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Dispersion of concentrated aqueous yttria-stabilized zirconia with ammonium polyacrylate

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Abstract

The dispersion of concentrated 0.53 μm yttria stabilized zirconia (YSZ) aqueous slip to achieve sintered compacts with high and uniform microstructure was investigated. 78 wt.% (37.5 vol%) and 83 wt.% (45.3 vol%) slips were prepared by dispersing the powder in water with ammonium polyacrylate (NH_4PA) at pH values in a range of 8–9.5. The influences of the amount of NH_4PA and pH on the rheological properties of 78 and 83 wt.% slips were studied. The minimum viscosities of 78 and 83 wt.% slips were obtained with the addition of 0.05–0.1 wt.% NH_4PA at pH 9. Increasing pH from 8 to 9.5 had no effect on the YSZ dispersion with NH_4PA. These dispersions yielded green densities of 63% of theoretical density (TD) and sintered to 98% TD at 1400 °C.

Keywords: A. Slip casting; Yttria stabilized zirconia; Dispersion properties; Sintering behavior

1. Introduction

The addition of 8 mol% Y_2O_3 stabilizes the cubic fluorite structure of ZrO_2, from room temperature to its melting point. YSZ is the most common electrolyte in oxide fuel cells because the material possesses an adequate level of oxygen-ion conductivity and exhibits desirable stability in both oxidizing and reducing atmospheres [1–3]. The excellent conductivity properties of this material can be achieved with fine and homogeneous microstructures. In order to obtain these microstructures the powder characteristics, the forming process and the sintering conditions should be controlled.

Slip casting is a suitable consolidation process to obtain materials with high green densities and microstructural homogeneity allowing the manufacture of components with complex shapes [4]. The goal of dispersion in this process is to achieve a high solids loading with a high degree of stability. Ceramic slips can be stabilized electrosterically by adsorption of polyelectrolyte additives such as NH_4PA [5,6].

In order to obtain well-dispersed concentrated aqueous slips, several critical factors related to the slip rheology were studied, such as the influence of the amount of NH_4PA solution added and pH on the viscosity of 78 and 83 wt.% slips. In addition, the density of green cast samples was studied and related to the degree of slip dispersion. Finally, the influence of the sintering temperature on the density and microstructure of cast samples was 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.

2.2. Slip preparation

YSZ slips with two different solid loadings, 78 wt.% (37.5 vol%) and 83 wt.% (45.3 vol%), were prepared. The

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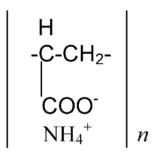
deflocculant used was a commercial ammonium polyacrylate solution (Dolapix, Zschimmer & Schwartz) with a low average molecular weight (≪10,000). The ammonium polyacrylate structure shown below illustrates that the functional groups are carboxylate ($RCOO^-$) groups:



The pH was adjusted with ammonia (25 wt.%). Aqueous slips were prepared by deagglomeration of the powder in de-ionized water by ultrasonic treatment, with additions of different amounts of NH_4PA at pH values in a range of 8–9.5. First distilled water with the pH adjusted at a desired value was added, then the dispersant and finally the powder. The powder was added in portions to the suspensions and the pH was manually adjusted to be maintained at a desired value during the additions.

2.3. Slip characterization

The particle size distribution of 4 wt.% YSZ slips with and without NH_4PA was measured using a Sedigraph (5000 D, Micromeritics).

Steady state flow curves of 78 and 83 wt.% YSZ slips were performed by measuring the steady shear stress as a function of shear rate in the range of 0.1–550 s^{-1} using a concentric cylinder viscometer (Haake VT550, Germany) at 25 °C. As soon as stationary conditions were reached at each shear rate, the shear rate was increased in steps up to the maximum value and then decreased.

2.4. Slip casting and characterization of green samples

Slips were cast in plaster molds into bars of dimensions (1 cm × 1 cm × 5 cm). The consolidated bars were removed from the mold after 6 h and dried slowly in air for 12 h at room temperature and 24 h at 100 °C.

