ELSEVIER

Ceramics International 33 (2007) 327–332

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Mullite compacts obtained by colloidal filtration of alumina powders dispersed in colloidal silica suspensions

Olga Burgos-Montes, Mª Isabel Nieto, Rodrigo Moreno *

Instituto de Cerámica y Vidrio, CSIC, c/ Kelsen n° 5, 28049 Madrid, Spain

Received 21 June 2005; received in revised form 25 August 2005; accepted 21 September 2005
Available online 28 December 2005

Abstract

This work deals with the manufacture of mullite-matrix composites by a colloidal filtration route. A variation of the transient viscous sintering process is studied in which submicrometer sized alumina particles are dispersed in a nanosize colloidal silica suspension. High solids loading suspensions (45 and 50 vol.%) are prepared by ultrasonic mixing and dispersed with citric acid. Rheological optimisation allows to obtain low viscosities and to reduce thixotropy and ageing effects. Specimens are obtained by slip casting and sintered to 1550 °C/2 h by using different heating cycles, the best results being obtained with a plateau after the maximum rate of sintering where reaction occurs.

Keywords: A. Suspensions; A. Shaping; A. Slip casting; D. Mullite; Alumina; Silica

1. Introduction

Mullite and mullite-matrix composites are attractive for high temperature structural applications due to their excellent thermo-mechanical properties [1,2]. However, sintering of mullite powders into dense compacts requires high temperatures due to its diffusion coefficient [3]. To enhance densification many studies have been directed toward reduction of particle size and improvement of the green microstructure [4].

Another approach to prepare mullite bodies at lower sintering temperature is by using mullite precursors that react after densification has occurred. The most popular way is by means of sol–gel techniques [5]. However, warpage and cracking is usual. Moreover, densification of mullite-matrix composites is difficult because once mullitization occurs densification is arrested until much higher temperatures [4,6].

Sacks et al. [3,4] proposed a transient viscous sintering (TVS) process in which α-alumina powders instead of alumina precursors were used and coated with amorphous silica source, like TEOS, as in other sol–gel processes. Silica was precipitated onto alumina by adding ammoniated water. These particles were dispersed in water to solids loadings of 30–35 vol.%, slip cast and sintered at 1500–1600 °C to produce mullite.

This work deals with the preparation of mullite bodies through a colloidal filtration route by using concentrated suspensions of submicrometer-sized α-Al_2O_3 powders dispersed in a commercial colloidal silica suspension. Colloidal silica suspensions are readily available and have a very low price, so that the process is cheaper than that reported by Sacks et al. and the use of organic precursors (i.e. TEOS) is replaced by a clean aqueous processing.

By optimising the dispersing conditions through rheological measurements, it is possible to produce uniform composite compacts by colloidal filtration that densify and react to produce mullite by reaction sintering.

2. Experimental

The following starting materials were used: a commercial α-alumina (ALCOA CT3000SG, USA), with average particle size of 0.6 μm and specific surface area of 8 m^2/g, and a colloidal silica suspension (LEVASIL 200A/40%) containing 40 wt.% particles with average size of 15 nm, specific surface area of 200 m^2/g and pH value of 9.

Mixtures were prepared with alumina/silica molar ratio of 13/5 (82/18, wt./wt.), with an excess of Al_2O_3 over the

---

* Corresponding author. Tel.: +34 91 735 5840; fax: +34 91 735 5843.
E-mail address: rmoreno@icv.csic.es (R. Moreno).

0272-8842/$32.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.09.018

stoichiometric ratio of mullite 3:2 (72/28, wt./wt.), which is expected to remain as a secondary phase. Suspensions were prepared in deionised water to total solids loadings of 45 vol.% (70 wt.%) and 50 vol.% (75 wt.%), including the water added with the colloidal silica suspension. Citric acid (PROBUS, Spain) was used as a dispersant in concentrations ranging from 0.1 to 0.5 wt.% on a dry solids basis. Homogenisation was carried out using an ultrasounds probe (IKA 400US, IKA, Germany) for mixing times of 1, 3, 5 and 10 min. The final pH of the mixtures was 6.5.

