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# The effect of shape forming and sintering methods on properties of 8 mol%-Y2O3 stabilized nano structured zirconia bodies

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**Abstract:** Among different types of ceramics, 8 mol%-Y2O3 stabilized zirconia (8YSZ) because of its high oxygen ionic conductivity and chemical stability over a wide range of temperature is a well known candidate for oxide fuel cells. In the present study, the effect of different shaping method on densification and grain growth of 8YSZ was studied. The slip casting was shown to be a more efficient method yielding homogenous green bodies with higher green density containing smaller pores with narrower distribution. The grain growth, consequently, was decreased significantly in nearly-full dense bodies formed by slip casting. Two steps sintering of nanocrystalline powder resulted in remarkable suppression of accelerated grain growth. High rate microwave sintering was also found to hinder the grain growth, resulting in finer microstructure. The fracture toughness and microhardness were taken as criteria to evaluate the microstructural evolution of 8YSZ bodies formed by different combination of shape forming-sintering methods. Interestingly it was shown that without applying any modified sintering technique the hardness and fracture toughness of slip casted bodies with coarser structure is completely close to those of samples sintered through microwave heating.

**Keywords:** Zirconia, Nanostructured, Shape forming

## Introduction

Zirconia is one of the most important ceramic oxides due to its traditional and advanced applications. Among the different types of the ceramics ,8 mol% yttria stabilized zirconia (8YSZ), because of its high oxygen ionic conductivity and chemical stability over a wide rang of temperature, is a well known candidate for oxygen sensors, oxygen pumps and oxide fuel cells [1].

Although there are many reports on slip casting of nanometric powder [2,3], the literature has not distinctly reported the efficiency of wet shaping methods in comparison with conventional uniaxial dry pressing. In other words, it is believed that wet shaping of nanopowder can lead to the more uniformity of green bodies as well as less and finer inter and intra agglomerated pores. This can cause a significant improvement in green density, as well as notable decrease in sintering temperature. The high green density means more contact points between particles which would have more mass transport during sintering and thus result in a faster densification rate. In addition to shaping method, sintering technique can considerably influence on densification and grain growth of nanopowders. Recently, Chen and Wang [4] showed that the grain growth would be suppressed significantly through two-step sintering (TSS) method. As another efficient technique, microwave heating was reported to hinder grain growth.

In the present study, nanocrysalline 8YSZ powder were shaped via uniaxial dry pressing (DP) as well as slip casting (SC) method. Pore distribution, densification, microstructural evolution and mechanical properties of the samples produced by DP and SC during sintering were compared. Also, the obtained results were compared with those sintered via microwave heating as well as two step sintering.

## Materials and Experimental methods

Nanocrystalline powder of 8 mol% yittria stabilized zirconia was synthesized through glycine-nitrate combustion process. The as-synthesized sheet-like nanocrystalline agglomerates were milled in a planetary ball mill to break foamy agglomerates. As shown in TEM micrograph (Fig. 1), the particle size ranges between 15-33 nm. Green bodies were shaped by two different processes of dry pressing and slip casting. The uniaxial pressing was performed at different pressures in a steel cylindrical die. The green pellets were characterized by density measurements using volumetric method. Aqueous slurries with different solid contents (42 wt%- 67 wt%) and a fixed amount (0.8 wt% solid) of Dolapix as sterically stabilizer of slurry used for slip casting. green bodies formed via DP as well as SC were conventionally sintering up to 1500 ˚C with heating rate of 5 ˚C $min^{-1}$ without holding. To investigate the effect of sintering technique, samples pressed at 600 MPa with the highest relative density (~ 48.5 % of the theoretical density) were sintered through microwave heating as well as two-step sintering method. Hardness ($H_v$) was calculated using the Vickers indentation method on polished surface of the sintered samples. Also, fracture toughness ($K_{IC}$) was determined using crack length emanating the indentation center.

