameters around 250 nm and ~800 nm length on the surface of metallic glass struts during the crystallization. As a result of hydrothermal reaction, oxides and intermetallic phases were growth on the surface of porous Ni59Zr20Ti16Si2Sn3 metallic glass under high pressure and temperature conditions during 24 hours and 72 hours, respectively. The characterization of phases was evaluated by SEM, XRD, DSC, XPS and BET.

(ICACC-S11-P153-2014) Effect of interlayer thickness on the structure and properties of TiAlN/CrN multi-layer coating

Y. Kim*, J. Kim, Hanbat National Univ., Republic of Korea; K. Moon, Korea Institute of Industrial Technology, Republic of Korea

TiAlN and CrN as a hard coating are well established in industrial use as tool and die coatings. The typical micro hardness values of such hard coatings are in the range of 30 Gpa. It is well known that the multilayer composed of two different hard coatings takes advantage of the superior properties of each constituent. It is possible to deposit TiAlN/CrN superlattice structure coating by PVD techniques. In this work we try to deposit TiAlN/CrN multi-layer by dual D.C magnetron sputtering using TiAl alloy and Cr targets in an Ar+N2 atmosphere. The TiAlN and CrN layer thickness were varied by changing the duration of substrate faced the target. The microstructures of the multi-layer were characterized by cross-sectional TEM and EDS. We will discuss the effects of interlayer thickness and substrate temperature on microstructures and properties of the multi-layers.

(ICACC-S11-P154-2014) Thermal stability of SiOxCy(-H) thin films deposited by atmospheric pressure dielectric barrier discharge

Y. Kim*, Y. Lee, Hanbat National Univ., Republic of Korea

Electrode materials such as copper and silver applied in PCB are easily oxidized in ambient air. A SiOxCy(-Hz) thin film is one of the good barriers to protect the metals from reacting with oxygen, SOx, and humid. In this study, we try to deposit SiOxCy(-Hz) films on the silver using atmospheric pressure dielectric barrier discharge (DBD) generated by 30 kHz AC. The SiOxCy(-Hz) films were deposited from a mixture of hexamethylcyclotrisiloxane (HMCTSO), oxygen, and nitrogen. We investigated the microstructure and chemical bonding of SiOxCy(-Hz) thin layers up to 300oC by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The protection ability of the barrier layer was evaluated by color change of the silver for duration at several temperatures. We will discuss the relationship between the microstructure and chemical bonding of the barrier layer with protection ability.

(ICACC-S11-P155-2014) The synthesis of WC-Co alloy sintered by planetary ball-milling and spark plasma sintering process

H. Lee*, K. Moon, C. Byun, KITECH, Republic of Korea

WC-Co alloys are used widely in cutting tools, dies and wear resistant parts, because of their high hardness tools and wear resistance, as well as the good combination of strength and fracture toughness. In this paper, a new process for the production of WC-6, 9, 12wt%Co cemented carbide was fabricated by planetary ball-milling and spark plasma sintering. Tungsten carbide powder was mixed with cobalt powder in the planetary ball-mill. After planetary ball milling, the powders had uniform distribution of Co and the same composition with the original premixed powders. With the increase of Co contents, the particle size and grain size were increased and hardness was decreased. The as-milled powders were sintered at 1200 C by spark plasma sintering. The sintered body had its theoretical density. The as-sintered WC-6wt%Co showed the smallest grain size and thus it had the highest hardness of 2510Hv1.0.

(ICACC-S11-P156-2014) The properties of nanocomposite TiAlBN coating synthesized by magnetron sputtering process with single composite target

D. Jung*, K. Moon, KITECH, Republic of Korea; N. Lee, Hanyang University, Republic of Korea

With its progress of machine tools and cutting technology, study of multi-funcrional matrials with high efficiency is becoming increasingly important in terms of productivity, cost reduction and from an environmental point of view. The role of adding third elements have been studied to improve the properties of TiAl-N films. In this study, Ti-Al-B based single alloying targets were prepared by powder metallurgy of mechanical alloying and SPS. Ternary TiAlBN based films were deposited by unbalanced magnetron sputtering method with various alloying targets. During deposition, the substrate temperature was kept constant at 25degree in the mixture of Ar+N2 atmospheres. The composition of the films was almost the same with that of the target. Their micro-structures and mechanical properties were investigated by XPS, XRD, SEM, nano-indenter, tribometer, corrosion test and etc. Also, the effects of the boron on the mechanical and corrosion properties of the TiAlBN films were studied by changing Ar:N2 ratio. They showed the highest hardness at the gas ratio of Ar:N2 being 3:1. It was found that adding boron elements results in increasing its hardness by 5~10Gpa compared with that of TiAlN films itself. Finally characterization of films was studied by comparing the single nitride films with its graded nitride films.

(ICACC-S11-P157-2014) Improved Corrosion Resistance of Stainless Steels by Atomic Layer Deposited Films

S. Jang*, Z. Wan, D. Kim, S. Kwon, KITECH, Republic of Korea

Herein, we examined the feasibility of using atomic layer deposition method for improving corrosion resistance of stainless steels. Atomic layer deposition (ALD) has been recently attracted much interests as an effective strategy for a corrosion resistant coating application. Due to the inherent characteristics of self-limiting and surface reactions, ALD enables a precise atomic scale control of thickness of inorganic insulating layers and the resultant ALD films are naturally dense, highly conformal and pinhole-free, which makes it suitable for the application of corrosion resistant coatings. In this study, we examined two different approaches: (1) Design of the stacking structures of corrosion resistive ALD-films (nanolaminated or nanomixed structures), and (2) development of a new type of hybrid process between PVD and ALD methods. Based on our results, the most feasible strategy using ALD for improving a corrosion resistance was to use a hybrid process between PVD and ALD methods. We will introduce the detailed results in the presentation.

(ICACC-S11-P158-2014) A study on the mechanical properties with Cu amount on thin films prepared by magnetron sputtering with Mo-Cu single alloying target

H. Lee*, P. Shin, K. Moon, KITECH, Republic of Korea

In this study, Mo-Cu alloying powders were fabricated by mechanical alloying (MA) method because it is a useful process for mixing alloying powders which are usually hard to be mixed by conventional methods. Alloy targets were sintered by spark plasma sintering (SPS) process because it has several advantages such as rapid cooling rate and possibility of sustaining metastable state. Finally, thin film of Mo-Cu alloy were prepared by magnetron sputtering technique. Process conditions of Mo-5~50at%Cu powders were fabricated in air atmosphere, 1wt% of dispersion agent, 300RPM and the ratio 10:1 between balls and powder by mechanical alloying. Process conditions of Mo-5~50at%Cu single alloying targets were manufactured in sintering temperature 1100°C, pressure 70MPa, process time for 20mins. The targets density of Mo-5~50at%Cu were about 99%. And then the thin films were coated on the Si-wafer by using manufactured alloying targets. As compared with two target and single target, the components of coated specimen by using single target were able to match the target. It was able to confirm that the film has features structure and speeder than deposition rate of about 38%.

(ICACC-S11-P159-2014) Microstructure and thermal shock resistance of (silica-based ceramic + steel) composites coated on plain carbon steel by a bottom pouring casting

H. Kim, Sejong University, Republic of Korea; K. J. Oh, N. K. Yi, S. K. Kim, S.M Metal, Republic of Korea; K. Park*, Sejong University, Republic of Korea

Recently, steel-based metal matrix composites (MMCs) have been intensively investigated and found to be one of the most promising structural materials due to their high hardness, high wear and corrosion resistance, and high stability at high temperatures. In the present work, we coated (silica-based ceramic + steel) composites on plain carbon steel by a bottom pouring casting and investigated their microstructure and thermal shock resistance. The morphology, phase composition, and crystal structure of the coatings were investigated with scanning electron microscope, energy dispersive X-ray spectrometer, and X-ray diffractometer, respectively. We found good interface between the silica-based ceramic and steel in the composites. In this study, the microstructure and thermal shock resistance of (silica-based ceramic + steel) composites coated on plain carbon steel will be discussed, considering the bottom pouring casting conditions.

(ICACC-S11-P160-2014) The new trend of DLC coatings

J. Moon*, K. Yeo, E. Shin, J. Yoo, J&L Tech Co., LTD., Republic of Korea

Diamond-like carbon (DLC) can be coated on a variety of substrates including metals, polymers and ceramics. The coating provides certain diamond attributes, such as high wear resistance, low frictional coefficient, and extreme chemical inertness. Recently, Development of new trends in the area of DLC coatings, an attempt to create new properties are underway by the appearance of nanostructured surface from DLC coating. In particular, soft materials such as polymers present themselves various types of nanostructures due to the residual stress in the DLC coating or damage caused by plasma. In addition, by controlling the characteristics of DLC-coated surfaces, it can be implemented as hydrophilic and hydrophobic. Additionally, we developed multi-layer type anti-static film including few nano scale thickness of hydrogenated amorphous carbon (DLC) layer and metallic conductive layer, by hybrid coating system which is comprised of linear ion gun and magnetron sputter. Surface resistance can be controllable in the range of 103~1010Ω/sq by controlling the thickness. With the benefit of few nano scale coating, this technique can have the maximum processing speed and save raw coating materials, compared to conventional coating method for processing anti-static film.

(ICACC-S11-P161-2014) Mechanical properties of ZrAlCu(M) nitride films synthesized by ion beam assist sputtering

K. Yeo*, N. Kim, J. Hong, S. Ahn, J&L Tech Co., LTD., Republic of Korea

The ZrAlCu(M) nitride films were synthesized on SCM415(Carburizing) by using ion beam assist sputtering deposition from ZrAlCu(M) amorphous target. The influences of ion assist source energy and Ar : N2 relative flow rate on the surface roughness, adhesion, friction and mechanical properties of ZrAlCu(M)N films were investigated systematically. The surface roughness was measured using AFM(Atomic Force Microscope) and the mechanical properties of ZrAlCu(M)N films were evaluated with nano-indenter, pin-on-disk and micro-scratch methods.

(ICACC-S13-P162-2014) Graphite foil-incorporated carbon-carbon composite used in molten fluoride salt environment

C. Ju*, H. Lin, National Cheng-Kung University, Taiwan; K. Lee, I-Shou University, Taiwan; J. C. Lin, National Cheng-Kung University, Taiwan

C/C composite has been recommended to be used for molten fluoride salt-cooled reactors as structural containment for the highly corrosive salts. Despite their excellent high-temperature mechanical properties and chemical compatibility with molten fluoride salts, the inherently high porosity level of C/C composites is one major challenge to the material for such applications. The numerous macrocracks and pores in C/C composites are difficult to be completely sealed by conventional methods such as CVD or CVI. To overcome the porosity-related molten salt permeation problem, a graphite foil-incorporated carbon-carbon composite has been developed in the authors' laboratory. Reported in the presentation are some preliminary results of the corrosion resistance of this composite in a molten mixture of LiF, NaF and KF salts. Cross-sectional scanning electron micrographs and EDS elemental maps indicate that the graphite foil has effectively sealed the underneath PAN fiber/phenolic resin matrix-derived C/C composite against permeation of the high-temperature molten salts. Furthermore, given appropriate process parameters, the graphite foil may remain tightly bonded to the C/C structure during the entire fabrication processes and subsequent tests. The research is supported by the National Science Council of Taiwan, Republic of China under research grant NSC101-2221-E-006-127.

(ICACC-S13-P163-2014) Microwaves ignited combustion synthesis as a rapid and pressure-less joining technique for SiC ceramics

R. Rosa, P. Veronesi, University of Modena, Italy; V. Casalegno, M. Salvo, Politecnico di Torino, Italy; C. Leonelli, University of Modena, Italy; M. Ferraris*, Politecnico di Torino, Italy

Combustion synthesis (CS) is here proposed as a promising joining methodology for SiC based ceramic materials. Particularly, CS intrinsic peculiarities/advantages over more conventional joining techniques include extremely short processing times, significant energy saving, substantially pressure-less characteristics and a heating generation which is strictly localized where it is really required, i.e. in the joining region. Moreover, further advantages arise from the exploitation of microwave energy as ignition technique for the exothermic reactions occurring in the powders mixtures, constituting the joining material, and particularly the possibility to transfer energy to the reacting system also after ignition, the selective and volumetric nature of the heating mechanism together with the possibility to exploit microwaves absorption by the silicon carbide substrates to be joined. Aim of the present work is to pursue the joining of SiC components by microwaves ignited and sustained combustion synthesis in the ternary Ti-Si-C system. Several compositions of the starting reactive powders have been investigated with the aim of highlighting the main refractory phases responsible for a good joint, including the possibility to in situ synthesise MAX phases. A special dedicated MW applicator has been used to sustain the exothermic reaction with the appropriate forward MW energy.

(ICACC-S13-P164-2014) Advanced Characterization of High Burn-up Oxide Fuel

M. Teague*, Idaho National Lab, USA; B. Gorman, Colorado School of Mines, USA; B. Miller, Idaho National Lab, USA

Development of new advanced characterization techniques have aided in understanding complex materials under a variety of conditions. The application of these techniques to radioactive samples, and specifically irradiated fuel have been delayed due to challenges of working with the samples. However, these advanced techniques such as electron backscatter diffraction, focused ion beam, and transmission electron microscopy when applied to these samples provide valuable new data that has been very difficult or impossible to generate previously. The results from characterizing high burn-up oxide fuels irradiated in the fast flux test facility to a range of burn-ups will be presented.

(ICACC-FS1-P165-2014) Design of wool-geopolymer pots

E. Papa*, A. Natali Murri, V. Medri, E. Landi, CNR-ISTEC, Italy

Disposal of wool waste still encounters significant problems due to the need to satisfy environmental legislation and to the increasing cost of landfilling. Conversely, given the high content of useful nutrients it contains, sheep wool waste could still have a great potential for many applications, such as crop plant fertilizer and growth medium. The aim of this work is hence to highlight the possibility of reusing wool scraps as a constituent material for plant pots, producing innovative wool-geopolymer composite artifacts. Environmental-friendly pots for plant growing have been designed by impregnating chopped or hank wool scraps with an inorganic geopolymer resin. Preliminary comparative evaluations conduced on plant crops grown in peat or wool-geopolymer vases demonstrated that the presence of the organic material positively influenced the plant growth ratio. Wool fibers and geopolymer matrix indeed act together in providing a controlled release of nutrients to the plants and maintaining a higher and longer lasting level of soil moisture.

(ICACC-FS1-P166-2014) Rice Husk Ash as a Silica Source in Geopolymer Formulation

U. Heo, W. M. Kriven*, University of Illinois at Urbana-Champaign, USA

South Korean rice husk ash (RHA) has been investigated as an alternative silica source to replace fumed silica currently used in geopolymer research. In order to acquire proper RHA from raw rice husk, the optimal calcination temperature, which produces the highest amount of amorphous silica, was studied. SEM-EDS and XRD were used to determine the RHA content. Previously many researchers have studied mixtures of RHA/fly ash (FA) or RHA/red mud (RM), resulting in a ratio of SiO_2/Al_2O_3 which varied for each mixture. In this paper, however, RHA only replaced a fraction of fumed silica. The fundamental ratio of each ingredient in the geopolymer ($K_2O/SiO_2/Al_2O_3/H_2O$ or 1:1:4:11) was strictly kept. Five variations of RHA/fumed silica mixture (0/100, 25/75, 50/50, 75/25, 100/0 by wt %) were studied. Each mixture was dissolved in potassium hydroxide (KOH) and water for 24 hours on a stirring plate forming “waterglass”. Metakaolin was added to the waterglass and mixed in a high shear mixer The geopolymer slurry was poured into a mold and cured at 50 C for 24 hours. After demolding the RHA geopolymer samples were cured for at least 3 days at room temperature. The flexural stress of RHA geopolymer samples were investigated by 3-point bending (ASTM C78) at room temperature. It was demonstrated that the RHA can clearly be used as a fumed-silica alternative.

(ICACC-S7-P167-2014) Self-sustained UV/visible-light photodetector based on hybrid heterostructures

A. A. Gad*, T. Fischer, S. Mathur, Inorganic and Materials Chemistry, Germany

A self- sustained, UV/visible-light photodetector has been fabricated based on the integration and correlation of complementary functionalities originating from multiple junctions in a singular nanostructure of CdS@ZnO/p-Si nanowires. The synergic overlap of the n-ZnO functionalities as part of the diode (n-ZnO/p-Si, signal generation unit) and its UV- light absorbing ability, which have been extended into visible region by decoration with CdS nanoparticles (CdS@ZnO, photodetection unit), enables a very simple and compact design of an autonomous photodetector that operates without the need of any external energy source. Under different wavelength of light illumination, the open circuit voltage produced under zero-bias by the photovoltaic cell of n-ZnO/p-Si diode act as self-generated signal sensitive to different wavelengths in the UV/visible-light region. Fast responses can be attributed to the efficient charge separation and transfer at the heterointerfaces of the system. These photodetector are promising candidates for the development of a new generation of technically feasible and easy to use energy neutral nanodevices.

(ICACC-S7-P169-2014) Core-shell and segmented metal oxide-metal composite nanowires for photocatalytic hydrogen formation

W. Maijenburg, J. E. ten Elshof*, University of Twente, Netherlands

Two novel types of photocatalytically active segmented nanowires are demonstrated. They were grown from electrolyte solutions by electrochemically induced sol-gel deposition in the pores of polycarbonate track-etched template membranes. Axially segmented nanowires such as ZnO|Ag were made by sequential deposition from different precursor solutions. Nanowires with core/shell morphologies like Ag/TiO2 were obtained via an electrodeposition strategy that involved the formation of a metal hydroxide gel by cathodic deposition, followed by a drying step in which the gel collapsed to form hollow metal oxide nanotubes. In a subsequent electrodeposition step, these tubes were then filled by a noble metal. The as-formed wires typically had a length of 3-6 micrometer, and 50-300 nm diameter. The combination of a photo-anodic metal oxide phase and a cathodic metal phase in a single wire enabled the formation of hydrogen from water/methanol solutions and water under UV radiation. To prevent recombination of excitons, we paid special attention to the realization of Schottky barriers between the metal and metal oxide phases. The electrical properties of individual wires were investigated by positioning them between macroscopic electrodes using dielectrophoresis, and monitoring their I-V response. The Schottky character of the metal oxide/metal interface was clearly demonstrated.

(ICACC-S7-P170-2014) Conformal Nanocoatings for Surface Engineering of Particles by Thermal and Plasma-Enhanced Atomic Layer Deposition using a Rotary Reactor

G. Rampelberg*, D. Longrie, D. Deduytsche, J. Haemers, Ghent University, Belgium; K. Driesen, Umicore, Belgium; C. Detavernier, Ghent University, Belgium

Surface engineering of micro- and nanoparticles is of great importance in fields such as catalysis, energy and sensing. In this work, a rotary reactor was used to agitate particles, enabling the deposition of conformal nanocoatings by thermal and plasma-enhanced atomic layer deposition (ALD). Particles ranging from nanometer size to millimeter size were successfully coated with nanolayers of Al2O3, TiO2, AlN and TiN. In-situ mass spectroscopy confirmed that ALD was performed by detecting the expected reaction products. By monitoring the formation of these reaction products over time, it was possible to optimize precursor and reactant usage, which is linearly dependent on the effective surface area of the particles. In the case of plasma-enhanced ALD, optical emission spectroscopy confirmed the mass spectroscopy data. X-ray fluorescence revealed the expected linear relationship between the amount of ALD cycles and the deposited amount of material. X-ray photo-electron spectroscopy confirmed the composition and purity of the coatings. Transmission electron spectroscopy showed that the individual particles were coated uniformly and conformally. Our results show that the proposed rotary reactor enables the conformal deposition of nanocoatings on nano- and microparticles by ALD. In this way, surface engineering of such particles can be achieved.

(ICACC-S7-P171-2014) Surface interaction control and characterization of microcapsule and biological molecules for pharmaceutical application

H. Kamiya*, Tokyo University of Agriculture and Technology, Japan; M. Iijima, Yokohama National University, Japan; H. Ichikawa, Y. Fukumori, Kobe Gakuin University, Japan; H. Takeuchi, Gifu Pharmaceutical University, Japan

For the development of drug delivery systems using particulate matters and microcapsules, the surface interaction between such materials and biological molecule was controlled by surface molecular and nanometer scaled structure design. The interactions between pharmaceutical particulate material and biological molecules such as mucin layers were successfully measured by using colloid probe atomic force microscopy (AFM) . Based on the measurement result, our group designed surface molecular structure to control surface interaction. One example is novel thermo- and pH-sensitive nanogel particle, which is a core-shell structured particle as a vehicle for the controlled release of peptide drugs. The pH depended change of surface interaction between p(MMA-g-EG) shell and mucin layer in small intestine were measured. The interaction between nanogel and mucin layer in each pH condition was able to be controlled by molecular level shell structure design. Next, chitosan-coated liposomes have been designed for same purposes. Carbon nano-tube (CNT) attached probe was immersed in PEI solution (3mg/ml) over night and then adsorbed mucin layer on CNT probe. Micro adhesion behavior of chitosan-coated liposomes was quantitatively assessed by using CNT probe with coated mucin layer.

Thursday, January 30, 2014

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing I

Room: Coquina Salon D
Session Chairs: Yiquan Wu, Alfred University; Emmanuel Boakye, UES Inc.

8:00 AM

(ICACC-S1-043-2014) New Concepts for Tailoring Mechanical Properties of Multilayer Ceramic Systems Designed With Compressive Residual Stresses

Y. Chang, G. L. Messing*, Penn State University, USA; R. Danzer, Almatis, Inc., Germany; R. Bermejo, Penn State University, USA

Multilayer ceramic composites are usually arranged with 2-2 connectivity (i.e., a periodic laminar architecture) in which relatively high compressive residual stresses can be tailored based on the elastic/thermal properties and volume ratio of the layers, yielding high crack growth resistance and mechanical reliability relative to the monolithic ceramic constituents. Recent work has shown that non-periodic layering can be more effective at arresting the propagation of cracks than periodic designs. In this work, new design concepts for tailoring the resistance to crack propagation in multilayer ceramic composites are shown based on 1-1 connectivity laminate composites fabricated using the co-casting technique. Experimental findings on alumina-zirconia composites, supported by a fracture mechanics analysis, demonstrate that placing the first compressive layer closer to the tensile surface and increasing this layer's thickness yields a significant increase in the threshold strength (up to 470 MPa) and apparent fracture toughness (up to 17 MPa.m$^{1/2}$). 1-1 multilayer architectures provide the opportunity to tailor the location and thickness of the compressive layers, thus providing a preferential fracture path for crack propagation independent of initial defect size. This opens new possibilities for design of multilayer structures with higher reliability.

8:20 AM

(ICACC-S1-044-2014) Thermo-mechanical properties of SOFC components investigated by a combined method

F. Teocoli*, V. Esposito, S. Ramousse, R. Kiebach, Technical University of Denmark - DTU, Denmark

Co-firing process of different ceramic materials can lead to significant stress and deformation at the multilayer. This is the net effect of a complex set of phenomena such as the removal of organic additives from the green tapes (de-binding), solid state diffusive phenomena during the sintering, and differential thermo-mechanical behavior at each layer. The combination of such factors can have a critical effect on the final shape and microstructure, and on the mechanical integrity. Thermo-mechanical properties and sintering mechanisms of important SOFC materials (CGO, YSZ, ScYSZ) were systematically characterized by mean of the combined use of optical dilatometry, cyclic loading thermo-mechanical analysis and scanning electron microscopy. The results from the different techniques were found complementary and the thorough understanding of viscoelastic properties of individual layers led to optimization of firing strategy and SOFC design, fundamental to avoid shape instability. Work sponsored by EUDP (Danish energy agency) project 64012-0225 "SOFC accelerated".

8:40 AM

(ICACC-S1-045-2014) Microstructural control of spark plasma sintered silicon nitride powder blends with low concentration magnesium nitride sintering additives

A. Ellis*, W. Pinc, L. S. Walker, E. L. Corral, University of Arizona, USA

Silicon nitride is densified with precise control of porosity and β-Si_3N_4 concentration by use of spark plasma sintering (SPS), a low concentration magnesium nitride sintering additive, and by altering starting β-Si_3N_4 concentration in starting powder blends. Powder blends are developed by optimization of particle dispersion and the mixing of magnesium nitride sintering aid into Si_3N_4. Higher concentration of β-Si_3N_4 in the starting powder blends are used to promote β-Si_3N_4 growth during SPS densification. Sintering temperature, pressure, and hold time are all found to have significant impacts on densification and β-Si_3N_4 growth rates. The effect of altering the powder blend and SPS processing parameters on grain size, morphology, and pore distribution is investigated along with flexural strength data. It is found that despite the low concentration of additive, our powder system can achieve the same microstructure and properties obtained in high concentration oxide aided systems.

9:00 AM

(ICACC-S1-046-2014) Spark Plasma Sintering of Ceramic Matrix Composites with self healing matrix

J. Magnant, L. Maillé*, R. Pailler, A. Guette, Laboratoire des Composites Thermostructuraux, France

The processing of dense Ceramic Matrix Composites (CMC) by a short time and so by low cost process was studied. This process is based on (i) the chemical vapor deposition of carbon interphase on the fiber surface, (ii) the introduction of mineral powders inside the multidirectional continuous fiber preform and (iii) the densification of the matrix by Spark Plasma Sintering (SPS). To prevent carbon fibers and interphase from oxidation in service, a self-healing matrix made of silicon nitride and titanium diboride was processed. A thermal treatment of 3 minutes at 1500°C allows to fully consolidate by SPS the composite without fiber degradation. The ceramic matrix composites obtained have an ultimate bending stress at room temperature around 300 MPa and show a self-healing behaviour in oxidizing conditions.

9:20 AM

(ICACC-S1-047-2014) Spark Plasma Sintering of Transparent Li4Ti5O12

Y. Wu*, Y. Yang, Alfred University, USA

Transparent Li4Ti5O12 was fabricated by a Spark Plasma Sintering (SPS) process using commercial nano-powders. Firstly, the Li4Ti5O12 nano-powder was ball-milled followed by the calcination to remove the remaining organics. After the pre-treatment, the powder was directly sintered by a SPS process to make transparent Li4Ti5O12 ceramics. The particle size distribution of the powder before and after the pre-treatment was measured. The phase purity of the final transparent ceramic was examined by X-Ray Diffraction (XRD). The microstructure of the sintered bodies was observed by Scanning Electron Microscopy (SEM). The transmissions were then characterized by Fourie Transform Infrared Spectrometry (FTIR). The heating rate, pressure and sintering temperature as well as the soaking time were varied to investigate the parameters during the SPS process.

10:00 AM

(ICACC-S1-048-2014) Mechanical Performance of Honeycomb-like Biomorphic Graphite/Copper Composites

A. Childers*, K. Faber, Northwestern University, USA

This work utilizes biomorphic graphite produced by catalytic pyrolization of wood, creating an anisotropically porous graphite scaffold with relative ease as compared to traditional porous ceramic-processing methods. The wood species of the scaffold precursor determines the pore size, volume fraction, distribution, and connectivity, offering a wide range of possible porous materials systems. The elongated channels are then infiltrated with copper using pressure-assisted melt infiltration to produce a composite with high connectivity in the matrix ceramic phase, and extended one-dimensional connectivity in the metal reinforcement phase. Due to the natural variations, imperfect (mechanically-bonded) interfaces, and interpenetrating phases, these composites present an interesting opportunity to compare composite mechanical theory with naturally derived structures. Several methods have been used to begin illuminating the mechanical properties of this class of material, including standard compression and flexure tests, synchrotron X-rays techniques, and manufactured material analogs. This talk will discuss the observed properties in these metal/ceramic composites, many of which vary between the brittle/ductile extremes depending on the precursor wood species, and compare and contrast the benefits of each experimental technique.

10:20 AM

(ICACC-S1-049-2014) Anisotropic creep behavior of a unidirectional all-oxide CMC

K. Artzt*, S. Hackemann, F. Flucht, M. Bartsch, DLR, Germany

All-oxide CMCs based on alumina fibers and matrices are favorable materials for use at high temperature in oxidizing atmospheres. Combining endless ceramic fibers with a highly porous matrix a material with high damage tolerance can be processed. However, given the comparably low creep resistance of alumina CMCs utilizing this class of materials for long term applications under mechanical load requires detailed knowledge about creep properties. Due to the fiber-matrix structure the CMC exhibits an inherent anisotropy, making experimental investigations and modeling quite challenging. Further complexity arises by asymmetric creep behavior in tension and compression and by matrix compressibility. Starting with unidirectional CMC specimens, tensile and compression experiments were conducted to identify the stress and temperature dependent creep parameters. Additional compressive off-axis tests provided shear parameters and identified a transition from fiber-dominated creep to matrix compaction. The matrix deformation in compression was investigated by visualization of fiber rearrangement, which simultaneously gave information about local displacements. First simulation results of compressive creep behavior based on a fiber-matrix unit cell and experimental results are presented and discussed with regard to the applicability and limitations of a commonly used approach after Hill considering creep anisotropy.

10:40 AM

(ICACC-S1-050-2014) Advanced ceramic composite using self-healing and fiber-reinforcement

W. Nakao*, D. Maruoka, Yokohama National University, Japan; M. Nanko, Nagaoka University of Technology, Japan; S. Ozaki, Yokohama National University, Japan; T. Osada, National Institute of Materials Science, Japan

Advanced fiber reinforced ceramic composite (FRC) having self-healing function has been developed. The composite includes the silicon carbide interlayer as healing agent at the interface between alumina fiber and alumina matrix. The healing agent interlayer caused the preferential fracture of the fiber/matrix interface and the interface fracture gave rise to the slip of the interface during crack propagation. Thereby the FRC could exhibit a large deformation at the fracture and large fracture energy. Moreover, the high temperature oxidation of the healing agent made the interface delimitation rebounded by the formed oxide and the reaction heat. As a result, the maximum strength and the stiffness degraded by the interface delimitation could be recovered by the healing. Consequently, it was found that the FRC containing the interlayer of the healing agent can survive the repeated crack propagation or initiation due to the large impact damage.

11:00 AM

(ICACC-S1-051-2014) Directional Crystallization of Columnar-Grained Monoclinic Y2O3 under Pressure

J. Al-Sharab*, NYU-Poly, USA; S. Deutsch, B. H. Kear, S. D. Tse, Rutgers University, USA

In a previous communication, we described a novel pressure-induced reversible phase transformation process to convert fine-grained (1.5 μm) cubic-Y2O3 directly into the nanocrystalline state. Briefly, polycrystalline cubic-Y2O3 is first exposed to 8.0 GPa/1000C/15min to generate nanocrystalline monoclinic-Y2O3, and then exposed to 1.0 GPa/1000C/15 min to regenerate cubic-Y2O3, but now with a nanocrystalline structure. In this paper, we report new results obtained for polycrystalline cubic-Y2O3 when processed at 1000C for 15-240 min, with pressures varying over the 1.0-8.0 GPa range. As will be shown, a remarkable transformation to columnar-grained monoclinic-Y2O3 occurs when polycrystalline cubic-Y2O3 is subjected to pressures >2.5 GPa at 1000C. The effect appears to be due to directional crystallization (DC), driven by the negative free volume change that occurs at the tips of the growing columnar grains, as the material transforms from c-Y2O3 phase to the higher density m-Y2O3 phase.

11:20 AM

(ICACC-S1-052-2014) Resin System Prepared via Ethanol Additions to Polyvinylsilazane

G. Richards*, J. Reutenauer, T. Coons, S. Frueh, S. Suib, University of Connecticut, USA; M. Kmetz, Pratt and Whitney, USA

This investigation focused on the synthesis and characterization of an ethanol-modified polyvinylsilazane (PVSZ) resin system. The PVSZ polymer has been previously shown to be a viable precursor for silicon nitride and silicon carbide based ceramics, but lacks stability when exposed to air. The PVSZ polymer was synthesized via the ammonolysis of trichlorovinylsilazane in tetrahydrofuran (THF). The PVSZ polymer and ethanol-modified PVSZ resin were each characterized with Attenuated Total Reflectance spectroscopy (ATR), 1H Nuclear Magnetic Resonance (1H-NMR), and Gel Permeation Chromatography (GPC). Both polymers were found to have an average molecular mass of about 950 g/mol. Ethanol-modified PVSZ was heated to 1400°C in Ar and found to have a char yield of 86% using Thermogravimetric Analysis (TGA). Residual Gas Analysis (RGA) was used to observe the removal of ethanol from the polymer when heated. X-ray powder diffraction (XRD) of the ceramic char showed that SiC was obtained in a He pyrolysis atmosphere. Ethanol-modified PVSZ yielded SiC when pyrolyzed in Ar, while neat PVSZ contained a mixture of SiC and Si3N4. Pyrolysis in N2 gave Si3N4 for the neat PVSZ, while ethanol-modified PVSZ contained a mix of SiC and Si3N4. Pyrolysis in NH3 gave Si3N4 for both materials. The ethanol-modified PVSZ maintains the desirable properties inherent in the original polymer, while having far superior stability.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Advanced Thermal and Environmental Barrier Coatings

Room: Coquina Salon G

Session Chair: Marie-Helene Vidal-Setif, ONERA; Kang Lee, Rolls-Royce Corporation

8:00 AM

(ICACC-S2-021-2014) Hot gas corrosion and EBC development for ceramic materials (Invited)

H. Klemm*, W. Kunz, A. Michaelis, FhG IKTS Dresden, Germany

Caused by the steady increasing energy price and the stronger requirements in environmental protection the main focus of future generations of gas turbines will be emphasized on an increased efficiency with a simultaneous reduction of the emissions. From technical point of view these goals can be obtained only by higher operating temperatures in the system in combination with lower amount of cooling air. Ceramic materials offer high potential for application in gas turbines. Significant progress has been achieved in the development monolithic materials and ceramic matrix composites; however, commercial applications in the hot gas path of gas turbines were rather limited. Caused by the high water vapor pressure in combination with high temperatures and gas velocities, corrosion processes at the surface and inside the materials were observed resulting in significant material loss. Hence, environmental barrier coatings (EBC) have been presented to be the solution to protect the surface of the ceramic materials. Systematic studies on the hot gas corrosion of ceramic materials have been performed with and without EBC. Based on a detailed understanding of these processes in the whole system, EBC and the ceramic base material during application in hot gas environments at elevated temperatures, general concepts for the development of environmental barrier coatings will be discussed.

8:30 AM

(ICACC-S2-022-2014) The structure design for the impact resistance of environmental barrier coatings (Invited)

Y. Wang*, J. Liu, Northwestern Polytechnical University, China

Fiber reinforced SiC ceramic composites (SiC-CMC) can be used as structural materials for next generation gas turbine due to their excellent high temperature mechanical properties. Ho wever, SiC matrix is very sensitive to the water-vapor in the combustion gas, which will lead to the degradation of the materials. The environmental barrier coatings (EBCs) are therefore required to protect the ceramics from corrosion. In the gas turbine, the combustion gas has a very high velocity. Any foreign objects in the combustion gas will impact on the components in the turbine. These foreign object impacts can case the damage to the EBC coatings, causing the corrosion to the fibers and matrix inside, further the failure of the components. In order to address this problem, a unique EBC structure was designed in this study. The structure includes an outerlayer with lower Young's modulus materials, a middle layer with higher Young's modulus materials, and a bonding layer. We simulated the impact damage using indentation with different loads. The indented samples were then corroded in water-vapor for 200 hours at high temperatures. Results indicated that such a unique structure can effectively suppress the crack propagation to the matrix. The SiC-CMC was well protected.

9:00 AM

(ICACC-S2-023-2014) Effect of periodical stress/strain distribution on fracture behavior of EBCs coated on woven continuous fiber-ceramic matrix composites

Y. Motoyama*, H. Kakisawa, Y. Kagawa, The University of Tokyo, Japan

Effect of local deformation behavior in surface of woven fabric continuous ceramic fiber-ceramic matrix composites on deformation and fracture behavior of EBCs have been studied to investigate the damage evolution of the EBCs under tensile overloading condition. Woven fabric carbon fiber or SiC fiber-SiC matrix composite is tensile tested and strain distribution at the surface of the composite is measured using DIC method. Model brittle layer coatings are applied on the surface of composite and cracking events under tensile loading is observed; the results are compared with the strain distribution pattern. Local periodical strain distribution obviously appears in the surface and cracking behavior of the brittle coating layer is correlated with the strain distribution. Mechanical model to describe the cracking behavior of the EBCs on woven fabric type ceramic composites is proposed based on experimental results. The effect of the local stress/strain distribution on damage evolution of EBC upon overloading condition is discussed especially from safety application points.

9:20 AM

(ICACC-S2-024-2014) Stress Relaxation in an Air Plasma Sprayed Silicate Coating

J. Wan*, E. Gamble, D. Lipkin, C. Johnson, GE Global Research, USA

Experimental measurement of stress relaxation as a function of time was performed on an air plasma sprayed rare earth silicate material. A coating of the silicate material was sprayed onto a relatively thin CMC substrate. A compressive stress in the coating was evolved during heating. The resulting stress was relaxed during dwell at high temperature. The stress in the coating was determined from in-situ measurements of the bilayer curvature. Stresses in excess of 120 MPa were observed. The stress data were fit to a power law creep model to predict the relaxation rate.

10:00 AM

(ICACC-S2-025-2014) Oxygen and water vapor permeability of $Y_2Ti_2O_7$ at high temperatures

M. Tanaka*, T. Matsudaira, Japan Fine Ceramics Center, Japan; H. Mukai, T. Sassa, Gifu University, Japan; S. Kitaoka, Japan Fine Ceramics Center, Japan; M. Yoshida, O. Sakurada, Gifu University, Japan

The environmental stability and durability of environmental barrier coatings (EBCs) for SiC fiber reinforced SiC ceramic matrix composites (CMCs) play a key role in their application to hot-section components of next-generation gas-turbine engines. We have proposed the new concept of advanced EBCs that effectively reflect the thermal energy radiated from a high-temperature heat source in addition to providing oxidation protection of the underling CMCs. The resulting significant decrease in EBC temperatures would inhibit the diffusion of oxidant species through the EBCs, drastically reducing the oxidation of the CMCs. Such thermal reflectivity can arise from the formation of periodic layered structures consisting of two kinds of oxides with large different refractive index (n). The combination of $Y_2Ti_2O_7$ (YT) and alumina is satisfying the condition of n, and they do not react with each other at high temperatures. Furthermore, YT has an excellent water vapor corrosion resistance. Thus, they are candidate for the EBC materials. In this study, oxygen and water vapor permeability of YT was evaluated at high temperatures to investigate the applicability of it. The corresponding permeation mechanisms were discussed.

10:20 AM

(ICACC-S2-026-2014) APS Y_2O_3 Environmental Barrier Coatings with high CMAS-Resistance

P. Mechnich*, W. Braue, German Aerospace Center (DLR), Germany

Al_2O_3/Al_2O_3 ceramic matrix composites (CMCs) are candidate materials for combustor walls of next generation gas turbines. The maximum CMC operation temperatures, however, are limited since Al_2O_3 is prone to thermochemical recession in combustion environments. The application of environmental barrier coatings (EBC) is considered a suitable way to overcome the recession problem. Y_2O_3 is a potential EBC material for Al_2O_3/Al_2O_3 CMCs due to its high thermal and chemical stability and a thermal expansion close to Al_2O_3. Different types of continuous fiber reinforced Al_2O_3/Al_2O_3 CMC substrates were coated with Y_2O_3 by air plasma spraying (APS). Upon isothermal and thermocyclic heat treatments APS Y_2O_3 coatings exhibit good adherence to Al_2O_3/Al_2O_3 CMCs. This is due to the low thermal mismatch and the formation of an approximately one micron thick reaction zone at the Y_2O_3-Al_2O_3 interface, comprising a thermodynamically stable sequence of garnet-type $Y_3Al_5O_{12}$, perowskite-type $YAlO_3$ and monoclinic $Y_4Al_2O_9$. The response of APS Y_2O_3 EBCs to high-temperature attack by deposited mineral dusts was studied using synthetic CMAS powders. It turns out that CMAS melt infiltration of APS Y_2O_3 is low, which is explained by the microstructure and a rapid formation of a continous Ca,Y-oxyapatite layer.

10:40 AM

(ICACC-S2-027-2014) Deposition parameter-microstructure study of ytterbium silicate based EBCs deposited via APS

B. T. Richards*, H. Zhao, H. Wadley, University of Virginia, USA

Ytterbium silicate based Environmental Barrier Coatings (EBCs) have been deposited via Air Plasma Spray (APS) and examined for five sets of deposition parameters. These coatings were used to assess the possible range of microstructures that may be achieved for EBC use in gas turbine hot sections. For each coating layer (ytterbium silicate/mullite/silicon), we have identified lower and upper torch amperage and secondary gas flow bounds required to deposit a structurally sound coating of near target stoichiometry (evaluated by SEM and EDS) using a trial-and-error approach. All coatings were deposited in a Praxair-TAFA spray cell with UPC7700 controls and SG100 torch. The window for achieving an adherent and reasonably dense coating with both acceptable deposition efficiency and no phase decomposition is small; varying structures are obtained across the acceptable parameter space. Secondary hydrogen gas flow and torch amperage both contribute to the spray power achieved but have slightly different effects on the deposited microstructure. Hydrogen flow, torch amperage, and powder feeder configuration must all be carefully optimized in order to deposit the most desirable coating structure.

11:00 AM

(ICACC-S2-028-2014) High Temperature Multilayer Environmental Barrier Coatings Deposited Via Plasma Spray–Physical Vapor Deposition

B. Harder*, D. Zhu, NASA Glenn Research Center, USA; M. P. Schmitt, D. E. Wolfe, Pennsylvania State University, USA

Ceramic matrix composites (CMCs) have the potential to significantly improve gas turbine engine efficiencies due to lower densities and higher thermomechanical stabilities than superalloy components. However, SiC/SiC CMCs require environmental barrier coatings (EBCs) in combustion environments to avoid rapid material loss. Candidate EBC materials have use temperatures only marginally above current technology, but the addition of a columnar oxide topcoat to the EBC can substantially increase the maximum temperature. Plasma Spray-Physical Vapor Deposition (PS-PVD) processing allows for this columnar topcoat to be incorporated onto dense EBC layers to form a multilayer EBC in a single deposition. The PS-PVD technique is a unique processing method that combines conventional thermal spray and vapor phase methods, allowing for tailoring of thin, dense layers or columnar microstructures by varying deposition conditions. Multilayer coatings were deposited on CMC specimens and assessed for durability under high heat flux and load. Coated samples were tested for up to 200 hours with surface temperatures ranging from 2400-2700F and 10 ksi loads using the high heat flux laser rigs at NASA Glenn. Coating morphology was characterized in the as-sprayed condition and after thermomechanical loading using electron microscopy and the phase structure was tracked using X-ray diffraction.

11:20 AM

(ICACC-S2-029-2014) Characterization of Desert Sand and Glass

N. Bansal*, NASA Glenn Research Center, USA; S. R. Choi, Naval Air Systems Command, USA

Future jet engines will operate at much higher temperatures than the current engines. Desert sand ingested into turbine engines will melt into glass at these elevated operating temperatures. Sand and molten glass may chemically interact and infiltrate into the TBC and EBC of various engine components and may adversely affect their performance and life. It will be useful to understand the characteristics of desert sand and various properties of the resulting glass. Desert sand was characterized by X-ray diffraction (XRD) and DTA-TGA. XRD analysis showed the presence of quartz (SiO2), calcite (CaCO3), gypsum (CaSO4.2H2O) and NaAlSi3O8 phases in as-received sand. TGA/DTA analysis of sand showed weight loss of ~35% due to decomposition of CaCO3 and CaSO4.2H2O when heated to 1400C. A batch of as-received desert sand was melted into glass. Various physical, thermal and mechanical properties of the glass have been evaluated.

11:40 AM

(ICACC-S2-030-2014) Interactions of Desert Sand Glass with Advanced $Y_2Si_2O_7$ and $HfSiO_4$ Environmental Barrier Coatings

V. L. Wiesner*, B. J. Harder, N. P. Bansal, NASA Glenn Research Center, USA

Particulates, such as sand and volcanic ash, pose a significant threat to the development of robust environmental barrier coatings (EBCs) that are used to protect silicon-based ceramic matrix composite (CMC) turbine engine components from corrosion and oxidation encountered in harsh combustion environments during service. When an aircraft engine ingests sand and similar small debris at elevated temperatures, the particulates transform into molten glassy deposits of calcium-magnesium-aluminosilicate (CMAS). In this study, CMAS glass was prepared by melting a sample of desert sand to evaluate and experimentally model high-temperature interactions between the sand glass and advanced EBC materials. Freestanding hot-pressed substrates of $Y_2Si_2O_7$ and $HfSiO_4$ were used, and cylindrical wells were drilled into the substrates. Desert sand glass powder was added to the well to subject the surface of the EBC substrate to a loading of ~35mg/cm^2. Heat treatments in air at 1200°C, 1300°C, 1400°C and 1500°C for 20h were performed. Scanning electron microscopy and X-ray energy-dispersive spectroscopy were used to evaluate the microstructure and phase compositions of specimens after heat treatment.

12:00 PM

(ICACC-S2-031-2014) The Influence of Ca-Mg-Al Silicates on Stresses, Phase Transformations, and Damage Evolution in Yb-Silicate Environmental Barrier Coatings

F. Stolzenburg*, Northwestern University, USA; P. Kenesei, J. Almer, Argonne National Lab, USA; K. N. Lee, Rolls-Royce Corporation,, USA; K. T. Faber, Northwestern University, USA

With the increasing importance of SiC/SiC composites for high-temperature structural applications and their known vulnerability to attack by water vapor at elevated temperatures, identifying environmental barrier coatings (EBCs) for these materials is paramount. Rare-earth silicates have been recognized as promising candidates for EBCs due to their excellent high temperature stability and well-suited thermal expansion coefficient. However, it is known that calcium magnesium aluminosilicates (CMAS), ubiquitous glassy engine deposits, react with EBCs, leading to changes in stress states, the formation of unwanted phases, and ultimately, premature failure. High-intensity X-rays in a transmission geometry at beamline 1-ID of the Advanced Photon Source were used to perform detailed analysis on these EBCs by combining wide-angle X-ray strain measurements, small-angle X-ray scattering, and X-ray computed tomography. This allowed for studying changes in these materials at several size scales, offering a better understanding of what changes take place in these EBCs when exposed to CMAS. Ex-situ studies were also performed to study the formation of new phases at the interface using a combination of electron and X-ray diffraction techniques.

