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Processing of porous yttria-stabilized zirconia by tape-casting

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Abstract

The tape-casting process was used to produce porous yttria-stabilized zirconia (YSZ) substrates with pore volume fraction from 14 to 44.7% 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 slip composition on the properties of green and sintered tapes were studied. In addition, the pore structure and final microstructure were investigated. The YSZ packing density of the tapes with amounts of starch from 13 to 33 wt% was dependent on the latex that remained between the YSZ particles, which was, in turn, controlled by the added latex and starch. The volume of starch in the green tape and consequently the volume fraction of porosity in the sintered tape could be controlled by the amount of starch added as well as by the latex content. As the volume fraction of starch increased from 17 to 33% there was a gradual increase in the openness of the pore structure; for 33 vol.% starch the porosity was completely open. The sintering shrinkage was dependent on the green density; for a constant amount of starch, the additional porosity created by the latex volume was removed upon sintering resulting in an increase in the sintering shrinkage.

Keywords: A. Tape-casting; Porous ZrO_2; Green and sintered properties

1. Introduction

Porous ceramics have a number of important applications in devices that include filters, gas burners, fuel-cell electrodes, battery separators, and membrane reactors [1,2]. Copper-based ceramic–metallic (cermet) tapes are used for anodes in solid oxide fuel cells [3]. The first step in the fabrication of the cermet is the synthesis of a porous YSZ matrix. Then, the Cu–YSZ cermet is prepared by impregnating soluble salts of copper into the porous YSZ structure after the YSZ has been sintered [3]. 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 using starch as pore-forming agent. Tape-casting suspensions are composed of ceramic powder dispersed in a solvent, with the addition of a dispersant, binder and plasticizer [4]. Organic solvents are frequently used to prepare the concentrated ceramic suspensions [5]. 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 [6]. These emulsions have useful and unique characteristics such as internal plasticization and controllable crosslinking [6]. We have developed an aqueous-based starch/YSZ/latex system for tape-casting of porous ceramics.

The amount of starch as well as the latex content added to the suspensions controlled the ultimate material properties in terms of pore structure and component dimensions.

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Therefore, in this work, the influence of the slip formulation on the properties of green and sintered tapes were studied. In addition, the pore structure and final microstructure were investigated.

2. Experimental procedure

2.1. Materials

A commercial yttria doped zirconia 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. Cornstarch commercially available in Argentina was used as pore former agent. The average size of the spherical granule of starch was 10 μm.

A commercial ammonium polyacrylate 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

Seventy-seven weight percent of YSZ slips were prepared by deagglomeration of YSZ and starch in de-ionized water with 0.3 wt% NH_4PA (dry weight basis of powder) by ultrasonic treatment. Then, the latex was added to the slurry, followed by additional stirring. The pH of the suspensions was adjusted at 9.0 with ammonia (25 wt%). The concentration of starch given as the ratio of weights for starch to starch plus YSZ as well as the latex contents were shown in Table 1. For each amount of starch, three latex contents were tested referred to minimum, medium and maximum. Minimum means the minimum latex content that is necessary to produce a crack-free flexible green tape.

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 at 0.4 mm. The cast tapes were dried in air at room temperature up to constant weight; afterwards, they were stripped from the film.

2.4. Characterization of green tapes

The tapes were weighted and measured to determine the green density. The thickness of the tapes was measured using a Mitutoyo absolute ID-S 1012 Digimatic Indicator.

2.5. Burnout and sintering

The burning out of organic additives were obtained by slow heating (1 °C/min) up to 1000 °C. Then, a heating rate of 5 °C/min was applied to achieve the final sintering temperature of 1500 °C and the tapes were sintered for 2 h.

Table 1
Compositions of YSZ slips with different amounts of starch and latex

Amount of starch (wt%)	Minimum latex[a] (wt%)	Medium latex[a] (wt%)	Maximum latex[a] (wt%)
0	25	30	35
13	25	30	35
23	25	30	35
33	30	35	40

[a] The latex contents were expressed as the dry weight base with respect to (YSZ + starch) powders.

