JOURNAL OF MATERIALS SCIENCE **40** (2005) 5161 – 5166

Mullite-zirconia composites: Effect of citric acid addition on slip and cast properties

L. B. GARRIDO*, E. F AGLIETTI‡
*CETMIC (Centro de Tecnología de Recursos Minerales y Cerámica) and
‡CONICET-UNLP-CIC, Cno. Centenario y 506. C.C.49 (B 1897 ZCA) M.B. Gonnet, Prov. de Buenos Aires, Argentina
E-mail: garridol@netverk.com.ar

Dispersion of mixed suspensions of zircon and α-alumina using citric acid as dispersant followed by pressure filtration produced after sintering (1600°C—2 h) dense mullite-zirconia composites. The effect of citric acid addition and pH on the rheological behavior of the mixed suspensions (57 vol%) was examined. Most of flow curves showed a shear thinning behavior at low shear rates reaching the viscosity a plateau at high shear rates. Newtonian viscosity at high shear rates values decreased to a minimum and then increased with increasing the amount of dispersant added. Compacts prepared from well stabilized suspensions achieved a maximum relative density of 72% (theoretical) which is slightly higher than that obtained from suspensions dispersed with a polyelectrolyte. Characteristics of sintered compacts such as density and crystalline phase composition by XRD were determined.

1. Introduction

Dispersion is a fundamental step in wet ceramic processing where small changes in suspension stability may produce significant variations of density and of microstructure of the resulting green and sintered bodies.

In order to stabilize ceramic suspensions different kinds and concentrations of dispersants can be used. Most of dispersants, such as citric acid, ammonium citrate, sodium oxalate, pyrophosphates, and polyphosphates contain potential determining anions. When adsorbed on the oxide powder surface, these anions decrease the pH of the isoelectric point (iep) with a consequent increase in the negative zeta potential at a given pH [1–3]. In such a case, the adsorbed anions can impart electrostatic stabilization of particles. Since, $\mathrm{pH_{iep}}$ reaches a constant value at higher additions of dispersant, the effect of increasing dispersant concentration on electrostatic repulsion is less effective.

Previously we used [4] a polyacrylate based dispersant to electrosterically stabilize mixed alumina-zircon suspensions. Anionic polyelectrolyte was adsorbed on the powder surfaces and shifted the iep to an acidic pH increasing the negative surface charge at pH 9 as shown by zeta potential measurements. Additionally, adsorbed molecules can produce an steric barrier that prevents close contact between particles. Well stabilized suspensions produced green bodies having high and homogeneous density. Also, a correlation between green and sintered densities indicated that high green density was desirable to obtain a high fired density. Dispersion of mixed powder was mainly controlled by the polyelectrolyte adsorption on the alumina surface since a weak adsorption on zircon was determined. Because citric acid was a better dispersant for alumina than the polyelectrolyte used [5], it was selected to achieve as lower viscosity as possible.

In this work, highly concentrated (57 vol%-85 wt%) aqueous suspensions of alumina-zircon mixture were prepared using citric acid as dispersant in a pH range of 7.5 to 9.1. Slip properties were optimized in order to improve the characteristics of mullite-zirconia composites obtained by sintering (1600°C—2 h) from the pressure filtrated compacts. Flow properties such as viscosity and zeta potential measurements were correlated with the characteristics of the resulting dried and sintered compacts.

2. Materials and methods

Alpha-alumina (A-16 SG, Alcoa Inc., USA) powder with a mean particle size of 0.4 μm and a BET surface area of 9.5 $\mathrm{m^2/g}$ was used. Zircon (Mahlwerke Kreutz, Mikron, Germany) powder was characterized by a large mean particle size (2 μm) and 4 $\mathrm{m^2/g}$ BET surface area. The contents of alumina and zircon in the mixture were 45.5 and 54.5 wt%, respectively. The mixture exhibited a mean particle size of 0.9 μm (Sedigraph 5000D, Micromeritics) with broad and bimodal particle size distribution.

Negative zeta potential vs. pH curves were determined through the electroacoustic technique (ESA 8000, Matec Instruments) on a 1 vol% suspension for powders with and without citric acid adsorption. Acid citric additions were 0.3 and 0.05 wt% for alumina and zircon, respectively that corresponds to amounts required to achieve optimum dispersion conditions.

