Calcium-Magnesium-Alumino-Silicates (CMAS) Reaction Mechanisms and Resistance of Advanced Turbine Environmental Barrier Coatings for SiC/SiC Ceramic Matrix Composites

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Advanced Ceramic Matrix Composites:
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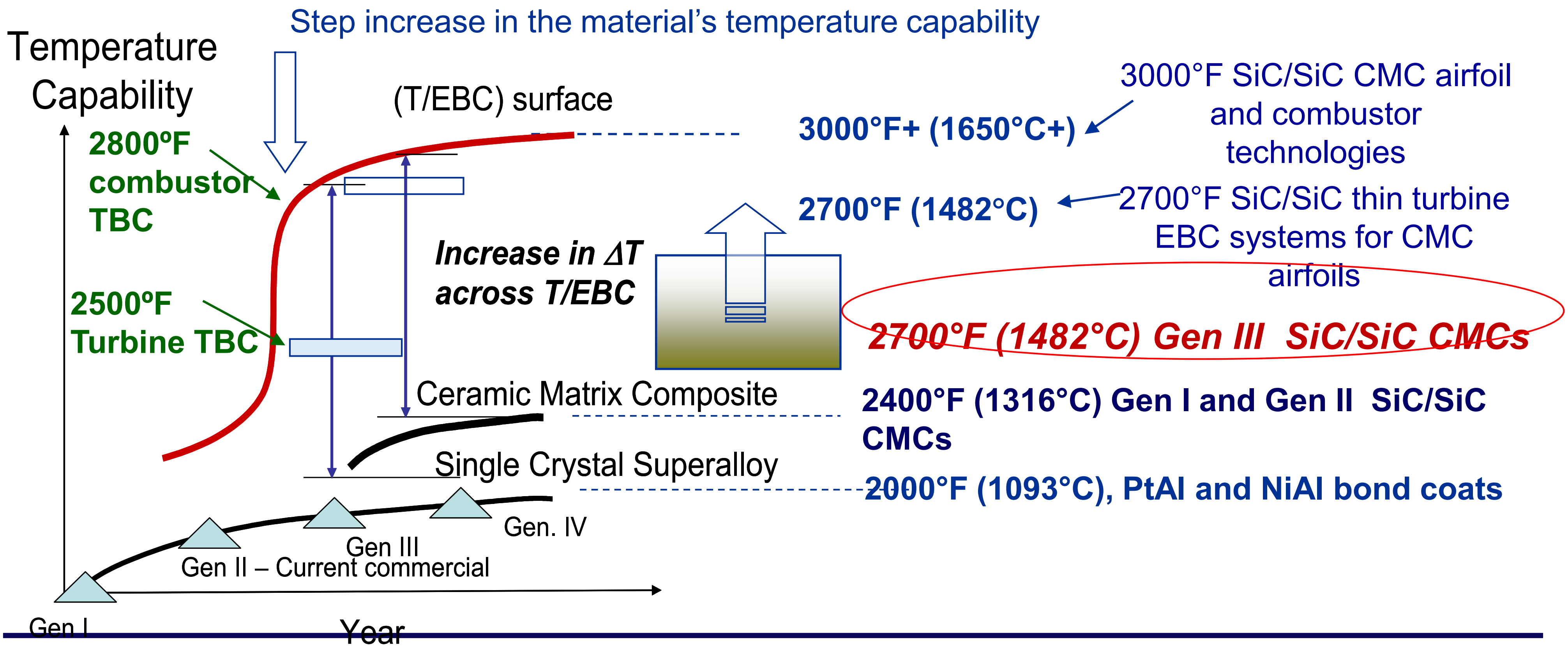
NASA Environmental Barrier Coatings (EBCs) and Ceramic Matrix Composite (CMC) System Development

- **Emphasize material temperature capability, performance and *long-term* durability-** Highly loaded EBC-CMCs with temperature capability of 2700°F (1482°C)
  - 2700-3000°F (1482-1650°C) turbine and CMC combustor coatings
  - 2700°F (1482°C) EBC bond coat technology for supporting next generation
    - Recession: <5 mg/cm^2 per 1000 h
    - Coating and component strength requirements: 15-30 ksi, or 100- 207 Mpa
    - Resistance to Calcium Magnesium Alumino-Silicate (CMAS)

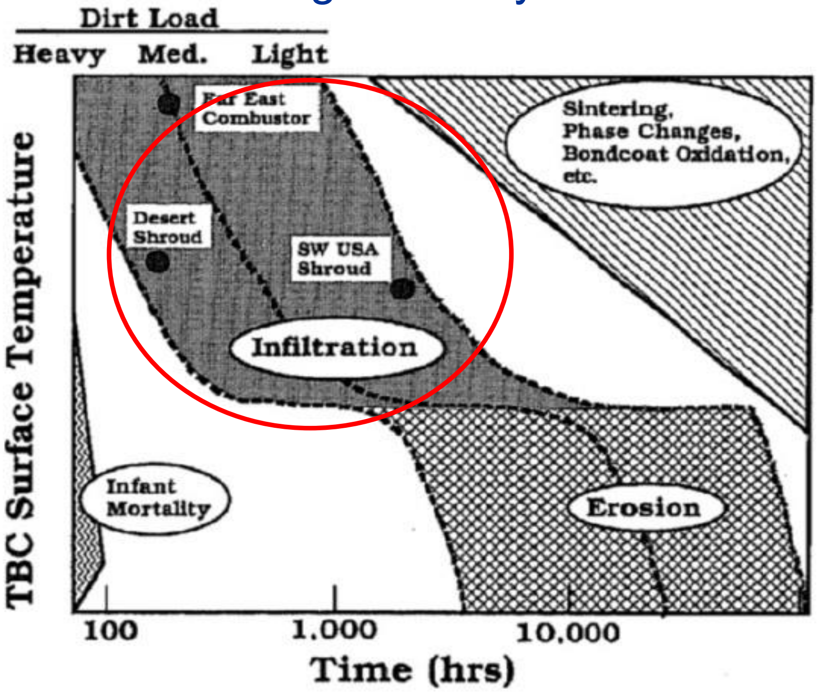


Outline

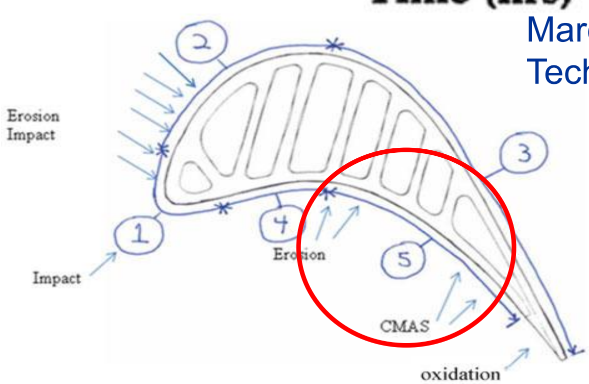
- **NASA environmental barrier coating (EBC) development: the CMAS relevance and importance**
  - EBC systems
  - CMAS compositions
- **Some generalized CMAS related failures**
- **CMAS degradation of environmental barrier coating (EBC) systems: rare earth silicates**
  - Ytterbium silicate and yttrium silicate EBCs
  - Some reactions, kinetics and mechanisms
- **Current advanced EBCs, HfO_2- and Rare Earth - Silicon based 2700°F+ capable bond coats**
  - Some CMAS durability tests and results
- **Summary**

EBC-CMAS Degradation is of Concern with Increasing Operating Temperatures

- **Emphasize improving temperature capability, performance and *long-term* durability of ceramic turbine airfoils**
  - Increased gas inlet temperatures for net generation engines lead to significant CMAS - related coating durability issues – CMAS infiltration and reactions



Marcus P. Borom et al, Surf. Coat. Technol. 86-87, 1996

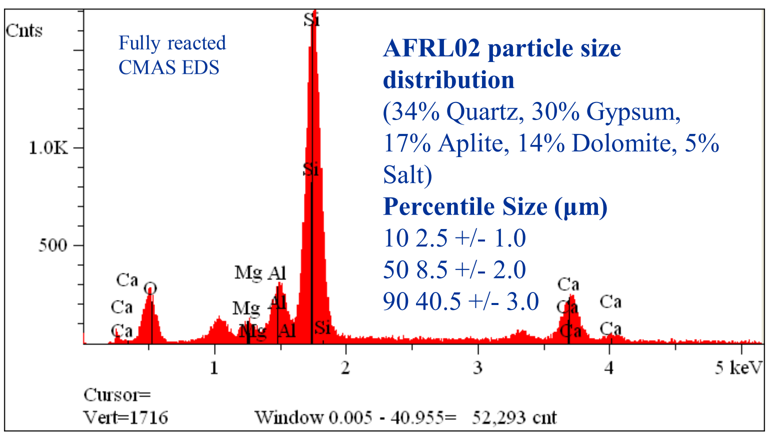


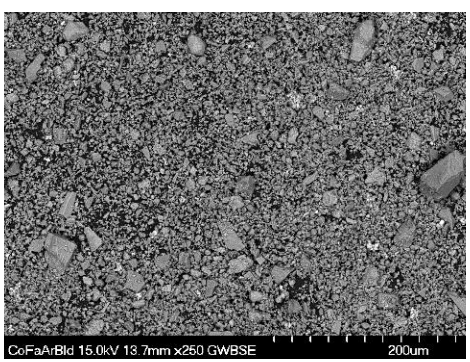
Current airfoil CMAS attack region - R. Darolia, International Materials Reviews, 2013

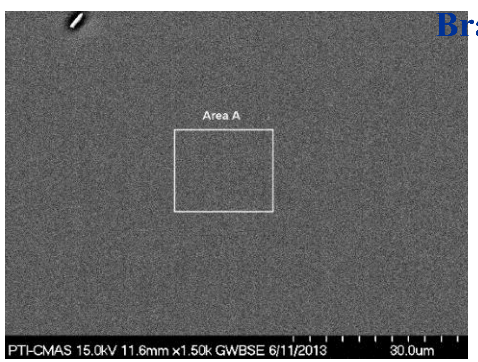
Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests

- NASA modified version (NASA CMAS), and the Air Force - Powder Technology Incorporated PTI 02 CMAS currently being used for advanced coating developments
- CMAS SiO_2 content typically ranging from 43-49 mole%; such as NASA's CMAS (with NiO and FeO)

ARFL PTI 11717A 02







As received　　Fully reacted

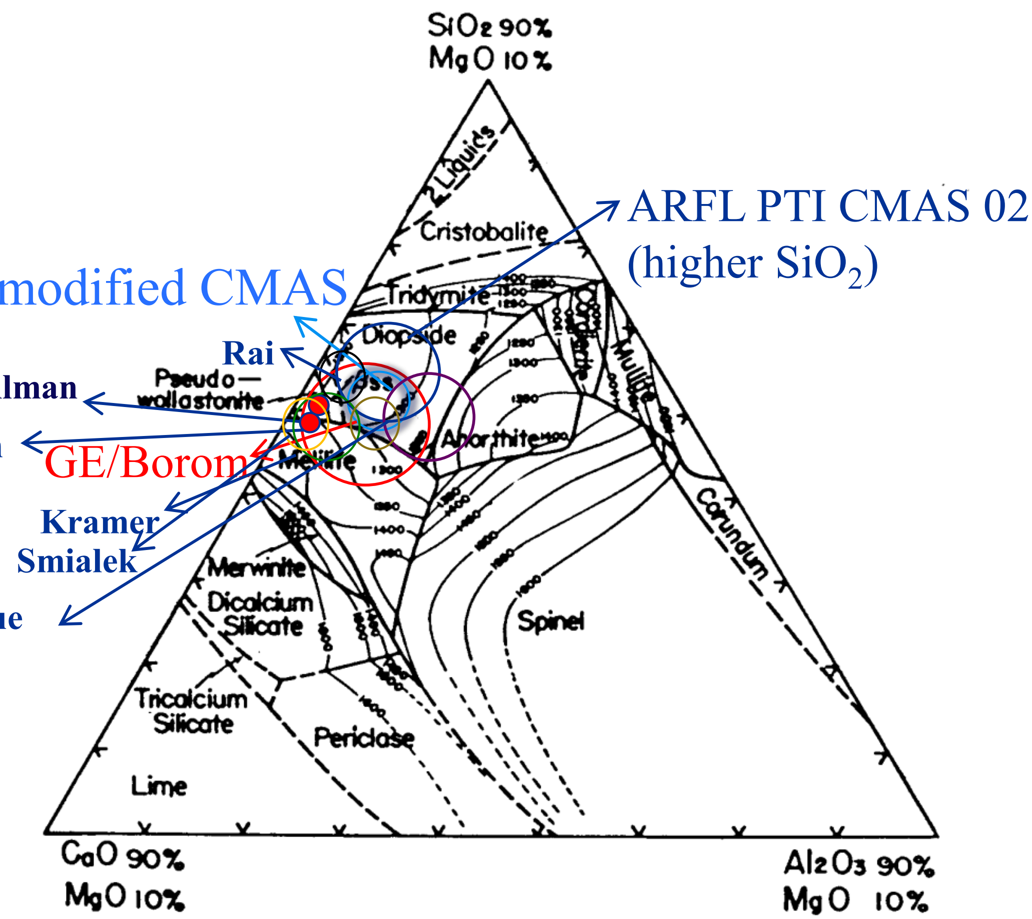


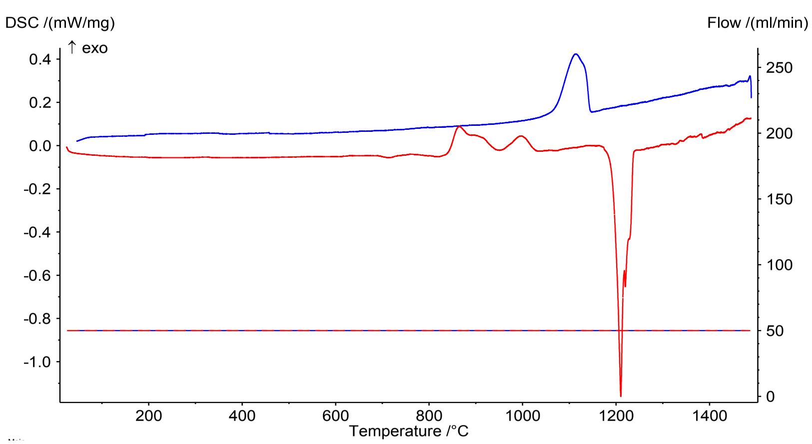
Fig. 4. The 10% MgO plane of the system $CaO-MgO-Al_2O_3-SiO_2$ showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests - Continued

