Processing of porous yttria-stabilized zirconia tapes: Influence of starch content and sintering temperature

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Abstract

The tape-casting process was used to produce porous yttria-stabilized zirconia (YSZ) substrates with volume fractions of porosity ranging from 28.9 to 53 vol.% by using starch as a fugitive additive. Concentrated aqueous YSZ slips with different amounts of starch and an acrylic latex binder were prepared. The influence of the volume fraction of starch and sintering temperature on the sintering behavior and final microstructure were investigated. The microstructure consisted of large pores created by the starch particles with lengths between 15 and 80 μm and smaller pores in the matrix with lengths between 0.6 and 3.8 μm. The pores in the matrix reduced the sinterability of the YSZ leading to the retention of closed porosity in the sintered tapes. The porosities were above those predicted for each of the starch contents. However, larger deviations from the predicted porosity were found as more starch was added. The open to total porosity ratio in the sintered tapes could be controlled by the volume fraction of added starch as well as by the sintering temperature. As the volume fraction of starch increased from 17.6 to 37.8 vol.% there was a gradual increase in the interconnectivity of the pore structure. The sintering shrinkage of the tapes at a given temperature could be directly related to the YSZ packing density in the matrix.
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1. Introduction

Porous ceramics find application in a variety of components, including fuel-cell electrodes, battery separators, filters and preforms used to manufacture metal/ceramic composites [1–3]. Copper-based ceramic-metallic (cermet) tapes are used for anodes in solid oxide fuel cells (SOFC) [4]. The synthesis of a porous YSZ matrix is the first step in the fabrication of the cermet. The Cu-YSZ cermet is then prepared by impregnating soluble salts of copper into the porous YSZ structure, after the YSZ has been sintered [4]. As the cermet anode should be 30 vol.% metal to ensure electronic conductivity, and should still remain highly porous to allow diffusion of fuel to the electrolyte interface, very high initial porosity (∼40 vol.%) is desirable for the YSZ substrate before the addition of soluble salts of copper.

The objective of this work was to develop a porous YSZ matrix by tape-casting. A way to produce porosity in the tape is to mix organic particles into the slurry preparation stage [5]. These organic particulates can be chosen so that they pyrolyze during the binder-removal step, leaving stable voids that are not removed during the subsequent sintering procedure [5]. This method of introducing porosity offers a direct control over the porous characteristics of the final ceramic. In addition, it may be possible to form open pore networks because of the potential percolation of these pyrolyzable particles in the green body [5]. Starch is one of the more frequently used pore-forming agents in ceramic technology [6]. Due to its chemical composition (a polysaccharide consisting essentially of C, H and O) this natural biopolymer is easily burnt out during firing without residues in the final ceramic body. It has also been shown that the morphology and the size of the pores are particular to the type of starch used to create the porosity [7].

The tape-casting process for porous ceramics involves the preparation of a concentrated YSZ suspension with the addition

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of a pore-forming agent, a binder and a plasticizer [8]. Organic solvents are frequently used to prepare the concentrated ceramic suspensions [9]. Due to the volatility and toxicity of these organic solvents, the development of water-based tape-casting systems is considered to be desirable. A water soluble binder such as an acrylic latex emulsion can be used to produce YSZ tapes [10]. These emulsions have useful and unique characteristics such as internal plasticization and controllable crosslinking [10]. In the present work we have developed an aqueous-based starch/YSZ/latex system for tape casting of porous ceramics.

It is well-known that SOFC performance is affected by the structure of the anode [11]. Therefore, it is very important to be able to control the overall porosity and structure of the pores in the porous YSZ matrix that is used to make the anode. In this work, the effect of the volume fraction of starch on the properties of green tapes was studied. In addition, the influence of the volume fraction of starch and sintering temperature on the sintering behavior and final microstructure were investigated.

2. Experimental procedure

2.1. Materials

A commercial yttria doped YSZ powder (Y8Z01, Saint-Gobain, France) was used in this study. The mean particle diameter and the specific surface area were 0.53 μm and 8.26 m^2/g, respectively. Potato starch commercially available in Argentina was used as pore former agent. The starch granules exhibit a small degree of anisotropy with a median equivalent diameter of about 50 μm.

A commercial ammonium polyacrylate (NH$_4$PA) solution (Duramax D 3500, Rohm & Haas, Philadelphia, PA) was used as a dispersant. The binder was an acrylic latex emulsion (Duramax B1000, Rohm & Haas, Philadelphia, PA) with solids loading of 55 wt.%, an average particle size of 0.37 μm, and a glass transition temperature of −26 °C.

2.2. Slip preparation

Concentrated aqueous YSZ suspensions with a solid loading of 77 wt.% were prepared by deagglomeration of the powder in distilled water with 0.3 wt.% NH$_4$PA (dry weight base of powder) using an ultrasonic bath. Different amounts of starch in the range of 13–33 wt.% (dry weight base of YSZ powder) were added to the stabilized YSZ slips, followed by ultrasonic treatment. Subsequent to this, 25 wt.% latex (dry weight basis with respect to (YSZ + starch) powders) was added to the slurry, followed by additional stirring. The pH of the suspensions was adjusted to 9.0 with ammonia (25 wt.%).

2.3. Tape-casting

The slips were cast manually on a Mylar film using an extensor. The gap between the extensor and the film was adjusted to 0.4 mm. The cast tapes were subsequently dried in air at room temperature up to constant weight; afterwards, they were stripped from the film.

2.4. Burnout and sintering

The burn out of organic additives was achieved by slow heating (1 °C/min) up to 1000 °C. Then, the pre-calcined tapes were sintered at 1300, 1400, 1500 and 1600 °C for 2 h, with a heating rate of 5 °C/min.

