

CHARACTERIZATION OF POROUS ZIRCONIA PREPARED FROM POTATO STARCH

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ABSTRACT

Porous zirconia (3 mol% yttria stabilized ZrO₂) was processed by the starch consolidation method using potato starch as a pore forming agent and binder. Various ZrO₂-starch compositions with volume fractions of starch (relative to the volume of solids) between 0.44 and 0.68 were prepared. Concentrated aqueous suspensions (near to 50 vol %) of the different compositions were consolidated in a plastic mold by controlled heating. The effects of the volume fraction of starch in the green body X_{st} and sintering temperatures (1000-1500 °C) on relative density and microstructure of sintered bodies were examined by scanning electron microscopy SEM and Hg porosimetry. The microstructure consisted of large spherical pores left by the starch granules, having diameters of 50 μm or higher and connected by channels of approximately 5 μm size. Total porosity of products sintered at 1500°C increased slightly from 49 to 54 vol. % for X_{st} of 0.23 and 0.54, respectively. The porosity was completely open for the different X_{st} values.

Key words: zirconia, porous ceramics, starch consolidation casting.

INTRODUCTION

The use of zirconia based materials either as dense or as porous ceramics in industrial applications seems to be increasing. Porous stabilized zirconia combines the mechanical requirements of a high-strength material with appropriate properties such as high temperature stability and corrosion and thermal shock resistance. Volume porosity, pore size and pore connectivity may be adjusted for ceramic filters, supports for catalyst and components for solid oxide fuel cells. To produce continuous porous materials several conventional ceramic processing techniques have been used such as foaming of ceramic suspensions, adding fugitive materials to the ceramic powder or infiltrating reticulated polymer foams with a ceramic suspension ⁽¹⁾. Among these techniques, starch consolidation casting has been successfully used to produce materials with complex shapes and high porosity at low cost ⁽²⁾. Starch has two functions in this process; primary is added to the ceramic composition as a fugitive additive. Pores are formed after burnout of granules by heating. Also, starch forms a gel during consolidation which provide green strength through formation of bonds with ceramic acting as a binder for the particles ⁽³⁾.

In this work, porous 3Y-ZrO₂ ceramics were produced by starch consolidation casting using a commercially available submicronic ZrO₂ powder and potato starch. Sintering temperature has a significant role in influencing the properties of porous ceramic, especially the nature and the amount of the porosity. Therefore the effect of sintering temperature between 1000 and 1500°C on the evolution of microstructure and pore volume and morphology of resultant material was examined, using Hg porosimetry and SEM.

MATERIALS AND METHODS

Starting materials

Fine commercial zirconia powder stabilized with 5.1 wt% Y₂O₃ in tetragonal phase was used. The average particle size was 0.6 μm. Potato starch used granules exhibited a bimodal size distribution with a main peak at 54 μm and a fine fraction of less than 10 vol% having a mean diameter of 10 μm.

Various ZrO₂-starch compositions with volume fractions of starch (relative to the volume of solids) between 0.45 and 0.71 were prepared.

Processing

To minimize the shrinkage of the ceramic, concentrated suspensions of zirconia containing starch with a minimum of 50 vol% of solid content were prepared. Stabilized suspensions were prepared by adding zirconia to aqueous solutions containing 0.3 wt% of dispersant (an ammonium salt of a polycarboxylic acid) at pH 9. The suspensions were ultrasonicated, and subsequently the amount of potato starch was mixed with the zirconia suspension. Then, the mixed suspensions were poured in plastic molds which were coated with a release agent and consolidated by a thermal treatment at 90 °C for 30 minutes. Cylindrical compacts were obtained, with approximate dimensions of 25 mm diameter and 15-20 mm thickness. In addition some zirconia compacts were prepared by slip casting in plaster molds to determine the relative increase in porosity created by the starch content. Compacts were dried firstly at room temperature and then at 110 °C up to a constant weight.

Sintering and characterization

The decomposition reaction of pure starch and that in the zirconia starch mixtures was previously analyzed by differential thermal analysis and thermogravimetry (ATD-TG). The results showed that elimination of starch occurred in steps below 400 °C and was completely decomposed at 600 °C. Thus, burning out of starch was done by slow heating up to 800°C, and then held for 2 h at 1000 °C. Finally, the precalcined cylinders were sintered at 1300, 1400 or 1500 °C for 2 h. The relative sintered density (% of the theoretical, density of 6.05 g/cm³ was used for ZrO₂) and open porosity were determined by the water absorption method. The microstructures of the porous ZrO₂ were observed by SEM, using the fracture surface of the sintered specimens. The channel size distribution of the samples was measured by mercury intrusion porosimetry.