0022–2461
DOI: 10.1007/s10853-005-4406-1

Concentrated aqueous 57 vol% suspensions for rheology measurements and consolidation were prepared by adding the powders to distilled water containing the appropriate amount of citric acid (commercial analytical reagent). To compare the effect of polyelectrolyte addition on suspension and compact properties, 57 vol% suspensions were prepared using Dolapix CE64 (Zschimmers and Schwartz, Germany). NH_4OH was used to adjust the pH of the suspension that were homogenized and dispersed by an ultrasonic process.

Flow curves of the suspensions were obtained using a rotational viscometer Haake vt550 of coaxial cylinders with NV measuring system at 25°C.

Slips were cast by pressure filtration using a metallic sintered filter at 8 MPa, uniaxial pressure was employed. The obtained disks (25 mm in diameter and 12–15 mm in thickness) were dried for 24 h at room temperature and then at 110°C to a constant weight. Dried density was measured by Hg immersion.

The pore-size distribution of green compacts was measured using a Carlo Erba Hg porosimeter (Porosimeter 2000).

Sintering was carried out in an electric furnace in air. After sintering (1600°C—2 h), density was determined by the water absorption method.

Crystalline phases present in the sintered bodies were analyzed by XRD with a Philips 3020 equipment (Cu-K_α radiation and Ni filter at 40 kV–20 mA). Phase composition was quantitatively determined using the Rietveld method.

3. Results and discussion

3.1. Effect of citric acid addition on zeta potential

Fig. 1 curve a shows the variation of zeta potential vs. pH for alumina, the iep determined through the electroacoustic technique on a 1 vol% suspension was about 9. Zeta potential slightly increased to −5 mV with increasing pH from 9 to 10.

Zeta potential vs. pH curve for zircon (Fig. 1 curve b) indicated that the iep was at pH 5. A nonsymmetric curve was obtained: in the acidic pH range the magnitude of the zeta potential was lower than that for the basic pHs. The negative zeta potential increased from −60 to −80 mV for pH 7 and 9, respectively.

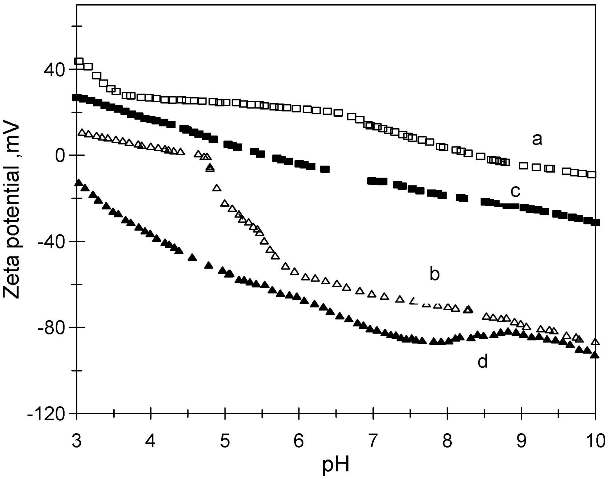

Figure 1 Zeta potential versus pH curves for 1 vol% suspensions of different powders: (a) alumina, (b) zircon, (c) alumina with 0.3 wt% citric acid and (d) zircon with 0.05 wt% citric acid.

In a weakly alkaline pH range (7–9), the powders exhibited opposite zeta potential values. Therefore, electrostatic attraction resulted in heterocoagulation of the particles reducing stabilization of the suspension.

Fig. 1 curves c and d show the variation of zeta potential as a function of pH after addition of citric acid for alumina and zircon, respectively. For alumina, pH iep shifted to 5.5. Negative zeta potential gradually increased from −10 to −25 mV for pH 7 and 9, respectively.

Citric acid shows high affinity for the alumina surface as was determined by Hidber *et al.* [1]. At pHs above 7, the citric acid molecule has a high negative charge due to dissociation of COOH groups which increases with increasing pH. Specific adsorption of citric acid on alumina involves a ligand exchange mechanism where hydroxyl of the surface Al-OH groups is exchanged for a carboxylate group [1]. In addition, in a range of pH 7.5 to 9.1, electrostatic attraction between the COO^- groups of the citric acid and the positive surface sites on the alumina (pH_{iep} 9) favored adsorption of citrate.