The rheological behaviour was studied using a rheometer (RS50, Haake,Germany) with a double-cone/plate sensor configuration (DC60/2°, Haake, Germany). Flow curves were obtained with a three-stage measuring program with a linear increase of shear rate from 0 to 1000 s^{-1} in 300 s, a plateau at 1000 s^{-1} for 120 s, and a further decrease to zero shear rate in 300 s. The influence of the volume fraction of solids, the citric acid concentration and the time of ultrasonic mixing on the flow behaviour was studied. Flow curves of every suspension were also determined after times of 30, 60, and 90 min, in order to establish the ageing behaviour. Thixotropy was calculated as the area enclosed between the up-curve and the down-curve in the controlled rate flow curves for the measuring conditions described above.

Ceramic pieces were obtained by slip casting on plaster of Paris moulds. Cast green densities were determined by Archimedes' method in mercury after drying for 48 h at room temperature. Dynamic sintering studies were performed with a differential dilatometer (Setsys 16/18, Setaram, France). For static sintering tests, green specimens were treated according to three different sintering schedules: (a) heating rate of 5 °C/min up to 1550 °C/2 h; (b) heating rate of 5 °C/min up to 1550 °C/2 h with an additional isothermal step at 1250 °C/1 h, considered as the temperature at which flow phenomena occur; and (c) heating rate of 5 °C/min up to 1550 °C/2 h with an isothermal step at 1350 °C/1 h, considered as the nucleation temperature of mullite.

Table 1
Thixotropy (Pa/s) of 50 vol.% Al_2O_3/SiO_2 fresh and aged suspensions prepared with different sonication times

Ageing time (min)	Thixotropy (Pa/s, × 10^4) Sonication time (min)			
	1	3	5	10
Fresh	0.03	0.26	0.20	0.02
30	3300	1.70	0.71	0.52
60	7300	5.10	1.90	1.50
90	12000	7.10	3.10	–

Microstructure of the sintered pieces was observed by scanning electron microscopy (SEM, Carl Zeiss, DSM-950, Germany) on polished and thermally etched surfaces. Sintered densities were measured by immersion in water. X-ray diffraction (D5000, Siemens, Germany) was used to determine the crystalline phases using ground materials.

3. Results and discussion

The effect of mixing and ageing times on the rheological behaviour of the suspensions were first studied. To do this, a constant concentration of dispersing aid (citric acid) of 0.3 wt.% was used. Fig. 1 shows the variation of viscosity (at a shear rate of 100 s^{-1}) with ageing time for 50 vol.% suspensions, prepared with different sonication times. The viscosity increases with ageing time for any ultrasounds treatment and thixotropy strongly increases. Table 1 shows the calculated thixotropy values of the different suspensions. The fresh slips always have the lowest viscosity and thixotropy, but for 1 min sonication time settling occurs rapidly, so that ageing leads to a significant increase of viscosity and very large increase of thixotropy. This means that 1 min US is not enough to homogenise the suspension and the dispersant is not readily adsorbed at the particles surface. The highest stability is reached after 5 min ultrasonic mixing, where both the increase of viscosity with ageing time and the thixotropy

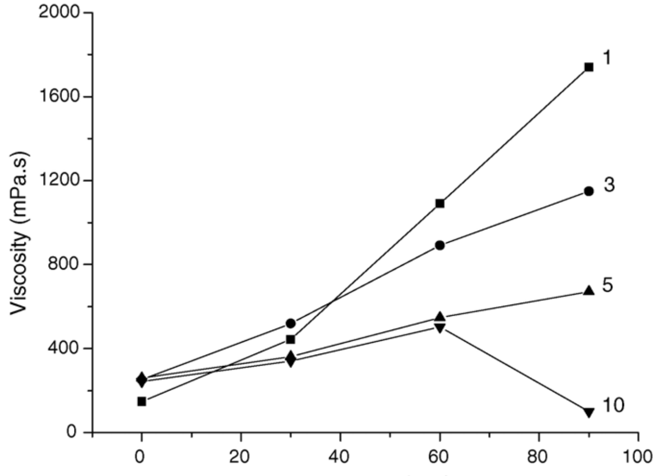

Fig. 1. Viscosity vs. ageing time of 50 vol.% suspensions dispersed with 0.3 wt.% citric acid after different sonication times (min).

