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Micro structural control of stabilized zirconia ceramics (8YSZ) through modified conventional sintering methodologies

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Abstract:

Slip cast Y₂O₃ stabilized Zirconia (8YSZ) ceramics was subjected to Conventional Ramp and Hold (CRH), Rate Controlled (RCS) and Two Stage Sintering (2SS) methodologies. Sintered samples were characterized for their densities and grain size analysis by Scanning Electron Microscopy. The slip cast samples sintered by CRH and 2SS have achieved 98 – 99 % of theoretical densities while RCS samples have exhibited a low density of 97 %. The samples exhibited an average grain size of 2.64 μm by 2SS sintering in comparison to 8.83 μm in case of CRH and 3.45 μm in case of RCS. Controlled pore growth associated with RCS, when compared to CRH methodology is mainly responsible for the relatively smaller grain size observed with RCS. A four fold decrease in grain size i.e. 2.64 μm observed with the two step sintering can be attributed to the fact that the first heating step to high temperature of 1550°C for a shorter duration closes the porosity without significant grain growth. The second step at 1375°C for a longer period of time imparts densification with limited grain growth.

Keywords: *Zirconia, Sintering, Rate controlled sintering, Two stage sintering, Grain size*

Introduction

Development of ceramic components using ultra fine powders has often been hindered by the challenges associated with its shaping and the control over grain growth during sintering [1-10]. The inherent tendency of fine sized powders to agglomerate not only prevents uniform mixing while processing but also are detrimental to densification during pressure less sintering processes. This is attributable to the differential shrinkage rates within and between these agglomerates leading to sintering defects. Further, the grain coarsening and pore growth associated with sintering also pose major challenges in obtaining fully dense ceramics with controlled microstructure. It is well known that zirconia with yttria content up to a concentration of 7–10 mol. % [11, 12] is a candidate material for solid oxide fuel cell and the ionic conductivity of zirconia increases with yttria content. However, increasing yttria content imparts grain growth resulting in poor mechanical properties [13-15]. Further, fully dense zirconia with nano sized grains provides a high level of grain boundaries, as potential sources of vacancies, favorable to promote ionic conductivity [16-19]. This has generated wide interests in sintering of cubic YSZ powders [20].

Extensive efforts have been made to develop fully dense ceramics by employing non conventional sintering methodologies like SPS, HIP etc which necessitates sophisticated

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infrastructural facilities and techniques. Modified conventional techniques like RCS [21-25] and 2SS [26-27] are possible alternatives with significant commercial viability. These techniques demand only the conventional furnaces and a careful choice of the sintering schedule during various stages of sintering can lead to the realization of twin objectives of full densification and fine sintered grain sizes.

The conventional ramp and hold sintering employs longer duration of soaking time at high temperatures for the elimination of residual porosity and often results in abnormal grain growth. RCS 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. It has been postulated that imposition of such a progressive densification rate could lead to significant changes in microstructure evolution. Unlike rate controlled sintering, the two stage sintering technique utilizes the principle that activation energy of grain growth is lower than the activation energy of densification [26]. A sintering schedule in 2SS is characterised by two regimes wherein the first regime at peak temperature dominates densification in combination with the complete elimination of residual porosity followed by a second regime at significantly lower temperatures effecting controlled grain growth during final stages of sintering.

In the present study, commercially available zirconia powder was slip cast by colloidal processing and was subjected to densification using the said techniques. A comparative evaluation of CRH, RCS and 2SS in achieving full dense ceramics with controlled microstructure is carried out.

Experimental Work

Slip Casting of Specimens

Zirconia powder (Tosoh TZ-8Y 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 were optimized with respect to their solid loading based on their rheological properties measured using Rheometer (MCR 51, Anton Paar, Austria) and were then cast 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.

Sintering methodologies

Sintering behavior was recorded from room temperature to 1550°C at a heating rate of 5, 10 and 20°C/min using a single pushrod dilatometer (Netzsch, Germany). An alumina sample holder and pushrod were employed for the measurements. Based on the dilatometric plots, Under CRH methodology the samples were subjected to a final sintering temperature of 1550°C with a heating rate of 10°C/min and a soaking period of 2 hrs in a PID controlled laboratory furnace. Rate Controlled Sintering was carried out by selecting the shrinkage plot with 10°C/min for application of the RCS protocol. Three shrinkage rates were applied identifying the three temperature regimes of significance and the temperature profile thus generated was programmed in a PID furnace where the samples are sintered. Under 2SS the samples were first heat treated at a temperature of 1550°C under heating rate of 10°C/min and was followed by a second step of hold at lower temperature of 1350°C for 4hrs. The sintered

samples were characterized for their density using Archimedes principle and microstructural analysis of polished and thermally etched samples were carried out using SEM (Hitachi 3200S, FE SEM, Japan). Grain size analyses of the samples were carried out by the linear intercept method.