2.5. Characterization of green and sintered tapes

The tapes were weighed and measured geometrically to determine the green density. The weight loss of the green tapes on sintering was also determined.

The bulk-sintered density was calculated from the dimensions and weight of the sintered pieces. In order to calculate the relative green and sintered densities, density values of 6.05 and 1.45 g/cm^3 were used for YSZ and starch, respectively. The sintering shrinkage was geometrically measured.

The open porosity and the pore size distribution of the sintered tapes were determined using mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy). The microstructure of green and sintered samples were observed on fractured surfaces using a field emission scanning electron microscopy (FE-SEM) (Hitachi S-4700).

3. Results and discussion

Table 1 shows the compositions of YSZ tapes with different amounts of starch. We can define the following expressions:

$$V_S = \frac{\text{volume of starch}}{\text{bulk green volume}}, (V_T) \tag{1}$$

$$V_S = \frac{\text{volume of starch}}{\begin{array}{c}\text{volume of starch} + \text{volume of YSZ}\\ + \text{volume of latex} + \text{volume of pores}\end{array}}$$

$$F_{VS} = \frac{\text{volume of starch}}{\text{volume of solids}}$$

$$F_{VS} = \frac{\text{volume of starch}}{\text{volume of starch} + \text{volume of YSZ} + \text{volume of latex}}$$

$$F_{VZ} = \frac{\text{volume of YSZ}}{\text{volume of solids}} \tag{3}$$

$$F_{VL} = \frac{\text{volume of latex}}{\text{volume of solids}} \tag{4}$$

Table 1
Compositions of YSZ tapes with different amounts of starch.

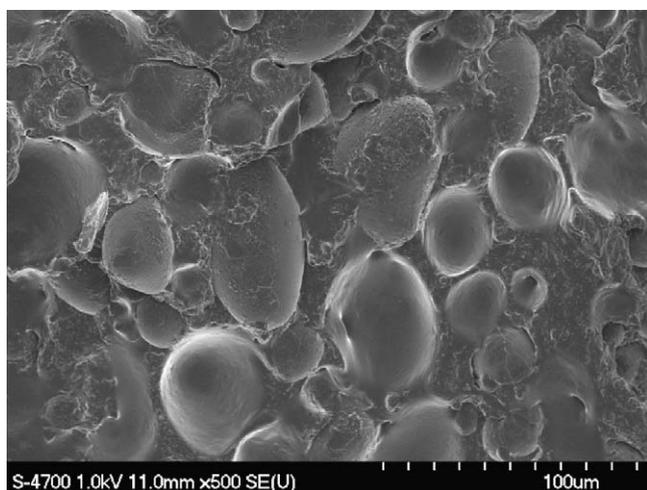| V_S (%)	F_{VS} (%)	F_{VZ} (%)	F_{VL} (%)	F_{VL}/F_{VZ}
0	0	42	58	1.38
17.6	19	31	50	1.61
28.4	30	25	45	1.82
37.8	40	19	41	2.16

Fig. 1. SEM micrograph of a green tape with 37.8 vol.% starch.

V_S indicates the volume of starch relative to the volume of the green tape; whereas, F_{VS} is the volume of starch with respect to the volume of solids.

The relative green density of the tapes with volume fraction of starch (V_S) between 0 and 37.8% was 93–95% of the theoretical density. The relative green density values were close to the theoretically predicted values. This indicates that some residual porosity, between 5 and 7% remained in the tapes. A certain amount of porosity can be generated by air trapped in the suspension or by incomplete mixing of the powders during processing [5]. In addition, drying can also create non-uniformly mixed powders in the green tape. Different settling behavior of the powder constituents and/or re agglomeration during solvent evaporation can also occur [5].

The relative green density was kept nearly constant with increasing the amount of starch from 0 to 37.8%. This suggested that the addition of starch to the YSZ tape did not introduce additional porosity. Fig. 1 shows a SEM image of a green tape with 37.8 vol.% starch. The latex filled the space between the s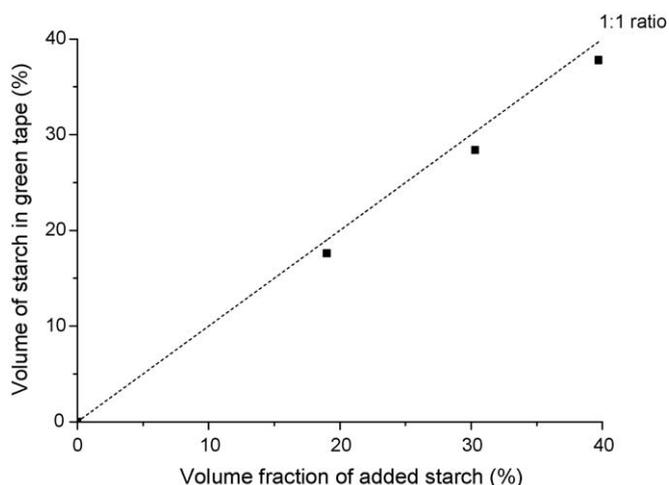tarch particles, and voids were not found at the starch particle contacts. Thus, as the starch content increased, the starch particle contact as a result of percolation did not contribute to a reduction in packing efficiency.

Fig. 2 shows the volume fraction of starch in the green tape (V_S) as a function of the volume fraction of added starch (F_{VS}). The 1:1 relationship between V_S and F_{VS} is also indicated in this figure. This relationship would be expected if residual porosity was not present in the green tape (Eqs. (1) and (2)). However, a slight deviation from the 1:1 relationship could be seen, this indicates that the volume fraction of starch in the green tape was slightly lower than the volume fraction of added starch, due to the presence of some residual porosity in the green body.