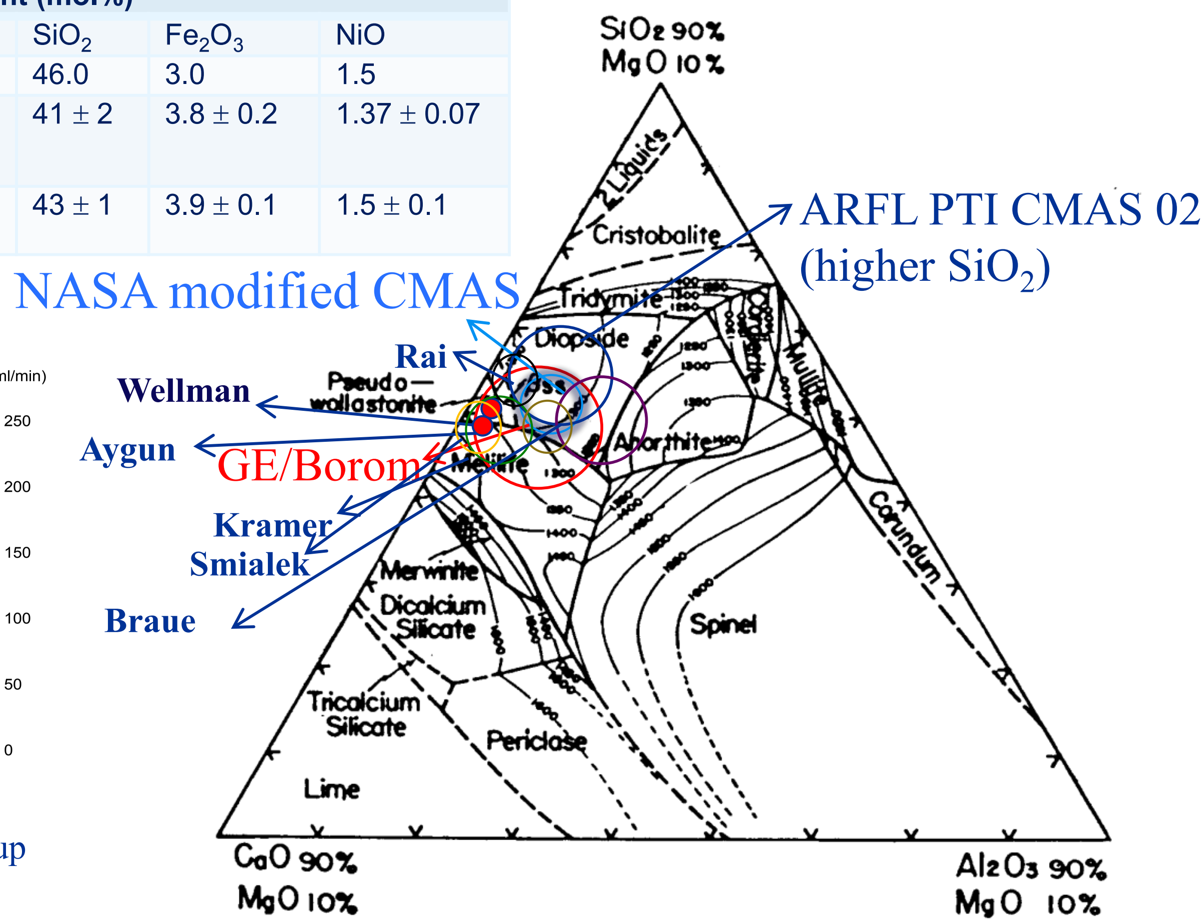
- NASA modified version (NASA CMAS)
- CMAS SiO_2 content typically ranging from 43-49 mole%; such as NASA's CMAS (with NiO and FeO)

NASA CMAS Compositions

Method	Content (mol%)					
	CaO	MgO	Al_2O_3	SiO_2	Fe_2O_3	NiO
(Designed/Targeted)	33.8	9.0	6.7	46.0	3.0	1.5
Measured by ICP-OES	38 ± 2	9.0 ± 0.5	6.9 ± 0.3	41 ± 2	3.8 ± 0.2	1.37 ± 0.07
Measured by EDS	36 ± 1	8.4 ± 0.3	7.5 ± 0.2	43 ± 1	3.9 ± 0.1	1.5 ± 0.1



DSC traces of CMAS during heating and cooling up to 1500 °C at 5 °C/min.



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Advanced NASA EBC Developments

	Gen I (EPM) R&D Award	Gen II (UEET) 2000-2004	Advanced EBC (UEET) 2000-2005 R&D Award (2007)	Advanced EBC (FAP) 2005-2011 R&D Award (2007) coating turbine development	**Advanced EBC (FAP - ERA) 2007 - present Advanced (FAP, ERA) Patent**13/923,450 PCT/US13/46946, and subsequent patents	
Engine Components:	Combustor	Combustor/ (Vane)	Combustor/ Vane	Vane/ Blade	**- Vane/Blade EBCs - Equivalent APS combustor EBCs**	**Airfoil components**
Top Coat:	BSAS (APS)	$RE_2Si_2O_7$ or RE_2SiO_5 (APS)	- *(Hf,Yb,Gd,Y)* $_2O_3$ - *ZrO_2/HfO_2+RE silicates* - *ZrO_2/HfO_2+BSAS* (APS and EBPVD)	RE-HfO_2-Alumino silicate (APS and/or 100% EB-PVD)	**RE-HfO_2-X advanced top coat RE-HfO_2Silica (EB-PVD, etc vapor deposition)**	**Advanced EBCs**
Interlayer:	--	--	RE-HfO_2/ZrO_2-aluminosilicate layered systems	Nanocomposite graded oxide/silicate	--	
EBC:	Mullite+ BSAS	$RE_2Si_2O_7$/and or BSAS+Mullite	RE silicates or RE-Hf mullite	RE doped mullite-HfO_2 or RE silicates	**Multi-component RE silicate systems**	**Multicomponent RE-silicate + Hf /self grown**
Bond Coat:	Si	Si	Oxide+Si bond coat	HfO_2-Si-X, doped mullite/Si SiC nanotube	**Optimized HfO_2-Si-X bond coat 2700°F bond coats**	**RE-Si+Hf systems**
Thickness	10-15 mil	10-15 mil	15-20 mil	10 mil	**5 mil**	**1 -3 mils**
Surface T:	Up to 2400°F	2400°F	3000°F/2400CMC	2700°F/2400F CMC	**2700-3000°F**	
Bond Coat T:	Limited to 2462°F	Limit to 2462°F	Limit to 2642°F	Proven at 2600°F +; Advancements targeting 2700°F	**2700°F**	

Challenges overcome by advancements:

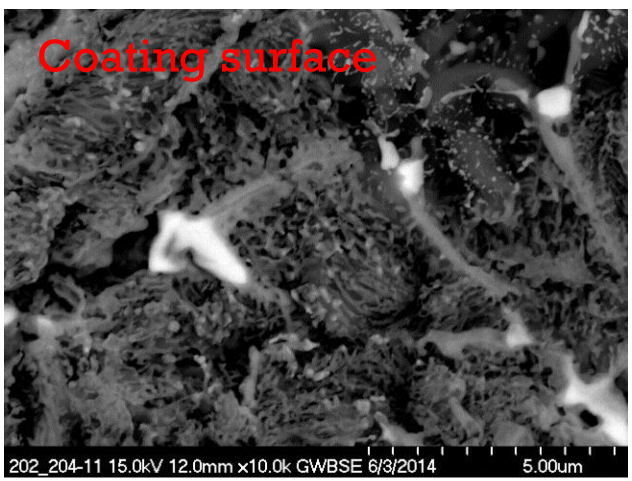
Improved temperature capability, sintering, phase stability, recession resistance, and high temperature strength

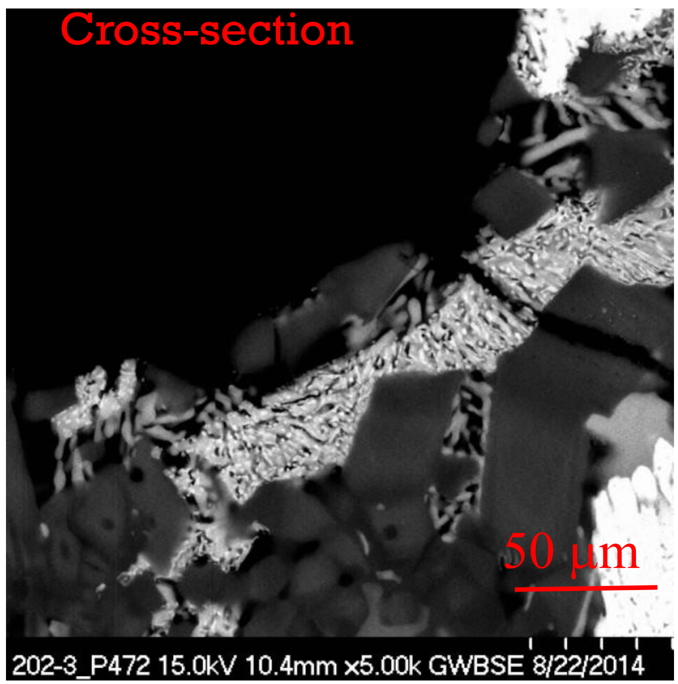
Advanced compositions & processing for combined thermomechanical loading and environments, higher stability and increased toughness towards prime-reliant

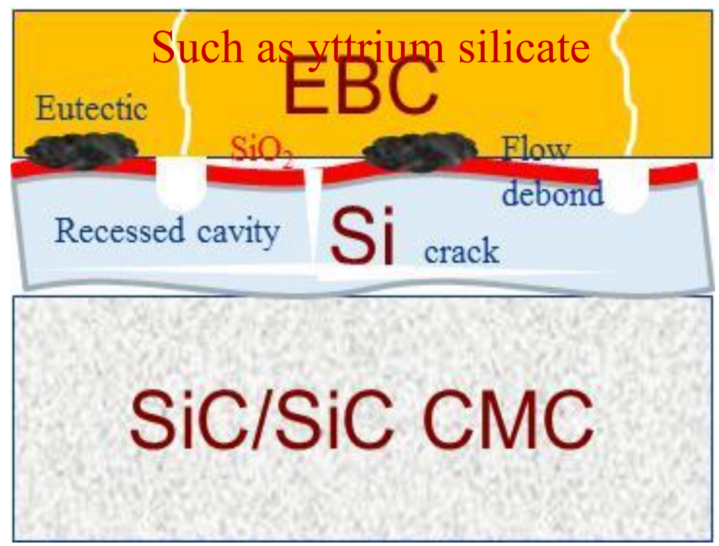
CMAS Related Degradations in EBCs

– CMAS effects

- Significantly reduce melting points of the EBCs and bond coats
- More detrimental effects with thin airfoil EBCs
- CMAS weakens the coating systems, reducing strength and toughness
- MAS increase EBC diffusivities and permeability, thus less protective as an environmental barrier
- CMAS interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue
  - Reaction layer spallations
  - Accelerated CMC failure when CMAS intact with CMCs





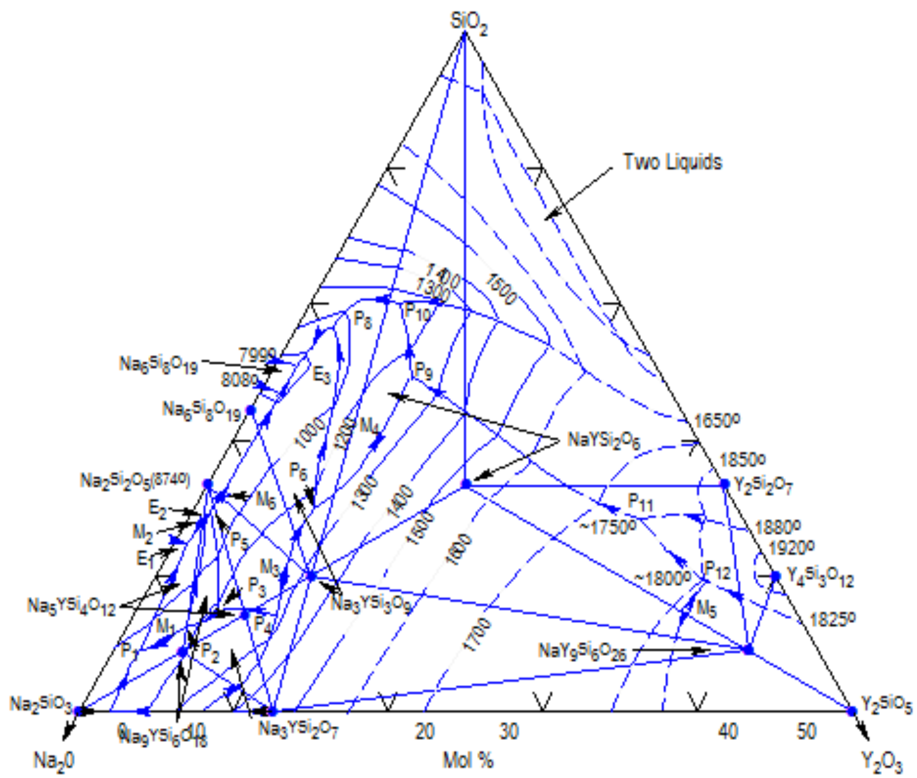


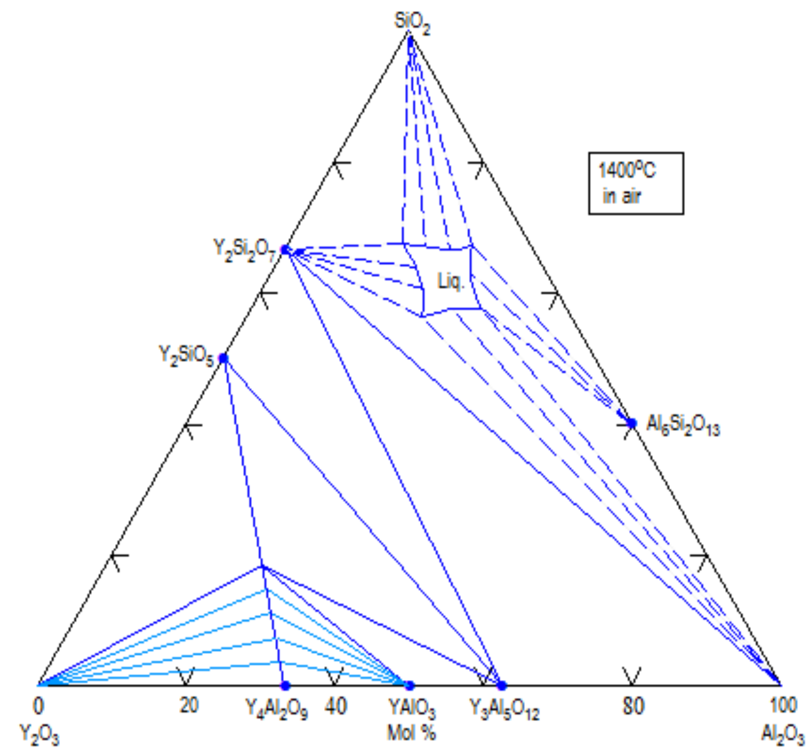
EBC and degradations

CMAS induced melting and failure $

CMAS Related Degradations in EBCs - Continued

– **CMAS effects on EBC temperature capability**
  - Silicate reactions with NaO_2 and Al_2O_3 silicate