Results and Discussions

The viscosity vs shear rate plots of zirconia slurries with 55-70 wt% solid loading is presented in Fig. 1. Viscosity is increasing for solid loading values > 60wt%. Additionally, flow behavior shift from Newtonian to shear thinning as the solid loading increases from 60 wt% to 70 wt%. The consistency of slip was quite conducive for casting even at 70 wt% solid loading. Scanning Electron Micrographs of the green compact of the slip cast samples are provided in Fig. 2. It is evident from the SEM micrographs that the casting technique has lead to a close packed and homogeneous green specimen. Further, the homogeneity in case of slip casting process can also be attributed to the key factors of suspension stability and its viscosity, controlled by the solid loading and additives [28-30].

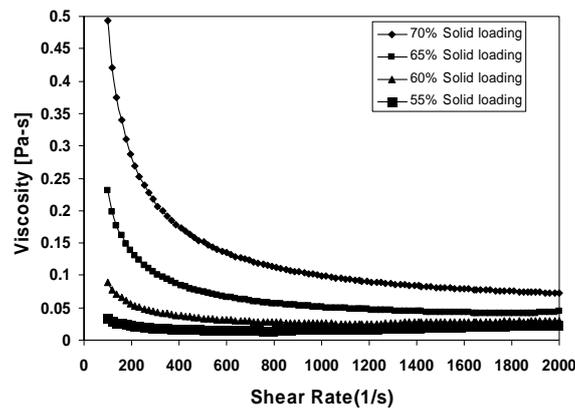


Fig. 1. Shear thinning behaviour of 8YSZ slurry

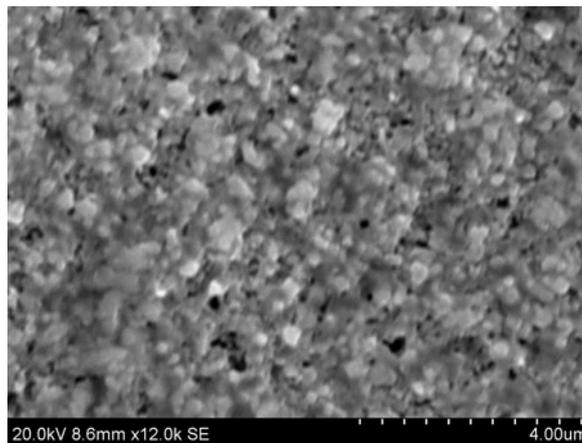


Fig. 2. Microstructure of 8YSZ green sample slip cast

The plot of dilatometric shrinkage for the constant heating rates of 5, 10, and 20 °C/min for slip cast samples are shown in Fig. 3. Samples exhibited almost a similar shrinkage pattern with an onset of shrinkage at temperatures around 1000°C and extending to

1550°C with a total shrinkage of 25.75 % at a heating rate of 10 °C/min. There is only marginal change on shrinkage rate as well as on final shrinkage with increase in heating rate from 5 to 20 °C/min. Plot of relative density derived from dilatometric plots vs. temperature for three different heating rates and the activation energy plots of $\ln(dp/dT \times T \times T^*)$ vs. $10^4/T$ are shown in Fig. 4 and further the activation energy for corresponding relative densities were estimated. Activation energy of 272 – 309 KJ/mol is found to be in good agreement with the activation energy reported 307 ± 10 KJ/mole for by Sharon et.al. [27].

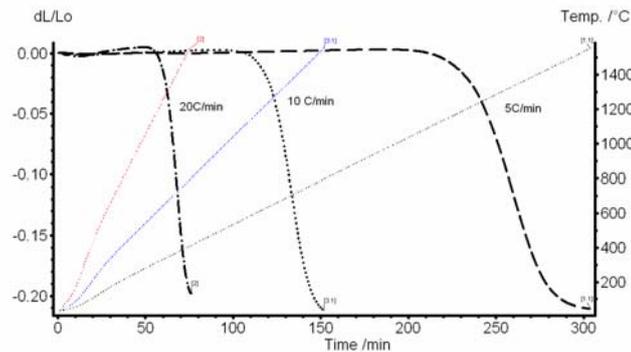


Fig. 3. Linear shrinkage of the 8YSZ Compacts during sintering at three different heating rates 5 (dashed line), 10 (dotted line) and (dot-dash line) 20 °C /min.