S3: 11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Air Electrode

Room: Coquina Salon H
Session Chairs: Peter Hendriksen, Technical University of Denmark; Nguyen Minh, University of California, San Diego

8:00 AM

(ICACC-S3-028-2014) Synthesis of SmBa0.5Sr0.5Co2O5+δ powder and its application as composite cathode for intermediate temperature solid oxide fuel cell

T. Lin*, The Institute of Nuclear Energy Research, Taiwan; M. Lee, The Institute of Nuclear Energy Research, Taiwan; R. Lee, The Institute of Nuclear Energy Research, Taiwan

The layered samarium and strontium doped perovskite oxide SmBa0.5Sr0.5Co2O5+δ (SBSC) is synthesized by glycine nitrate combustion process. The crystallinity of SBSC powder with calcination temperatures shows that the perovskite phase is completely formed above 1000 °C. SBSC powders mixed with Sm0.2Ce0.8O2-δ (SDC) have been utilized as cathode materials to form a composite cathode which provides better compatibility with electrolyte and enhances the catalytic property for the cell. The single cell of yittria-stabilized zirconia (YSZ) based electrolyte with structure of NiO-YSZ // YSZ // SDC / SDC-SBSC, is operated from 700 to 800 °C with H2 as a fuel and ambient air as oxidant. The maximum power densities are 603, 449 and 321 mW cm-2 at 800, 750 and 700 °C, respectively. The fixed-current treatment of the cell results in an ultimate power density of 652 mW cm-2 at 800 °C with a slight cell degradation. According to the electrochemical impedance spectroscopy, the charge-transfer resistances of the electrodes are 0.10, 0.14, and 0.87 Ω cm2, and the non-charge-transfer resistances are 0.27, 0.97, and 1.09 Ω cm2 at 800, 750, and 700 °C, respectively. The experimental results indicate that SBSC is a promising cathode material for intermediate temperature solid oxide fuel cell (IT-SOFC).

8:20 AM

(ICACC-S3-029-2014) Defect Equilibria of (Pr0.6Sr0.4)(Co0.2Fe0.8)O3-δ

C. S. Barclay*, L. Zhao, S. Bishop, Kyushu University, Japan; K. Duncan, University of the West Indies,Mona Campus, Jamaica

In the present work defect chemistry of PSCF was studied. Nitrates of the individual elements (Praseodymium, Cobalt, Iron, Strontium) were used as precursors for synthesis of PSCF according to the Pechini method. The XRD results showed that the material crystallized in an orthorhombic cell type. The nonstoichiometry of single-phase perovskite Pr0.6Sr0.4Co0.2Fe0.8O3-δ (PSCF) was measured using Thermogravimetric Analysis technique in the temperature range (800°C – 600°C). The nonstoichiometry for PSCF was found to be greater than LSCF for all measured temperatures and oxygen partial pressures (Po2) tested. A defect equilibria model was developed based on small polaron formation on both A-and B-sites of the perovskite. Good fits of the model to the experimental data were obtained. The model showed that PSCF is a p-type semi-conductor with holes dominating at high Po2. PSCF is a potentially good mixed ionic and electronic conductor (MIEC) for use as cathode in solid oxide fuel cells.

8:40 AM

(ICACC-S3-030-2014) Increasing the oxygen exchange rate of CeO2 based materials for SOFC electrodes

L. Zhao*, N. Perry, T. Diao, K. Sasaki, S. Bishop, Kyushu university, Japan

Reducing the operation temperature of solid oxide fuel cells (SOFCs) will aid in extending their durability and lifetime. With decreasing temperature, the barrier to oxygen exchange is a key limitation in achieving high power density. In this presentation, we demonstrate a dramatic increase in oxygen surface exchange rate with the addition of a second phase oxide on the surface of (Pr,Ce)O2-δ. The origins of the large increase will be discussed. A novel optical absorption approach to studying oxygen exchange on "native" thin film materials is used, thereby deconvoluting the impact of second phase material, and often catalytic, electrical contacts used in more conventional measurements.

9:00 AM

(ICACC-S3-031-2014) Mechanism for Enhancement of Electrochemical Performance on LaNi0.6Fe0.4O3-δ – Ce0.9Gd0.1O1.95 Composite Electrode

R. A. Budiman*, S. Hashimoto, Tohoku University, Japan; K. Yashiro, K. Amezawa, Tohoku University, Japan; T. Kawada, Tohoku University, Japan

Mixed conducting LaNi0.6Fe0.4O3-δ (LNF) electrode was combined with an ionically conducting oxide Ce0.9Gd0.1O1.95 (GDC) resulting high area specific conductivity (ASC). The electrochemical performance of LNF is enhanced with mixing GDC might be not only due to the extension of triple phase boundary since LNF itself has sufficient ionic conductivity to reduce the oxygen at some portion of the electrode surface. Using dense film electrode which prepared by pulsed laser deposition to simplify the reaction pathway we examined the enhancement factor on area specific conductivity. The surface of the LNF film electrode has been coated with GDC particles, and the electrochemical performance is compared with the bare LNF film electrode under the same condition of sample preparation and measurement to determine the effect of the GDC porous layer. The LNF film electrode coated with GDC porous layer on the top showed higher ASC compared to the bare LNF film electrode. In this case, besides the extension of triple phase boundary, the catalytic activity itself could also be enhanced at the junction of the two oxides. The enhancement of ASC will be also proved by making the hetero-structured electrode, LNF film – GDC film layer electrode, which is measuring its oxygen exchange rate by secondary ion mass spectrometry (SIMS).

9:20 AM

(ICACC-S3-032-2014) High performance and highly durable infiltrated cathodes using Pr-modified Ce0.9Gd0.1O1.95 backbone

A. Samson*, M. Søgaard, N. Bonanos, C. Chatzichristodoulou,
P. Hendriksen, Technical University of Denmark, Denmark

Infiltration of electrocatalysts into ionic conducting backbones is an attractive way of preparing cathodes for SOFCs. The high surface area nanoparticle grains of the electrocatalysts obtained in the method enhances the area for oxygen surface exchange. However, during long term operation, the nanoparticles exhibit significant grain growth and subsequent loss of percolation thus increasing both the ohmic (Rs) and polarization (Rp) resistance. Here, we present a way to mitigate the problem by doping a Ce0.9Gd0.1O1.95 (CGO) backbone with Pr through infiltration into the structure followed by firing. The modified backbone is then infiltrated with La0.6Sr0.4Co1.05O3 (LSC). The electrochemical performance of the infiltrated cathodes with and without Pr modification in the backbone was studied by impedance spectroscopy on symmetric cells during 1000 h operation and under varying firing temperatures. The cathodes with Pr – modified backbone are found to exhibit lower Rp and are more tolerant to heat treatments as evidenced by a smaller increase in Rp and Rs at 600°C after heating at a maximum temperature of 900°C (without Pr: Rp=0.094 to 0.45 Ω cm2, Rs=0.74 to 0.79 Ω cm2; with Pr: Rp=0.051 to 0.32 Ω cm2, Rs=0.74 to 0.71 Ω cm2). The improved performance and heat treatment tolerance is thought to originate from the increased electronic conductivity in the CGO backbone due to Pr doping.

Air Electrode / Interfacial Reactions

Room: Coquina Salon H
Session Chair: Ji-Won Son, Korea Institute of Science and Technology (KIST)

10:00 AM

(ICACC-S3-033-2014) Donor Doping of a P-Type SOFC Cathode: Influence of La on Sr(Ti,Fe)$O_{3-\delta}$ Defect Chemistry and Performance

N. H. Perry*, J. W. Druce, Kyushu University, Japan; D. Pergolesi,
Paul Scherrer Institut, Switzerland; J. A. Kilner, Imperial College,
United Kingdom; S. R. Bishop, Kyushu University, Japan; H. L. Tuller,
Massachusetts Institute of Technology, USA

Solid oxide fuel cell cathodes exhibiting fast oxygen exchange and durability are required for efficient, long-term operation. The oxygen exchange rate-limiting step for the cathode Sr(Ti,Fe)$O_{3-\delta}$ was reported to be electron transfer from the cathode to the adsorbed oxygen, as the exchange rate activation energy correlated with the energy difference between the conduction band minimum and the Fermi level (Jung *et al. Adv. Energy Mater.*, 2011). In the present work, donor doping with La was pursued to raise the Fermi level, to test this model and to potentially improve the oxygen exchange rate by facilitating electron transfer. The influence of La on surface chemistry and aging rate was also studied. $Sr_{1-x}La_xTi_{0.65}Fe_{0.35}O_{3-\delta}$ thin films were grown by pulsed laser deposition. Oxygen exchange rates and corresponding defect chemistry were characterized by *in situ* optical absorption, Kelvin probe, and impedance spectroscopies. Surface monolayer chemistry was analyzed by low energy ion scattering. La doping (x≤0.35) raised the Fermi level but lowered the hole and oxygen vacancy concentrations. La lowered the activation energy of the area specific resistance (ASR) but barely altered the ASR magnitude and relaxation time for changing oxygen stoichiometry. La also lowered the concentration of surface Sr in as-deposited films and shows promise for delaying the Sr-mediated aging process.

10:20 AM

(ICACC-S3-034-2014) Effects of Sr Doping on the Conductivity and ORR Kinetics of La2NiO4

X. Liu, B. Guan*, H. Zhang, West Virginia University, USA

Sr doped lanthanum nickelates i.e., La2-xSrxNiO4+δ (0≤x≤0.4), have been prepared and investigated as candidates for SOFC cathode. With increasing dopant content, the lattice parameters a and b decreased while the c increased resulting from the increase amount of Ni3+ due to neutralization compensation. Electrical conductivity after doping was tested and maxima was obtained at 10% Sr doping, 110 Scm-1 at 600oC. Electrochemical impedance spectroscopy (EIS) under different oxygen partial pressures at open circuit voltage (OCV) condition was measured. Sr-doping first enhanced the polarization resistance with 10% doping level, 0.17 Ωcm2 at 800oC. But increased resistances were observed with heavier doping. Judged from EIS results, the rate-limiting step was assigned to surface diffusion process.

10:40 AM

(ICACC-S3-035-2014) Effect of dopants on the lattice structure, electrical and electrochemical properties of La2NiO4+δ

Y. Shen, H. Zhao*, J. Xu, C. Yang, University of Science and Technology
Beijing, China

Identifying suitable cathode materials has been one of the challenges to develop intermediate temperature fuel cell (IT-SOFC). As a family of mixed ionic and electronic conductors, La2NiO4+δ has attached considerable attentions due to its high oxygen surface exchange and diffusion coefficients, good electrocatalytic properties and moderate thermal expansion coefficient compatible with commonly used electrolyte. However, its electronic conductivity and electrochemical properties are not satisfactory when used as cathode. To improve these properties, alkaline earth elements Ba, Sr, Ca were doped on the A site and Cu on the B site of La2NiO4+δ to form La2-xMxNi1-yCuyO4+δ. All the investigated A-site dopants improve the electronic conductivities of La2NiO4+δ with the order of Ba < Sr < Ca, due to the increased oxygen interstitial with decreasing ionic radius of dopants. Ba-doped sample exhibits the lowest ASR and highest maximum output power densities. Substitution Ni by Cu can significantly improve the sintering behavior, electrical and electrochemical properties of La1.7Ca0.3Ni1-yCuyO4+δ. The increasing electrical conductivity is mainly caused by the contract of Ni-Oequatorial bonds, while the enhanced electrochemical properties are correlated with the elongated rocksalt layers.

11:00 AM

(ICACC-S3-036-2014) Infiltrated lanthanum nickelate cathodes on protonic ceramic fuel cells utilizing thin $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ electrolytes

S. M. Babiniec*, S. Ricote, N. P. Sullivan, Colorado School of Mines, USA;
A. Manerbino, CoorsTek, Inc., USA

We discuss the processing and performance of infiltrated La_2NiO_4 cathodes for use with $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY27)-based proton-conducting fuel cells and electrolysis/H_2 separation cells. It has been shown that the BCZY27 material is a good candidate material as a protonic-ceramic membrane due to its phase stability and high protonic conductivity. Traditional SOFC MIEC materials do not have protonic conductivity, making them a poor choice for PCFC cathodes. The development of cathodes for proton-conducting fuel cells started with EIS studies to determine the polarization resistance and total ASR of the materials. It was found that infiltrated catalysts performed very well in these experiments as compared to traditional cathodes. Creation of a two-phase cathode by infiltrating catalyst nano-particles into a proton-conducting backbone increases the three phase density by extending the three phase region and by increasing catalyst surface area. It is our goal to characterize infiltrated lanthanum nickelate cathodes in fuel cell and electrolysis operation. Lanthanum nickelate has shown water uptake properties, an indicator of both protonic conduction and water splitting catalysis. Using solid-state reactive sintering, anode-supported half-cells are fabricated with an anode support, a dense thin-film electrolyte, and an infiltrated La_2NiO_4 cathode.

11:20 AM

(ICACC-S3-037-2014) Investigating Humidity Effects on LSM/YSZ Cathodes of Anode-Supported SOFCs using In-Operando X-ray Diffraction

J. S. Hardy*, J. W. Templeton, J. W. Stevenson, Pacific Northwest National Laboratory, USA

X-ray diffraction (XRD) of the LSM/YSZ cathode on anode-supported solid oxide fuel cells was performed continuously for 1000 hours while the cells were operated at constant current approximating an operating voltage of 0.8 V at a temperature of 775C. The cathode of one cell was exposed to dry air while the other was exposed to moist air (~3% H2O). The air was delivered to the cell at a flow rate of 350 sccm. The resulting XRD patterns were inspected to detect what changes occurred in the atomic structure of each cathode during 1000 h of cell operation. Summation of the XRD patterns taken over the entire test duration results in cumulative count times that greatly enhance the signal to noise ratio of peaks associated with minor phases, making it possible to identify phases present in the cathode in quantities as low as tenths of a percent as well as the changes that occur in those phases.

11:40 AM

(ICACC-S3-038-2014) A study of cathode contact strength of solid oxide fuel cells: effect of particle size and sealing temperature

Y. Chou*, F. Spadoni, E. Riel, J. Choi, J. W. Stevenson, Pacific Northwest National Lab, USA

Good contact at electrode was considered vital for solid oxide fuel cells. A poor contact may lead to poor cell performance, especially after routine thermal cycling in SOFC operations. In this work, cathode contact strength was studied. Both LSM and LSC contact materials were tested with different particle size and sealing temperatures. Both as-received and attrition milled powders will be used. Small cells with LSM cathode and contact materials are fired to elevated temperatures. The bonded couples were tested in uniaxial tension at room temperature to determine the nominal contact strength. Fracture surface analysis with optical microscopy and SEM will be conducted to shed the lights of the effect of particle sizes and final sealing temperature.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics I

Room: Coquina Salon E

Session Chairs: Min Wang, The University of Hong Kong; Akiyoshi Osaka, Okayama University

8:00 AM

(ICACC-S5-001-2014) Multifunctional Hybrid Scaffolds for Bone Tissue Engineering (Invited)

M. Wang*, C. Wang, The University of Hong Kong, Hong Kong

Electrospinning is a versatile technique for fabricating nanofibrous tissue engineering scaffolds which can be used for regenerating human tissues such as skin, bone and peripheral nerve. However, scaffolds constructed are normally simple porous structures which provide a substrate for cells and a framework for tissue formation. Owing to the bioinertness of polymers for scaffolds and shortcomings of conventional electrospun scaffolds, most nanofibrous scaffolds cannot result in successful regeneration of targeted tissues. Creating multifunctional nanofibrous scaffolds by using the hybrid, nanocomposite approach can be a successful strategy for regenerating tissues such as bone. To demonstrate our hybrid, nanocomposite approach, assisted by composite fiber electrospinning and emulsion electrospinning, angiogenic, osteoconductive and osteoinductive tricomponent scaffolds for bone tissue engineering were formed through multi-source dual-power electrospinning. These novel scaffolds consisted of rhVEGF/(PLGA/PEG), rhBMP-2/PLGA and Ca-P/PLGA fibers which were evenly distributed in the scaffolds. In vitro biological investigations employing mesenchymal stem cells showed superior biological performance of tricomponent scaffolds over mono- or bicomponent scaffolds. Furthermore, scaffolds were shown to have angiogenic property, which would facilitate vascularization, a critical issue in bone tissue engineering.

8:20 AM

(ICACC-S5-002-2014) Freeze-Cast Methods to Make Porous Ceramics (Invited)

M. White*, R. Chen, Dalhousie University, Canada

The control of porosity in technical ceramics is very important because of its relationship to physical properties, such as toughness, strength, thermal conduction, etc. Furthermore, porous ceramics can form the basis for hybrid materials, including bioceramics. Here we summarize the use of freeze-cast methods to make porous ceramics. As an example, we present our studies of Al2O3 ceramic prepared by a freeze-casting process, yielding a porous scaffold. The structure can be modified by physical and chemical changes in the freeze-cast process, and morphological control will be described.

8:40 AM

(ICACC-S5-003-2014) Open porous ceramic TiO_2 foams for bone regeneration

H. Tiainen*, D. Wiedmer, J. C. Wohlfahrt, S. P. Lyngstadaas, H. J. Haugen, University of Oslo, Norway

Synthetic bone scaffolds can be used in assisting the repair and regeneration of bone tissue in critical size bone defects. In this study, the objective was to fabricate highly biocompatible ceramic titanium dioxide (TiO_2) scaffolds with pore architectural and mechanical properties suitable for bone regeneration. For this purpose, porous TiO_2 foams were produced using polymer sponge replication. SEM imaging and micro-CT analysis were used to examine the pore architectural features of the scaffolds, while the mechanical properties were assessed by compression test. For an in vivo animal study, 15 scaffolds were implanted in extraction sockets in minipig mandibles. Bone ingrowth and biocompatibility were evaluated using micro-CT and histology 6 weeks after implantation. The produced TiO_2 scaffolds were highly porous (~90 %) with well-interconnected pore network and mean pore size of ~400 μm, while the average compressive strength of the scaffolds was 3.4 MPa. Combined with the excellent biocompatibility of TiO_2, the highly interconnected pore structure provided a favourable microenvironment for bone regeneration. This was manifested by good osteointegration and extensive bone ingrowth and vascularisation within the scaffold structure in vivo. Therefore, the fabricated TiO_2 scaffolds show great promise as load-bearing bone scaffolds for applications where moderate mechanical support is required.

9:00 AM

(ICACC-S5-012-2014) Osteoconductive and Osteoinductive Implants Composed of Hollow Hydroxyapatite Microspheres (Invited)

M. N. Rahaman*, W. Xiao, Missouri University of Science and Technology, USA

The regeneration of craniofacial bone defects resulting from periodontal disease, trauma and congenital diseases represents a common and significant clinical problem. Bone autografts and allografts are commonly used but they suffer from problems. Synthetic bone graft substitutes are commercially available but concerns have been expressed about the high doses of bone morphogenetic proteins (such as BMP2) required for bone regeneration at a clinically acceptable rate. We have been developing hollow hydroxyapatite (HA) microspheres that have a high surface area (>100 m2/g) and a mesoporous shell wall (pore size 10–20 nm) for applications in bone regeneration The hollow HA microspheres are osteoconductive and, when loaded with BMP2 (1 μg/defect), showed a significant capacity to induce bone growth in rat calvarial defects within 3–6 weeks. The optimal characteristics of the hollow HA microspheres such as size, surface area, geometry and BMP2 loading for regenerating bone in rat calvaria will be discussed. These BMP2-loaded hollow HA microspheres could provide novel osteoconductive and osteoinductive implants for regenerating bone in craniofacial and other non-loaded bone defects.

9:20 AM

(ICACC-S5-005-2014) Porous TiO_2 bone grafts promote healing in rabbit peri-implant cortical defect model

H. J. Haugen*, S. P. Lyngstadaas, University of Oslo, Norway; M. Monjo, M. Rubert, University of Balearic Islands, Spain; J. E. Ellingsen, J. C. Wohlfahrt, University of Oslo, Norway

A variety of bone substitutes from natural to synthetic materials have been developed. One of the major obstacles with synthetic bone grafts is their lack of mechanical strength to carry load after insertion into the adult body. The bone grafts produced in this study combine porosity as high as 91% with compressive strength of 1.2 MPa. The aim was to evaluate the performance of these bone grafts in a rabbit peri-implant tibial bone defect model. A modification of a well-established rabbit tibial model was used in which the cylindrical TiO_2 bone grafts were placed in a defect extending from the cortical bone region to the bone marrow space of the tibia. The cortical side of the defect was covered with a titanium disc that was in direct contact with the bone graft material. Micro-CT and histology was used to evaluate bone healing, while inflammatory markers were quantified with real-time PCR. All samples showed de novo bone formation at the surface of the bone graft material and the new bone bridging the defect mostly seemed to emerge from the grafted area. There were no signs of inflammatory or foreign body reactions or fibrous encapsulation were observed. These results demonstrate that the novel porous TiO_2 bone graft promotes new bone formation in a peri-implant critical size defect, and that the open porosity of this scaffold promotes bone growth onto the adjacent implant surface.

9:40 AM

(ICACC-S5-006-2014) Intelligent Bio-Materials for Tissue Engineering and Nanomedicine (Invited)

A. Tampieri*, S. Sprio, M. Sandri, M. Iafisco, S. Panseri, CNR - Institute of Science and Technology for Ceramics, Italy

The present work illustrates how bio-mineralization, an amazing natural process that Nature puts in place to realize and optimize a profuse collection of living organisms endowed with astonishing abilities, can be used to guide efforts for developing biomaterials for bone and osteochondral regeneration. In particular it will be illustrated how the self-assembling and bio-mineralization of natural polymeric fibres can be induced by reproducing the conditions of formation of new bone tissue in mammals, thus obtaining a hybrid composite formed by collagen-based matrix mineralized with biomimetic apatite. Such a mineral phase is nucleated upon guidance of the chemical features and physical confinement imposed by the polymeric matrix, so that to impart, chemical and ultra-structural resemblance with mineral bone and providing very high osteogenic activity when implanted in vivo. Pinning on recent developments superparamagnetic hydroxyapatite have been prepared upon crystallographic and chemically controlled doping with Fe(II)/Fe(III) ions . The new phase can be used to design smart scaffolds able to trigger cell phenotype and promote their osteogenic and angiogenic potential. Moreover, the new magnetic bioreabsorbable nanoparticles able to be moved and driven by magnetic force and enter into the cells are very promising materials for therapies in regenerative medicine.

10:00 AM

(ICACC-S5-007-2014) Electrospinning Preparation of PVA-Ceramic Nano-Particle Composite Fiber Mats for Tissue-Engineering Applications (Invited)

Y. Shirosaki, Kyushu Institute of Technology, Japan; H. Yoshihara, S. Hayakawa, Y. Nakamura, Okayama University, Japan; A. Stamboulis, University of Birmingham, United Kingdom; A. Osaka*, Okayama University, Japan

Micro- and nano-composite fiber mats of silica, titania, hydroxyapatite (HAp), heavy-metal oxide (Fe, Zn, Cu) or other biocompatible oxides find biomedical applications. Attempts were reported to fabricate HAp-involved and biodegradable fiber mats due to electrospinning precursor suspension of submicron size HAp particles in poly-L-lactic acid and poly(caprolactone), though the HAp particles frequently aggregate themselves in the polymer solution and were likely to be precipitated. In contrast, acidic aqueous solution of biodegradable poly(vinyl alcohol) (PVA) can involve certain concentration of calcium and phosphate ions, as the source of HAp, and it deserves electrospinning to yield fiber mats of ~100μm fibrils. In this study, we first fabricate the PVA fiber mats by electrospinning aqueous solution of PVA, Ca(NO3)2, and NaH2PO4, where the atomic ratio Ca/P was set to 5/3 equivalent to that of stoichiometric HAp, and pH was adjusted at ~5 with HCl. Then, we exposed the obtained mats to dry ammonia vapor to deposit apatite in the fiber mat. The microstructure of the HAp-PVA mats was compared with that derived from similar solution containing Ca(HPO4)-2H2O and calcium chloride due to the Fourier Transform infrared spectroscopy, X-ray diffractometry, and scanning electron microscopy.

10:20 AM

(ICACC-S5-008-2014) Bioactive and Resorbable Composite As Drug Delivery System for Bone Substitution and Repair (Invited)

C. Combes*, S. Jacquart, INPT - CIRIMAT, France; S. Girod-Fullana, UPS - CIRIMAT, France; C. Roques, UPS - LGC, France; R. Bareille, Inserm U1026, France; F. Anagnostou, Université Denis-Diderot Paris 7, Laboratoire de Bioingénierie et Biomécanique Ostéo-articulaire, France; F. Brouillet, UPS - CIRIMAT, France; C. Rey, INPT - CIRIMAT, France

With the development of minimally invasive surgical techniques, there is a growing interest in the development of injectable biomaterials especially for orthopedic applications. We aim at preparing a composite for bone regeneration exhibiting bioactivity, antibacterial properties and easiness of use to broaden the application domains of the actual bone mineral cements and improve their resorbability, injectability while preventing the risks of infection. Composites have been prepared by associating calcium carbonate-calcium phosphate (CaCO3-CaP) cement, carboxymethyl cellulose (CMC) and silver as antibacterial agent directly included in the solid phase as silver salt or as Ag-loaded CMC microspheres obtained by spray-drying. The study of the release properties of various composite formulations at 37°C and pH 7.4 showed the sustained release of Ag controlled by the way of incorporation of Ag into the composite. Antibacterial activity tests and in vitro cytotoxicity tests showed that silver-loaded composites had antibacterial properties (anti-adhesion and anti-biofilm formation) for concentration of Ag as low as 0.0375 % w/w without a toxic effect on HBMSC cells, making these composites promising candidates (confirmed by the results of the animal study) for the prevention of bone implant-associated infections.

10:40 AM

(ICACC-S5-009-2014) The Utility of Calcium Phosphate Bioreactor Cores in Culturing Primary Human Liver Cells

I. Nettleship*, A. Finoli, E. Schmelzer, J. Gerlach, University of Pittsburgh, USA

At present the only clinical treatment for chronic liver disease is liver transplantation for which there are too few donors. Future regenerative medicine solutions to this problem including, cell therapies transplantable tissue formation and extracorporeal liver support will require in-vitro expansion and maintenance of large volumes of human liver cells from available cell sources. Bioreactor systems will be well suited to this task. This presentation will focus on material selection and biocompatibility of porous calcium phosphate-hydrogel composite bioreactor cores in which the levels of structure are informed by key features of the natural microenvironment in the liver. Hydroxyapatite and alumina ceramics were evaluated in the presence of hydrogels for culture periods up to 28 days. The effect on the different cell types in the culture were evaluated using: gene expression, ELISA for the study mature liver function and immunohistochemistry was used to examine morphology. Only the bioreactor cores made of hydroxyapatite and collagen 1 maintained increasing albumin production (indicator of mature liver function) over a period 28 days and hydroxyapatite was found to promote the expansion of the endothelial cell population needed for the formation of blood vessels. The implications for design and material selection of bioreactor cores will be discussed.

11:00 AM

(ICACC-S5-010-2014) Mimicking the Formation of Bones, Stones, and Teeth through Biomimetic Processing (Invited)

L. Gower*, University of Florida, USA

Our group's work has focused on developing in vitro model systems for studying the physico-chemical mechanisms involved in biomineral formation. More specifically, we have focused on the role that biopolymers play in modulating the formation of these hierarchically-structured organic-inorganic composites. We originally discovered that acidic polypeptides that are simple mimics to the acidic proteins associated with biominerals could induce a polymer-induced liquid-precursor (PILP) process, and that the fluidic character of the amorphous calcium carbonate precursor enabled many of the enigmatic features found in invertebrate biominerals to be mimicked in the beaker. In recent years, our focus has turned to examining the issues associated with the calcium phosphate biominerals found in invertebrates, such as in bones, teeth, and pathological deposits. In particular, we have shown that these acidic peptides (and non-collagenous proteins) can lead to intrafibrillar mineralization of collagen fibrils, which is a key characteristic of these hard tissue biominerals. Here, I will discuss our latest results related to mimicking bone structure and properties, remineralization of dentin lesions, and emulating Randall's plaque, the latter of which is thought to be the initial nidus of kidney stone formation.

11:20 AM

(ICACC-S5-011-2014) Polymorphic phase transitions in nanocrystalline binary metal oxides (Invited)

S. Sood, P. Gouma*, State University of New York, Stony Brook, USA

Structural changes often occur in binary metal oxides due to polymorphic phase transitions. The latter result in multiple phases with distinct physical and chemical properties, thus providing us with a "toolbox" of materials with variable functionality yet of a simple and fixed composition. For nanostructured materials, it has been observed that particle size and temperature are the main factors affecting i) the onset of the phase transformations and ii) controlling the relative phase stability. Key functional binary metal oxides are discussed here in terms of their observed polymorphism as a function of the synthesis techniques used and the conditions of temperature and particle size. Further, a heuristic approach to particle size dependence of polymorphic reactions is put forth considering factors like surface energy, surface tension, and particle shape. This approach enables us to deduce a value for the critical particle size upon which the phase stability fails and a phase transformation begins.

11:40 AM

(ICACC-S5-004-2014) Highly porous wollastonite-diopside and wollastonite-apatite ceramic foams from low temperature foaming and reactive ceramization of silicone-based mixtures (Invited)

E. Bernardo*, L. Fiocco, P. Colombo, University of Padova, Italy

A commercial liquid silicone resin, filled with inexpensive CaCO3 and Mg(OH)2 microparticles, has been successfully converted into highly porous wollastonite-diopside and wollastonite-apatite ceramic foams, by low temperature foaming, at only 350°C, and ceramization at 900-1100°C. In the first case, operating with CaCO3 and Mg(OH)2, extensive foaming and phase development were promoted by the use of borax microparticles as secondary, multifunctional filler. In fact, borax contributes to the foaming, owing to a significant water release at 350°C, and to ionic interdiffusion, by formation of a sodium-borate liquid phase, upon firing at 1100°C. In the second case, operating with only CaCO3 microparticles as main fillers, the foaming was due to the control of solvent release, addition of borax and/or specific foaming additive (DCH). The apatite phase was developed by application of a novel treatment, based on phosphatization of samples preceramized at 700°C and final firing at 900°C.

S7: 8th International Symposium on Nanostructured Materials and Nanocomposites

Nanocomposites

Room: Coquina Salon B
Session Chairs: Franz Faupel, Christian-Albrechts University at Kiel; Makio Naito, Osaka University

8:00 AM

(ICACC-S7-049-2014) Formation and Characterization of Nanoparticle based Sub-micron Structures (Invited)

K. Lu*, Virginia Tech, USA

Patterning using focused ion beam lithography has been an interesting approach of producing small feature arrays for nanoparticle-based material systems. This patterning ability can be used to create re-usable molds for casting nanoparticle suspensions. The current study investigates the casting and stamping processes of nanoparticle and polymer precursor suspensions in forming nanoparticle-based arrays and the sintering process of as-cast nanoparticle based structures fabricated through such a technique. A PDMS mold is used to cast a nanoparticle suspension consisting of feature sizes ranging from 2 micron to 500 nm. Feature-level shrinkage and the correlation with the particle-level interactions are examined. The scalability of shrinkage during sintering is studied as feature sizes approach that of particle size.

8:30 AM

(ICACC-S7-050-2014) Hybrid Processing of Nanostructured Materials for Energy Applications (Invited)

B. Vaidhyanathan*, S. Saremi, K. Annapoorani, J. Binner, V. Venkatachalam, Loughborough University, United Kingdom

The merits and limitations of using microwave assisted heating for the fabrication of nanostructured ceramic films and bulk materials for energy applications will be discussed here using four exemplar case studies: (i) α-Fe2O3 films for solar-driven hydrogen/energy generation (ii) nano barium titanate multilayer ceramic capacitors (MLCCs) for energy storage, (iii) nano YSZ layers for SOFCs and (iv) Li-phosphates for batteries. It is demonstrated for the first time that significant enhancement of photoelectrochemical performance could be achieved by using microwave annealing for the fabrication of α-Fe2O3 thin films. Undoped and Si-doped iron oxide samples showed that microwave-annealing resulted in superior structural and performance enhancements. The lower processing temperature needs of the microwave process also opened up the possibility of fabricating hematite thin films on conducting, flexible, plastic electronic substrates. Interest in the fabrication of nanostructured barium titanate (BT) capacitor devices is huge owing to the requirements of miniaturization, multifunctionality and improved reliability. Using a methodical study, microwave power was identified as a new tool for altering tetragonal BT phase evolution. Also nano YSZ ceramics were prepared for SOFCs and volatile phosphate losses were minimised significantly in the case of Li-battery materials using microwaves.

8:30 AM

(ICACC-S7-051-2014) Functional nanocomposites prepared by vapor phase deposition (Invited)

F. Faupel*, Christian-Albrechts University at Kiel, Germany

Nanocomposite films consisting of metal nanoparticles in a dielectric matrix have unique functional properties with hosts of applications. The present review demonstrates how vapor phase deposition techniques can be employed for tailoring the nanostructure and the resulting properties. Vapor phase deposition, inter alia, allows excellent control of the metallic filling factor as well as the incorporation of alloy nanoparticles with well-defined composition. Various methods such as sputtering, evaporation, and plasma polymerization have been applied for the deposition of the matrix component, while the metallic component has mostly been sputter-deposited, evaporated or generated in a gas aggregation cluster source. Examples presented include optical composites for plasmonic applications, magnetic high frequency materials with cut-off frequencies well above 1 GHz, sensors that are based on the dramatic change in the electronic properties near the percolation threshold, and antibacterial coatings.

9:00 AM

(ICACC-S7-064-2014) Fabrication of CNT/Alumina composites compatible with high strength and high electrical conductivity by control of dispersing and networking of CNTs

J. Tatami*, M. Matsuoka, Yokohama National University, Japan

Carbon nanotubes (CNTs) are used to improve electrical conductivity and to reinforce mechanical properties of many kinds of materials. In this study, networking of CNT in ethanol was carried out by adding a surfactant. Furthermore, CNT/alumina composites compatible with high strength and electrical conductivity were fabricated by spark plasma sintering. At first, uniform dispersion of CNTs by the bead milling technique using polyethylene imine as a cationic surfactant. Optical microscopic observation showed that networking of CNTs in the slurry ccurred by adding ammonium polycarboxylate as an anionic surfactant. Electrical conductivity of CNTs dispersed slurry increased with an increase in quantity of the added ammonium polycarboxylate and with an increase in the soaking time due to development of CNT network. It was shown that the CNT/alumina composites prepared by adding ammonium polycarboxylate had higher electrical conductivity than those without ammonium polycarboxylate while having high strength. The improvement of these properties resulted from homogeneous networking of CNTs formed by adding ammonium polycarboxylate to increase the conduction paths in the sintered body.

Thin Film Technology

Room: Coquina Salon B
Session Chairs: Thomas Fischer, University of Cologne; Junichi Tatami, Yokohama National University

10:00 AM

(ICACC-S7-053-2014) Atomic Layer Deposition: a 3D surface engineering technique for nanomaterials (Invited)

C. Detavernier, G. Rampelberg*, J. Dendooven, D. Deduytsche, Ghent University, Belgium

This general introduction to atomic layer deposition (ALD) will explain how this technique enables 3D surface engineering on the nanoscale. Since the invention 40 years ago, ALD has attracted researchers from many fields to benefit from its unique properties. Due to the layer-by-layer growth mechanism, thin films can be grown with a thickness down to the subnanometer scale. In addition, an exceptional degree of uniformity and conformality on 3D structures such as fibrous or nanoporous materials and nanosized particles can be achieved. ALD can therefore be considered as an ultimate method for controlling surface properties (adhesion, hydrophobicity), surface functionalization (catalysis) and surface passivation (diffusion barriers, encapsulation, anti-corrosion). Although ALD is a slow technique that often limits the applicability, its future is very promising because the technology is still developing and ALD is taking entrance in fields that are just learning how to take advantage of this 3D surface engineering technique.

10:30 AM

(ICACC-S7-054-2014) The effect of Ti addition on the properties of DLC films (Invited)

K. Moon*, D. Jung, N. Lee, KITECH, Republic of Korea

DLC films is widely used in machinery and medical industries due to high hardness, low friction, high wear resistance and chemical stability. However, the problems of DLC films such as thermal unstable, poor adhesion on ferrous material is limited on its wide uses. So, there have been developed the modified DLC films by doping or alloying of different elements to improve the properties in respect to pure DLC films. In this study, the effect of Ti addition has been studied on the properties of DLC films. Especially, the improvement of the conductivity of DLC films without losing the chemical intentness have been examined to find out the usefulness of DLC films for the application in fuel cell. In this study, DLC films were deposited by PECVD equipped with sputter gun and Ti was added to DLC film with increasing RF power. On sputter gun as a result, Ti content in DLC films could be controlled by varying RF power and process pressure for Ti target. Also Ti-DLC films were deposited by PECVD of C2H2, Ar and precursor of tetrakis(dimethylamino)titanium (TDMAT, Ti[(CH3)2N]4). The crystal structure of DLC films were measured by Raman, XPS. The mechanical properties of DLC films was investigated by scratch test, nano-indenter, wear test with the type of ball on disc. The chemical properties of the DLC films was measured with dynamic tests and four point probe methods.

11:00 AM

(ICACC-S7-055-2014) *In-situ* investigations during CVD growth of nanostructured metal oxide thin-films and nanowires (Invited)

T. Fischer*, S. Mathur, University of Cologne, Germany

The chemical vapor deposition (CVD) is a well established tool for the synthesis of homogeneous thin films and anisotropic nanostructures, but the details during film growth still remain unclear. Using metal organic precursors with complex decomposition and reaction pathways a deeper insight into the film formation relies on *in-situ* diagnostic tools like for example mass spectrometry and electrical spectroscopy resolving the chemical composition of the gas phase products as well as the evolution of the electrical properties, respectively. Especially the direct monitoring of the materials electrical resistance during the CVD process is a suitable tool in tailoring the materials properties needed for the targeted application. In addition the application of the as prepared nano structured films of SnO_2, TiO_2 and Fe_2O_3 as gas sensors and photo catalysts will be presented, correlating the depostion parameters with material morphology and device performance.

11:20 AM

(ICACC-S7-056-2014) Plasma Deposition and Modification of Semiconducting Thin Films for Photoelectrochemical Hydrogen Production

A. Mettenbörger*, S. Mathur, University of Cologne, Germany

The PE-CVD is a unique technique for thin film deposition, since it provides a good control over several parameters (time, plasma power and reactive gas composition) and therefore over the properties of the resulting films. In addition PE-CVD processes show a high reproducibility and they are scalable for large area productions. It finds applications in growth and processing of nano-materials, such as semiconductor thin films or carbon structures like graphene, carbon nanotubes (CNT), or DLC. Since the PE-CVD is a low temperature process it is possible to deposit under mild conditions onto sensitive materials like polymers. In this work we present the deposition and modification of semiconducting metal oxides (TiO_2, Fe_2O_3) for photoelectrochemical (PEC) hydrogen production. The deposition parameters for thin film creation were optimized with respect to the PEC performance of the resulting materials. Furthermore the as deposited films were modified using plasma techniques. Namely those modifications were the partial reduction of the metal oxides by hydrogen plasma, anion doping (F^-) and the doping with different metal cations. All this techniques allowed the selective tuning of the optical and electrical properties of the films and therefore lead to a substantially enhanced PEC performance.

11:40 AM

(ICACC-S7-022-2014) Fine-tuning Thermophysical Properties of Graphitic Nanofluids with Surface Treatment and Particle Morphology for Advanced Heat Transfer (Invited)

E. V. Timofeeva*, D. Singh, W. Yu, K. Velvadapu, M. J. Nawrocki, J. E. Graviria, Argonne National Laboratory, USA

Nanofluids with carbon nanoparticle additives have shown a wide range of thermal conductivity increases from insignificant in carbon blacks to a 2-3 fold increase in thermal conductivity in suspensions with carbon nanotubes and graphenes. Besides thermal conductivity other thermo-physical properties of suspensions such as viscosity and specific heat are important for heat transfer efficiency. Viscosity of nanofluids with high aspect ratio particles is incredibly high resulting in pumping power penalties that are higher than the benefits in thermal conductivity of those systems. Therefore such nanofluids are not practical for commercial applications. We investigated the effects of nanoparticle morphology and surface treatment on the thermo-physical properties of nanofluids with graphitic nanomaterials in EG/H2O base fluid. Using simple, low cost, and up-scalable surface modification method for graphitic nanoparticles we were able to formulate the nanofluid coolant with advanced combination of properties that allows 90+% improvement in heat transfer coefficient when used in laminar flow and 30+% enhancements in heat transfer coefficient when used in turbulent flow. The implementation of this technology in HEV's and EV's will result in reducing the size, weight and number of heat exchangers and improving overall vehicle efficiency.

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

Novel Sintering & Forming III

Room: Coquina Salon A
Session Chairs: Soshu Kirihara, Osaka University; Vojislav Mitic, University Nis and ITN SASA Belgrade

8:20 AM

(ICACC-S8-044-2014) A New Aqueous-Organic Tape Casting System for Fabrication of Transparent Ceramics (Invited)

Y. Yang, Y. Wu*, Alfred University, USA

Yttrium Alumina Garnet (YAG) and alumina transparent ceramics were prepared by tape-cast processing with a new system of water-soluble organics binders. Different plasticizers were tested with various amount of binder for the tape-casting process. The suspension were made by mixing water, YAG or Al2O3 powders, and water-soluble organics in a planetary ball mill and de-aired by a vacuum system. The viscosity of the suspension and the shrinkage behavior of the green body were tested. The thermal analysis (TG-DTA) and transmittance were also characterized. The solid loading, binder addition, and the choice of different plasticizers were optimized for the tape-casting process. Finally, homogeneous microstructures of calcined and sintered transparent ceramics were obtained.

8:40 AM

(ICACC-S8-045-2014) Mechanical Behavior of Green Ceramic Tapes Used in A Viscoelastic Shaping Process

M. Pan*, S. Wimmer, V. DeGiorgi, US Naval Research Laboratory, USA

In this study, we work to develop an understanding of green ceramic tapes' stress-strain behavior and ability to deform due to applied pressure and temperature. The knowledge gained will be used to fabricate complex ceramic components with microchannels by laminating paper patterns with the green ceramic tape to form the desired geometry. The paper sacrificial phase is removed during the subsequent sintering process. The ceramic tape consists of mullite powder, polyvinyl butyral (PVB) binder, benzyl butyl phthalate plasticizer, and fish oil dispersant. Both tensile and compressive tests are conducted at several temperatures. The tension samples are dogbone-shaped cutouts from the ceramic tape and the compression samples are short cylinders made by slip casting. Five different tapes are prepared: baseline, 10% extra binder, 10% extra plasticizer, 10% extra of both binder and plasticizer, and a different grade of PVB binder. This will allow for the impact of the organic content and processing temperature on the stress-strain behavior to be quantified. Finally, the experimental results are used as material property input in the computational simulation of the lamination process. Examples of the numerical simulation will be given.

9:00 AM

(ICACC-S8-046-2014) Stress Estimation for Multiphase Ceramics Laminates during Sintering

K. Yasuda*, Tokyo Institute of Technology, Japan; T. Nakayama, S. Tanaka, Nagaoka University of Technology, Japan

Ceramics laminates are widely used in ceramics products, but combination of different phases leads to internal stress during sintering. The authors propose a theory to estimate internal stress during sintering of multiphase laminates, based on sintering strain and thermal expansion strain. The authors also show how to get the parameters to be needed in this calculation by using lamina specimens. With comparison between the estimated stress and the strength of intermediately sintered lamina, possible cracking behavior is discussed. Finally, this theory can be extended into the materials having continuous composition like functionally gradient materials.

9:20 AM

(ICACC-S8-047-2014) The Effects of Na_2O, SiO_2 and MgO on the Sintering Behavior and Microstructure Evolution of Bayer Processed Alumina

I. O. Ozer, E. R. Kupp*, Penn State University, USA; C. Compson, Almatis, Inc., USA; M. Spreij, Almatis, Inc., Germany; G. L. Messing, Penn State University, USA

Sintering behavior and microstructure evolution of Bayer processed alumina is strongly influenced by powder chemistry (i.e., impurities and dopants). Bayer processed alumina is usually classified based on its Na_2O content, i.e. normal and low soda alumina. The soda is a remnant of the Bayer process itself, having been introduced during the digestion stage in the form of caustic. A small amount of this impurity may form sodium β-alumina ($Na_2O.11Al_2O_3$). Most commercial alumina grades are doped with MgO to prevent abnormal grain growth during sintering. MgO may stabilize sodium β”-alumina. Despite the strong effect of dopants on microstructure evolution, the number of systematic studies is scarce. In this study, we report the effects and co-effects of the two most common impurities, Na_2O and SiO_2 on sintering behavior and microstructure evolution. In addition, the role of MgO doping on sodium β”-alumina formation was studied. Sintering activation energies were determined as a function of impurity/dopant type and concentration using master sintering curves.

Advanced Integration & Joining

Room: Coquina Salon A
Session Chair: Vojislav Mitic, University Nis and ITN SASA Belgrade

10:00 AM

(ICACC-S8-048-2014) Thermal Diffusion Processing for the Hard Boride-Based Coatings for Wear- and Corrosion-Resistant Applications (Invited)

E. Medvedovski*, F. A. Chinski, J. Stewart, Endurance Technologies Inc., Canada

Engineering components, e.g. tubing systems for down-hole applications in oil and gas industry, slurry pump components, gears, turbine components for power generation and some other large size complex-shape components made of steels and alloys, require protection against slide abrasion, friction, impact and corrosion. CVD coatings consisted of the borides obtained through thermal diffusion of boron into the metallic base of the components provide significant improvement of the properties of the surfaces designated for the contacts with abrasive and corrosive environments and enhance the integrity and service life of the components in several times. The principles of the thermal diffusion process are outlined. Thermal diffusion process and quality of the coatings are defined by the batch composition providing the boron deposition and diffusion, temperature and time of the process, type of the metallic base and its surface quality and engineering design of the CVD process system. The obtained hard boride coatings with thicknesses of 50-250 up to 400 μm (depending on the application) are uniform through the entire length of the components, do not have delamination issues, and they are successfully used in industry. The wear and corrosion test results, as well as the structural features affecting the application properties, are discussed.

10:20 AM

(ICACC-S8-049-2014) Diffusion Bonding and Interfacial Characterization of Sintered Fiber Bonded Silicon Carbide Ceramics Using Boron-Molybdenum Interlayers

H. Tsuda*, S. Mori, Osaka Prefecture University, Japan; M. C. Halbig, NASA Glenn Research Center, USA; M. Singh, Ohio Aerospace Institute, NASA Glenn Research Center, USA; R. Asthana, University of Wisconsin-Stout, USA

Advanced silicon carbide-based ceramics and composite materials are currently undergoing significant technology development and testing for a wide variety of aerospace and energy applications. Robust and affordable ceramic joining and integration technologies are critically needed for the successful implementation of these systems. In previous studies, we have utilized physical vapor deposited (PVD) titanium and titanium metal foil interlayers for the diffusion bonding of chemical vapor deposited (CVD) SiC and sintered fiber bonded SiC ceramic (SA-Tyrannohex). In this work, boron-molybdenum foils of ~25 micron thickness were used as joining interlayers. Also, SA-Tyrannohex, which has a dense and highly ordered structure consisting of small SiC grains with a carbon interlayer, was used as the substrate in parallel and perpendicular fiber weave orientations relative to the joint interface. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were conducted on polished cross-sections and on specimens prepared by focused ion beam (FIB), respectively. Results from the analysis of the formed phases in the bonded regions will be presented. The detailed microstructures will be compared to those obtained from bonded region using titanium foil interlayers.