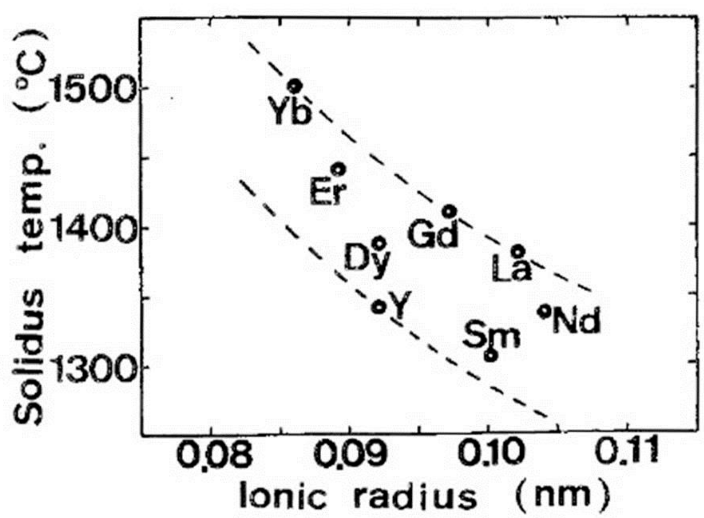




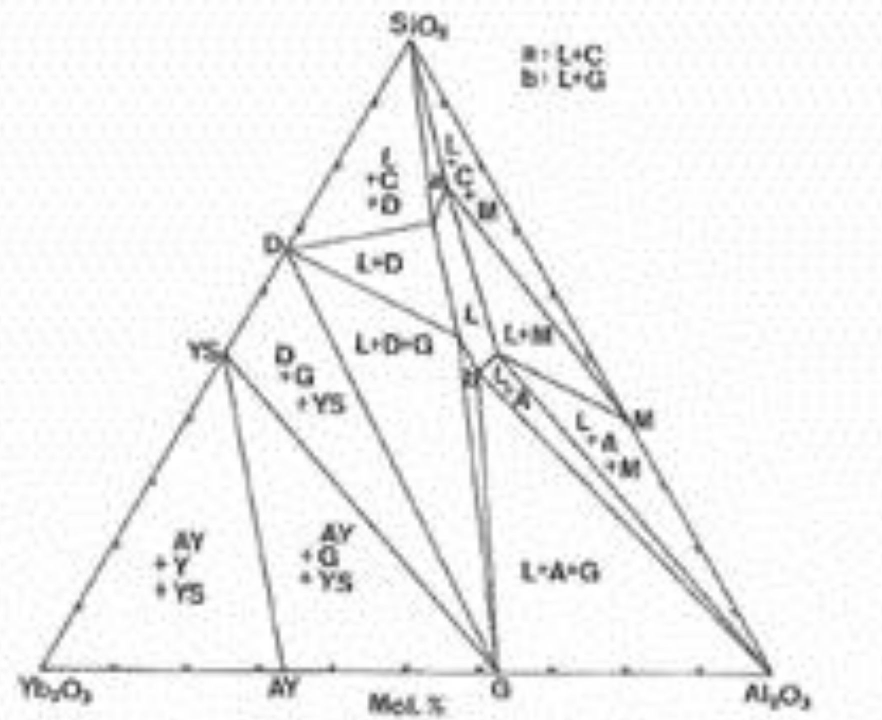
Phase diagrams showing yttrium di-silicate reactions with SiO_2, NaO and Al_2O_3

CMAS Related Degradations in EBCs - Continued

– **CMAS effects on EBC temperature capability**
  - Rare earths generally have limited temperature capability below 1500°C in the RE_2O_3-Al_2O_3-SiO_2 based systems,
  - Smaller ionic size REs have higher melting points



Solidus temperature in $Ln_2Si_2O_7$-$Al_6Si_2O_{13}$-SiO_2 system as function of ionic radius

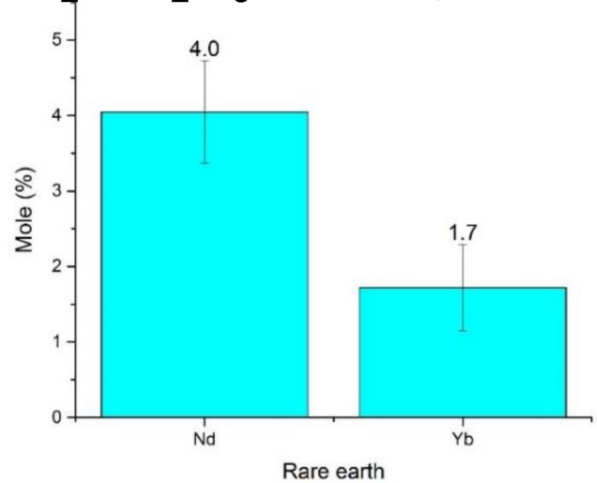


Phase diagram of the Al_2O_3–Yb_2O_3–SiO_2 system at 1550°C.
L: represents liquid phase, C: SiO_2 (cristobalite), D: $Yb_2Si_2O_7$, YS: Yb_2SiO_5, Y: Yb_2O_3, AY: $Al_2Yb_4O_9$, G: $Al_{1.xx}Yb_{x.xx}O_3$, A: Al_2O_3, M: $Al_6Si_2O_{13}$.

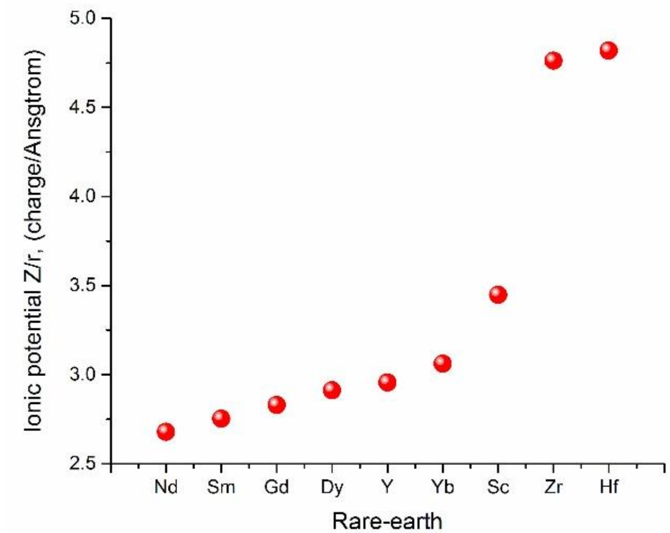
Y. Murakami and H. Yamamoto, *J. Ceram. Soc. Jpn.*, **101** [10] 1101-1106 (1993).

Rare Earth Dissolutions in CMAS Melts

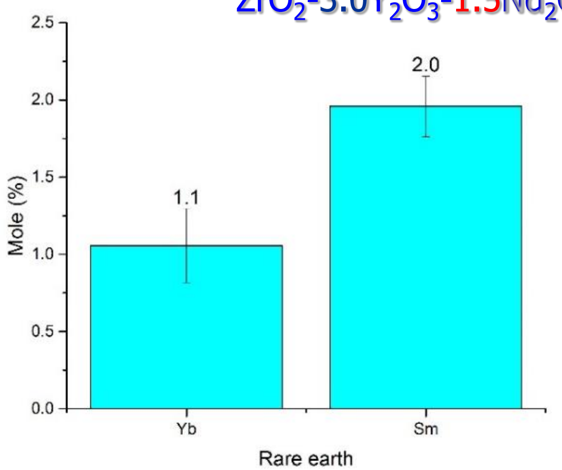
− Large ionic size rare earths showed higher concentration dissolutions in the CMAS melt for ZrO_2-RE_2O_3 oxide systems



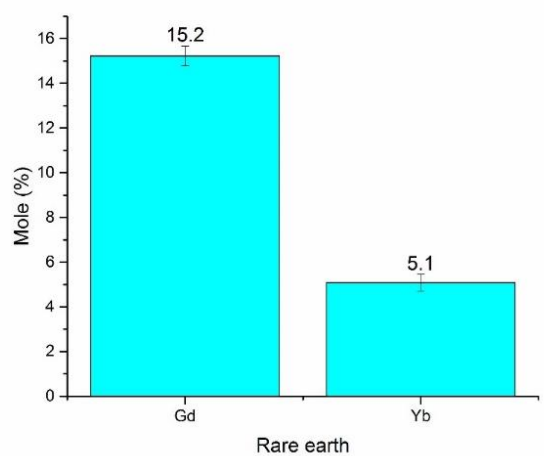
ZrO_2-3.0Y_2O_3-1.5Nd_2O_3-1.5Yb_2O_3-0.3Sc_2O_3



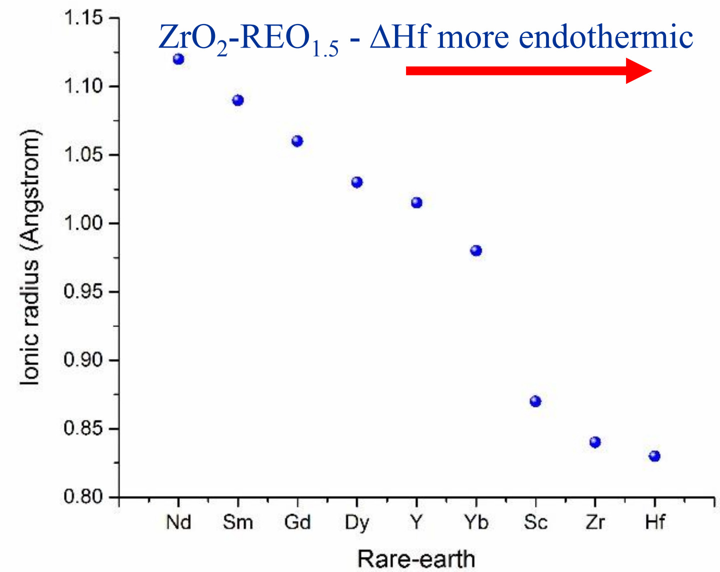
Ionic potential trend of RE



ZrO_2-3.0Y_2O_3-1.5Sm_2O_3-1.5Yb_2O_3



ZrO_2-9.6Y_2O_3-2.2Gd_2O_3-2.1Yb_2O_3



Radius size trend of RE

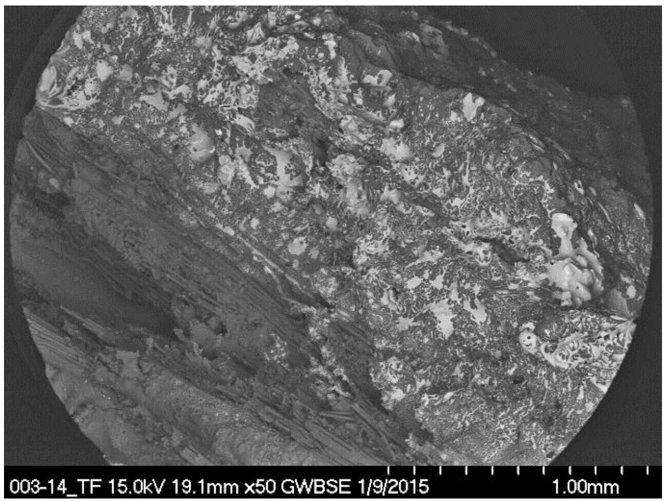
Gustavo and Zhu, International Conference on Advanced Ceramics and Composites, 2016

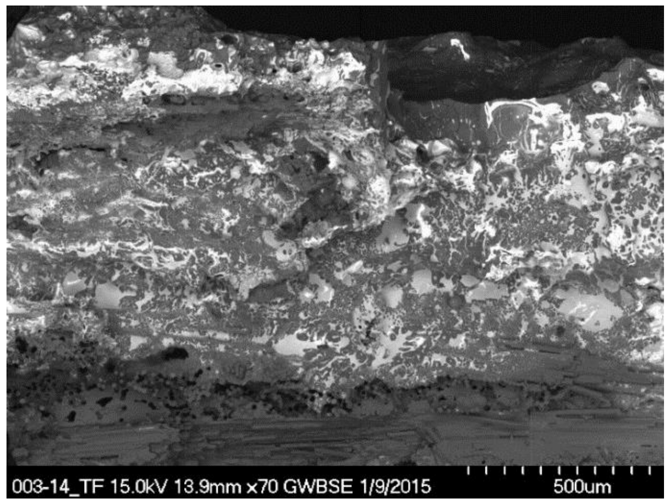
CMAS Related Degradations in EBC coated CMCs – Laboratory Heat Flux Tests

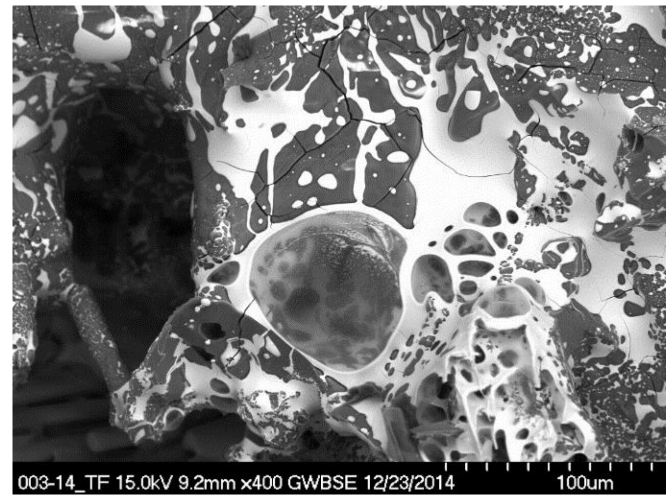
– **CMAS effects on EBC-CMC temperature capability tested in laser high heat flux creep-rupture rig**