The density of green compacts was determined by the Archimedes method using mercury displacement.

2.5. Sinterization and characterization of sintered samples

Green bars were sintered in air at temperatures in a range of 1250–1650 °C for 3 h using heating rates of 5 °C/min up to the final temperature.

The bulk density of the sintered bars was determined by water inmersion (Standard Method ASTM C20). The microstructures were observed by scanning electron microscopy (SEM, Jeol JSM 6360LV) on polished sections after thermal etching.

3. Results and discussion

3.1. Influence of the amount of NH_4PA solution added and pH on the rheological properties of 78 and 83 wt.% YSZ slips

Fig. 1 shows the mean particle diameter (d_{50}) as a function of pH for 4 wt.% YSZ slips with and without NH_4PA. A maximum d_{50} of 14 μm was found for the slip without NH_4PA at pH 7. The particles in a flocculated suspension form floc groups because of the mutual attraction between particles and the d_{50} increases. This behavior occurred at the isoelectric point of the powder (IEP) which was about 7. This IEP value was in agreement with that previously reported for this YSZ powder [7]. Therefore, the YSZ powder had negative surface charge at pH > 7. The d_{50} was reduced to 0.9 μm for pH < 6.5 and >8; thus, at these pH values the slips were stabilized electrostatically.

The ammonium carboxylate groups dissociates according to the reaction

$$RCOONH_4 = RCOO^- + NH_4^+$$

begins at pH > 3.5; at pH ≥ 8.5 the polymer charge is negative with the degree of ionization approaching 1 [6]. The $RCOO^-$ groups of the deflocculant are adsorbed at the minority of positive surface sites of YSZ, even though the net surface charge is negative at alkaline pH [7]. Thus, the amount of NH_4PA adsorbed contributed to an increase of the negative surface charge of the powder and shifted the maximum of the d_{50} versus pH curve toward a lower pH value (Fig. 1). Thus, the pH_{IEP} of the powder with NH_4PA adsorbed was slightly lower than 7.

Fig. 2a and b shows the flow curves of viscosity versus shear rate as a function of the amount of NH_4PA solution added at pH 9 for 78 and 83 wt.% YSZ slips, respectively. Fig. 3 shows the viscosity at a shear rate of 550 s^{-1} versus the amount of NH_4PA solution added at pH 9 for the different slip concentrations. The viscosity values of the slips were strongly dependent on the

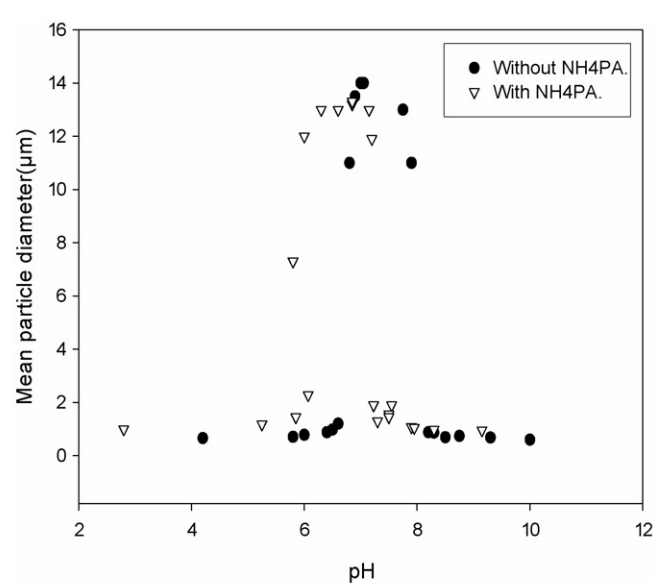


Fig. 1. Mean particle diameter as a function of pH for 4 wt.% YSZ slips with and without NH_4PA.

