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Comparative Evaluation of Spark Plasma (SPS), Microwave (MWS),Two stage sintering (TSS) and Conventional Sintering (CRH) on the densification and Micro structural Evolution of fully Stabilized Zirconia Ceramics

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Abstract:

Yttria stabilized zirconia (8YSZ) powders were subjected to densification studies employing various sintering techniques like spark plasma sintering (SPS), microwave sintering (MWS) and two-stage sintering (TSS). The densification and microstructural evolution of the samples are studied and compared with that of conventionally sintered samples (ramp and hold). Depending on the technique employed the samples were sintered at different temperatures to arrive at a minimum density of 99%TD. Detailed microstructural evaluation indicated that a low temperature densification leading to finer sintered grain sizes (~1 μm) could be achieved by spark plasma sintering followed by the two stage sintering technique with an average sintered grain size of 2.6 microns.

Keywords: *Yttria stabilized zirconia; Spark plasma sintering; Microwave sintering; Two stage sintering; Grain size; Microstructure*

1. Introduction

Densification strategies are vital in the fabrication of ceramic components in order to achieve the twin objectives of full densification and finer sintered grain sizes. Various sintering methodologies based on diverse mechanisms are currently available to engineer the densification kinetics enabling the realization of above cited objectives. The conventional ramp and hold sintering, employing a longer duration of soaking time at high temperatures for the elimination of residual porosity, often results in abnormal grain growth thereby adversely affecting the mechanical characteristics and other functionalities like ionic conductivity and optical properties. Modifications on this conventional technique have been attempted earlier by engaging rate controlled sintering (RCS) and recently by two stage sintering (TSS). The concept of RCS, originally introduced by H. Palmour III and D. R. Johnson in 1967 [1] employs a progressive reduction (fast to slow) in densification rates, accomplished by a feedback-controlled dilatometer, to develop fine-grained microstructures in dense sample. The density-time profile is characterized by three regimes corresponding to linear, slower linear and log decreasing dependence of relative density with time after onset of shrinkage. The profile thus derived is converted to optimized sintering schedules that can be applied to a

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PID controlled conventional furnace for the sintering of samples with varying sizes, geometry and shape. The technique has met with limited success though studies are available on its use as an effective technique for sintering nano powders. Ragulya et al carried out the RCS sintering of ultra fine nickel by optimizing the temperature-time path to achieve specific density of 0.99 and a sintered grain size of 100 nm [2]. The study has further been extended to various ceramic systems like $BaTiO_3$, $3Y_2O_3$-ZrO_2 and nanocomposites of Si_3N_4-TiN, AlN-TiN etc [3, 4]. Remarkable improvements in mechanical and microstructural features of yttria doped zirconia has also been demonstrated by employing RCS for the sintering of zirconia containing varying mole % of yttria [4]. Fracture toughness values as high as 15 $MPam^{1/2}$ was reported for the composition 1.4 mole%Y_2O_3-ZrO_2. Hardness values of 26 GPa was obtained in nano TiN system by following a RCS protocol for sintering. Nearly full dense (99.9%) $BaTiO_3$ ceramics with mean grain size of 0.35 μm has been obtained by applying a constant densification rate of 0.5%/min on the initial and intermediate stages of sintering Ragulya has derived an optimum protocol for RCS by the creation of a kinetic field of response by a careful choice of shrinkage rate with temperature [3].

Two stage sintering methodology introduced by Chen and Wang utilizes the principle that the activation energy for grain growth is lower than the activation energy of densification [5]. The suppression of the final-stage grain growth is achieved by exploiting the difference in kinetics between grain-boundary diffusion and grain-boundary migration. Such a process should facilitate the cost-effective preparation of other nanocrystalline materials for practical applications. The sintering schedule is characterized by two regimes wherein the first regime at peak temperature dominates densification and complete elimination of residual porosity followed by a second regime at significantly lower temperatures effecting controlled grain growth during final stages of sintering. Various systems are investigated engaging TSS and the technique has been proven successfully for sintering ceramics with controlled grain sizes. Yu et al demonstrated the suitability on injection molded 3YSZ samples by engaging TSS at the peak temperature of 1350°C followed by a low temperature soaking at 900°C resulting in finer microstructures [6]. Mehdi Mazaheri et al. employed two stage sintering on slip casted 8YSZ powders arriving at sintered grain sizes finer then 300 nm [7]. The efficiency of TSS sintering technique on the densification and microstructure of oxide ceramics with different crystal structures was studied by Maca et al [8]. It was demonstrated that the technique was successful in densifying cubic zirconia ceramics with a reduction in grain size but its effect was negligible in tetragonal zirconia and hexagonal alumina ceramics.