- Accelerated failure of CMC in loading high heat flux conditions

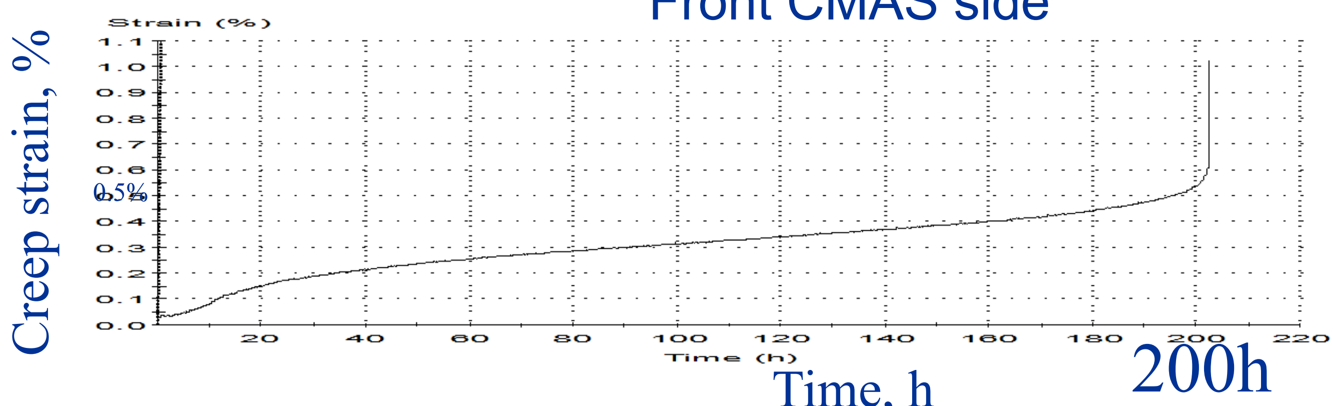
EBC coated CVI-MI CMC with NdYb silicate RESi bond coat, tested Tsurface 2600°F; T_{CMC} 2450°F





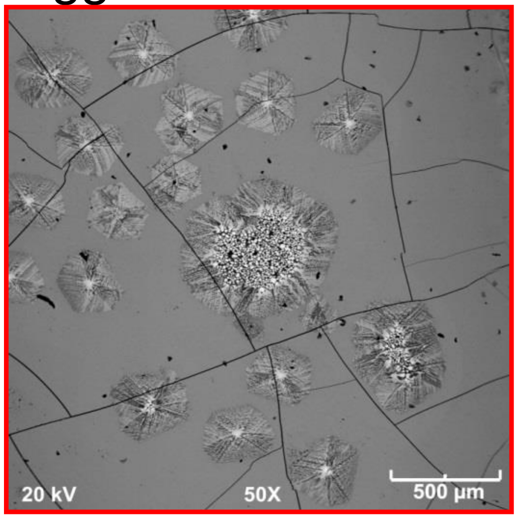


Front CMAS side

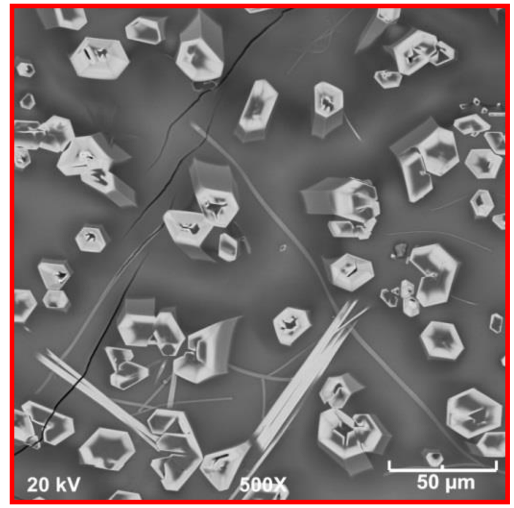


EBC CMAS Surface Initial Nucleation, Dissolution Reactions

- Ytterbium- and yttrium-silicate silicates reactions and dissolutions in CAMS
- More sluggish dissolution of ytterbium as compared to yttrium



Ytterbium di-silicate surface CMAS melts: 50 h 1300°C



Ytterbium di-silicate surface CMAS melts: 5 h 1500°C $

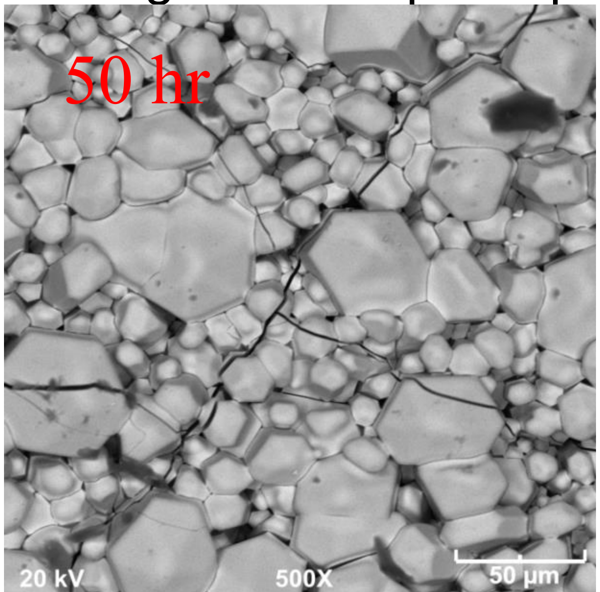
Yttrium mono-silicate surface CMAS melts: 50 h 1300°C

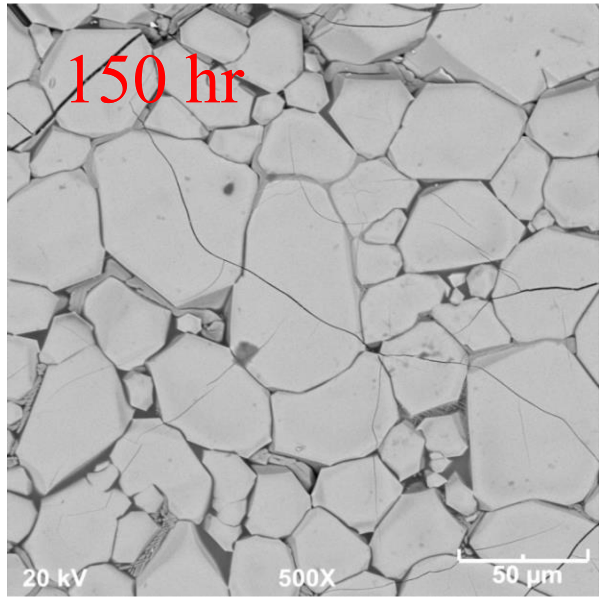
Yttrium silicate surface CMAS melts: 5 h 1500°C

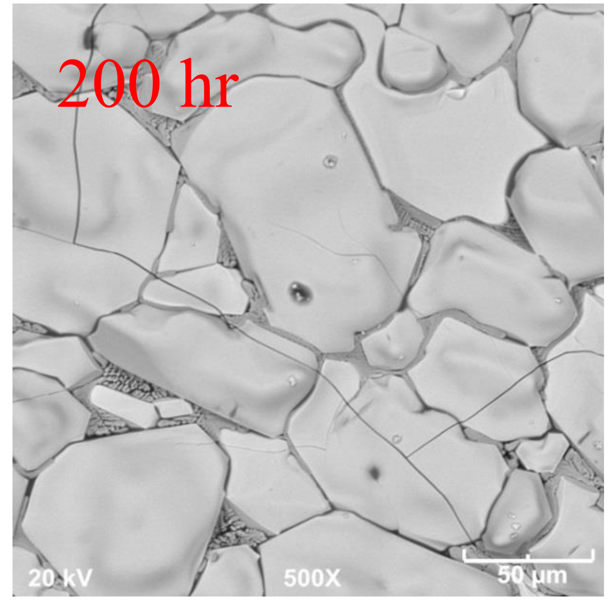
Ahlborg and Zhu, Surface & Coatings Technology 237 (2013) 79–87.

Rare Earth Apatite Grain Growth

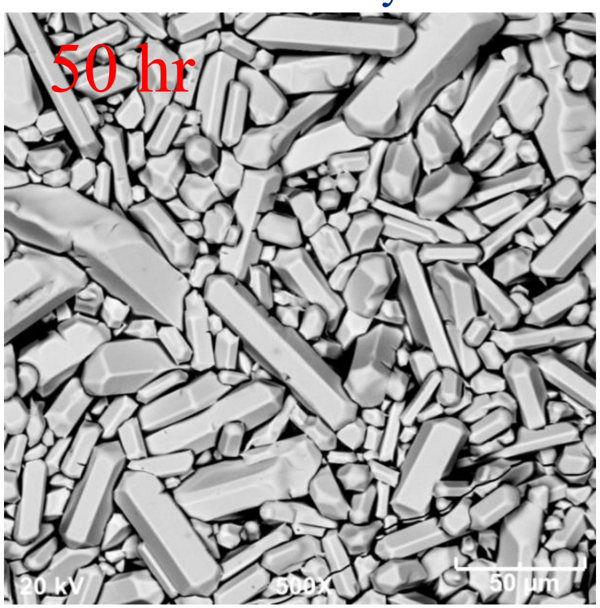
– Grain growth of apatite phase at 1500°C at various times

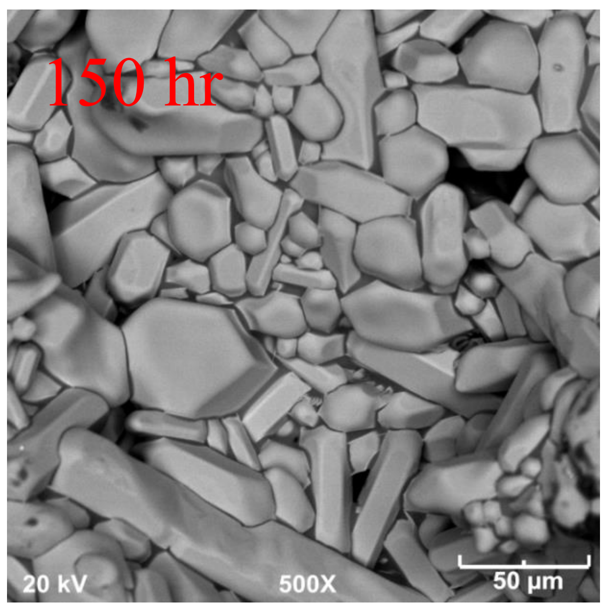


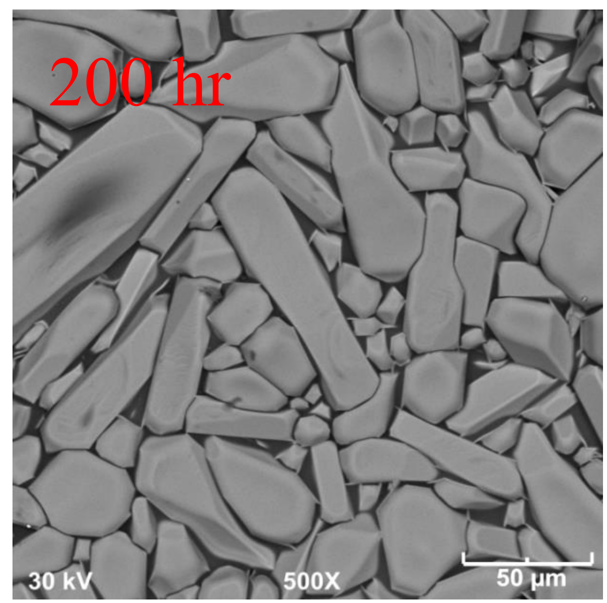




Ytterbium silicate system



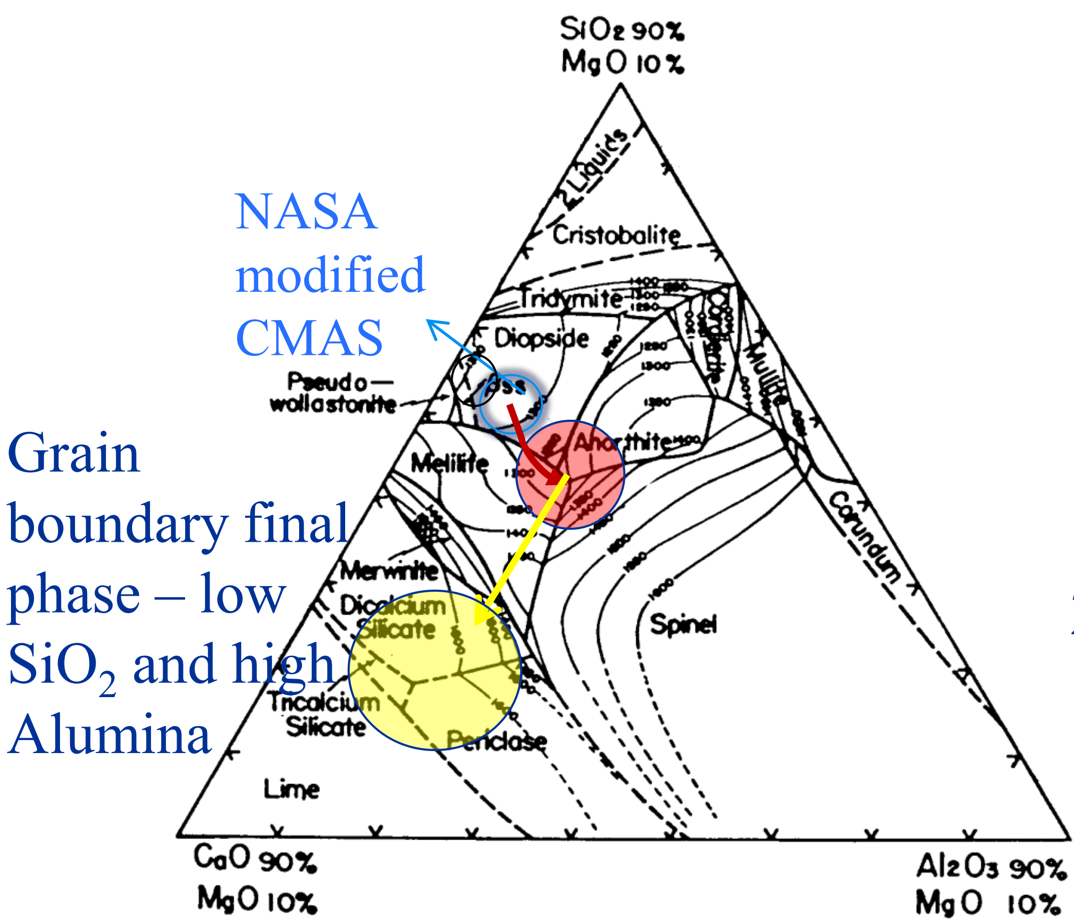




Yttrium silicate system $

Effect of CMAS Reactions on Grain Boundary Phases

- CMAS and grain boundary phase has higher Al_2O_3 content (17-22 mole%)
  - Eutectic region with high Al_2O_3 content ~1200°C melting
  - Loss of SiO_2 due to volatility