Fig. 3 shows the F_{VL}/F_{VZ} ratio and the bulk YSZ packing density (δ_{YSZ}) in the matrix versus the volume fraction of starch in the green tape (V_S). The bulk YSZ packing density in the matrix can be expressed by:

$$\delta_{YSZ} = \frac{\text{volume of YSZ}}{V_T - \text{volume of starch}} \tag{5}$$

This parameter indicates the bulk packing density of the YSZ within the matrix, which is formed by the binder and pores, surrounding the starch particles.

As the amount of starch increased more latex was required to bind the particles, thereby increasing the F_{VL}/F_{VZ} ratio. The added latex along with the starch decreased the bulk packing density of the YSZ powder within the matrix. Thus, as the volume fraction of starch in the green tape increased the F_{VL}/F_{VZ} ratio also increased, thereby decreasing the YSZ packing density. This behavior has also been observed by our group in a previous study [12].

Fig. 4 shows the relative sintered density as a function of the sintering temperature for tapes with different volume fraction of starch: 0, 17.6, 28.4 and 37.8%. The relative sintered density of the tapes without starch increased from 56.7 to 90.3% of the theoretical density with increasing the sintering temperature from 1000 to 1600 °C. Thus, the YSZ tapes did not achieve full

Fig. 2. Volume fraction of starch in the green tape as a function of the volume fraction of added starch.
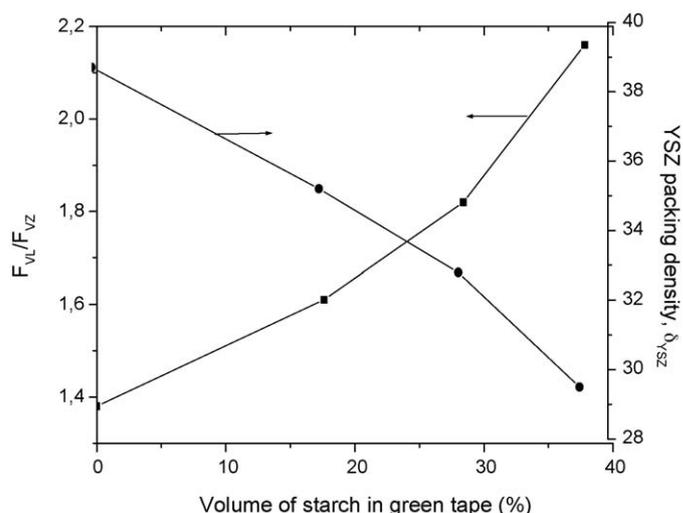

Fig. 3. F_{VL}/F_{VZ} ratio and bulk YSZ packing density in the matrix versus the volume fraction of starch in the green tape.
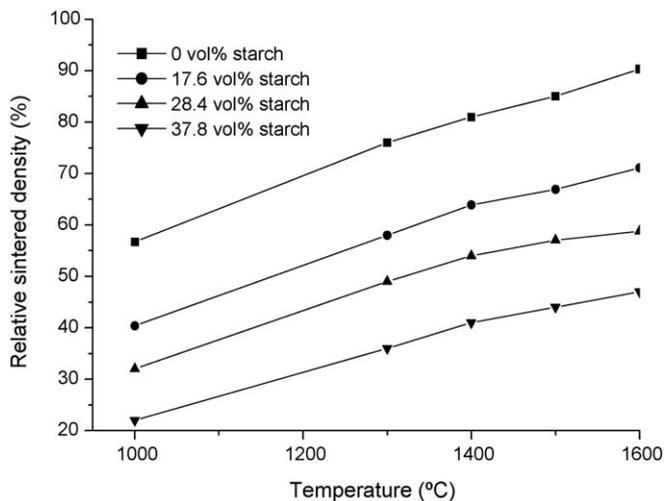
Fig. 4. Relative sintered density as a function of the sintering temperature for tapes with different volume fractions of starch.

densification at 1600 °C. This behavior will be explained in a subsequent paragraph.

The relative sintered density of the porous tapes, which was significantly lower than that of the tapes without starch, increased with increasing the sintering temperature up to 1600 °C due to the densification of the YSZ matrix. At a given temperature, the relative sintered density of the tapes decreased as more starch was added.

Fig. 5 shows SEM images of the tapes with 17.6 vol.% starch sintered at different temperatures. The YSZ matrix with some elongated pores left by the starch were observed. A reduction in the porosity of the matrix with increasing the sintering temperature could be seen; however, at 1600 °C the matrix was still not fully densified. This observation was also noted for the tapes prepared without starch sintered at 1600 °C (Fig. 4).

Some of the large pores left by the starch particles were empty but others had inner shells of YSZ separated from the rest of the YSZ matrix. Similar observations have previously been made by Lyckfeldt and Ferreira [13], who reported that there was some contraction of the starch particles during heating. A shell of ceramic particles, adhering to the surface of each starch particle, in the surrounding matrix is released from the rest of the matrix and follows the shrinking starch particles during heating [13]. Hence, a space between the formed shell of ceramic and the main ceramic matrix is left after sintering [13].