Also, for zircon, pH_{iep} shifted bellow pH 3 as indicative of citrate anion adsorption. Negative zeta potential of zircon reached a maximum value of −85 mV at pH 7.5. Further increase in pH caused a minor effect on zeta potential probably due to double layer compression as concentration of alkali increased in solution.

When the zircon surface is in contact with water two different types of surface functional groups develop: Si—OH silanol and Zr—OH because of breakage of silicate Si—O and Zr—O bonds. As iep of SiO_2 is usually below pH 2, for a pH range above iep the dominant surface groups are SiO^- due to a proton dissociation mechanism with the silanol group. The iep of pure ZrO_2 was reported in the range of pH 7–7.4 [6]. For zircon an iep at pH 5 which is nearly intermediate between 2 and 7, may be explained by a similar relative amount of these groups on the exposed surface. Consequently, as citrate anion adsorbs specifically on ZrO_2 [7] only a part of surface sites present on the zircon was able to adsorb citric acid.

3.2. Effect of citric acid concentration on rheology of 57 vol% suspensions

Fig. 2 shows apparent viscosity vs. shear rate curves for 57 vol% mixed suspensions with different citric acid concentrations in a pH range between 7.5 and 9.1.

Suspensions exhibited a shear thinning behavior reaching the apparent viscosity a plateau at high shear rates. Several suspensions showed a shear thickening behavior at elevated shear rates.

Fig. 3 shows the Newtonian viscosity at high shear rates (obtained from Fig. 2) as a function of the amount of citric acid added for pHs between 7.5 to 9.1.

Newtonian viscosity at high shear rates values of suspensions at pH 7.5–9.1 showed a minimum for citric acid concentrations of 0.13–0.16 wt%. This result indicated that the degree of dispersion of the particles

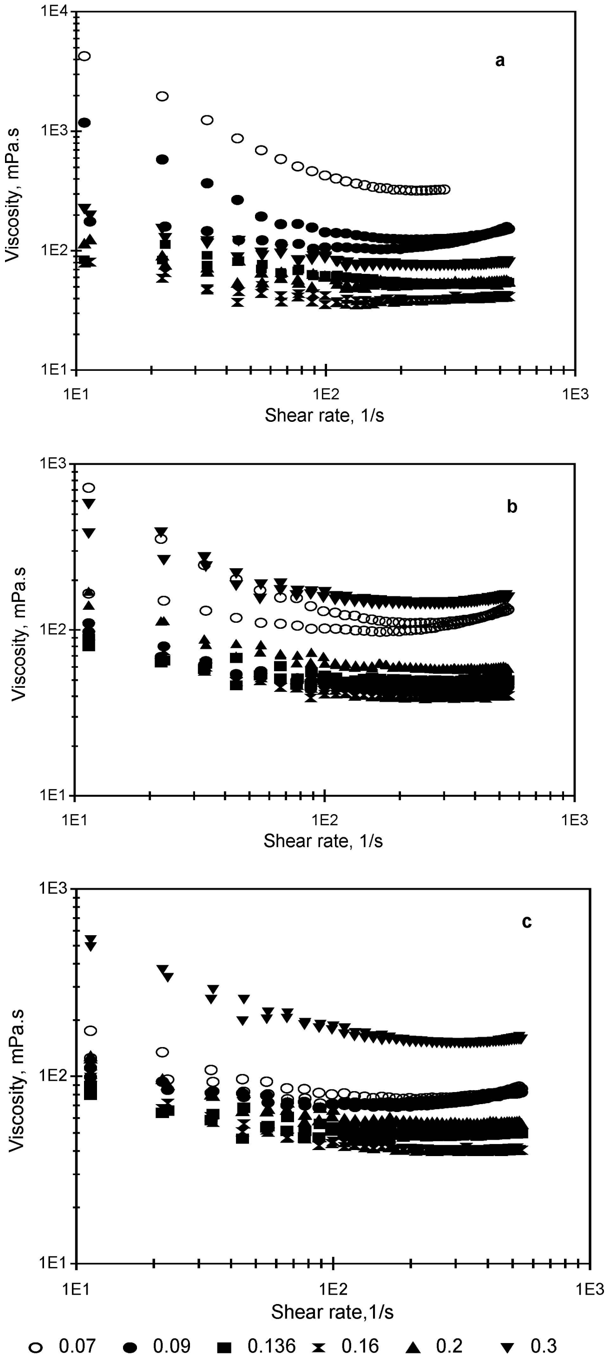

Figure 2 Apparent viscosity versus shear rate curves of 57 vol% suspensions in the presence of citric acid (○: 0.07, ●: 0.09, ■: 0.136, x: 0.16, ▲: 0.2, ▼: 0.3 wt%) at different suspension pH: (a) pH 7.5, (b) pH 8.5 and (c) pH 9.1.

increased to a maximum. These suspensions exhibited a nearly Newtonian flow behavior with a viscosity of 45 mPa·s.