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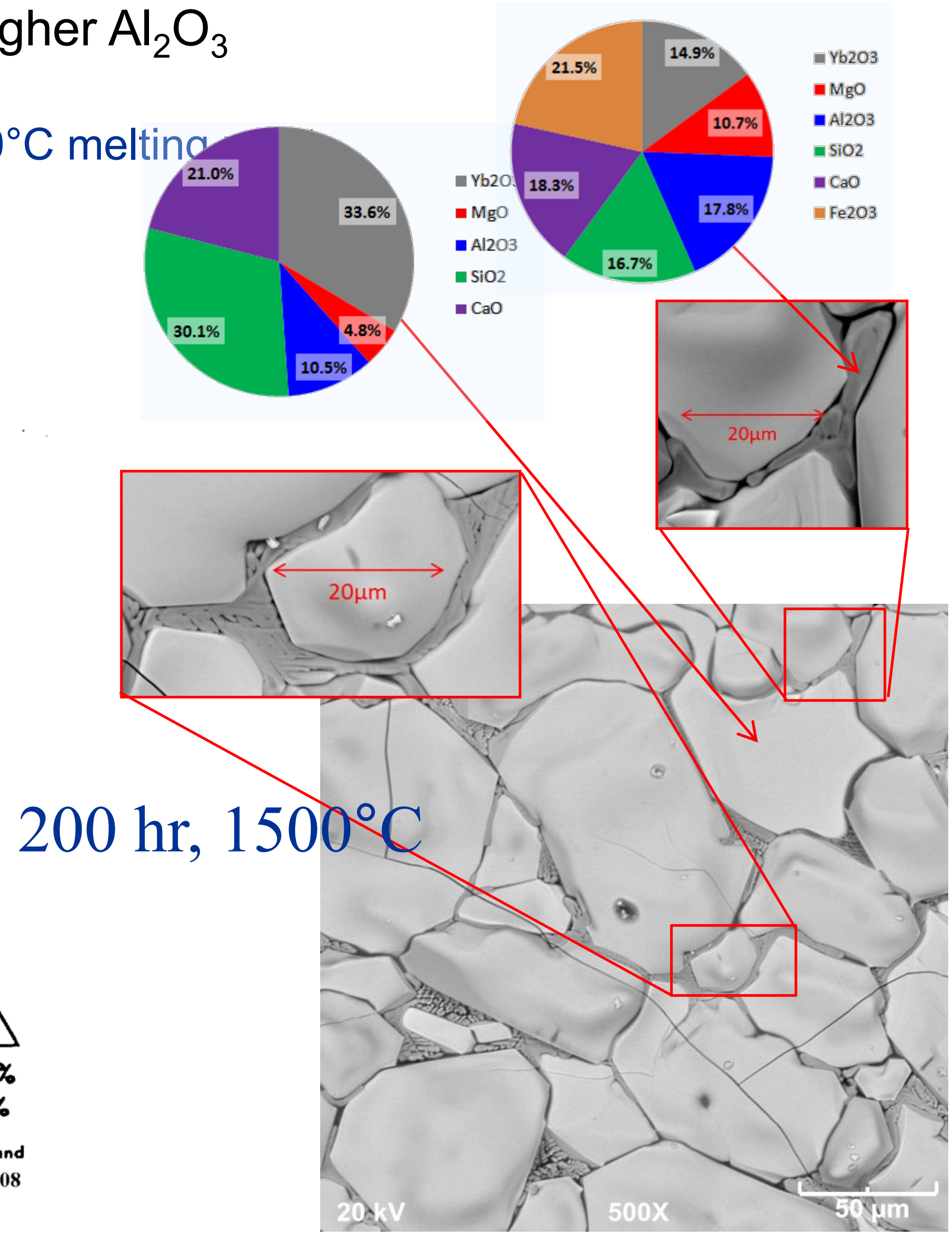
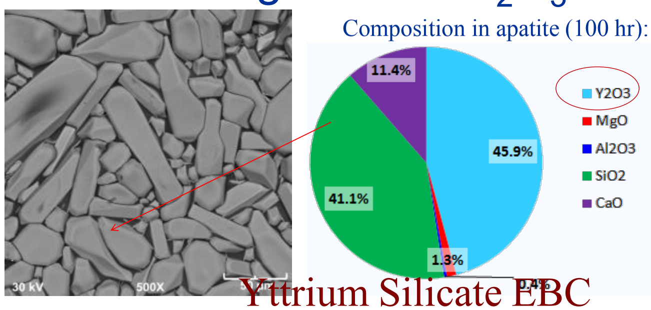
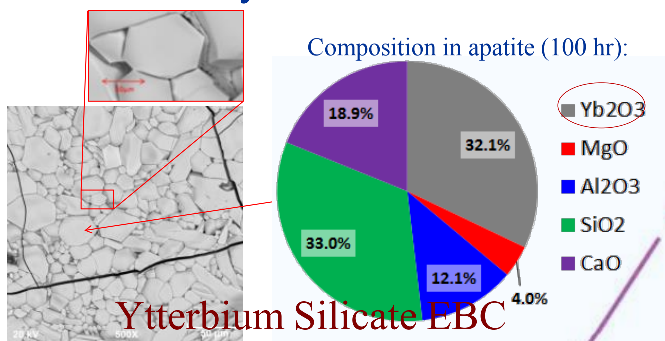


Rare Earth Dissolution in CMAS Melts

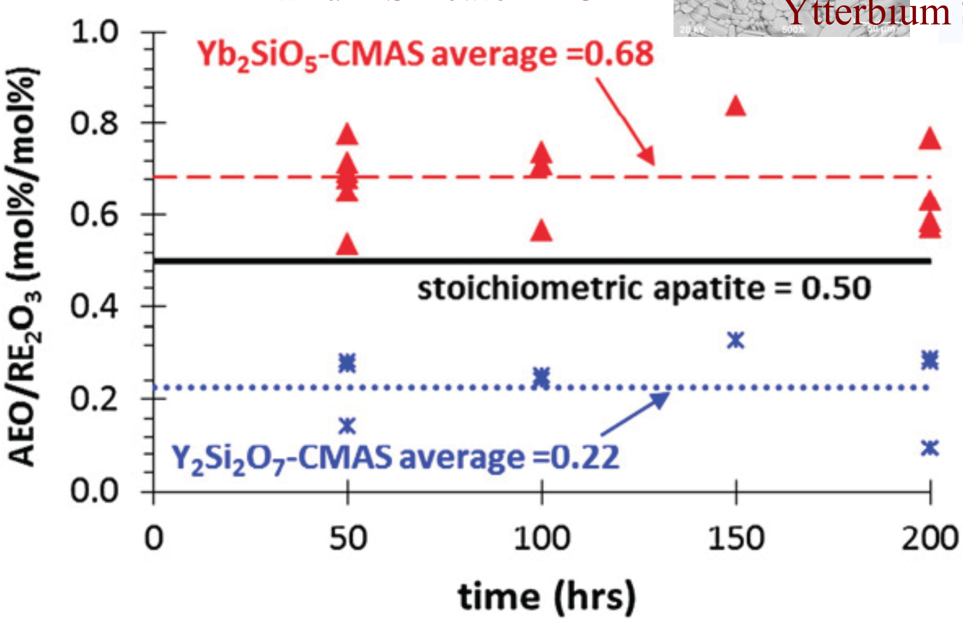
- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases – up to 200 h testing
- Difference in partitioning of ytterbium vs. yttrium in apatite
  - Average AEO/RE_2O_3 ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE_2O_3 ratio ~ 0.22 for yttrium silicate – CMAS system

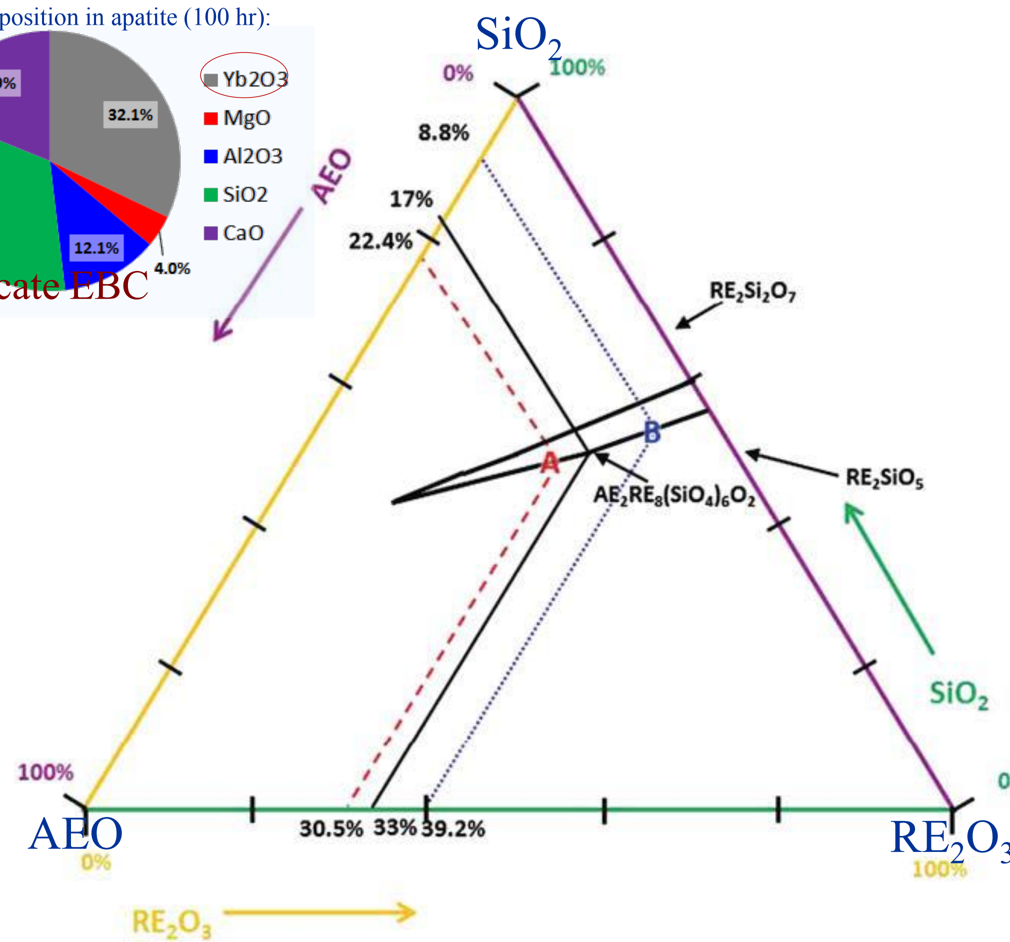


Yttrium Silicate EBC



Ytterbium Silicate EBC

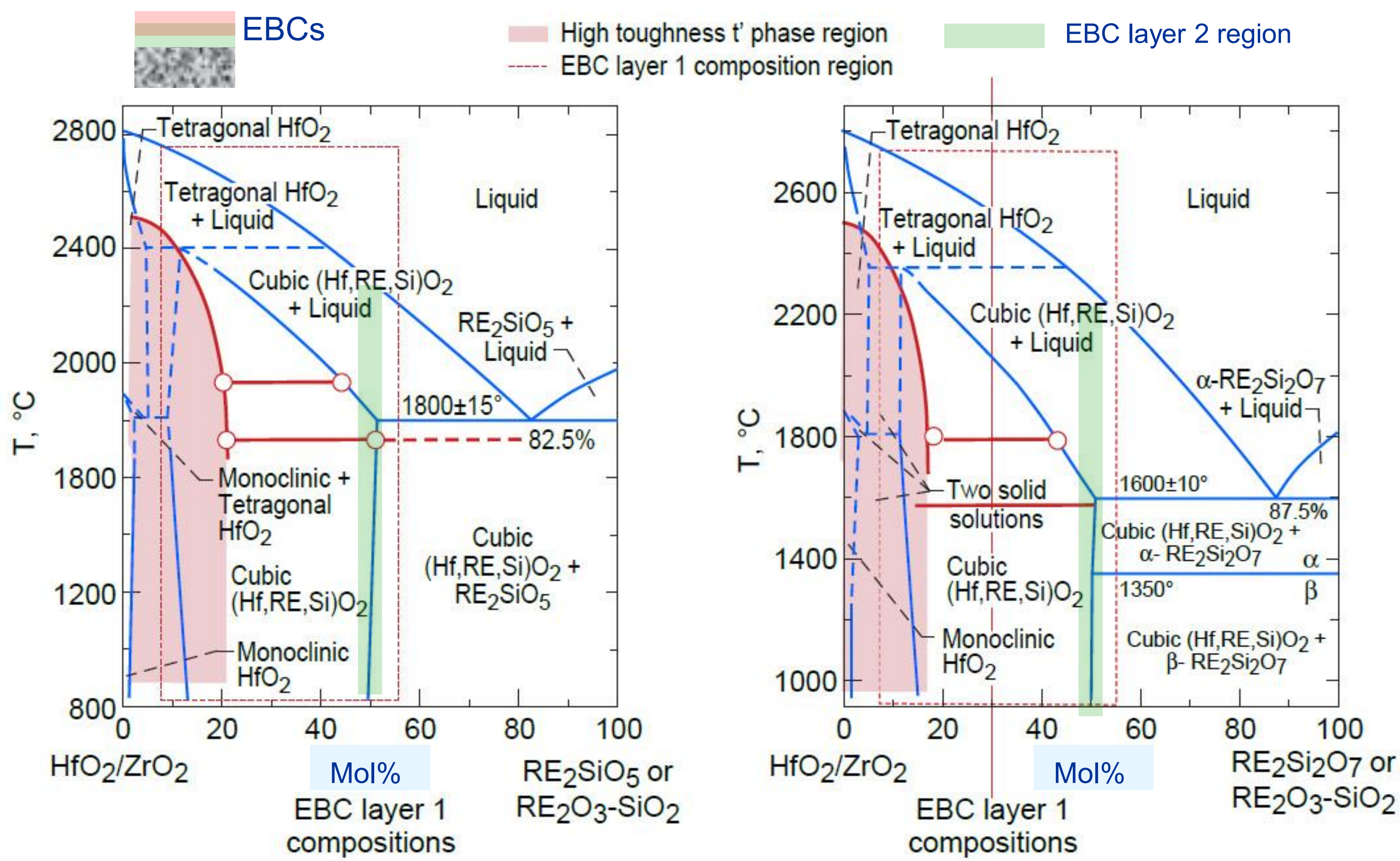


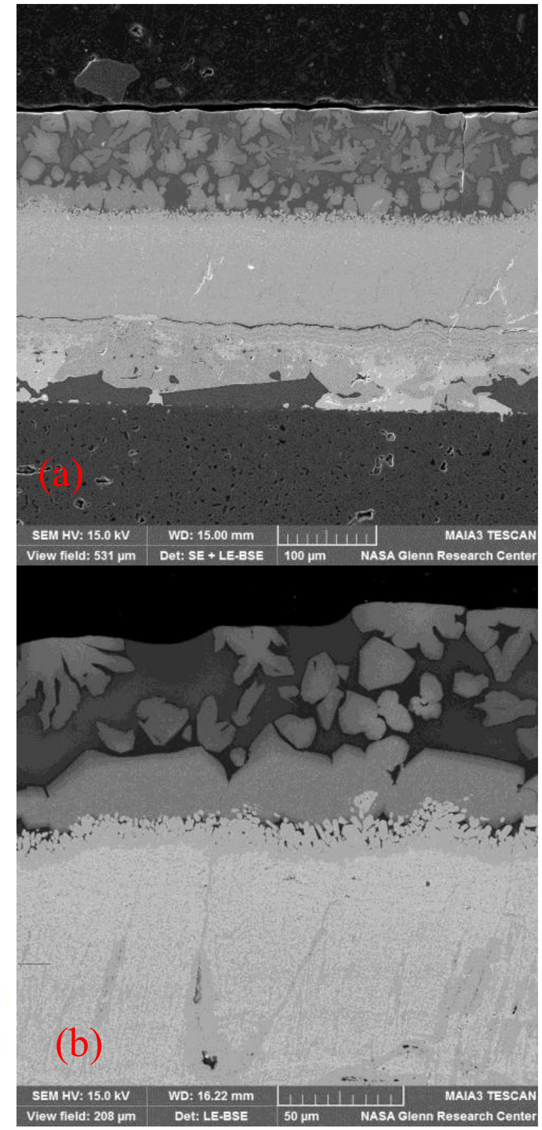


Ahlborg and Zhu, Surface & Coatings Technology 237 (2013) 79–87.