## Results and Discussion

Fig. 2 shows the fractional green density of dry pressed and slip cast bodies as a function of applied pressure (in logarithmic scale) and solid load (wt%), respectively. As shown, with increasing the solid content a continuous increase of green density was observed while in the case of dry pressed bodies two break points ($P_y$, $P_c$) separates three distinct linear parts. Previously, the authors reported [5] $P_y$=370 MPa as the agglomerate strength of the combustion synthesized nanocrystalline 8YSZ powder. Interestingly, upward trend was ceased at 600 MPa in which further increase of pressure did not enhance the green density any further. Inspection of green bodies reveals the occurrence of lamination transverse to the load direction at higher pressures (e.g. 900 MPa) resulting in no further advancement in densification. Using wet shaping, a significant increase in green density was obtained. The results show that slip casting of slurry containing ~ 65 wt% of nanocrystalline powder led to formation of green bodies with relative green density of ~ 60% TD. The higher the solid content is, the higher the green density would be achieved.

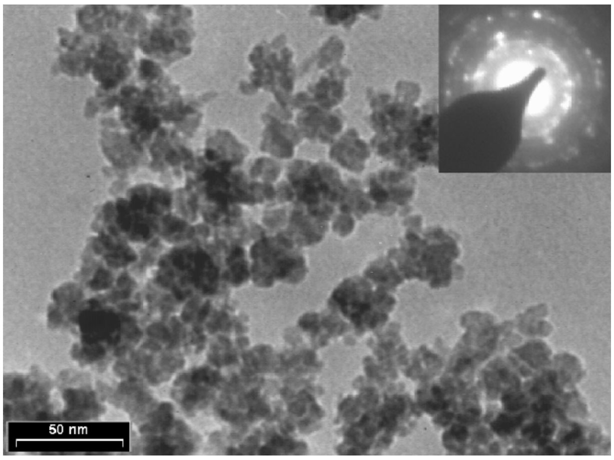

Figure 1. TEM image of nanocrystalline 8 mol% yittria stabilized zirconia (8YSZ) powder.

Figure 2. Effect of applied pressure and solid load on the fractional green density of nanocrystalline 8YSZ compacts shaped through dry pressing and slip casting.

To have a better insight on sintering behavior of green bodies shaped differently; one can consider density of samples (with identical green density) sintered through heating up to 1500 ˚C without holding. Fig. 3 exhibited the fractional fired density of DP samples and SC bodies as a function of fractional green density. Fig. 3 implies that higher green density led to higher fired density, this figure also shows that even with identical green density SC was more successful than DP.

Figure 3. Fired density of dry pressed and slip cast bodies as a function of fractional green density. All of the samples were sintered through heating up to 1500 ˚C with the heating rate of 5 ˚C min$^{-1}$.

To investigate the main reason of this phenomenon, pore size distribution of bodies with the same green density of 41% TD prepared by DP (at 400 MPa) and SC (with solid load of ~ 50 wt%) was presented in Fig. 4. Comparing the curves reveals two considerable differences: I) A significantly larger pores exhibit in DP samples (with an average diameter > 375 nm), while the size of largest pores formed in SC bodies is less than 80 nm, II) SC bodies also show narrower pore size distribution while the DP bodies have a wide pore size distribution. The pore size distribution can be a reliable evidence for achieved homogeneity degree of particle coordination. Wider pore size distribution can be originated from agglomeration of particles which depicts a poor homogeneity of particle coordination as a general feature of DP samples. Larger pores through green bodies can result in locally different shrinkage in subsequent sintering. From the microstructural point of view, it is the reason of the lower sintering temperature of SC bodies.

To find how efficiently shaping method as well as sintering technique influences on densification and grain growth of a nanopowder, one can consider sintering path (grain size versus fractional density). Fig. 5 represents the sintering path of nanocrystalline 8YSZ bodies formed by SC and DP with the maximum obtainable green density. The result of two-step sintering [5] as well as microwave sintering [6] for bodies formed by DP was also added. As shown in this figure, the parabolic grain growth at the final stage of sintering (TD > 90%) in conventionally sintered bodies shaped via SC and DP was observed but this exaggerated grain growth in SC bodies is more moderate than DP compacts. Application of a better shaping method i.e. SC, to obtain bodies with higher green density resulted in an increase in densification kinetic. However, the grain growth is not generally related to the shaping method. And the effect of shaping method is more effective in systems where grain growth rate relative to densification rate is high such as DP samples (Fig. 5). As the densification rate enhanced by higher green density as well as finer residual pores through green bodies, the sintering temperature as well as sintering time can be reduced and grain growth further suppressed (Fig. 5). As mentioned before, for instance sintering temperature of SC bodies were decreased 200 ˚C rather than DP compacts. As presented in pervious publications [5,7,8], the efficiency of TSS method to control grain growth during densification at the final stage of sintering is drastically high. As shown in Fig. 5, no parabolic growth was observed in TSS (details of TSS condition for nanocrystalline 8YSZ is available in [5]). The lower temperature in the second step of TSS ($T_2$ makes accelerated grain growth be suppressed. The immobile triple point junctions at the second sintering temperature ($T_2$) pin grain boundaries while grain boundary diffusion is active to obtain nearly-full dense samples. Microwave sintering shows similar trend such as conventionally sintered SC bodies. Seemingly, the effect of SC is similar to that of microwave sintering. Shorter sintering time as well as fast firing led to an increase of densification rate to grain growth one.