Fig. 6 shows the total bulk porosity of the tapes sintered at 1600 °C versus the volume fraction of starch in the green tape; the 1:1 relationship between the bulk porosity and the amount of starch is shown. This relationship assumed that a full densification of the YSZ matrix occurred and consequently the remaining porosity corresponds to the volume fraction of starch originally added. Deviations from the 1:1 relationship could be seen, the porosities were above the predicted amount for all starch contents. Figs. 4 and 5c confirmed that the YSZ matrix was not fully densified at 1600 °C. Therefore, the higher porosity observed with respect to the amount of added starch was due to an incomplete densification of the YSZ matrix during sintering.
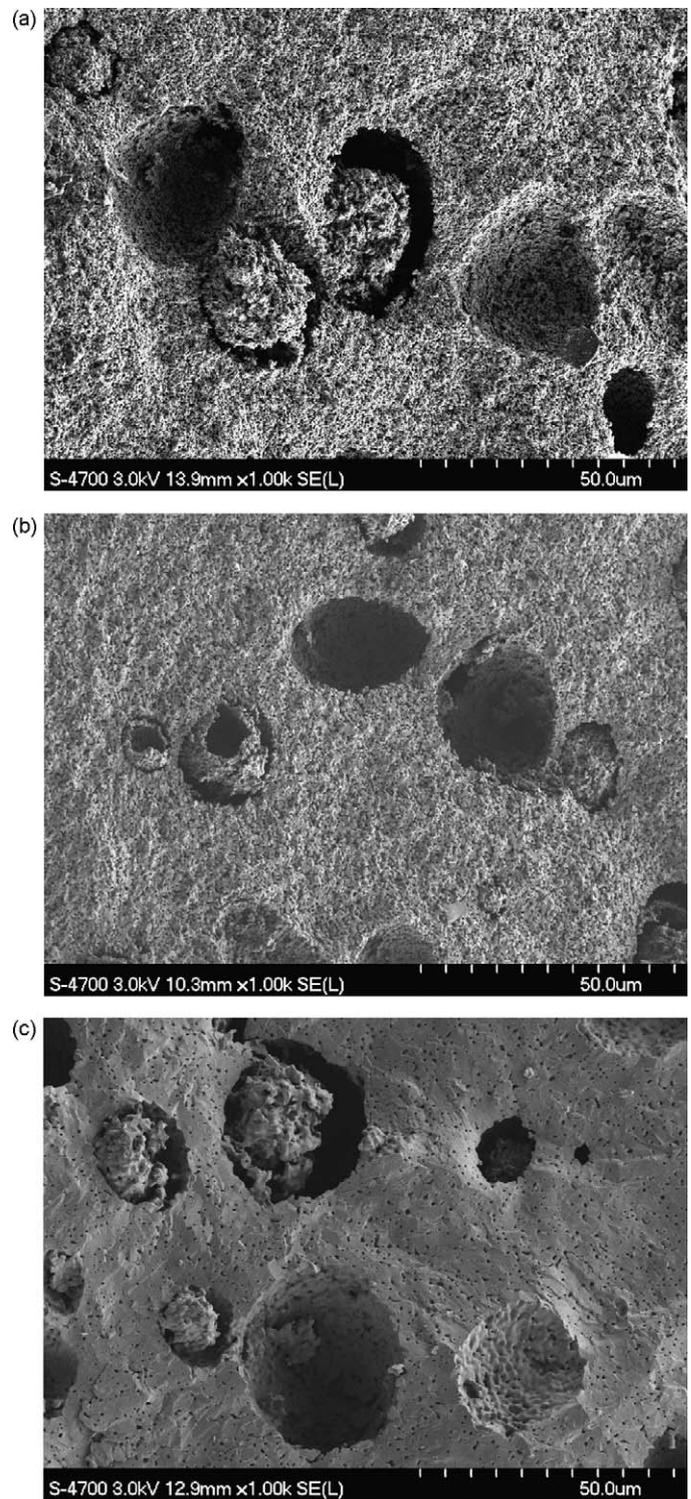
Fig. 5. SEM micrographs of tapes with 17.6 vol.% starch sintered at different temperatures: (a) 1300 °C; (b) 1400 °C; (c) 1600 °C.