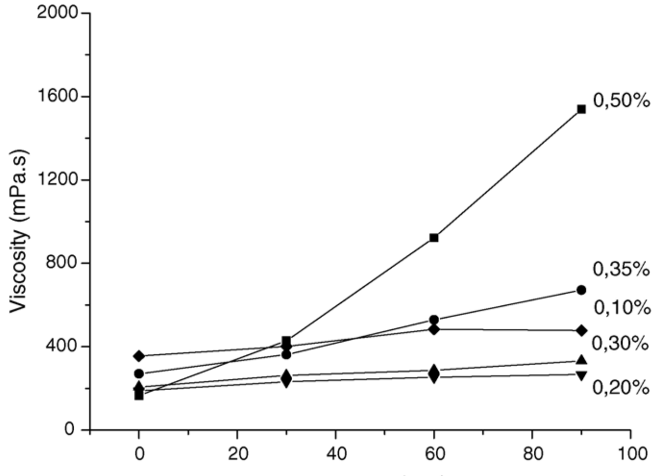

Fig. 2. Viscosity vs. ageing time of 50 vol.% suspensions dispersed with different concentrations of citric acid after sonication time of 5 min.

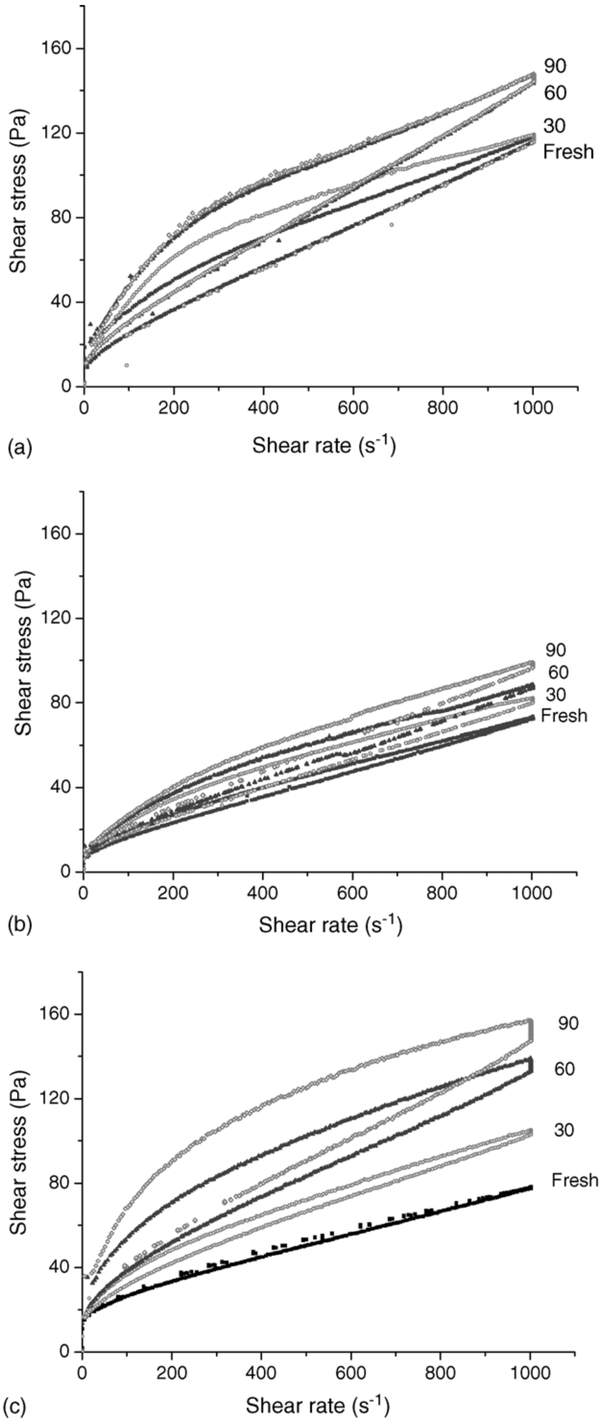

Fig. 3. Flow curves of 50 vol.% suspensions as-prepared and after different ageing times with concentrations of citric acid of 0.1 (a), 0.2 (b), and 0.5 wt.% (c).