The non-conventional methodologies for sintering ceramics primarily comprises of spark plasma sintering (SPS) and microwave sintering (MW). Spark plasma sintering simultaneously applies pulsed electrical current and pressure directly on the sample leading to densification at relatively lower temperatures and short retention times. As both the die and sample are directly heated by the Joule effect extremely high heating rates are possible due to which non densifying mechanisms like surface diffusion can be surpassed. The technique is widely explored for the development of nanostructured ceramics and has found commercial applications in the fabrication of cutting tools and piezoelectric ceramics. The densification, grain growth kinetics, hardness and fracture toughness of sub-micrometer sized alumina sintered by SPS was systematically investigated by Shen et al leading to the development of alumina samples with superior hardness and toughness [9]. Tamburini et al obtained dense zirconia and ceria ceramics with grain sizes as low as 10 nm by employing SPS at pressures up to 1 GPa [10]. Transmission electron microscopy studies were engaged on SPS sintered TZ3Y (3 mole % yttria stabilized zirconia) samples to elucidate the sintering path and densification mechanisms by Granger et al [11]. In a review on the sintering and densification of nanocrystalline ceramic oxide powders, Chaim et al analyzed various techniques and opined that the low temperature mass transport by surface diffusion can lead to rapid densification kinetics with negligible grain growth during spark plasma sintering of nanoparticles [12]. The densification behaviour of nano 8YSZ powder by SPS was compared

with hot pressing and conventional sintering techniques by Dahl et al and sintered samples with 96% TD and grain size of 200nm were obtained by SPS [13]. Takeuchi demonstrated the use of SPS for the preparation of dense barium titanate and lead titanate ceramics and correlated the electrical properties with fine grained microstructures [14, 15].

Microwave sintering, also in presence of an electromagnetic field, exploits the tendency of a dielectric material to couple with the microwave resulting in the generation of heat within. The technique generally uses a frequency of 2.45 GHz resulting in relatively rapid heating rates with uniform grained microstructures and has been employed for the sintering of a wide variety of ceramics ranging from dielectric materials to transparent ceramics. Clark et al analysing microwave processing of materials demonstrated low temperature densification and enhanced mechanical behavior of alumina ceramics [16]. Yadoji et al reported microwave sintering of Ni-Zn ferrites leading to lower dielectric constant values compared with the samples sintered conventionally, making microwave sintering particularly suitable for high frequency applications [17]. Microwave sintered Y-TZP/20 wt. % Al_2O_3 composites were shown to exhibit superior bending strength, fracture toughness and Vickers hardness compared with conventionally sintered materials by Travitzky et al [18]. Structural, dielectric, piezoelectric, and ferroelectric properties of Zirconium-doped barium titanate ($BaZr_{0.10}Ti_{0.90}O_3$) ceramics prepared by microwave and conventional sintering process are compared by Mahajan et al demonstrating improved room temperature performance of electrical properties [19].

The objective of the present study is therefore a comparative evaluation of the densification and microstructure development in fully stabilized zirconia ceramics by the sintering methodologies of conventional ramp and hold (CRH), two - stage sintering (TSS), microwave sintering (MW) and spark plasma sintering (SPS).