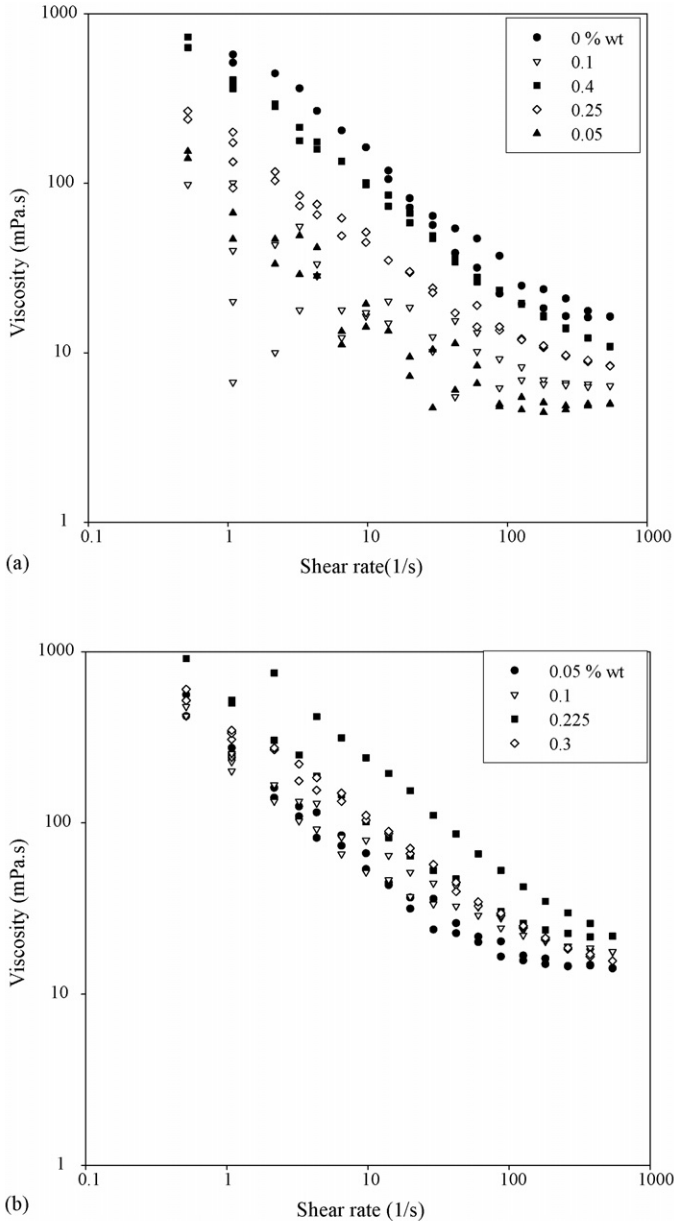


Fig. 2. Flow curves of viscosity vs. shear rate as a function of the amount of NH_4PA solution added at pH 9 for different YSZ slip concentrations: (a) 78 wt.% and (b) 83 wt.%.

shear rate; thus, the suspensions exhibited a pseudoplastic behavior (Fig. 2a and b). The degree of shear thinning at the different NH_4PA concentrations was nearly the same.

For 78 wt.% slips the addition of NH_4PA up to 0.05 wt.% resulted in a significantly lower viscosity. The decrease in the slip viscosity was attributed to the adsorption of NH_4PA on the YSZ powder. The adsorption of the negatively charged polyelectrolyte enhanced the surface charge of the powder and consequently the electrostatic repulsion between particles. In addition, the electrostatic repulsion between the charged carboxylate groups avoids the accumulation of groups at the surface, the polyacrylate adsorbs in a stretched-out configuration which results in long-range steric interactions of the NH_4PA at the solid–liquid interface [8]. Thus, the steric interaction of the adsorbed