RESULTS AND DISCUSSION

Effect of sintering temperature on properties of sintered bodies

The production of a sintered body involves several stages (drying of the consolidated sample, decomposition of starch and sintering) associated with important density and volume changes. Because the starch granules were soluble in

hot water, they partially formed a gel in the current consolidation process (90°C-30 min). This means that the starch gel would leave additional pores in the green body after drying and shrinkage as was showed before ⁽⁴⁾. After drying and burnout of the starch, the weight loss was near to 21-29% and 19-51 %, for 44 to 68 vol% of potato starch in the composition, which were originated from the evaporation of water and the pyrolysis of starch at 1000°C respectively. Shrinkages of samples after drying was 4 (linear %) and precalcining was 7 vol%. Increasing starch content to 68 vol% the respective values were 13 (linear %) and 12 vol% indicating that the removal of more starch affected slightly the sintering shrinkage. However, a higher shrinkage in the green body was found with increasing added starch from 44 to 68 vol%, and thus the volume fraction of starch relative to the volume of the green compact X_{st} increased from 0.23 to 0.54, respectively.

The effect of sintering temperature on relative density of zirconia compacts prepared by slip casting without starch and porous samples obtained from suspensions containing 44 and 68 vol% of potato starch is showed in Figure 1. For these starch contents in the suspension, the X_{st} resulted 0.23 and 0.47, respectively.

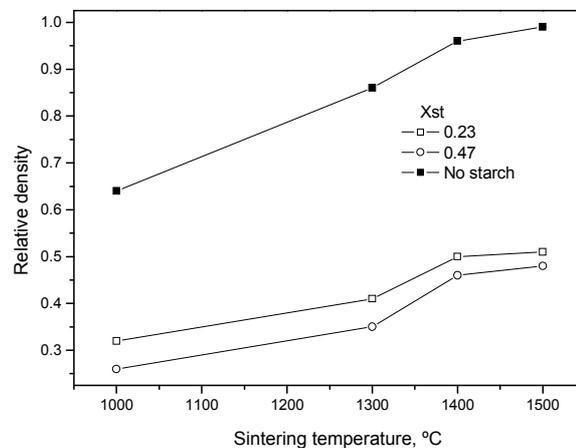


Figure 1: Relative density vs. sintering temperature for volume fraction of starch in the green compact X_{st} of 0.23 and 0.47 and for compacts obtained from slip casting without adding starch.

The relative sintered density of compacts without adding starch increased from 0.64 to 0.96, by increasing the sintering temperature from 1000 to 1400°C, and bodies achieved higher densification at 1500°C.

In the case of porous samples the relative sintered density gradually increased by increasing the sintering temperature up to 1400°C due to densification of zirconia matrix but reached a value significantly lower than that of the samples without starch. Consequently a pronounced reduction in porosity occurred as zirconia matrix densified.

Density of porous samples with nearly full density in the matrix (i.e. sintered at 1400°C) slightly changed with a further increase in temperature. In this condition, the maximum relative density achieved was 0.48 and 0.45 for starch volume content X_{st} of 0.23 and 0.47, respectively indicating no significant difference in porosity between the samples.

Effect of starch content on characteristics of porous samples.

Typical microstructures of a fracture surface of porous materials prepared from different compositions and sintered at 1400°C are showed in Figure 2.

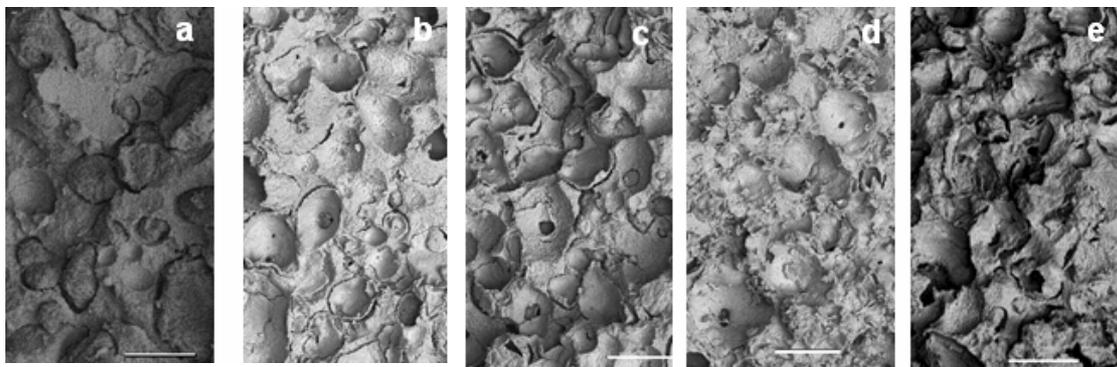


Figure 2: SEM micrographs of the fracture surfaces of porous ZrO_2 sintered at 1400°C for different volume fraction of starch in the green body (a) 0.23, (b) 0.27 (c) 0.29 (d) 0.38 and (e) 0.47 .(Bar 50 μm)