The adsorption isotherm of citric acid on alumina showed a plateau in the adsorbed amount at high equilibrium concentrations in solution [1]. Maximum adsorption value of citric acid on alumina at pH 7 was 1.2 μmol/m^2 which corresponds to a concentration of 0.2 wt% (with respect to solid weight). This concentration is higher than that required to obtain low viscosity suspensions of the mixture (0.13 wt%) indicating a low adsorption of citric acid on the zircon surface.

Fig. 1 curve d showed that citrate anion adsorbs specifically on $ZrSiO_4$. However, in a pH range of

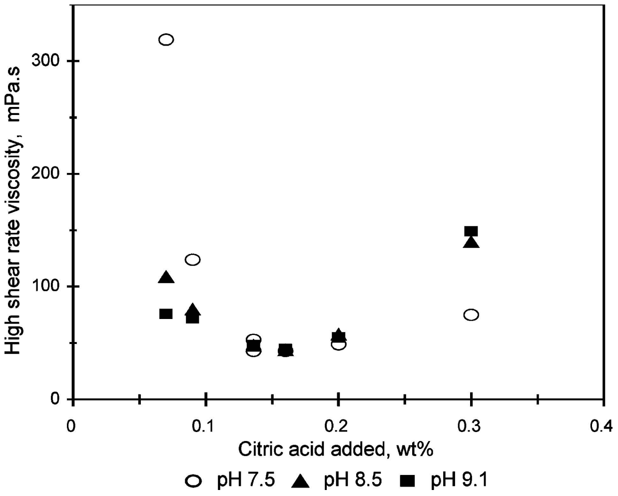

Figure 3 Viscosity at the high shear rate region (200 s^{-1}) versus citric acid concentration (wt%) for different suspension pH.

7.5–9.1 zircon particles had a very high negative surface charge (or few positive surface groups) generating an electrostatic repulsion between the zircon surface and the negatively charged citric acid in solution, which probably resulted in a low amount of dispersant adsorbed. Weak adsorption on the zircon surface was also expected because of the low specific surface area. Thus, citric acid adsorption on the mixed powder may be controlled by the adsorption on the alumina surface. At pH 9, negative zeta potential of alumina with adsorbed citrate increased to −25 mV. As thickness of adsorbed citrate layer on alumina particle is close to 0.5 nm [1], the steric contribution is expected to be significant at small interparticle distances or for low surface potentials [3]. Therefore, simultaneous dispersion of both components may be attributed to the high electrostatic repulsion between negatively charged alumina and zircon and consequently, a low suspension viscosity was obtained.

For 0.2 wt% citric acid addition, viscosity of the mixed suspension increased from 45 to 60 mPa·s. Since the surface of alumina became saturated at 0.13–0.16 wt%, high equilibrium concentrations only produces a small increase in citrate anion adsorption with more citric acid remaining in solution [1]. Suspension viscosity higher than the minimum may be attributed to an excess of citric acid in solution. An increase in ionic strength reduced zeta potential and consequently the degree of dispersion of the particles decreased.

Further additions of citric acid caused a gradual reduction of the dispersion and an increase in viscosity is observed.

To get an indication of the degree of dispersion, we compared viscosity results of Fig. 3 with those obtained using a polyacrylate solution as dispersant. Fig. 4 curve a shows Newtonian viscosity at the high shear rate region of 57 vol% suspension vs. polyacrylate concentrations at pH 9. Suspensions of the mixture of alumina and zircon exhibited a minimum viscosity near to 50 mPa·s. Minimum viscosity using 0.13 wt% of citric acid was slightly lower than that obtained with the polyelectrolyte indicating a relatively high degree of dispersion of particles.