Fig. 7 shows the matrix of the tapes with 0 and 37.8 vol.% starch sintered at 1600 °C. The micrographs show rounded and elongated pores with length between 0.6 and 3.8 μm. The coalescence of the latex particles during drying and the pore coalescence during sintering might contribute to the enlargement of the pores in the matrix. The onset of the latex coalescence is expected to occur during the drying of the cast-
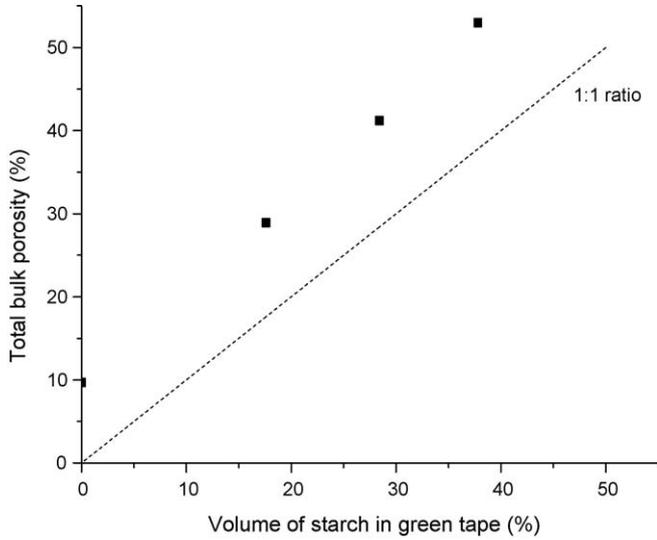
Fig. 6. Total bulk porosity of tapes sintered at 1600 °C versus the volume fraction of starch in the green tape.
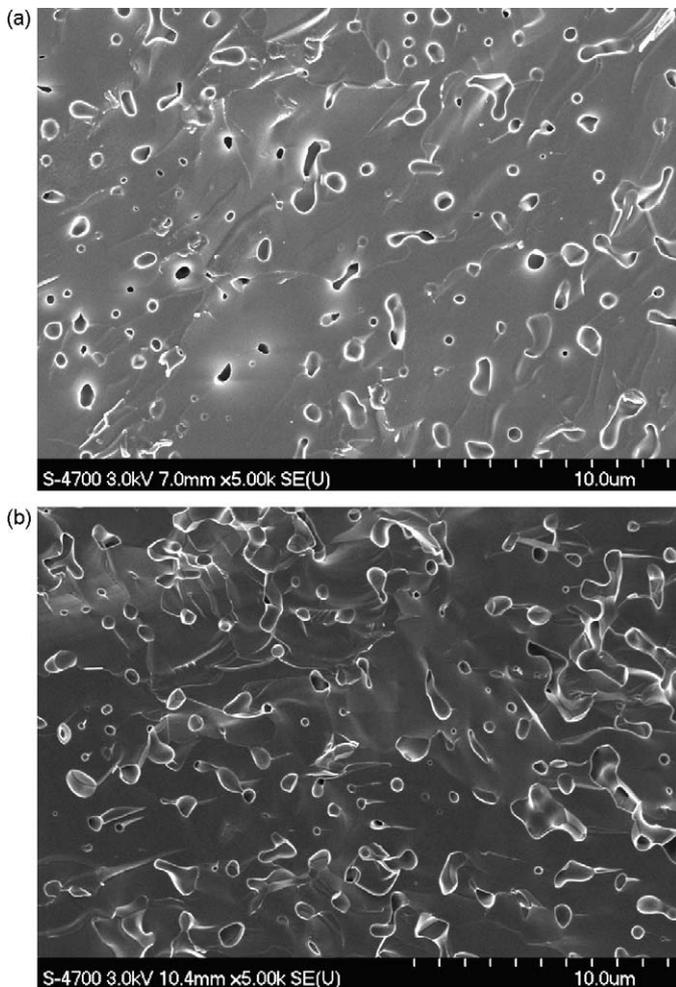
tapes when the volume fraction of latex particles approaches 0.6, its maximum solids loading [14]. The latex coalescence resulted in an increase in the particle size of the latex, thereby increasing the pore size left by the latex during burnout. The pores could also coalesce during sintering so that the pore size increased. The greater the pore size, the lower the driving force for sintering and shrinkage [15]. Consequently, enlargement of the pores leads to a decreased sintering rate [15]. Therefore, the large pores in the matrix reduced the sinterability of the YSZ leading to retained closed porosity in the sintered tapes.

Larger deviations from the predicted porosity as more starch was added were observed in Fig. 6. An increase in the matrix porosity with increasing volume fraction of starch in the green tape was found (Fig. 7). The added latex, along with the starch, reduced the packing density of the YSZ within the matrix (Fig. 3), thereby increasing the matrix porosity after sintering at 1600 °C. Consequently, the larger deviations from the predicted porosity with increasing added starch were attributed to the reduction in the YSZ packing density.

The total bulk porosity of the tapes sintered at 1600 °C is re plotted against $V_S + P_0$ ($F_{VL}/F_{VZ}/F_{VL0}/F_{VZ0}$) in Fig. 8; P_0 is the total porosity of the tapes without starch and the factor $F_{VL}/F_{VZ}/F_{VL0}/F_{VZ0}$ is the F_{VL}/F_{VZ} ratio of the green tapes with starch with respect to that of the tapes without starch. The term P_0 ($F_{VL}/F_{VZ}/F_{VL0}/F_{VZ0}$) represents the additional porosity produced by the latex volume added with respect to the YSZ which increased with increasing added starch. Clearly, the total porosity of the tapes followed that predicted based on the volume fraction of starch in the green tape plus the additional porosity described above.

The SEM images demonstrate visually that the overall pore structure is dominated by the large pores left by the starch particles. On the other hand, Hg porosimetry was used to measure
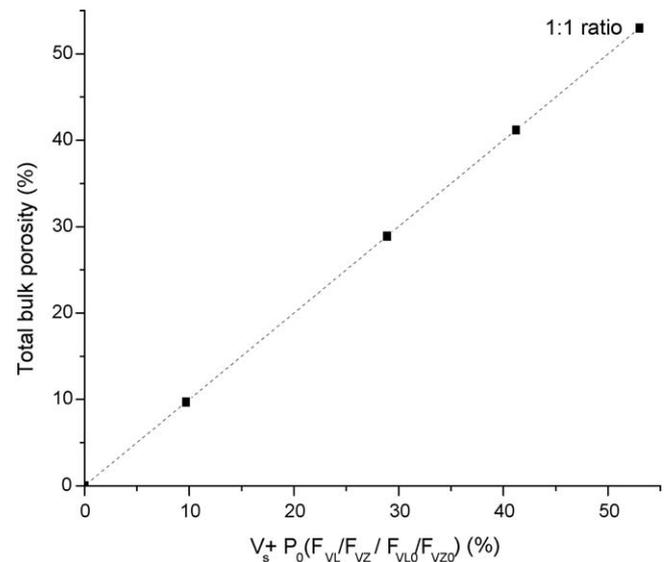

Fig. 7. The matrix microstructure of tapes sintered at 1600 °C with different volume fractions of starch: (a) 0; (b) 37.8%.