2. Experimental

2.1 Slip Casting of Specimens

Commercially available zirconia powder (TZ-8Y, Tosoh, Tokyo, Japan) with an average particle size of 205 nm was dispersed in aqueous medium to form slurries having solid loading in the range of 55 - 65 wt% using 1% Darvan 821A (R. T. Vanderbilt Co., Inc., Norwalk, CT, USA) as dispersant and octanol as the antifoaming agent. The slurries, optimized with respect to their solid loading based on their rheological properties measured using Rheometer (MCR 51, Anton Paar, Austria), were then casted into circular discs of 30 mm diameter in porous plaster of Paris moulds followed by drying under controlled humidity conditions of 50°C and 75% RH. The green densities were calculated and are found to be in the range of 50-51% of the theoretical density.

3. Sintering methodologies

3.1 Conventional sintering (CRH and TSS)

Under conventional sintering methodologies, specimens were sintered under two sintering techniques namely conventional ramp and hold (CRH) and two step sintering (TSS). The specimens were first subjected to dilatometry (Netzsch, Germany) and the shrinkage curve was recorded from room temperature to 1550°C as shown in Fig1.

Based on the dilatometric plots three different temperatures of 1500°C, 1525°C and 1550°C were selected as the peak temperatures for sintering and the samples were sintered in a PID controlled laboratory furnace (Nabertherm R, Model: HT 64/17, Germany) as per the sintering schedule shown in Fig 2. Under TSS methodology the specimens were first heat

treated to a temperature of 1525°C followed by a second step of hold at lower temperatures of 1300°C, 1350°C and 1375°C for 4 hrs as per the sintering schedule shown in Fig 2.

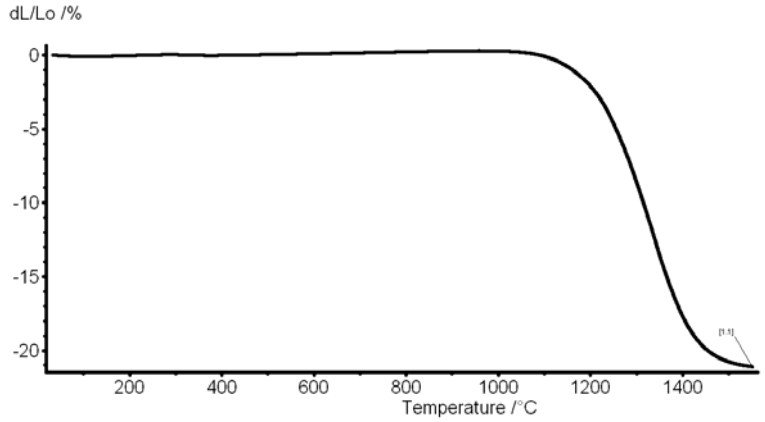

Fig. 1 Dilatometric shrinkage curve of 8YSZ sample

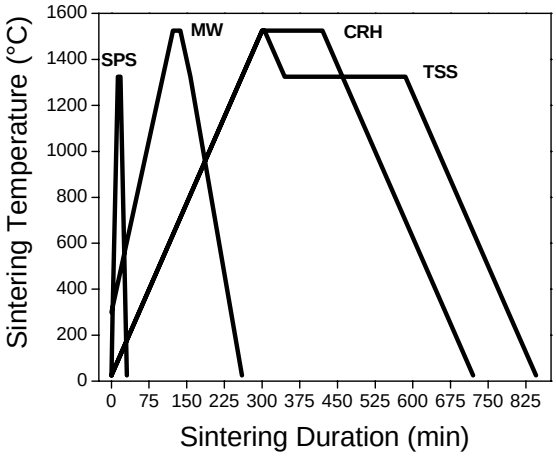

Fig. 2 Heating schedule employed for 8 YSZ specimens during CRH, TSS, MWS and SPS methodologies samples for which >99% theoretical density is achieved using minimum processing time.

3.2. Non-conventional sintering (SPS and MW)

Under non conventional sintering methodologies the specimens were sintered by SPS (Model Dr. Sinter 1050) with a heating rate of 100°C/min to peak temperatures of 1250°C and 1325°C at a pressure of 50 MPa with a holding time of 5 minutes as presented in Fig 2. Microwave sintering was carried out (Linn High Therm MHTD 1800-6, 4/2, 45 with 2.45 GHz frequency) at a heating rate of 10°C/min to peak temperatures of 1475°C, 1525°C and 1550°C with a holding time of 15 minutes as per Fig 2. SiC tubes were used as susceptors, since it is known that MW sintering of stabilized zirconia at 2.45GHz needs susceptors.