Advanced NASA EBC Developments

NASA advanced EBC systems emphasizing high stability HfO_2- and ZrO_2-RE_2O_3-SiO_2 EBC system, $RE_2Si_{2-x}O_{7-2x}$, such as $(Yb,Gd,Y)_2Si_{2-x}O_{7-2x}$
- Controlled dissolution and maintaining coating stability

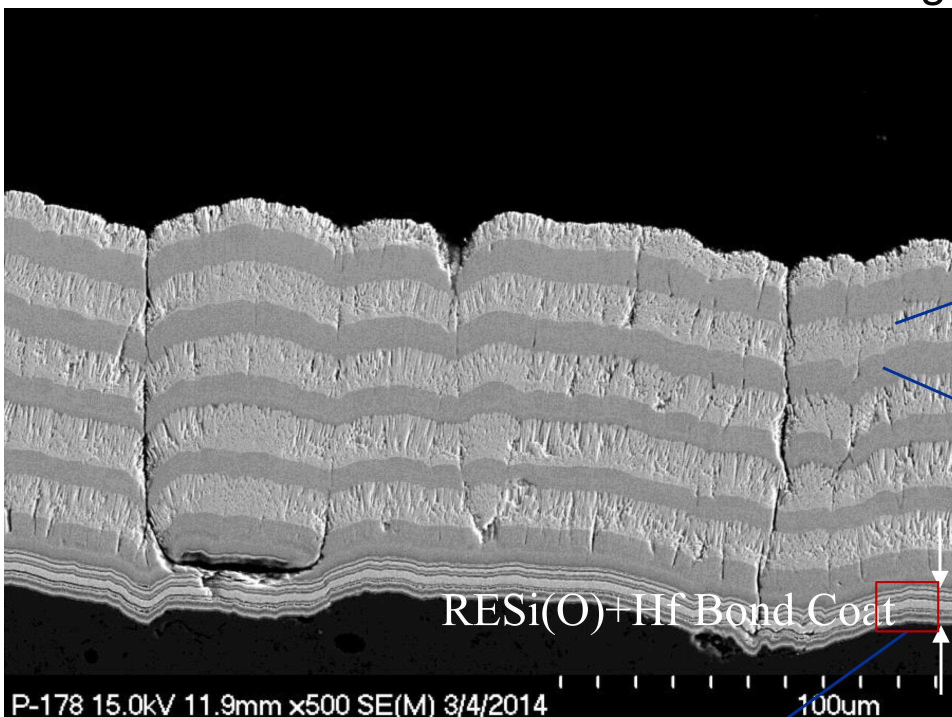


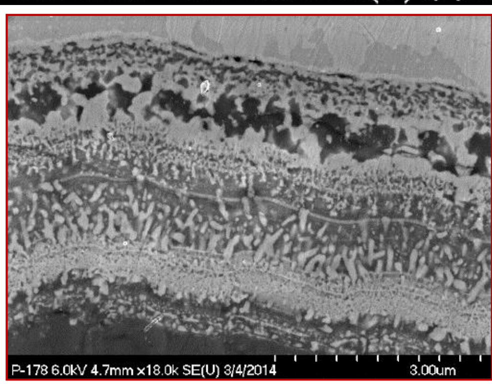


$(Yb,Gd,Y)_2Si_{2-x}O_{7-2x}$ in CMAS, 1300°C

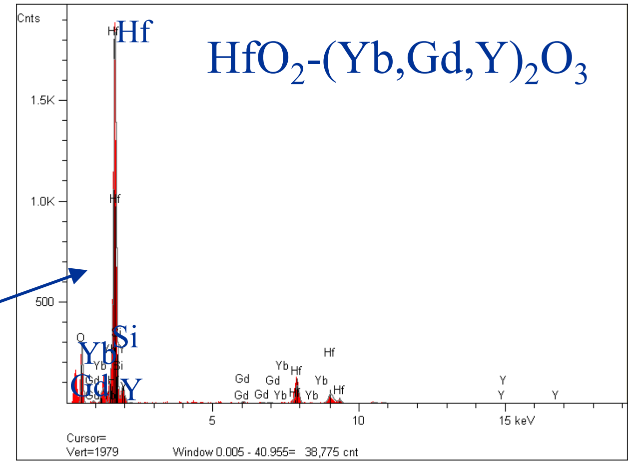
Example of NASA Advanced Environmental Barrier Coating on SiC/SiC CMC Systems

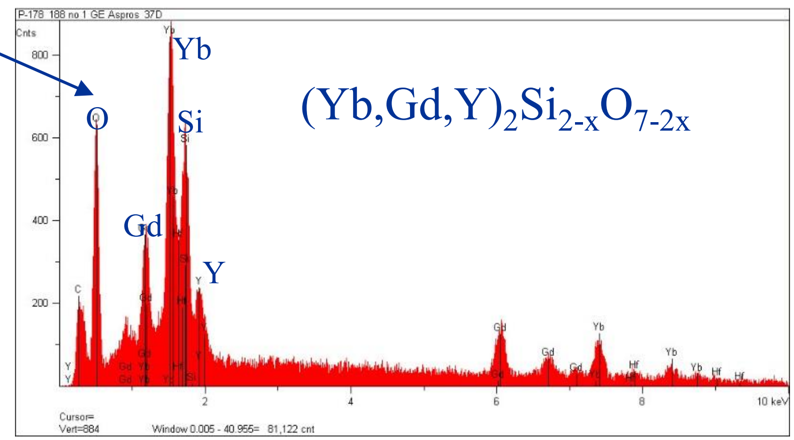
- Alternating layered HfO_2- Multicomponent Rare Earth silicate EBCs used, for fundamental stability studies
- 2700°F capable Yb/Gd-YbO+Hf based bond coats
- Coated onto SiC/SiC CMC substrates using EB-PVD





The bond coat region

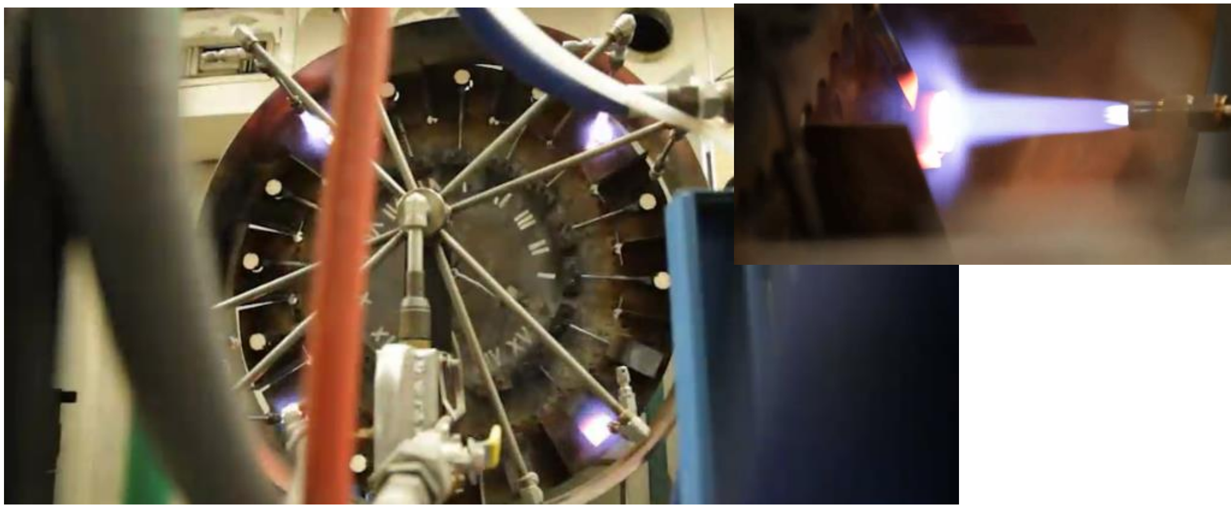


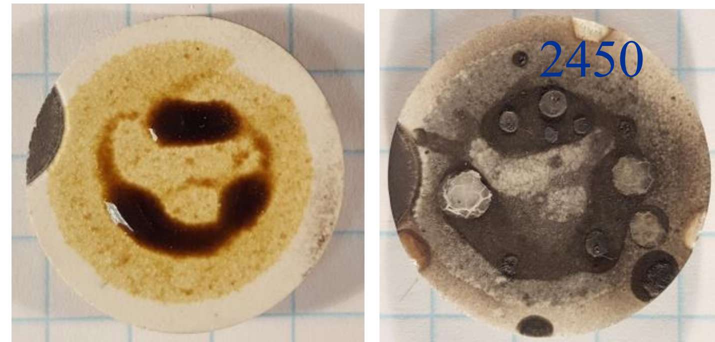


Advanced EBC coated vanes

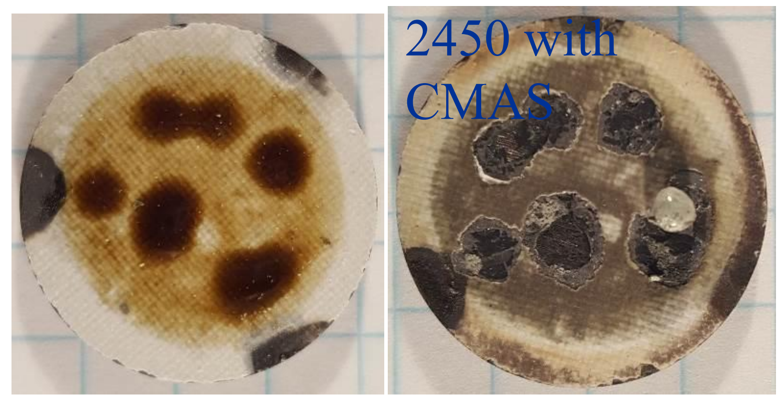
CMAS Resistant Tests

– JETs test of more advanced coating systems at 2700F

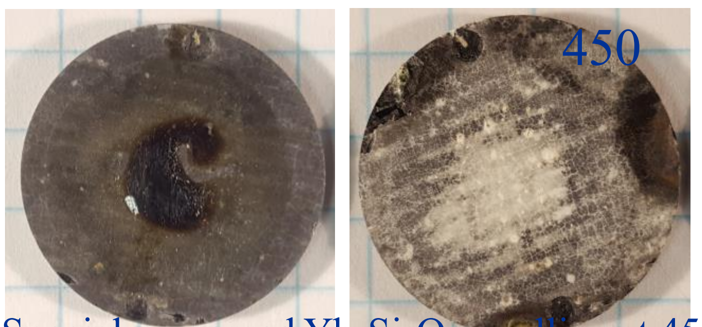




Plasma sprayed $(Gd,Y)_2Si_2O_7$, 2450 cycles



EB-PVD $(Yb,Gd,Y)_2Si_2O_7$, total 4450 JETS cycles, 100h



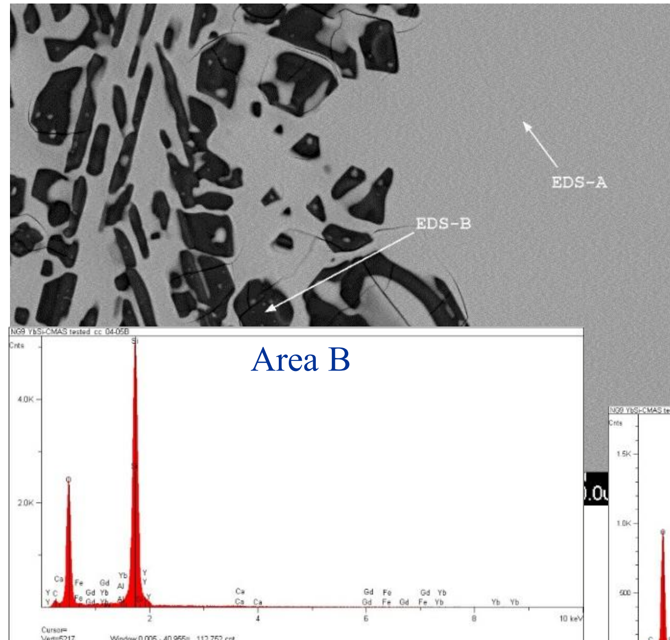
Special processed $Yb_2Si_2O_7$, spalling at 450 Cycles

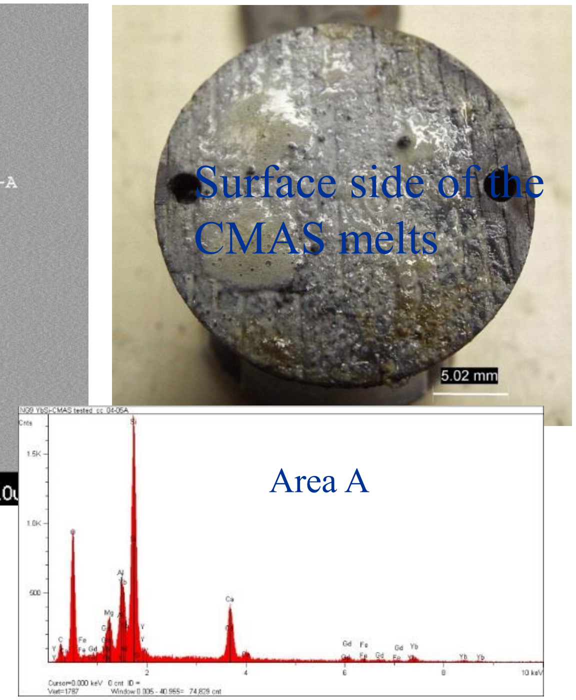
Hybrid Hf-rare earth aluminate silicate, completed 4450 cycles, 100h