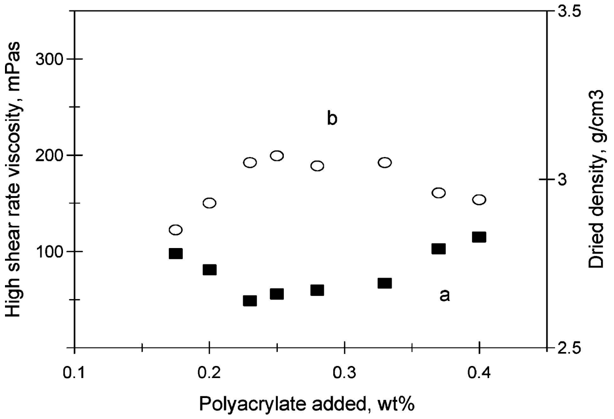

Figure 4 Effect of polyelectrolyte addition on suspension and cast properties: (a) Newtonian viscosity of 57 vol% mixed suspension at pH 9 and (b) dried density of compacts obtained by pressure filtration.

3.3. Effect of pH on viscosity

Fig. 3 shows the effect of citric acid additions on the Newtonian viscosity for different suspension pH. At pH 7.5 viscosity increased up to 319 mPa.s for citric acid concentrations lower than 0.13 wt%. With increasing suspension pH to 9.1, viscosity decreased to 76 and 72 mPa·s for 0.07 and 0.09 wt%, respectively.

Based on the maximum adsorbed amount of citric acid on alumina at pH 9 (0.52 μmol/m^2) [1], most of 0.1 wt% of amount of added dispersant was adsorbed on the surface. At pH 7.5, Fig. 1 curve a shows a positive zeta potential for alumina. Since more positive groups developed mainly on alumina surface, citrate adsorption capacity of the mixture increased. Thus, for mixed suspensions containing less than 0.1 wt% of citric acid, the amount of dispersant added became insufficient with decreasing pH. Also, at low pH dissociation of carboxilate groups is reduced and citric acid existed in solution in the form of a less negatively charged species. A decrease of the negative charge of alumina may result in a low degree of dispersion of the mixture and consequently in an increase of viscosity.

Moreover, at pH 7.5, high suspension viscosity may be explained by an electrostatic attraction (heterocoagulation) between the fine and positive to neutral alumina particles (uncovered) and the coarse and negatively charged zircon particles.

At pHs higher than 7.5, the negative effect of the low adsorbed amount of dispersant on viscosity was less pronounced. Although the dispersant content was low, the degree of dispersion of the particles improved due to negative zeta potential of the powders gradually increased with increasing pH from 7.5 to 9.1 (Fig. 1).

For citric acid concentration of 0.3 wt%, viscosity increased from 75 mPa·s at pH 7.5 to 149 mPa·s at pH 9.1. As the maximum adsorbed amount of citric acid decreased with increasing pH [1], more nonadsorbed dispersant remained in solution. Also, the concentration of NH_4OH required to adjust suspension pH at 9.1 increased from 0.05, 0.11 to 0.18 M, for citric acid additions of 0.16, 0.2 and 0.3 wt%, respectively. Thus, an increase in viscosity may be explained by excess of dispersant and high NH_4OH concentration. High ionic strength decreased zeta potential by double layer compression [1, 2].

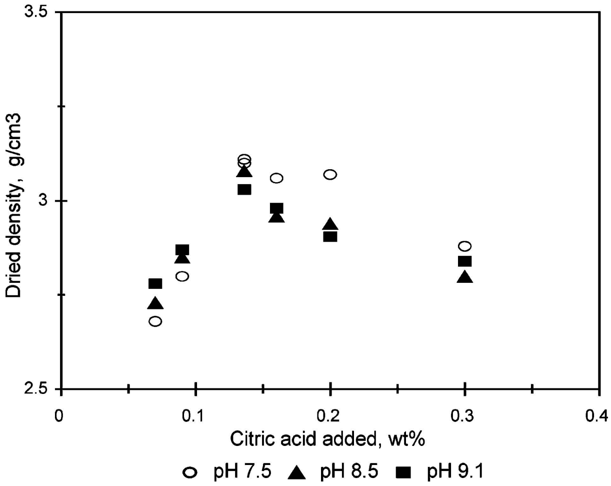

Figure 5 Dried density of compacts obtained by pressure filtration from 57 vol% suspensions as a function of the amount of citric acid added for different suspension pH.

