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Effect of Processing Methodology on Microstructure and Ionic Conductivity of Yttria-Stabilized Zirconia

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In this study, different methodologies were used for preparing commercial zirconia-8 mol% yttria sintered specimens. Powder compacts were conformed by uniaxial or by a combination of uniaxial and cold isostatic pressing. The sintering of powder compacts was carried out by the two-step sintering process and the results were compared to those of conventionally sintering specimens. The use of combined pressing procedures and two-step sintering process allowed for obtaining sintered specimens with high densities, small grain sizes and with minor differences in the electrical conductivity, which should improve the mechanical properties without compromising the electrical behavior at high temperatures.

Introduction

Zirconia containing 8 mol% yttria (8YSZ) is the most studied material for use as solid electrolyte in high temperature solid oxide fuel cells (SOFCs) (1). This ceramic material exhibits a cubic fluorite-type structure and high ionic conductivity. Compared to other yttria-doped zirconia compositions, the cubic material has relatively low fracture toughness, which can lead to crack formation and, consequently, compromise the cell performance. Reduction of the sintering temperature may decrease the grain size resulting in increased mechanical strength. However, to achieve high ionic conductivity the solid electrolyte must be dense and uniform with a well-controlled stoichiometry.

The ionic conductivity of yttria-stabilized zirconia is influenced by the microstructure attained during sintering, that is one of the most important steps in the processing of ceramic materials, in which a compacted powder reaches its final geometry and properties. The microstructure of commercial 8YSZ usually consists of micron-sized grains along with residual porosity inside the grains, whereas for lower yttria contents the grain size is in the sub-micrometer range. This is attributed to the thermodynamics and kinetics of grain growth in the different zirconia polymorphs (2).

Recently a two-step sintering process was proposed as a mean to obtain ceramic materials with high density along with reduced grain size (3). This process takes advantage of grain boundary diffusion with no or negligible grain boundary migration. In the two-step sintering process, the powder compacts are initially heated up to a high temperature (peak temperature). After a short holding time at that temperature, the compacts are cooled down to a dwell temperature, remaining at that temperature for a sufficiently long time. This sintering process has been successfully applied to a number of ceramic materials, like $BaTiO_3$ (4), SiC (5) and Al_2O_3 (6). In these studies, it was

shown that some parameters may influence the final density and grain size, such as the heating and cooling rates and the green microstructure of the powder compacts. Agglomerate-free nanocrystalline 8 mol% yttria-stabilized zirconia powders prepared by coprecipitation (7) or glycine-nitrate (8) methods reached high density (> 95% of the theoretical value) and sub-micrometer grain sizes using this sintering process. In these studies, conducted in homemade powders, the mechanical properties of the product materials were improved.

In this work, the two-step sintering process was applied to commercial 8YSZ aiming to obtain sintered ceramics with a homogeneous distribution of grain sizes, reduced mean grain size and suitable ionic conductivity.

Experimental

Zirconia-8 mol% Y_2O_3, 8YSZ, (99.6%, Tosoh Co.) was used as starting material. Cylindrical pellets were prepared by uniaxial pressing at 196 MPa or by a combination of uniaxial (30 MPa) and cold isostatic pressing (30,000 psi) followed by sintering. Sintering experiments were conducted in air by a two-step sintering process, where the samples were heated up to the peak temperature at $10^{o}C.min^{-1}$ and cooled down at $20^{o}C.min^{-1}$ to the dwell temperature. The holding time at each dwell temperature varied from 4 to 20 h. Powder compacts for linear shrinkage experiments were prepared by uniaxial followed by cold isostatic pressing.

The apparent sintered density was determined by the water immersion method. Linear shrinkage of powder compacts was studied by dilatometry (Labsys model, Setaram) up to 1380ºC in stagnant atmosphere of synthetic air. Phase characterization was studied by Raman spectroscopy (Renishaw InVia Raman Microscope), coupled to an optical microscope (Leica DM 2500M), using a He-Ne laser with 633 nm wavelength as excitation source. Microstructural observations were carried out by scanning electron microscopy (FE-SEM, Quanta 600F, FEI) on polished and thermally etched surface of sintered pellets. The medium grain size was estimated using the intercept method. Electrical conductivity measurements were carried out using a LF impedance analyzer (HP4192A) in the 5 Hz to 13 MHz frequency range. Silver was used as electrode material for electrical measurements.