Table 2
Thixotropy (Pa/s) of 50 vol.% Al_2O_3/SiO_2 fresh and aged suspensions as a function of citric acid concentration

Ageing time (min)	Thixotropy (Pa/s, $\times 10^4$) Citric acid concentration (wt.%)				
	0.1	0.2	0.3	0.35	0.5
Fresh	1.10	0.37	0.11	0.20	0.40
30	2.00	0.77	0.10	0.71	1.40
60	2.00	0.77	0.37	1.90	5.20
90	3.20	0.84	0.67	3.10	7.60

are significantly reduced. As a more efficient adsorption of dispersant on the surface occurs, a higher stability is reached and thus, the influence of time is less important. For longer sonication times (10 min) the viscosity is rather the same as for 5 min US but sedimentation takes place after 1 h ageing. Probably, an excess of sonication time leads to an excessive heating of the suspension, which has a direct influence on the state of adsorption of the dispersant and the number of free-sites at the alumina surface increases, thus leading to isolated flocs. In addition, the commercial silica suspension has a small, uncertain fraction of additives and organic precursors, and the particles agglomerate on heating. The increase of viscosity indicates irreversible damage through the onset of a cross-linking reaction to form silica gel. In this work, experiments were carried out using open vessels for shake of simplicity, thus allowing the adsorption of CO_2 from the air, which increases slightly the tendency of gelling. The goal is to find the simplest processing conditions without affecting significantly the dispersing behaviour.

Once the mixing time was fixed to 5 min US, the concentration of deflocculant was optimised. Fig. 2 shows the variation of viscosity with ageing time for 50 vol.% suspensions dispersed with different concentrations of citric acid. There is a minimum viscosity for 0.2–0.3 wt.% citric acid, where the differences of viscosity of aged slips are rather small. Higher concentrations of deflocculant ($\geq$0.35) lead to a more pronounced effect of ageing. The pH of the suspensions maintains always in the range between 6 and 7, where the surface charge of silica is negative and that of alumina, in the absence of citric acid, would be positive. The suspension of the mixture only contains the water present in the silica suspension, so that the role of citric acid in the dispersion is crucial, as it must maintain the alumina particles separated each other to avoid agglomerates that could reduce excessively the separation distance among the nanoparticles of silica, which would

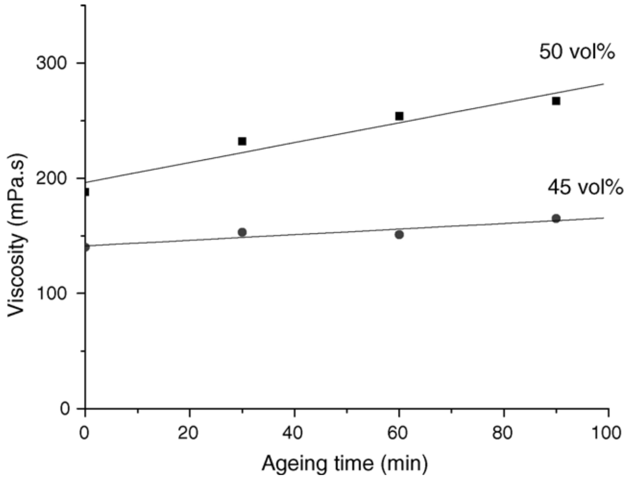

Fig. 4. Evolution of viscosity (at 100 s^{-1}) with ageing times for 45 and 50 vol.% suspensions (0.2 wt.% citric acid, US time, 5 min).

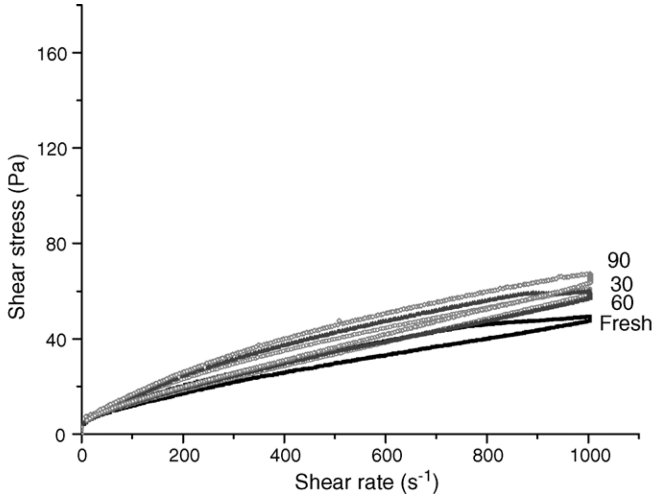

Fig. 5. Flow curves of 45 vol.% suspensions as-prepared and after different ageing times with 0.2 wt.% of citric acid.