The sintering schedules were optimized to arrive at sintered densities of > 99% of theoretical density for the conventional and non conventional sintering. The sintered specimens were characterized for their density using Archimedes principle and

microstructural analysis of polished and thermally etched specimens were carried out using Field Emission Scanning Electron Microscope (Hitachi 3200S, FE SEM, Japan). Grain size analyses of the specimens were carried out by the linear intercept method as elaborated by Mendelson [19].

4. Results and Discussions

4.1. Densification

Tab. I presents the sintering parameters, densities and sintered grain sizes of zirconia samples densified using the sintering methodologies of CRH, TSS, MWS and SPS. In CRH mode, the samples could be sintered to densities >99% TD in the temperature range of 1525-1550°C. When the methodology is modified as per TSS technique selecting a peak temperature of 1550°C, zirconia samples densified to >99%TD at a lower soaking temperature of 1350°C. The samples were first subjected to high temperature of 1525°C (first stage) for a shorter duration to ensure the closure of porosity and the second stage of firing was attempted at the lower temperatures of 1300°C, 1350°C and 1375°C, for four hours of dwell time. It is evident from the density plot that temperatures greater than 1300°C is essential to arrive at densities of 99%TD. On increasing the temperature to 1375°C no significant improvement in densification (99.50%) is observed. Thus the second temperature regime of T> 1300 and < 1375°C is found to be desirable to achieve maximum density > 99 % TD. The second step at 1350°C imparts densification with limited grain growth and can be attributed to grain boundary diffusion remaining active while grain boundary migration is suppressed through triple junction drag.

Tab. I: Sintering Parameters and Sintered densities of the 8YSZ Specimen

Specimen Identity	Sintering technique	Sintering temperature (°C)	Dwell Time	Density (g/cc)	Theoretical Density (% TD)	Average grain size (μm)
1	CRH					
	(a)	1500	2 hr	5.810	98.50	4.12
	(b)	1525	2 hr	5.867	99.44	4.67
	(c)	1550	2 hr	5.870	99.49	8.83
2	TSS	T1:1525	5minutes			
	(a)	T2:1300	4 hr	5.830	98.81	2.64
	(b)	T2:1350	4 hr	5.865	99.40	2.64
	(c)	T2:1375	4 hr	5.870	99.50	4.14
3	MWS					
	(a)	1500	15minutes	5.820	98.64	2.77
	(b)	1525	15minutes	5.850	99.15	3.70
	(c)	1550	15minutes	5.850	99.15	5.22
4	SPS					
	(a)	1250	5 minutes	5.846	99.10	1.30
	(b)	1325	5 minutes	5.870	99.50	1.16

In MWS, the temperature regime for good densification (>99%TD) matched that of the CRH mode (1500-1550°C) but at substantially low soaking periods of 15 minutes

compared to 2 hr in CRH. During microwave heating energy is transferred to the material electro-magnetically and not as a thermal heat flux enabling the material to be heated at rapid rates. The higher oxygen vacancies associated with 8 mol% yttria stabilized zirconia provides higher ionic conductance at elevated temperatures leading to high dielectric losses and enhanced absorption of microwaves. This mechanism could be one possible reason for the shorter sintering times in MWS. It is also to be observed that at identical temperatures the density attained in MWS samples and CRH samples are similar.

Maximum densification at the lowest sintering temperature was provided by SPS wherein samples could be sintered to >99%TD at a temperature of 1250°C for 5 minutes. The rapid densification of samples by SPS is attributed to the enhanced densification rate due to mechanisms like particle rearrangement and breaking up of agglomerates aided by the applied pressure and faster heating rates. By rearrangement of particles, the SPS process also impedes the pore size increase generally observed in the first and intermediate stages of sintering. Further, applied electric field also promotes the diffusion of ions and vacancies which enhances the sintering rate.