3.4. Dried density and pore volume of compacts vs. rheological properties

Fig. 5 shows the density of dried compacts prepared by pressure filtration of 57 vol% suspensions as a function of the added amount of citric acid. Density increased to a maximum and then gradually decreased with increasing citric acid concentrations.

Density behavior was dependent on suspension pH. Compacts prepared from well dispersed suspensions with 0.13–0.16 wt% of citric acid at pH 7.5 achieved the maximum density of 3.11 g/cm^3 (72% TD) The presence of electrostatic (long-range) repulsive potentials between particles facilitated a dense particle packing during consolidation [1, 2]. When suspension pH increased, the range of dispersant concentration appropriate to obtain a high-density compact decreased and the mean density reached 3.02 g/cm^3.

Density reduced to 2.83 g/cm^3 for compacts prepared from flocculated suspensions due to an excess of dispersant and/or NH_4OH in solution. Increasing citric acid addition to 0.3 wt%, degree of dispersion of particles decreased due to high ionic strength as shown by viscosity measurements (Fig. 3). Compacts obtained from strongly flocculated suspensions due to insufficient amount of dispersant added (low negative surface charge) only reached a density of 2.70 g/cm^3. These strongly flocculated suspensions can not reach close packing.

Fig. 4 curve b shows the dried density of compacts prepared from 57 vol% suspensions dispersed with a polyelectrolyte. Maximum density of green compacts produced from well dispersed suspensions containing 0.22–0.33 wt% of polyelectrolyte (3.05 g/cm^3, 71%TD) was slightly lower than that of compacts prepared using citric acid. Density variation as a function of added polyacrylate concentration was similar than that previously reported for 48 vol% suspensions. At high solid content of suspensions (i.e., low interparticle distances) an adsorbed dispersant layer on surface enhanced the contribution of steric repulsion. Similar short-range repulsion forces between citrate and polyacrylate adsorbed on ZrO_2 were previously reported [2, 7]. In the alkaline pH range, high ionic strength in the solution produced a change in the conformation of polyacrylate molecule [8, 9]. As electrostatic repulsion between charged segments of polyelectrolyte reduces, coil configuration causes an adsorbed layer with low thickness [8, 9]. Nevertheless, interparticle distances decreased as the solid content increased during consolidation and therefore steric hindrance may favor particle arrangement.

Different compaction behavior of suspensions flocculated by the two mechanisms (low surface charge or high ionic strength) have been previously discussed [10–13]. Attractive networks produced adjusting pH towards iep were stronger than those produced flocculating the suspension by increasing ionic strength. Particles with low surface charge are strongly bound to each other and the strength of the resulting network is strong enough to resist rearrangement during processing. Whereas increasing the ionic strength leads to the development of a secondary minimum in the interparticle potential curve. The adsorbed layer acts as steric barrier and prevents that particles reach the primary minimum. Because of the weak attraction particles can move easier than those flocculated via low surface charge, and consequently, rearrangement during consolidation could take place [10–13].

The effect of the two different mechanisms of flocculation on the microstructure of the resulting green compacts was examined. Fig. 6 shows the pore size distribution curves for green compacts prepared by pressure filtration. Large (micrometer-sized) pores were absent and narrow distributions were obtained. Unimodal pore-size distribution curves were obtained indicating an uniform distribution of the two types of particles [14]. At high solid loading, segregation of particles due to different density or size was avoided.

The most frequent pore radius increased from 280 Å for a well-dispersed suspension to 310 and 360 Å for flocculated suspensions due to high ionic strength and to low negative surface charge, respectively. Heterocoagulation between alumina and zircon powders resulted in compacts having high total pore volume and pores of large size.

3.5. Sintering of dried compacts

Reaction sintering of alumina and zircon powders conducts to a mullite-zirconia formation at temperatures up to 1600°C depending on sintering time. If reaction is complete, the composite reaches a density of about 3.84 g/cm^3 depending on the relative content of tetragonal and monoclinic zirconia (t or m-ZrO_2) [15].

Fig. 7 shows the density of compacts prepared by pressure filtration after sintering (1600°C—2 h) for different processing conditions. Sintered density increased linearly with increasing green density. Highly dense compacts reached a sintered density of 3.75 g/cm^3.