Results and Discussion

Linear Shrinkage and Density

The commercial 8YSZ powder used in this work consists of granules of varying sizes prepared by spray drying (or atomization) of a mixed solution containing the desired cations. The atomization process is responsible for the good packing properties of this relatively fine powder (average crystallite size = 25 nm), resulting in good homogeneity of the green compact. The linear shrinkage of 8YSZ is shown in figure 1.

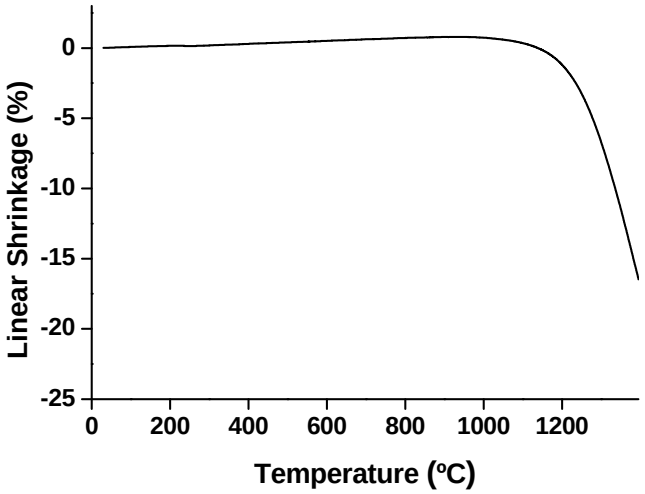

Figure 1. Linear shrinkage of 8YSZ.

The linear shrinkage of compacts prepared from commercial powders starts around 1000ºC and finishes only above 1400ºC. Then, in a conventional sintering process, temperatures in excess of 1350ºC are required to attain high density. The maximum shrinkage rate temperature is 1345ºC. Thus, above that temperature the grain growth plays an increasing role in the sintering process.

According to previous results (3,4) on the two-step sintering process, a minimum relative density of about 75% must be reached in the first step, in order to obtain high densification after the second step of sintering. In addition, the peak temperature determines the grain size, once negligible grain growth occurs during the second step of sintering. Then, the processing steps of the powders must allow for obtaining high density at not much higher temperatures, specifically below the maximum shrinkage rate temperature of the powder compacts.

Specimens prepared by uniaxial pressing attained 75% of relative density when the peak temperature is about 1375ºC, whereas for those prepared by combined uniaxial and isostatic pressing a peak temperature of 1330ºC is sufficient to accomplish that. Additionally, the dwell temperature for specimens prepared by uniaxial pressing cannot be lower than 1300ºC. Therefore, specimens prepared by uniaxial and isostatic pressing are preferred for obtaining lower medium grain size. Table I shows relative density values of sintered specimens.

TABLE I. Relative density values of 8YSZ specimens sintered at different dwell temperatures and soaking times. Conformation: uniaxial and isostatic pressing.

Sintering Profile (ºC/h)	**Relative Density (%)**
1400/2	98.5
1330/0 + 1230/12	93.0
1330/0 + 1230/20	97.0
1330/0 + 1250/4	92.5
1330/0 + 1250/8	95.5
1330/0 + 1250/12	98.5
1330/0 + 1280/4	96.5
1330/0 + 1280/8	99.8
1330/0 + 1280/12	96.0

The relative density is high for specimens sintered at 1400ºC for 2 h, which corresponds to the conventional sintering profile. Specimens sintered by the two-step process may also attain high densification by suitable choice of the dwell temperature and soaking time. In general, increase of the soaking time at a fixed dwell temperature results in increased density. Increase of the soaking time at the dwell temperature of 1280ºC beyond 8 h, in contrast, decreased the relative density indicating overfiring of 8YSZ specimens, in those conditions.

Structural and Microstructural Characterization

Figure 2 shows Raman spectroscopy spectra of sintered 8YSZ after uniaxial (left) and uniaxial followed by isostatic pressing (right).