2.6. Characterization of sintered tapes

The weight loss of the green tapes on sintering was determined. The bulk density was calculated from the dimensions and weight of the sintered pieces. The sintering shrinkage was geometrically measured.

The open porosity and the pore size distribution, characterizing the interconnecting pores between the large ones left by the starch particles, were determined using mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy). Pieces of the materials were impregnated with polymer resin under vacuum and polished to observe the microstructure in a scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1 shows the green density of the tapes as a function of the latex content for different weight percentage of starch. The densities of the tapes without starch prepared with the minimum, medium and maximum latex content were higher than those with starch. A reduction in the green density occurred as the larger starch particles (inclusions) of lower density (1.4 g/cm^3) were added to the smaller YSZ particles (matrix) of higher density (5.9 g/cm^3). It has been proposed [7] that disruptions in the local matrix packing density can occur at the surface of inclusion particles and when inclusions contact each other by percolation.

For the four-weight percentage of starch, the green density decreased with increasing the latex content. The addition of

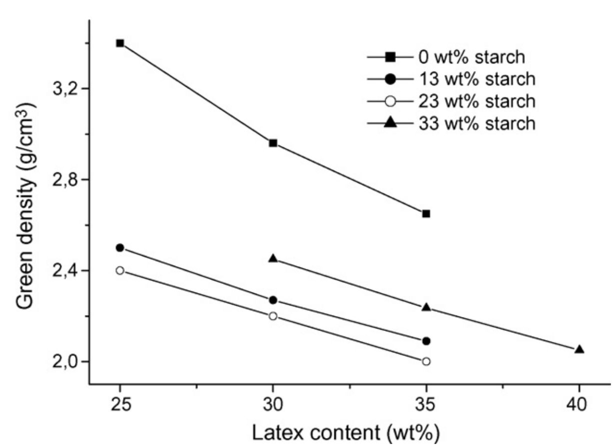

Fig. 1. Green density of the tapes as a function of the latex content for different weight percentage of starch.

latex reduced the packing density of the ceramic powder. Only a little portion of the latex was required to bind the starch particles in the green tape. The remainder was distributed throughout the rest of the green tape. This distribution effectively diluted the packing density of the YSZ powder.

For each latex content the addition of 13 wt% starch decreased the green density, further increasing in the starch content up to 23 wt% scarcely produced a decrease in the green density. For 13 and 23 wt% starch the experimental green density values were close to the theoretical ones. This indicated that most of the latex added was distributed uniformly throughout the green tape and that there was no residual porosity in the tape. Although the starch content increased the minimum latex content required to produce a crack-free flexible green tape was the same.

As the starch content increased from 23 to 33 wt%, the minimum latex content that was necessary to prepare a crack-free flexible green tape increased 5%. Thus, the density curves shifted to higher latex content in a quantity of 5%. For 33 wt% starch the measured green density values were slightly higher than the theoretical ones. This behavior could be expected if a lesser increase in the volume of the green tape occurred. Since more latex was required to bind the starch particles, a lower latex content was uniformly distributed between the YSZ particles resulting in a minor increase in the volume of the green tape and consequently in a higher green density.

The compositions with added starch from 13 to 33 wt% prepared with the minimum, medium and maximum latex content (Table 1) had nearly the same green density. This result showed that the green density of the tapes with starch contents from 13 to 33 wt% was dependent on the amount of latex that remained between the YSZ particles, which was, in turn, controlled by the added latex and starch.

Fig. 2 shows the green density as a function of the volume percentage of starch in the green tape for different starch contents. For the compositions with the minimum, medium and maximum latex content which had nearly the same green density (Fig. 1), the volume of starch in the green tape increased with the addition of starch. For each starch content the volume of starch in the green tape increased with the reduction of the tape volume and consequently with the increase in the green density. Thus, the volume of starch in the green tape could be controlled by the amount of starch added as well as by the latex content.