Composition of crystalline phases present in compacts sintered at 1600°C—2 h was near to 66 mullite-23 vol% zirconia. The presence of alumina and zircon, 6 and 5 vol% respectively, indicated that reaction was not complete. The residual molar ratio of Al_2O_3 to zircon increased from the initial 1.5 (stoichiometric) to 2–3 due to a lower mullite formation than that of zirconia. The amount of t-ZrO_2 was near to 8 wt% with respect to total ZrO_2 content.

Sintered compacts obtained from flocculated suspensions had a relatively constant zirconia content (23 vol%) whereas the proportion of mullite slightly reduced from 66 to 64 vol%. Minor formation of mullite took placed than that predicted from alumina and silice assuming complete zircon dissociation. Flocculation of fine alumina particles and heterocoagulation in the suspension resulted in a slight increase of amount of non reacted alumina. During reaction sintering, SiO_2 formed traverses to the nearest Al_2O_3 to form mullite

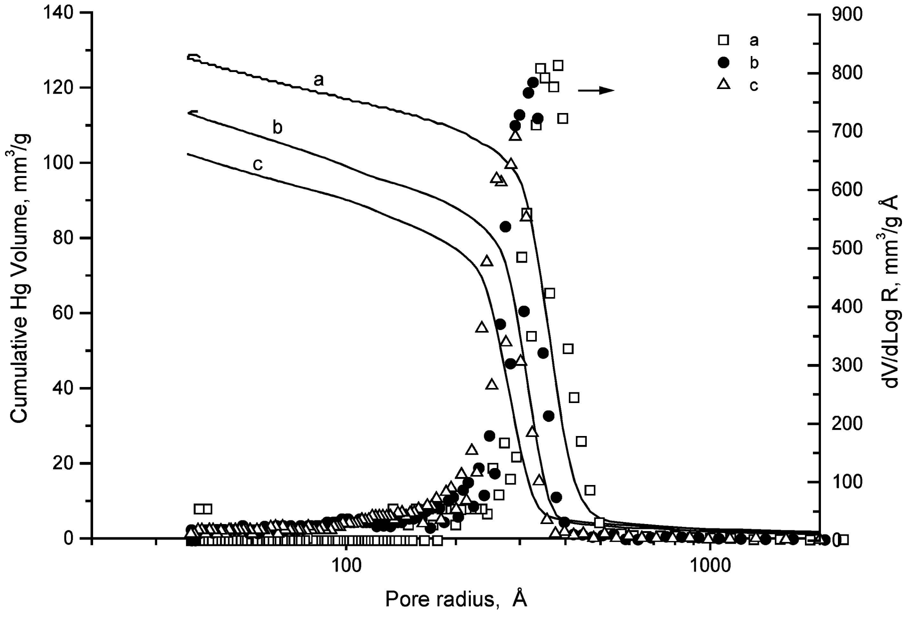

Figure 6 Pore-size distribution curves of dried compacts prepared from 57 vol% suspensions at pH 7.5 for different citric acid addition: (a) 0.09 wt% (strongly flocculated), (b) 0.3 wt% (weakly flocculated) and (c) 0.16 wt% (well dispersed).

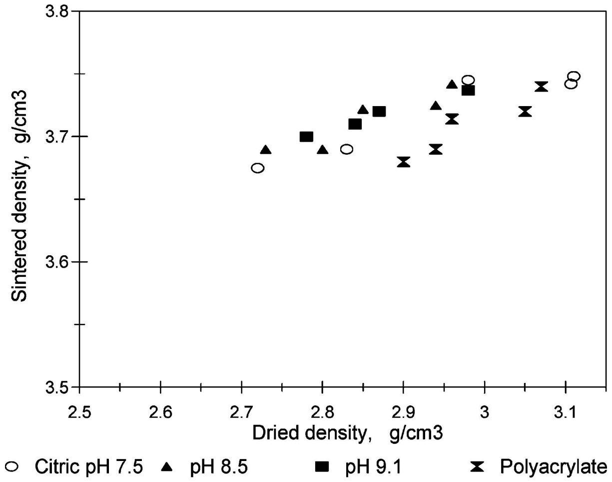

Figure 7 Sintered density versus dried density of compacts prepared using: citric acid pH 7.5; pH 8.5; pH 9.1 and polyacrylate as dispersants.

[16]. Thus low degree of dispersion of fine alumina particles in suspension as well as high total pore volume in the green compact reduced the amount of mullite formed on sintering.