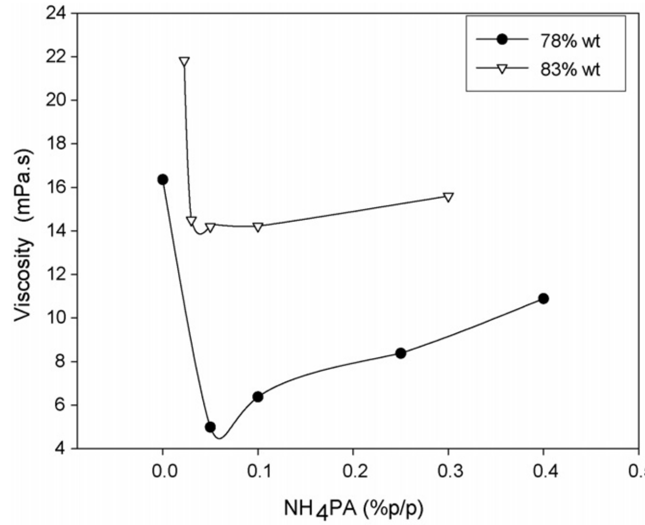


Fig. 3. Viscosity at a shear rate of 550 s^{-1} vs. the amount of NH_4PA solution added at pH 9 for the different slip concentrations.

polyacrylate has a positive contribution to the dispersion. The viscosity was reduced to as low as 4 mPa s.

For polymer additions <0.05 wt.% the increase in the viscosity was due to incomplete adsorption which resulted in lower electrostatic repulsion between particles, thereby forcing particles together (Figs. 2a and 3). Additions of polymer above 0.05 wt.% increased the viscosity due to a probably excess of polymer in solution. This free-polymer increased the ionic strength of the solution and resulted in a decrease in the negative surface charge of the powder due to the large compression of the double layer [5]. Consequently, the electrostatic repulsion between particles was reduced increasing the slip viscosity (Figs. 2a and 3).

The viscosity curves for 83 wt.% slips (Figs. 2b and 3) were similar to that obtained for 78 wt.% slips. The minimum viscosity occurred at 0.05–0.1 wt.% NH_4PA. The increase in the solids loading increased the hydrodynamic interactions between particles, thereby increasing the magnitude of the slip viscosity. As the solids loading increased from 78 to 83 wt.%, the minimum viscosity increased from 4 to 14 mPa s, respectively.

Fig. 4 shows the flow curves of viscosity versus shear rate as a function of pH for 83 wt.% slips with 0.1 wt.% NH_4PA in the 8–9.5 pH range. Almost the same viscosities and degree of shear thinning were found for the different pH values in the range of 8–9.5. This indicated that the slip dispersion was nearly the same at that pH range. The increase in pH from 8 to 9.5 might not contribute significantly to the negative surface charge of the NH_4PA-adsorbed YSZ particles and consequently to the electrostatic repulsion between them.

The measured flow curves were fitted with various rheological models. The best fit was obtained with the Casson model equation:

$$\tau^{1/2} = \tau_c^{1/2} + (\eta_c D)^{1/2}$$

were τ is the shear stress (Pa), D the shear rate (s^{-1}), τ_c the yield stress and η_c is the Casson viscosity. The shear rate exponent

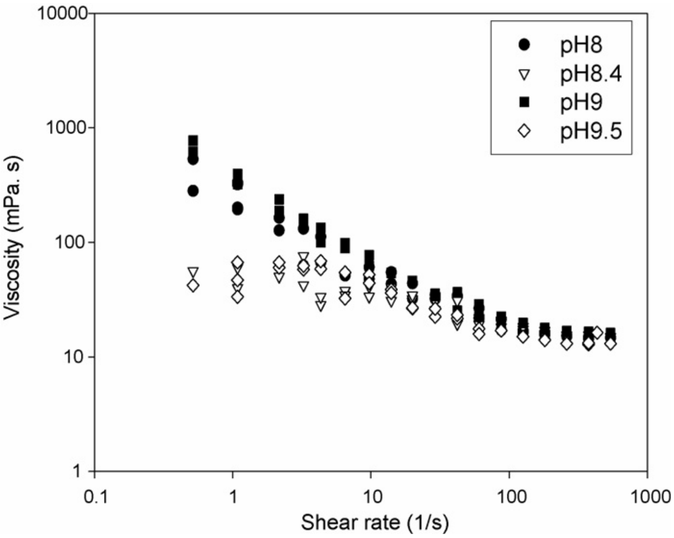


Fig. 4. Flow curves of viscosity vs. shear rate as a function of pH for 83 wt.% slips with 0.1 wt.% NH_4PA.