10:40 AM

(ICACC-S8-050-2014) High Temperature Approaches for Joining of SiC-Based Ceramic Composites

M. Halbig*, NASA Glenn Research Center, USA; M. Singh, C. E. Smith, Ohio Aerospace Institute, USA

Silicon carbide-based ceramic matrix composites (CMCs) are being developed for turbine engine applications. To allow for many of the complex shaped components, the joining and integration of CMCs will be a critically needed enabling technology. In this presentation, four joining approaches will be discussed. They include ARCJoinT (Affordable, Robust Ceramic Joining Technology), diffusion bonding, REABOND (Refractory Eutectic Assisted Bonding), and SSRF (Single Step Reaction Forming) of SiC-based joint interlayers. Results from joining using ARCJoinT and diffusion bonding will be discussed. Emphasis will be placed on the REABOND technology which utilizes refractory eutectic alloys such as Si-8.5Hf, Si-16Ti, and Si-18Cr. An overview of SSRF method, which uses carbonaceous tapes containing primarily Si, C, and SiC powders of varying sizes, will be presented. The approach provides SiC based joint compositions with simplified processing and high compatibility to the SiC based composites. Microstructural analysis of the joints was conducted using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) to evaluate bond quality and identify reaction formed phases. Mechanical tests were conducted to evaluate the effective shear strength at room temperature and elevated temperatures. Technical advantages and limitations of different techniques will also be presented.

11:00 AM

(ICACC-S8-051-2014) Characterization of Reactive Air Brazed Ceramic-Metal-Joints with Unadapted Thermal Expansion Behavior

K. Bobzin, M. Öte, S. Wiesner*, surface engineering institute, Germany

The increasing demands on components for energy generation are often met by combining the advantages of different groups of materials. Reactive Air Brazing (RAB) has proven to be an efficient and effective joining technology for joints consisting of ceramic and metals. The main challenges in combining these different groups of materials are the high residual stresses accumulated during cooling and the resulting crack formation. To reduce these stresses the joining partners for demanding applications are chosen considering the linear thermal expansion coefficient. In this study joints of materials with unadapted expansion coefficient (yttria-stabilized zirconia-X15CrNiSi25-20 and Ba0,5Sr0,5Co0,8Fe0,2O3-δ-X1CrWNbTiLa22), were reactive air brazed with different Ag based filler metals. In addition to the examination of the microstructure and the crack formation after brazing, the expansion behavior of the brazed joint was determined. Moreover, for a better comparability the linear expansion coefficient of the base materials after the brazing process was determined. The difference in the thermal expansion coefficient in the YSZ-X1CrWNbTiLa22-joints is compensated sufficiently by using a ductile silver based filler material. On the other hand the residual stresses accumulated in the BSCF-X15CrNiSi25-20-joint still exceed the strength of the ceramic.

11:20 AM

(ICACC-S8-052-2014) Effect of annealing on Microstructure and mechanical strength of reactive air brazed BSCF-steel-joints

A. Kaletsch*, A. Bezold, E. M. Pfaff, C. Broeckmann, RWTH-Aachen, Germany

The material Ba0.5Sr0.5Co0.8Fe0.2O3 δ (BSCF) is a technological important ceramic and can be used as oxygen transport membrane (OTM) material for oxygen supply in high temperature applications. BSCF cannot be brazed in vacuum due to thermodynamic instability at low oxygen partial pressures. In case of BSCF reactive air brazing (RAB) is the only technical applicable solution for a heat resistant and gas tight sealing to metals. BSCF exhibits low strength and low Weibull module. After brazing BSCF to steel the room temperature (RT) strength of the joint is additionally decreased by internal stresses due to thermal misfit. Also a change in microstructure of the BSCF appears at the interface due to reactions with the copper oxide (CuO) from the AgCuO braze alloy. This change in microstructure results in a decrease of the RT strength of BSCF-steel joints and fracture always appears in the damaged microstructure of the ceramic. In case of high temperature (HT) tensile testing another fracture mode appears: Most specimens fail at the braze-steel-interface due to insufficient adhesion between silver and the reaction layer which is built during brazing. This study presents results of mechanical testing of reactive air brazed BSCF-steel-joints before and after annealing in air atmosphere and the correlation between microstructure and mechanical strength.

11:40 AM

(ICACC-S8-053-2014) Phase field simulations of the microstructure evolution in Ag-Cu brazing fillers during reactive air brazing

R. Berger*, B. Böttger, M. Apel, ACCESS Materials and Processes, Germany

Reactive air brazing utilizing Ag-Cu brazing alloys is used in joining metallic and ceramic parts in the context of different applications, e.g. SOFCs. The multiphase field method, in particular in combination with computational thermodynamics based on the CALPHAD method, allows quantitative numerical simulations of the microstructure evolution in the brazing filler. In this presentation the effect of the ambient oxygen partial pressure and oxygen transport on the microstructure evolution in the filler metal is investigated. For the Ag-Cu-O system especially the amount of nonmetallic CuO and the later formation of Cu2O are determined by the availability of oxygen, this becomes clear by thermodynamic equilibrium calculations. The kinetic phase field simulations suggest that the phase formation rate is determined by the oxygen transfer between the ambient gas and the liquid brazing alloy. The simulations are compared to experimental results, i.e. DTA measurements and post mortem microstructure analysis, which qualitatively confirm the simulation results. Challenges, prospects and first results for a comprehensive simulation including the reaction between brazing alloy and dissimilar base materials will be discussed.

S9: Porous Ceramics: Novel Developments and Applications

Processing Methods for Porous Ceramics II

Room: Coquina Salon C
Session Chair: Manabu Fukushima, National Institute of Advanced Industrial Science and Technology (AIST)

8:00 AM

(ICACC-S9-010-2014) Fabrication and Properties of Ultra-High-Porous Ceramics for Energy Saving Insulator (Invited)

K. Sekine*, Y. Tanaka, A. Tsujino, Mino Ceramic Co.,Ltd., Japan

Porous ceramics have a significant position in industry for a variety of applications related with environmental protection and energy saving. Especially, ceramic thermal insulators utilized in many kinds of industrial furnaces at elevated temperature contribute the improvement of energy efficiency and the prevention of heat leakage, such as fibous insulator and refractory insulator. Fibous insulator has low thermal conductivity but low compressive strength. On the other hand, refractory insulator has high compressive strength but high thermal conductivity. Then, these insulations are used for each suitable applications. However, a new insulation with lower thermal conductivity and higher compressive strength is expected for other applications in the future. We currently have focused on the gelation-freezing (GF) method to fabricate highly porous ceramics composed of ordered micrometer-sized cells. Porous ceramics prepared by GF method showed very high porosity (>70vol%) with uniform orientation and excellent near-net shape forming. Scanning electron microscopy (SEM) observations of the zirconia based insulators showed a unique bamboo like microstructure composed of ordered micrometer-sized cylindrical cells with joint cell walls. Results presented were compared to commercial available insulators and, it was found that the porous ceramic manufactured by GF method was promising material.

8:30 AM

(ICACC-S9-011-2014) Mechanical Response of Graphene-based Complex Porous Networks

N. Ni*, S. Barg, F. M. Perez, E. Saiz, Imperial College London, United Kingdom

Graphene has the potential to form novel platforms for a wide range of functional systems demanding strong, lightweight porous structures able to provide multiple functionalities. The challenge is to fabricate graphene three-dimensional structures in practical dimensions with an accurate control of the chemistry and architecture while maintaining the desirable properties of the pristine graphene. In this work, porous graphene networks with ordered lamellar structures were successfully fabricated by unidirectional freeze casting of graphene oxide (GO) water suspensions followed by thermal reduction. Different processing parameters including the GO flake size, the freezing rate, the use of organic additives and the reduction temperature were studied systematically. The mechanical response of the structures was investigated with compression tests, cyclic compression, indirect tensile testing and energy absorption measurements. Results are compared with the behaviour of isotropic cellular graphene networks. The mechanical behaviour of the porous networks varied from elastomeric to elastic-brittle depending on the architecture and chemistry. The energy absorption was largely influenced by reduction degree. This work provides fundamental information needed to understand how architecture determines the mechanical response in porous nanocarbon materials to guide the design of structures with improved mechanical properties.

8:50 AM

(ICACC-S9-012-2014) Ice templating of ZrB2-based ceramics

V. Medri*, D. Sciti, CNR-ISTEC, Italy; E. Sani, CNR-INO, Italy; E. Landi, CNR-ISTEC, Italy

Porous architectures of ZrB2 ceramics and ZrB2-SiC composite were prepared, where the pores are the replica of the ice crystals developed by freeze casting. The effects of solid content, suspension stabilization and cold transmission depending on mold type were studied since micro and macrostructure and, hence, the properties of the sintered body are determined by controlling the growth direction of the ice crystals during freezing. Monophasic ZrB2 powders suspensions produced porous architectures with main unidirectional anisotropic pores interconnected by diffuse globular-isotropic pores. Improved mechanical performance, due to the formation of thinner and homogenously distributed ceramic lamellae, were obtained changing the process parameters. With ZrB2-SiC composite suspensions, the ice networking resulted in macro-pores arranged into dendritic distributions which were randomly distributed in the samples or in porous domains of elongated voids with irregular boundary. Samples showed intrinsic spectral selectivity, which can be interesting for high-temperature solar absorber applications.

9:10 AM

(ICACC-S9-013-2014) Processing and Testing of Ultrahigh Temperature Structural Ceramic Foams

J. J. Stiglich*, B. E. Williams, Ultramet, USA

Ultramet has developed innovative processing for ultrahigh temperature structural ceramic foams that can be produced in various pore sizes from various ceramic materials. Highly insulating and lightweight thermal protection materials have been produced by combining an open-cell carbon or ceramic foam skeleton with an ultralow density aerogel filler material. The foam serves as an easily machinable structural reinforcement for the very low-strength aerogel insulator and defines the shape of the component. In the foam-aerogel composite structure, the aerogel exists in small discrete cells and is supported by the foam skeleton. The combined density of the composite insulator is as low as 0.1 g/cm3, and the thermal conductivity is <1 W/m×K at 2000°C. Single-piece panels up to 30” square are feasible. In addition to thermal insulation, ceramic foams have been used as catalyst supports and for turbine engine noise reduction. Processing and testing of ceramic foam materials will be discussed.

9:30 AM

(ICACC-S9-014-2014) Cellular glass-ceramics from self-foaming mixtures of recycled glass and inorganic waste

E. Bernardo*, M. Mauro, I. Ponsot, P. Colombo, University of Padova, Italy

Glass-based foams are generally obtained by gas evolution, in a pyroplastic mass of softened glass, provided by foaming agents. These substances can be roughly divided into those undergoing thermal decomposition (such as carbonates and sulphates) and those undergoing oxidation (such as C-containing compounds, typically carbon black and SiC), and often imply extra costs in the manufacturing (e.g. SiC, recognized as a very versatile foaming agent, is quite expensive). The present investigation aims at evidencing an inexpensive further possibility, provided by iron-rich waste of natural or industrial origin. When fired mixed with recycled glasses (mainly common soda-lime glass), the waste releases oxygen, owing to the reduction of Fe2O3 into FeO. The optimization of the glass/waste balance, considering the origin of the iron-rich waste (basalt mining residues, metallurgical waste), yields glass-ceramic foams with a homogeneous microstructure and good mechanical properties, to be applied as lightweight thermally insulating building materials.

Processing Methods for Porous Ceramics III

Room: Coquina Salon C
Session Chair: Alberto Ortona, SUPSI

10:10 AM

(ICACC-S9-015-2014) Functionalizing Cellular Ceramics by Coating (Invited)

J. Adler*, D. Boettge, U. Petasch, Fraunhofer Institute for Ceramic Technologies and Systems, Germany

New challenges in process engineering and environmental technologies require cellular materials that offer corrosion resistance, catalytic activity or adhesion characteristics as well as high open porosity, low pressure drop and a high degree of homogeneity. One option to reach these goals is the functionalization by coating of cellular substrates. Beside typical laboratory methods like repeated dip coating, technologies for coating of cellular substrates are not well-described in literature. Moreover, coating of honeycombs with catalyst/washcoat slurries is state-of-the-art, but not applicable to other cellular substrates, like foams. Therefore, there is a need for coating technologies, which can be adjusted to the structure of the cellular substrate. Two special techniques are presented using water-based slurries to apply coatings to honeycombs and open-celled foams. It was the main idea both to prevent repeated coating steps and to get a controllable amount of coating thickness at a high degree of homogeneity. Open-celled foams were coated by a combined dip- and spincoating process, whereas honeycombs were pressure flooded by slurry and blown out by air. By using both techniques controllable and homogeneous coatings could be applied to different cell sizes. Some examples are presented, like catalyst coated foams for burner applications and VOC treatment, DeNOx catalyst on honeycombs and soot oxidation catalyst in wall-flow DPF.

10:40 AM

(ICACC-S9-016-2014) Open-interconnected–network structures by Electrospinning of Preceramic Polymers

A. Guo, M. Roso, M. Modesti, P. Colombo*, University of Padova, Italy

Ceramic open-interconnected–network structures based on SiOC nano-fiber mats were obtained by electrospinning of silicone preceramic polymers. Several fabrications conditions were investigated in order to optimize the processing procedure, and the impact on the morphology and some properties of the produced fiber mats was evaluated. Doping of the fibers with metal precursors was explored, for the development of functional ceramic nano-fiber based devices. In addition, ceramic nanowires were grown on the fibers by the VLS method, to produce components possessing hierarchical porosity and higher specific surface area. Deposition of fibers on open cell ceramic foams was also pursued, for the development of advanced filters.

11:00 AM

(ICACC-S9-017-2014) Synthesis and 3d-printing of silicate bioceramics from preceramic polymers and fillers

A. Zocca*, BAM, Federal Institute for Materials Research and Testing, Germany; H. Elsayed, University of Padova, Italy; C. Gomes, BAM, Federal Institute for Materials Research and Testing, Germany; E. Bernardo, University of Padova, Italy; J. Guenster, BAM, Federal Institute for Materials Research and Testing, Germany; P. Colombo, University of Padova, Italy

The polymer-derived route is a unique approach for the production and shaping of ceramic materials. The incorporation of active fillers to a preceramic polymer opens the possibility of generating ceramics with a controlled phase composition. New compositions for the production of silicate bioceramics from mixtures of a preceramic polymer and fillers will be discussed. Different phase assemblages can be achieved by incorporation of calcium and zinc oxide precursors, resulting in different bio-related properties, such as solubility and ions release. A proprietary apatite-wollastonite glass-ceramic is also mixed as additional filler. A possible application of these mixtures is the shaping by the indirect three-dimensional printing. In this context, the preceramic polymer acts as a binder, selectively gluing the ceramic filler particles layer-by-layer. The preceramic polymer acts as a non-sacrificial binder that leaves a silica residue with a high yield (84 wt%), which can furthermore react with the fillers to generate the desired ceramic phases upon heat treatment. The preliminary results on the three-dimensional printing and characterization of some of these mixtures will be discussed. This process allows the generation of 3D-printed porous components, possessing a hierarchical porosity deriving from the inherent porosity of the struts in addition to the geometrically designed macro-porosity.

11:20 AM

(ICACC-S9-018-2014) Robocasting of porous inorganic hollow fibers for membrane applications

B. Michielsen*, M. Mertens, M. Jacobs, V. Middelkoop, S. Mullens, F. Snijkers, Flemish Institute for Technological Research, Belgium

Inorganic membranes can be used in harsh operating conditions such as corrosive environments and high temperatures. We propose a new method for producing porous hollow fiber membranes using phase-inversion robotic fiber deposition. The method uses a suspension consisting of inorganic powder, polymer and solvent which is extruded through a concentric nozzle. By exchanging the solvent with a non-solvent the paste solidifies. After calcination and sintering a hollow fiber with a well-defined pore structure is obtained. The technique has the advantage that preparation is not limited to straight hollow fibers but that continuous patterns and three-dimensional structures can also be accurately reproduced. The feasibility of the method was tested using stainless steel and alumina as the membrane materials. We have successfully prepared hollow fibers with a variety of outer diameters (1 to 4 mm) wall thicknesses (200 to 700 μm) and shapes. The morphology of the obtained fibers was characterized and the effect of the sintering temperature on properties such as porosity, mechanical strength and nitrogen permeation was investigated.

11:40 AM

(ICACC-S9-019-2014) From Advanced Ceramics To Engineered Ceramics: Optimization of Cellular Structures

S. Gianella*, EngiCer SA, Switzerland

Technological advancement increase the demand for better performing materials, with no exception for the field of cellular ceramics. The performance of cellular structures depend on bulk material properties and on their structures. Thus, along with material optimization, structure optimization represents a crucial factor for the final performance of cellular materials. The present work focuses on cellular ceramics optimization, driven in these cases by the need of specific thermo-mechanical and fluid dynamic performances of the component, in which the long and expensive prototyping phase is entirely carried via computer simulation. This allows to shorten the development of the component and start its testing phase on its quasi-final configuration. To show the feasibility of this approach some case-study will be presented in the aerospace and combustion industry. It starts from common random foam structures, to end up with structures first digitally optimized and then produced by rapid prototyping of the template and replication.

S11: Advanced Materials and Innovative Processing Ideas for the Industrial Root Technology

Next Generation I

Room: Ponce De Leon
Session Chairs: Jindrich Musil, University of West Bohemia; Trilok Singh, Institute of Inorganic and Materials Chemistry

8:20 AM

(ICACC-S11-011-2014) Advanced hard nanocomposite coatings: Flexible and functional nanocomposites (Invited)

J. Musil*, University of West Bohemia, Czech Republic

The lecture reports on new advanced hard nanocomposite coatings with unique properties. A special attention is devoted to flexible hard nanocomposite coatings which exhibit an enhanced resistance to cracking in bending. The principle of the formation of hard nanocomposite coatings resistant to cracking is explained in detail. It is shown that there are three necessary conditions which must be fulfilled simultaneously in formation of these nanocomposite coatings. Flexible nanocomposites have to exhibit (1) the low effective Young's modulus E* which gives a high ratio H/E* and a high elastic recovery We, (2) the compressive macrostress and (3) the dense, free of voids microstructure; here H is the hardness of nanocomposite. The way how to form such nanocomposite coatings is given. It is shown that properties of nanocomposites are controlled by the energy delivered to the growing coating and by the kind and amount of element added in the base material. The addition of the selected element in a base material of the coating can strongly influence not only its flexibility but also its other properties, for instance, mechanical protection of the substrate surface, friction, wear, antibacterial activity, optical transparency, electrical conductivity, etc. At the end, new trends of the next development of new advanced nanocomposite coatings are outlined.

8:50 AM

(ICACC-S11-012-2014) Plasma-enhanced CVD and Atomic Layer Deposition of Metal Oxide Nanostructures for Functional Applications (Invited)

T. Singh*, A. P. Singh, T. Fischer, N. Tosun, A. Mettenbörger, S. Mathur, University of Cologne, Germany

Application of tailor-made molecular precursors in low pressure or plasma-enhanced chemical vapor deposition techniques offers a viable solution for overcoming thermodynamic impediments involved in thin film growth. The use of cold plasmas enables the realization of various functional coatings whose application spectrum spans from transparent conductive coatings, scratch-proof films to anti-bacterial materials. Over the past decade, we have developed several new precursor systems in order to demonstrate the competitive edge of molecule-based plasma coatings. Our work on a large number of metal oxide systems and their characterization towards microstructure, compositional and functional properties supports the advantages of chemical design in simplifying deposition processes and optimizing functional behavior This talk will present how PE-CVD processed nanostructured films of different metal oxides open up new vistas of material properties, which can be transformed into advanced material technologies. The examples will include application of thin glassy films as barrier and corrosion-resistant coatings, metal oxide nanowires and heterostructures for photoelectrochemical applications.

9:20 AM

(ICACC-S11-013-2014) Encapsulation of polyaniline in hollow silica nanospheres by using an in-situ synthesis in Water-in-Oil (W/O) microemulsion

M. Pyeon*, G. Kim, T. Hwang, KITECH, Republic of Korea

An encapsulation of active components in hollow silica nanosphere was tested through a facile one-pot synthesis using water-in-oil microemulsion. The encapsulation of not only pre-prepared materials (TiO2 solid particles and aqueous solution of ascorbic acid), but also, as a novel trial, in-situ synthesized polyaniline was carried out. As long as the aqueous droplet in the microemulsion was maintained strong-acidic, the synthesis of silica shell along the soft template, micelle, persisted regardless of the phase of encapsulated materials, and the hollow silica nanospheres successfully encapsulated both the pre-prepared TiO2 solid particles and ascorbic acid, and in-situ synthesized polyaniline. Transmission electron microscopy combined with line-scanned EDS analysis has confirmed the encapsulation of each of the designated materials inside the hollow silica particles. From the obtained experimental results, a schematic illustration was proposed to explain the encapsulation process, where the synthesis of silica shell starts from the border of micelles encapsulating the incorporated second materials. The encapsulation of the in-situ synthesized compound, would increase the application degree of freedom of core-shell type composite materials with tailored functionalities.

Next Generation II

Room: Ponce De Leon
Session Chair: Jung-Pyung Choi, Pacific Northwest National Lab

10:00 AM

(ICACC-S11-014-2014) Knowledge based material design approaches for industrial applications based on property predictions by quantum mechanics and verification by combinatorial materials science (Invited)

J. Schneider*, RWTH Aachen University, Germany

This lecture provides an overview of modern materials development, from discovery and optimization towards materials design, based on combinatorial thin film materials science. Implications for bulk materials are discussed. The combinatorial approach, combining combinatorial materials synthesis of thin film composition-spreads with high-throughput property characterization has proven to be a powerful tool to delineate composition-structure-property relationships, and hence to efficiently identify composition windows with enhanced properties. These results are relevant for the design of coating and bulk materials. Furthermore, and most importantly for materials design, theoretical models and hypotheses can be critically appraised. The combination of modern electronic structure calculations with the highly efficient combinatorial thin film composition-spread method constitutes an effective tool for knowledge based materials design of hard and wear resistant coatings, nanolaminates, thermoelectrics, metallic glasses and steel. Quantum mechanically guided design strategies for Mo2BC as well as FeMn alloys are examples where the data obtained for thin films is relevant for bulk materials as well.

10:30 AM

(ICACC-S11-015-2014) Reactive Air Aluminization Process for Planar SOFC Stacks (Invited)

J. Choi*, J. W. Stevenson, M. Chou, Pacific Northwest National Lab, USA

Generally, low-cost chromia-forming ferritic stainless steels are used as interconnect materials for planar type SOFC, because of their oxidation resistance and good thermal expansion match at high operating temperatures. However, volatile Cr-containing species, which originate from the steel's oxide scale, can poison the cathode material in the cells and subsequently cause power deterioration in the device. Moreover, this interconnect should separate the fuel and air for operating this SOFC. Usually, a glass sealant is used for this purpose. However, chromium reacts with glass sealants to form high CTE phases that can cause leakage of fuel or air, leading to degradation of SOFC performance. To prevent this, the novel Reactive Air Aluminization process has been developed. This paper will present recent progress regarding these novel coatings.

11:00 AM

(ICACC-S11-016-2014) Corrosion and electrical properties of the metallic glass thin films for bipolar plate in proton exchange membrane fuel cell

J. Sun*, J. Choi, K. Moon, S. Shin, KITECH, Republic of Korea

The bipolar plates play vital functions in the proton exchange membrane (PEM) fuel cell stack. Metallic materials for PEM fuel cell have advantages over graphite-based ones because of their higher mechanical strength, better electrical conductivity and lower production cost. However, they have a significant handicap, the susceptibility to corrosion in the acid and humid environment, which may decrease its performance. Recently some research groups have tried to use metallic glass alloys in bipolar plates because of their unique properties such as higher mechanical strength and corrosion resistances. But few researchers have tried to use the metallic glass thin films for bipolar plate due to differences of sputtering yield of the constituent elements of the target. In this study, we tried to synthesize the metallic glass thin films and investigated their electrical and corrosion properties. Zr-Al-Cu and Zr-Co-Cu amorphous thin film are deposited on SUS316L substrate by DC magnetron sputtering process with an alloyed single target. Current density of the films were under 10-8 A/cm2 and there were no changes of the current density in the range of 0.6 ~ 1.2V which is operating voltage of the fuel cell stack..

11:20 AM

(ICACC-S11-017-2014) Polarization properties of self-supported bismuth sodium titanate thick films prepared by using AD method

M. Suzuki*, J. Akedo, National Institute of Advanced Industrial Science and Technology, Japan

Bismuth sodium titanate [$(Bi,Na)TiO_3$; BNT] is an attractive piezoelectric material because it has a high Curie temperature (T_C) of 320 °C and a large spontaneous polarization. Aerosol Deposition (AD) method, which is based on room temperature impact consolidation (RTIC) phenomena, is attracting attention because it can form thick ceramic layers of simple or complex compositions at a room temperature. In this study, microstructure observation of self-supported BNT ceramics films prepared by the AD method has been performed. BNT films with thickness of around 20 μm were deposited on sapphire single crystal substrates deposited by the AD method. The self-supported films were obtained to be peeled from sapphire single crystal substrates the by a heat treatment of 500–1000 °C for 30–60 min in the air. Furthermore resultant films peeled by the heat treatment of 500 °C for 30min were annealed at 900–1000 °C for 60 min in the starting raw powder. A single phase of perovskite structure was confirmed for specimens prepared. While abnormal grain growth was confirmed for the heat treatment in the air, films annealed at 900 °C in the starting raw powder had uniformly-sized grain.

11:40 AM

(ICACC-S11-018-2014) Development and Integration of Innovative Glass Fibre Sensors into Advanced Composites for Applications in Hostile Environments

B. Milsom*, D. Milanese, Politecnico Di Torino, Italy; M. Roseman, S. Giannis, R. Martin, Element, United Kingdom; M. Salvo, Politecnico Di Torino, Italy

This research was focused on the development and integration of innovative glass fibre sensors into glass reinforced polymer (GRP) composites for applications in hostile environments. GRPs are increasingly used in the petrochemical industry, but there is a reluctance to use them in extreme conditions due to unknown long term stability. They are cheaper, lighter and easier to install than traditional steel pipes. However it must be possible to give accurate, non-invasive data on the degradation rate during component lifetimes of up to 30 years. These sensors will enhance the performance of GRP components, and increase the confidence in their use by providing real time monitoring of the composites integrity. This research enables monitoring of the degradation through the thickness of the protective liner of a petrochemical pipeline or component, where degradation is caused by a corrosive gaseous mixture at high temperatures and pressures. The sensors used were evanescent field optical glass fibre sensors based on commercially available multimode fibres. Fibres sputtered with metallic thin films were compared with bare fibres to determine the optimal configuration. The chemical degradation through the composite has been monitored to provide information on the penetration depth of the corrosive species and the depth of structural failure of the sample.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

Novel Processing III

Room: Coquina Salon F
Session Chair: William Pinc, University of Arizona

8:00 AM

(ICACC-S12-053-2014) High temperature solution growth of Cr2AlC MAX-phase single crystals (Invited)

T. Ouisse*, E. Sarigiannidou, O. Chaix-Pluchery, H. Roussel, B. Doisneau, D. Chaussende, Grenoble INP, France

Single crystalline platelets of the Cr2AlC MAX phase have been produced by high temperature solution growth, with typical areas in the range of a few mm2. We present a set of characterization experiments which confirm the single crystalline character of the samples and focus on some specific aspects, all related to the nano-lamellar structure of this material. We show that the crystals can be cleaved or delaminated parallel to the basal plane, and we present AFM observations of those cleaved surfaces.

8:20 AM

(ICACC-S12-054-2014) Layer-by-layer growth of Ti3SiC2 thin films

V. Vishnyakov*, J. Colligon, MMU, United Kingdom

Ti3SiC2 ceramic in crystalline form is a member of a large class of materials - so called MAX-phases. It has many unique properties and at the moment is extensively studied. In bulk form temperatures in excess of 1200 0C are needed to create crystalline nanolaminated structure. We have recently succeeded in growing the material by sequential layer-by-layer deposition on silicon substrate at 650 0C from three elemental magnetron targets. The question if the further reduction of synthesis temperature is possible by optimisation of deposition parameters remains open. We have used silicon and nickel superalloy substrates and composite targets in order to see how the enthalpy of the surface growth assists formation of desired nanolaminated structure. The results show that the type of composite target significantly affects resulting crystalline structures and further annealing at temperatures up to 900 0C further stabilise the structures created during deposition. In both cases when instead of all pure elemental targets silicon carbide and/or titanium carbide targets are used the nanolaminated ternary structure cannot be achieved on the non-epitaxial substrate at substrate temperatures up to 900 0C. This demonstrates that the heat of ternary compound formation on the surface during deposition plays an important role in the possibility to create Ti3SiC2 in the right form at the lowest possible temperature.

8:40 AM

(ICACC-S12-055-2014) Melt Infiltration based on Spark Plasma Sintering Technique: a Novel, Versatile Route for Producing Interpenetrating Ceramic-Metal Composites

L. Hu*, A. Kothalkar, M. O'Neil, I. Karaman, M. Radovic, Texas A&M University, USA

A novel technique is proposed for fabricating interpenetrating ceramic-metal composites by spark plasma sintering (SPS) assisted infiltration on porous ceramic preforms with molten metals and alloys. The porous Ti2AlC preform was simply and inexpensively prepared using sodium chloride powder as pore former, and the preform has a very open and interconnected structure that could be easily infiltrated by the molten metals/alloys. Different metals and alloys, including pure magnesium and aluminium alloy 6061 (AA6061), have been incorporated into the Ti2AlC preform, resulting in Mg/Ti2AlC composite and AA6061/Ti2AlC composite, respectively. The microstructure, phase composition and distribution in these composites were studied using a combination of X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy-Dispersive Spectroscopy (EDS). The AA6061/Ti2AlC composites are characterized in compression testing, and the results are compared with that of its pure components, i.e. AA 6061 and Ti2AlC. Comparisons with existing infiltration technology are presented.

9:00 AM

(ICACC-S12-056-2014) On the Development of Novel MAX-Al Composites

T. Hammann*, R. Johnson, M. F. Riyad, S. Gupta, University of North Dakota, USA

Mn+1AXn (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates displaying unusual, and sometimes unique, properties. The MAX phases are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously soft for transition metal carbides and nitrides. The composites of MAX phases with metals (MAXMET) are also important from both fundamental and applied perspective. MAX Phase-based composites have the potential to be used as shafts against SA (Super Alloys) foils for different foil bearing applications at 50,000 rpm from RT till 550 oC during thermal cycling. By making composites with hexagonal metals, it is also possible to enhance the damping behavior of these materials. In this presentation, we will present different studies about the development of MAX-Al composites as a potential structural material. It is expected that due to light weight these materials can be used for different tribological and engineering systems, for example, air-foil bearings, gas turbine seals, cylinder wall/piston ring lubrication for low-heat rejection diesel engines, various furnace components, among many others.

9:20 AM

(ICACC-S12-057-2014) Synthesis and properties of novel UHTC composites matrixes

J. Hu*, M. Tao, Y. Zhou, Science and Technology of Advanced Functional Composite Laboratory, China

UHTC composites matrixes were prepared via introducing ceramic powder (SiC, ZrC, Si or Zr etc.) to allyl-hydride-polycarbosilane (AHPCS). Its rheology investigated by rheometer. The cross linking and polymer-to-ceramic conversion of as-synthesized matrix was characterized by means of TGA, SEM and XRD. The results suggested that active ceramic powder reacted and C or CH4 in high temperature, and then produced ultra-high temperature resistant and antioxide component such as ZrC and SiC ceramic etc. The effect of the active ceramic powder are also studied in the work.

Structure-Property Relationships III

Room: Coquina Salon F
Session Chair: Laura Pienti, CNR

10:00 AM

(ICACC-S12-058-2014) Synthesis and characterization of bulk $(Cr_{1-x}Mn_x)_2AlC$ (0<x<0.2)

H. Gao*, Texas A&M, USA; A. Bandyopadhyay, I. Karaman, Texas A&M University, USA; M. Radovic, Texas A&M, USA; M. Radovic, Texas A&M University, USA

In this paper, we report on reactive synthesis of bulk $(Cr_{1-x}Mn_x)_2AlC$ (0<x<0.2) MAX phases by Spark Plasma Sintering (SPS) of Cr, Mn, Al and Cr_3C_2 powders. All samples were processed at the temperature of 1250°C and a load of 20MPa for 15-30 minutes to obtain high purity samples. XRD analysis showed that the c-axis lattice parameter of $(Cr_{1-x}Mn_x)_2AlC$ decreased slightly with increasing amount of Mn on M site. Additional studies using TEM equipped with EDX analysis indicated that the $Cr_{2-x}Mn_xAlC$ could form homogeneous solid solution with up to 10 at.% of Mn substituting Cr on M site. Magnetic properties of all processed samples were studied using SQUID magnetometer in 5-400K temperature range and 0.05-1T magnetic fields. The temperature dependent magnetization M(T) and the isothermal magnetic hysteresis loop M(H) indicate that Cr_2AlC has typical paramagnetic behavior. However, although isothermal M(H) for $(Cr_{1-x}Mn_x)_2AlC$ low increases in an essentially linear fashion with magnetic field at low temperature, tiny anomaly around low magnetic field indicates possible weak ferrimagnetism.

10:20 AM

(ICACC-S12-059-2014) Determination of Thermal Expansion Coefficients of $(Cr_{0.25}, V_{0.75})_3AlC_2$ and $(Cr_{0.25},V_{0.75})_4AlC_3$

J. Halim*, Drexel University, USA; E. N. Caspi, Nuclear Research Center, Israel; T. Cabioch, CNRS-Université de Poitiers-ENSMA, France; P. Eklund, Linköping University, Sweden; M. W. Barsoum, Drexel University, USA

Among the MAX phases, Cr_2AlC has excellent oxidation resistance. However, its thermal expansion coefficient (TCE) is too high relative to the protective Al_2O_3 layer that forms during oxidation causing spallation of the latter. Introducing a second transition element, such as vanadium, is one method to tune the TECs. Herein $(Cr_xV_{1-x})_{n+1}AlC_n$ solid solutions were synthesized by annealing Cr, V, Al, and C mixed powders for 8 h at 1450°C under Ar flow. Each TEC for the solid solutions $(Cr_{0.25}, V_{0.75})_3AlC_2$ and $(Cr_{0.25}, V_{0.75})_4AlC_3$ was determined by measuring the temperature dependencies of the lattice parameters obtained by Rietveld refinement analysis of X-ray diffraction patterns of a bulk sample containing both phases. The TECs (α_a and α_c) for $(Cr_{0.25}, V_{0.75})_3AlCr_2$ were found to be $12.0x10^{-6}$ and $7.5x10^{-6}$ deg^{-1} respectively. For $(Cr_{0.25},V_{0.75})_4AlCr_3$, α_a and α_c were calculated to be $9.5x10^{-6}$ and $8.7x10^{-6}$ deg^{-1} respectively. The difference between the TEC for both phases is in the range of 13 to 26%. $(Cr_{0.25}, V_{0.75})_3AlC_2$ shows an anisotropic behavior compared to that of $(Cr_{0.25}, V_{0.75})_4AlC_3$ whose TEC is almost isotropic, quite low and a better match for alumina.

10:40 AM

(ICACC-S12-060-2014) Constitutive Behavior and Fracture Toughness of Ti2AlC under Dynamic Thermo-mechanical Loading

P. Naik Parrikar*, S. Abotula, University of Rhode Island, USA; H. Gao, R. Benitez, M. Radovic, M. Radovic, Texas A&M University, USA; A. Shukla, University of Rhode Island, USA

An experimental investigation was conducted to evaluate the constitutive behavior and fracture initiation toughness of Ti2AlC under dynamic thermo-mechanical loading. All samples were processed from using Spark Plasma Sintering from commercially available Ti2AlC powder. A Split Hopkinson Pressure Bar (SHPB) apparatus was used in conjunction with an induction coil heating system for applying dynamic loads at elevated temperatures. The SHPB apparatus was modified to investigate the dynamic fracture initiation toughness. High speed photography was used to determine the fracture initiation time and the associated failure load. The results reveal that the peak compressive failure stress in dynamic conditions decreases with increase in temperature, from 1540 MPa at 25 °C to 950 MPa at 900 °C. The failure remains brittle even at temperatures as high as 900 °C. The fracture experiments show that the dynamic fracture toughness is higher than the quasi-static value by approximately 35 %. Also, the fracture toughness decreases with increase in temperature. The post mortem analysis of the fracture surfaces was conducted using Scanning Electron Microscopy to identify deformation and failure mechanisms in the examined samples. It was found that kinking together with intergranular cracking and delamination play important role in constitutive behavior of Ti2AlC under dynamic loading conditions.

11:00 AM

(ICACC-S12-061-2014) Interfaces between Shape Memory Alloy (SMA) and MAX Phases: A Comparison Study of Interpenetrating and Bilayer Composites

L. Hu*, A. Kothalkar, Texas A&M University, USA; G. Proust, University of Sydney, Australia; I. Karaman, M. Radovic, Texas A&M University, USA

Shape memory alloy (SMA)/MAX phase interpenetrating and bilayer composites were processed using spark plasma sintering (SPS) and pressureless sintering. NiTi/Ti2AlC and NiTi/Ti3SiC2 powder mixtures, each with a 50/50 volume ratio, were sintered in the 960~1100 oC temperature range under 100-300 MPa uniaxial pressure for various times, ranging from 3 to 30 minutes. NiTi bulk and Ti3SiC2 bulk were diffusion bonded using both spark plasma sintering (SPS) and pressureless sintering. The microstructure, phase composition and distribution in these two-phase composites were studied using a combination of X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy-Dispersive Spectroscopy (EDS), and Electron Backscatter Diffraction (EBSD). While good diffusion bonding between these two phases was observed between 960 and 1000 oC, they completely reacted with each other at 1100 oC. The overall thickness of the reaction layers and their phase compositions, and the density of composites were found to depend significantly on the composition of starting powders, sintering temperature, and soaking time. The reaction mechanisms between NiTi and MAX phases, Ti3SiC2 and Ti2AlC, for the first time proposed.

11:20 AM

(ICACC-S12-062-2014) Effects of concentration modulation on high temperature mechanical properties of silicon carbide/aluminium nitride ceramics

N. Minhas*, T. Boll, D. H. Anjum, King Abdullah University of Science and Technology, Saudi Arabia; J. Evans, J. Wang, F. Giuliani, Imperial College London, United Kingdom; T. Al-Kassab, King Abdullah University of Science and Technology, Saudi Arabia; L. J. Vandeperre, Imperial College London, United Kingdom

High temperatures are one of a range of possible extreme environments. Where at room temperature ceramics are hard and brittle, at high temperature the resistance to dislocation glide or creep can control the lifetime of components. In general, phase separation in composites via a spinodal reaction might induce a compositional modulation and enhances the resistance to dislocation movement in the lattice. In this paper, a possible spinodal decomposition of solid solutions of SiC and AlN is investigated as a means to ascertaining whether benefits in mechanical behaviour can be achieved. Hereto blends of SiC and AlN powders were hot pressed and homogenized at 2100 °C for 30 h. X-ray diffraction showed that a single solid solution of 2H SiC-AlN had been achieved. Part of the samples was treated for another 20 h or 40 h at 1900 °C to induce decomposition into a modulated pattern of SiC rich and AlN rich regions. Characterisation of the microstructure was performed using various imaging and analytical techniques. Results on high temperature creep testing and nano-indentation experiments to determine the effect of the concentration modulation on the high temperature mechanical properties will be presented and discussed within this contribution.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Materials Science and Technologies for Advanced Reactors III

Room: Oceanview
Session Chairs: Lionel Gelebart, CEA; Juergen Knorr, GWT-TUD GmbH

8:00 AM

(ICACC-S13-019-2014) Experimental study and modeling of the mechanical behavior of SiC/SiC composite tubes (Invited)

L. Gelebart*, F. Bernachy, CEA DEN, DMN, SRMA, France; M. Bornert, Université Paris Est, Laboratoire Navier, Ecole des Ponts ParisTech, France; J. Crépin, Mines ParisTech, Centre des Matériaux, UMR CNRS 7633, France

Because of their stability at high temperatures and under irradiation, SiC/SiC composites could be used as fuel cladding tubes in the next generation of nuclear reactors. In that context, these new materials (with the last generations of SiC fibers) are elaborated, optimized and studied at CEA. An important issue is related to the mechanical behavior of the fuel cladding tube when considering in-service or accidental conditions. For that purpose, the anisotropic behavior of the tubes must be precisely characterized and modeled. The key point of that talk relies on the close connection between mechanical testing and damage characterization to build and identify a new damage model for SiC/SiC composites. The anisotropic behavior is characterized from various kinds of combined solicitations (traction or compression, torsion and internal pressure). Digital Image Correlation, specifically adapted to the tube geometry, allows for a complete description of the macroscopic strain (in-plane). In addition, the orientation of cracks (at the surface of the sample) can be evaluated and related to strain heterogeneities. In parallel, a micromechanically based model is built from this new set of experimental characterizations. The model differs from the others previously proposed in the literature from its ability to reproduce and take into account the orientation of cracks observed experimentally.

8:30 AM

(ICACC-S13-020-2014) Ceramic nuclear fuel cladding with SiC hollow bodies

J. Knorr*, GWT-TUD GmbH, Germany; A. Kerber, SiCeram GmbH, Germany

The goals set for Gen IV nuclear energy systems can be met only with innovative solutions for fuel element cladding: use ceramics instead of metals. Fuel elements for different reactor types show two basic geometries: cylinders and spheres, simple forms, which can be manufactured as hollow bodies of high-tech ceramics like SiC. Laser beam joining is now available for SiC components, so the envisaged manufacturing technology consists of following steps: selection of appropriate SiC, manufacturing of robust pressureless sintered SSiC hollow body, filling with fuel matrix (preferably TRISO coated particles), densification, hermetical sealing with a lid, armouring with fibres (optional). Hollow bodies offer also possibility to precipitate an additional special layer on inner surface for enhancing retention capability and SSiC protection. With SICANA@ a new SiC composition was developed for advanced in-core application. A simple and effective method for manufacturing SiC hollow spheres has promising capability for production on industrial scale like capsules or compacts as fuel elements for block type (V)HTR. Stacks of small capsules armoured by ceramic fibre braids are proposed as rods for water-cooled reactors. Prototypes of discribed geometries and materials will be presented. Great efforts are still necessary to obtain qualified fuel elements and to demonstrate their superiority under operational conditions.

8:50 AM

(ICACC-S13-021-2014) A new model explaining silver migration through SiC coatings in TRISO particle fuel

X. Geng*, N. Rohbeck, F. Yang, P. Xiao, University of Manchester, United Kingdom

In-reactor experiments showed extensive release of the metastable silver nuclide Ag-110m from fully intact tristructural isotropic (TRISO) fuel particles. The insufficient retention of silver by the silicon carbide (SiC) layer is a major safety concern and needs to be resolved. Until now, the mechanism of silver migration though the SiC layer remains controversial. In this paper, we propose a new model to interpret the observed silver penetration of the SiC layer in TRISO fuel particles. Within experiments, a thin film of silver was trapped between two SiC layers in the simulated TRISO particles, which were subjected to high temperature heat treatment. Microstructural observations showed that silver located inside the SiC grains and along the SiC grain boundaries. Results from various characterisation techniques indicated that the migration of silver in the SiC layer involved dissolution of SiC in Ag, reaction between Ag and SiC, and formation of new SiC grains. Based on the experimental results, a new silver migration mechanism was proposed, termed as the “dissolution/reaction-recrystallization” model. Thermodynamic calculations supported the validity of the above model.

9:10 AM

(ICACC-S13-022-2014) Extending the Application and Functional Range of SiC Irradiation Temperature Monitors

L. L. Snead*, Y. Katoh, W. Porter, M. A. Fechter, Oak Ridge National Laboratory, USA

Silicon carbide, due to the irradiation formation and subsequent annihilation by isochronal annealing during of simple point defects and defect clusters, has been used to determine experimental irradiation temperature since the mid-60s. The primary technique utilized over the decades has been a simple measurement of length change, though due to limitations in absolute swelling of SiC bars the accuracy of the technique was somewhat limited and depended on dose and temperature. Generally, as the technique was driven by interstitial swelling the application range was limited to the "saturation regime" of SiC, or about 200-800°C. The purpose of this paper is to demonstrate how the technique of SiC-thermometry has been significantly improved both in terms of accuracy (through the use of advanced measurement techniques) and by measuring properties both in the amorphization regime of SiC and in the void swelling regime. Today, these monitors are in use from 100°C to well over 1200°C, essentially covering the typical experimental range of today's materials irradiation experiments.

9:50 AM

(ICACC-S13-023-2014) Porous Silicon Carbide Composites Development by Various Fabrication Methods

T. Hinoki*, S. Maeta, M. Lee, K. Shimoda, Kyoto University, Japan

Porous silicon carbide (SiC) composites were developed applying porous SiC matrix. The composites consist of just SiC fiber and crystalline porous SiC matrix without fiber/matrix interphase like carbon. The SiC matrix was formed with carbon sources. The porous SiC matrix was formed following decarburization process in air at high temperature. The porous SiC matrices were formed by liquid phase sintering method, reaction sintering method and chemical vapor infiltration method. The composites showed pseud-ductile behavior and complicated fracture behavior due to enhanced debonding at fiber/matrix interface attributed from partial interfacial bonding and frictional stress at the debonded fiber/matrix interface. The porous SiC composites were exposed at elevated temperature up to 1200C in air. No apparent degradation of flexural strength was observed compared to that of the as-received material. Effect of fabrication method on properties of the composites is discussed.

10:10 AM

(ICACC-S13-024-2014) Single-Source-Precursor Synthesis and Processing of Dense Metal-Modified Silicon Carbide Monoliths and Their Behavior in Ultraharsh Environments

E. Ionescu*, S. Kaur, Q. Wen, R. Riedel, Technische Universitaet Darmstadt, Germany

In this work, dense SiC-based monoliths were prepared upon processing of preceramic polymers and without using additives. Thus, a polycarbosilane was converted by means of cross-linking, warm-pressing and pyrolysis into SiC ceramic monoliths with low residual porosity. Subsequent infiltration with polycarbosilane followed by pyrolysis furnished after few steps fully dense SiC parts. Additionally, different metals (B, Y, Hf) have been incorporated into SiC. The metals were introduced upon chemical modification of the polycarbosilane with suitable metal organic precursors, followed by polymer-to-ceramic conversion. The incorporation of B into SiC has been shown to be beneficial for the densification behavior; whereas Y strongly enhanced the environmental stability of SiC (i.e,. high-temperature corrosion resistance). Hafnium incorporation into the polycarbosilane delivered an ultrahigh temperature ceramic nanocomposite (UHTC-NC) consisting of hafnium carbide nano-precipitations finely dispersed within β-SiC matrix, which exhibited excellent high-temperature oxidation behavior. The present study indicates that polymer processing of ceramics is a versatile technique to prepare dense SiC-based ceramic parts with tailor-made phase compositions, microstructures and property profiles.