Fig. 8. Total bulk porosity of tapes sintered at 1600 °C versus $V_S + P_0$ ($F_{VL}/F_{VZ}/F_{VL0}/F_{VZ0}$). V_S = volume fraction of starch in the green tape; P_0 = total porosity of the tapes without starch; $F_{VL}/F_{VZ}/F_{VL0}/F_{VZ0}$ = volume fraction of added latex/volume fraction of added YSZ, of the green tapes with starch relative to that of the tapes without starch.
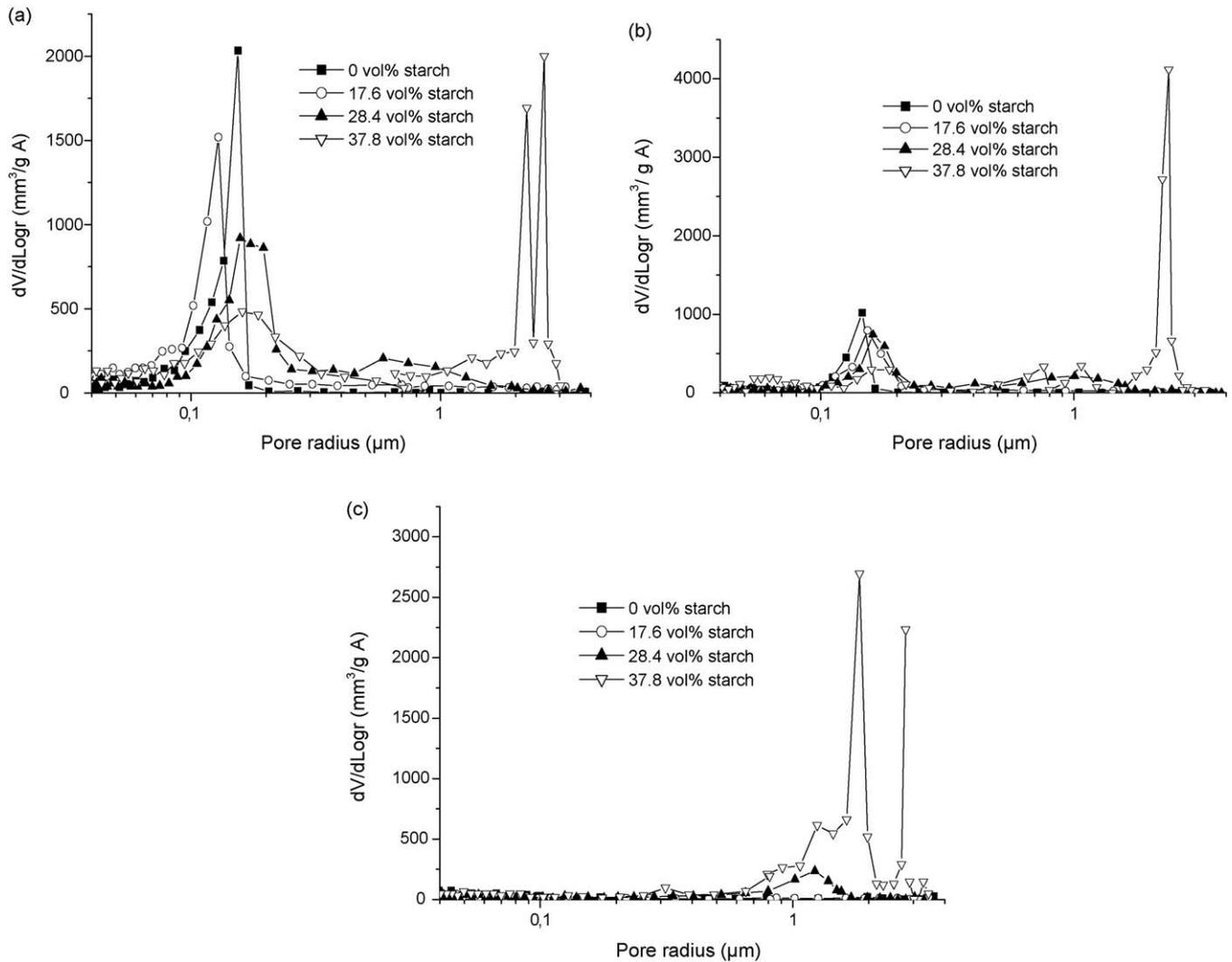
Fig. 9. Pore size distribution curves of tapes with 0, 17.6 and 37.8 vol.% starch sintered at different temperatures: (a) 1000 °C; (b) 1300 °C; (c) 1600 °C.

the smaller channels which corresponded to the connecting contacts areas, or necks, between much larger pores created by the original starch particles. Fig. 9a–c shows the differential pore size distribution curves of tapes with 0, 17.6, 28.4 and 37.8 vol.% starch, sintered at 1000, 1300 and 1600 °C, respectively. At 1000 °C a unimodal distribution of pore sizes was observed for 0 and 17.6 vol.% starch. The most frequent pore radius were 0.16 and 0.13 μm, respectively, which corresponded to the pores between the YSZ particles. For the tapes with 28.4 and 37.8 vol.% starch sintered at 1000 °C channels with sizes between 0.5 and 3 μm appeared, resulting in a bimodal distribution. These channels corresponded to the necks between the larger pores created by the starch particles. For the tapes with 37.8 vol.% starch, the volume of the small pores between the YSZ particles was lower than the volume of the connecting channels, since the volume fraction of starch in the green tape was higher than the volume fraction of YSZ (Table 1). As more starch was added the number of contacts between the YSZ particles decreased, thereby decreasing the volume of pores between YSZ particles.

The pore size distribution curves at 1300 °C were similar to those observed at 1000 °C. At 1600 °C, for the final stage of

sintering, the open pores between YSZ particles disappeared due to the development of necks between the YSZ grains. Consequently, for 0 and 17.6 vol.% starch there was no measurable open porosity; in this instance the open porosity was completely removed by sintering. For 28.4 and 37.8 vol.% starch, the open porosity corresponded to the connecting channels between the overlapping starch pores which resulted in a connected porous network in the sintered body. Thus, at 1600 °C the porosity was open for amounts of starch ≥28.4 vol.%. The most frequent channel radius were 1.29 μm for 28.4 vol.% starch and 1.82–2.75 μm for 37.8 vol.% starch.