4.2 Microstructure development

Fig. 3a represents the SEM microstructure of 8YSZ samples sintered by CRH at 1525°C. The structure is dense with very few isolated pores. Dark spots, presumably segregations of yttria are also observed. Average grain size measurement by linear intercept method provided a value around 4.6 µm.

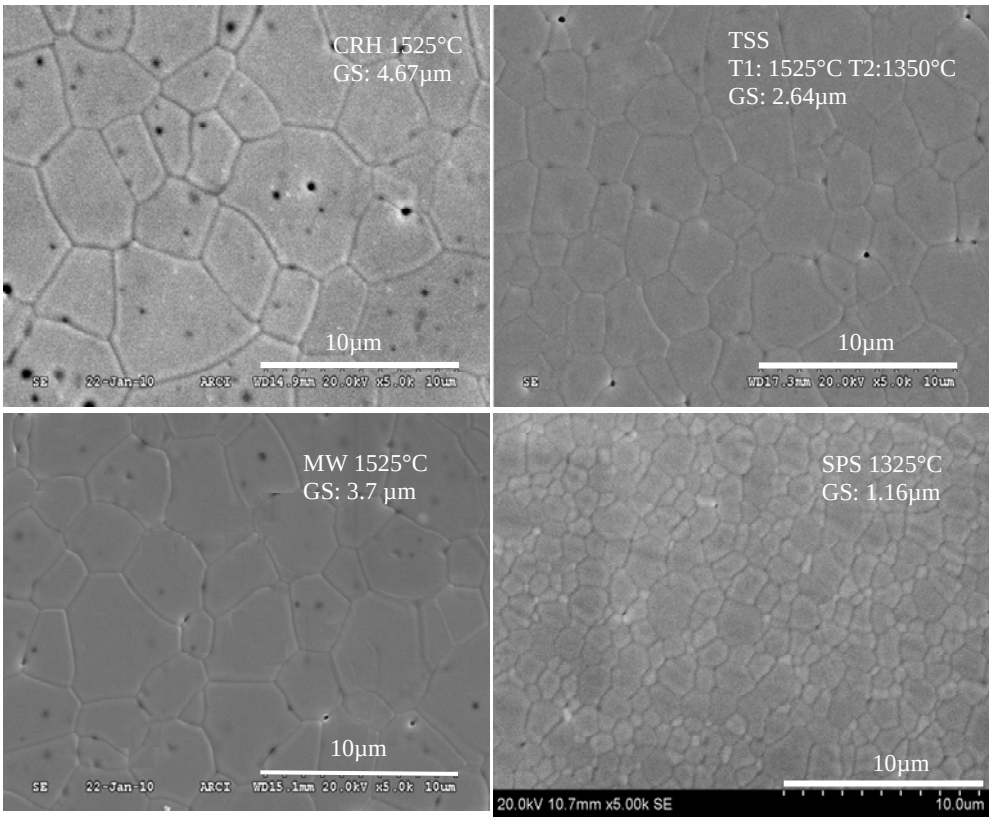

Fig. 3. A comparison of the microstructure of sintered 8YSZ specimens > 99 %TD of (a) CRH - 1525°C, (b)TSS - T1:1525°C - T2:1350°C, (c)MWS -1525°C and (d)SPS -1325°C

The variation of density and grain size with temperature is provided in Figure 4a. The grain growth is limited during a temperature increase from 1500-1525°C while it is significantly increased on a further increase of 25°C to 1550°C (~9 µm). A reverse trend is observed for the densification behaviour on increasing the temperature from 1500-1550°C. 8YSZ sample sintered by the TSS technique at the lower soaking temperature of 1350°C indicate relatively finer microstructure with few scattered inter-granular pores (Fig 3b). The grains are of uniform sizes averaging around 2.6 microns. The plot of density and grain size with temperature provided in Fig 4b indicated negligible grain growth on increasing the soaking temperature from 1300°C to 1350°C. However, the growth is substantial as the temperature is further increased to 1375°C with an increase in average grain size from 2.6 to 4 µm.