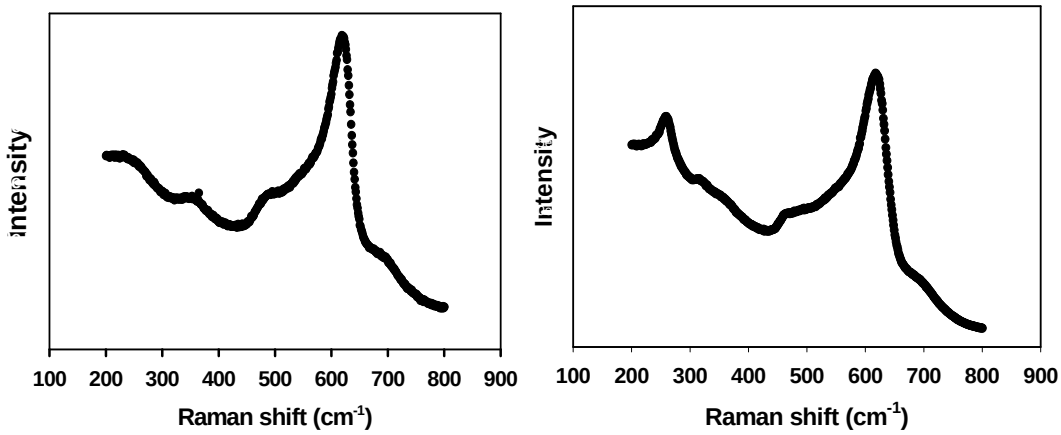

Figure 2. Raman spectra of 8YSZ specimens. Processing conditions: uniaxial (left) and combined uniaxial followed by isostatic (right) pressing; sintering at 1330ºC/0 h + 1250ºC/8 h.

These Raman spectra are qualitatively similar. A strong band is detected at ~ 610 cm^{-1}, which is attributed to F_{2g} mode of the cubic lattice. Other bands with weak intensities are observed in these plots. These bands are related to the tetragonal phase, which is usually detected on the surface of cubic specimens. Although the relative fraction of the tetragonal phase was not determined, it should be very small once it could not be detected in conventional X-ray diffraction experiments.

The main difference between these two spectra is related to the intensity of the band at ~ 260 cm^{-1}. Strengthening of this soft mode with cold isopressing suggests that it is somewhat related to the packing of powder particles due to the conformation process.

Figure 3 shows scanning electron microscopy micrographs of specimens sintered by the two-step process at 1330ºC/0 h + 1230ºC/12 h (left) and 1330ºC/0 h + 1280ºC/8 h (right).

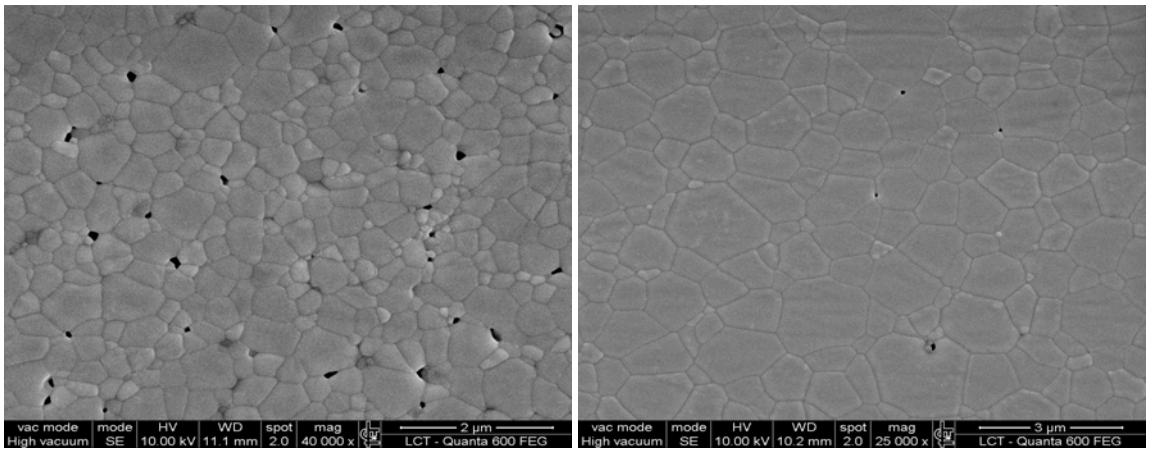

Figure 3. Scanning electron microscopy micrographs of 8YSZ specimens after sintering at (left) 1330ºC/0 h + 1230ºC/12 h, and (right) 1330ºC/0 h + 1280ºC/8 h.