As the volume fraction of starch increased from 28.4 to 37.8 vol.% at all the temperatures, the volume and size of the most frequent channels increased. Thus, when the amount of starch increased, the number of contacts between the starch particles also increased, resulting in more channels of larger sizes. Consequently, there was a gradual increase in the openness of the pore structure. This openness could be due to the gradual creation of percolating starch networks that extend through the green body and lead to connected porous networks in the sintered body. The level of interconnectivity between
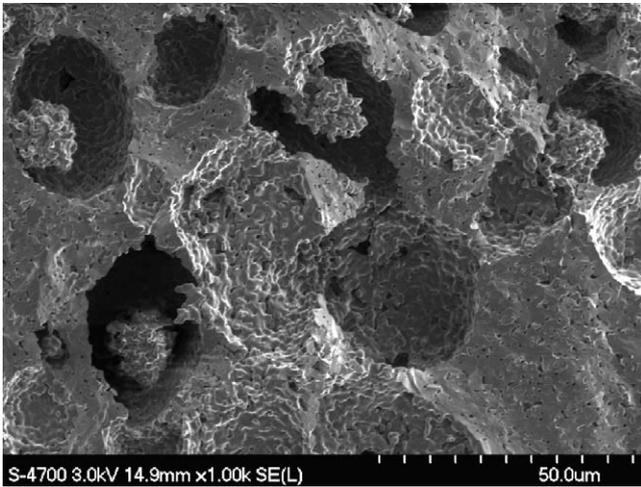
Fig. 10. SEM micrograph of a tape with 37.8 vol.% starch sintered at 1600 °C.

Fig. 11. Open to total porosity ratio versus the volume fraction of starch in the green tape for different sintering temperatures.

pores increased with increasing starch addition. Higher interconnectivity will open paths and channels between pores, which finally result in open porosity [16]. The channels radius were between 0.5 and 3 μm for all the temperatures.

Fig. 10 shows a SEM image of a tape with 37.8 vol.% starch sintered at 1600 °C. For 17.6 vol.% starch (Fig. 5c) isolated pores left by the starch could be found throughout the microstructure; thus, there was no pore contact effect. However, as the concentration of starch increased to 37.8 vol.% (Fig. 10), the individual pores started to interact and an open structure interconnecting the coarse pores was being gradually established. The higher interconnection between pores shown in Fig. 10 resulted in larger cavities.

Fig. 11 shows the open to total porosity ratio versus the volume fraction of starch in the green tape for different sintering temperatures. The porosity was completely open for the tapes with different amounts of starch sintered at 1000 and 1300 °C. This was expected since only limited densification of the YSZ matrix had occurred at these temperatures (Fig. 9a and b). At 1600 °C all the porosity was closed for amounts of starch ≤17.6 vol.%. There was a gradual increase in the openness of the pore structure with increasing the amount of added starch from 17.6 to 37.8 vol.%. This was consistent with the results shown in Fig. 9c. For 37.8 vol.% starch open porosity was predominant in the microstructure. The degree of open and closed porosity produced in the sintered tapes was dependent on the volume fraction of starch added and the sintering temperature.

Fig. 12a and b shows a green tape with 37.8 vol.% starch and the corresponding microstructure of the sintered tape at 1600 °C, respectively. It was evident that the shape and size of the pores corresponded well to the shape and size of the starch particles in the green body. Contraction of the tape was observed in the thickness direction. However, since the pores left by the starch were larger than the interstitial voids between the YSZ particles, they were not removed during sintering.

Fig. 13 shows the volumetric sintering shrinkage of the tapes as a function of the YSZ packing density in the matrix for different sintering temperatures. A linear correlation between
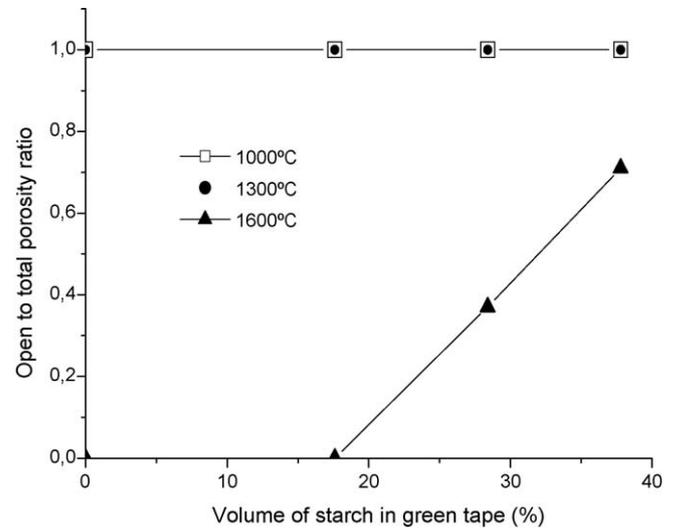
the sintering shrinkage and the YSZ packing density could be found; the sintering shrinkage decreased with increasing YSZ packing density for all the temperatures. A matrix with low density had a tendency to shrink during sintering due to the
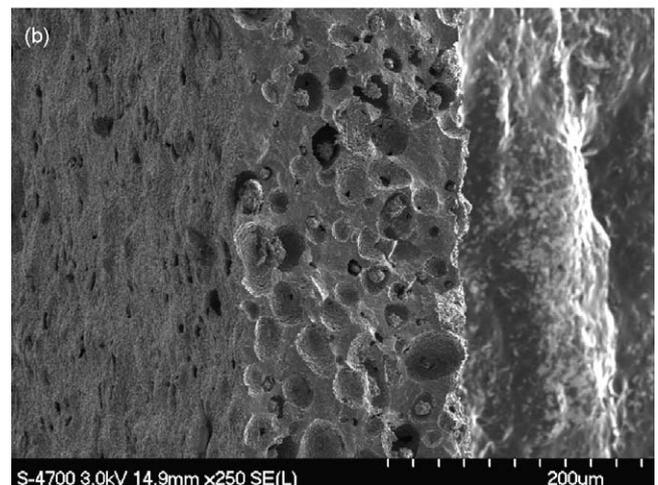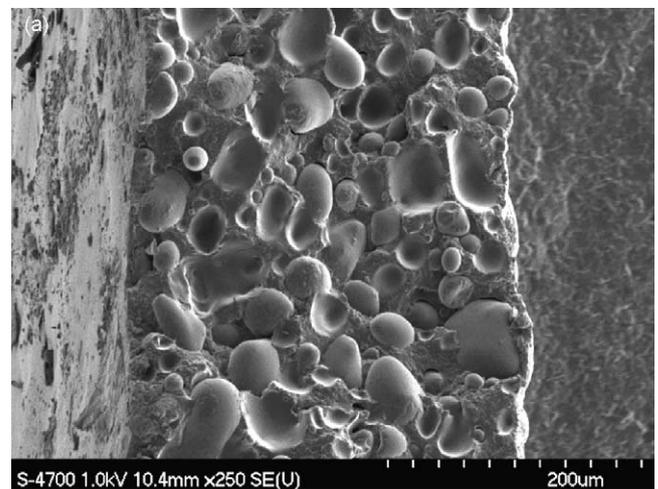