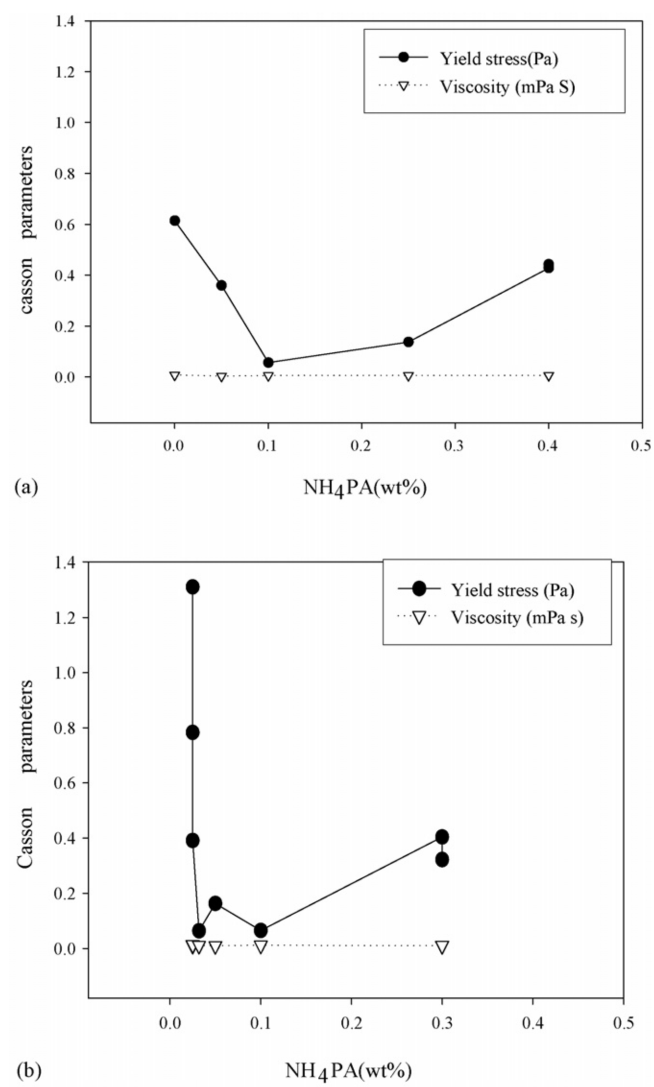


Fig. 5. τ_c and η_c values versus the amount of NH_4PA solution added at pH 9 for different YSZ slip concentrations: (a) 78 wt.% and (b) 83 wt.%.

which indicated the relative degree of shear thinning was 1/2. This constant value could be expected since the degree of shear thinning of the different slips were nearly the same (Figs. 2a and b and 4).

The particles in a flocculated suspension form floc groups or a network, because of the mutual attraction between particles, and the yield value τ_c of the Casson model could be used as a parameter that indicated the degree of flocculation. Fig. 5a and b shows the effect of the amount of NH_4PA concentration on the τ_c and η_c values at pH 9 for 78 and 83 wt.% YSZ slips, respectively.