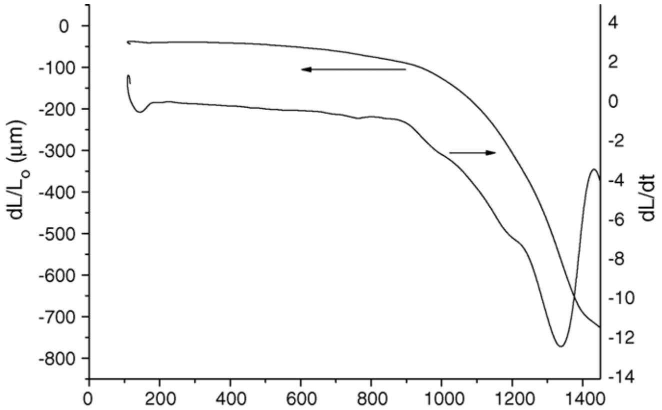

Fig. 6. Dynamic sintering curves of the Al_2O_3/SiO_2 compacts, showing the linear shrinkage, $\Delta L/L_0$, and the linear shrinkage rate, $d(\Delta L/L_0)/dT$, vs. temperature.

lead to gelling. The dispersing mechanism of alumina suspensions by citric acid has been studied in detail by Hidber et al. [7], who stated that small additions of citric acid (<0.2 wt.%) at pH < 7 led to full adsorption, as confirmed in our experiments. As a consequence, the isoelectric point of alumina shifts down below pH 5. Hence, in the presence of citric acid both the alumina and the silica particles are negatively charged.

To illustrate the combined action of deflocculant content and ageing time, Fig. 3 shows the flow curves of fresh and aged suspensions with citric acid contents of 0.10 wt.% (poor dispersion, Fig. 3a), 0.20 wt.% (homogeneous dispersion,