10:30 AM

(ICACC-S13-025-2014) Development of porous SiCf/SiCm composite for industrial use

S. Maeta*, T. Hinoki, Kyoto University, Japan

Porous silicon carbide composites reinforced with silicon carbide fibers (porous SiCf/SiC composites) are novel material that can be used at high temperature in air atmosphere because of no fiber/matrix interface layer like carbon. In this study, a low-cost and simple-manufacturing process for the porous SiCf/SiC composites was developed for industrial use. The preform for porous SiCf/SiC composites was prepared by stacking the SiC green sheets with carbon and plain woven SiC fibers. The preform was sintered by hot-pressing in argon atmosphere. The porous matrix structure was obtained by heat-treatment in air atmosphere by oxidation of carbon. Yield rate for the process was good, whereas scattering of properties of the composites was limited. In order to optimize the porous SiC composites, porous SiC ceramics without SiC fibers were fabricated and evaluated as reference matrix materials. The mechanical and physical properties of the porous SiC ceramics and the porous SiC composites fabricated by different conditions were compared, respectively. The porous SiCf/SIC composites were optimized in terms of mechanical properties.

10:50 AM

(ICACC-S13-026-2014) High temperature water vapor oxidation behavior of various SiC ceramics for nuclear fuel cladding materials

M. Lee*, S. Kondo, T. Hinoki, Kyoto University, Japan

The oxidation behavior in water vapor environment at high temperature was studied for chemical vapor deposited (CVD) SiC and liquid phase sintered (LPS) SiC, which are candidates for new nuclear fuel cladding material, to evaluate their performance under severe accident. The polycrystalline CVD-SiC samples from Rohm and Haas Electronic Materials, L.L.C are highly pure and fully dense material. The LPS-SiC samples were fabricated by hot press with SiC powders and sintering additives such as Al2O3 and Y2O3 powders. Effects of impurities in LPS-SiC samples on the behavior of water vapor oxidation were evaluated based on the comparison in results of microstructural analysis by SEM and nano-indentation testing with the results of CVD-SiC samples. Especially, the influences of amount of impurities and exposed temperatures on the oxidation reactivity and modulus degradation of SiC samples will be presented. Moreover, the underlying mechanisms of the significant reaction between water vapor and impurities, and upper limit of the impurities will be discussed. This work was performed under contract with Toshiba Corporation in "Research and Development of Innovative Technologies for Nuclear Reactor Core Material with Enhanced Safety" entrusted to Toshiba by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

11:10 AM

(ICACC-S13-027-2014) Neutron irradiation effects on textured AlN prepared by slip casting in strong magnetic field

T. S. Suzuki*, National Institute for Materials Science, Japan; K. Yoshida, A. Rueanngoen, Tokyo Institute of Technology, Japan; T. Uchikoshi, National Institute for Materials Science, Japan; T. Yano, Tokyo Institute of Technology, Japan; Y. Sakka, National Institute for Materials Science, Japan

The development of crystallographic orientation is an interesting topic in ceramics and one of the effective ways to improve their properties. Recently, superconducting magnet technologies have been developed and used for various applications, and we reported that the successful control of the development of a textured microstructure even in diamagnetic ceramics was achieved by a colloidal processing in a strong magnetic field. The starting materials were commercially available AlN powders. The suspension with this powder was consolidated by a slip casting in a rotating strong magnetic field of 12 T. The green compacts after slip casting were isothermally sintered at the desired temperature for 2 h without applying a magnetic field. The c-axis of AlN was aligned perpendicular to the rotating magnetic field. The c-axis of the 61% of grains were aligned with less than 20 degree of tilting angle between c-axis and the rotating plane of a magnetic field in the c-axis oriented AlN. The random and textured AlN were neutron-irradiated to fluences of 1x10^24 and 2x10^24 n/m2. Neutron irradiation increased lattice parameters both in the textured and random AlN. Effect of irradiation on the a-axis was more sensitive in random sample than textured sample. The increments in lattice parameter of the c-axis in random AlN were similar to the textured sample.

11:30 AM

(ICACC-S13-028-2014) A Unified Predictive Tool for Thermal Conductivity and Mechanical Properties of SiC/SiC Composites

B. Nguyen*, C. H. Henager, Jr., R. J. Kurtz, Pacific Northwest National Laboratory, USA

SiC/SiC composites are being developed as structural materials for fusion power reactors. In such applications, the composite is subjected to high heat and neutron fluxes that impose extremely stringent requirements on the thermophysical properties of the components. Exploiting the complete analogy between the variables used in elasticity and those in steady-state heat conduction, this paper develops a unified tool to predict the thermal conductivity and mechanical properties of SiC/SiC composites using an Eshelby-Mori-Tanaka approach (EMTA). EMTA accounts for the constituent properties and features to first compute the properties of a reference unidirectional (UD) composite. The properties of the as-formed composite are obtained by averaging the solution for the UD composite over all possible fiber orientations using an orientation averaging algorithm. A damage mechanics approach is used to describe matrix cracking and fiber/matrix debonding for SiC/SiC composites loaded to failure. EMTA carries out the homogenization to compute the response of the as-formed composite incrementally. This damage model is implemented in ABAQUS and applied to predict the behavior of SiC/SiC composites subjected to monotonic loading. EMTA predictions for thermal conductivity and mechanical properties are compared to the corresponding experimental results to validate the models.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Synthesis, Processing and Microstructure

Room: Coquina Salon F
Session Chair: Waltraud Kriven, University of Illinois at Urbana-Champaign

1:30 PM

(ICACC-FS1-001-2014) Evidence of a fractal percolating network during geopolymerisation (Invited)

J. Rouyer, P. Steins, T. Piallat, CEA Marcoule, France; O. Diat, ICSM, France; F. Frizon, A. Poulesquen*, CEA Marcoule, France

The aim of the study is to describe the evolution of the microstructure during the alkali activation of a metakaolin by using original rheological method named Optimal Fourier Rheology (OFR) coupled to scattering experiments SAXS and SANS. The OFR technique consists in a continuous frequency strain solicitation in order to probe viscoelastic properties (G' and G'') on the full bandwidth of the rheometer in a short duration. The use of SANS with contrast matching method allows to visualise the growth of the geopolymer after the gelling time whereas SAXS gives an insight of the aggregation kinetic before the gelling time. The results show that the number of oligomers increases into the solution due to the dissolution of the metakaolin leading to a constant increase of the viscoelastic parameters until the gradual appearance of the percolating networks. The gelling time can be rigorously assessed by using the Winter and Chambon criterion. Analysis of the results clearly shows that a fractal percolating networks is formed inside the material after a reaction time depending on the formulation parameters. This percolating process is quite long due to the constant connexion of oligomers which continuously consolidated the geopolymer. After this period of gelling, the elasticity (G') becomes constant and the viscous parameter (G'') strongly decreases which means that the solid porous network is under formation.

2:00 PM

(ICACC-FS1-002-2014) Effect of aging and alkali activator on the porous structure of geopolymer (Invited)

P. Steins*, A. Poulesquen, F. Frizon, CEA, France; S. Rossignol, GemH, France

Nitrogen sorption, Small Angle X-ray and Neutron Scattering (SAXS, SANS) techniques were used to study the porous structure of geopolymer. Geopolymer are inorganic polymers synthesized by reaction of a strongly alkaline silicate solution and an aluminosilicate source (metakaolin). Effect of aging and alkali activator (Na+, K+) differing by their size, were investigated at room temperature. Influence of aging time on microstructure of both geopolymers matrix was verified in terms of pore volume and surface area. Results suggested a segmentation of the porosity and therefore a reduction in the pore volume over time. Regardless of maturity considered, some characteristics of the porous network such as pore size, shape and distribution depend on the alkali activator used. Whatever the technique considered, potassium-geopolymer has a greater specific surface area than sodium-geopolymer. According to SANS results, characteristic distances in the porous network increase for potassium-geopolymer whereas it remains substantially constant for sodium-geopolymer over time. The increase of the correlation length between two pores for potassium-geopolymer may be related to the densification of the porous structure. This densification over time is favored with potassium-geopolymer because the pores are smaller and closer than the sodium-geopolymer.

2:30 PM

(ICACC-FS1-003-2014) ^{29}SI NMR Study of the Si/K Molar Ratio Influence on the Geopolymerization Mechanisms (Invited)

A. Autef*, CEC-ENSCI-GEMH, France; E. Joussein, GRESE, France; G. Gasgnier, Imerys Ceramic Centre, France; J. Sanz, I. Sobrados, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain; S. Rossignol, CEC-ENSCI-GEMH, France

Geopolymers are amorphous three-dimensional alumino-silicate binders which may be obtained at slightly temperature by a reaction of an alumino-silicate source with an alkaline solution, generally potassium or sodium silicate. The aim of this work is to study by infrared and NMR spectroscopy the influence of the Si/K molar ratio on the reactivity of a potassium silicate solution and then on the structure of the obtained geopolymers. Then, this study is focused on the evolution of the mechanical properties according to the Si/K molar ratio. Geopolymers were synthesized from a mixture containing alkaline silicate solution obtained by dissolution of KOH pellets in water and metakaolin. Several solutions presenting Si/K molar ratio varying from 0.35 from 1.4 were used. Finally, the metakaolin was added to the alkaline mixture. The obtained results give information on the environment of the silicon in the silicate solution and on the nature of the silicate species. The Si/K molar ratio seems to play an important role on the reactivity of these species. The Si/K molar ratio value in the silicate solution strongly influences the structure of the strengthened material and consequently its mechanical properties. A too high Si/K molar ratio limits the dissolution of raw materials while a too much concentrated environment in alkaline hydroxide opposes to the polymerization of the species in solution.

Composites

Room: Coquina Salon F
Session Chair: Hubert Rahier, Vrije Universiteit Brussel

3:20 PM

(ICACC-FS1-004-2014) Influence of fly ash reactivity on geopolymerization behavior: An isothermal conduction calorimetric study

S. K. Nath*, CSIR-National Metallurgical Laboratory, India; S. Mukherjee, Jadavpur University, India; S. Maitra, Govt. College of Engineering & Ceramic Technolog, India; S. Kumar, CSIR-National Metallurgical Laboratory, India

Geopolymers represent a new class of binder materials characterized by excellent mechanical properties, as well as low manufacturing energy consumption. In geopolymerization synthetic alkali activated alumino-silicate material is produced by reaction of a solid alumino-silicate with a highly concentrated aqueous alkali hydroxide or silicate solution. Use of fly ash in geopolymer is getting increased attention as it is most abundantly available by-product comprising of alumino-silicates desirable for geopolymerization. In the present work class F fly ashes of different reactivity were subjected to geopolymerization. The kinetics of geopolymerization was monitored using Isothermal conduction calorimeter. The variable parameters were alkali concentration, particle size of fly ash, mineralogy of fly ash and temperature of geopolymerization. It was found that the peak heat values corresponding to dissolution and precipitation of alumino-silicate gel was more intense in the samples with higher glassy phase content. The isothermal calorimetric curves were correlated with the FTIR spectra of the treated fly ash samples. Higher intensity of the Si-O-Si stretching peaks were observed in the fly ash samples having relatively more glassy phase content. The reactivity of fly ash was correlated with microstructure and properties of produced geopolymer.

3:40 PM

(ICACC-FS1-005-2014) Production of in situ silicon nitride reinforced geopolymer composites, made by carbothermal reduction and nitridation (Invited)

C. Bagci, Hitit University, Turkey; G. P. Kutyla, W. Kriven*, University of Illinois at Urbana-Champaign, USA

Alkali-based geopolymer (M2O•Al2O3•5SiO2•14H2O+9C), where M = Na, K, or Cs composite, reinforced with in situ Si3N4 was produced by carbothermal reduction and nitridation (CRN). For this purpose the geopolymer was prepared by mixing metakaolin (Al2O3•2SiO2) with alkaline water glass solution and then the activated carbon nano powder was added the prepared geopolymer by hand. The viscos and homogenous slurry was poured into the mold to obtain bar samples at ambient temperature and cured in a humidity controlled, constant temperature oven at 50 °C. The CRN process of the bar samples was carried out in an atmosphere controlled tube furnace under a nitrogen flow of 5 cm3.min-1 at a temperature varying of 1100-1400 °C for 1h. XRD and SEM analysis were used to determine in situ transformation, morphology of all products after carbothermal reduction.

4:00 PM

(ICACC-FS1-006-2014) Flexural creep evaluation of polycrystalline Nextel and single-crystal mullite fiber reinforced pollucite composites using the geopolymerization technique (Invited)

S. Musil*, W. M. Kriven, University of Illinois at Urbana-Champaign, USA; S. T. Mileiko, A. A. Kolchin, Solid State Physics Institute of the Russian Academy of Sciences, Russian Federation

Geopolymers are an inorganic polymeric material composed of alumina, silica, and alkali metal oxides. Caesium-based geopolymer has shown good high temperature (>1200 degrees C) strength retention, as well as a very low coefficient of thermal expansion when crystallized into pollucite. These qualities make caesium geopolymer an attractive matrix material for creep resistant applications. Caesium geopolymer binders are combined with Nextel fibers and single crystal mullite fibers, then the matrix is crystallized to form pollucite. Single crystal mullite fibers were obtained by the internal crystallization method and show excellent creep resistance up to 1400 degrees C. High temperature flexural strength and creep resistance of pollucite and polycrystalline/single-crystal fibers are evaluated at 1000-1400 degrees C.

4:30 PM

(ICACC-FS1-007-2014) Properties of SiC/SiC composite prepared by polymer infiltration and pyrolysis process (Invited)

M. Lodhe*, IIT Madtas, India; A. Selvam, FRP Institute, India; A. Udayakumar, National Aerospace Laboratories, India; M. Balasubramanian, IIT Madtas, India

A high ceramic yield polycarbosilane (PCS) precursor for SiC was synthesized and characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis and gel permeation chromatography. Silicon carbide whiskers and particles were prepared from a mixture of rice husk, coconut shell and polycarbosilane. The synthesized SiC whiskers and particles were mixed with PCS solution and green compacts were prepared by cold compaction after the evaporation of solvent. The compacts were pyrolyzed at 1400 °C for 3 h under Ar atmosphere to get the SiC/SiC composites. The composites were obtained without any macro-defects, and their initial observed porosity was reduced by repeated polymeric infiltrations of PCS precursor and subsequent pyrolysis cycles. These composites were characterized by X-ray diffractometer and scanning electron microscope, in addition to density and mechanical property measurements.

5:00 PM

(ICACC-FS1-008-2014) The Potential of Geopolymer Composites as Castable Refractory Materials

G. P. Kutyla*, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Potassium geopolymers are easily made, and have shown chemical stability to temperatures in excess of 1500 °C. The fact that they can be produced inexpensively and do not require firing opens up many niches of application. Yet, they remain unutilized for refractory roles due to dehydration cracking and thermal shrinkage. Alumina platelets with a mean diameter of 50 microns and mean thickness of 10 microns were mixed with metakaolin-based potassium geopolymer to enhance performance at high temperatures. Four-point flexure tests show the composite remains stronger than 5 MPa until over 1400 °C in situ. Additionally, samples showed no cracking or friability on heating, even in response to extreme thermal shock. Thermal shrinkage measurements show less than 2% linear shrinkage to 1200 °C, and less than 3% to 1500 °C. Analysis with XRD and SEM did not show reactivity between the geopolymer and alumina platelets. These results indicate that geopolymers can be strong candidates for castable refractory applications.

5:20 PM

(ICACC-FS1-009-2014) Synthesis of Hierarchical Zeolites via in situ Alkalinity Control of Geopolymer Resin (Invited)

D. Medpelli*, D. M. Ladd, J. Seo, D. Seo, Arizona State University, USA

While geopolymers are of a great interest as green building materials, they may have a significant potential in production of new nanomaterials due to both the inherent nanostructures and the robust three-dimensional network structure of corner-sharing AlO4/SiO4 tetrahedra. Herein, we present a new scalable synthetic method for producing hierarchical zeolites by taking advantage of geopolymer chemistry. By carefully controlling the alkalinity and by employing vegetable oil as an emulsion template mixed into a geopolymer resin, hierarchical zeolites with good crystallinity can be produced in high yields (>500 g/L) through a one-pot top-down process that operates at relatively low temperatures. During geopolymerization and zeolitization, the vegetable oil undergoes saponification reaction by consuming the alkali present in the geopolymer resin, thereby reducing its alkalinity and simultaneously generating soap molecules in situ. Generation of soap molecules and reduction in alkalinity are found to be critical in creating meso- and macropores in the products and also in achieving the desired zeolitic crystallinity. After subsequent removal of organics by washing with water, the zeolitic products exhibited a faujasite structure with characteristic microporosity. Role of various synthetic parameters are to be discussed in determining the morphology and structure type of the zeolite products.

5:40 PM

(ICACC-FS1-010-2014) Sodium Geopolymer Reinforced with Jute Weaves or Fique Fibers (Invited)

K. Sankar*, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Geopolymers or polysialates are inorganic polymeric ceramics formed by mixing an aluminosilicate powder with sodium or potassium or cesium waterglass. Geopolymers can be reinforced with various materials to enhance the mechanical properties. Jute fibers (*Corchorus capsularis or Corchorus olitorius*) are a good choice for reinforcements because they are abundant, cheap, eco-friendly and offer good mechanical properties. Teixeira–Pinto et al.[ref.1] performed dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), tensile and flammability testing on jute weave reinforced, sodium geopolymer composites, in which the jute fibers were not pre-treated with NaOH. In this work, the mechanical properties of jute weave reinforced sodium geopolymer composites were measured according to ASTM standards and the variation was studied by reinforcing with as-received versus alkali-treated jute fibers. The mechanical properties were measured by tensile, impact and four-point flexure testing. Thermogravimetric analysis was used to study the behavior of jute in the geopolymer matrix, at high temperatures. X-ray diffraction was used to confirm the formation of geopolymer and scanning electron microscopy (SEM) and optical microscopy (OM) were used to examine the fiber-matrix interaction. Ref. 1. 1Teixeira-Pinto, A., Varela, B., Shrotri, K., Panandiker, R. S. P. and Lawson, J., CESP vol 28, Issue 9 (2009)

6:00 PM

(ICACC-FS1-011-2014) Tailoring of the porosity in geopolymers (Invited)

E. Papa*, E. Landi, ISTEC-CNR, Italy; P. Benito, A. Vaccari, University of Bologna, Italy; V. Medri, ISTEC-CNR, Italy

The production process in aqueous medium of geopolymers allowed the tailoring of the porosity from the nanometric to the millimetric range. Different techniques were used in order to fulfill the porosity requirements for many various purposes. Water contents in the starting mixtures affected the intrinsic meso-porosity of the geopolymer matrix, since water acted as pore former during the polycondensation stage. Moreover, ultra-macro-porosity were obtained by direct foaming, using additions of metallic silicon powder that, in alkali aqueous conditions, produced hydrogen bubbles which generate foamed structures with interconnected rounded pores. Furthermore, porous architectures with main unidirectional anisotropic macro-pores were gained by freeze-casting, where the ice crystals acted as pore network template, forming unique lamellar morphology. It is important to highlight that, if the skeletal material is originally meso-porous, a hierarchical pore system in which mesopores are directly connected to macro- and finally to ultra-macro pores can be constructed. Geopolymer matrices and foams were deeply investigated in order to optimize the consolidation process and to design the desired porosity. The microstructure, the intrinsic and induced porosity were fully characterized in view of potential applications.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing II

Room: Coquina Salon D

Session Chairs: Dileep Singh, Argonne National Laboratory; Swapan Das, CSIR-Central Glass & Ceramic Research Institute

1:30 PM

(ICACC-S1-053-2014) Enhancement of oxidation resistance of graphite foam by SiC coating for concentrated solar power application

T. Kim*, D. Singh, Argonne National Laboratory, USA; M. Singh, A. Gyekenyesi, Ohio Aerospace Institute, USA

Graphite foam has been considered to improve thermal performance of latent heat thermal energy storage system for concentrated solar power (CSP) plant. However, poor oxidation resistance of graphite foam at high temperature limits the use of graphite foam for these elevated temperature applications. Method to enhance oxidation resistance of graphite materials was investigated in this study. Oxidation resistance of uncoated graphite foam and SiC coated graphite foam were investigated by measuring weight changes with increasing exposure time at various elevated temperatures. Experiments were conducted under two conditions: flowing and static argon atmosphere in a furnace. After the experiments, weight loss rate (%/hour) and life time (time to reach 90% of initial weight) were calculated. It is shown that SiC coating can significantly improve the oxidation resistance of the graphite foam such that the estimated weight loss of graphite foam over CSP plant life time will be less than 10% of the initial weight.

1:50 PM

(ICACC-S1-054-2014) Melt infiltration of HfSi2 into porous C/C composites

T. Aoki*, Japan Aerospace Exprolation Agency, Japan; T. Yano, K. Wada, S. Umezu, Tokai University, Japan; T. Ogasawara, Japan Aerospace Exprolation Agency, Japan; H. Ohmori, RIKEN, Japan

Silicon melt infiltration(MI) has been conducted for the fabrication of C/C-SiC composites. Heat resistance of C/C-SiC composites in oxidation environment is limited to up to 1600C because active oxidation occurs above this temperature. In order to increase heat resistance, the authors tried to infiltrate HfSi2 to form HfC-SiC ceramics within C/C composites. MI of HfSi2 was conducted at temperatures 1550-2000C. Formation of HfC and SiC was confirmed within C/C composite by XRD analysis. Observations revealed that volume ratio between HfC and SiC is about 6:4. Moreover, only HfC was observed on external surfaces of C/C composite. This greater amount of HfC is inconsistent with the result of following simple reaction: $HfSi_2+3C \rightarrow HfC+2SiC$. Greater amount of SiC is expected according to above reaction. In order to investigate reaction mechanisms between HfSi2 and carbon, dense graphite specimen was used as substrates. Just above melting point of HfSi2(1550C), both HfC and SiC were observed within reaction layer. However, with increasing processing temperature, SiC disappeared and only HfC was observed. These results indicate that formed SiC further reacted with HfSi2, remaining HfC by following reaction: $SiC+HfSi_2 \rightarrow HfC+3Si(g)$. This secondary reaction is beneficial to increase the heat resistance of C/C-HfC-SiC composites. Reaction mechanisms, bending strength and arc-jet test results of C/C-HfC-SiC composites will be presented.

2:10 PM

(ICACC-S1-055-2014) Fabrication of SiCf/SiC composites by low temperature melt infiltration method using Si-Y alloy

Y. Okubo*, Tokyo Institute of Technology, Japan

Continuous silicon carbide fiber-reinforced silicon carbide matrix composites (SiCf/SiC) have been expected to be used for aerospace industry and energy fields because of its low density, high fracture toughness, high mechanical strength at high temperature and good oxidation resistance. However SiCf/SiC composites have not been commercially applied because the production cost of SiCf/SiC composites is very expensive. Melt infiltration (MI) method is simple and short term processing of SiCf/SiC composites, and it will contribute to reduce the processing cost of SiCf/SiC composites. Moreover, lower proceesing temperature is so attractive to inhibit the degradation of amorphous SiC fiber at high temperature. In this study, the author could decrease the MI fabrication temperature by 100oC using Si-Y alloy compared to Si. Si-Y alloy have the potential to lower the melting temperature to 1230oC. However, the alloy did not melt and not infiltrated into the fiber preform. This is because the Si evaporation during heat-treatment from Si-Y alloy. It changed the composition of Si-Y alloy, and finally higher the alloy's melting temperature. The three-point bending strength of SiCf/SiC composites fabricated by the MI method using Si-Y alloy shows about 580 MPa, and this value was higher than that of SiCf/SiC composites fabricated by conventional MI method using Si.

2:30 PM

(ICACC-S1-056-2014) Dense matrix formation and high temperature mechanical properties of C/SiC composite by multiple melt infiltration

T. Hara*, M. Ishikawa, Y. Kogo, Tokyo University of Science, Japan; T. Aoki, T. Ogasawara, Japan Aerospace Exploration Agency (JAXA), Japan

A rapid and low-cost manufacturing process of a carbon-fiber-reinforced SiC matrix (C/SiC) composite was examined in this study. The composites were produced by a chemical vapor infiltration combined with multiple melt infiltration process. First, pyrolytic carbon interfacial layer and SiC barrier layer were deposited on carbon fiber surfaces by CVI process. Then, remaining unfilled spaces in the pre-coated preform were filled with carbon particles by infiltration of carbon black slurry. The carbon filled preform was infiltrated with molten silicon to form SiC. Then, residual Si was eliminated by heat treatment at 1650 °C. Those composites were further densified by several cycles of polymer impregnation and pyrolysis of phenolic resin and the Si-MI followed by Si elimination. Through these processes, residual Si was reduced and the pores in the composite were filled successfully. Then, three point bending tests of the C/SiC composites at room temperature, 1200, 1500 and 1600 °C were carried out. Experimental results revealed that those composites possessed dense SiC matrix and exhibited the high flexural strength of approximately 500 MPa at 1600 °C.

2:50 PM

(ICACC-S1-057-2014) Enhanced Diffusion of Oxygen in Alumina Exposed to Water Vapor

J. P. Angle*, P. Morgan, M. L. Mecatney, University of California, Irvine, USA

Faster effective diffusion of oxygen was observed for α-Al_2O_3 exposed to high temperature water vapor versus dry air. Oxidation of Ni metal nanoparticles in α-Al_2O_3 to form $NiAl_2O_4$ was used to determine relative oxygen diffusion rates in dry air versus humid atmospheres at 0.2 to 0.8 atm $P_{H}2_{O}$. Temperatures from 1300 – 1500°C, and exposure times from 2 to 20 hours were used. The apparent kinetic rate-constant for oxygen diffusion in alumina at 1300°C in the presence of water vapor was 80% higher ($1.4x10^{-13}$ m^2/s for 0.2 atm $P_{H}2_{O}$ versus $7.9x10^{-14}$ m^2/s for dry air). The role of (OH^-) ions and proton hopping and tunneling will be discussed in relation to observations of faster diffusion. This effect of water vapor on oxygen diffusion can potentially impact sintering, creep, corrosion, oxidation, and the performance of thermal barrier coatings (TBC).

3:30 PM

(ICACC-S1-058-2014) Development of high performance proppants for gas and oil recovery

J. R. Hellmann*, B. E. Scheetz, Penn State, USA

Stimulation of gas and oil wells via hydrofracturing is commonly achieved by introducing a slurry of ceramic aggregates under pressure to induce and maintain fractures emanating from the well bore. The aggregates are pinned by closure stresses after the pressure is relieved, and "prop" the fracture open, thereby providing a more highly permeable pathway for oil and gas to migrate to the well. Hence, the aggregates are commonly referred to in the industry as proppants. This presentation summarizes our work on the development of high strength proppants from ion exchanged mixed glass cullet, doped low-grade alumina-bearing ores, andesite- and shale-based glass-ceramics, and spinel-based ferrimagnetic materials. These materials rival commercially available sintered bauxite-based materials with regard to strength, hardness, specific gravity and fracture behavior in American Petroleum Institute testing (ISO 13503). Transient liquid phase sintering processes have been developed for tailoring the microstructure, crush strength, fracture toughness, specific gravity, and catalytic activity in bauxite based proppants. Related technology for achieving enhanced fracture resistance of glass based proppants through ion exchange treatments and/or controlled devitrification in rhyolite-, andesite-, and shale-based proppants has been demonstrated, and is currently being transitioned to large scale manufacturing.

3:50 PM

(ICACC-S1-059-2014) Microstructural evaluation in a zirconia–spinel processed by a current-activated pressure-assisted densification method

M. Shirooyeh*, University of Southern California, USA; J. E. Garay, University of California, USA; T. G. Langdon, University of Southern California, USA

Quantitative investigations including measurements of crystallographic orientations as well as microscopic observations were conducted on a two-phase superplastic ceramic material after deforming in tension under a constant-stress condition. Yttria-stabilized zirconia-spinel (3Y-TZP – 30 vol% MgAl2O4) composite was produced via a micro-emulsion synthesis method. A Current-Activated Pressure-Assisted Densification (CAPAD) method was employed as a one-step consolidation process to produce a dense nanostructured zirconia–spinel ceramic with an average grain size of about 150 nm. Preliminary creep experiments were conducted at 1623 – 1723 K to investigate the plastic deformation behavior of the composite. Microstructure texture characterizations using SEM and EBSD provided an understanding of the characteristics of the flow mechanisms.

4:10 PM

(ICACC-S1-060-2014) High Thermal Conductivity Aluminium Nitride Polycrystals

D. Kata*, J. Lis, AGH University of Science and Technology, Poland

The AlN is used in electronic devices thus squeeze out conventional materials like SiO2, Al2O3 or BeO. The thermal conductivity (λ) of AlN mainly depends on the three factors: (1) level of oxygen content dissolved in crystallographic structure, (2) microstructure appearance, (3) nature of points and linear defects. These factors can radically reduced λ factor from 320 W/mK to 70 W/mK unless they are controlled well at every stage of manufacturing procedure. The aim of this study was to obtain aluminum nitride samples by rapid densification process – PPS. The AlN polycrystals were prepared by the PPS technique. Starting mixtures were composed with addition of 3.0 wt. %, 5.0 wt. % and 10 wt. % of yttrium oxide. Relative density of each polycrystals was measured by hydrostatic method. The XRD method was used for phase examination of samples after heat treatment. Microstructure examination supported by computer add analysis was performed by scanning electron microscope SEM and energy dispersive spectrometry EDS. The results were correlated with thermal conductivity of the samples measured by the laser pulse method on LFA 427 apparatus. The influence of the rapid sintering technique and yttria additive content on thermal conductivity and microstructure appearance of aluminum nitride polycrystals was clearly showed.

4:30 PM

(ICACC-S1-061-2014) Mechanical Behavior and Ionic conductivity of Sol-gel Derived Silica-Based Porous Organic-Inorganic Hybrid Materials

W. Wang*, H. Ahmadi, J. Kieffer, University of Michigan, USA

Porous organic-inorganic composite materials have been synthesized via the sol-gel process, tetraethoxysilane (TEOS) and poly(ethylene glycol) of low molecular weight as precursors. 3-aminopropyl triethoxy silane (APTES) is used as a silane-coupling agent to ascertain chemical bonding between organic and inorganic components at the molecular level. The materials exhibit enhanced elastic moduli and toughness compared to their constituents. The insertion of PEG into the porous silica network also improves Li ion conductivity of the hybrid materials doped with lithium salt, thus affording potential application as solid-state battery electrolytes. We use concurrent Raman and Brillouin light scattering, IR and dielectric impedance spectroscopy, and nitrogen adsorption porosimetry to characterize these materials. Concurrent Raman and Brillouin scattering reveals chemical characteristics and the complex mechanical moduli of the network at the molecular level. We report on the roles of the pore size, shape, porosity, and chemistry of the organic phase on the materials performance. Of particular interest is the inverse correlation between elastic moduli and ionic mobility we observe, and how these quantities depend on the atomic packing density of the materials. From these structure-property relationships we derive design criteria for high-mobility solid electrolytes.

4:50 PM

(ICACC-S1-062-2014) Thermo-chemo-mechanical induced expansion and stress in non-stoichiometric oxides

S. Bishop*, Kyushu University, Japan; D. Marrocchelli, Trinity College Dublin, Ireland

Ionic materials, particularly oxides, have shown advantageous properties in energy conversion and storage applications, such as solid oxide fuel cells (SOFCs), photoelectrochemical cells, and batteries, due in part to their high temperature stability, corrosion resistance, and foreign cation solubility (e.g. Li), respectively. Additionally, as a support material, oxides have been increasingly shown to influence catalytic activity. In addition to their electrochemical properties, thermo-chemo-mechanical coupling often plays a key role in device stability. In this presentation, the relationship between point defect concentration (e.g. oxygen vacancies), environmental variables, and mechanical properties (e.g. strain and elastic modulus) will be introduced. Results of a predictive stress model describing these relationships for an SOFC material in operation will be presented. New insight, aided by computational studies, in understanding the atomistic origins of chemo-mechanical coupling which have resulted in the development of new materials with reduced defect induced expansion will also be discussed.

5:10 PM

(ICACC-S1-063-2014) Highly Efficient Dye-Sensitized Solar Cells (Invited)

L. Han*, National Institute for Materials Science, Japan

In this presentation, strategy for improving efficiency of dye-sensitized solar cells (DSCs) was reported. The method for improvement of shirt circuit density (Jsc), open circuit voltage (Voc) and fill factor (FF) were investigated based on the equivalent circuit. It is found that the series-internal resistance decreases with increase of the roughness factor of the counter electrodes, the decrease of the thickness of the electrolyte layer and the sheet resistance of the transparent conducting oxide, and Jsc, increase with increase of the haze of TiO2 film. Futhermore, a small donor-acceptor type co-adsorbent for black dye sensitized DSCs was designed and synthesized, which can effectively increase JSC by offsetting the competitive light absorption of I-/I3- and improve VOC by introducing butyloxyl chains into the molecule to avoid dye aggregation and reduce the charge recombination. The certified efficiency record of 11.6% was achieved by using the novel co-adsorbent. Finally, the current state and futher respect of comicatisation of DSCs will be detailed.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Advanced Multifunctional Coatings I: Processing and Characterization

Room: Coquina Salon G

Session Chair: Eric Jordan, University of Connecticut; Federico Cernuschi, RSE

1:30 PM

(ICACC-S2-032-2014) Design of High Emissivity Coatings for Hypersonic Applications using Plasma Spray (Invited)

R. Trice*, W. Tan, Purdue, USA; C. Petorak, Praxair Surface Technology, USA

Hypersonic vehicles require sharp-featured nose tips and wing leading edges to reduce aerodynamic drag. However, the geometry of these edges increases heat transfer to the surface. This temperature can be reduced via increasing the radiation heat transfer away from the surface which is controlled by maximizing the emissivity of the surface material. In our work, a rare-earth emissivity modifier is incorporated into the ZrB2/SiC system to improve its surface radiation heat transfer. Two approaches have been used: 1. Mechanically mixing rare-earth oxide powders into the ZrB2 and 2. Doping rare-earth nitrates into the spray dried ZrB2. Each has been plasma sprayed using a unique shrouded gun that minimizes oxidation of the ZrB2. X-ray diffraction data suggests that the dopants have been integrated into the coatings while retaining the ZrB2, and further investigations reveal the doped rare-earth ions still reside in the coatings after oxidization at 1500oC for an hour. Total hemispherical emissivity and oxyacetylene ablation results will be presented.

2:00 PM

(ICACC-S2-033-2014) High Velocity Flame Spraying of Nano-structured Materials and Related Industrial Applications (Invited)

R. Gadow*, A. Killinger, University of Stuttgart, Germany

Thermal Spraying of fine structured powder materials require either the application of agglomerated powders that can be processed using HVOF (High Velocity Oxy Fuel Flame Spraying) based processes or the conversion of these fine powders into a finely dispersed suspension together with an organic solvent, appropriate for suspension spraying (HVSFS: High Velocity Suspension Spraying). HVOF using liquid fuels is a flame spray technique that is especially appropriate to process high-grade cermet materials containing submicron and nano-sized carbides in form of agglomerated powders. With HVSFS on the other hand, micron, sub-micron and nano-oxide particle containing suspensions can be processed. Both methods are suitable for the manufacturing of finely structured and dense coatings and offer new possibilities in functional coating development for new application fields. Due to their refined microstructure, mechanical and physical coating properties can differ significantly from their conventionally sprayed counterparts. The paper will give an overview about current development activities at the IFKB and will present numerous industrial application examples in the field of tribo-functional and wear protection applications, biomedical applications, energy conversion and armor.

2:30 PM

(ICACC-S2-034-2014) Tribological Studies of the Boride-Based Thermal Diffusion Coatings

E. Medvedovski*, J. Jiang, Endurance Technologies Inc., Canada;
M. Robertson, NRC - EME, Canada

Engineering components, e.g. valves, tubing for the artificial lifting systems for the down-hole applications in the oil and gas industry, require protection against friction and sliding abrasion service conditions. The hard boride coatings on steels and alloys obtained through the thermal diffusion process have a high potential for these severe application conditions over many other types of coatings as they can be obtained on the entire working surfaces of large size and complex shape products. The tribological studies of the boride-based coatings obtained at Endurance Technologies Inc. have been conducted using the Cameron-Plint testing unit (reciprocating sliding of the metallic rod under the load over the flat surface of coated samples). The friction wear loss, friction coefficient and structural changes of the coatings have been studied in dry and lubricating (water-oil) friction conditions, which simulate actual application conditions. The obtained boride coatings have the friction loss significantly smaller than electroless nickel coatings and untreated steel (e.g. ~10-30 times in the dry conditions and at least 5 times in the lubricating conditions) with no flaking-off. The friction coefficients of the boride coatings are steady over the test duration. The encouraging results are explained by the specific structure of the hard coating obtained through the thermal diffusion process.

2:50 PM

(ICACC-S2-035-2014) Effect of microstructure and thickness on the friction and wear behavior of CrSiCN coatings

O. Ajayi*, C. Lorenzo-Martin, S. Torrel, A. Erdemir, Argonne Nat Lab, USA;
R. Wei, Southwest Research Institute, USA

One of the emerging composite/alloy coatings for tribological applications is CrSiCN, typically deposited by physical vapor deposition. Examples of potential applications of this coating include cutting and forming tools, dies and automotive components, such as injection valves and piston rings for diesel engines. In selecting coatings for different tribological applications, one of the critical parameters is the coating thickness. In the present work, the effects of microstructure and coating thickness on the friction and wear behavior of CrSiCN coatings were determined under unidirectional sliding conditions. Tests were conducted with a dry ball-on-flat contact configuration using ~ 1-, 3.5-, and 7-μm thick coatings deposited on a hardened H-13 steel substrate by plasma enhanced magnetron sputtering. The ball specimen was made of WC. The friction behavior was observed to be strongly dependent on coating thickness and microstructure, especially at relatively low loads (5 N). At higher loads, however, the thinnest coating (1 μm) was quickly worn through, while the thicker ones (5 and 10 μm) remained intact. Wear in both the counterface WC ball material and the coatings also depended on coating thickness and microstructure. In all coatings, there was localized damage but minimal wear.

Advanced Thermal Barrier Coatings II: New Compositions, Processing, Testing Development

Room: Coquina Salon G
Session Chair: Peter Mechnich, German Aerospace Center (DLR); Bryan Harder, NASA Glenn Research Center

3:30 PM

(ICACC-S2-036-2014) Structure and Thermal Conductivity of (La1-xGdx)2Zr2O7 TBCs Fabricated by Suspension Plasma Spray

S. Kim*, C. Kwon, Y. Oh, S. Lee, H. Kim, Korea Institute of Ceramic Engineering and Technology, Republic of Korea; B. Jang, National Institute of Materials Science, Japan

Zirconate-based oxides with fluorite and/or pyrochlore have been investigated as candidate materials for future TBCs. Fluorite and pyrochlore have analogous cubic structures with a space group of Fm3(-)m for the former and Fd3(-)m for the latter. The general formula of the fluorite and pyrochlore oxides is AO2 and A2B2O7, respectively. The low thermal conductivities of rare earth oxides with these structures are attributed to the phonon scattering by point defects in the crystallographic structures. In this study, (La1xGdx)2Zr2O7 TBCs are fabricated by suspension plasma spray with a variety of suspension conditions. (La1-xGdx)2Zr2O7 systems are comprised by selecting La3+ /Gd3+as A-site ions and Zr4+ as B-site ions in A2B2O7 pyrochlore. Phase formation, microstructures, and thermal conductivities are examined with the deposited coatings of (La1-xGdx)2Zr2O7 compositions. The possibilities of these coatings for TBC application are also discussed.

3:50 PM

(ICACC-S2-037-2014) La2Zr2O7 (LZ) coating by liquid feedstocks plasma spraying: Role of precursor

W. Duarte*, S. Rossignol, ENSCI-GEMH, France; M. Vardelle, SPCTS, France

To increase the efficiency of aerospatial and aeronautic engines, new thermal barrier coatings operating at high temperature (>1200°C) need to be developed. Indeed, Yttria-Stabilised-Zirconia (YSZ) obtained by atmospheric plasma spraying is the industrial solution for aircraft propulsion. Nevertheless, YSZ exhibits some limits: phase transformation after thermal cycling or sintering temperature of 1200°C. Lanthanum zirconate (LZ) with pyrochlore structure shows better properties than YSZ i.e. low thermal conductivity, phase stability or high melting point (>2000°C). Moreover, new thermal spraying processes: Suspension Plasma Spraying (SPS) and Solution Precursor Plasma Spraying (SPPS) permit to obtain LZ coating with fine microstructure which increase coating properties. Both processes require the dissolution of zirconium and lanthanum metallic salts to prepare solution either to synthesize powder for SPS or to be directly sprayed with SPPS. This work aims to study the different precursors of zirconium and lanthanum in aqueous or alcohol solutions in particular thermal decomposition and rheological properties. But also, to characterise LZ powders synthesized by three processes: citrate route, sol-gel and coprecipitation using various precursors. The first results evidenced the possibility to spray solution containing metallic precursors. Controlled parameters will be concentration and viscosity.

4:10 PM

(ICACC-S2-038-2014) Interface chemistry of rare-earth added YSZ films for TBC prepared by EB PVD

Y. Oh*, C. Park, S. Kim, S. Lee, H. Kim, KICET, Republic of Korea; D. Lim, Korea University, Republic of Korea; B. Jang, NIMS, Japan

Interface structure and compositions, specially related with TGO (Thermally Grown Oxide), are critical issues in durability of thermal barrier coating (TBC). Control of TGO formation and growth behavior has been studied by many researchers because those are directly related with lifetime of TBC. EB PVD coating, as an emerging technology for TBC application such as airfoils in turbine engines, is known to better to withstand high temperature thermal resistance than conventional plasma spray coating for their unique columnar structure which can have outstanding thermal strain tolerance. In this research, we tried to find out compositional change of interface and related phase evolution between YSZ based top layer and Ni-Cr alloy bond coat. TEM with compositional profile anaysis used to invesigate the interface chemistry. LFA used for anayzing of thermal conductivity of specimen. La2O3 added YSZ film shown cross-linked interface which might affect to adhesion and thermal durability of film.

4:30 PM

(ICACC-S2-039-2014) Non-line-of-sight vapor deposition of thermal barrier coatings

T. M. Rodgers*, H. Zhao, H. Wadley, University of Virginia, USA

Controlling deposition of thermal barrier coatings onto complex-shaped engine components is highly desirable. A combination of vapor-phase direct simulation Monte Carlo and surface assembly kinetic Monte Carlo methods was used to study deposition performance onto a doublet guide vane substrate at various conditions. The combined simulation techniques were used to determine both coating thickness and microstructural uniformity. Experimental coatings were then deposited via directed vapor deposition to confirm simulation results. Both coating thickness and microstructural uniformity were found to vary greatly with deposition conditions and substrate configuration. Improved coating uniformity was achieved by increasing carrier gas velocity and finely tuning the deposition chamber pressure. Increasing the separation distance between vanes also improved coating uniformity. Adjustment of deposition parameters reduced coating thickness variation along the inner vane surfaces by 35%.

4:50 PM

(ICACC-S2-040-2014) Engineered multi-layered thermal barrier coatings for enhanced durability

V. Viswanathan, G. Dwivedi*, M. Flynn, M. Miller, S. Sampath, Stony Brook University, USA

The durability of plasma sprayed thermal barrier coatings has been of significant interest ever since their inception in gas turbine engine components. Although several novel materials are being developed, 7-8 % YSZ continues to serve as the industry standard. One of the major reasons being the penalty of lower fracture toughness that is associated with these novel TBC materials. While toughness is an essential component in determining the spallation life of coatings, the elastic energy present in the coating is almost equally critical. Since the failure of typical APS coatings occur at the interface of the bond coat and topcoat due to the strains associated with TGO growth, the toughness is most critical at that particular interface. We experimentally demonstrate that by functionally optimizing the location specific needs of toughness and modulus via a multi layered TBC architecture, the furnace cyclic life of coatings can be significantly improved. Thus by leveraging the benefits of process science we present a durability strategy for APS YSZ coatings.

5:10 PM

(ICACC-S2-041-2014) Measuring thermal barrier coating's thermal conductivity on as-manufactured and ex-service components

G. Witz*, M. Esquerre, H. Bossmann, Alstom (Switzerland) ltd, Switzerland

To assess the effectiveness of a thermal barrier coating, it is important to measure its thermal conductivity. The most common method used to measure the coating thermal conductivity is the laser flash method. Unfortunately, this method can be performed only on small samples that are specially manufactured for this purpose. A method allowing measurement of thermal barrier coatings thermal conductivity on complete parts without sample preparation is necessary for coating production quality control. Such a method has been developed in Alstom and its results have been compared to the ones produced by standard methods showing a very good correlation. The principles of the method will be presented and its accuracy will be discussed and compared to the one of other methods.

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(ICACC-S2-042-2014) Study on hot corrosion behavior of YSZ-Ta2O5 thermal barrier coating in turbine simulated environment

H. Habibi*, S. Guo, Louisiana State University, USA

Zirconia stabilized with 3.2–4.2 mol% (6–8 wt. %) yttria (3–4YSZ), the current material of choice for thermal barrier coating applications, is susceptible to hot corrosion by acidic oxides such as vanadia in high temperatures. Chemical interaction is found to be the major corrosive mechanism for the deterioration of zirconia based coatings at high temperatures. This study compares the hot corrosion performance of yttria stabilized zirconia (YSZ), and YSZ-Ta2O5 (TaYSZ) composite samples in the presence of molten mixture of Na2SO4 + V2O5 at 1100C. Characterizations using X-ray diffraction (XRD) and scanning electron microscope (SEM) indicate that in the case of YSZ, the reaction between NaVO3 and Y2O3 produces YVO4 and leads to the transformation of tetragonal ZrO2 to monoclinic ZrO2. Results show that the TaYSZ is more resistant to destabilization by NaVO3. For TaYSZ, minor amount of NaTaO3, TaVO5 and Ta9VO25 are formed as the hot corrosion products with only traceable YVO4. Due to synergic effect of co-doing of zirconia with Y2O3 and Ta2O5, TaYSZ sample is more stable, both thermally and chemically in Na2SO4+V2O5 media at 1100C, than YSZ, and shows a better hot corrosion resistance.

S3: 11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Interfacial Reactions / Fuel Electrode

Room: Coquina Salon H

Session Chairs: Victor Orera, C.S.I.C.; Denis Klemm, sunfire GmbH; Sean Bishop, I2CNER Kyushu University

1:30 PM

(ICACC-S3-039-2014) Solid Oxide Fuel Cell Interface Dynamics and Associated Electrochemical Performance Degradation

C. Zhang, D. R. Mumm*, University of California, Irvine, USA

The stability and degradation mechanisms of perovskite cathode/electrolyte interfaces were systematically investigated by correlating long term electrochemical performance change to the nano-scale structural and chemical evolution, assessed using advanced electron and X-ray characterization techniques. A significant increase in cathode polarization resistance was observed over the duration of testing, and the performance degradation was attributed to either the formation of a less catalytic phase, or a change in perovskite stoichiometry at the interface (depending upon the system studied). The mechanisms underpinning the structural and chemical evolution revealed characteristics with strong diffusion related kinetics. Based on the mechanistic understanding of factors that constitute interfacial instability, approaches to stabilize perovskite cathode/electrolyte interfaces were experimentally explored. Exploratory studies with each approach are discussed.