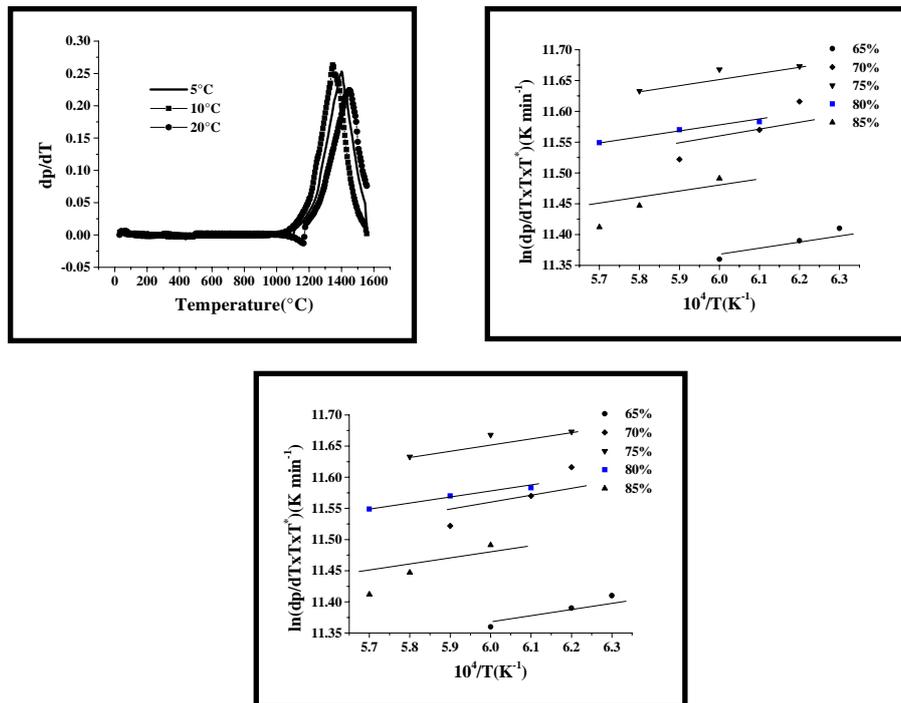


Fig. 4. Plot of Relative density Vs. Temperature for heating rates 5, 10 and 20 °C / min and activation energy plots of $\ln(dp/dT \times T \times T^*)$ vs. $10^4/T$

The above heating schedule followed in a PID controlled sintering furnace for CRH, RCS and 2SS are shown in Fig. 5 a, b and c respectively. As per RCS protocol the temperature regime, wherein the shrinkage was observed from the dilatometric curve with

10°C/min, was split into three segments. The first linear region wherein, the fastest shrinkage rates can be functional is applied to the temperature regime of 1105 - 1395°C. The sample attains a density of ~75% TD at this stage. In the next region, where there is a slower linear rate dependence of temperature on densification, the shrinkage rates are to be lowered. In this temperature region between 1395-1415°C, density of 85% TD was obtained. The last regime, where a log decreasing dependence on densification rate is prevailing, occurred in the temperature zone of 1415-1550°C.

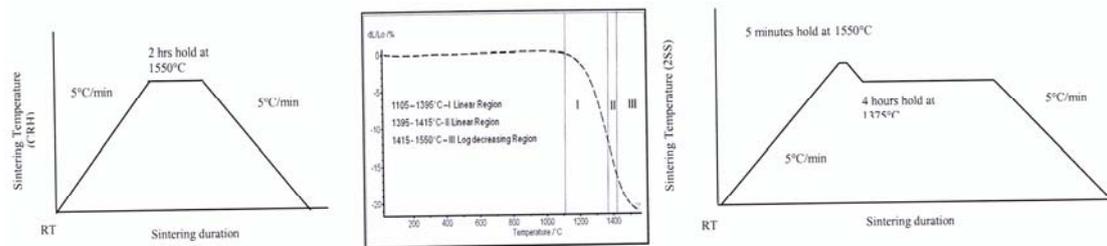


Fig. 5 (a) Heating schedule and Linear Shrinkage of the 8 YSZ compacts during (a) CRH (b) RCS (c) 2SS

The sintered densities and grain sizes of sample sintered by CRH, RCS and 2SS is shown in Tab. I. Samples sintered vide CRH has achieved the highest density of 99.49 % followed by 2SS where the samples were 98.81 % TD dense. However, RCS samples have exhibited a relatively low density of 97 %. Residual pores were observed in case of RCS and 2SS samples in the grain boundaries corresponding to their lower densities in comparison to CRH. The dark spots in the micrographs are attributed to the ZrO_2 inclusions originating from milling process as observed by Karel et al (31). The samples exhibited an average grain size of 2.64 μm by 2SS sintering in comparison to 8.83 μm in case of CRH and 3.45 μm in case of RCS. A comparison of microstructure is shown in Fig. 6.