Microstructure consists in a dense zirconia matrix due to high temperature used and large rounded pores with a size of approximately 50 μm and larger homogeneously distributed. Small circumferential cracks developed in the spacing surrounding the pores due to the shell formation. These shells were previously observed using the

starch processing method ⁽²⁻⁴⁾. Shell formation resulted from the gel shrinkage that takes place during drying. Further pyrolysis and heating produced a nonuniform differential shrinkage due to different densification rates between high and low density regions.

As shown in Figures 2 a and e microstructure was modified by increasing the amount of starch. Low Xst originated large rounded pores which were in close contact each other and homogeneously distributed in the matrix. In contrast, the porous structure for high Xst became less uniform and pore shape was difficult to determine. Moreover, a complex pore structure with a broader size distribution resulted at high Xst due to the initial high overlapping and interpenetration between starch granules in the green body.

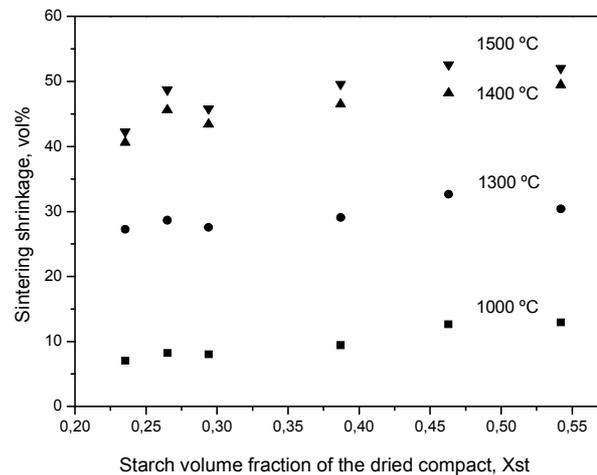


Figure 3: Sintering shrinkage vs. starch content in the green compact Xst for different sintering temperatures

Pores with diameters in the range 40–60 μm were found in the samples. However, the ceramic grain size was very fine (0.6 μm). Slamovich and Lange ⁽⁵⁾ demonstrated that organic inclusions larger than the size of ceramic particles originate large pores which persist even after prolonged sintering times. Thus, the large spherical pores created by the starch remained thermodynamically stable during sinterization due to the relatively large area in relation with the size of interstices between the zirconia particles.

The effect of the starch volume fraction in the green body Xst on physical properties of porous samples sintered was examined. Figure 3 shows the sintering shrinkage vs. Xst curves for different sintering temperatures. The shrinkage remained almost constant or slightly increased in the range of xst studied. The shrinkage of products sintered at 1500°C increased from 42 to 51 vol % for Xst 0.23 and 0.54 respectively, because of the small reduction in the ZrO₂ packing density in the green body.

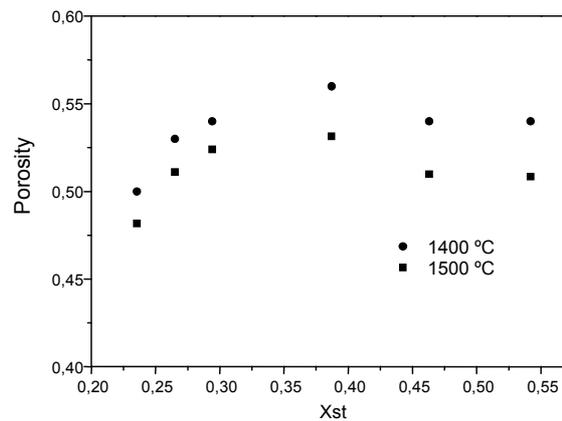


Figure 4: Total porosity vs Xst curves for porous samples sintered at 1400 and 1500 °C.

Figure 4 shows the variation of total porosity with Xst ranging between 0.23 and 0.54 for samples with nearly full density in the matrix; similar curves resulted at higher temperatures used. Total porosity increased by increasing the amounts of starch in the green body until Xst 0.4, then it remained unchanged or slightly reduced with a further increase in the starch content to 0.54. The variation in porosity did not follow a general linear increase predicted by the Xst (i.e. porosity identical to Xst) as previously reported using several organic inclusions as fugitive pore former ⁽⁶⁾. Greater porosity than expected from Xst was obtained at low starch additions due to the swelling of starch granules while low porosity resulted at high Xst due to high initial overlapping and interpenetration of granules.