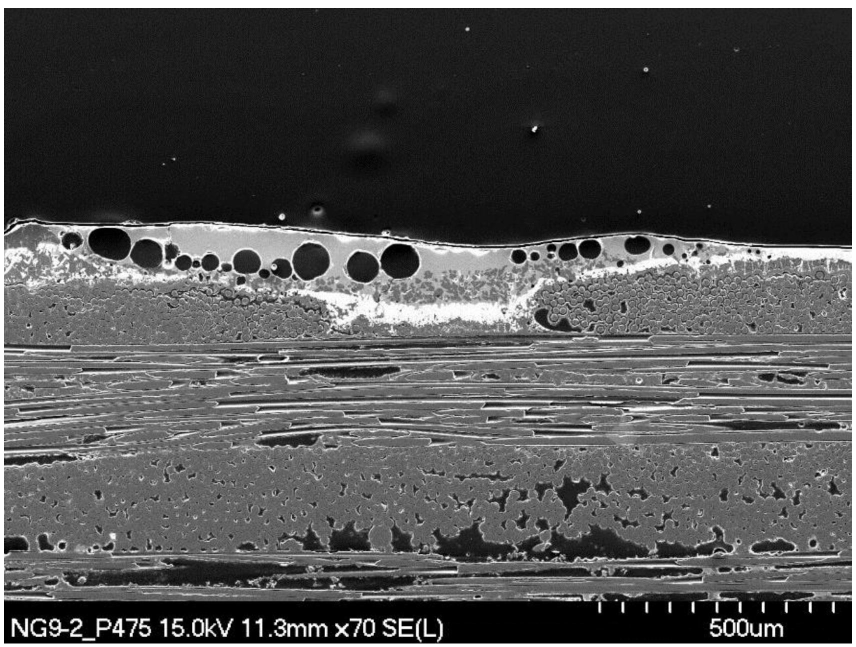
Hybrid Hybrid Zr-rare earth silicate, completed 4450 cycles, 100h

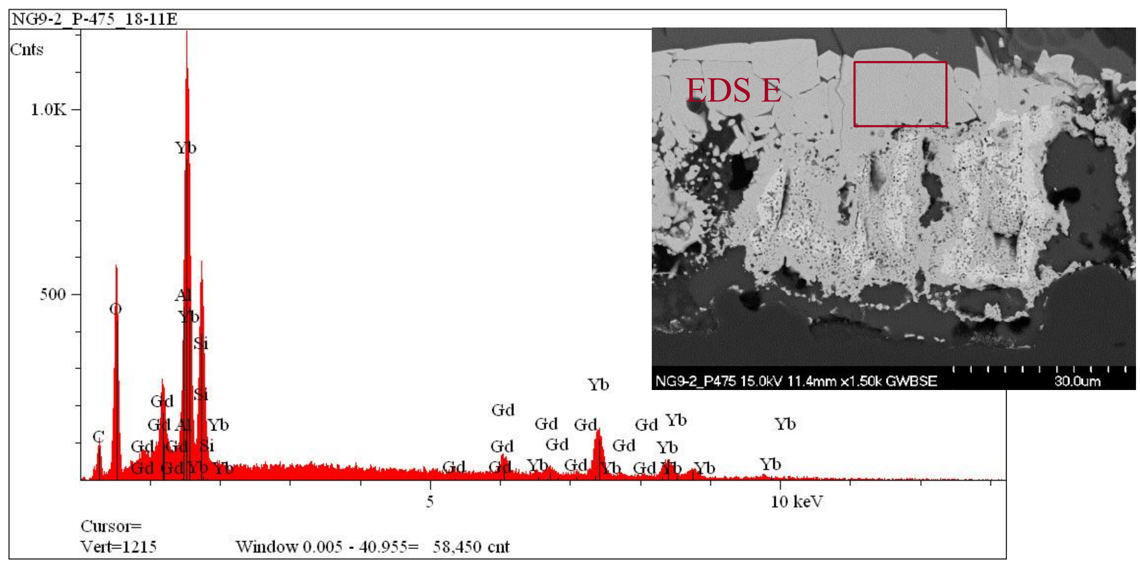
High Stability and CMAS Resistance are Ensured by Advanced High Melting Point Coating, and Multi-Component Compositions

- Generally improved CMAS resistance of NASA RESi System at 1500°C, 100 hr
- Silica-rich phase precipitation
- Rare earth element leaching into the melts (low concentration ~9mol%)









Advanced EBC-CMC System Demonstrated 300 hr High Cycle and Low Fatigue Durability in High Heat Flux 2700°F Test Conditions

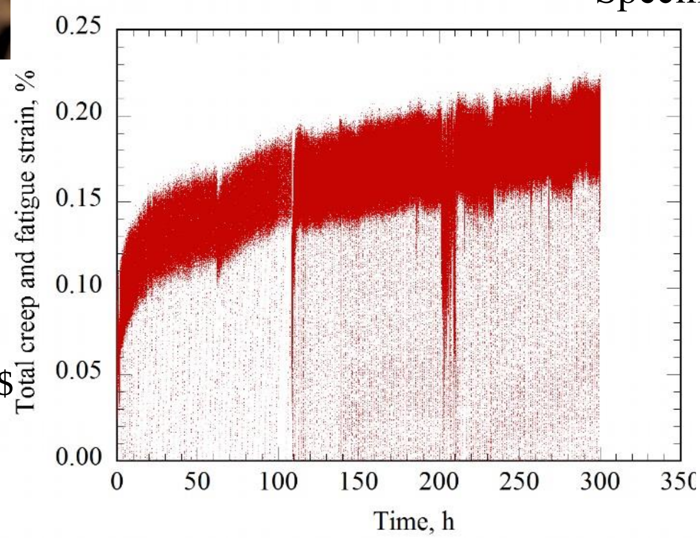
- A turbine airfoil EBC with HfO_2-rare earth silicate and GdYbSi bond coat on CVI-MI CMC substrate system selected for heat flux durability testing
- Laser high heat flux rig High Cycle and Low Cycle Fatigue test performed at Stress amplitude 10 ksi, fatigue frequency 3 Hz at EBC, and 1 hr thermal gradient cycles
- Tested EBC surface temperature 1537°C (2800°F) and T bond coat temperature 1482°C (2700°F), with CMAS
- Demonstrated 300 hour durability at 2700°F+
- Determined fatigue-creep and thermal conductivity behavior of the EBC-CMC system

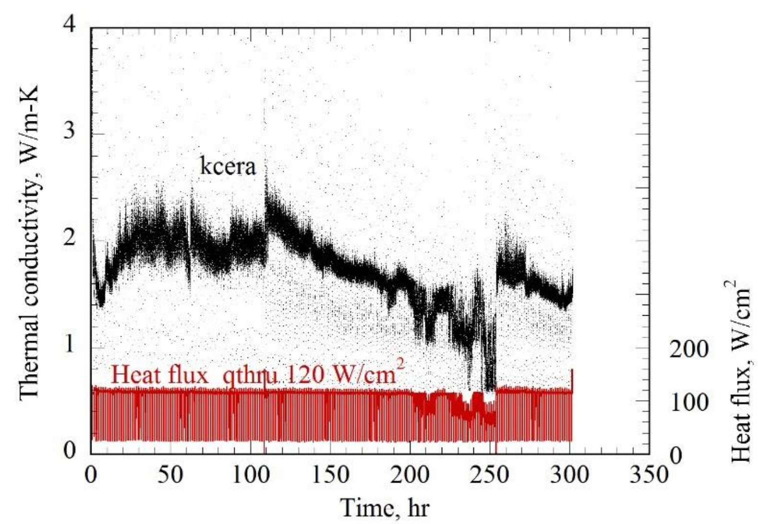
Specimen in rig testing

Specimen after 300 h testing

Test Condition Summary

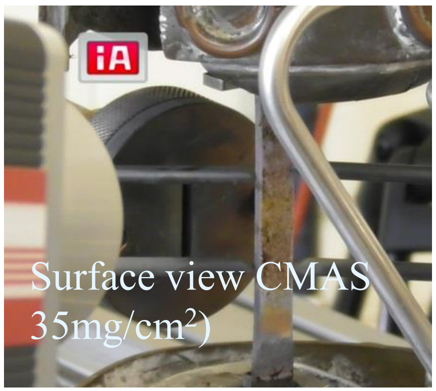
- EBC/CVI-MI, Fatigue $ loading 10 ksi (69 MPa), R=0.05, with 1 hr Thermal LCF $
- $T_{EBC\text{-}surface}$ 1537°C (2800°F) $
- $T_{bond\ coat}$ 1482°C (2700°F) $
- $T_{back\ CMC\ surface}$ 1250°C (2282°F)

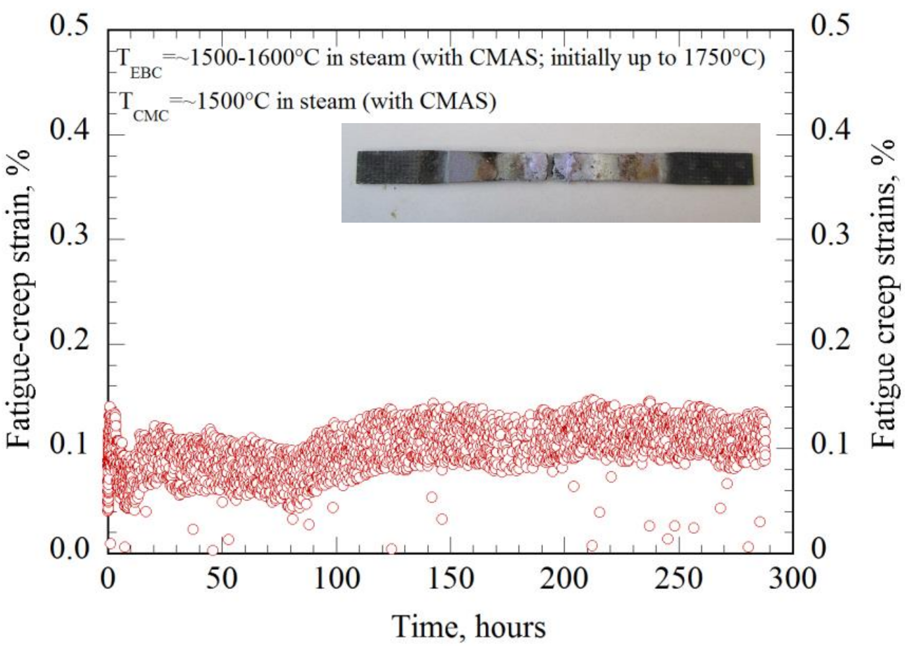


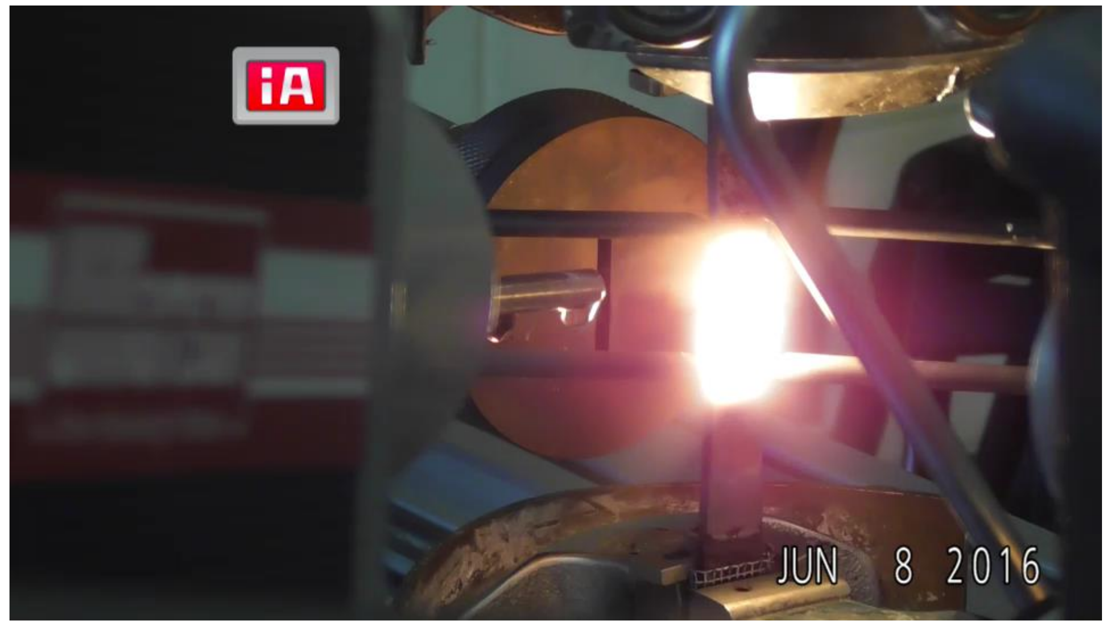


Advanced EBC-CMC Fatigue Test with CMAS and in Steam Jet: Tested 300 h Durability in High Heat Flux Fatigue Test Conditions

- Advanced Hf-NdYb silicate-NdYbSi bond coat EBC coatings on 3D architecture CVI-PIP SiC-SiC CMC (EB-PVD processing)
- Further understanding water vapor - environmental interactions necessary