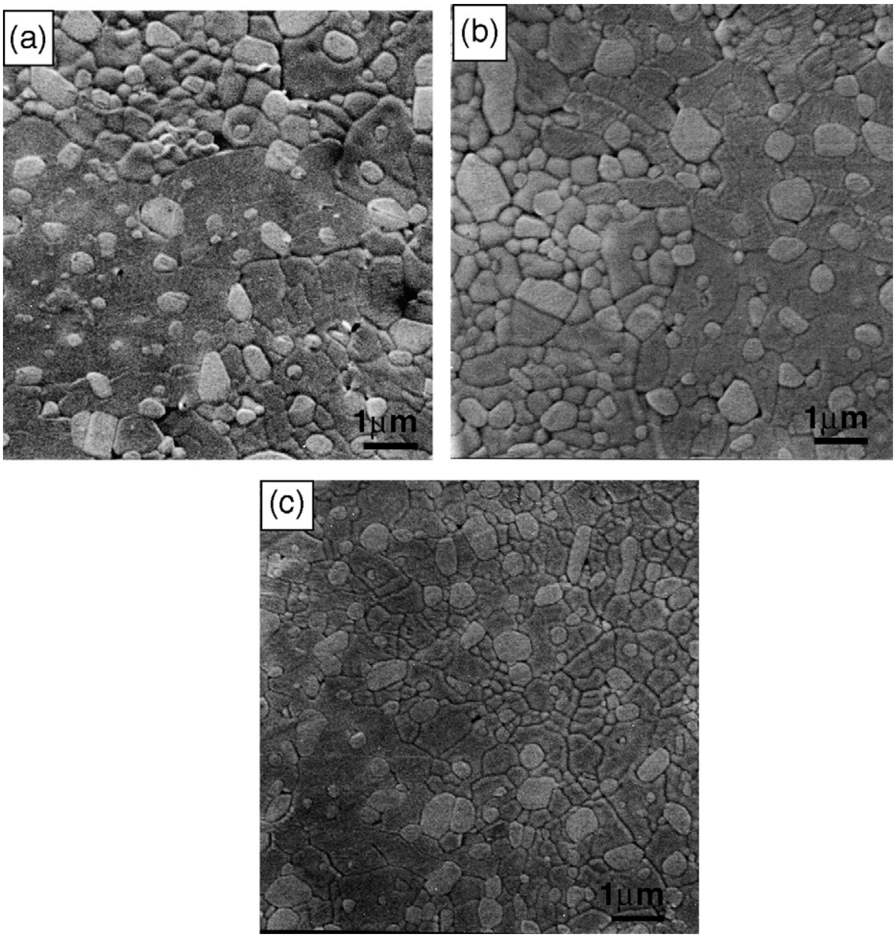

Fig. 7. SEM microstructures of samples prepared from 50 vol.% suspensions and sintered according to cycles a, b, and c (pictures a, b, and c, respectively).

Fig. 3b), and 0.5 wt.% (excess of deflocculant, Fig. 3c). The thixotropy of suspensions with different concentration of citric acid is shown in Table 2, as calculated from the flow curves. Suspensions with 0.1 wt.% citric acid have a shear-thinning behaviour with a significant time-dependency (thixotropy), which is significantly reduced for a deflocculant content of 0.2 wt.%. An excess of deflocculant seems to have a more detrimental effect on thixotropy and ageing viscosity than the lack of deflocculant (Fig. 3d.). This is probably related to some incipient gelling of silica nanoparticles induced by heating during the longer sonication time, as discussed above.

Since the viscosity of these suspensions may be too high for a suitable casting, similar studies were carried out using suspensions prepared in the same way but with lower solids loading (i.e. 45 vol.%). Fig. 4 compares the viscosity of suspensions prepared to 45 and 50 vol.% solids with 0.2 wt.% citric acid as a function of ageing time. In Fig. 5, the flow curves of the 45 vol.% suspensions are plotted. When the solids loading decreases, the viscosity decreases and the thixotropy practically disappears and hence, the suspension stability is preserved for longer times.

Fresh suspensions with 45 and 50 vol.% solids were slip cast on plaster moulds to obtain solid discs with 2 cm in diameter. The green densities of cast samples after drying at open conditions for 48 h are 2.45 and 2.50 g/cm^3 for solids loadings of 50 and 45 vol.%, respectively. Assuming that the theoretical green density of the mixtures is 3.59 g/cm^3 relative densities as high as 68 and 70 % of theoretical were obtained, thus demonstrating that a suitable slip casting performance has been reached. Although the differences in the green density are rather small, it is significant that the less concentrated suspensions led to higher densities, thus indicating that a better dispersion (i.e. packing of particles) is reached.

Dynamic sintering studies were performed using differential dilatometry. In the sintering curve (Fig. 6), two differentiated zones can be seen; the first one in the temperature range 1000–1350 °C is attributed to viscous flow phenomena with a maximum sintering rate at ~1330 °C, and the second, between 1350 and 1450 °C exhibits a lower shrinkage, due to the nucleation and growth of mullite, as like as the behaviour observed in mullite gel [8,9].

Considering the dilatometric studies three sintering cycles were designed for slip cast bodies obtained from suspensions with 45 and 50 vol.% solids loading. A first cycle with no intermediate steps (a), a second one with a plateau before the temperature of maximum sintering rate (b), and the third with a plateau above that temperature (c).