The Casson viscosity remained nearly constant with increasing the amount of NH_4PA solution added and pH. This behavior was previously observed in suspensions by Guo et al. [9]. The 78 wt.% slips without NH_4PA and the 83 wt.% slips with 0.02 wt.% NH_4PA were flocculated; therefore high τ_c values were obtained. The decrease in viscosity with the addition of NH_4PA up to 0.1 wt.% resulted in a decrease in τ_c. For NH_4PA additions between 0.05 and 0.1 wt.%, the viscosity and consequently τ_c attained the minimum values. Thus, as the NH_4PA addition increased the slips were changed from being flocculated for about 0 wt.% NH_4PA to weakly flocculated and eventually well stabilized for 0.05–0.1 wt.% NH_4PA. The adsorbed polymer generated repulsive interactions caused by electrostatic and steric effects. At 0.05–0.1 wt.% NH_4PA the electrostatic repulsion was strong enough to overcome the Van der Waals forces and the suspensions were dominated by repulsive forces; thus, they were stabilized. NH_4PA additions above 0.1 wt.% resulted in an increase in the slip viscosity and consequently in the τ_c value.

The τ_c value was nearly constant in the pH range studied (8–9.5) in accordance with the viscosity values (Fig. 4).

3.2. Green and sintered densities

Fig. 6 shows the green density of cast samples versus the amount of NH_4PA solution added at pH 9 for the different slip concentrations. The better slip dispersion of 78 and 83 wt.%

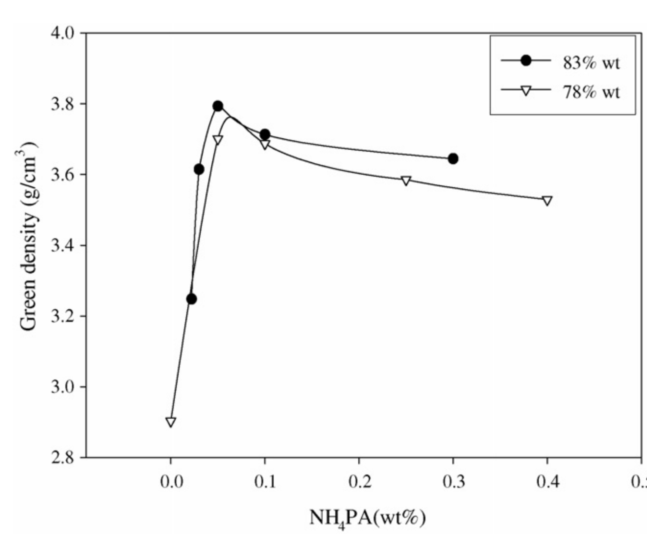


Fig. 6. Green density of cast samples vs. the amount of NH_4PA solution added at pH 9 for the different slip concentrations.

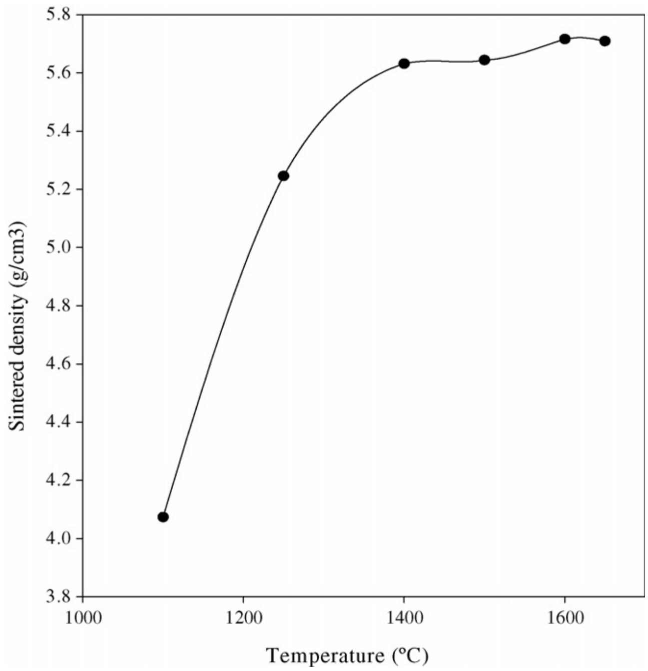


Fig. 7. Sintered density of cast samples as a function of the temperature after sintering for 3 h.