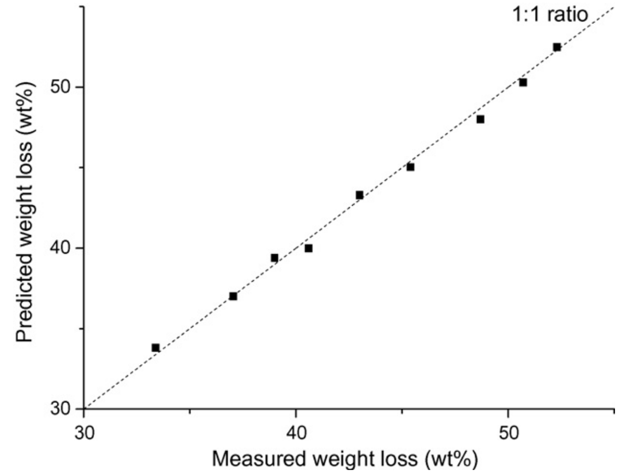

Fig. 3. Predicted weight loss after sintering vs. measured weight loss.

Fig. 3 shows the predicted weight loss after sintering versus the measured weight loss. The relationship 1:1 between predicted and measured weight loss was indicated in this figure. A very good agreement between measured and predicted weight loss for all the tapes was achieved. This confirmed that all the organic additives initially present in the dry tape were removed during sintering.

Fig. 4 shows the sintered bulk porosity as a function of the amount of starch in the green tape; the 1:1 relationship between the bulk porosity and the volume of starch in green tape was indicated. This relationship assumed that the porosity left corresponded to the volume fraction of originally added starch. This behavior would be expected if the porosity created by the latex volume was removed upon sintering and a full

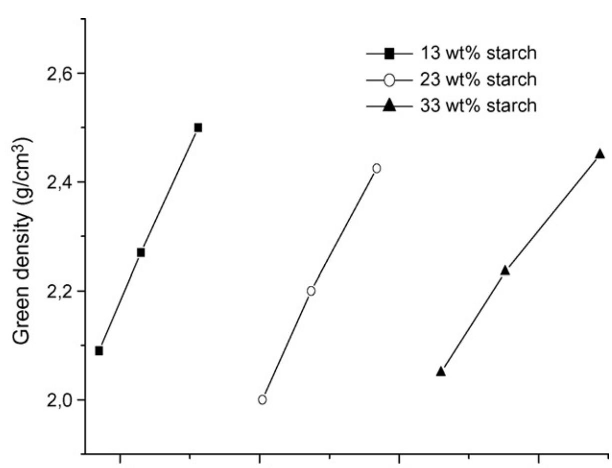

Fig. 2. Green density as a function of the volume percentage of starch in the green tape for different starch contents.

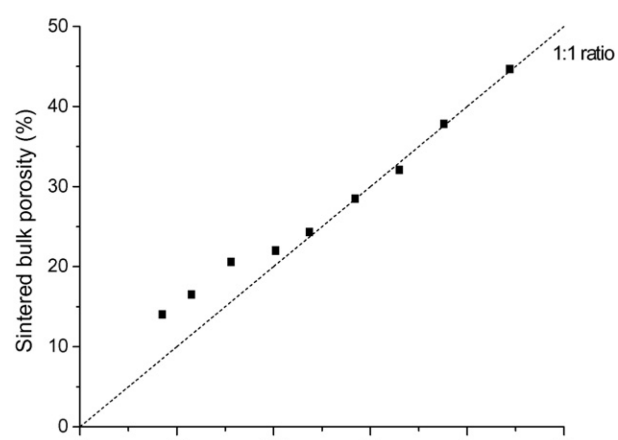

Fig. 4. Sintered bulk porosity as a function of the volume of starch in the green tape.