Figure 5 shows open porosity versus total porosity of materials prepared from Xst between 0.23 and 0.54 and different sintering temperatures.

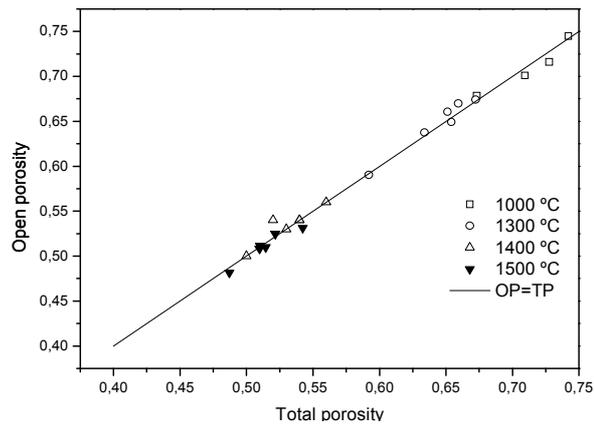


Figure 5: Volume fraction open porosity OP versus total porosity TP for a range of Xst between 0.23 and 0.54 and different sintering temperatures.

The line represented the volume fraction of open porosity that would occur if 100 % of the porosity was completely open. Figure 4 shows that pores resulted completely interconnected even at 1500°C.

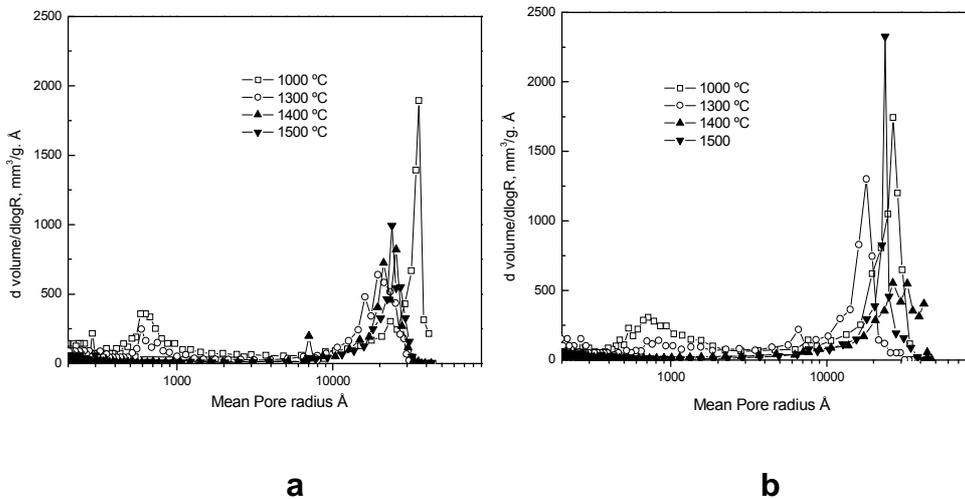


Figure 6: Channel-size distributions of samples produced from xst 0.23 (a) and 0.47 (b) sintered at different temperatures.

Figure 6 shows the channel-size distributions of samples produced from xst 0.23 and 0.47 measured by mercury porosimetry for different sintering temperatures. The sample prepared from Xst 0.23 sintered at 1000 °C had a bimodal distribution which was composed by channel populations having peaks at $\sim 3.5 \mu\text{m}$ and $\sim 0.07 \mu\text{m}$ (caused by the interstices between zirconia particles). At 1400 °C, the peak at

~0.1 μm disappeared and that at ~3.5 μm slightly reduced to ~2.5 μm . The sample prepared from Xst 0.47 exhibited a wider channel size distribution in good agreement with Figure 2e. After sintering at 1000°C also exhibited two peaks at ~2 μm and ~0.05 μm . Similarly, the distribution changed to monomodal at 1500°C for which the radius of large channels increased to 2.6 μm .

CONCLUSIONS

Yttria-stabilized zirconia ceramics with a range in porosity between 50 to 63 vol% were processed using a starch consolidation casting with potato starch. In the experimental conditions used, the higher porosity combined with relatively lower sintering shrinkage could be obtained with zirconia- 60 %vol starch composition. Nearly spherical pores of 50 μm and higher resulted totally interconnected by channels of approximately 5 μm . Materials with these textural properties are potentially useful for applications that require high permeability as filters, catalyst supports and for the preparation of composites by infiltration.

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