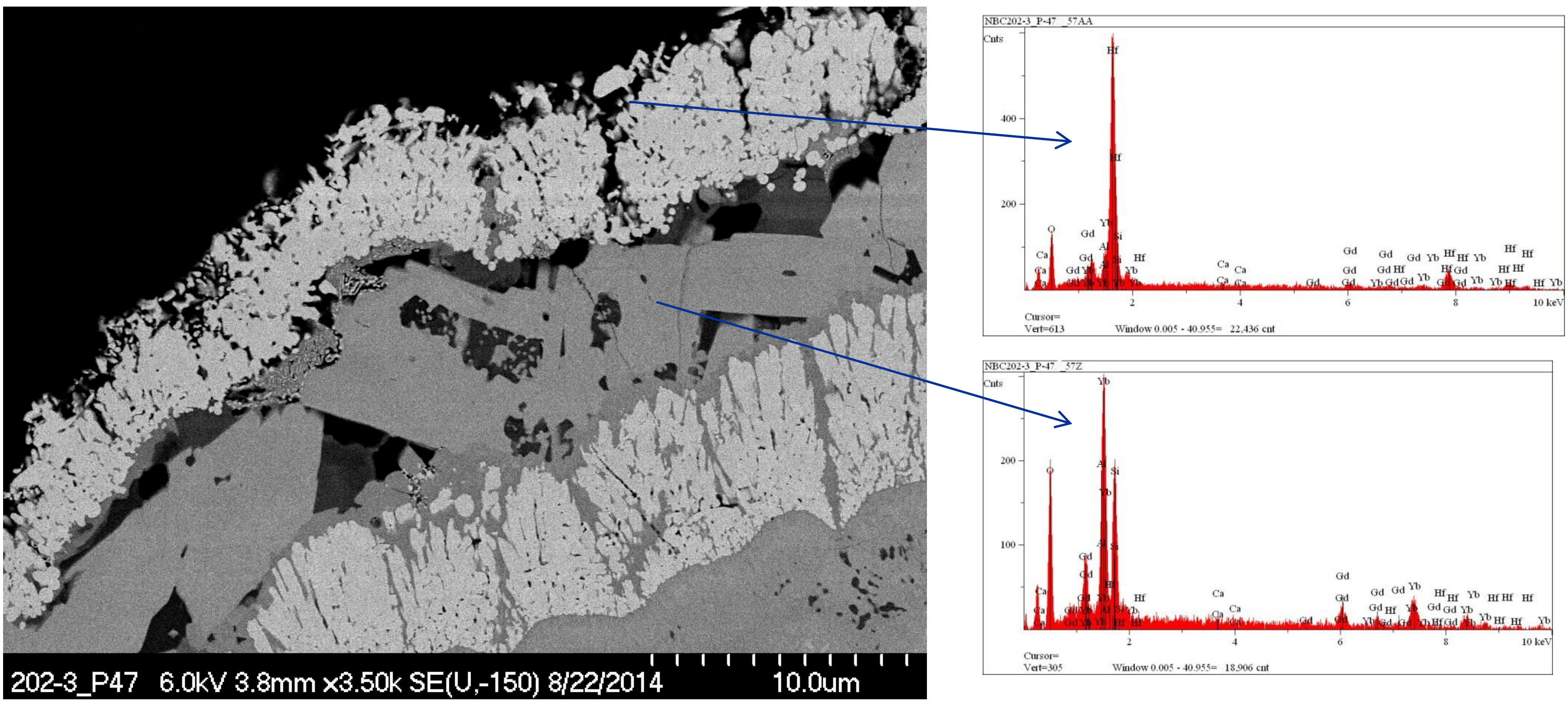






EBC System Designs – Effects of Composites and Clustered Compositions?

- An alternating HfO_2-and RE-silicate coatings (EB-PVD processing) – HfO_2- layer infiltration and rare earth silicate layer melting



EB-PVD Processed EBCs: alternating HfO_2-rich and ytterbium silicate layer systems for CMAS and impact resistance?

Summary

- CMAS degradation remains a challenge for emerging turbine engine environmental barrier coating – SiC/SiC CMC component systems
- CMAS leads to lower melting point of EBC and bond coat systems, with accelerated EBC and CMC degradations
- NASA advanced EBC compositions showed some promise for CMAS resistance at temperatures up to 1500°C in high velocity, high heat flux and mechanical loading tests
- Currently focus on better understanding of EBC compositions, and EBC-CMAS interactions particularly with hafnium, zirconium and rare earth silicates, for improved temperature capability and CMAS resistance
- Also standardize CMAS testing, and quantify CMAS induced life debits, helping validate life modeling;
- Controlling the compositions for CMAS resistance while maintaining high toughness continued to be a key emphasis

Acknowledgements

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- **The authors are grateful to Dr. Michael Helminiak in the assistant of JETS tests.**

CMAS Reaction Kinetics in Bond Coats

- SiO_2 rich phase partitioning in the CMAS melts
- Rare earth content leaching low even at 1500°C
- More advanced compositions are being implemented for improved thermomechanical – CMAS resistance

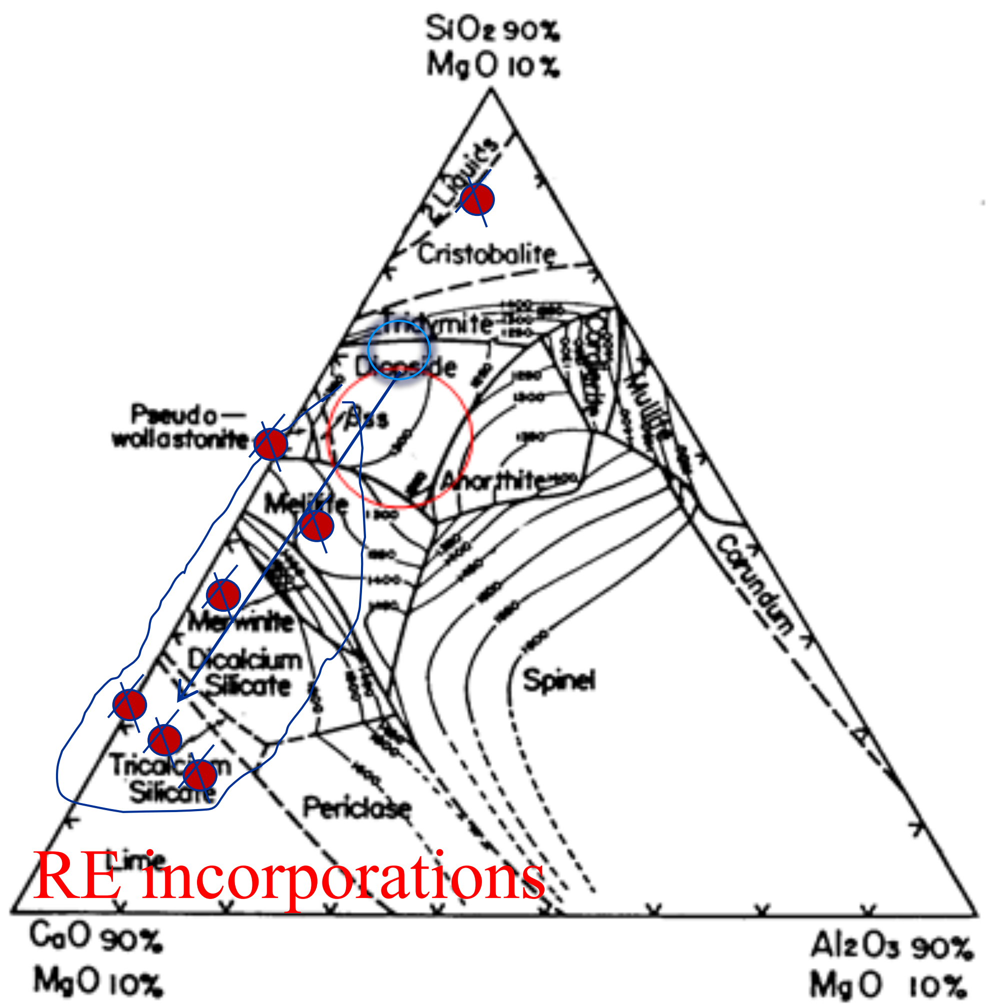
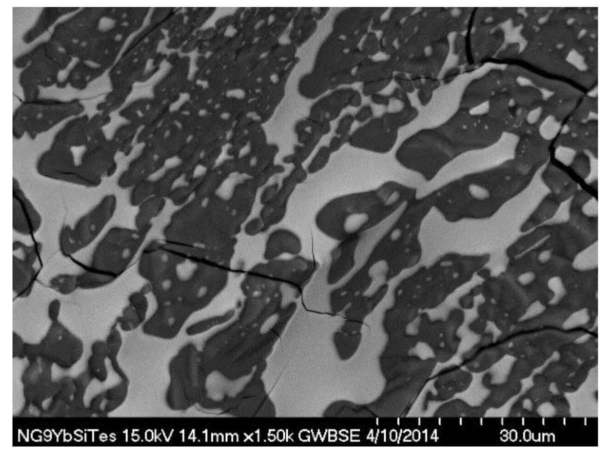


Fig. 4. The 10% MgO plane of the system CaO–MgO–Al_2O_3–SiO_2 showing the isotherms and fields of primary crystallization. A.T.Prince, J.Amer.Ceram.Soc., 37(9)1954 p402-408

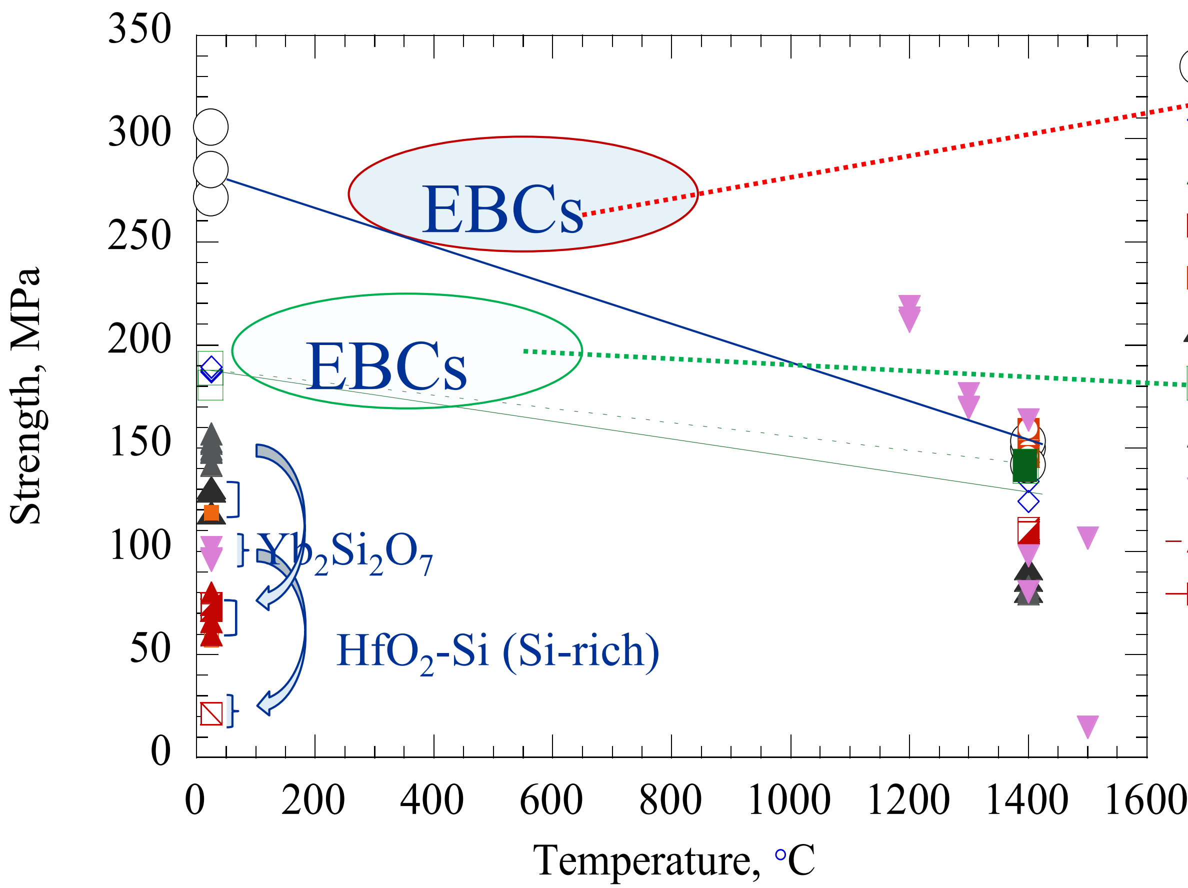
CMAS Partitioning on RE-Si bond coat, 1500°C, 100hr



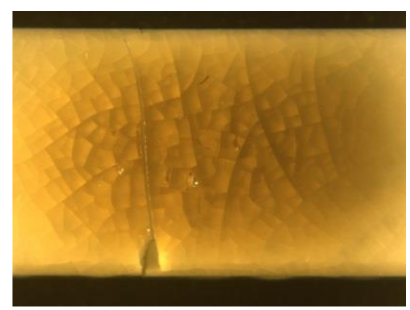
Strength Results of Selected EBC and EBC Bond Coats - CMAS Reaction Resulted in Strength Reduction in Silicates

Selected EBC systems

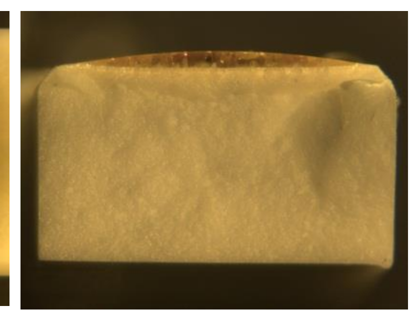
– HfO_2-RE-Si, along with co-doped rare earth silicates and rare earth alumino-silicates , for optimized strength, stability and temperature capability
– CMAS infiltrations can reduce the strength



Strength test data compared



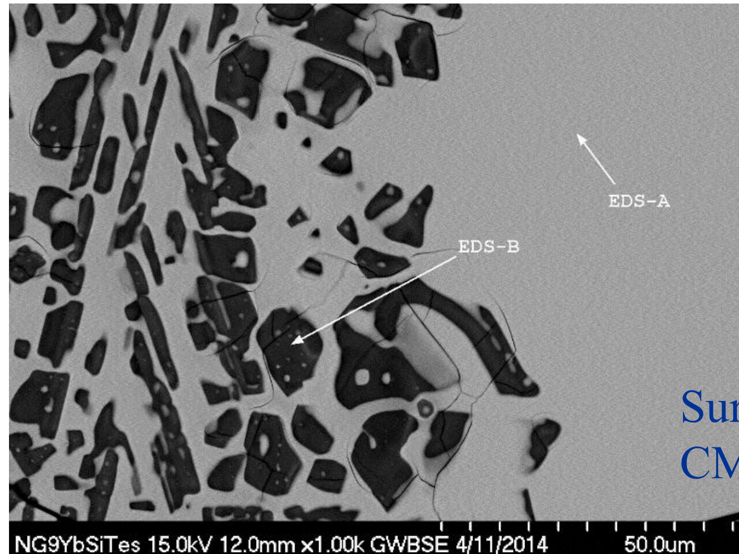
$Yb_2Si_2O_7$ CMAS reacted tensile surface



$Yb_2Si_2O_7$ CMAS reacted specimen fracture surface

High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

- Demonstrated CMAS resistance of NASA RE-Si System at 1500°C, 100 hr
- Silica-rich phase precipitation
- Rare earth element leaching into the melts (low concentration ~9 mol%)



Surface side of the CMAS melts