1:50 PM

(ICACC-S3-040-2014) Process Specific Degradation Analysis of SOFCs

J. Hjelm*, C. Graves, P. Hjalmarsson, Technical University of Denmark, Denmark

The solid oxide fuel cell (SOFC) is an attractive technology for the generation of electricity with high efficiency and low emissions. The current focus in the area of anode supported (ceramic) SOFCs is on cells and components suitable for operation in the temperature range 600 - 750 °C. Lifetime limiting effects and lifetime prediction are becoming more important as SOFC technology moves closer to commercialization, with lifetime targets of 40000 – 60000 hours for many stationary applications such as co-generated heat and power (CHP). Demands of max 10-20% voltage drop during such long lifetimes translates to degradation rates of approximately 5-20 mΩ cm^2 kh^{-1}, which must be accurately measured, preferably in a component or process specific manner. Durability testing and quantitative degradation analysis using both ac and dc data obtained before, during, and after long-term tests of anode-supported solid oxide fuel cells with mixed electronically and ionically conducting cathodes, will be discussed in this contribution.

2:10 PM

(ICACC-S3-041-2014) Fuel distribution in SOFC stacks derived from the gas conversion impedance

R. R. Mosbæk*, J. Hjelm, DTU Energy Conversion, Denmark; R. Barfod, Haldor Topsøe A/S, Denmark; P. V. Hendriksen, DTU Energy Conversion, Denmark

As SOFC technology is moving closer to a commercial breakthrough, methods to measure the "state-of-health" of operating stacks are becoming of increasing interest. This requires application of advanced methods for detailed electrochemical characterization during operation. An experimental stack with low ohmic resistance from Topsoe Fuel Cell A/S was characterized in detail using Electrochemical Impedance Spectroscopy (EIS). The stack geometry was optimized for EIS by optimal geometrical placement of the current feeds and voltage probes were carried out in order to minimize measurement errors caused by stray impedances. The SOFC stack was tested at 750°C with hydrogen as fuel at OCV with different partial steam pressures (4%, 20% and 50%), and at different current loads (0 A cm^{-2}, 0.1 A cm^{-2}, 0.2 A cm^{-2}, 0.25 A cm^{-2}) with 4% partial steam pressure. Existing diffusion and conversion impedance models was fitted to the impedance data to identify the gas distribution in the stack. This tool can be used to detect possible minor changes in the supply of gas to the individual cells, which is important when going to high fuel utilizations.

2:30 PM

(ICACC-S3-042-2014) Interaction of perowskite type lanthanum-calcium-chromites-titanates La1-xCaxCr1-yTiyO3-δ with solid electrolyte materials

C. Belda, E. Dietzen, M. Kusnezoff*, N. Trofimenko, Fraunhofer IKTS, Germany; U. Vasook, Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V., Germany; A. Michaelis, Fraunhofer IKTS, Germany; U. Guth, Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V., Germany

Lanthanum-calcium-chromites-titanates have been proposed as alternative anode material [1, 2], or diffusion barrier layer material in metal supported cells, due to the electrical conductivity and coefficients of thermal expansion. However interactions of perovskites with electrolyte materials such as doped zirconia are known to cause zirconate formation depending on temperatures and oxygen partial pressure [3]. In this study we demonstrate how the metallic nickel phase affect the zirconate formation at the solid state Perowskite-Fluorite interface. Different compositions of La1-xCaxCr1-yTiyO3-δ (x = 1 - 0.5; y = 1 – 0.8) have been synthesized and reactivity with yttria doped zirconia (8YSZ) and nickel-8YSZ-cermets was investigated by X-ray diffraction, field emission scanning electron microscopy and energy dispersive X-ray spectroscopy after 80 hours at 1300 °C in reducing atmosphere (H2). The results indicate that there is no zirconate formation in the absence of metallic nickel, while in the presence of metallic nickel, calcium- and or lanthanum zirconate formation takes place, depending on the La/Ca-ratio of the A-site doping. Thermodynamic calculation and EDX spectra consistently indicate nickel-titanium alloy formation as a reason for the destabilization of the perovskite lattice within a oxygen partial pressure of 7*10-20 Pa < p(O2) < 3*10-17 Pa.

3:10 PM

(ICACC-S3-043-2014) Nanostructured Electrodes for Solid Oxide Fuel Cells (Invited)

F. Dogan*, A. Buyukaksoy, A. Sarikaya, V. Petrovsky, Missouri University of Science and Technology, USA

Recent results on development of SOFC electrodes prepared by co-sintering of starting powders and infiltration methods will be reviewed. While co-sintering of powders leads to achieving of relatively high power densities, redox stable SOFCs are obtained by electrode infiltration techniques. Infiltration of a polymeric nickel oxide precursor into a sintered porous ytrria –stabilized zirconia (YSZ) skeleton is a promising approach to achieve redox stable cells. In order to ensure that the porous YSZ skeleton was mechanically strong enough to withstand the stresses caused by the volumetric expansion of the Ni phase upon oxidation, a polymeric YSZ precursor was infiltrated into the porous YSZ skeleton, prior to NiO infiltration. It was shown that infiltration of YSZ precursor strengthened the porous YSZ skeleton without compromising from the porosity or initial YSZ particle size significantly. Electrolyte supported SOFC (electrolyte thickness ~ 180 µm) with redox stable anode prepared by YSZ and NiO infiltrations showed a power density of ~0.41 Watt/cm2 at 800 °C which remained stable after 20 redox cycles in 10%H2 – 90% Ar fuel. Impedance spectroscopy measurements at 800 °C showed significantly low electrode polarization resistances (anode + cathode ~0.07 Ohm.cm2). The relationship between the processing, microstructural development and electrochemical performance of SOFC electrodes will be discussed.

3:40 PM

(ICACC-S3-044-2014) Titanate perovskites designed to exsolve Cu-based alloy nanoparticles for SOFC applications

S. M. Bukhari*, D. Neagu, J. Irvine, University of St Andrews, United Kingdom

Copper based solid oxide fuel cell anodes have been considered as an alternative of typical Ni/YSZ cermet to tackle the coke and/sulphur poisoning issues. However, high mobility of Cu on the surface of oxides is problematic. In-situ exsolution could be a way to fabricate such Cu based anodes. Compared to initial approaches of this technique, our approach employs advanced control over perovskite nonstoichiometry and subsequent defect chemistry to tailor the exsolution process. The nanoparticles produced by this method have good anchorage onto the host lattice which enhances not only the stability of the catalyst but also reduces the aging effect of the catalyst. Therefore, in-situ exsolution can be considered a way to produce robust catalyst and thus it can play a vital role in tackling improved performance and long term stability issues of SOFCs. In this study we developed new compositions with copper doping in titanate perovskites. We adopted various strategies to tune defect chemistry for optimal copper solubility in the perovskite lattice and the exsolution itself from the resulting perovskites. We further replaced some of the copper with very catalytic active metals like Ni, Co and Fe to produce Cu-M (M= Ni, Co, Fe) alloy nanoparticles. We will demonstrate the potentials of Cu-M alloy nanoparticles produced by in-situ exsolution for SOFC anode applications.

4:00 PM

(ICACC-S3-045-2014) Ordered Mesoporous cermets as anodes for intermediate temperatures Solid Oxide Fuel Cells

L. Almar, M. Torrell, A. Morata, IREC, Spain; L. Yedra, LENS-MIND-IN2UB, UB, Spain; S. Estradé, TEM-MAT, Scientific and Technological Centers, (CCiT), UB, Spain; B. Colldeforns, IREC, Spain; F. Peiró, LENS-MIND-IN2UB, UB, Spain; T. Andreu, A. Tarancón*, IREC, Spain

High temperature stable ordered mesoporous metal oxides were prepared from a silica hard template.The self-supported replicas maintain the periodic mesoporous structure and a high surface area at temperatures as high as 1000°C. The proposed route has low dependency on the material to prepare allowing its use for synthesizing a wide variety of mesostructures based on metal oxides. In particular, mesoporous nickel based cermets were synthesized and characterized by using this approach. Finally, fuel cell tests were carried out using an electrolyte-supported SOFC and a mesoporous layer working as anode. A maximum value of power density of 435 mW/cm2 was achieved at 800°C in H2. Moreover, virtually no degradation of the microstructure and the electrochemical performance was demonstrated for the cermet after more than 200h of test at 800°C in a water satured 5%H2 in argon atmosphere. This methodology could represent a step forward towards the implementation of mesostructures in applications where high thermal stability is required such as solid oxide fuel/electrolysis cells, gas separation membranes or high temperature catalysis..

4:20 PM

(ICACC-S3-046-2014) Method for Calculating Effective conductivity of SOFC electrodes from 3D tomography images

D. Roussel*, C. L. Martin, D. Jauffrès, University of Washington, USA; A. Lichtner, R. Bordia, Grenoble INP, France

We validate an image-based method for computing the effective conductivity of both simulated and real SOFC electrode microstructures, taking into account their electronic, ionic and electrochemical resistances. The simulated microstructures are created by numerically sintering a mixture of ionic and electronic particles using the Discrete Element Method (DEM). Three types of contacts are considered: ionic-ionic, electronic-electronic and ionic-electronic. TPBs between the ionic and electronic particles are used to account for the electrochemical reaction. A network of resistances is then built and, the effective conductivity is calculated. A second method relying on image analysis was used to calculate the effective conductivities of these same numerical microstructures by voxelizing the 3D images and assigning a specific conductivity to voxels defining TPBs. A fast-fourier transform approach is used to compute the effective conductivity of the voxelized images (GEODICT commercial software). The results from the image-analysis method were in agreement with the resistance-network method, validating its use on other microstructures. Finally, 3D tomography images of anisotropically porous, freeze-cast samples were voxelized and analyzed to identify active TPBs within the microstructure. Using the image analysis method, the effective conductivities of real 3D microstructures were calculated.

4:40 PM

(ICACC-S3-047-2014) Structure characterization and transport properties of Mn-CeO2 and Fe-CeO2

L. Zhao*, Kyushu university, Japan; J. Hyodo, T. Ishihara, Kyushu University, Japan; K. Sasaki, Kyushu university, Japan; S. Bishop, Kyushu University, Japan

Mn or Fe doped Ceria, known as good catalysts for the oxidation of hydrocarbons, have received much attention as candidates for intermediate temperature solid oxide fuel cell (IT-SOFC) anodes. In this presentation, we present an investigation of the phase stability of Mn-CeO2 and Fe-CeO2 solid solutions. 3 – 60 mol% Mn and 3-50 mol% Fe mixed with CeO2 compositions were prepared using the Pechini method, and the crystal structure was characterized by XRD and Raman spectroscopy. For the present preparation conditions, the maximum solubility of Fe and Mn is less than 3 at% in CeO2. Bulk and interfacial defect transport and thermodynamic equilibria, investigated using impedance spectroscopy (bulk samples) and thermogravimetry (powders) on Mn-CeO2 compositions will also be presented. Additionally, oxygen surface exchange of the Mn-CeO2 and Fe-CeO2 films, measured using a novel in situ optical absorption method, will be discussed.

5:00 PM

(ICACC-S3-048-2014) Characterization of Doped Yttrium Chromites as Electrode for Solid Oxide Fuel Cell by Impedance

X. Liu, W. Li*, M. Gong, West Virginia University, USA

Co and Ni doped yttrium chromites as potential anode and cathode materials for solid oxide fuel cell are characterized by impedance in various PO2 and PH2 atmosphere. The polarization resistances for Y0.8Ca0.2Cr0.8Co0.2O3 (YCCC) and Y0.8Ca0.2Cr0.9Ni0.1O3 (YCCN) on yttrium stabilized zirconia (YSZ) electrolyte are 0.96 and 8.4 Ωcm2 in wet H2, 1.2 and 36.7 Ωcm2 in air at 850 oC, respectively. In anode part, the rate-limiting steps (rds) are indentified as charge transfer and surface diffusion for both electrodes. The primary active zone is three-phase boundary (3PB) for YCCN but it extends to a small portion of electrode bulk in YCCC anode. In the cathode part, O2 dissociative adsorption or diffusion is one of the rds for both electrodes, and the active zone is limited to the 3PB area. The influence of electrolyte to electrode performance is investigated by replacing YSZ electrolyte with scandium stabilized yttrium (SSZ). Smaller polarization resistances are observed on each electrode in both wet H2 and air atmospheres. Replacement of electrolyte can alter not only the rate of charge transfer process but also in some cases other surface processes not related to the electrolyte directly. The best performance is obtained from the YCCC/SSZ combination, which is 0.49 and 1 Ωcm2 in wet H2 and air at 850oC respectively, making it a promising electrode material.

5:20 PM

(ICACC-S3-049-2014) Electrocatalysis for Solid Oxide Fuel Cells with Proton-Conducting Oxides in the Anodes

Z. Cheng*, Florida International University, USA

Solid oxide fuel cells (SOFC), as a relatively new power generation technology, offer several major advantages including high energy conversion efficiency, high energy density and power density, fuel flexibility, and reduced emission of CO2 and NOx. Conventional SOFCs are based on oxygen ion conducting electrolytes such as yttria-stabilized-zirconia (YSZ), and the anodes are typically nickel-YSZ (Ni-YSZ) cermets. This presentation will focus on some alternative SOFC architectures that incorporate proton-conducting oxides into the Ni-containing cermet anodes and provide examples of the intriguing electrocatalytic behaviors that have been demonstrated for those SOFCs. Specifically, interesting phenomena such as improved tolerance to sulfur poisoning (up to tens of ppm level), tolerance to carbon deposition (coking), and improved (higher) open circuit voltage when using mixed ionic-electronic conducting (MIEC) oxides such as doped ceria as the electrolyte have been observed on button cells of those alternative SOFC architectures. The above phenomena will be discussed in terms of the possible changes in the underlying electrochemical reaction mechanisms when proton conducting oxides are incorporated into the Ni-containing cermet anodes for SOFCs, and the directions for future research to try to capitalize on those observations in real world applications will be pointed out.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics II

Room: Coquina Salon E

Session Chairs: Christian Bonhomme, UPMC; Florence Babonneau, UPMC/CNRS/Collège de France

1:30 PM

(ICACC-S5-013-2014) Physicochemical description of synthetic and natural biomaterials (Invited)

C. Bonhomme*, UPMC, France

In this contribution the latest developments in NMR and first principles calculations will be highlighted. Various examples taken in the field of calcium phosphates and oxalates will be presented. The detailed characterization of organic inorganic interfaces will be emphasized.

2:00 PM

(ICACC-S5-014-2014) Fractographic Analysis of Broken Ceramic Dental Restorations

G. D. Quinn*, American Dental Association Foundation, USA

This presentation will provide new fractographic analyses of several in vivo fractured ceramic crowns and bridges made with modern dental restorative materials. It is part of an ongoing study to understand the mechanisms of fracture of such restorations. Cases will include a 3-unit zirconia bridge with very unusual fracture markings, a 3-unit lithium disilicate bridge, a zirconia crown, and others time permitting. Recommendations for manufacturers, laboratories and clinicians will be made.

2:20 PM

(ICACC-S5-015-2014) Multifunctional Glass Microspheres for Medical Applications (Invited)

D. E. Day*, Missouri University of Science and Technology, USA

This paper describes how the inherent versatility of glass is used to create multifunctional glass products for treating diseases in humans. An example is the bioinert aluminosilicate glass microspheres which are being used to destroy malignant tumors in the liver by delivering a lethal dose of localized beta radiantion and by reducing the blood suppy to the tumors, radioembolization. These glasses can also be modified to elevate the temperature of the tumor, hyperthermia, which make the tumor more susceptible to radiation. Other examples include microspheres which can deliver radiation and/or release drugs to a target organ, but which also biodegrade in the body in a unique way so that no radiation escapes from the site, radiation synovectomy. Other examples of multifunctional, biodegradable glasses are also described, including those that can function as tissue (vessel) guides and which simultaneously release drugs or antimicrobial agents at a chosen site.

2:40 PM

(ICACC-S5-016-2014) Enhanced mechanical properties of ATZ for biomaterials applications

S. Soares*, N. Neves, M. Rodrigues, A. L. Lagoa, J. Calado, INNOVNANO – Materiais Avançados, S.A., Portugal

Alumina toughened zirconia (ATZ) composites are being widely used in the production of implants for surgery due to its biocompatibility, good mechanical properties and high lifetime. This work is focus on the development of ATZ nanocomposites based on nanostructured powders synthesized by Emulsion Detonation Synthesis (EDS). The high pressures (1-10 GPa) and temperatures (1000 – 4000C) reached during synthesis combined with ultrafast quenching allows to form small primary particles and consequently produce ATZ with improved homogeneity. The influence of the alumina content in zirconia was study with the intention of attaining a good compromise between mechanical performance and lifetime. INNOVNANO ATZ ceramic pieces were prepared by hot isostatic pressing and values as high as 2000 MPa of flexural strength were achieved as well as 1400 MPa of hardness. Fracture toughness achieved values around 5 MPa.m1/2 with low aging. The SEM analysis demonstrated that the nanocomposites have high chemical and microstructural homogeneity with grain sizes below 300 nm and full densification, being responsible for the enhanced of the mechanical properties (fracture toughness and flexural strength).

3:20 PM

(ICACC-S5-017-2014) Diffusion Coating for Increasing the Biocompatibility of Conventional Metal Implant Alloys (Invited)

J. J. Stiglich*, B. E. Williams, ultramet, USA

Ultramet has been developing and commercializing refractory metal and ceramic coatings and freestanding parts for corrosive and high temperature environments for more than 42 years. Tantalum has a long history of use as an implant material in both bone and soft tissue. Ultramet developed and licensed a process for fabricating open-cell tantalum metal foam that closely resembles the structure and properties of human bone for use as FDA-approved orthopedic bone implants. Under NASA funding Ultramet developed a process to diffuse highly corrosion-resistant tantalum metal into the surface of conventional stainless steels and superalloys to improve the acid corrosion resistance of components used in precision space shuttle orbiter propellant transfer valves. A thin, metallurgically bonded tantalum surface layer was established that graded from pure tantalum at the surface to a mixture of tantalum and the substrate elements. The tantalum surface layer precisely replicates intricate substrate features and does not require post-process machining or polishing. The potential exists to use this coating to increase the biocompatibility of conventional metal implant alloys, and the processing allows the application of various surface textures. Ultramet's experience with tantalum foam structures and coatings will be reviewed.

3:40 PM

(ICACC-S5-018-2014) One-pot synthesis of monodisperse nanospheres of amorphous calcium phosphate in a simple biomineralization medium (Invited)

A. Tas*, University of Illinois, USA

An inorganic solution similar to the inorganic electrolyte compartment of the DMEM (Dulbecco's modified Eagle medium) cell culture medium is developed. This biomineralization medium contains 44.05 mM HCO3-, 126.86 mM Na+, 93.37 mM Cl-, 5.33 mM K+, 2.26 mM Ca2+, 0.905 mM H2PO4-, and 0.81 mM Mg2+. Its Ca/P molar ratio is set to be identical with that of human blood plasma, i.e., 2.50. The medium is free of any Tris or Hepes but maintains a pH of 7.45 both at 37 and 65 C. The first novelty of this solution is it has the unique ability to homogeneously coat x-ray-amorphous calcium phosphate (ACP) on glass slides vertically immersed in it and kept at 37 C for less than 48 h. The second innovative aspect of this solution is it has the unprecedented ability to produce monodisperse ACP nanospheres with diameters less than 180 nm when simply heated at 65 C for 1 h while being stirred. The third novelty of this solution is it only forms ACP and it does not form apatite in stark contrast to many other synthetic calcification or biomineralization media known. Samples were characterized by x-ray diffraction, energy-dispersive x-ray spectroscopy, Fourier-transform infrared spectroscopy, BET surface area, contact angle goniometry, field emission-scanning and transmission electron microscopy analyses.

4:00 PM

(ICACC-S5-019-2014) Multi-physic degradation mechanisms of zirconia and alumina-zirconia composites for implants : interactions between fatigue, wear and hydrothermal ageing (Invited)

L. Gremillard*, L. Preiss, L. Martin, INSA, France; R. Kohal, B. Spies, University of Freiburg, Germany; J. Chevalier, INSA, France

Biomedical implants are submitted in-vivo to a wide range of solicitations, triggering many degradation mechanisms from different physical origins. Mechanical stresses are of course important but they are coupled with specific solicitations related to the environment: presence of water, enzymes, cells, potentially high local temperatures… Moreover, the degradation mechanisms are not always independent, and multi-physic degradation may occur. However, international standards principally deal with the mechanical solicitations, mostly forgetting the others. Moreover, most of the time existing literature considers separately the different degradation mechanisms. We seek here to explore the combined effects of fatigue, wear and hydrothermal ageing on zirconia and zirconia-toughened alumina components. In particular, we will show that friction increases the ageing rate of the zirconia components in total hip prostheses. This mechanism may explain some of the poor long-term in-vivo results of zirconia hip prostheses reported in the literature. On the contrary, zirconia-toughened alumina components may be free from this combined degradation. Finally, preliminary results on spine and dental implants submitted to such multi-physic degradation tests will be discussed.

4:20 PM

(ICACC-S5-020-2014) Nanostructural Ca-Aluminate Based Biomaterials

L. Hermansson*, J. Lööf, Doxa AB, Sweden

The presentation deals with nanostructural chemically bonded bioceramics with Ca-aluminate (CA) as main raw material, and which dental applications these bioceramics are suitable for. Due to a low solubility product of the phases formed, nanocrystals are easily formed. The nanocrystal size is in the range 10-50 nm with an open porosity with a nano-channel width in the range 1-3 nm. General properties of CA-based bio-materials due to the nanostructures developed deal mainly with 1) High mechanical strength, 2) Reduced porosity, and 3) Complete sealing of contact zones to tissue and other biomaterials due to the nanostructural hydration mechanisms. CA-based biomaterials are close in chemistry to apatite, the main chemical constituent in hard tissue. The CA-based materials can favorably be produced at body temperatures. Theses bio-materials tolerate moist conditions. The hardening can be controlled to avoid shrinkage, and the thermal and electrical properties of CA-based materials are close to those of hard tissue. A specific interesting combination of properties is the simultaneous appearing of bioactivity, and bacteriostatic and antibacterial properties, as well as reduced microleakage. More than ten different dental applications have been found possible to produce. These deal with dental filling materials, dental luting cements, endodontic materials, stabilising materials and as coatings on other implant materials.

4:40 PM

(ICACC-S5-021-2014) γ -ray imaging enhancement using nanoscience (Invited)

R. L. Leonard*, J. King, J. Johnson, UTSI, USA; S. Schweizer, South Westphalia University of Applied Sciences, Germany

The purpose of this work is to develop a γ-ray glass-ceramic scintillator to enhance imaging capabilities in computed tomography, positron emission spectroscopy and single photon emission computed tomography. Glass ceramics can be made in any shape or size and at a low cost. Samples have been synthesized based on a ZPBL (zirconium, lead, barium, and lanthanum fluoride) formulation additionally doped with chlorine and one or two rare-earth halides. The glasses are prepared in an inert atmosphere and later heat-treated in order to develop $BaCl_2$ nanocrystals within the glass matrix. Depending on size and number of the embedded nanocrystals they are optically transparent in the visible spectral range and offer the potential of high spatial resolution. Characterization methods include differential scanning calorimetry (DSC), photoluminescence (PL), photostimulated luminescence (PSL), x-ray diffraction (XRD), Mössbauer spectroscopy, and transmission/scanning electron microscopy. Results will be presented assessing the suitability of such a material for γ-ray scintillation.

5:00 PM

(ICACC-S5-022-2014) Antimicrobial Effects of Formable Gelatinous Hydroxyapatite-Calcium Silicate Nanocomposites For Biomedical Applications (Invited)

C. Ko*, University of North Carolina-Chapel Hill, USA

The nanocomposite Gemosil made of gelatinous hydroxyapatite with animosaline and pozzolanic crosslinking was developed. The mechanical performance of Gemosil approximated that of cortical bone. The composite formed formable cement, which allowed approximately 5 minutes solidifying in water. This study was aimed to test if adding chlorhexidine (CHX) to Ca(OH)2 could provide antimicrobial effects of the cement. Four materials, including the CHX control in paper discs, Gemosil with and without CHX, and mineral trioxide aggregate (MTA used in clinical dentistry) were tested. Each material was prepared in disc samples. The E. Faecalis and S mutans were cultured at 37 degrees C. Bacterial suspensions were evenly distributed on the blood-agar plate surface. The MTA/Gemosil/CHX discs were placed on the blood-agar plate after inoculation and immediately placed for incubation at 37 degrees for 72 hours. Results showed that the control and Gemosil with CHX provide similar antimicrobial effect to E. Faecalis while Gemosil without CHX and MTA did not show antimicrobial effect to E. Faecalis. All four materials showed a significant antimicrobial effect to S mutans. In combination with previous reports showing osteogenesis of Gemosil, the CHX incorporated Gemosil may be applicable to both orthopedic cement and dental cement.

5:20 PM

(ICACC-S5-023-2014) Strengths of Solid State NMR to investigate silicate- and carbonate-substituted hydroxyapatites (Invited)

F. Babonneau*, C. Coelho, UPMC/CNRS/Collège de France, France;
D. Marchat, Ecole Nationale Supérieure des Mines, France

The richness of the apatite structure is an extraordinary ability to accept substitutions and vacancies. The apatite structure can incorporate a wide variety of ions, of the same or of different charge, which affect both its cationic and anionic sub-lattices. This property is intimately related to its adaptability to the biological functions of different tissues. This presentation will illustrate how multinuclear solid-state NMR methods can be efficiently used to characterize hydroxyapatites substituted by silicate and carbonate ions.

S7: 8th International Symposium on Nanostructured Materials and Nanocomposites

Synthesis, Functionalization and Assembly of Metal Oxide Nano Materials

Room: Coquina Salon B

Session Chairs: Kathy Lu, Virginia Tech; Mauro Epifani, CNR-IMM

1:30 PM

(ICACC-S7-058-2014) Developement of microstructure-controlled nanocomposites by use of nano-integrated composite particle (Invited)

H. Muto*, Toyohashi University of Technology, Japan

So far we have been developing a method for preparation of composites particles, composed of matrix and filler particles, based on the electrostatic interaction between the particles bearing opposite surface charges. This preparation process can be applied for various kinds of powder materials with different sizes; up to now, we have been successfully in preparation of nano- and micro- size composites particles. By using the obtained composites particles as raw materials, the agglomeration of filler materials can be avoided and the composite material with uniform microstructure can be produced. In this study, the microstructure controlled Alumina – Zirconia composite material with different vol. ratios were successfully synthesis by using the composites particles obtained via the colloidal process. The microstructure of obtained 15vol% zirconia – alumina composites show that zirconia particles were uniformly distributed in alumina matrix without large aggregation.

2:00 PM

(ICACC-S7-007-2014) Enhanced Molecular Adsorption and Photocatalytic Properties of Tinania Nanotubes by Cation Doping (Invited)

T. Sekino*, H. Tsukamoto, Tohoku University, Japan; T. Kim, S. Lee, Sun Moon University, Republic of Korea; S. Tanaka, Tohoku University, Japan

Titania nanotube (TiO_2 nanotube, TNT) is known as one of the promising low-dimensional nanostructured oxides. In this study, TNTs have been modified by doping various metals such as Cr, Nb, Sm and so on. Their physical and photochemical properties have been investigated and discussed. Metal-doped TNTs were successfully synthesized by solution chemical synthesis route at temperature around 110°C. It was found that the doping of aliovalent metal ions enhances methylene blue (MB) molecules adsorption properties by maintaining and/or enhancing their photocatalytic properties. When Nb was doped to TNT, high MB adsorption performance was confirmed. Photocatalytic degradation of MB was investigated under the UV and visible light irradiation condition. It was found that the doped TNTs exhibited better visible light responsibilities, provably due to the formation of optical absorption bands owing to the doped elements. In addition, co-doping of metal ions exhibited further enhancement of the both properties. These results rationalized that modification of low-dimensional oxide semiconductor nanomaterials provide excellent environmental and/or energy multifunctions. Detailed processing-structure-physical/chemical properties will be discussed.

2:30 PM

(ICACC-S7-060-2014) Synthesis and processing of nanostructured YAG ceramics

P. Ramanujam*, B. Vaidhyanthan, J. Binner, Loughborough University, United Kingdom

Nanocrystalline yttrium aluminium garnet (nYAG) has been synthesized using a solvothermal method. The optimised solvothermal conditions for the formation of nYAG were examined using XRD, TEM, NMR, GC-MS and FT-IR and it was found that highly crystalline and non-agglomerated spherical particles could be obtained. The centrifuged and washed particles were redispersed with NH4PAA to produce colloidal YAG suspension. The rheological behaviour and the electrokinetics of the nYAG suspensions were characterised to optimise the desired solids content and suitable pH to achieve maximum suspension stability. The 55 wt% YAG suspension was further spray-freeze dried (SFD) to produce soft and crushable granules and green compacts were made by uniaxial pressing at 75 MPa followed by isopressing at 200 MPa. The defect free green bodies were pre-sintered to 97-99% theoretical density at 1600°C / 5 h and hot isostatically pressed from 1500-1650°C. The HIPped samples were characterised for microstructure, optical and mechanical properties.

2:50 PM

(ICACC-S7-061-2014) Growth and Characterization of Eco-friendly Lead-Free Ferroelectric ZnSnO3 Nanostructures

C. Kons*, A. Datta, University of South Florida, USA

Ferroelectric (FE) materials exhibit polarization-reversal under an external electric field and are essential components in non-volatile memory devices such as in iPhones, notebooks, and other portable media offering higher storage density and faster access speeds. Moreover, FE nanomaterials have become the focus of intensive research due to their size and shape dependent enhancement in functional properties. Worldwide regulatory restrictions on the use of lead (Pb) have resulted in search for eco-friendly, Pb-free, efficient FE materials to replace lead-zirconium-titanate (PZT), which was the most popular FE material till-date. To this end, ZnSnO3 (ZSO) with stable, noncentrosymmetric crystal structure holds great promise. In this work, we report novel and facile physical-chemical combined synthesis methodologies encompassing pulsed laser deposition, electroplating and solution phase methods towards FE ZSO nanostructures in large scale on a variety of substrates. The carefully grown and optimized nanostructures are characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy and Raman spectroscopy. Electronic properties of these nanostructures are measured and the results are discussed in context of understanding the potential of these nanostructures for advanced device applications.

Nanostructured Carbon, CNT and Graphene Composites: Synthesis, Characterization and Application

Room: Coquina Salon B

Session Chairs: Masahiro Yoshimura, National Cheng Kung University; Anuja Datta, University of South Florida

3:20 PM

(ICACC-S7-062-2014) Hydrothermal Carbons: Synthesis and Reaction of Various Carbon Materials under Hydrothermal Conditions (Invited)

M. Yoshimura*, National Cheng Kung University, Taiwan

Ours ystematic study showed following results: [I] Under 100 MPa water 1)Carbon itself has not corroded below 300oC.2)Organic and/or inorganic impurities can be decomposed and/or extracted by hydrothermal water in those conditions.3)Corrosion of carbon can be observed above 400-500oC particularly disordered parts in the carbon materials.4)Carbon nano-cell might be formed from amorphous carbons above 600oC. 5)Fulleren and single wall carbon nanotube (SWCN) started to change into amorphous carbon above 600oC, then might produce multiwall carbon nanotube (MWCN) above 700oC.6)Carbon nano-materials (nanofilament, nanopipe, MWCN, etc.) could be produced from many hydrocarbon materials like polyethylene with use of catalysts like Ni powders.7)Those nanopipes might have encapsulated water .8)Diamond crystals (>100 µm) would not be corroded even under hydrothermal conditions of 800oC.9)Spherical carbons with µm sizes could be fabricated in supercritical C-H-O fluids. [II] In Local Hydrothermal Conditions under ambient pressure 1)Carbon films and/or patterns could be produced by the electro deposition from organic solvents like alcohols at ambient temperatures.2)Nano-structured carbons can be formed by electrochemical corrosion with HF.3)Nano –carbons can be formed by submerged iquid plasma processing.4)Those interesting results can be seen in many (>30) papers.

3:50 PM

(ICACC-S7-063-2014) The use of XAFS to study the internal structure of iron-molybdenum loaded PS-b-P2VP micelles during bimetallic nanoparticle synthesis

A. Riskin*, Hasselt University, Belgium; A. M. Beale, Utrecht University, Netherlands; H. Boyen, Imecvzw, Belgium; A. Vantomme, KULeuven, Belgium; A. Hardy, M. K. Van Bael, Hasselt University, Belgium

The poly(styrene)-block-poly(2-vinylpyridine) (PS-b-P2VP) micelle route is a well established method for the preparation of bimetallic nanoparticles used for the catalysis of carbon nanotubes (iron-molybdenum) and other applications like ultrahigh density storage devices (iron-platinum), yet to date no information is available concerning the internal structure of the P2VP–metal salt complex. For the first time, XAFS measurements were performed on micelles loaded with either iron(III) chloride or molybdenum(V) chloride and combinations of both. Analysis of the data revealed that iron is tetrahedrally coordinated within the core, whereas molybdenum is octahedrally coordinated in the pure loaded micelles and tetrahedrally coordinated in the mixed micelles. For the bimetallic samples, analysis of the Fe and Mo K-edge data revealed the existence of an interaction between iron and molybdenum. This approach to obtain detailed structural information during the preparation of these catalyst particles will allow for a deeper understanding of the effects of structure on the function of catalysts used for CNT growth i.e. to explain differences in yield as well as potentially providing a deeper understanding of the CNT growth mechanism itself.

4:10 PM

(ICACC-S7-052-2014) Development of Al_2O_3/SiC nanocomposites through a polymer precursor method: processing variables vs. microstructure

Y. Zhu*, J. Binner, H. Wu, B. Vaidhyanathan, Loughborough University, United Kingdom

1 vol% SiC/Al_2O_3 nanocomposites have been prepared via an aqueous route based on adding a Si-containing preceramic polymer, polycarbosilane, to an alumina slurry with the aim of synthesising SiC nanoparticles *in-situ*. An antisolvent precipitation process was employed to prepare a well-dispersed polymer/Al_2O_3 suspension and spray freeze drying was used to generate flowable and crushable granules, which were subsequently die and isostatically pressed to yield green bodies. A heat treatment was applied to either the granules or the pressed bodies to complete the polymer-to-ceramic transformation and subsequently densify the green bodies by pressureless sintering. The transformation was studied by a combination of thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), infra-red spectroscopy (FT-IR) and X-ray diffraction (XRD). The influence of the different processing parameters, including those associated with the anti-solvent precipitation, heat treatment conditions and sintering conditions, on the microstructural features of the composites, e.g. grain size, grain morphology, distribution of SiC and presence of porosity, are discussed with a view to determining the 'optimum' processing conditions to achieve fully dense, homogenously dispersed nano SiC particles in an Al_2O_3 matrix.

4:30 PM

(ICACC-S7-065-2014) Pull-out of Rough Multiwall Carbon Nanotubes: a Parametric Study

E. M. Byrne*, M. A. McCarthy, University of Limerick, Ireland;
W. A. Curtin, Ecole Polytechnique Federale de Lausanne, Switzerland

A Finite Element study of MWCNT pull-out from a ceramic matrix with a rough fiber-matrix interface is presented to study the effect of interfacial/sliding parameters on fiber pull-out behaviour, and nanocomposite strength and toughness. Interfacial roughness, due to missing CNT walls and other fabrication defects, is represented as an axisymmetric sinusoidal fiber-matrix interface with Coulomb friction. Our results indicate that even though an individual rough fiber requires high peak pull-out forces, a cracked nanocomposite with an array of rough MWCNTs is likely to experience both crack closing and opening stresses. The net average pull-out stress due to a bundle of fibers is then quite low relative to the peak values, reducing energy dissipation. Furthermore, during pull-out, roughness leads to significant stress concentrations over the innermost walls of the MWCNT that can lead to premature fracture. We conclude that deliberately using interface roughness to achieve higher interfacial friction is not an effective strategy to improve composite strength and toughness, and that even atomic-scale roughness can be detrimental to composite performance. Results also demonstrate that for MWCNTs, increasing interfacial friction parameters is the most effective way to improve composite performance, accomplished by inserting interstitial atoms which act as covalently-bonded bridges between the CNT and the matrix.

4:50 PM

(ICACC-S7-066-2014) Processing and properties of ceramic matrix composites with nano- and micro- reinforcements (Invited)

H. Mei*, L. Cheng, School of Materials Science and Engineering, China

Silicon carbide ceramic matrix composites (SiC-CMCs) reinforced by carbon nanotubes (CNTs) and silicon carbide whisker (SiCw) were prepared by chemical vapor infiltration (CVI). Bulk and aligned CNTs, buckypaper, and SiC whisker were used as the reinforcements. Microstructures, mechanical, and functional properties of the prepared SiC-CMCs were investigated. It was found that as increase of CNT quantity during electrodeposition, both tensile strength and fracture toughness of CNT-C/SiCs increased substantially, by 10.7%, 39.3%, and 45.2% for the tensile strength corresponding to the CNT deposition times of 5, 8, and 10 minutes, respectively. The buckypapers have good electrical conductivity with the average conductivity of 17.2 S/cm. Optical transmittance test showed that during 500 to 1700 nm, the transmittance of the buckypapers was mainly within the range of 5-10%, and during 1700 to 4000 nm, about 1%, which indicates a low wave-transparent material. SiC-CMCs reinforced by the aligned CNTs were found to be denser and to dissipate energy in the form of CNT pull-outs opposed to their bulk CNT-reinforced counterparts. The strength of C/SiCs reinforced with 5 wt% and 15 wt% SiCw increased by 98.5% and 64.3%, respectively. The major strengthening and toughening mechanism of nano- and micro-reinforcement ceramic composite materials are related to the reinforcement bridging and pull-outs.

5:20 PM

(ICACC-S7-067-2014) Mechanistic Studies of Graphene-Gold Nanocrystal Hybrids

S. Kodepelly*, H. Cho, J. Wu, J. Ting, National Cheng Kung University, Taiwan; Y. Gogotsi, Drexel University, USA; M. Yoshimura, National Cheng Kung University, Taiwan

Graphene as a new two-dimensional and π-networked macromolecule is received great interest due to its unique electrical, optical and mechanical properties. Graphene has emerged as a potential partner for the synthesis of hybrid materials. Due to the promising properties, graphene hybrids play strategic roles in the fields of electronics, organocatalysis, energy storage and biomedical applications etc. Recently graphene-metal hybrids such as reduced graphene oxide-gold nanocrystal (RGO-AuNC) hybrids are received great attention. The literature reported studies of those hybrids described the effects of reducing agents, surfactants, stabilizers and/or capping agents phenomenologically, however their real effects have not well understood yet. Our proposed mechanistic studies of those hybrids are based upon the polymerization of complexed Au species in the precursor solution and/or on the surface of RGO. Our model considered a new approach for the decoration mode of AuNCs on the surface of RGO sheet. In addition, the functional groups (epoxides, hydroxyls, phenols and carboxylic acids) transformation of graphene oxide (GO) during the reduction process and also the binding process of citrate moieties to the resulted RGO surface is well discussed. We believe that this proposed novel model is more reasonable for understanding the formation mechanism of RGO-AuNC hybrid.

5:40 PM

(ICACC-S7-068-2014) Bulk Mechanical Properties of Graphene-Silicon Nitride Ceramic Nanocomposites Densified by Spark Plasma Sintering

K. Schnittker*, L. S. Walker, E. L. Corral, The University of Arizona, USA

Silicon nitride (Si_3N_4) is an attractive technical ceramic due to its mechanical properties and thermal shock resistance. The properties can be controlled during processing to form either a high hardness ceramic with pure alpha phase or a high toughness ceramic consisting of beta phase, but high hardness and toughness cannot be achieved simultaneously. To improve mechanical properties graphene is added to a Si_3N_4 ceramic as uniformly dispersed nanophase reinforcement through aqueous colloidal processing and rapid densification by spark plasma sintering. The ceramic nanocomposites retain a high hardness while increasing both flexural strength and toughness of the ceramic with low graphene concentrations (<1.5 vol. %). The graphene alters the bulk fracture properties of the composite and is found to interact with the crack over a range of scale lengths. Crack deflection is observed in addition graphene sheet crack bridging prior to sheet tearing.

6:00 PM

(ICACC-S7-069-2014) Synthesis and Characteristics of Heteroatom-doping Carbon Nanotubes

Q. Zhen*, S. Dong, Y. Kan, Shanghai Institute of Ceramics, Chinese Academy of Sciences, China; Y. Leng, Shanghai Institute of Ceramics, Chineses Academy of Sciences, China

Carbon nanotubes have attracted many attentions due to its super mechanical and electrochemical properties, and show great application prospects in the fields of Li-ion batteries, supercapacitors and gas sensors. The structure of carbon nanotubes can be changed as heteroatoms are inserted into the lattice, which may create innovation in electrochemical properties. Here, heteroatom N or P were introduced to the structure of CNT array via in-situ CVD method. Influence of preparing parameters on the growth of CNTs was considered. The morphologies and structures of doping CNTs were characterized by scanning electronic microscope (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Raman microscopy was used as diagnostic tool for estimating the amount of disorders by comparing D and G bands. Doping effects on the structure variation were discussed. The electrochemical properties were also studied by galvanostatic method and electrochemical impedance spectroscopy (EIS).

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

Advanced Micro & Composite Processing I

Room: Coquina Salon A

Session Chairs: Michael Halbig, NASA Glenn Research Center; José Ferreira, University of Aveiro

1:30 PM

(ICACC-S8-054-2014) Nanoceramics Processing: Revolutionizing Medicine (Invited)

T. Webster*, Northeastern University, USA

Ceramics have been a critical part of medicine for numerous years. However, with the advent of nanoceramics, over the past several decades, there has been a resurgence in the exploration of ceramics in medicine, including improved prevention, diagnosis, and treatment of numerous diseases. This talk will emphasize implantable and non-implantable devices and will summarize efforts over the past decade that have created novel ceramic nanoparticles, nanotubes, and other nanomaterials to improve health, energy, and society. Efforts focused on the use of nanomaterials to minimize immune cell interactions, inhibit infection, and increase tissue growth will be especially emphasized. Tissue systems covered will include the nervous system, orthopedics, bladder, cardiovascular, vascular, and the bladder. Due to complications translating in vitro to in vivo results, only in vivo studies will be emphasized here. Novel ways to process ceramics and ceramic polymer composites will be emphasized as a means to improve medical applications. Efforts to decrease bacterial attachment and growth on surfaces (such as door knobs, bed railings, etc.) will also be covered. In addition, efforts to develop in situ sensors that can measure cell responses and then respond to such cellular responses will be covered. Growing concerns over the toxicity of manufacturing nanoceramics for various products will also be covered.

2:00 PM

(ICACC-S8-055-2014) Microfabrication of functional ceramic devices from aqueous suspensions (Invited)

J. M. Ferreira*, S. M. Olhero, A. Kaushal, University of Aveiro, Portugal

The state of the art micro-machining technologies (dry-etching, plasma-etching or even photolithography) that selectively etch away parts of the substrate (usually silicon) or add new structural layers to form mechanical and electromechanical devices are onerous and time consuming. Therefore, finding alternative cost effective technologies is of crucial importance to fabricate ceramic micro components such as Micro Electro Mechanical Systems (MEMS) or Bio-MEMS medical sensors, microneedles for drug delivery, and microfluidic systems. In the present communication a new processing route suitable for the fabrication of micro devices will be presented. Different electroceramics, including ferroelectic alkaline earth titanates and lead free piezoelectric materials were studied. The strategy used includes the following steps: (i) surface treating the powders to hinder hydrolysis reactions in the aqueous dispersion media; (ii) preparation of suspensions with high solids loading containing the ceramic powders dispersed in a mixture of suitable epoxy-based self-setting additives; (iii) casting the suspensions into soft silicone rubber molds with the desired shape and size features, followed by curing; (iv) drying and sintering. Examples of piezoelectric pillar arrays for high-frequency transducers that enable more than triplicating the resolution of actual ultrasound medical imaging devices will be presented.

2:30 PM

(ICACC-S8-056-2014) Biocompatible TiC/ hydroxyapatite implant materials

K. Balazsi*, MTA Research Centre for Natural Sciences MFA, Hungary;
C. Balazsi, Bay Zoltan Nonprofit Ltd for Applied Research ATI, Hungary

Biomaterials used for implant should posses some important properties. Materials used as different biomaterials should be made with certain properties as excelent biocompatibility, corrosion resistance and be without toxicity. The creation of nanocomposites with particle size few ten nanometers can significantly improve the bioactivity of implants. One of most used biomaterials is hydroxyapatite. The major inorganic constituent of bones is calcium phosphate similar to the synthetic hydroxyapatite (HAp). Titanium (Ti) is used as orthopedic implants. One negative property of Ti is a low abrasion resistance and minute Ti abrasion powders may cause inflammatory reactions. From this point of view, TiC is a very stable phase. TiC is useful material for bio instruments because has a range of desirable properties. In this work, the combination of excellent bioactive HAp with very stable and mechanicaly strong TiC has been studied. The nanostructured hydroxyapatite has been prepared by attritor milling from biogenic eggshells. TiC thin films were deposited by dc magnetron sputtering in argon atmosphere at different deposition temperatures. Spin coating was applied to obtain HAp decorated TiC films. Structural, mechanical and biological properties of TiC/ HAp coatings are being presented in this study. Acknowledgement This work was supported by OTKA PD101453, K105355 and Bolyai János Research Scollarship and EU FP7 HypOrth project.

3:10 PM

(ICACC-S8-057-2014) BaTiO3 -ceramics electronic thermal capacity within the fractal and Brownian motion structure analysis relations (Invited)

V. Mitic*, V. V. Paunovioc, L. Kocic, Faculty of Electronic Engineering, University of Nis, Serbia; V. Pavlovic, Institute of Technical Sciences of SASA, Serbia

The intergrain ceramic structures are very complex and difficult to describe by using traditional analytical methods. In this study, in order to establish grain shapes of sintered ceramics, new approach on correlation between microstructure and properties of doped $BaTiO_3$ -ceramics based on fractal geometry has been developed. $BaTiO_3$ ceramics doped with CeO_2,Bi_2O_3, Fe_2O_3, Er_2O_3, Yb_2O_3, Ho_2O_3, La_2O_3, $MnCO_3$ and $CaZrO_3$ were prepared using conventional solid state procedure and sintered at 1350 °C. The microstructure of sintered specimens was investigated by SEM-5300 and capacitance has been done using LCR-metre Agilent 4284A. Using method of fractal modelling a reconstruction of microstructure configurations, like shapes of grains or intergranular contacts has been successfully done. Furthermore, the area of grains surface was calculated using fractal correction that expresses the irregularity of grains surface through fractal dimension. The main goal of this research is to apply the fractal analysis and Brownian motion within the structure of electronic thermal capacity. Microstructure properties of barium-titanate based materials, expressed in grain boundary contacts, are of basic importance for electric properties of these material in this case special electric thermal capacity.