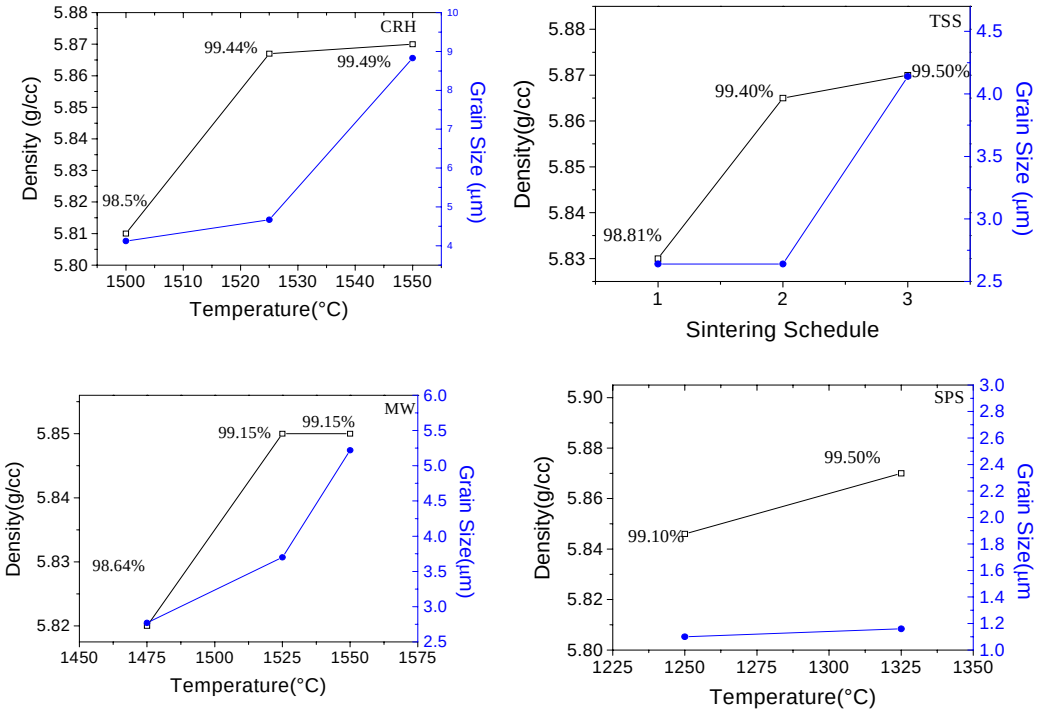

Fig 4. Temperature vs. density and grain size plots of 8YSZ specimens ((a) CRH, (b) TSS, (c) MWS and (d) SPS methodologies)

MW sintering of samples provided 99%TD at 1525°C and is similar to the value attained during CRH. The advantage with MWS was that the grain sizes are lower than that of CRH (3.6 µm compared to 4.6 µm in CRH) at nearly identical density values, primarily due to shorter soaking times. Microstructure presented in Fig 3c represents that of a dense sample with very few inter-granular pores. Grain growth with temperature was prominent during the increase of temperature from 1525°C to 1550°C without appreciable density changes (Fig 4c).

The microstructure of SPS sintered specimen at 1325°C is provided in Fig 3d. Dense microstructure with extremely fine grain sizes was observed and the average grain size was found to be ~1 µm. The particle size to sintered grain size ratio is quite low (a factor of 5) compared to the other sintering techniques employed. The plot of density and grain size with temperature provided in Fig 4d.

The effect of sintering technique on grain size distributions in microstructure is presented in Fig 5. The CRH technique produced a larger distribution of sizes in sintering at 1525°C and grain sizes ranging from 1 - 7 μm were observed (Fig 5a). There is significant grain size control and uniformity as the schedule is modified as per TSS technique at the lower soaking temperature of 1350°C (Fig 5b). In MWS, the distribution falls between that of CRH and TSS and is dominated by larger grains in the 3-5 μm range (Fig 5c). The grain size distribution is most favorable in SPS technique with the majority of grains having sizes close to 1 μm (Fig 5d).