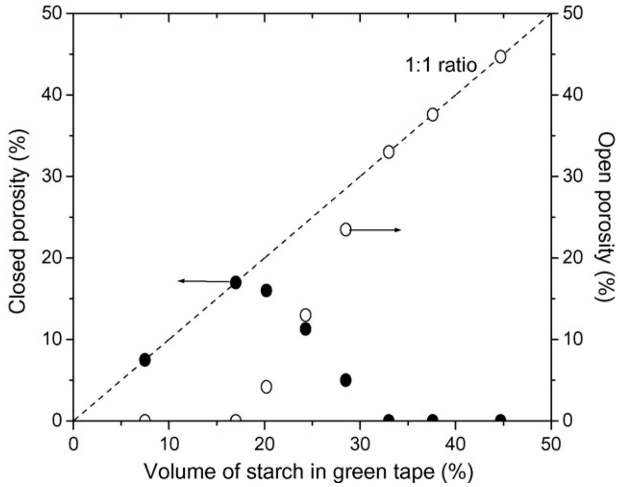

Fig. 5. Closed and open porosity as a function of the volume of starch in the green tape.

densification of the YSZ matrix occurred. For amounts of starch lower than 20 vol.% a slight deviation from the 1:1 relationship could be seen; the porosities were slightly above the predicted. Deviations were not detected for amounts of starch ≥20 vol.%. These deviations will be explained in a posterior paragraph.

Fig. 5 shows the closed and open porosity as a function of the volume of starch in the green tape. All the porosity was closed for amounts of starch ≤17 vol.% and was completely open for amounts of starch ≥33 vol.%. Thus, open porosity started to be measurable for 20 vol.% starch. As the volume fraction of starch increased from 17 to 33%, 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 pores increased with increasing starch added.

Higher interconnectivity will open paths and channels between pores, which finally result in open porosity [8]. Hg porosimetry was used to measure the smaller channels which corresponded to the connecting contacts areas or necks between much larger pores created by the original starch particles. Fig. 6 shows the pore size distribution curves of sintered tapes with different starch contents. For 20 vol.% starch the porosity began to open (Fig. 5) consequently a small channels volume of about 0.15 and 0.24 μm were found. As the volume percentage of starch increased the volume and size of the most frequent channels also increased; the most frequent channel radius for 24.3 vol.% starch was about 0.62 μm. The porosity was completely open for 33 vol.% starch, the higher interconnectivity increased the number of contacts between the starch particles opening more paths and channels between pores. The most frequent channel radius were 0.28, 0.53, 0.9 and 1.2 μm. Thus, as the starch content increased more channels of larger sizes were opened. The increase in the volume and size of the connecting channels with increasing the starch content was consistent with the gradual openness of the pore structure observed in Fig. 5.

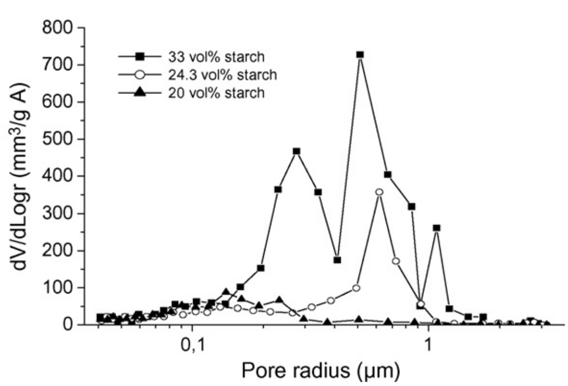

Fig. 6. Pore size distribution curves of sintered tapes with different starch contents.

Fig. 7 shows SEM images of sintered tapes with 20 and 44 vol.% starch. A very uniform pore distribution with an average pore size of about 11 μm was observed for 20 vol.% starch (Fig. 7a). The spherically shaped pores corresponded well to the shape and size of the individual starch particles used to create the porosity.