3:30 PM

(ICACC-S8-058-2014) Mechanical behavior of foamed insulating ceramics

V. R. Salvini*, D. Spinelli, University of Sao Paulo, Brazil; V. C. Pandolfelli, Federal University of São Carlos, Brazil

In recent years, increasing interest in the development and use of insulating foamed ceramics has been observed due to energy costs and environmental concerns. These porous ceramics present key properties such as low density and thermal conductivity, controlled permeability and high surface area allowing their use in many industrial processes aiming to reduce heat losses and energy consumption. However, they are subjected to mechanical stresses and cycled thermal shocks when used as a structural material. The analysis of foamed ceramics suggests that there is a strong interaction of cracks with their porous in the microstructure. Therefore, the understanding of the mechanical behavior of these materials is an important aspect for selection and design for structural applications. In this paper, the two fracture surface energies based on concepts of crack initiation energy, γ_{NBT}, and the crack propagation energy, γ_{WOF}, of foamed insulating ceramics are presented and correlated to their microstructure. Alumina (Al2O3), mullite (3Al2O3.2SiO2) and silica (SiO2) foamed ceramics with high porosity (70 to 80%), low thermal conductivity (0.1 to 2 W/mK) and flexural mechanical strength in the range of 2 to 10 MPa were specially designed for this work and produced by the foaming method developed by the authors.

3:50 PM

(ICACC-S8-059-2014) Electrically Conductive Y-TZP/TiN Ceramic Composites with Reduced Amount of Conductive Phase

K. Krnel*, A. Lazar, T. Kosmac, Jozef Stefan Institute, Slovenia

Zirconia (Y-TZP) is a versatile oxide ceramic material with outstanding properties, which is useful in various applications. The aim of our work was to prepare Y-TZP/TiN electro-conductive ceramic composite with reduced amount of conductive phase that can be shaped by an electrical discharge machining. Electrically conductive composites based on zirconium oxide with dispersed nanoparticles of titanium nitride were successfully prepared by controlled precipitation of titanium hydroxide on the surface of Y-TZP powder, which was followed by thermo-chemical conversion of titanium oxide to titanium nitride by nitridation process and densification using spark plasma sintering technique The impact of the quantity and size distribution of conducting phase on the density, mechanical and electrical properties was investigated. The above approach resulted in the composites with required electrical conductivity and significantly lower amount of conductive phase. The possibility of machining of such composites with electrical discharge was also investigated.

4:10 PM

(ICACC-S8-060-2014) Electromagnetic properties of silicon nitride based ceramics (Invited)

X. Yin*, L. Zhang, L. Cheng, Northwestern Polytechnical University, China

Silicon nitride (Si3N4) based ceramics possess not only excellent mechanical properties but also attractive electromagnetic (EM) response characteristics, which make them enabling materials in various applications requiring both EM and mechanical properties. Si3N4 exhibits small complex permittivity and dielectric loss tangent, so that Si3N4 based ceramics offer large possibility to be tailored into EM transparent, absorbing and shielding ceramics when the phase composition of the second phase in Si3N4 ceramics is adjusted. Two main approaches are developed to fabricate Si3N4 based ceramics: polymer-derived ceramics (PDCs), and chemical vapor infiltration (CVI). The key developments and future challenges in this field are summarized. The main issues regarding permittivity of Si3N4 based ceramics are discussed, with an emphasis on the EM response mechanisms. References: [1] Int J Appl Ceram Techn 7:391(2010). [2] Scrip Mater 63: 657(2010). [3] Scrip Mater 66:33(2012). [4] Scrip Mater 67:380(2012) [5] J Am Ceram Soc 95:1038(2012). [6] J Europ Ceram Soc 32:1485(2012). [7] J Europ Ceram Soc 32:4025(2012). [8] J Europ Ceram Soc 33:647(2013). [9] J Europ Ceram Soc 33:1469 (2013). [10] J Europ Ceram Soc 33:2173(2013). [11] J. Phys. Chem. C 117:2135(2013). [12] J Am Ceram Soc 96:979(2013).

4:30 PM

(ICACC-S8-061-2014) Sintering, Microstructure and Piezoelectric Properties of Laser-fused K0.5Na0.5NbO3 Glass Microspheres

F. Hmood*, J. Heinrich, Clausthal University of Technology, Germany

Transparent ceramics with piezoelectric properties have acquired considerable attention in recent years. Low weight noise cancelling windows are one of the anticipated applications for such ceramics. Sintering of nanopowder compacts has been a popular method in preparing transparent ceramics from high melting temperature systems such as Al2O3 and MgAl2O4. Spark Plasma Sintering (SPS) and hot pressing followed by Hot Isostatic Pressing (HIP) represent the main sintering processes in this field. Transparent ceramics can also be synthesized by sintering glass granules, which in this case represents a competition between the viscous flow and the crystallization of the glass granules surfaces. In this study, K0.5Na0.5NbO3 (KNN) glass granules have been sintered using SPS method. The glass microspheres were prepared by laser fusing with a cooling rate of 105 K/s, where 5 kW CO2 laser beam has been used to yield a material with 75% transparent fraction. Considering the DSC measurement, 525 °C has been chosen as a sintering temperature which lies into the kinetic window of the KNN glass has been set at 26°C. Sintering behavior and microstructure of the sintered samples have been investigated and the relationship between the microstructure and the piezoelectric properties will be discussed.

S9: Porous Ceramics: Novel Developments and Applications

Processing Methods for Porous Ceramics IV

Room: Coquina Salon C

Session Chair: Joerg Adler, Fraunhofer Institute for Ceramic Technologies and Systems

1:30 PM

(ICACC-S9-020-2014) The manufacture of porous 3D ceramic structures using a modified weaving technique

S. O. Matthews*, J. Matthews, SCF Processing Ltd, Ireland

A new technique to manufacture 3D ceramic structures has been under development at SCF Processing. The technique combines extrusion, supercritical fluids and weaving techniques, and resulted in 3D carbon, stoneware and alumina structures. The key to the technology development has been the ceramic fibre formulation and the manufacturing process. This paper will highlight the most recent developments, namely development of the fibre formulation for long term flexibility, controlled fibre porosity and the scaling up of the weaving technique. A number of case studies will also highlight the broad range of end-user applications that can benefit from this technique.

1:50 PM

(ICACC-S9-021-2014) Novel Cold-set Ceramics for CO2 Capture

H. Sarma*, S. Ogunwumi, Corning Incorporated, USA

Porous ceramic honeycomb structures are being explored as purely structural members to support catalysts used in various filtration application like CO2 capture. High temperature firing, an essential part of conventional ceramic fabrication, is highly complex and capital intensive, besides having a large CO2 footprint. Also, unlike the underlying ceramic, most of the catalysts cannot withstand high temperatures. Hence, the manufacture of these articles is a two–step process: (1) Production of the ceramic substrate; (2) Subsequent application of the catalyst. In this paper, a novel cold set approach for ceramic processing is proposed, so as to render high temperature firing unnecessary. Preliminary data indicating that this cold set approach could yield extruded ware with sufficient strength so as to be attractive to applications where refractoriness is not a premium, is also presented. Such a low temperature processing would render co-extrusion of catalysts and sorbents (e.g., zeolites) feasible. This in turn would not only lead to a simple, one step process, but also result in a "greener" process with low CO2 footprint, thus making it a sustainable and attractive approach for filtration and sequestration of CO2 applications.

2:10 PM

(ICACC-S9-022-2014) Innovations and novel techniques used to manufacture low cost environmentally friendly porous ceramics

J. E. Lancien*, E. E. Branigan, S. Clarke, S. O. Matthews, SCF Processing Ltd, Ireland

Commercial routes used to manufacture open porous ceramic components are generally based on the use of polyurethane sacrificial scaffolds. These porous ceramics are expensive to manufacture, are not environmentally friendly and generally secondary processing is required in order to achieve the desired part geometry. SCF Processing Ltd has undertaken an extensive R&D program to assess and optimize alternative routes to manufacture open porous ceramic foams. This paper reports on the low cost, environmentally friendly and innovative techniques used, such as starch scaffolds, natural fiber scaffolds, supercritical fluids and most recently 3D printing of ceramics. These techniques will be compared to the conventional polyurethane route for a variety of ceramics so that cost and property assessments can be made.

2:30 PM

(ICACC-S9-023-2014) Novel Processing Methods for Developing Porous Oxides and Carbide Ceramics

M. F. Riyad*, R. Johnson, T. Hammann, S. Gupta, University of North Dakota, USA

Porous ceramics are used for numerous structural applications, for example, lightweight sandwich structures, heat sinks, electrodes, heat exchangers, photocatalysis, biological scaffolds, filtration, insulation applications etc. However, the manufacturing steps required to produce porous ceramic materials are tedious and time consuming, for example, replica technique, gel casting, hollow bead method, freeze-casting, physical and chemical foaming etc In this presentation, authors will present novel methods for manufacturing structural ceramics, for example, oxide, ternary carbide and nitrides, among others. The microstructure and mechanical properties of these novel porous materials will be presented in detail.

2:50 PM

(ICACC-S9-024-2014) Effects of SiC Particle Size and Sintering Temperature on Microstructure of Porous SiC Ceramics Based on In–Situ Grain Growth

K. Yoshida*, C. See, S. Yokoyama, T. Yano, Tokyo Institute of Technology, Japan

Silicon carbide (SiC) is expected to be an attractive material for structural applications such as aerospace industries, nuclear applications and high-temperature gas turbine. Furthermore, porous SiC has been commercially used as the material for diesel particulate filter. Recently, porous ceramics have received great attention in many fields, and present authors have proposed the surface functionalization of porous ceramics based on in-situ grain growth. In this study, porous SiC ceramics were fabricated based on in-situ grain growth using SiC powder with different particle sizes and the effects of SiC particle size and sintering temperature on their microstructures were investigated. Submicron- (0.3 μm) or micron-sized β-SiC powder (2.3 μm and 5.3 μm) was used as the starting material, and aluminum, boron and carbon were added to SiC powder as the sintering additives. In order to fabricate porous SiC, polymeric pore former (spherical PMMA particles) was used. SiC ceramics using micron-sized SiC powder had larger plate-like grains than porous SiC ceramics using submicron-sized SiC powder. Plate-like grain growth in porous SiC ceramics using micron-sized SiC powder proceeded above the sintering temperature of 2000ºC. In the case of porous SiC ceramics using β-SiC particles with the size of 5.9 μμm, plate-like SiC grains did not grow during sintering.

Modeling and Properties of Porous Ceramics

Room: Coquina Salon C
Session Chair: Randall Stafford, Cummins Inc

3:30 PM

(ICACC-S9-026-2014) Characterization of Porous Ceramics via Micro X-Ray Tomography (Invited)

S. Nickerson*, Corning, Inc., USA; R. Fertig, University of Wyoming, USA; C. Koenke, Bauhaus University, Germany

This work focuses on the measurement and analysis of various open porosity ceramics via X-Ray tomography with sub-micron resolution. This technique enables estimates of elastic anisotropy to be made and compared with alternative indirect methods. This technique also provides a methods estimating non-microcracked elastic moduli which are used to confirm empirical methods of estimation. Notes will be made on limitations of these measurement and analysis methods as well as example implementations on computer generated synthetic microstructures.

4:00 PM

(ICACC-S9-027-2014) Reticulated ceramics under bending: the non-linear regime before their catastrophic failure

E. Rezaei, A. Ortona*, SUPSI, Switzerland; S. Gianella, Erbicol, Switzerland

Our early experiences with reticulated ceramics under mechanical loads was always showing a behavior which is not typical for monolithic ceramics which, under different types of loading, are characterized by a sudden and catastrophic failure. Conversely, as the material takes the morphology of a solid foam, before collapsing, local failure of its struts and nodes is occurring. This phenomenon motivated us to further study this non-linear regime in their mechanical behavior. In this work, Si infiltrated SiC foams and lattices were mechanically tested by four point bending. In order to better understand this phenomenon we coupled standard sensing devices (a LVDT and a load cell) with electrical resistance and acoustical emissions sensors. The results show a strong correlation between local failures, electrical resistance and acoustical output. We observed that, unlike monoliths, reticulated ceramics experience local cracks in multiple zones at the same time. As a result of this, ceramic foams present a certain degree of toughness which could not be possible if they were monolithic . We show also that the quantity of molten Si employed in liquid silicon infiltration, which fills first the intra particle porosity and then if in excess, the cavity of the struts, has a great influence on the final strength of the foam.

4:20 PM

(ICACC-S9-029-2014) Control of the microstructure of porous oxide materials – Characterization of the thermal properties

C. S. Peyratout*, A. De Marcos, B. Nait Ali, C. Pagnoux, ENSCI, France

Control of the microstructure is a key factor regarding thermal performances of insulating porous materials. In silicate based materials, adjusting the porosity can lead to a final product with a thermal conductivity of the order of 0.1 W.m-1.K-1. In addition to insulating behavior in a given direction, a potential application of anisotropic porous materials could be to vehicle heat in other directions. This control of the microstructure can be achieved through the drying process since this step influences the pore size distribution. Freeze drying, which consists in sublimating solid water, can induce pore orientation resulting in an anisotropic porous material. Furthermore, this process does not disturb the arrangement of clay particles and does not lead to defects (cracks) in the material. The influence on pore formation (mostly pore orientation and size) after freeze drying of α-alumina (used as a model system) and of natural clay mineral (bentonite) suspensions has been studied using scanning electron microscopy and the laser flash technique for thermal conductivity measurements. The purpose of this study is to understand the effect of the organic or inorganic nature of the binder and of the freezing rate on the microstructure (pore orientation and size) of the final material in relation with the thermal conductivity.

4:40 PM

(ICACC-S9-031-2014) Effect of humidity on the thermal conductivity of porous ceramics

B. Nait-Ali*, D. S. Smith, H. Goure-Doubi, J. Tounzi, G. L. Lecomte, S. Rossignol, S. Nichenko, A. Smith, GEMH - ENSCI, France

Thermal conductivity has been widely studied in the case of porous ceramic materials with the aim of identifying the parameters which govern its value. However the influence of humidity has been somewhat neglected. This study focuses on the role of the water content on the effective thermal conductivity of porous ceramics. As a model case, we first studied zirconia samples. Then, clay materials and geomaterials were investigated in view of insulating applications. For all materials, the experimental values of the effective thermal conductivity increase significantly with water content. Using an approach based on the rule of mixtures, this increase can be explained by the volume of air in the material which is replaced by a volume of water with a higher thermal conductivity. Experimental results on zirconia samples agree closely to analytical predictions based on the Hashin and Shtrikman upper bound for calculating the thermal conductivity of the pores (water + air) and Landauer's effective medium expression for calculating the effective thermal conductivity of the material. For clay materials and geomaterials, analytical predictions differ from experimental results, indicating that the role of water is not just limited to a contribution as an additional phase with its intrinsic conductivity. The localization of water in the porous material may also affect the contact between grains.

5:00 PM

(ICACC-S9-033-2014) The stress analysis of porous ceramic support tube in module of ceramic separation membranes

S. Honda*, S. Hashimoto, Y. Daiko, Nagoya Institute of Technology, Japan; T. Eda, H. Watanabe, K. Miyajima, Noritake Corporation Limited, Japan; Y. Iwamoto, Nagoya Institute of Technology, Japan

Thermal stress in the module of ceramic separation membranes was simulated by the finite element method (FEM). The simulated module was consisted of porous ceramic support tube, metal junctions, and sealing materials. In this simulation, the thermal expansion coefficient of the glass seal was closely to the support tube, while that of the commercially available fluoroelastomer o-ring was apparently higher than those of other components. In order to simulate a drop in temperature from a typical operating temperature of the membrane module for dehydration of isopropyl alcohol, the temperature condition was applied from 135 to 35 degree Celsius. Then, the maximum thermal stress caused by the difference of the thermal expansion among the components of the membrane module during the increasing or decreasing temperature in service was estimated for the porous ceramic support tube. The longitudinal tensile thermal stress in the porous ceramic support tube due to the higher shrinkage of the metal junctions was observed when the both edges of the support tube were fixed, and the thermal stress was found to increase with decrease of the support tube length or diameter.

5:20 PM

(ICACC-S9-035-2014) Preparation and properties of reticulated porous γ-Y2Si2O7 ceramic with high porosity and relatively high strength

Z. Wu*, J. Wang, Institute of Metal Research, Chinese Academy of Sciences, China

Dense γ-Y2Si2O7 ceramic is a promising silicate with very low thermal conductivity, good damage tolerance and hot corrosion resistance. However, processing of porous γ-Y2Si2O7 was not reported in early literatures. In this work, we successfully fabricated reticulated porous γ-Y2Si2O7 ceramic with high porosity (~85%) and relative high compressive strength (~1.28 MPa) by the polymeric sponge impregnation method. The sponge was pretreated by various methods, and the influence of pretreatment on the compressive strength was investigated. The slurries consisted of Y2SiO5 powers and silica sol, and were used to reactively sinter the porous γ-Y2Si2O7 ceramic. Deionized water, 0.2 wt% sodium carboxymethyl cellulose, 0.2 wt% kaolin and 0.3 wt% of polyglycol were used as the dispersing medium, dispersant, rheological agent and surfactant, respectively. The ceramic-coated polymeric templates were heated in a sintering furnace at 1550 oC for 2 h to burn out the polyurethane sponge and to densify the γ-Y2Si2O7 skeleton. Scanning electron microscopy (SEM) and 3-D X-ray tomography (XRT) showed that the as prepared porous ceramic possessed highly interconnected pores with sizes from 200 to 700 μm. This work presents novel results to develop light-weight component of porous γ-Y2Si2O7 ceramic.

S11: Advanced Materials and Innovative Processing Ideas for the Industrial Root Technology

Beyond Critical Technology I

Room: Ponce De Leon

Session Chairs: Taejin Hwang, Korea Institute of Industrial Technology; Kyoung Il Moon, KITECH

1:30 PM

(ICACC-S11-019-2014) Influence of the Field and Current Limit on Flash Sintering at Isothermal Furnace Temperatures (Invited)

J. Francis*, R. Raj, University of Colorado Boulder, USA

Flash Sintering is characterized by densification in just a few seconds at a threshold condition of temperature and applied DC electrical field. Experiments on 3Y-Stabilized Zirconia have been performed to investigate the incubation time and temperatures required for the instability condition, preceding the flash-sintering behavior. These experiments are done by holding the temperature constant and supplying the voltage as a step function, measuring the time until instability. While the onset of the flash-sintering is related to the field and temperature, the magnitude of densification is proportionally related to the current. Grain growth behavior in relation to the flash sintering condition is also investigated. Measurements of the incubation time suggest a nucleation like event that precipitates a sudden and simultaneous increase in conductivity and mass transport, defect concentrations are show to exist in the flash-sintered samples. The results continue to reinforce the hypothesis that a combination of electric field and temperature produce a defect avalanche that underlies the flash-sintering behavior.

2:00 PM

(ICACC-S11-020-2014) Fast infiltration process for in-line continous siliconization

M. Chiodi*, M. Valle, Petroceramics SpA, Italy

C-Si-SiC composites are produced using liquid infiltration. In such process, spontaneous diffusion of molten Si inside a carbon preform and SiC formation is achieved in vacuum-operated furnaces. High temperature is necessary to melt the Si, while vacuum is needed to activate the capillarity forces driving the process. Here we present a new approach to infiltration in which the furnace is heated up to Si melting point while maintaining a high pressure of inert gas (500mbar). As long as the pressure in the chamber is kept high, the capillarity does not act and the infiltration does not start. Beyond the Si melting point (1414°C) the infiltration is activated anytime simply dropping the gas pressure, even beyond 1414°C. At high temperatures the process is so fast that the system can be considered as adiabatic and the thermal energy of the exothermic Si-C reaction is kept inside the preform and contribute to further accelerate the infiltration. Thus, the capillarity forces are so strong that pores are filled simultaneously, regardless their size. The result is a fast siliconization (minutes vs. hours) with virtually 0% porosity. Also, the reaction-layer thickening is minimized, litimiting the SiC growth and preserving the carbon fibers. This approach is applied to an innovative siliconization oven where differential vacuum is applied locally to a single crucible, allowing a process of a few minutes for each preform.

2:20 PM

(ICACC-S11-021-2014) Effect of bimodal porous structure on the gas adsorbability of copper oxide fabricated by powder metallurgy process

M. Lee*, Korea Institute of Industrial Technology, Republic of Korea

Porous metallic oxides have high potential for applications as lightweight functional materials, particularly when they are comprised of structures with high specific surface areas. Especially, nanocrystalline transition-metal oxides are promising candidates for functional applications such as magnetic resonance imaging, biosensing and ferrofluids. Among the transition-metal oxides, Cu oxide is an attractive choice and has been extensively studied due to its narrow band gap and lower surface-potential barrier with high superconductivity transition temperature. In this study, we describe a novel method for creating macroscopic monolithic structures of nanoporous copper oxide derived from extruded composite bulk precursor forms comprised of Cu and carbon nanotubes (CNTs) using a simple gas-solid reaction during a heating process in air. The final porous copper oxide architecture has a hybrid structure consisting of ~500 nm sized macropores, which are separated by ligaments that contain copious quantities of ~20 nm sized nanopores. The hybrid structure promotes high surface area and furthermore facilitates more rapid adsorption rate of permeating gases, as compared to traditional porous metal oxides having a single distribution of nanopores.

2:40 PM

(ICACC-S11-022-2014) Flash sintering Remediates Constrained sintering

S. K. Jha*, R. Raj, University of Colorado, USA

In conventional sintering of composite with components of different particle sizes, the big rigid inclusions inhibits the densification of matrix phase, which has been so called as constrained sintering. The retardation of densification is much more pronounced than what is expected from the rule of mixture. A work by Bordia et. al. (1988) shows the case of TiO2 matrix containing large non-sintering particles of Al2O3 retarding the sintering rate, depending on the volume fraction of dispersed phase. In the present work, we show flash sintering under suitable electric field and current density can overcome the retardation caused by constraining phase, at a significantly lower temperature in few seconds. Experiment involves sintering of 20 nm particle sized TiO2 matrix with Al2O3 particles of 10 μm size dispersed in it. In the isothermal experiments (850 oC) an applied field of 250Vcm-1 and 40 mAmm-2 gives near full densification compared to 1400 oC required for conventional sintering. XRD analysis confirms the absence of interoxide phase formation, while the microstructure and EDS analysis reveal a better contact at the interfaces of two phases with no processing defects. Results suggest an entirely different and much effective transport mechanism during flash which overcomes the barrier of constraining. Flash sintering has also shown to control the problem of grain growth in TiO2, as found in conventional sintering (1400 oC).

Beyond Critical Technology II

Room: Ponce De Leon
Session Chairs: Wulf Pfeiffer, Fraunhofer IWM; Kouichi Yasuda, Tokyo Institute of Technology

3:20 PM

(ICACC-S11-023-2014) Peen Forming of Ceramics – A New Chipless Shaping Technique (Invited)

W. Pfeiffer*, H. Höpfel, Fraunhofer IWM, Germany

Thin ceramic components are often distorted during production due to anisotropic shrinkage and/or residual stresses due to machining. If unwanted distortion is detected in a component in its final shape, the distortion cannot be eliminated by an additional material removal. Such ceramic components are usually discarded since the brittleness does not permit further flattening. Ceramic parts with complex shapes must be fabricated by, for example, a sintering close to the desired shape followed by a costly 3D machining process. This paper describes the first successful experiments aimed at shaping ceramic specimens using shot peening. Strips of different thicknesses, made of silicon nitride ceramic, were shot-peened using different shot peening parameters. The residual stress-depth distributions were determined using X-ray diffraction. Based on the experimentally determined stress states, the curvatures of the strips were determined analytically and using Finite Element calculations (FEM). Silicon nitride flat springs and a concave mirror could be peen formed without the need of additional hard machining. Finite Element calculations demonstrated the capability of designing peen forming processes on basis of experimentally determined peening stresses.

3:50 PM

(ICACC-S11-024-2014) Preparation of CrN-Ni composites by hot press sintering

T. Fukushima*, Extreme Energy-Density Research Institute, Japan

Tungsten carbide-cobalt (WC-Co) is used for cutting tools such as drills or end-mills. Since minor metals including W and Co are expensive and development of new materials having superior mechanical properties and chemical stability without rare metals is required. CrN-Ni bulks of CrN ceramics and nickel binder are considered to be superior material for above purpose, since the thin films of CrN has high hardness, superior oxidation resistance and corrosion resistance. In this study, CrN-Ni sintered composites were prepared by using mixed powder of Cr2N and Ni. The amount of added Ni in sintered compacts was changed with mole ratio of Cr : Ni from 10 : 0 to 8 : 2. In order to obtain CrN phase from Cr2N, the mixture powder was sandwiched between layers of Mg3N2 powder which generates nitrogen by decomposition at elevated temperature. This green compacts were loaded with upper and lower graphite punches at 70 MPa in a hot press sintering system. After evacuation in the hot press down to 3.6 Pa, nitrogen gas was supplied up to 3.3×103 Pa. The sintered bulks were characterized by X-ray diffraction, scanning electron microscopy, Vickers hardness and fracture toughness. The density of prepared sample was about 6.7 g cm-3. It was found that bulks consisted for CrN and Ni. The fracture toughness was increased up to 8.0 MPa m1/2 with the increase of Ni content, and Vickers hardness was around 800 HV.

4:10 PM

(ICACC-S11-025-2014) Fabrication and Electrical Properties of Cup-stacked Carbon Nanotubes/polymer Nanocomposite Films as an Electrode Sensor for Brain-wave Detection

M. T. Huynh*, H. Cho, T. Nakayama, S. Nguyen, H. Suematsu, T. Suzuki, W. Jiang, K. Niihara, Nagaoka University of Technology, Japan

Polymer-based composites films with cup-stacked carbon nanotubes (CSCNTs) are fabricated with objectives to enhance the electrical sensitivities for brain-wave detection without artifact of electroencephalography-computed tomography (EEG-CT). The CSCNTs are homogeneously dispersed in pre-polymer of polysiloxane using a high speed mixer. The pre-polymer suspension including CSCNTs fillers underwent air removal by vacuum treatment. The artificial image from the composite films, which can be generated while using electrode sensors during operation and also hinder the proper detection of brain-wave, was evaluated using X-ray CT scanning. Effects of solvent and vacuum treatment are performed during fabrication in order to motivate denser packing of the nano inclusions resulting in the reduced inter-phase gaps in the matrix. X-ray transmission, electric resistivity and pressure sensitiveness are analyzed. Analysis shows that the composite films enhance the X-ray transmission as well as high electrical conductivity without generation of artificial images. Since this fabricated composite films possesses to compensate the disadvantageous things of typical metal electrodes that causes uneasy feeling to subjects as well as disturbance of image capturing, the CSCNTs hybrid film are regarded as a promising material for EEG-CT recording system.

4:30 PM

(ICACC-S11-026-2014) Conventional DC magnetron sputtering of Mo/Cu seed layer on high aspect ratio vias by tilting

Y. Song*, T. Yim, KITECH, Republic of Korea; J. Lee, Hongik University, Republic of Korea; J. Kim, Hanyang University, Republic of Korea

3D ICs involve interconnected ICs as they contact each other by means of through-silicon-vias (TSVs). Although it is a cheap process and suitable to mass production, the conventional sputtering method has not been widely used to fabricate high aspect ratio vias due to its more or less rectilinear propagation property. In this study, the effect of sputtering conditions on the growth mechanism of seed layers was investigated to fabricate 10:1 high aspect ratio TSVs through the conventional sputtering method. In order to improve the quality of Cu seed layers, a Mo buffer layer was pre-deposited because Mo has a good conductivity and an intermediate thermal expansion coefficient between Si and Cu. To obtain a homogeneous and continuous Mo layer on TSV, the effect of sputtering conditions and substrate tilting was examined. In the Cu sputtering conditions, Cu seed layers with low electrical resistivity of 2.25 μΩ cm were obtained when the working pressure was maintained below 3 mTorr. This indicates that low sputtering pressure should reduce the scattering chance of Cu and Ar gas and then enhance the rectilinear propagation. For the formation of Mo/Cu seed layers, low sputtering power and short sputtering process time were desirable to obtain the high opening percentage.

4:50 PM

(ICACC-S11-027-2014) Optimization of the industrial synthesis of Silicon Carbide-Reaction Bonded Silicon Nitride (SiC-RBSN)

M. Rosa, Petroceramics SpA, Italy; F. Casaril, Università degli Studi di Milano, Italy; M. Valle*, Petroceramics SpA, Italy; S. Poli, Università degli Studi di Milano, Italy

Si_3N_4 is a suitable material for many industrial applications because of its high thermomechanical properties and good chemical stability, especially the β-Si_3N_4 phase. In this work the industrial production of SiC-RBSN has been optimized, focusing on the control of the α/β Si_3N_4 ratio and on the understanding of the nitridation mechanism. The Si_3N_4 bonding phase has been synthesized in a flowing N_2+H_2 atmosphere via $Si_{(s)}+N_{2(g)}\rightarrow Si_3N_{4(s)}$ reaction or $Si_{(l)}+N_{2(g)}\rightarrow Si_3N_{4(s)}$ reaction, above Si melting point. The starting materials were mixtures of slip casted SiC and free Si in a range of 15-60 %wt. The Si-N-O system has been investigated with both experimental runs and correlated industrial firings: different H_2 percentages (0-4%), solid mass/gas flow ratios and additives have been considered, and the main variables such as time, temperature and pO_2 have been monitored. For large solid mass/gas flow ratios, the reaction progresses in a self-buffering atmosphere, where most of the oxygen is consumed leading to the extremely O_2-depleted conditions required for the stability of the nitrides. Our results clearly show that the most important parameter is the solid mass/gas flow ratio which allows to regulate the matrix composition and consequently the composite microstructure. This variable is often underrated in experimental tests but is extremely important on the industrial scale.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Codes, Standards and Design Methodology

Room: Oceanview
Session Chair: Michael Jenkins, Bothell Engineering and Science Technologies

1:30 PM

(ICACC-S13-029-2014) Developing Codes and Specifications for Ceramic Composites in Nuclear Reactors within the ASME BPV Framework (Invited)

S. T. Gonczy*, Gateway Materials Technology, USA; Y. Katoh, Oak Ridge National Laboratory, USA; M. Mitchell, Eon Consulting, South Africa

Ceramic matrix composites are being considered for fuel cladding and for high temperature reactor components, offering higher temperature capabilities and improved durability compared to metals. As new materials, these ceramic composite components will have to meet the stringent licensing and operational regulations of the United States Nuclear Regulatory Commission (NRC). The NRC uses provisions of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel (BPV) Code as one part of the framework to establish the design, fabrication, construction, testing, and performance requirements for structures, systems, and components important to nuclear safety. The ASME codes are extensively detailed documents that address engineering factors (classification, materials, design, NDE, fabrication and installation, and in-service inspection, etc.), as well as management and regulatory issues (legal responsibilities of designers, producers, and owners; certification requirements; quality assurance systems). As ceramic composites are developed for fission nuclear power applications, appropriate codes, specifications, and standards will have to be written and approved that meet the NRC regulations and address the scope and detail of the ASME BPV code.

2:00 PM

(ICACC-S13-030-2014) Hoop Tensile Strength of Composite Tubes for LWRS Applcations Using Elastomeric Inserts: Draft ASTM Test Method (Invited)

M. G. Jenkins*, Bothell Engineering and Science Technologies, USA; J. A. Salem, NASA Glenn Research Center, USA

The US DOE plans to replace conventional zirconium-alloy fuel rod tubes in light water reactors (LWR) with those consisting of SiC/SiC CMCs to enhance fuel performance and accident tolerance. SiC/SiC CMCs show tolerance to the irradiation and chemical environments of LWRs. Failure modes in LWR fuel cladding include loss of gas tightness and mechanical integrity due to the build-up of internal gas pressure and the swelling of fuel pellets. Therefore, determination of the hoop tensile strength is critically important for evaluation of SiC/SiC CMC fuel claddings. A draft ASTM test method has been developed and submitted for full consensus balloting that uses axial compression of elastomeric inserts to introduce hoop stresses in composite tubuluar test specimens from the resulting internal pressures. This test method is based on sound, theoretical analysis of the stresses developed in tubes subjected to internal pressure over a finite length inside a semi-infinitely long tube. The draft ASTM test method contains test specimen dimensions, testing geometries, test conditions and results interpretation based on this theory and subsequent empirical tests applied to various materials and geometries. This test method (a.k.a., overhung tube method) is for material development, material comparison, material screening, material down selecting and quality assurance.

2:30 PM

(ICACC-S13-031-2014) Flexural Strength of Composite Tubes for SMR Applications Using Pure Bending: Draft ASTM Test Method

M. G. Jenkins*, Bothell Engineering and Science Technologies, USA; T. L. Nguyen, Levitas Consultants, USA; J. E. Gallego, Bothell Engineering and Science Technologies, USA

US DOE is planning to use advanced materials for the core and the reactor unit components in various advanced Small Modular Reactor (SMR) concepts. Ceramic matrix composites (CMC), in particular silicon carbide (SiC) fiber SiC-matrix (SiC/SiC) composites, could revolutionarily expand the design window for various components in terms of operating temperature, applicable stress, and service life, as compared to heat-resistant metallic alloys, while significantly improving safety margins and accident tolerance. Examples of CMC tubular components include control rod sleeves, control rod joints, and fuel rods. Anticipated failure modes for these components include axial and hoop tension, axial flexure, axial and diametral compression, and axial shear. An ASTM draft test method has been developed and submitted for full-consensus ballot to determine the flexural strength of composite tubes subjected to pure bending. Numerical modeling and empirical tests of composite tubes provided validation of the parameters specified in the test method. The draft test methods addresses the following experimental issues — test specimen geometries/preparation, test fixtures, test equipment, interferences, testing modes/procedures, data collection, calculations, reporting requirements, precision/bias.

Fuel and Cladding Evolution and Performance Modeling

Room: Oceanview
Session Chair: Veena Tikare, Sandia National Laboratory

3:10 PM

(ICACC-S13-032-2014) Modeling Structural Loading of Used Nuclear Fuel under Conditions of Normal Transportation (Invited)

K. J. Geelhood*, H. Adkins, Pacific Northwest National Laboratory, USA; J. Orchard, U.S. Department of Energy, USA

The U.S. Department of Energy has established the Used Fuel Disposition Campaign (UFDC) to conduct research and development activities related to storage, transportation, and disposal of used nuclear fuel (UNF) and high-level radioactive waste. The UFDC established a multi-laboratory, multi-disciplinary team to model UNF under rail related normal conditions of transport (NCT) and evaluate the potential for rod failure due to the shock and vibration loads associated with this transportation. This team identified a high burnup Westinghouse 17x17 OFA and generic burnup cask-32 as the reference fuel assembly and transportation package. Typical accelerations imparted to the cask were calculated using the NUCARS® program which was validated against similar rail data. Material properties for all components were identified with irradiated fuel and cladding properties taken from fuel performance modeling experience. The mechanical modeling was performed at three distinct levels with communication between each level. Modeling was performed at the cask level, the fuel assembly level, and the fuel rod level. Calculated fuel rod stress and strain histories were assessed against fatigue and plastic strain failure criteria. Analyses were performed to assess the impact of uncertainties in material properties, initial conditions, and modeling assumptions on the failure predictions.

3:40 PM

(ICACC-S13-033-2014) A micromechanical model of hydrided cladding under long-term storage and transport (Invited)

R. Dingreville*, G. Hansen, Sandia National Laboratories, USA

There are many mechanisms that can impact the behavior of used reactor fuel when it is subjected to handling loads. Radial hydrides formed during drying and storage may be one of the most significant. The combination of the temperature drop and the hoop stresses present during the drying process form radial hydrides within the cladding that can weaken it significantly. Computational approaches capable of reproducing the behavior of hydrides within the cladding must consider both the hydride morphology and the mechanical behavior of hydride inclusions within the metal matrix. We present a multiphysics modeling approach that estimates the hydride morphology at the completion of the drying phase coupled with a mechanical model designed to model the behavior of the hydrided cladding under load. The mechanical model treats the zircaloy matrix as a J2 plastic material hydride “fibers” oriented in particular directions, while the formation of hydrides is evaluated based on a mean field model for the kinetics of nucleation and precipitation of a secondary phase under an applied stress and irradiated environment. Results from this model are compared with experimental characterization of cladding materials.

4:10 PM

(ICACC-S13-034-2014) Hybrid Potts-Phase Field model for coupled microstructural-compositional evolution in U-Pu-Zr nuclear fuels (Invited)

E. R. Homer*, J. J. Cox, Brigham Young University, USA; V. Tikare, Sandia National Laboratories, USA

A recently introduced hybrid Potts-Phase Field method has demonstrated the ability to evolve microstructural networks in conjunction with compositional fields of the existing phases. In this method, Monte Carlo Potts methods are used to evolve the microstructure while phase field methods are used to evolve the composition, and the two fields are coupled through the free energy of the system. By handling the microstructure with Potts and the composition with phase field, the solutions balance efficiency with accuracy. Recent developments of the model allow different alloy systems to be simulated through the use of thermodynamic databases and kinetic quantities that dictate the behavior. The method is demonstrated for a binary alloy along with techniques for extending the framework to multi-component alloy systems. Finally, we present efforts to implement the technique to simulate the significant evolution that U-Pu-Zr nuclear fuels experience while in service.

4:40 PM

(ICACC-S13-035-2014) Simulation of Hydride Formation in Zr-Based Claddings during Dry Storage

V. Tikare*, Sandia National Laboratory, USA

Dry storage is the only currently available option for long-term storage of used nuclear fuels. Until a permanent storage solution is found, used fuel must be held in dry storage for an indeterminately long time. This requires that the safety and security of the storage be ensured for containment of radioactive materials during storage and subsequent transport. One of the barriers available for containment is the Zr-based cladding. Ensuring the structural integrity of the cladding is a key component in developing the technical basis for long-term dry storage. The most likely failure mechanism for the cladding is hydride formation and reorientation and may lead to structural instability of the fuel cladding. A model for simulating hydride formation and growth is based on a hybrid Potts-phase field model and has the ability to simulation nucleation and growth of hydride precipitates by diffusional phase transformation.

Friday, January 31, 2014

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Novel Applications

Room: Coquina Salon F
Session Chair: Claus Rüscher, Leibniz Universität Hannover

8:00 AM

(ICACC-FS1-012-2014) Alkali activation of basalt (Invited)

H. Rahier*, M. Esaifan, J. Wastiels, Vrije Universiteit Brussel, Belgium; H. Khoury, University of jordan, Jordan

To further reduce the emission of greenhouse gasses, raw materials that can be directly alkali activated are looked for. In this study the reaction of basalt with concentrated NaOH or KOH solutions to form geopolymer like materials is investigated. A comparison with alkali activated kaolinite is made. The reactivity and the mechanical properties are investigated and a preliminary study into the structure of the material is made. The workability of the mixture basalt/NaOH solution is better, but the reactivity is much lower (DSC study). A wet compressive strength of about 20MPa can be reached, depending on the amount of NaOH added. SEM-EDX and XRD show that not all crystals in the initial basalt react with the alkaline solution. This hampers a deeper study of the reactions going on during polymerization. With XRD it was possible to show that the main reactive phases in basalt are nepheline (NaAlSiO4) and anorthite (CaAl2Si2O8) whereas the main reaction products are hydrated hydroxysodalite and gehlenite (Ca2Al2SiO7). According to the TGA measurements the hydroxysodalite is probably the dihydrate Na8[AlSiO4]6(OH)2.2(H2O). The results show that basalt can indeed be alkali activated, but it needs a cure temperature of about 80°C (24h).

8:30 AM

(ICACC-FS1-013-2014) NaBH4-geopolymer composites (Invited)

L. Schomborg, C. H. Rüscher*, J. C. Buhl, Leibniz Universität Hannover, Germany

Mixtures of sodium silicate and aluminate solutions are known to undergo sol-gel type condensation reactions. Such gels are used as mother compounds for the synthesis of various types of zeolites but are also known to set rapidly and harden at ambient temperature forming geopolymer binders. In this respect a new approach is the enclosure and handling of NaBH4 in such type of geopolymer-matrix. It will be shown that high amounts of NaBH4 can easily be solved in aluminate and silicate solutions. Mixing of these solutions leads to sol-gel type reactions as described above for the pure solutions. During further drying either at temperatures between 40 and 120 °C or in a desiccator by evacuating a re-crystallisation of NaBH4 occurs in the geopolymer type matrix. The handling of the NaBH4 containing geopolymer gel is easy even under moisture. Highest contents of NaBH4 are about 72 wt% which can be used in a rather controlled reaction for hydrogen release. Advantages and disadvantages of the new composite compared to the pure NaBH4 salt, NaBH4 in alkaline solutions, NaBH4 enclosed in zeolite type structure (the only case known is NaBH4-SOD) or even H2 pressed into zeolites may be discussed.

9:00 AM

(ICACC-FS1-014-2014) Nanoporous Geopolymers and Composites for Environmental Remediation and Catalysis (Invited)

D. Seo*, D. Medpelli, K. Hristovski, R. Sandoval, Arizona State University, USA; C. Wang, D. Ladd, Nanovoltaics, USA

Geopolymers are inherently nanostructured and exhibit chemical features that are closely related to zeolites and clays, two of the most produced and utilized nanomaterials. Unlike those two materials, however, geopolymers have a unique gel-like structure made up of strongly fused nanoparticles of amorphous aluminosilicates. Therefore, harnessing the innate potential of geopolymers may lead to new chemical applications that have not been addressed by zeolites and clays. Herein, we report new synthetic approaches for nanoporous geopolymers and their composites for environmental remediation and catalysis. The nanoporous geopolymers are produced by employing a reactive emulsion templating method in which intimate mixing of potassium-based geopolymer resin with vegetable oil leads to hierarchically porous geopolymer with co-existing interconnected mesopores and spherical macropores. The nanoporous geopolymers are further treated to form hydrous ferric oxide (HFO) coating on the internal pore surfaces. The nanoporous HFO-geopolymer has been demonstrated to be a sustainable adsorbent for the arsenic from the ground water. Alternatively, the nanoporous geopolymer has been ion-exchanged with Ca2+ ion and the resulting material showed excellent catalytic properties in transesterification of biorenewable oil to produce biodiesel. Detailed experimental results will be discussed in the presentation.

9:20 AM

(ICACC-FS1-015-2014) Microstructural evolution study of geopolymers obtained with feldespars

H. Balmori-Ramirez*, D. Gonzalez-Garcia, L. Tellez-Jurado, National Polytechnic Institute, Mexico

The microstructural evolution of geopolymers obtained by the alkaline activation of a natural pozzolan composed by a mixture of albite, anorthite, calcite and quartz was followed for 28 days. The geopolymers were synthesized using a sodium silicate solution with an activator/pozzolan ratio = 0.6 curing at room temperature and 40°C. The microstructural evolution was followed by XRD, FT-IR and MEB. The XRD results show that albite and anorthite dissolve and produce a gel that was identified by an increment of an amorphous hallo in the XRD pattern between 20°and 40° (2θ) that is characteristic of geopolymers. These phases reappear after 14 days. The FT-IR results display a decrease in the OH-bounds and a shift to the right of the Si-O-Si and Si-O-Al bounds as the curing time increases. These changes denote that a depolymerisation and a structural reorganization occur during curing, in accordance with a geopolymerization mechanism. The microstructure observed by MEB-EDS shows that the final product is a densified material which is less porous than cement. Compression test was carried following ASTM-C91 obtaining a Cold Crushing Strength of 13.2 MPa at 28 days of curing.

Alternative Chemistries and Construction Materials

Room: Coquina Salon F
Session Chair: Henry Colorado, Universidad de Antioquia

10:00 AM

(ICACC-FS1-016-2014) Immobilization of Simulated Cesium Radionuclide in CFBC Fly ash-based geopolymer (Invited)

Y. Xu*, Q. Li, H. Cui, Y. Deng, Z. Sun, H. An, J. Zhai, Nanjing University, China

CFBC is an advanced, clean and reliable coal firing technology, which has been widely used all over the world. But the low combustion temperatures of 800-950°C lead to the low pozzolanic activity, which made CFBC fly ash difficult to use. In this study the CFBC fly ash-based geopolymer was synthesized for solidification/stabilization of simulated radionuclide waste solution(133Cs+). The activator of the geopolymer were alkalis hydroxides and/or sodium silicate solutions. Leaching tests of the geopolymer solidified waste blocks were conducted according to the Toxic Characteristic Leaching Procedure (TCLP). The mechanical property, acid and salt corrosion resistance of the solidified blocks were tested. All these results showed that the CFBC fly ash-based geopolymer samples had significant advantages, comparing with the reference cement samples. Considering the heat effect of exothermic geological activity and radioactive waste disintegration, the high temperature(600-1000°C) resistant performance of the geopolymer blocks was also studied. After roasting at 1000 °C, the strength of the geopolymer blocks was increased with little extra effort, while the cement ones was all broken. This work indicated that the CFBC fly ash-based geopolymer could be used for solidification/stabilization of radioactive wastes instead of cement materials.

10:30 AM

(ICACC-FS1-017-2014) Alumina-based Phosphate Cement (Invited)

H. A. Colorado*, Universidad de Antioquia, Colombia; J. Yang, University of California, USA

In this paper alumina based acid-base phosphate cement (PC) composites are studied when exposed to temperatures up to 1000 C. The cements were synthesized at room temperature. Samples were exposed to different temperatures (up to 1000 C) in air environment and then tested in compression tests. The characterization was conducted by optical and scanning electron microscope and by x-ray diffraction. The thermal stability of the samples was also evaluated by Thermo-gravimetric analysis. It was found the material increases the compressive strength when exposed to 1000C. The mechanisms are discussed and all phase changes were identified.

11:00 AM

(ICACC-FS1-018-2014) Alternative Sustainable Materials for use in Portland Cement Concrete (Invited)

J. M. Paris*, C. C. Ferraro, T. G. Townsend, University of Florida, USA;
H. D. Deford, Florida Department of Transportation, USA

The Portland cement concrete industry has a standard group of pozzolanic and cementitous materials for use as supplementary cementitious material: class F and class C fly ashes, metakaolin and granulated blast furnace slag. The more commonly used supplementary cementitious materials (fly ash and blast furnace slag) rely on the fossil fuel and steel industry for production as they are byproducts of those industries. Recently, the increase of natural gas production has caused a shortage of fly ash due to an increased demand for alternative fuel sources. This paper investigates to viability of alternative pozzolans to ease the demand of standard pozzolans while finding alternative uses for byproducts of other industries that are not currently used in infrastructure or Portland cement concrete mixes. We intend to investigate the viability of rice husk ash and sugar cane bagasse ash as pozzolans, as well as ternary or quaternary mixes to stabilize class C fly ash. The incorporation of alternative pozzolans into Portland cement concrete mixes can create a greener, more sustainable product. Encapsulation of these alternative pozzolans in concrete mixes will utilize material that would otherwise be destined for landfills as solid waste into a more environmentally friendly product.

11:30 AM

(ICACC-FS1-019-2014) Investigation of ettringite binder hydration at early age for Glass Fiber Reinforced Concrete application (Invited)

E. Prud'homme*, J. Georgin, M. Michel, J. Ambroise, LGCIE - INSA Lyon, France

In building area, the use of Glass Fiber Reinforced Concrete (GFRC) based on ettringite binder is a possible way to reduce CO2 emissions. Indeed the use of an ettringite binder permits to reduce manufacturing cycles, thickness and weight without mechanical properties loss. An ettringite binder is an ecofriendly material by using a mix of calcium aluminate cement (CAC) and calcium sulfate (C$). The respective amount of hydrates formed (ettringite, monosulfate or aluminum hydroxide) determine the binder intrinsic properties. It is therefore necessary to control the formulation parameters to optimize a building material made from this binder. This study focuses on monitoring the hydration of an ettringite binder at early age. The different kinetics of hydrate formation are evaluated as a function of the ratio between CAC and C$, and of the kind of sulfate used (hemihydrate or anhydrite). Investigations are realized by using in-situ infrared spectroscopy, XRD, DTA-TGA and isothermal calorimeter. The correlation of the infrared signal with the heat generated by the chemical reaction in isothermal configuration allows to truly emphasizing the characteristics of the kinetics of hydrate formation and their respective quantities that are specific to each study parameter. This study is fundamental for the development of GFRC explaining some phenomena of shrinkage and carbonation.