slips was achieved with about 0.05 wt.% NH_4PA and resulted in the highest green density values. The maximum green density values were 62.1% TD and 63.6% TD for 78 and 83 wt.% slips, respectively. For NH_4PA additions lower than 0.05 wt.% a marked decrease in the green density was found in accordance with the increase in the slip viscosity (Figs. 3 and 8). The lesser decrease in the green density for NH_4PA additions higher than 0.05 wt.% was consistent with the lesser increase in the slip viscosity (Figs. 3 and 8). Thus, a correlation between the green density and the viscosity was found; as the slip viscosity decreased a denser packing of the samples could be obtained.

Cast samples prepared from the 83 wt.% slips with 0.1 wt.% NH_4PA at pH 9 were chosen to study the sintering behavior. Fig. 7 shows the sintered density as a function of the temperature after sintering for 3 h. An important increase in the density was found up to 1400 °C followed by a lesser increase with further increasing of the sintering temperature. Therefore, the YSZ samples could be sintered at 1400 °C and a sintered density of 98% TD could be achieved.

Fig. 8 shows a SEM micrograph of the sample after sintering at 1400 °C. The open porosity was low (0.95%) and the mean grain size was 2.65 μm.

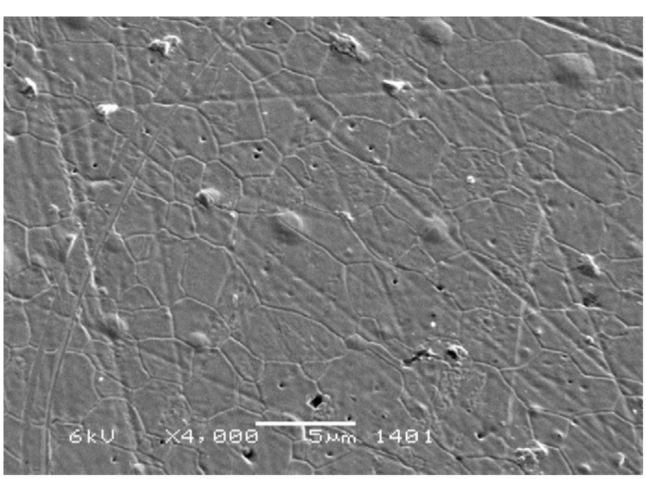


Fig. 8. SEM micrograph of the sample after sintering at 1400 °C. Bar = 5 μm.

4. Conclusions

The 78 and 83 wt.% YSZ slips were prepared by dispersing the powder in water with NH_4PA at pH values in a range of 8–9.5.

The flow curves of the slips followed the Casson model; the τ_c constant of the model was used to indicate the degree of flocculation. The minimum viscosity and τ_c values of 78 and 83 wt.% slips at pH 9 were obtained with the addition of 0.05–0.1 wt.% NH_4PA; the adsorbed polymer generated repulsive interactions caused by electrostatic and steric effects. For polymer additions <0.05 wt.% an increase in the slip viscosity and consequently in the τ_c value was found due to incomplete adsorption of the polymer on the surface powder. Additions of polymer over 0.1 wt.% increased the viscosity and the τ_c value due to an excess of polymer in solution.

The increase in pH from 8 to 9.5 had no effect on the YSZ dispersion with NH_4PA since the slip viscosity and the τ_c values were nearly the same in that pH range.

Lower viscosities of the YSZ slips resulted in higher slip cast packing density compacts. The highest green density values (63.6%TD) were obtained from 78 and 83 wt.% slips with 0.05 wt.% NH_4PA at pH 9 which had the lowest viscosities.

An important increase in the sintered density was found up to 1400 °C followed by a lesser increase with further increasing of the sintering temperature. A sintering temperature over 1400 °C did not contribute significantly to the densification and promoted an important grain growth. At 1400 °C a high sintered density of 98% TD could be achieved.

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