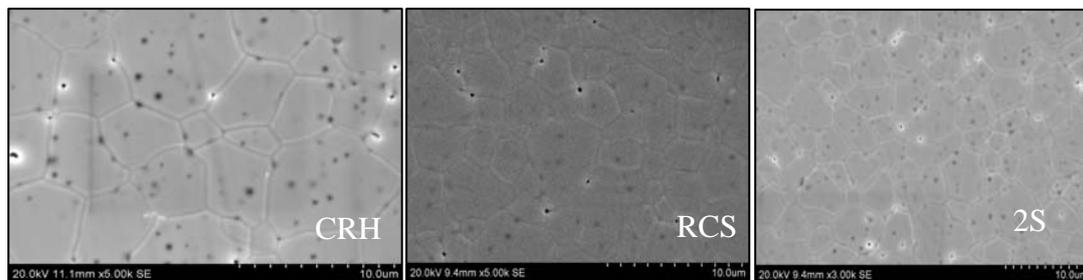


Fig. 6. Microstructures of 8YSZ samples of CRH, RCS, and 2SS samples

Tab. I. Densification data of 8YSZ Samples heat treated under CRH, RCS and 2SS

Sample Identity	Sintering technique	Density g/cc	% Theoretical Density	Average grain size (μm)
8 YSZ Slip Cast	CRH	5.87	99.49	8.83
8 YSZ Slip Cast	RCS	5.72	96.95	3.45
8 YSZ Slip Cast	2SS	5.83	98.81	2.64

This significant decrease in grain size during the 2SS can be attributed to the fact that the first heating step to high temperature of 1550 °C for a shorter duration closes the porosity and the second step at 1375°C, the lower temperature, for a longer period of time imparts

densification with limited grain growth. In addition to 2SS, RCS also exhibited significant decrease in grain size ($3.45\ \mu\text{m}$) in comparison to the CRH methodology but with a lower density of 97 %. The observed reduction in grain size in RCS can be attributed to the following proposed mechanisms [29-31]. It has been postulated that, in RCS all mass transfer mechanisms competing in the sintering process are in balance and their particular rates follow the minimum free energy dissipation principle. The driving forces for these mechanisms change non-linearly and RCS establishes a variable and non linear dependence of densification with temperature. In the case of conventional sintering when the density is around 88-90 % TD, the topology of the pores changes from open cylinder to close spherical shapes, as a result of which the concentration of pores is reduced leading to enhanced grain growth. The pore growth is controlled to a minimum in RCS, when compared to conventional ramp and hold method. At the same porosity level the number of cylinder shaped pores before their splitting and the number of isolated spherical shaped pores are much higher in case of RCS than that during conventional sintering at the same porosity. However, it is evident that the presence of pores is much higher along the grain boundaries as revealed by the lower densities.

Conclusions

Densities close to 99% of the TD could be achieved in slip cast zirconia ceramics with CRH and 2SS sintering methodologies while rate controlled sintering could achieve only approximately 97 %. A major difference is observed with respect to the grain growth accompanied with densification. The average grain size of sintered zirconia grains after conventional sintering was $8.83\ \mu\text{m}$. A four fold decrease in grain size i.e. $2.64\ \mu\text{m}$ was observed with the two stage sintering. This decrease in grain size during the two-step sintering, significantly controls the grain growth which can be attributed to the fact that the first heating step to high temperature of 1550°C for a shorter duration closes the porosity without significant grain growth. The second step at 1375°C the lower temperature for a longer period of time imparts densification with limited grain growth.

Rate controlled sintering also exhibited a decrease in grain size $3.45\ \mu\text{m}$ however, with a lower density of 97 % in comparison to the 99.45 % with conventional sintering methodology. Unlike in CRH, topology of the pore and pore growth is controlled to a minimum in RCS leading to much higher cylindrical shaped pores at same porosity level resulting in reduced grain growth.

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Садржај: Ливена керамика цирконијума стабилизованог са Y_2O_3 (8YSZ) је подвргнута методама конвенционалног синтеровања са рампом и држањем (CRH), са контролом брзине загревања (RCS) и двостепеног синтеровања (2SS). Густина и величина зрна синтерованих узорака је карактерисана скенирајућом електронском микроскопијом. Ливени узорци синтеровани методама CRH и 2SS су достигли густину од 98'99% теоријске густине док су RCS узорци имали мању густину од 97%. Узорци су имали просечну величину зрна од 2.64 μm коришћењем методе 2SS у поређењу са 8.83 μm у случају методе CRH и 3.45 μm у случају методе RCS. Контролисани раст пора који је асоциран са RCS у поређењу са методом CRH је углавном одговоран за релативно мању величину зрна. Четвороструко опадање величине зрна од 2.64 μm у случају двостепеног синтеровања се може приписати чињеници да први корак синтеровања до високе температуре од 1550°C за краће време затвара порозност без значајног раста зрна. Други корак на 1375°C за дуже време доводи до згучњавања са ограниченим растом зрна.

Кључне речи: Цирконијум, синтеровање, синтеровање контролисаном брзином, двостепено синтеровање, величина зрна.