FS4: Ion-Transport Membranes

Ion-Transport Membranes

Room: Coquina Salon B
Session Chairs: Charles Lewinsohn, Ceramatec, Inc.; Neal Sullivan, Colorado School of Mines

8:00 AM

(ICACC-FS4-001-2014) Mixed conducting membranes for oxygen separation (Invited)

H. J. Bouwmeester*, University of Twente, Netherlands

Mixed oxide ionic-electronic conductors hold promise for use as oxygen separation membrane for direct oxygen production or integrated in, e.g., an oxyfuel power plant design. The perovskite-type oxide Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF) has emerged as an exceptional mixed conducting oxide. The material exhibits extremely fast oxygen transport and associated surface exchange kinetics at elevated temperatures as measured using a variety of techniques, e.g., electrical conductivity relaxation, 18O-16O isotopic exchange and oxygen permeation. Thin-film asymmetric (supported) membranes of BSCF show unprecedented oxygen fluxes. However, BSCF suffers from poor structural and chemical stability. The present paper highlights oxygen transport, oxygen nonstoichiometry, and phase stability of BSCF and related perovskite-type compositions, and discusses a number of research challenges in the field. Attention is also drawn to the creep behavior of these solids, and to the influence of CO2 adsorption on the kinetics of oxygen surface exchange.

8:30 AM

(ICACC-FS4-002-2014) Oxygen Transport Membranes: Prospects and Challenges (Invited)

M. Søgaard*, A. Kaiser, P. V. Hendriksen, Technical University of Denmark, Denmark

Prospects and challenges of Oxygen Transport Membranes (OTMs) in different applications will be described. The benefits of close thermal and, to some extent, chemical integration of the OTMs with a high temperature process will be explained. Some of the major membrane activities that have taken, or are taking, place in Europe and the most significant results reported in the last decade from this work will be reviewed. Based on this review, our group proposes that ceria-based membranes offer some advantages. Recently, we have demonstrated fluxes of more than 18 Nml min^{-1} cm^{-2} at 900°C using a membrane of $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (CGO). It is predicted that fluxes of this magnitude also can be obtained at a significantly lower temperature if the electronic conductivity of the material can be increased. Permeation results on thick membranes (~1 mm) with improved electronic conductivity will be presented. The strategy for increasing the electronic conductivity includes *i*) co-doping CGO with cobalt and praseodymium, or *ii*) composite membranes of CGO and a good electronic conductor. Aspects relating to ceramic processing will be discussed, including thin film membrane deposition using dip coating and optimization of both porous ceria and magnesia supports with respect to mechanical properties and permeability.

9:00 AM

(ICACC-FS4-003-2014) Composite ceramic membranes for hydrogen separation

N. P. Sullivan*, Colorado School of Mines, USA; P. Chitta, S. Elangovan, Ceramatec, Inc., USA; W. A. Rosensteel, Colorado School of Mines, USA; S. Dierickx, Karlsruhe Institute of Technology, Germany; S. Ricote, S. Babiniec, Colorado School of Mines, USA; A. Manerbino, W. Coors, CoorsTek, Inc., USA

This report details our development of composite ceramics for high-temperature hydrogen separation for methane dehydroaromatization (MDA) applications. The composite ceramics are based on a yttria-doped barium cerate (BCY) / yttria-doped ceria (YDC) composition. BCY serves as the proton conductor, while YDC provides electronic conductivity for charge compensation. The dense membranes are fabricated through solid-state reactive sintering in which a small amount of nickel oxide (NiO) is added to the parent oxides or precursors to promote simultaneous formation of the two phases and membrane densification in a single high-temperature sintering step. A host of diagnostic techniques are used to characterize membrane microstructure and electrochemical performance. X-Ray diffraction (XRD) is used confirm the presence of the desired phases, and the absence of undesired phases. Electron microscopy is used to characterize the morphological structure of the composite ceramics, and to confirm density as measured by Archimedes method. A test stand is used to hermetically package the membrane and quantify hydrogen transport under a hydrogen partial-pressure gradient using gas chromatography. Reasonable flux (0.1 μmoles / cm2 s) is observed under a 0.1 bar H2 pressure gradient in idealized H2/Ar gas streams and hydrocarbon-containing synthetic-MDA streams.

9:20 AM

(ICACC-FS4-004-2014) Thermo-mechanical Characterization of Ba0.5Sr0.5(Co0.8Fe0.2)1-xZrxO3-δ and La5.4WO12-δ Membrane Materials for Carbon Capture Processes

V. K. Stournari*, J. Malzbender, T. Beck, L. Singheiser, Forschungszentrum Jülich GmbH, Germany

The investigation of mechanical properties of membrane materials is critical to warrant the long term reliability of the entire separation system. Two groups of materials were studied with respect to their mechanical properties with emphasis on creep behavior since associated elevated temperature deformation would lead to mechanical instability and eventually failure. The first group involves mixed ion electron conducting materials and the second the ambipolar proton electron conductor La5.4WO12-δ (LWO54). Regarding the first group, a doped modification of the perovskite BSCF, known to have high oxygen permeability, was investigated as basic component for OXYFUEL process. The material was doped with Zr to overcome the elevated temperature structural instability. Creep investigations were carried out to examine the effect of doping level on the mechanical properties for the series Ba0.5Sr0.5(Co0.8Fe0.2)1-xZrxO3-δ with Zr = 0.01, 0.03, 0.05 and 0.1. Complementary microstructural data are presented. The second part of the work focuses on the initial mechanical investigations of LWO54. This novel fluorite structured material can be applied for the capture of CO2 directly in the Pre-Combustion process. The effect of temperature and atmosphere on the creep behavior was investigated. Furthermore data on elastic and fracture behavior are discussed.

10:00 AM

(ICACC-FS4-005-2014) Advances in Ion Transport Membrane Technology for Syngas Production (Invited)

J. C. Chen*, Ceramatec, Inc., USA; C. F. Miller, M. F. Carolan, T. Foster, Air Products and Chemicals, Inc., USA

Ceramic, ion transport membranes for the production of Syngas (ITM Syngas), produce high pressure synthesis gas in a single unit operation from low pressure air and pre-reformed natural gas. Oxygen transport through ITM Syngas membranes occurs through a series of processes, including solid phase oxygen anion diffusion through the dense membrane and surface reactions on the air and reducing sides of the membrane. This paper focuses on the effect of adding porous layers to the syngas side or both sides of the membrane to increase the available surface area for the surface reactions. The highest fluxes are achieved by increasing the surface area on both sides of the membrane, indicating that both surface reactions are a significant resistance to oxygen transport.

10:30 AM

(ICACC-FS4-006-2014) Oxygen permeability and structural stability of BaCo(Fe)O3-δ-based ceramic membranes (Invited)

H. Zhao*, Y. Cheng, N. Xu, Y. Li, X. Liu, Y. Lu, J. Zhang, University of Science and Technology Beijing, China

Oxygen permeation membranes have received considerable attention due to their potential applications in separation of oxygen from air or other oxygen containing atmospheres, conversion of natural gas to syngas, oxidative coupling of hydrocarbon to value-added products and oxy-fuel combustion for CO2 capture. BaCo(Fe)O3-δ is good parent compounds for oxygen permeation materials due to the large lattice parameter, high catalytic activity and weak Co(Fe)-O bond. However, several problems restrain their practical applications, such as the phase transformation from cubic to hexagonal during cooling course in the preparation step, the poor chemical stability towards reducing atmosphere. From the viewpoints of lattice geometric structure, defect chemistry and bonding energy, with the aim of stabilizing the cubic structure, enhancing the chemical stability and improving the permeation performance, the potential elements are selected as dopants to optimize the lattice structure of BaCo(Fe)O3-δ material. The experimental results revealed that Nb, Y and In as B-site dopant and Sr as A-site dopant as well as A-site deficiency can enhance the structure stability and improve the permeation property of BaCoO3-δ-based membrane. The role of the dopants on the oxygen permeation and the structure stability was discussed based on lattice defect analysis and first principle calculation.

11:00 AM

(ICACC-FS4-007-2014) Reliability Assessment of Ceramic Membranes for Oxygen Separation

M. K. Ferber*, MTIC, USA; C. Lewinsohn, Ceramatec, Inc., USA

Ion transport ceramic membranes are under extensive development for a variety of high-quality and high-tonnage O2 delivery systems used in the conversion of natural gas to hydrogen and synthesis gas, fuels for transportation, and IGCC used in clean coal power plants. While much progress has been made in the fabrication of membrane structures (tubular and planar) that exhibit impressive fluxing performance, the short and long-term mechanical reliability of these structures is still of concern. To address the long term performance of O2 delivery systems, one must implement a thorough reliability assessment that is capable of predicting (1) the probability of survival of membrane components operating under a variety of conditions: startup, shutdown, steady state, unexpected transients and (2) changes in probability of survival occurring over time due to time dependent phenomena including slow crack growth, creep, and deleterious environmental reactions. This presentation will describe results of reliability assessment applied to a typical oxygen membrane. Data collection techniques, finite element modeling, and prediction of the probabilities of survival as a function of time will be discussed. The importance of non-destructive testing in the early detection of life-limiting defects will be briefly described.

11:20 AM

(ICACC-FS4-008-2014) Manufacturing and Performance of supported BSCF-Membranes for oxygen separation

P. Niehoff*, F. Schulze-Kueppers, S. Baumann, R. Vassen, H. Buchkremer, W. Meulenberg, Forschungszentrum Juelich, Germany

Major industrial applications require large quantities of oxygen, normally generated by cryogenic air separation which requires significant amounts of energy. Estimates show, that the use of ceramic oxygen transport membranes (OTMs) can result in higher efficiencies. In this context, planar OTMs were manufactured by tape casting and lamination. The material used is Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF), a mixed ionic-electronic conductor (MIEC), showing the highest oxygen permeability so far. In order to increase the oxygen permeation, the membrane thickness was minimized until surface limitations become rate limiting. For small thicknesses (<200 μm), porous supports are necessary to ensure mechanical stability, but also introducing additional permeation resistances, which in turn can become rate limiting. This work presents the manufacturing of supported membranes made of BSCF with varying microstructure and membrane thickness. The performance is discussed by systematically varying operation conditions (e.g. temperature, feed/sweep flow). Transport limitations are identified and stepwise minimized by adjusting experimental conditions and sample structure. The samples' microstructure is analyzed using SEM/X-ray computer tomography. Basic model approaches for the complex permeation processes are presented. The development and manufacturing of a planar design for a modular membrane unit is discussed.

11:40 AM

(ICACC-FS4-009-2014) High Oxygen Permeance ITM from Plasma Sprayed LaSrCoFeO on Porous Metallic Supports

M. Jarligo, R. Vassen*, M. Bram, IEK-1, Forschungszentrum Jülich GmbH, Germany; J. M. Serra, J. Garcia-Fayos, Instituto de Tecnología Química, Universidad Politécnica de Valencia, Spain

The severe demands in property requirements and performance of ion transport membranes (ITMs) for oxygen separation in integrated power plants have promoted research and development efforts to combine promising materials with advanced processing techniques. This paper presents the fabrication of an asymmetric membrane assembly made of porous metallic support and dense ceramic membrane as well as their good performance with respect to high oxygen fluxes. The support composed of fine spherical particles of NiCoCrAlY was fabricated by free-sintering. A robust technique known as plasma spray - physical vapor deposition (PS-PVD) was adopted to deposit the gastight membrane layer made of thermally stable La-Sr-Co-Fe ceramic oxide. PS-PVD allows for high deposition rate of dense coatings on large substrates even with complex geometries. The membrane layer was activated using Ba-Sr-Co-Fe-O and Pd. When air was used as feed gas and CH4 was added to Ar in the sweep gas, high oxygen fluxes between 5.7 and 7.5 ml/min-cm2 were achieved at 800°C to 1000°C.

12:00 PM

(ICACC-FS4-010-2014) Contribution of Surface Exchange Kinetics on the Mixed Ionic/Electronic Conduction of Fluorite-Perovskite Composite Membranes

J. Joo, Korea Institute of Energy Research, Republic of Korea; M. Shin, University of Science and Technology, Republic of Korea; G. Park, Chungnam National University, Republic of Korea; C. Yoo, J. Yu*, Korea Institute of Energy Research, Republic of Korea

MIEC perovskite (ABO3) materials have been intensively studied owing to their high oxygen permeability. However, their chemical instability in CO2-containing atmospheres limits their practical applications. Since fluorite structured oxygen ion conductors have good phase stability under CO2 and reducing atmospheres and relatively low thermal expansion coefficients, the addition of fluorite has the possibility of improving the chemical and structural stabilities of dense ceramic membranes. In this study, Sr0.95Fe0.5Co0.5O3-δ and La0.6Sr0.4Co0.2Fe0.8O3–δ perovskite-type oxides were mixed with Ce0.9Gd0.1O2-δ, a nearly pure ionic conductor. The effects of electronic percolation depending on the volume fraction of the perovskite material and the surface exchange rate on the oxygen transport have been investigated. The characteristic thickness of the composite membrane was evaluated by using permeation data with a modified Wagner equation.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Tribology and Materials

Room: Coquina Salon D
Session Chairs: Oyelayo Ajayi, Argonne Nat Lab; Lalit Sharma, Central Glass & Ceramic Research Institute

8:00 AM

(ICACC-S1-064-2014) Practical Aspects of Using Hertzian Ring Crack Initiation to Measure Surface Flaw Densities in Glasses: Influence of Humidity, Friction, and Searched Areas

R. Tandon*, Sandia National Lab, USA; B. Paliwal, George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0405, USA and Unite Mixte Internationale Georgia Tech Lorraine/CNRS, UMI-2958, 57070, France; C. Gibson, Sandia National Lab, USA

Hertzian ring crack initiation loads on glass, using spherical WC and glass (G) indenters, are measured and analyzed. Our measurements demonstrate that humidity plays a key role in determining load to fracture; experiments conducted without controlling this variable cannot be used to obtain material properties. The role of friction is explicitly considered for dissimilar (WC-G) elastic contacts. For this material pair, the stresses at fracture are well described by a boundary lubrication value of friction coefficient. The fracture loads are used in a fracture-mechanics formulation to calculate crack sizes on glass surfaces. The "searched-area" concept for dissimilar contacts is described, and used to estimate crack density values for these surfaces. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:20 AM

(ICACC-S1-065-2014) Friction induced plastic deformation and cracking of silicon carbide

G. Bian, Loughborough University, United Kingdom; E. Claffey, BENTLEY MOTORS LIMITED, United Kingdom; A. Smith, Alcon components Limited, United Kingdom; H. Wu*, Loughborough University, United Kingdom

Silicon carbide is a key matrix constituent in carbon-fibre/ceramic composites that have been extensively explored as a replacement of metals for light and durable brake rotors. However, little knowledge is available in literature on the tribological behaviour of silicon carbide under similar braking conditions used in transportation vehicles. We conducted an investigation of the friction surfaces of carbon fibre/silicon carbide composite rotors that were tested against organic pads on an industry-scale dynamometer or a vehicle. It was found that the as-braked silicon carbide regions suffered severe deformation - cracking and plastic deformation. To understand such deformation, an experimental simulation on a laboratory-scale dynamometer was conducted on monolithic silicon carbide ceramic discs tested against metallic materials, key constituents in organic pads, to understand the development of cracking and plastic deformation. The plastic deformation on the surface was characterised with analytical transmission electron microscopy (TEM). Discussion is provided on the possible mechanisms of friction-induced plastic deformation and cracking on the surface of silicon carbide.

8:40 AM

(ICACC-S1-066-2014) Tribological background for the use of Niobium Carbide (NbC) as cutting tools and for wear resistant tribosystems

M. Woydt*, BAM Federal Institute for Materials Research and Testing, Germany

The tribological profile of rotating disks made in binderless niobium carbide (NbC) and cobalt-bonded NbC dry sliding against alumina (99.7%) were determined under unidirectio nal sliding tests (0.1 m/s to 8.0 m/s; 22°C and 400°C) as well as in oscillation tests (f= 20 Hz, dx= 0.2 mm, 2/50/98% rel. humidity, n= 105/106 cycles) under unlubricated (dry) conditions. In addition, the microstructure and mechanical properties of NbC cobalt-bonded NbC were determined as well. The room temperature wear rates of HP-NbC were low and less sensitive to increasing sliding speeds, where as increasing sliding speeds to 8.0 m/s decreased the wear rates of NbC-8Co down to outstanding low values of kV of 1-5 10-7 mm3/Nm. The wear rates at 400°C of HP-NbC and NbC-8Co remained generally below 10-6 mm3/Nm regardless of the applied sliding speed. Cutting tests underlined the suitability of NbC as a cutting tool material. As a refractory carbide, niobium carbide (NbC) is today still a forgotten carbide with hidden properties, such as wear resistance, thus qualifying NbC for the group of tribological materials with enhanced wear resistance.

9:00 AM

(ICACC-S1-067-2014) Cavitation erosion behavior of siliconized graphite composite in Water

C. Long*, X. Hong, W. Li, R. Tang, H. Liu, Nuclear Power Institute of China, China

Siliconized graphite composite (SGC) has been used as excellent self lubricated sliding bearings in hydraulic machines due to its high resistance against abrasive wear and a very low friction coefficient. SGC components have been occasionally damaged by cavitation erosion. In the present work, the microstructure and mechanical properties of SGC had been characterizied, and the cavitation erosion behavior of SGC had been investigated by laboratory cavitation erosion tests of SGC specimens and the examination of failed SGC components in water pumps. SGC consisted of graphite, SiC and Si. The cavitation damage of SGC was mainly initiated at the graphite, SiC and Si grains cracked due to fatigue processes and resulted in detachment of large chunks of material from the loaded surface. A cavitation erosion mechanism of SGC has been proposed.

9:20 AM

(ICACC-S1-068-2014) Plasticity Mechanisms in Tantalum and Hafnium Carbides

N. De Leon*, X. Yu, B. Wang, The University of Alabama, USA;
C. R. Weinberger, Sandia National Laboratory, USA; G. B. Thompson, The University of Alabama, USA

Transition metal carbides have a large assortment of applications because of their high hardness, chemical resistance, and high melting temperatures. At elevated temperatures, these ceramics can exhibit significant plasticity depending on the metal: carbon ratio. In the present study, the mechanisms of slip in the TaC, Ta2C and HfC systems are studied. Hot isostatic pressed tantalum and hafnium carbides bars were flexural tested near 2000 deg. C. The Ta2C phase was most plastic followed by HfC and then TaC. Dynamical electron diffraction confirmed slip systems in each material. These results were compared to generalized stacking fault energies computed by density functional theory. Basal and nonbasal plane slip is accounted as Ta2C mechanisms for accommodating deformation. Additionally, Ta2C has a local Ta-Ta bond that contributes to the hierarchy of slip activation. Mixed <110>/{111} and <110>/{110} slip was observed in the monocarbides and compared to similar ab initio energy landscape calculations of stacking fault energies.

10:00 AM

(ICACC-S1-069-2014) The Mechanical Properties of Sandwich Structures based on a Metal Ceramic Core and Fiber Metal Laminates Skin Material

P. Cortes, M. Curl, K. Myers*, Youngstown State University, USA;
W. Whitman, B. Hetzel, K. Peters, Fireline, Inc., USA

A sandwich structure consisting of Fiber Metal Laminates (FMLs) skins and Ceramic Metal Matrix (CMM) core is under development. A manufacturing process of the sandwich system has been achieved by incorporating a thin polyimide interlayer at the FML-CMM interface, yielding fracture toughness well above 2000 J/m2. Fracture tests on the CMM suggest that their mechanical performance is strongly related to their physical composition. Here, the compressive properties of CMM based on Al2O3-Al are at least two times higher than those associated with CMM based on Al2O3-Al/SiC-Si. Low velocity impact tests on Al2O3-Al based CMM have also shown impact energies up to 5 times higher than those displayed SiC based CMM. The evaluation of the constituent materials of the FML-CMM sandwich structure has lead into the development of an enhanced sandwich system based on foam CMM core material. The incorporation of a low density CMM as the core structure in sandwich materials, in addition to high-impact skin FMLs, will represent a new breed of hybrid structures for the transportation sector. The present paper will address the mechanical performance achieved on the constituent materials of the FML and the CMM, as well as on the FMLs-foam CMM structures under a wide range of loading rates conditions.

10:20 AM

(ICACC-S1-070-2014) Superior fracture toughness and flexural strength for Zirconia-TZP nanoceramics

S. Soares, N. Neves*, M. Rodrigues, A. L. Lagoa, J. Calado, INNOVNANO – Materiais Avançados, S.A., Portugal

The aim of this work was to maximize both fracture toughness and flexural strength taking advantage of INNOVNANO novel emulsion detonation synthesis method (EDS) for the production of nanostructured powders. The simultaneous high pressures (1-10 GPa), high temperatures (1000 – 4000°C) and the dynamic shock waves during synthesis induce a high concentration of defects and solid state amorphization resulting in small primary particles with improved chemical homogeneity. A complete study was made in order to correlate powder properties, grain growth, mechanical properties and low temperature degradation. Stable tetragonal zirconia phase ceramic pieces with yttria contents varying from 2.5 to 1.7 mol% were produced in order to find a compromise between mechanical performance and lifetime of the ceramic pieces. Decreasing the amount of yttria, small grain sizes were achieved (lower than 150 nm) and values as high as 15 MPa.m1/2 can be obtained for the fracture toughness, 1300 MPa for the biaxial flexural strength and 1400 MPa for the hardness HV10. This work demonstrated the feasibility of EDS method to produce Zirconia-TZP nanopowders with very attractive properties for ceramics for advanced structural ceramics applications.

10:40 AM

(ICACC-S1-071-2014) Study of bulk TiC/C produced via a pressure-less DC focus plasma arc technique (Invited)

R. Mahmoodian*, R. Yahya, M. Hassan, M. Hamdi, University of Malaya, Malaysia

Titanium carbide-graphite (TiC/C) composite was successfully synthesized from starting elemental powders using self-propagating high temperature synthesis technique in an ultra-high plasma inert medium in a single stage. The Ti+C pellet was kept exposed to high temperature inert medium to allow recrystallization. The product was then characterized using field emission scanning electron microscopy (FESEM) coupled with Energy Dispersive X-ray Analysis (EDX), X-ray diffraction (XRD) and micro-hardness and nano-indentation to determine the properties of the product. The product's micro-hardness recorded 3660 HV which is enhanced by 14% and comparable to TiC materials.

11:00 AM

(ICACC-S1-072-2014) Alkali Treatment of Sugarcane Bagasse to Improve Properties of Sugarcane Bagasse Fibers-Polypropylene Composites

J. Anggono*, N. R. Habibi, S. Sugondo, Petra Christian University, Indonesia

This work evaluates the improved performance of sugarcane bagasse fibers-polypropylene (PP) composites as a result of alkali treatment done on sugarcane bagasse as reinforcing fibers. Alkali solution of 10% NaOH with a temperature of 60-70°C was used to soak the bagasse for 2-6 hours. Hot pressed samples were prepared from a mixture of sugarcane bagasse fibers and polypropylene with fibers/PP weight ratios are 20/80, 25/75, and 30/70. Untreated bagasse fibers were also used for a comparison. Tensile test was performed to all samples and their fractured surface was observed using SEM to study how the presence of reinforcement in PP matrix and its alkali treatment influence the strengthening and failure characteristics of the composites. The alkali treatment carried out resulted in a relevant increase of tensile strength of the composite. Microstructural study using SEM shows a different outlook on the fiber's surface after alkali treatment which the treatment caused the elimination of the impurities, waxy materials, lignin as well as hemicellulose, which is responsible for an easy deformation of the cellular networks. Alkali treated-sugarcane bagasse gives the best as reinforcement in composites at 2 hours of treatment which resulted from the best fiber-resin bonding.

11:20 AM

(ICACC-S1-073-2014) Development of electrical porcelain insulators from ceramic minerals in Uganda

P. W. Olupot*, Makerere University, Uganda; S. Jonsson, Royal Institute of Technology, Sweden; J. K. Byaruhanga, Makerere University, Uganda

Characterisation studies on ceramic minerals in Uganda have revealed their possibility for application in ceramic insulator production. Sand, feldspar and clay were used to formulate porcelain bodies based on established theories for ensuring high dielectric and mechanical strength. Sintering profiles and their effects on strength, crystalline phase content and morphology were investigated

using dilatometry, 4-point bending strength, XRD and FEG-SEM. Optimum properties of insulators from these minerals were attained with heating/cooling rates of 6°C/min to peak temperature of 1250°C with dwell time of 2h. The quartz content of the sintered body decreased as peak temperature was increased beyond 1250°C along with a decline in strength of the bodies. Neither increasing dwell time at 1250°C nor reducing the heating/cooling rate to less than 6°C/min for a peak temparature of 1250°C were shown to result in improvement of strength. The morphology of mullite crystals did not change with change in either heating/cooling rate or dwell time at peak temperature of 1250°C. The industrial sized specimens produced exhibited dry and wet flashover voltages of 20.3kV and 9.3kV respectively, transverse strength of 12.5kN and bulk density of 2.27g/cm3. These are satisfactory for low voltage insulation applications.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Advanced Multifunctional Coatings II: Processing and Characterization

Room: Coquina Salon G

Session Chair: Doug Wolfe, Pennsylvania State University; Hideki Kakisawa, University of Tokyo

8:00 AM

(ICACC-S2-043-2014) Ceramics Coating by Thermal Nanoparticles Spraying and Filler Rods Feeding

S. Kirihara*, Osaka University, Japan

Thermal nanoparticles spraying were newly developed as novel technologies to create fine ceramics layers for alloy substrates. Nanometer sized alumina particles of 200 nm in average diameter were dispersed into liquid resins at 40 % in volume fraction. The obtained slurries were solidified through heat polymerization to crate composite rods of ϕ4×100 mm in dimensions. The solid rods including with the nanoparticles were introduced into the argon arc plasma at 5.0 mm/s in supplying speed by using a mechanical actuator. On the steels substrates, the fine surface layers of 500 μm in thickness with high wear resistance were formed at 100 μm/s in layer formation speed. Microstructures and compositional distributions in the coated layers were observed and analyzed by using a scanning electron microscopy and energy dispersive spectroscopy. X-diffraction spectroscopy was used to analyze the residual carbon elements produced by imperfect combustions of the liquid resin. Effective dielectric constants of the ceramics layers were measured successfully to calculate the porosities of air defects volume contents by using time domain spectroscopy of electromagnetic waves in a terahertz frequency range. The porosity decreasing by optimization of the filler rods feeding speeds during the thermal nanoparticles spraying technique will be discussed.

8:30 AM

(ICACC-S2-044-2014) A Chemical Solution Approach for Thin Films' Growth

G. Zou*, Soochow University, China

Thin films are widely applied in our real life. Materials in thin film form can be grown by physical/chemical vapor deposition and chemical solution deposition technique. Developing a new easy-setup, versatile, low cost, and coating of large area route is requisite to thin film growth for modern industry. In this talk, I will present a chemical solution approach, polymer-assisted deposition (PAD), to grow diverse thin-film materials including oxides, nitrides, carbides, and even single component Ge/Si. We use a new strategy to control the metals' distribution in solution at a molecular level, utilizing polymer to bind the mental ion and control solution viscosity. Herein, polymer-bound metal prevents the hydrolysis of metal ion in the aqueous solution. This ensures a homogeneous metal distribution and state of precursor solution. We have demonstrated the diverse materials' growth with desirable physical properties by PAD. This illustrates that PAD is an alternative technique for growth of high quality thin films.

8:50 AM

(ICACC-S2-045-2014) Effect of annealing atmosphere on structure, composition and optoelectronic properties of sputtered Cu-Al-O thin films

L. Feng*, Northwestern Polytechnical University, China

The Cu-Al-O thin films were prepared by magnetron reactive sputtering and annealed at 900 °C for 3h in air and Ar. Influence of annealing atmosphere on the structure, composition and optoelectronic properties of sputtered Cu-Al-O films have been investigated. Results show that annealing atmosphere has a great effect on the structure, composition and optoelectronic properties of the sputtered Cu-Al-O films. XRD analysis showed that the as-deposited Cu-Al-O films were amorphous. After the annealing treatment in air, the Cu-Al-O thin films were composed of the CuO, CuAl2O4 and CuAlO2 phases. The surface morphology of the films annealed in air was rough and non-uniform because of the impurity phases existing in the films. After the annealing treatment in Ar, amorphous Cu-Al-O films were converted to crystalline CuAlO2 thin films. The surface morphology of the films annealed in Ar was dense and uniform. XPS spectra indicated that Cu2+ was observed in the films annealed in air. However, Cu+ became the main valence state for the films annealed in Ar. XRD and XPS results imply that CuAlO2 films were formed by annealing the sputtered Cu-Al-O films in Ar. In particular, the CuAlO2 films have low resistivity of about 29.7 ± 4.1 Ω.cm and high transmittance more than 78% in the visible region.

9:10 AM

(ICACC-S2-046-2014) Air Plasma sprayed catalytic coatings for DeNOX applications

F. Cernuschi, M. Notaro, RSE, Italy; A. Moscatelli*, Flame Spray, Italy; S. Capelli, RSE, Italy; P. Mor, Flame Spray, Italy

The selective catalytic reduction (SCR) of NOx by NH3 is the best developed and most widely applied method for removing these pollutants formed from flue gases of fossil fuelled power plants and engines. Commercial catalysts are composed mainly of TiO2, WO3 and V2O5 plus other compounds without catalytic function. TiO2 in the anatase form acts as high specific surface support material and shows the most effective dispersive capacity for the catalytically active phases (V2O5 and WO3). Nowadays the installation of SCR DeNOx plants is usually limited to coal, oil and waste fired power plants. In fact, NOx emissions of natural gas combined cycles are still below the threshold fixed by the law but if this threshold will be further reduced, new combined cycles will have to be equipped with DeNOX plants or with very low NOx burners. On the other hand, to upgrade the already existing plants, a retrofitting technology is required. In this perspective, a possible solution would consist in depositing a catalytic coating on heat exchange pipes in the heat recovery steam boiler of combined cycle power plants in the region where the temperature of flue gases is in the range of operation of the catalyst. In this work the first results of the development of air plasma sprayed catalytic coatings will be presented.

S3: 11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Interconnects / Coatings

Room: Coquina Salon H

Session Chairs: Federico Smeacetto, Politecnico di Torino; Chien-Kuo Liu, Institute of Nuclear Energy Research

8:00 AM

(ICACC-S3-050-2014) Reactive Air Aluminization with Dip coating process for Planar SOFC Stacks (Invited)

J. Choi*, J. W. Stevenson, J. F. Bonnett, M. Chou, Pacific Northwest National Lab, USA

Generally, low-cost chromia-forming ferritic stainless steels are used as interconnect materials for planar type SOFC,, because of their oxidation resistance and good thermal expansion match at high operating temperatures. However, volatile Cr-containing species, which originate from the steel's oxide scale, can poison the cathode material in the cells and subsequently cause power deterioration in the device. To prevent this, a conductive MnCo spinel coating has been developed. However this coating is not compatible with the formation of hermetic seals between the interconnect frame component and the ceramic cell. Thus, a new aluminizing process has been developed to enable durable sealing, prevent Cr evaporation, and maintain electrical insulation between stack repeat units. This paper will present recent progress regarding these novel coatings.

8:30 AM

(ICACC-S3-051-2014) Interplay Among Chemistry, Microstructure and Functional Properties of Plasma Sprayed Lanthanum Strontium Manganite

S. Han*, Y. Chen, R. J. Gambino, S. Sampath, Stony Brook University, USA

LSM perovskite coatings are produced via air plasma spray (APS) to protect Cr-poisoning into the cathode side from the metallic interconnect of SOFC. Various spray conditions are manipulated such as fuel ratio, current and mass flow rate to understand process effect on the coating properties and performances. Particle temperature (T) and velocity are investigated to visualize particles' thermal and kinetic energies in the plasma plume by particle diagnostics. Coating density increases with increasing thermal and kinetic energies. However, phase decomposition also occurs when the material is exposed to high T for longer periods because of preferential loss of O and Mn. The amount of Mn loss is primarily governed by the T. La_2O_3 phase is formed in high T processed coatings with residual La^{3+} after breaking stoichiometry by Mn loss. Due to hygroscopic property of La_2O_3, the oxide scale grows faster than without LSM, but lower T processed coatings show oxide scale blocking effect with lowering rate about 70% at 800 °C for 600 hours. Moremore, electrical conductivity (σ) of lower T processed coatings show up to 60 S/cm at 800 °C and higher than those of high T processed about 1 order of magnitude despite porous microstructure. Both oxidation and σ results indicate keeping LSM stoichiometry plays important role in protection performance without impeding electron flow.

8:50 AM

(ICACC-S3-052-2014) Development of materials systems for SOFC interconnector application

Y. Chen*, A. Yeh, National Tsing Hua University, Taiwan; W. Shong, C. Liu, Institute of Nuclear Energy Research, Taiwan

The present research investigates materials systems as SOFC interconnectors based on a low thermal expansion superalloy HRA929 as the substrate, and thermodynamically stable coating compositions designed by CALPHAD-based Jmatpro and Thermo-calc. The coating method is RF sputtering for deposition. Experimental results of isothermal oxidation, area specific resistances, thermal expansion and chromium poisoning tests at 800°C will be presented in comparison with some commercial systems. Furthermore, the stability of the interface between coating and the substrate will be presented with respect to the degree of interdiffusion after thermal exposure at 800°C.

9:10 AM

(ICACC-S3-053-2014) NTN Composite Interconnect for SOFC

A. Malakhov*, Solid Cell Inc, USA; S. Ghosh, RocCera LLC, USA

High temperature metallic alloys and conductive ceramic oxides are traditional interconnect materials for SOFCs. Unfortunately, these materials have shortcomings that limit SOFC performance and often increase stack cost. Solid Cell has developed a novel interconnect, that consists of Nickel and Titania doped by Niobium (NTN Interconnect). The NTN Interconnect has several advantages over common interconnect materials like 441 stainless steel and lanthanum chromite, mainly mechanical and chemical stability in air and fuel at >900 deg. C; excellent electrical conductivity (>3,000 S/cm) and high thermal conductivity (>40 W/m*K) at the SOFC operating temperature of 900 deg. C; and a coefficient of thermal expansion that may be adjusted by varying the ratio of metallic to ceramic components. The NTN also contains no chromium or other materials that are poisonous to common SOFC cathodes, thus not requiring any barrier coatings. The NTN is manufactured from readily available low cost materials. Solid Cell has conducted durability testing of the NTN interconnect under varying conditions and in contact with different electrode materials. Critical changes and modifications to the fabrication process have also been shown to improve the properties of the NTN interconnect, resulting in a potentially new approach to resolving cell-to-cell connectivity challenges in an SOFC, without sacrificing performance or adding to stack cost.

9:30 AM

(ICACC-S3-054-2014) Mn1.5 Co1.5 O4 coatings on Crofer22APU obtained by Electrophoretic Deposition (EPD) for application in Solid Oxide Fuel Cells (SOFCs)

A. De Miranda*, Politecnico di Torino, Italy; S. Cabanas-Polo, University of Erlangen-Nuremberg, Germany; F. Smeacetto, M. Salvo, Politecnico di Torino, Italy; A. Boccaccini, University of Erlangen-Nuremberg, Germany; M. Ferraris, Politecnico di Torino, Italy

Cr-containing stainless steels have been widely used as metallic interconnects for SOFCs. Volatile Cr-containing species, which originate from the steel, can poison the cathode material in the cells and subsequently cause power degradation in the stack. Mn1.5Co1.5O4 spinel is one of the most promising coating materials due to its high electrical conductivity, good CTE match with the stainless steel substrate and an excellent chromium retention capability. In this work Mn1.5Co1.5O4 spinel coatings were obtained on Crofer22APU substrates by cathodic electrophoretic deposition (EPD) followed by sintering at 800-1000°C. Highly concentrated suspensions (37.5 g/L) in a mixture of water/ethanol (40/60 vol.%) were prepared and the coatings were obtain by applying 50 V for 1 min. Dense, homogeneous and crack free coatings (with thickness ranging from 5 to 30 micron) were obtained. Cross-scale conductivity measurements on Mn1.5Co1.5O4 coated Crofer22APU samples were carried out. The compatibility between Mn1.5Co1.5O4 coated Crofer22APU and glass-ceramic sealants is also reviewed and discussed.

Electrolytes and Membranes

Room: Coquina Salon H

Session Chairs: Mihails Kusnezoff, Fraunhofer IKTS; Albert Tarancón, IREC

10:10 AM

(ICACC-S3-055-2014) Oxygen Ion Conductors with Enhanced Properties for SOFC Applications (Invited)

K. Fung*, S. Tsai, C. Ni, C. Liu, National Cheng Kung University, Taiwan

Oxygen ion conductors are mostly found to exhibit either fluorite or perovskite type of structures. Enhanced structural and/or conducting properties are demonstrated using Bi_2O_3 and $LaAlO_3$. The enhanced stability of fluorite structure in doped Bi_2O_3 system was obtained by the partial elimination of oxygen vacancies. The enhanced conductivity in doped $LaAlO_3$ perovskite system was obtained by an approach of charge compensation and lattice expansion. As a result, the conductivity of the doubly doped $LaAlO_3$ was enhanced to $184x10^{-4}$ S/cm which is about 50 times higher than that of the undoped one at 800°C. A single cell using doubly doped $LaAlO_3$ as solid electrolyte was successfully assembled and tested. On the contrary, using doped Bi_2O_3 directly as a solid electrolyte for SOFC has not been successful due the instability of Bi_2O_3 systems in the reducing environment. On the other hand, a composite cathode based on doped Bi_2O_3 and electronic conductors such as Ag or Sr-doped $LaMnO_3$ has shown significantly reduced cathodic polarization that is crucial for SOFC to operate at lower temperatures.

10:40 AM

(ICACC-S3-056-2014) Rational Approach for Designing Cathode Materials for Proton Conducting Electrolytes Operating at 600°C (Invited)

E. Traversa*, King Abdullah University of Science and Technology, Saudi Arabia

The high cost of solid oxide fuel cells (SOFCs), related to their high operating temperatures, hinders their general use and causes long-term stability problems. Chemically stable high temperature proton conductor oxides are promising electrolytes for operating SOFC at 600°C. However, for such a low temperature efficient cathodes need to be developed to avoid polarization losses. Several good cathode materials have been developed for oxygen-ion conducting electrolytes, and in early works those same materials have been used also for proton conducting electrolytes. Though, using a proton-conducting electrolyte, protons migrate through the electrolyte from the anode to the cathode side, where they react with oxygen ions generating water. Thus, in principle a cathode material that performs well with an oxygen-ion conductor is not adequate for a proton-conducting electrolyte. This work will show the rational approach used to tailor cathode materials with low overpotential, taking into account the different species involved in the cathode reactions. The materials should concurrently possess electron, proton and oxygen-ion conductivities. In fact, the most performing cathode was made of a mixed oxygen-ion/electron conductor and a mixed proton/electron conductor composite, which allow extension of the cathode reaction sites to the whole cathode bulk.

11:10 AM

(ICACC-S3-058-2014) Effect of manganese dioxide addition to cubic phase stability, densification and electrical conductivity of scandia-stabilized zirconia

R. Muccillo*, E. Z. Santos, IPEN, Brazil

Zirconia: 8-12 mol% scandia shows the highest value of oxide ion conductivity among zirconia-based oxides. However, the cubic-rhombohedral phase transition at approximately 600 °C prevents its use as high temperature solid electrolyte in solid oxide fuel cells. To circumvent this problem, additives have been proposed. Here, ZrO2:10 mol% Sc2O3 was mixed to MnO2 to evaluate its effect on phase transformation, sintering and electrical conductivity. Pressed ceramic pellets of zirconia stabilized with 10 mol% scandia were sintered at 1200 °C/2 h + 1450 °C/2 h with addition of 0.5, 0.75, 1.0 and 1.3 mol% MnO2. All specimens were analyzed by X-ray diffraction for structural phase evaluation and dilatometry for monitoring shrinkage. The surfaces of the sintered pellets were observed in SEM and SPM. Impedance spectroscopy measurements were carried out from 300 to 500 °C. The results show that additions of 2.0 and 2.5 mol% of MnO2 prior to sintering at 1450 oC leads to i) single cubic fluorite phase, ii) the reduction of the maximum shrinkage temperature, and iii) an increase of the total electrical conductivity at 480oC from 1.4 x 10-5 S/cm (10ScSZ) to 2.6 x 10-4 S/cm (10ScSZ+1.3mol%MnO2), ~20x increase.

11:30 AM

(ICACC-S3-057-2014) Enhanced mass diffusion phenomena in highly defective doped ceria

V. Esposito*, D. Ni, Z. He, W. Zhang, J. Glasscock, C. Chatzichristodoulou, S. Ramousse, A. Kaiser, Technical University of Denmark, Denmark

The densification and grain growth of the solid state ionic conductor material Ce0.9Gd0.1O1.95-δ (i.e. GDC10, gadolinium doped-ceria Gd-10 mol. %) are analyzed for nanometric and fine powders of different particle size, both in air and in a 9 vol. % H2-N2 mixture. Due to a dominant solute drag effect in aliovalent highly doped ceria, the starting morphology of the powders controls the diffusion mechanisms of the material in air. Conversely, highly enhanced densification and grain growth are achieved by firing the materials at reduced temperatures (800 < T < 1200 °C) in low oxygen activity atmospheres (pO2 < 10^-12 atm). Solute drag is not the rate limiting step in highly defective GDC and the densification mechanisms are nearly independent of the starting powder properties. Fast diffusion is activated under low oxygen activity with high grain boundary mobility (e.g. Mgb ca. 10^-10 m3N-1s-1 at 1100 °C). The change of the dominant sintering mechanisms under low oxygen activity is attributed to the formation of a large concentration of oxygen vacancies, electronic defects, and reduced Gd/Ce cation mismatch. High densification and electric conductivity are achieved in Ce0.9Gd0.1O1.95-δ at low temperatures (1000 °C) and low oxygen activity, preserving the mechanical integrity of the material.

11:50 AM

(ICACC-S3-059-2014) Electro-chemo-mechanical properties of the non-stoichiometric oxide Pr doped ceria

S. Bishop*, Kyushu University, Japan; D. Marrocchelli, Trinity College Dublin, Ireland; D. Chen, J. Kim, H. L. Tuller, Massachusetts Institute of Technology, USA

Ionic materials, particularly oxides, have shown advantageous properties in energy conversion and storage applications, such as solid oxide fuel cells (SOFCs), photoelectrochemical cells, and batteries, due in part to their high temperature stability, corrosion resistance, and foreign cation solubility (e.g. Li), respectively. Additionally, as a support material, oxides have been increasingly shown to influence catalytic activity. In these applications, kinetics of charge transport (ionic and electronic), electrochemistry at interfaces, and chemo-mechanical coupling often play key roles in device functionality. Though these principles are certainly recognized, few systematic studies have been performed examining all three systematically, nor their behavior upon moving to the nanoscale. In this presentation, new insights into the thermodynamic equilibria and kinetics of oxygen exchange of thin films will be discussed. Key breakthroughs in understanding the atomistic origins of chemo-mechanical coupling are achieved with the aid of computational simulations.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics III

Room: Coquina Salon E

Session Chairs: Leena Hupa, Åbo Akademi University; Gianluca Malavasi, University of Modena and Reggio Emilia; Thierry Azaïs, Paris 6 University

8:00 AM

(ICACC-S5-025-2014) The role of Cerium oxidation state in bioactive glasses used as biomaterial with antioxidant properties

G. Malavasi*, F. Pincelli, S. Pierini, L. Menabue, University of Modena and Reggio Emilia, Italy; P. Luches, Istituto Nanoscienze, S3, Italy; F. Benedetti, S. Valeri, Università di Modena e Reggio Emilia, Italy

Cerium oxide (ceria) is one of the most versatile rare earth oxide materials, in particular in biological field it can be used for protection against oxidative stress. In particular nanoparticles of ceria (CeNPs) were used as superoxide radical and hydrogen peroxide scavenger and these biological properties strictly depend by the Ce^{3+}/Ce^{+4} ratio present on the oxide surface. Our purpose is to dope bioactive phospho-silicate glass with cerium allowing us to prepare a biomaterial able to join the bioactivity (bioactivity=capacity to bond hard and soft tissues trough the formation of a hydroxyapatite layer) with the antioxidant properties in terms of H_2O_2 reduction to H_2O. In fact one of the most relevant problems in the biomaterial field is the oxidative stress caused by the introduction of biomaterial into the body. To our knowledge bioactive glasses that can show the same properties of CeNPs have not yet been studied. In this study it has been possible through a spectroscopic UV-Vis and XPS study to define the ideal conditions (Ce^{3+}/Ce^{+4} ratio and glass composition) to obtain a reduction of the hydrogen peroxide to H_2O. In particular, the bioactive glass system $46.1\%SiO_2$-$24.4\%Na_2O$-$26.9\%CaO$-$2.6\%P_2O_5$-$5.3CeO_2$ was able to reduce the concentration of H_2O_2 to the half in 24 hours.

8:20 AM

(ICACC-S5-026-2014) Characterization of bone mineral surface layer (Invited)

T. Azaïs*, S. Von Euw, Y. Wang, G. Laurent, F. Babonneau, N. Nassif, Paris 6 University, France

Bone is a natural biomaterial mainly composed of an organic matrix made of collagen and a mineral phase compositionally close to hydroxyapatite Ca10(PO4)6(OH)2. In this communication, we demonstrate the existence of a distinct mineral layer through advanced ssNMR experiments validating the consensual hypothesis in the literature. This layer is highly hydrophilic and is identified as an amorphous calcium phosphate (ACP) related-phase as previously stated for dentin apatite. Our results rely on the use of freshly extracted intact bone kept in its native hydration state and on specific NMR experiments allowing the selection of protons from bone apatite. Numerical modeling leads to determine H-P distances (2.1-2.3 Å) characteristics of HPO42- ions. Spin diffusion-based experiment proves the “core-layer” organization of bone mineral. Moreover, NMR experiments conducted on selectively labeled biomimetic apatites suggest that the ACP layer of bone mineral is composed of divalent ions: Ca2+, HPO42-, CO32-. The role of such distinct surface mineral domain is not still well understood. Nevertheless, CryoTEM observations show that such water molecules play an unexpected structuring role by orienting apatite crystals in vitro. We propose that, besides its probable biochemical function, the hydrated ACP layer mediates the orientation of the bone mineral in vivo.