It is noted the homogeneous microstructure with different fractions of porosity, which is confined at the grain boundaries. Thus, in a first approach, this residual porosity can still be eliminated by increasing soaking time. No abnormal grain growth was observed in the studied specimens. Specimens sintered at different dwell temperatures by the two-step process exhibited similar microstructure features. The medium grain size determined by the intercept method is listed in table II.

TABLE II. Medium grain size of sintered specimens. Conformation: uniaxial and isostatic pressing.

Sintering Profile (ºC/h)	**Mean Grain Size (µm)**
1400/2	2.98 ± 0.33
1330/0 + 1230/12	0.58 ± 0.01
1330/0 + 1230/20	1.40 ± 0.32
1330/0 + 1250/8	0.69 ± 0.01
1330/0 + 1250/12	0.80 ± 0.05
1330/0 + 1280/4	0.87 ± 0.02
1330/0 + 1280/8	1.18 ± 0.23

The medium grain size of specimens sintered at 1400ºC/2 h is ~ 3 µm, whereas those of specimens sintered by the two-step process are, in most cases, in the sub-micrometer range. For all studied dwell temperature, the mean grain size increases with increasing soaking time. This result shows that for commercial 8YSZ there will be always grain growth in the second stage of sintering. However, specimens with mean grain sizes in the sub-micrometer range may be readily obtained, which should exhibit improved mechanical properties.

Electrical Conductivity

The electrical conductivity of specimens sintered at the dwell temperature of 1280ºC for several soaking times is shown in figure 4.

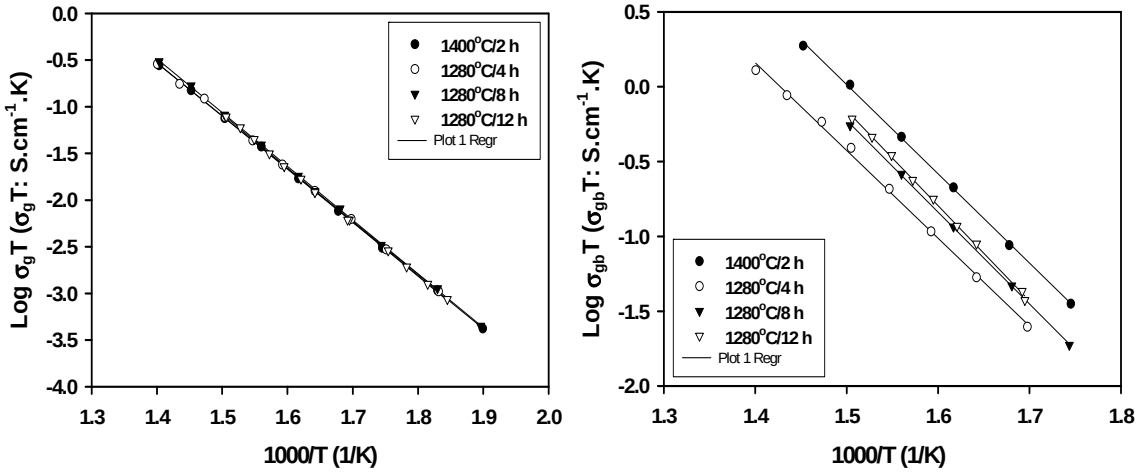

Figure 4. Arrhenius plots of grain (left) and boundary (right) for 8YSZ sintered at 1400ºC/2 h and at several soaking times at the dwell temperature of 1280ºC.

The grain conductivity (left) is similar to that of the specimen sintered at 1400ºC/2 h, whereas the grain boundary conductivity (right) is high for the latter. The grain boundary blocking effect for specimens sintered at 1280ºC is higher for soaking times of 4 h, and similar for 8 and 12 h.