Figure 4. Pore size distribution of n-8YSZ compacts shaped through dry pressing (pressed at 400 MPa) and slip casting (with solid load of ~ 0.50 wt%) with an identical green density of 41 % TD.

Hardness and fracture toughness (FT) of nearly-full dense samples are summarized in Table 1. As seen, there is no significant change in hardness with varying grain size. However, DP samples which were conventionally sintered show the minimum hardness. This observation confirms the strong effect of final density and available porosity on hardness of the sintered specimens. Table 1 shows the FT values increased from 1.61 (for CS) up to 3 MPa $m^{1/2}$ (for SC, MS and TSS).  In other word, regardless of the grain size the effect of slip casting on improvement of FT is equal to those of TSS and microwave sintering. For TSS samples this behavior can be attributed to refining of microstructure which is a well-known method to enhance mechanical properties.

Figure 5. Effect of shaping method as well as sintering technique on the sintering path of nanocrystalline 8YSZ compacts. Two-step sintering and microwave heating were conducted on green samples shaped through dry pressing.

Table 1. Mechanical properties of nearly-full dense 8YSZ specimens processed via different methods

| Processing Method | Fractional Density | Grain Size (μm) | Hardness (GPa) | Fracture Toughness (MPa $m^{1/2}$) |
|---|---|---|---|---|
| CS[1] | 97.4 | 2.15 | 12.87 | 1.61 |
| SC[2] | 97.6 | 1.3 | 13.5 | 3.01 |
| TSS[3] | 97.6 | 0.295 | 13.5 | 3.16 |
| MS[4] | 98 | 0.9 | 13.72 | 3.17 |

[1] Dry Pressing + Conventional sintering
[2] Slip casting + Conventional sintering
[3] Dry Pressing + Two-step sintering
[4] Dry Pressing + Microwave sintering

Improvement of FT of SC bodies in comparison with CS ones can be originated from two different sources. Comparison between the results of SC and CS bodies indicate that two different mechanisms can enhance the FT of the system. First effect is grain size which decreased from 2.15 μm for CS bodies to 1.3 μm for SC ones and the second mechanism is higher homogeneity of SC green bodies as well as smaller residual pores with narrower size distribution. Lower pore density can lead to formation of smaller flaws with minimum density and so can optimize the fracture toughness. On the base of the SC and TSS result, the authors think the dominate mechanism to increase the fracture toughness of SC bodies related to the seconded mechanism (effect of homogeneity) because the grain size of SC bodies is higher than that of TSS samples but their fracture toughness are approximately equal. The authors previously reported the same reason (higher microstructural homogeneity) for higher fracture toughness of microwave sintered samples.

## Conclusions

The effect of shaping method and sintering technique on densification and grain growth of nanocrystalline 8YSZ powder was investigated. The results show that slip casting led to a significant increase of green density up to 12% of the theoretical one in comparison with dry pressing. As a consequence, the final grain size of slip cast bodies relative to dry pressed ones after sintering was decreased from 2.15 to 1.3 μm. An investigation on the effect of sintering technique on densification and grain growth of dry pressed samples revealed that instantaneous heating of green bodies through microwave radiation suppressed the grain growth of nanocrystalline powder. While the grain size of microwave sintered samples was ~ 0.9 μm, the application of two-step sintering technique yielded nearly-full dense structures with a mean grain size of 295 nm.

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