The *m*-ZrO$_2$ was the dominant phase. The proportion of *t*-ZrO$_2$ remained low and it did not depend on the different processing condition employed. Probably, other critical factors such as size, shape, location (inter-, intragranular) and addition of stabilizing agents may be useful to control the stability of dispersed *t*-ZrO$_2$ particles in the mullite matrix.

4. Conclusions

Aqueous 57 vol% suspensions of a mixture of zircon and α-alumina containing citric acid as dispersant were cast by pressure filtration to produce after sintering dense mullite-zirconia composites.

Citrate anion specifically adsorbed on alumina and zircon surfaces as shown by zeta potential measurements. The iep of powders shifted to an acidic pH indicating an anion form adsorption. A low citric acid concentration (0.13 wt%) was effective to enhance electrostatic repulsion between both components in the alkaline pH range.

Dispersion and rheological behavior of the mixed suspensions using citric acid as dispersant slightly improved with respect to those obtained using a polyacrylate solution. Therefore, green compacts prepared from well-stabilized suspensions achieved a maximum relative density of 72% TD which is slightly higher than that obtained using a polyelectrolyte. Green compacts prepared from well dispersed suspensions exhibited unimodal and sharp pore size distribution curve. At high solid loading phase segregation during consolidation were avoided.

Sintered compacts at 1600°C—2 h were composed of 66 and 23 vol% of mullite and zirconia, respectively, with monoclinic as dominant phase. The amount of *t*-ZrO$_2$ was 8 wt% with respect to total ZrO$_2$ content. The contents of zirconia and *t*-ZrO$_2$ remained relatively constant whereas the proportion of mullite slightly decreased for compacts prepared from flocculated suspensions. Low formation of mullite (more amount of non reacted alumina) may be explained by flocculation of fine alumina particles and heterocoagulation in the suspension.

References

1. P. H. HIBDER, T. J. GRAULE and L. J. GAUCKLER, *J. Amer. Ceram. Soc.* **79** (1996) 1857.
2. E. P. LUTHER, J. A. YANEZ, G. V. FRANKS, F. F. LANGE and D. S. PEARSON, *ibid.* **78** (1995) 1495.
3. Y. K. LEONG, P. J. SCALES, T. W. HEALY, D. V. BOGER and R. BUSCALL, *J. Chem. Soc. Faraday Trans.* **89** (1993) 2473.
4. L. B. GARRIDO and E. F. AGLIETTI, *Ceram. Intern.* **27** (2001) 491.
5. A. SALOMONI, C. GALASSI, E. RONCARI, J. STAMENOVIK and E. RASTELLI, in Proceedings of the Fourth Euroceramic, 1994, edited by C. Galassi (Gruppo Editoriale Faenza Editrice SpA, Italy, 1995) p. 453.
6. J. W.-CH. WEI, S.-CH. WANG and F.-Y. HO, *J. Amer. Ceram. Soc.* **82** (1999) 3385.
7. Y. K. LEONG, P. J. SCALES, T. W. HEALY and D. V. BOGER, *Colloids Surf. A: Physicochem. Eng. Aspect.* **95** (1995) 43.
8. J. CESARANO, I. A. AKSAY and A. BLEIER, *J. Amer. Ceram. Soc.* **71** (1988) 250.
9. L. GUO, Y. ZHANG, N. UCHIDA and K. UEMATSU, *ibid.* **81** (1998) 549.
10. B. V. VELAMAKANNI and F. F. LANGE, *ibid.* **74** (1991) 166.
11. J. C. CHANG, F. F. LANGE and D. S. PEARSON, *ibid.* **74** (1991) 2201.
12. L. BERGSTRÖM, C. H. SCHILLING and I. A. AKSAY, *ibid.* **75** (1992) 3305.
13. S. KLEIN, M. FISHER, G. FRANKS, M. COLIC and F. F. LANGE, *ibid.* **83** (2000) 513.
14. J.-L. SHI and J. D. ZHANG, *ibid.* **83** (2000) 737.
15. N. CLAUSSEN and J. JAHN, *ibid.* **63** (1980) 228.
16. N. KAPURI, K. N. RAI and G. S. UPADHYAYA, *Interceram* **45** (1996) 427.

Received 30 October 2003
and accepted 31 August 2004