Figure 5 shows Arrhenius plots of grain (left) and grain boundary (right) conductivities for specimens sintered with varying dwell temperatures and soaking times.

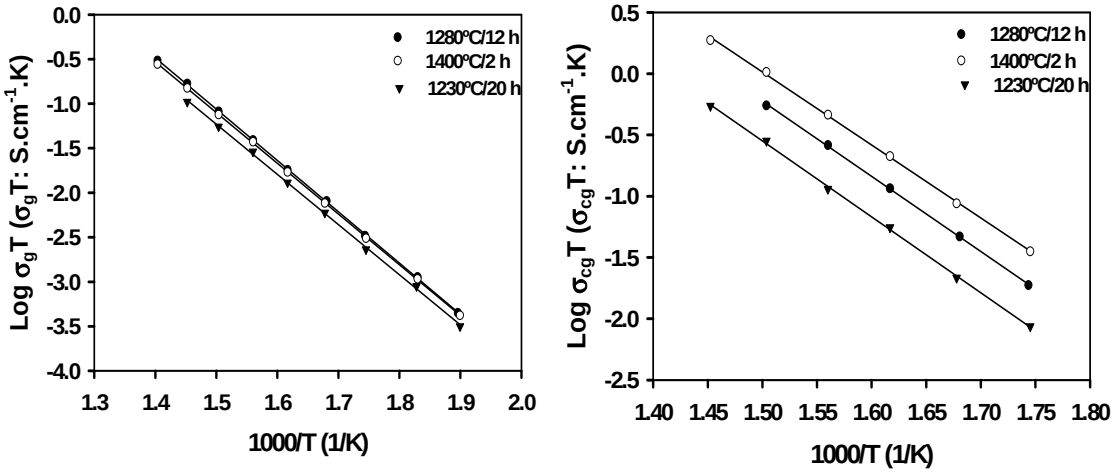

Figure 5. Arrhenius plots of grain (left) and boundary (right) for 8YSZ sintered at several dwell temperatures and soaking times.

The conductivity of grains is slightly lower for specimens sintered at 1230ºC. This result may be a consequence of residual impurity dissolution inside the grains or segregation of the stabilizer (yttrium ions) at the grain boundaries, due to the relatively large soaking time. The grain boundary blocking decreases steadily with increasing dwell temperature, and this effect can be attributed to the grain boundary area, which is different in these specimens. It should be remarked that the grain boundary blocking

effect disappears for temperatures above ~ 700ºC and, then, do not impose any restriction to the use of the two-step sintering process for technological purposes.

The capacitance of grains for all studied specimens determined in the apex of the high-frequency semicircle in impedance diagrams is 6.5-7.0 pF/cm, showing that no significant differences may be found in the composition and structure of grains. The capacitance of grain boundaries, calculated in the same way for the semicircle at intermediate frequencies, increases with the dwell temperature (at a fixed soaking time) and with soaking time (at a fixed dwell temperature). This effect is directly related to variation in the grain boundary area. Apparent activation energy values are 1.13 ± 0.02 eV and 1.20 ± 0.04 eV, respectively, for grains and grain boundaries.

Conclusions

Sintered specimens of commercial 8YSZ powders were prepared by the two-step sintering process. These specimens have a range of grain sizes and densities depending on the sintering profile. The combined uniaxial and isostatic pressing allowed for reducing the peak temperature below that of the maximum shrinkage rate, and the dwell temperature to about 1230ºC. All sintered specimen exhibited cubic fluorite-type lattice with small amount of tetragonal phase. Growth of the grain size occurred during the second step of sintering, although most of the studied specimens exhibited grain sizes in the sub-micrometer range. The grain conductivity is slightly lower for the lower dwell temperature and longer soaking time, when compared to that of specimens sintered at 1400ºC/2 h. The use of combined pressing procedures and two-step sintering processes allowed for obtaining sintered 8YSZ specimens with high density, small grain size and with minor differences in the electrical conductivity, which should improve the mechanical properties without compromising the electrical behavior at high temperatures.

Acknowledgments

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