Shells separated from the rest of the YSZ matrix could be seen at the outer part of the pores left by the starch particles. This was previously observed by Lyckfeldt and Ferreira [9],

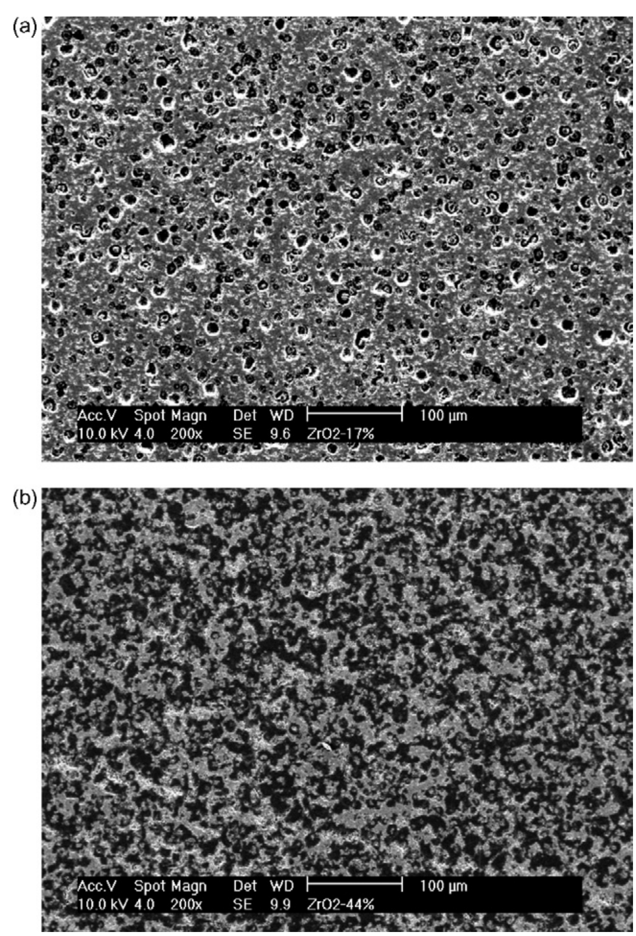

Fig. 7. SEM micrographs of sintered tapes with different starch contents: (a) 20 vol.% and (b) 44 vol.%.

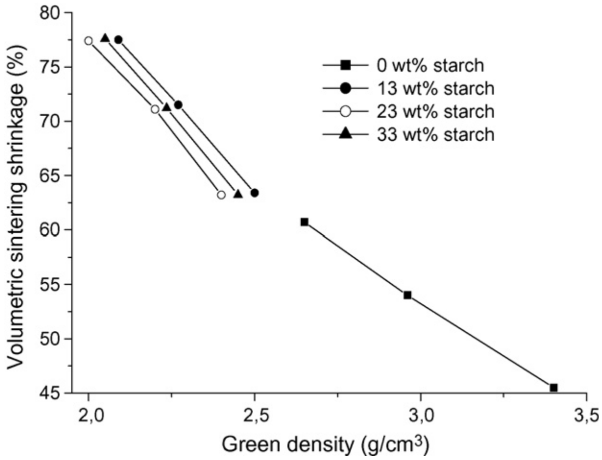

Fig. 8. Volumetric sintering shrinkage as a function of the tapes green density for the different starch contents.

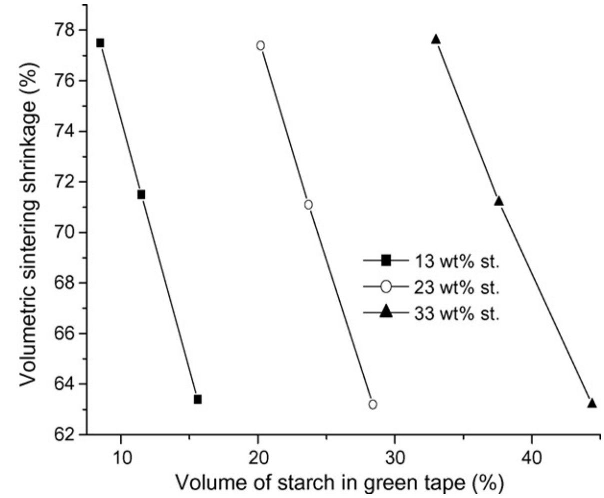

Fig. 9. Volumetric sintering shrinkage vs. starch volume percentage in the green tape.

who reported that there was some contraction of the starch particles during drying. A shell of ceramic particles, adhering to each starch particle, in the surrounding matrix is released from the rest of the matrix and follows the shrinking starch particles during drying [9]. Hence, a space between the formed shell of ceramic and the main ceramic matrix is left after sintering [9].