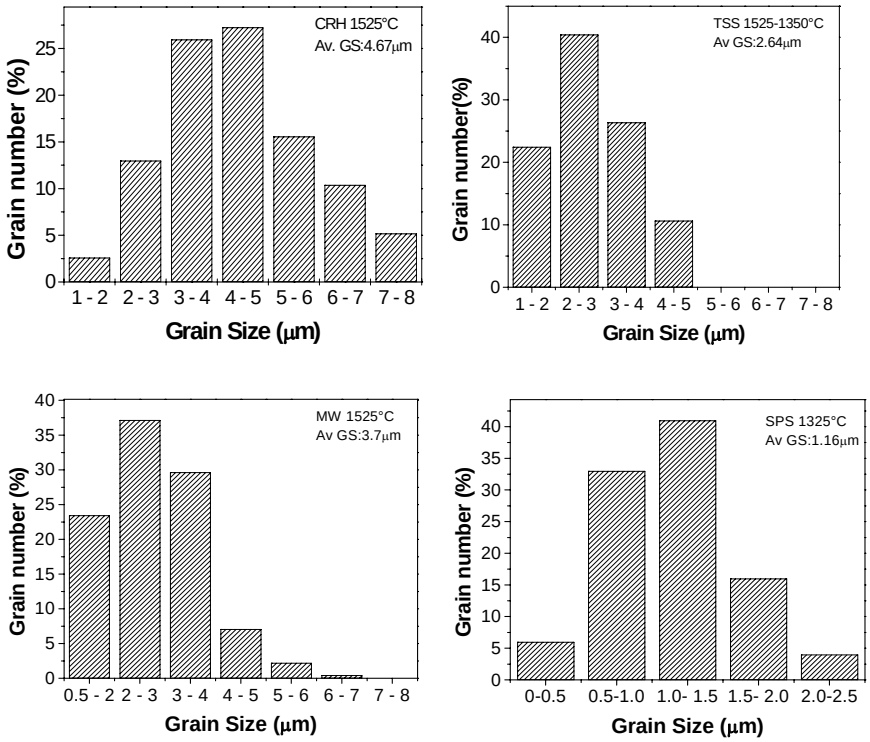

Fig 5. Grain size distribution of sintered 8YSZ specimens > 99 % of (a) CRH -1525°C , (b) TSS-1525°C -1350°C , (c) MWS - 1525°C and (d) SPS -1325°C methodologies

5. Conclusions

Yttria stabilized zirconia specimens sintered through Spark Plasma Sintering at 1325°C for a period of 5 minutes have exhibited the highest sintered density of 99.89 % with lowest grain size of ~1 μm . Slip cast specimens sintered by microwave technique at the temperature of 1525 °C have shown a density of 99.15 % at an average grain size of 3.7μm with grain size distribution similar to conventional sintered specimens. A significant decrease in grain size to 2.6 μm was observed with the two stage sintering in comparison to conventional sintering and is attributed to the lower soaking temperatures compared to conventional CRH. The microstructure was found to be more homogeneous with a narrow grain size distribution during two stage sintering.

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Садржај: *Проучено је згушњавање цирконијума стабилисаног итријумом коричћењем различитих техника синтеровања као што су варнично плазма синтеровање, микроталасно синтеровање и двостепено синтеровање. Проучено је згушњавање и еволуција микроструктуре узорака која је упоређена са конвенционално синтерованим узорцима (рампа и држање). У зависности од употребљене технике узорци су синтеровани на различитим температурама да би се добила минимална густина од 99% теоријске густине. Детаљна анализа микроструктура је указала да се згушњавање на нижим температурама које доводи до мањих величина зрна (~1 μm) може добити варничним плазма синтеровањем које је праћено двостепеним синтеровањем са просечном величином зрна од 2.6 микрона.*

Кључне речи*: Цирконијум стабилисан итријумом, варнично плазма синтеровање, микроталасно синтеровање, двостепено синтеровање, величина зрна, микроструктура.*