8:40 AM

(ICACC-S5-027-2014) Improved tetragonal stabilized zirconia for bioceramic applications

S. Soares, N. Neves*, M. Rodrigues, A. L. Lagoa, J. Calado, INNOVNANO – Materiais Avançados, S.A., Portugal

High fracture toughness and flexural strength associated with the stress-induced phase transformation of the metastable tetragonal phase into the stable monoclinic phase makes yttria-stabilized tetragonal zirconia (Y-TZP) a promising bioceramic material. The main goal of this work was to maximize mechanical, optical and aging properties of 3 mol% yttria-stabilized zirconia (3YSZ) produced by Emulsion Detonation Synthesis (EDS). INNOVNANO 3YSZ ceramic pieces prepared by hot isostatic pressing reached values as high as 1800 MPa for the flexural strength, 1400 MPa for the hardness and fracture toughness of 6 MPa.m1/2. Low aging and high translucency (30-35%) were also observed. These values of mechanical and optical properties were correlated with the manufactured method (EDS). The synthesis at high pressures (1–10GPa) and the dynamic shock waves induce a high concentration of defects and solid state amorphization which cause higher chemical reactivity and sinterability in zirconia powders. Consequently high density sintered pieces can be achieved at lower temperatures contributing to avoid grains overgrowth with improving mechanical properties. Small particles are less opaque because of less refraction and absorption which are responsible for the improvement in translucency. EDS method shows to be a suitable method for the production of tetragonal yttria-stabilized zirconia for biomedical applications.

9:00 AM

(ICACC-S5-028-2014) Ultrastructral investigations into the hard and tough shell of a bioluminescent gastropod

C. L. Salinas*, S. Herrera, Univeristy California Riverside, USA; R. Shimada, D. Deheyn, University of California San Diego, USA; D. Kisailus, Univeristy California Riverside, USA

Through hundreds of millions of years of evolution, gastropods have developed a diverse range of shell morphologies to survive in a vast array of different ecological niches. Gastropod shells are most commonly composed of an aragonitic Crossed Lamellar structure; there exist a wide range of shell thickness, ranging from thin shells that are transparent and brittle to thick heavy shells that are opaque and extremely tough. Hinea brasiliana, has evolved a thick hard shell that has the ability to transmit/diffuse bioluminescent light produced by the body of the snail through the shell. The ultrastructure of the H.brasiliana shell was investigated using a combination of scanning electron microscopy, synchrotron 2d-xrd, and Nano indentation. The shell is comprised of three distinct layers, which differ in appearance, crystallographic orientation, and mechanical properties, while still being composed of crossed lamellar aragonite. Here we examine the relationship between the mechanical properties and the crystallographic arrangement within the shell; in addition we examined the effect on light diffusion through gastropod shells of the different ultrastructural design.

9:20 AM

(ICACC-S5-029-2014) Effects of surface modification of 45S5 bioactive glass on mechanical and in vivo remodeling properties of polymeric biocomposites

A. Harmata*, K. Zienkiewicz, S. Uppuganti, Vanderbilt University, USA; D. Shimko, K. Kalpakci, Medtronic, Inc, USA; J. Nyman, S. Guelcher, Vanderbilt University, USA

The effects of surface polymerization of ε-caprolactone on 45S5 bioactive glass (BG) particles on the mechanical and in vivo remodeling properties of settable BG/polyurethane (PUR) composites were investigated. BG particles were functionalized with grafted PCL before combined with the PUR. The quasi-static and dynamic fatigue mechanical properties, compression and torsion, of composites made with various lengths of PCL-BG and PUR network mesh sizes were tested. For the in vivo study, a 11mm diam X 18mm length defect was created in the diaphysis of sheep femur and BG composites were implanted. After 16 weeks, the defect site was harvested and embedded for histological analysis. Modifying the BG surface increased the compressive fatigue life and quasi-static strength three-orders of magnitude and approximately 6- to 10-fold (8.9 to 53.8 MPa), respectively, making the composites stronger then human trabecular bone. The strength and modulus can be controlled by the length of the surface-polymerized chains relative to the mesh size of the in situ-formed PUR network. Substantial bone growth throughout the composite was observed 16 weeks after implantation in the large animal model. The initial bone-like mechanical and in vivo remodeling properties of grafted BG/PUR composites underscore their potential as settable grafts for weight-bearing bone defects.

10:00 AM

(ICACC-S5-030-2014) Bioactive Glasses – Composition Matters (Invited)

L. Hupa*, Åbo Akademi University, Finland

Since the very first findings of the ability of certain silicate glasses to chemically bond with living tissue, the influence of composition of these so called bioactive glasses has been studied intensely. Adjusting the composition not only allows different degrees of dissolution of the glass in the body but also enables manufacture of highly porous scaffolds and implants. For some glasses the degradation is connected with a bioactive action, i.e. the dissolution process simultaneously promotes new tissue growth at the glass surface. Other glasses just dissolve gradually with no direct bioactive reactions. Both types of glasses are interesting for different medical applications, and it is of vital importance to be able to tailor glasses with controlled degradation behavior. This presentation summarizes the most important results produced during the past thirty years related to the influence of the oxide composition on the reactivity and chemical and physical properties of bioactive and biodegradable glasses. The in vitro results of several glasses are compared with the observations of their capability to bond to bone. Further, interactions between bioactive glasses with biodegradable polymers in composites will be discussed. These results pave the road to tailoring glass compositions for future applications, such as optical glass fiber based sensors monitoring in-body healing processes, or novel multifunctional dressings for wounds.

10:20 AM

(ICACC-S5-031-2014) Mg incorporation into beta tricalciumphosphate (β*TCP) powder for high temperature phase stability*

R. Sasidharan Pillai*, S. Dirè, V. M. Sglavo, University of Trento, Italy

The synthesis and characterization of Mg doped- beta tricalcium phosphate (β*TCP) powders have been investigated in the present work. The* βTCP powders were synthesized by conventional solid-state reaction at 1200-1300°C, starting from brushite and calcium carbonate. MgO and $Mg(NO_3)_2$ were added as phase - stabilizers in different amounts (1-15 mol%). According to XRD and TG/DTA analyses, the MgO addition allows to stabilize the β*TCP phase at temperature as high as 1500°C, preventing the transformation into alpha TCP. It is shown also that MgO load in excess of 1 mol% causes the formation of hydroxyapatite.*

10:40 AM

(ICACC-S5-032-2014) Evaluation Of Antibacterial Activity Of Metal Oxide Nanoparticles For Water Disinfection Applications

A. Jurewicz*, O. Arslan, S. Mathur, Institute of Inorganic Chemistry, Germany

In the last years the progress accomplished on the synthesis of inorganic nanostructures has been gone together with exploitation of these systems in various fields, amongst them are biology and medicine. Strong antibacterial properties of inorganic metal oxides and their low toxicity towards mammalian cells is one of great interest in the development of new products. Antibacterial agents are of significant importance in several industries, e.g., water disinfection, textiles, packaging, medicine and food. Metal oxides may serve as effective disinfectants, due to their relatively non-toxic profile, chemical stability and efficient antibacterial activity. Among metal oxide nanoparticles, zinc oxide is an extremely versatile industrial chemical. Antibacterial activity of the zinc oxide@gluconate nanoparticles were investigated against common bacterial pathogens. Our results suggest its significant bacterial growth inhibition on a broad spectrum of bacteria such as Staphylococcus aureus and Escherichia coli.

11:00 AM

(ICACC-S5-033-2014) Formation of alumina layer on Ti-6Al-4V alloy for artificial hip joint application

R. Khanna*, T. Matsushita, T. Kokubo, H. Takadama, Chubu University, Japan

We attempt to prepare a new hip joint by forming alumina layer on Ti-6Al-4V alloy by deposition of Al metal powders on the alloy and its subsequent oxidation. The Ti-6Al-4V alloy has good biocompatibility and high mechanical strength, but does not show high wear resistance. Alumina shows high wear resistance, but is brittle in nature. High wear resistance of alumina and high mechanical strength of Ti-6Al-4V alloy can be applied by formation of alumina layer on Ti-6Al-4V alloy. In this study, fine powders of Al metal were deposited onto the alloy by high pressure cold spraying. Cold spraying was performed in N2/He atmosphere to form a dense layer of Al metal onto the alloy. Cold spraying in He gas atmosphere led to delamination of Al layer due to poor adhesion with the alloy as compared to that in N2 gas atmosphere. Cross-sectional analysis of as-prepared samples revealed that some gap was present between Al layer and the alloy. To close this gap, the Al coated-Ti alloy sample was heated at 640oC for 1h in air or Ar gas to form a reaction layer at the interface between Al layer and Ti alloy. X-ray diffraction revealed that the reaction layer is composed of Al3Ti. The adhesion between Al metal layer and Ti alloy was improved by formation of the reaction layer. The Al metal thus obtained will be subjected to oxidation to form a dense alumina layer under the varying temperatures and atmospheres.

11:20 AM

(ICACC-S5-034-2014) Assessment of hydraulic reactivity and mechanical properties of alpha-tricalcium phosphate:polycaprolactone composite bone cements

G. Alkan*, C. Durucan, METU, Turkey

Composites of calcium phosphate(s) exhibiting cement-type hardening, blended with polymers can be used for shaped bone defect filling operations. In this respect, α-tricalcium phosphate (α-TCP) can be considered as inorganic component; given its ability to hydrolyze hardened HAp from a single precursor. Here, preparation of α-TCP:polycaprolactone (PCL) composites have been reported. A comparative/parametric study was performed to elucidate the hydraulic reactivity of α-TCP in presence of PCL by isothermal-calorimetry studies. It was found that PCL addition hampers α-TCP to HAp conversion. However, it improves mechanical strength/integrity of pre-hydrated compacts and HAp-based cement products by providing interlocking between the inorganic granules. The strength α-TCP and α-TCP:PCL (3 wt.%) compacts prior to hydration were determined as 0.17±0.05 and 0.38±0.05 MPa, respectively. α-TCP cement demonstrated a strength value of 4.3±0.1 MPa after complete conversion to HAp in 42 h. Meanwhile, PCL-containing blend exhibited higher strength (6.6± 0.1 MPa) after hydration for 68 h.

S8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT8) In Honor of Prof. Stuart Hampshire

Advanced Micro & Composite Processing II

Room: Coquina Salon A
Session Chairs: Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology (AIST); Yiquan Wu, Alfred University

8:30 AM

(ICACC-S8-062-2014) Carbon Hybrids with Polymer-Derived Ceramics (Invited)

Y. Blum*, SRI International, USA; D. Hourlier, IEMN UMR, France;
G. Soraru, Università di Trento, Italy

The concept of polymer derived ceramics (PDC) has been evolved as a "carbon copycat", trailing more than a decade behind the rapidly growing and successful market for structural and fibrous carbon products. Both technologies share the same principles of polymer synthesis, shaping and pyrolysis and have scaled up as high performing fibers, composites and porous materials. While the carbon fiber composite market is booming, the PDC field is still very narrow and hindered by very high costs of polymers and expensive processes. This far, very limited effort has been attempted to combine advantageous characteristics of both carbon and PDC materials. This presentation will discuss reported synthesis capabilities to hybridize between the two disciplines at the homogeneous (molecular) and heterogeneous levels. Understanding of the mechanisms in which the precursor's organic groups are transformed in-situ into graphene nanodomains will be discussed in an effort to better control the evolved nanostructures and derived future application.

9:00 AM

(ICACC-S8-063-2014) Thermodynamic Control of Phase Composition and Crystallization of Metal-Containing SiOC Ceramic Nanocomposites

E. Ionescu*, Technische Universitaet Darmstadt, Germany; A. Navrotsky, UC Davis, USA; R. Riedel, Technische Universitaet Darmstadt, Germany

Silicon oxycarbides modified with main group or transition metals (SiMOC) are usually synthesized via pyrolysis of sol-gel precursors from suitable metal-modified orthosilicates or polysiloxanes. In the present study, the phase composition of different SiMOC systems (M = Sn, Fe, Mn, V, and Lu) was investigated. Depending on the metal, the formation of different ceramic systems was found. Thus, in case of M = Mn and Lu MOx/SiOC ceramic nanocomposites were formed, whereas other compositions revealed the formation of M/SiOC (M = Sn), MSix/SiOC (M = Fe) or MCx/SiOC (M = V) upon pyrolysis. The different phase compositions of the SiMOC materials are rationalized by a simple thermodynamic approach which generally correctly predicts which type of ceramic nanocomposite is expected upon ceramization of the metal-modified precursors. Calculations reveal that the thermodynamic stability of the MOx phase with respect to that of the C-O system is the most important factor to be taken into account to predict phase formation in polymer-derived SiMOC ceramic systems. A secondary factor is the relative stability of metal oxides, silicates, carbides, and silicides.

9:20 AM

(ICACC-S8-064-2014) Particle Size Reduction of Ceramic Powders: Wet Grinding

S. D. McManus*, Hockmeyer Equipment, USA

To explore the techniques of deagglomeration and particle reduction of ceramic powders with wet grinding media mills. Testing Method. A Comparison of particle distributions created when processing: Alumina Oxide in water. Processed for 2 hours with 1.5 mm ytz media in an Immersion Mill. Alumina Oxide in water. Processed for 2 hours with .8 mm ytz media in an Immersion Mill. Alumina Oxide in water. Processed for 2 hours with .3mm ytz media in an Immersion Mill. Mill tip speed will be maintained at 12 m/s for each media size and media loading will be 49 ml per liter of product. Alumina oxide loading will be 30% by weight per liter of material. Alumina Oxide processes to an average particle size of 1 um with 1.5 mm media, .7 um with .8 mm media and 200 nm with .3 mm media. Conclusions smaller media and high energy input generate more efficient particle reduction and tighter particle distribution bands.

10:00 AM

(ICACC-S8-065-2014) Colloidal processing of yttria powders: effects of powder dissolution on suspension stability

X. Li*, J. He, J. Li, S. Liu, X. Sun, Northeastern University, China

Yttrium oxide (Y2O3) with cubic symmetry is one of the important oxide hosts for the solid state lasers, as well as for infrared ceramics. Colloidal processing method has been adopted in this work for the fabrication of transparent yttria ceramics. Aqueous suspensions were prepared by dispersing yttria powders of various origins in de-ionized water with the addition of dispersants. Effects of the characteristics of starting powders, adsorption of dispersants, the pH of the suspending medium and solid loadings on the stability of the suspensions were characterized by means of sedimentation test, Zeta potential and viscosity measurements. Dissolution of yttrium ions into the suspension readily changed the viscosity of the suspensions and greatly reduced the long time stability of the suspensions. The prepared suspensions were subsequently consolidated into green compacts via centrifugation. The sintering behavior and microstructure of the sintered ceramics were compared for the green compacts consolidated from various suspensions.

10:20 AM

(ICACC-S8-066-2014) Isothermal kinetic laws of TiSi2 nitridation

J. Roger*, L. Maillé, M. Dourges, Université Bordeaux 1, Laboratoire des Composites ThermoStructuraux, UMR 5801, France

Our work deals with the reaction kinetic of in situ formation of a nanostructured ceramic matrix by reaction between a powder with a gas which is in the present case nitrogen. Isothermal nitridation behavior of powdered TiSi2 with fine (1.4μm) and medium (4.5μm) particle size has been studied in nitrogen ranging from 1000 to 1200°C for durations up to 100 hours. The isothermal nitridation kinetics of TiSi2 powders was investigated by thermogravimetry. The nitridation rate strongly depends on the particle size and temperature. The smaller particles size exhibits the higher nitridation rate due to its larger surface area. It was found that Johnson-Mehl-Avrami model appropriately explained the thermal reaction between the powder and gaseous nitrogen. The apparent activation energies for the two sizes of powder have been calculated. The type of rate law suggests that the conversion proceeds by nucleation and growth model.

10:40 AM

(ICACC-S8-067-2014) Glass fiber relaxation at temperatures close and below Tg

Y. Vulfson*, Hollingsworth & Vose, USA

Specialty glass fibers are widely used in the filtration industry and in lead acid battery electrode separators. The technology used in the manufacturing of glass fibers affects properties of filtration media and performance of valve regulated acid batteries. For the production of non-woven glass fibers two major methods are used: rotary and flame attenuation. In both processes glass fibers are attenuated and cooled within parts of milliseconds. The very fast heating and then cooling of fibers creates significant tension in the glass. This stress influences the properties of products made using glass wool. This study shows that fiber tension is determined by the method of fiberization and the numerous fiberization settings. In this work, stress has been determined as a function of fiberization method using thermal analysis. It has been shown that internal stress can be released at temperatures close and even below Tg. The mechanism of relaxation apparently is not related to the viscous flow of the bulk glass and can be explained using a similar model to that described recently for the flat sheet glass. It has been shown that the process of relaxation in micron-size fibers occurs much faster and has its characteristic properties. This can be explained by the size of the fibers, fiberization conditions, and the fast cooling rates.

11:00 AM

(ICACC-S8-068-2014) Novel Green Manufacturing Technologies

S. Gupta*, M. F. Riyad, T. Hammann, R. Johnson, University of North Dakota, USA

Green manufacturing is defined as a method for manufacturing that conserves resources, and minimizes waste and pollution. The aim of this presentation is to show that it is possible to develop novel materials by using green manufacturing technologies. This presentation will be divided in two parts: (a) novel methodologies for studying manufacturing to enhance productivity, and (b) sustainable cementitous materials by using waste materials. In part A, we will present different thermomechanical techniques for studying and optimizing manufacturing. Some of the techniques which will be presented in this talk are sinter forging, cyclic loading dilatometry, among others. In part B, we will present recent studies about developing novel cementitous materials by using waste materials like fly ash etc. Detailed mechanical behavior, and microstructure study of these solids will be presented.

11:20 AM

(ICACC-S8-069-2014) Potential of ceramics for thermal energy storage using the mixed chloride salt

K. Kita*, T. Nagaoka, T. Ohji, N. Kondo, AIST, National Institute of Advanced Industrial Science and Technology, Japan

The solar thermal power plant needs thermal energy storage system. At present, nitrate salt is used as the thermal energy storage material. However, thermal density of chloride salt is higher than that of nitrate salt, because the melting point and latent heat of fusion of chloride salt are higher than those of nitrate salt. Therefore, chloride salt would be needed as the thermal energy storage material in the future. However, chloride salt has some problems for the use as the thermal energy storage material. Solid chloride salt has poor thermal conductivity, so it takes time for thermal charge/discharge. In addition, molten chloride salt is severely corrosive, so the container for the chloride salt needs extraordinary corrosion resistance. To overcome these problems, we paid attention to ceramic and investigated the potentiality of ceramic. We chose the mixed chloride salt which contains 50 wt% of NaCl and 50 wt% of KCl. The mixed salt is known as the high thermal energy storage and has satisfactory results in industry. Alumina and silicon carbide was chosen as the materials for container and the corrosion tests in the molten mixed salt were carried out. In addition, alumina fillers with various shapes were prepared, and the suitable blend ratios and thermal density of the blended material including the chloride salt and fillers were investigated.

S9: Porous Ceramics: Novel Developments and Applications

Processing Methods for Porous Ceramics V

Room: Coquina Salon C
Session Chair: Siobhan Matthews, SCF Processing Ltd

8:00 AM

(ICACC-S9-025-2014) Silicon Nitride Foams Sintered by Pressure-less Spark Plasma

E. Guzi de Moraes*, University of Padova, Italy; D. Li, Stockholm University, Sweden; P. Colombo, University of Padova, Italy; Z. Shen, Stockholm University, Sweden

Si3N4 foams with high thermochemical and mechanical stability were developed from emulsions using proteins as stabilizers. Macrocellular foams were strengthened by rapid sintering under pressure-less spark plasma sintering conditions. The effect of the various processing parameters on structure and characteristics of the foams will be discussed. The morphology of the silicon nitride grains in the foams was investigated using SEM, so did the overall microstructure of the sintered foams. It was found that the foams were comprised of cells with interconnected pores in the range of 10 to 500 μm, and high level of porosity (> 80%). The formation of interconnected elongated silicon nitride grains favoured the increase of the mechanical strength of the foams. This processing approach enables to rapidly fabricate highly porous components with a homogeneous microstructure, suitable for several engineering applications.

8:20 AM

(ICACC-S9-028-2014) Highly porous reaction bonded silicon nitride foams; foam strength and reaction bonding parameters

A. Alem*, M. Pugh, R. Drew, Concordia University, Canada

Recently, many technological applications have been found in which porous ceramics have been utilized due to their unique characteristics. Although silicon nitride ceramics have many remarkable potentials and properties, silicon nitride foams have not received sufficient attention. In this study highly porous silicon nitride foams with open-cell structures have been fabricated via a sacrificial template technique. In this newly designed fabrication procedure, gel-casting and reaction bonding processes were combined in order to make a homogeneous reaction bonded silicon nitride foam without the normal issues of working with Si3N4 materials namely the high sintering temperature, the large linear shrinkage, costly post-sintering machining steps, and poor rheological behaviors. The fabricated foam has a controlled level of porosity which varies up to 87 vol% with a highly interconnected network. The high level of porosity in the foam and its large surface area significantly affect the reaction bonding process. It was observed that due to the large surface area of the foam, vapor-phase reactions resulted in α-Si3N4 whiskers as the dominant phase but under specific conditions, β-Si3N4 can form in a major quantity. The reaction bonding process was also designed and optimized in terms of the nitriding conditions to get the highest strength while the pore-interconnectivity is maintained.

8:40 AM

(ICACC-S9-030-2014) Porous Si3N4 ceramics prepared via nitridation of Si powder

Y. Zeng*, Shanghai Institute of Ceramics, China

Porous silicon nitride ceramics (Si3N4) show superior properties compared with other porous ceramic materials in strength, toughness, thermal shock resistance due to the interlocking microstructure of β-Si3N4 grains. In this work, porous silicon nitride matrix composites were prepared via reaction bonded Si3N4 (RBSN) and post-sintering, the influence factors, such as, heating program, silicon particle size, Y2O3 content on the mechanical properties were investigated. To investigate the relationship bending strength and microstructure porous Si3N4, different processing methods, such as, conventional powder forming processing, slip casting, and freeze-drying process, were used in preparation Si green bodies and the second phase, such as BN, C/SiC etc. were added to modify the mechanical properties of porous Si3N4. The results indicated that processing methods, second phase, as well as the sintering program have great effect on the mechanical properties and microstructure of porous Si3N4 ceramics. The oxidation resistance properties, high temperature properties, as well as thermal shock properties of porous Si3N4 ceramics were also investigated.

9:00 AM

(ICACC-S9-032-2014) Fabrication of Porous Silicon Nitride Ceramics with High Porosity and Mechanical Properties

Z. Xu, J. Yang*, W. Jing, B. Liu, Xi'an Jiaotong University, China

Porous Si3N4 ceramics with high porosity and mechanical properties was prepared by using α-Si3N4 as raw materials and talc, clay and Al2O3 as sintering additives. The Si3N4 ceramics consisted of fine, fibrous β-Si3N4 and small Si2N2O grains. The addition of the cheaper talc and clay helped to form the co-melting phase with low melting point, enhancing the transformation from α to β phase. The mechanical properties of the Si3N4 have porosity of 45.39%; density of 1.663 g/cm3; flexural strength of 131.59MPa. Porous β-Si3N4 ceramics fabricated with Al2O3 as additive exhibited the increased flexural strength, toughness and hardness and decreased porosity with the Al2O3 content. The flexural strength was over 170 MPa and the dielectric constants 3.0~3.2. Sintering densification behavior of different purities of α-Si3N4 powders and sintering nitrogen pressure are also studied. Since sintering liquid phase forming from low purity of α-Si3N4 powders has low viscosity, the obtained ceramics possessed high sinter shrinkage and low porosity, where high purity of powders shows inversely. With the increasing of nitrogen pressure, sintering shrinkage decreases, while porosity and aspect ratio of grain increase. With the nitrogen pressure increased from 0.1MPa to 0.5MPa, the shrinkage decreased by 26% and porosity increased by 17.3%.

9:20 AM

(ICACC-S9-034-2014) Template sacrificed fabrication of porous SiBCN ceramic foam

F. Zeng, Y. Li, Y. Luo, C. Xu*, Institute of chemistry, Chinese Academy of Sciences, China

The porous SiBCN ceramic foam had been successful fabricated by using template-sacrificed method. The structure and mechanical property of SiBCN ceramic foam were investigated with Fourier Transforms Infrared Spectroscopy (FTIR), Solid Nuclear Magnetic Resonance (Solid-NMR), Inductive coupled plasma emission spectrometer (ICP), Element Analysis (EA), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Mercury Intrusion Porosimetry (MIP), and mechanical properties instrument. It was found that the pore size and thermal conductivity of the ceramic foam became larger with the increase of oxidation temperature. The content of boron and silicon kept stable after oxidation at different temperatures. While the compressive strength data showed that the ceramic foam had relative high residual mechanical property after oxidation at 1300C.

Mechanical Properties of Porous Ceramics

Room: Coquina Salon C
Session Chair: James Zimmermann, Corning Incorporated

10:00 AM

(ICACC-S9-036-2014) Thermal Fatigue Analysis of Active Catalytic Diesel Particulate Filter Regeneration (Invited)

C. Su, Y. Yuan, R. Stafford*, Cummins Inc, USA

A method for lifetime prediction of DPF (Diesel Particulate Filter) will be presented. This method compares lifetime prediction against the thermal stress from DPF regeneration. In the method, experimentally measured material properties (strength, elastic modulus, coefficient of thermal expansion) and DPF temperature distributions under various conditions including regeneration mode were used in FEM (Finite Element Method) stress analyses. The estimated stress value through analysis on thermal stress is compared with the experimentally measured material strength by four point flexure testing method. Subsequently, the life time of the DPF under thermal fatigue was determined from Weibull parameters in a Principal of Independent Action (PIA) model. The effect of changes in material properties on the life time of the specific DPF will also be discussed.

10:30 AM

(ICACC-S9-037-2014) The uniaxial tensile response of β-eucryptite with varying levels of microcracking: experiments and modeling

M. Wheeler, A. Pandey, Oak Ridge National Laboratory, USA; G. Bruno, Federal Institute for Materials Research and Testing (BAM), Germany; A. Shyam*, Oak Ridge National Laboratory, USA

In this paper, we report the uniaxial tensile stress-strain response of three types of β-eucryptite (LiAlSiO4) specimens with different grain sizes and levels of microcracking. In addition, the uniaxial tensile response of the precursor glass with the nominal composition of β-eucryptite is also reported. The uniaxial tensile tests were performed using a microtensile system, and strains were obtained using non-contact 2D digital image correlation (DIC). The elastic moduli of the specimens were determined and compared with published values obtained using resonant ultrasonic spectroscopy (RUS). In order to link the mechanical response to the microstructure in this material, a micromechanical model that rationalizes the non-linear tensile behavior of ceramics in terms of levels of microcracking was used. Results show that microcracking dominates over other contributions in determining the non-linear tensile behavior of this material.

10:50 AM

(ICACC-S9-038-2014) Mechanical Modeling of Microcracked Porous Ceramics (Invited)

R. S. Fertig*, University of Wyoming, USA; S. Nickerson, Corning Incorporated, USA

The focus of this work is to develop an approach for predicting microcracking in porous ceramics with anisotropic thermal properties, such as cordierite, arising from combined thermal and mechanical loading. A previous model for predicting thermally-induced microcracking based on the distribution of grain boundary tractions is expanded upon to predict the increase in grain boundary microcracks with increasing applied tensile load. A method for linking isotropic distributions of thermally-induced microcracks with tensile load-induced anisotropic distributions of microcracks is proposed. The developed model contains only a single additional parameter beyond the thermal model, which characterizes load transfer from the macroscopic structure to grain boundary tractions. The model is used to predict microcrack-controlled nonlinear constitutive tensile behavior of a microcracked porous ceramic at any temperature.

11:20 AM

(ICACC-S9-039-2014) Determination of Elastic Moduli for Porous Ceramic Films Using Nanoindentation and FEM

Z. Chen*, X. Wang, F. Giuliani, A. Atkinson, Imperial College London, United Kingdom

The aim of this work was to present the methodology for reliably determining the elastic moduli of SOFC cathodes by appropriate nanoindentation experiments and analysis. The 3D microstructures of the porous crack-free perovskite LSCF films, which were prepared by sintering at 900-1200°C, were reconstructed based on dual-beam FIB/SEM tomography, followed by FEM to compute the elastic moduli. Detailed analysis of the nanoindentation results was also made to estimate the film-only elastic modulus for each film. The experiments showed that reliable measurements of the true film properties were obtained by data extrapolation provided that indentation depth was 0.1-0.2 of the film thickness. Effects from surface roughness and substrates responsible for the data deviation were taken into account. It was found that the elastic modulus increased from 32-122GPa as the sintering temperature raised from 900–1200°C and the porosity decreased from 47-15%. Further insights were gained into the porosity evolution, plastic deformation and substrate effect in the indented films with the aid of FIB/SEM. Excellent agreement was found when comparing the elastic moduli derived from nanoindentation and FEM, implying the present method could be an effective tool for investigating the way in which the mechanical properties of porous ceramic films is influenced by their microstructures.

S11: Advanced Materials and Innovative Processing Ideas for the Industrial Root Technology

New Concept & Emerging Technology I

Room: Ponce De Leon

Session Chairs: Changwoo Lee, KITECH; Hong Joo Rhee, Missouri University of Science and Technology

8:20 AM

(ICACC-S11-028-2014) Study of Mechanical Properties of CNT composite Solder Ball

C. Lee*, Y. Ko, J. Bang, KITECH, Republic of Korea

It is investigated shear strength of BGA(Ball Grid Array) electric chip which packaged by used CNT-composite solder ball. The CNT composite ball was manufactured with ball milling system. The CNT and the solder ball used in this study were multi-wall structures and SAC305(Sn-3.5Ag-0.5Cu), respectively. The spherical shape of composite ball was controlled by milling speed and atmosphere in milling system. Also the range of amount of CNT in solder ball was 0.05wt% to 0.01wt%. The packaging samples used CNT composite solder was fabricated by hot air Reflow process. The microstructure of the joined solder ball was observed by using FE-SEM and EDS. From the results, CNT was observed mostly in grain boundaries and shear strength of the BGA electric chip was increased about 8%, comparing with the strength of chip joined with SAC305 solder ball. It was seems to be caused by distributed hardening of CNTs. Additionally, it was possible to guess that the CNTs distribution arrested the crack propagation in the composite solder. Also, other manufacturing factors of CNT composite solder ball are discussed.

8:40 AM

(ICACC-S11-030-2014) Kinetics of IMC growth induced by Electromigration for Sn-0.7Cu/Cu solder

M. Heo*, Pusan National University, Republic of Korea; K. Cheong, SAMSUNG Electro-Mechanics, Republic of Korea; N. Kang, Pusan National University, Republic of Korea

Fine pitch technology has been developed for miniaturization and high performance of PCB(Printed Circuit Board). The reliability of PCB has emerged as a critical concern. Because size of solder bump that chip and substrate connect decreases, current density to solder bump increases by fine pitch formation. Main failure mode is the open-circuit failure due to void formation at the intermetallic compounds growth. This failure mode has been reported as a result of electromigration damage. Therefore, this study is needed to predict and prevent for open circuit failure by intermetallic compounds growth. This study predicted IMC growth kinetic by electromigration in Sn-0.7Cu solder bump. The intermetallic compounds during reflow process grow again by electromigration due to the application of current density. The intermetallic compounds under electromigration grow in proportion to current density. Consequently, crack that the main factor cause open circuit failure is formed by void formation and propagation at the intermetallic interface. Therefore, Fick's law and Nernst-Einstein equation are used for modeling of growth kinetics of intermetallic compounds. Consequently, this study compared modeling results and experiment results.

9:00 AM

(ICACC-S11-031-2014) Joint Property of Sn-Cu-Cr(Ca) High Temperature Solder for High Reliability of Automobile ECU

J. Bang*, KITECH, Republic of Korea

In this study, mother alloy of eco-friendly Sn-Cu-Cr-Ca solder was fabricated based on Sn-Cu alloy and its melting point was 230. Then, the alloy was produced in the types of ball and paste. The spread ability of the alloy was about 84% from the measuring of contact angle of the ball. The average shear strength of the modules which was manufactured by using the solder paste, were 1.9 kg/mm2.

New Concept & Emerging Technology II

Room: Ponce De Leon

Session Chairs: Derek King, Missouri University of Science and Technology; Inki Min, KITECH

10:00 AM

(ICACC-S11-032-2014) Mechanical Properties of Fusion Welded ZrB_2 containing 20 vol.% ZrC (Invited)

D. King*, G. Hilmas, W. Fahrenholtz, Missouri University of Science and Technology, USA

Plasma arc welding was used to join ZrB_2 containing 20 vol.% ZrC (ZrB_2-20ZrC). The billets were prepared by ball milling ZrB_2 and ZrC powders in acetone with phenolic resin as a sintering aid. Billets nominally 64 mm by 64 mm by 5 mm were hot pressed to near theoretical density, ground to a thickness of 4 mm, and then sliced in half with a diamond saw using an automated surface grinder. The cut halves were fusion welded using a plasma arc welder. To combat oxidation and thermal shock, welding was carried out under an inert argon atmosphere in a sealed furnace designed to preheat the samples prior to welding. The strengths of the joints were compared to that of the parent material following the guidelines of ASTM C1469-10. Hardness was also used to determine if a heat affected zone was apparent in the joint. Scanning electron microscopy and x-ray diffraction were used to evaluate the microstructure and composition of the fusion zone.

10:30 AM

(ICACC-S11-033-2014) High Strain Rate Material Testing and Internal State Variable / Damage Model Development on the Eco-Friendly Processed Lightweight Alloys

H. Rhee*, KITECH, Republic of Korea; W. Whittington, M. Horstemeyer, MSU, USA; S. Lee, K. Lee, J. Lee, J. Song, KITECH, Republic of Korea

The objective of this research is to characterize the high strain rate response and response variations of materials used in ground vehicles through experimentation and development of model parameters, and to develop an internal state variable (ISV/damage) model solution tool. 6000 and 7000 series aluminum alloy automotive bumpers, manufactured by a newly developed eco-friendly process, were compared to conventionally manufactured aluminum alloys with respect to microstructure and mechanical properties. Low and high strain rate tension experiments were performed for comparison of the mechanical response. Results showed that the eco-friendly processed bumpers were comparable in strength and ductility as well as microstructure.

10:50 AM

(ICACC-S11-034-2014) Development of Glass Fiber Reinforced Polymeric Worm Wheel for Automobile MDPS by Injection Molding Process

G. Kim*, J. Park, G. Yoon, J. Lee, KITECH, Republic of Korea

The plastic gear is widely used in the automobile manufacturing field because it is favorable to the weight-lightening of automobile, vibration and noise reduction, as well as corrosion resistance. However, it is very difficult to guarantee the physical properties required for driven or steering equipment of automobile only using engineering plastic materials. If the engineering plastic resin is reinforced by glass fiber or carbon fiber in those cases, it is possible to achieve the physical properties of metallic material levels. In this study, for fabrication of composite worm wheel for the luxury automobile MDPS(Motor Driven Power Steering) module, the physical characteristics analysis of the glass fiber reinforced composite worm wheel according to the weight-fraction of glass fiber and resin fluidic structure is performed by analytic modeling, simulation and experimental methods. In the case of the glass fiber reinforced plastic composite, the orientation and weight-fraction of glass fibers can influence the physical properties. For the characteristics prediction of composite worm wheel, computer-aided engineering(CAE) modeling and simulation processes such as structural and injection molding analysis were executed with the various conditions such as resin fluidic structure, injection molding condition and the weight-fraction of glass fiber(25, 50wt%).

11:10 AM

(ICACC-S11-035-2014) A Study on the Optimization of Optical and Dimensional Properties Using Hybrid Injection Molding Process for 7 Inch LGP

I. Min*, DanKook University, Republic of Korea; S. Hong, J. Kang, KITECH, Republic of Korea; K. Yoon, DanKook University, Republic of Korea

As the adoption of injection molding technology increases, injection-molded optical products require higher dimensional accuracy and optical stability than ever before. Recently, many alternative injection molding techniques have been adopted to increase the stability of optical and dimensional characteristics such as injection/compression molding or rapid heat cycle molding. In the present study, the hybrid process called RICM which is combination process of Rapid Heat Cycle Molding(RHCM) and Injection/Compression Molding(ICM) was developed and evaluated its characteristics through the comparison with other molding processes. Four different molding methods, i.e., conventional injection molding(CIM), injection/compression molding(ICM), rapid heat cycle molding (RHCM) and RICM(ICM+RHCM) were chosen to compare the dimensional stability and optical anisotropy of 7 inch LGP by examining the gap-wise distribution of birefringence and extinction angle. The dimensional stability was evaluated by measuring the thickness and the replication ratio of micro pattern at every nine points from the gate to the end of part. The gap-wise birefringence was measured at every 5 mm following the center line of flow direction from gate to the end of the part by a polarizing microscopy, too.

11:30 AM

(ICACC-S11-036-2014) Observation of the pore size and 3D distribution of the ZrO2 sintered ceramics (Invited)

H. Murayama*, T. Nakayama, Nagaoka University of Technology, Japan; B. Kim, T. Kim, Korea Institute of Industrial Technology, Republic of Korea; H. Suematsu, T. Suzuki, K. Niihara, Nagaoka University of Technology, Japan

Ceramics have excellent strength, toughness, abrasion resistance, wear resistance, heat and corrosion resistance. Among them, mechanical properties such as strength and toughness are most important property to use in various fields. But, It are gradually lost by the influence of degradation. If fracture strength can predict, It will expect application to another new areas can't use so far. Therefore, in the present study, we have demonstrated that examined internal structure by using X-ray CT scans and predicts the fracture strength. After that, predicted date compared to existing date. Employed material is 3Y-ZrO2. Method of create a sample is prepared by pressureless sintering. Evaluation method was using the following method. XRD as phase identification, X-ray CT scan as structural analysis, SEM as a surface observation and Archimedes method to measure density. After create sample, It measure X-ray CT scans. From the X-ray CT scans result, fracture strength predicted. After that, It did bending test to compare to the predicted date. Result of compared, showed a nearly equivalent results of both. Namely, fracture strength can predict.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Joining and Coating for Reactor Components

Room: Oceanview

Session Chairs: Monica Ferraris, Politecnico di Torino; Stephen Gonczy, Gateway Materials Technology

8:00 AM

(ICACC-S13-036-2014) Joining of SiC Ceramics Using a Laser Beam-Aided Interlayer Forming

Y. Jung*, H. Kim, J. Park, W. Kim, Korea Atomic Energy Research Institute, Republic of Korea

A SiC-based ceramic composite is one of the most spotlighted materials for future nuclear power plants. Recently, a SiCf/SiC fuel cladding tube for application into a light water reactor was developed to enhance safety against accidents. However, there are several technical issues that should be resolved before its application; and the joining technology of SiC ceramics is one of them. In this investigation, SiC monoliths were bonded using a laser beam scanning method by forming an interlayer structure in-situ. The laser was operated in a continuous wave condition. During the scanning of laser beam, metallic powders of Ti or Si with 50–70 μm in an average particle size were supplied to form the bonding interlayer. The powders were melted instantaneously under a laser beam irradiation, and then solidified with cooling. The SiC was joined with the melted interlayer materials by forming a Ti3SiC2 and/or TiSi2 phase. The effect of interlayer types was also investigated. Metallic foils of Ti or Mo were inserted between the SiC plates during the laser beam scanning with and without the powder supply. When the metallic foils were applied to the laser beam scanning under the powder supply, deeper bonding layers and increased bonding

strength were obtained. In addition, glass-ceramics and lots of braze fillers developed for the joining of SiC ceramics were also tested as interlayer-forming materials in this study.

8:20 AM

(ICACC-S13-037-2014) Pressure-less joining materials for silicon carbide based components

M. Ferraris*, M. Salvo, V. Casalegno, S. Rizzo, Politecnico di Torino, Italy; A. Czyrska-Filemonowicz, T. Moskalewicz, AGH-University of Science and Technology, International Centre of Electron Microscopy for Materials Science and Faculty of Metals Engineering and Industrial Computer Science, Poland; M. Reece, Queen Mary, University of London and Nanoforce Technology, United Kingdom; S. Grasso, Queen Mary, University of London and Nanoforce Technology, United Kingdom; D. Blagoeva, P. van den Idsert, NRG, Netherlands

Joining of SiC-based materials for nuclear applications is of interest in particular if the joining process can be done without using any pressure. Pressure-less joining offers greater possibilities for joining dissimilar materials and for on-site or in the field joining processes and repairs. Several materials and techniques have been tested for pressure-less joining of SiC-based materials within an international cooperation involving EU, USA, and Japan. Three silica and non-silica based glass-ceramics and several non-oxide joining materials based on Ti-Si-C have been used to join SiC and SiC/SiC by pressure-less joining techniques such as slurry methods and spark plasma sintering. The glass-ceramic micro-structure and their interface with SiC have been investigated by transmission electron microscopy and selected area electron diffraction before neutron irradiation and by scanning electron microscopy after neutron irradiation.

8:40 AM

(ICACC-S13-038-2014) Processing and characterization of diffusion-bonded SiC for nuclear application

T. Koyanagi*, J. O. Kiggans, C. Shih, Y. Katoh, Oak Ridge National Laboratory, USA

Development of robust and irradiation-resistant joining technologies is critical for nuclear energy systems utilizing SiC and its composites. A collaboration project among U.S., Japan, and Italy recently demonstrated the irradiation tolerance of diffusion-bonded SiC at low to intermediate neutron doses. Based on this result, the next step of joining technology development is to identify the process conditions for optimized strength and microstructures. The joining methods studied in this work include the Ti or Mo diffusion bonding. Flat plates of chemical vapor deposition-SiC were joined by hot pressing with inserts of Ti or Mo foil of 0.025 mm thickness. The strength of the joints was evaluated by a double-notched shear testing for the initial estimate, then by a torsional shear testing for the quantitative measurement. Nano-indentation was also used to investigate the mechanical properties of the joint layers. Microstructures were examined mainly by scanning electron microscopy. X-ray diffraction analysis was used for phase identification. More than 100 MPa of nominal shear strength was obtained from both Ti and Mo diffusion joints by the torsion test. Specimens appeared to fail at the SiC base, indicating the adequate bonding strength. The paper will provide the detailed discussion on relationships among the process conditions, microstructure, and the mechanical properties of these joints.

9:00 AM

(ICACC-S13-039-2014) Comparison of shear strength of ceramic joints determined by various test methods with small specimens

C. Shih*, J. O. Kiggans, Oak Ridge National Laboratory, USA; H. E. Khalifa, C. A. Back, General Atomics, USA; T. Koyanagi, Y. Katoh, Oak Ridge National Laboratory, USA; M. Ferraris, Politecnico di Torino, Italy

Mechanical testing of the joint is an important part of the development of ceramic joining and integration technology. In this study, shear strength values were compared for various test methods, including asymmetric four point bend, double notched shear, Iosipescu shear, and torsion of solid hourglass, for SiC to SiC brittle joints. Emphasis has been put on the establishment of test schemes that are capable of applying true shear loading to small size specimens. For neutron irradiation stability studies, small specimens are beneficial because the reduction of expenses, radioactive wastes, and radiation exposure to personnel. The initial result confirmed reasonable statistics for the shear strength determined by the double notched shear test. The apparent shear strength of the joints strongly depends on the test method. The apparent shear strength values determined by these test methods are discussed in relation with various factors including the stress state and distribution, fracture process, and the effective volume/area of the maximum shear stress. The outcome from this study will support the test standard development for shear strength of ceramic joints in the ASTM C28 on Advanced Ceramics.

9:20 AM

(ICACC-S13-040-2014) Development of an ASTM C28 Test Standard for the Torsional Shear Strength of Adhesive Bonds for Advanced Ceramics

S. T. Gonczy*, Gateway Materials Technology, USA; Y. Katoh, Oak Ridge National Laboratory, USA; M. Ferraris, Politecnico di Torino, Italy

High temperature adhesive bonding (sintered bonds, fused glass-ceramic, brazes, etc) of ceramic parts (monolithic and composite) to form complex components is a critical engineering technology in the application of ceramics in high temperature, harsh service environments, such as nuclear power, aerospace, and heat transfer. The bond strength in shear and tension is a fundamental engineering property that needs to be determined across the entire temperature range. The ASTM C1469 shear strength test (asymmetrical 4 point bend) has size, relative strength, alignment, and temperature limitations. Recent work (at Politechnico di Torino and Oak Ridge National Laboratory) on torsional shear tests of adhesive face bonds in ceramics shows advantages in specimen size, simpler stress states, and gage section failure. That work is being used to develop a new ASTM C28 standard test method for the torsional shear strength of adhesive bonds in ceramics. The new test standard is addressing the full range of test factors –different specimen geometries, size effects, edge and notch stress concentrations, gripping methods, torsion fixtures, specimen alignment, bond uniformity, adhesive failure modes, failure analysis, and high temperature testing.

Fundamental Science of Microstructural Evolution under Irradiation

Room: Oceanview
Session Chair: Takaaki Koyanagi, Oak Ridge National Laboratory

10:00 AM

(ICACC-S13-041-2014) Understanding Radiation Damage in Zirconium Carbide

C. Ulmer*, A. Motta, Pennsylvania State University, USA; M. Zheng, I. Szlufarska, D. Morgan, University of Wisconsin-Madison, USA

Zirconium carbide is considered for use in the intermediate layers of TRISO-type fuel structure of Generation IV high temperature, gas-cooled reactors. A fundamental understanding of the microstructural evolution under irradiation, including defect formation, clustering and temperature dependence is needed in order to evaluate its potential to function in this role. To that end, in situ ion irradiations with 1 MeV Kr ions were performed using the IVEM at Argonne National Laboratory at temperatures ranging from 20 to 1073 K. The evolution of the microstructure with dose, temperature and sample characteristics such as foil thickness and orientation was determined by detailed analysis of TEM micrographs. A rate theory model of dislocation loop growth is developed to simulate the microstructural evolution of ZrC under irradiation conditions, where the parameters including migration energies and displacement energies were determined by detailed first principles calculations. Solution of the rate theory equations provides information on loop size distribution and concentration. The results of the rate theory model are compared with experimental data.

10:20 AM

(ICACC-S13-042-2014) Nanocrystalline ZrN behaviors under intensive radiation conditions

F. Lu, J. Lian*, RPI, USA

Nitride fuels such as (U, Pu)N have high fissile element density and thermal conductivity similar to metallic fuels and excellent thermal and radiation stability comparable to oxide fuels. Zirconium nitride (ZrN) is considered as a promising inert matrix for actinide incorporation, and bulk ZrN displays excellent radiation tolerance. In this study, nanocrystalline ZrN thin films, with an average grain size of 5 nm, were prepared by ion beam assisted deposition and irradiated by energetic ion beam. Their microstructural evolution and mechanical properties upon intensive radiation damage were investigated. The nanocrystalline ZrN maintained its isometric structure upon intensive displacive and ionizing irradiations. However, a unique structural contraction up to 1.42% in lattice parameter occurred only in nano-sized ZrN upon displacive irradiation 300 keV Ne+ and 350 keV O+. A significant nitrogen loss occurred with the reduction of the N:Zr atomic ratio to 0.88, probably a result of the production of displaced nitrogen atoms and fast diffusion along grain boundaries in nanocrystalline ZrN matrix. The hardness of the nanocrystalline films as measured by nano-indentation decreases with radiation damage level. Nitrogen vacancy accumulation and strain relaxation may be responsible for the unique structural contraction of nanocrystalline ZrN and radiation-induced softening.

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