The higher interconnection between pores shown in Fig. 7b resulted in bigger cavities or channels. The SEM images also showed that the YSZ matrix was not fully densified. For the tapes without starch a closed porosity of about 5–6% was measured. Therefore, the higher porosity observed with respect to the amount of added starch for the lower starch contents (Fig. 4) was due to an incomplete densification of the YSZ matrix during sintering. The closed porosity of the matrix only had an appreciable effect on the total porosity for amounts of starch lower than 24.3 vol.%. For higher amounts of starch the contribution of the matrix porosity to the total porosity was not significant, therefore, deviations from the predicted porosity were not detected (Fig. 4).

Fig. 8 shows the volumetric sintering shrinkage as a function of the tapes green density for the different starch contents. As the densities of the tapes without starch were higher than those with starch the volumetric sintering shrinkage was significantly lower. The compositions of the tapes with added starch from 13 to 33 wt% which had nearly the same green density showed similar sintering shrinkage. This indicated that the sintering shrinkage was only dependent on the YSZ packing density. Davis et al. [10] studied the sintering behavior of alumina with starch and showed that the added pores from the starch are too large to contribute to the shrinkage. Thus, the sintering shrinkage was not dependent on the added starch.

For each starch content the addition of latex diluted the YSZ packing density (Fig. 1) and consequently increased the sintering shrinkage. Clearly, the additional porosity created by the latex volume was removed upon sintering resulting in an increase in the sintering shrinkage.

Graded porous structures are made by laminating green tapes with different amounts of added starch. When differential shrinkage between dissimilar porous tapes exceeds ≈5%, fairly severe warpage and cracking occur during burnout and sintering [7]. The relative success in producing porosity without altering sintering shrinkage can be determined by plotting volumetric sintering shrinkage versus starch volume percentage in the green tape (Fig. 9). The tapes prepared with the minimum latex content with different volume percentage of starch had similar green density (Fig. 2) and consequently nearly the same sintering shrinkage (Fig. 9). A similar behavior was found for the tapes produced with the medium and maximum latex content.

Porous structures with bulk porosities ranging from 14 (8.5 vol.% starch, Fig. 4) to 33%, 16.5 (11.5 vol.% starch, Fig. 4) to 37.6% and 20.6 (15.6 vol.% starch, Fig. 4) to 44.7%, would be created by laminating together green ceramic tapes with starch content in the range 13–33 wt% prepared with the maximum, medium and minimum latex content, respectively, without significantly altering sintering shrinkage. This would allow the production of sintered structures with graded porosity via lamination of various tape compositions, while avoiding the detrimental effects of warping and cracking during fabrication.

4. Conclusions

Porous YSZ tapes with volume fraction of porosity from 14 to 44.7% were produced using starch as a fugitive additive.

For the starch contents used (0–33 wt%), the addition of latex diluted the YSZ particle packing within the green tape. The YSZ packing density of the tapes with amounts of starch from 13 to 33 wt% was dependent on the latex remained between the YSZ particles, which was, in turn, controlled by the added latex and starch.

The volume of starch in the green tape and consequently the volume fraction of porosity in the sintered tape could be controlled by the amount of starch added as well as by the latex content.

The porosity was closed for amounts of starch ≤17 vol.% and was completely open for amounts of starch ≥33 vol.%. As the volume fraction of starch increased from 17 to 33% 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 shrinkage after sintering was dependent on the green density. For a constant amount of starch, the additional porosity created by the latex volume was removed upon sintering resulting in an increase in the sintering shrinkage.

Graded Porous structures with bulk porosities ranging from 14 to 33%, 16.5 to 37.6% and 20.6 to 44.7%, would be produced by laminating together green ceramic tapes with starch content in the range 13–33 wt% prepared with the maximum, medium and minimum latex content, respectively. The tapes had the same sintering shrinkage so that warping and cracking would be avoided upon sintering.

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