Fig. 12. SEM micrographs of (a) a green tape with 37.8 vol.% starch; (b) a tape with 37.8 vol.% starch sintered at 1600 °C.
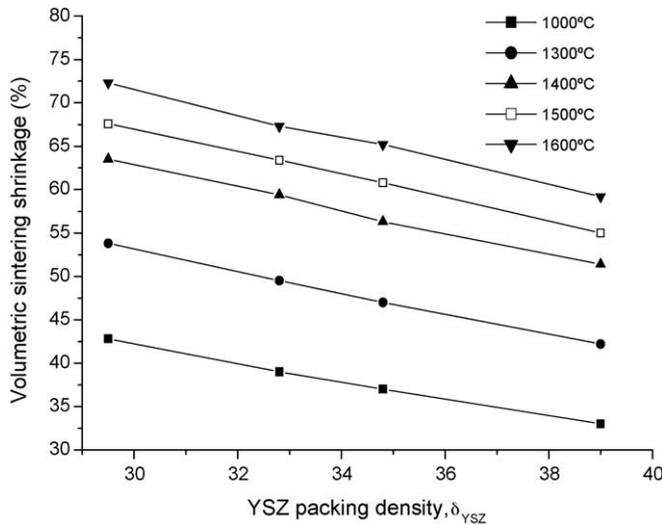
Fig. 13. Volumetric sintering shrinkage of tapes as a function of YSZ packing density in the matrix for different sintering temperatures.

empty space existing between the matrix particles. The addition of latex, along with the starch, diluted the YSZ packing density within the matrix (Fig. 3) and consequently increased the sintering shrinkage (Fig. 13). Thus, for each temperature the sintering shrinkage could be controlled by the green tape formulation. For each YSZ packing density, the increase in sintering shrinkage with increasing sintering temperature could be attributed to the sintering of the YSZ particles.

4. Conclusions

Porous YSZ tapes with volume fraction of porosity from 28.9 to 53% were produced using starch as a fugitive additive. The YSZ packing efficiency in the green tape was not reduced by the addition of starch. The relative green density values were close to the theoretical ones for all the starch contents.

The microstructure consisted of large pores created by the starch particles with length between 15 and 80 μm and smaller pores in the matrix with length between 0.6 and 3.8 μm. The coalescence of the latex particles during the drying of the cast-tapes and the pore coalescence during sintering, might contribute to the enlargement of the pores in the matrix, reducing the sinterability of the YSZ and leading to closed porosity in the sintered tapes. Consequently, the porosities were above those predicted for all the starch contents examined.

The higher F_{VL}/F_{VZ} ratio for the tapes with increasing added starch was responsible for the reduction in the YSZ packing density within the matrix. The larger deviations from the predicted porosity as more starch was added were attributed to the reduction in the YSZ packing density. The total porosity of the tapes with starch followed that predicted, based on the volume fraction of starch in the green tape, plus the additional porosity created by the adjustments of the formulation (higher F_{VL}/F_{VZ} ratio with increasing added starch).

The porosity was completely open for the tapes sintered at 1000 and 1300 °C for the different starch contents. The open pores between the YSZ particles were removed by sintering at 1600 °C. For the tapes with 0 and 17.6 vol.% starch sintered at 1600 °C, there was no measurable open porosity; for amounts of starch ≥28.4 vol.% the open porosity corresponded to the connecting channels between the overlapping starch pores which resulted in a connected porous network in the sintered body. As the volume fraction of starch increased from 17.6 to 37.8 vol.%, there was a gradual increase in the volume and size of the connecting channels between pores, and consequently in the openness of the pore structure.

The open to total porosity ratio in the sintered tapes could be controlled by the volume fraction of added starch, as well as by the sintering temperature.

The sintering shrinkage of the tapes at a given temperature could be directly related to the YSZ packing density in the matrix. The higher F_{VL}/F_{VZ} ratio for the tapes with increasing added starch diluted the YSZ packing density within the matrix, thereby increasing the sintering shrinkage.

Acknowledgements

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