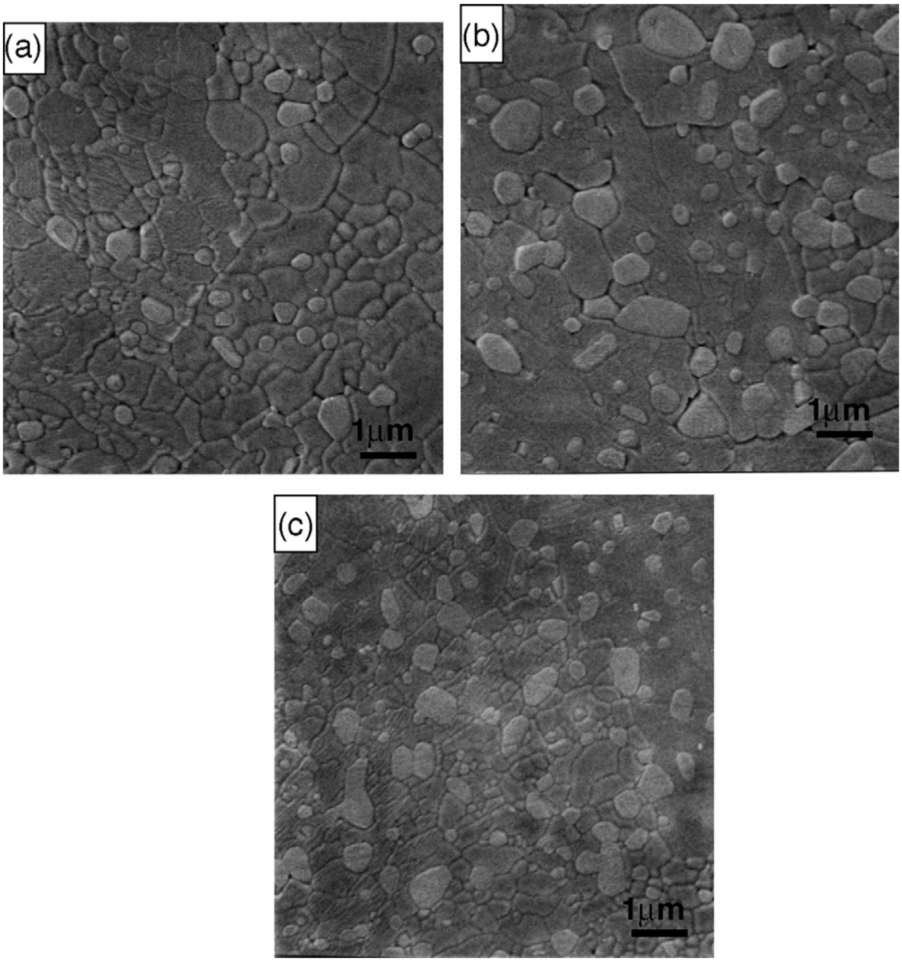

Fig. 8. SEM microstructures of samples prepared from 45 vol.% suspensions and sintered according to cycles a, b, and c (pictures a, b, and c, respectively).

The values of the densities of the specimens sintered with different cycles are similar thus the sintering cycle has no influence on the final relative density. The sintered densities are 3.30 ± 0.05 g/cm^3, higher than the theoretical density of mullite (3.16 g/cm^3), demonstrating that unreacted Al_2O_3 is present in the sintered specimens. To confirm this point, XRD analysis and SEM studies were performed for samples sintered with the three selected heating schedules. In all cases, both mullite and α-Al_2O_3 are clearly detected.

Figs. 7 and 8 show the SEM microstructures of specimens obtained with every sintering cycle from 50 to 45 vol.% suspensions. The presence of dispersed α-Al_2O_3 grains (clear grains in the pictures) was confirmed by EDX analysis. It can be observed that quite different microstructures were obtained depending on both the solids loading of the casting suspension and the sintering schedule. According to above results, suspensions with 45 vol.% solids are less viscous (i.e. have better flowability) and much more stable against time. As a consequence, the microstructure of 45 vol.% samples is much more homogeneous as compared to that of samples prepared with 50 vol.% suspensions and lower remaining porosity is observed. The dilution to 45 vol.% solids helps the particles to maintain far apart each other and to prevent cross-linking of the silica suspension to form a gel structure. In the concentrated suspension, the SEM microstructure reveals the existence of zones with different densification, as a consequence of agglomerated regions where incipient gelling has probably occurred.

In addition to solids loading the microstructure is strongly influenced by the heating cycle, as expected for a reaction sintering process. The better uniformity and the lowest grain size and porosity are reached for sintering cycle c, using an isothermal step at 1350 °C/1 h, just at the maximum sintering rate when the nucleation and growth of mullite begin. According to Osendi el al. [9], if the sintering curve has not isothermal step or this is at temperatures below that corresponding to mullite nucleation, exaggerated grain growth occurs and unreacted alumina particles remain. For sintering schedules with isothermal treatment above the temperature for mullite formation, the microstructure shows narrower grain size distribution with a smaller average grain size, but trapped porosity maintains in the microstructure and no further densification occurs.

Optimised sintering schedule leads to a dense microstructure without defects, where the α-Al_2O_3 grains are homogeneously distributed, their average size being <0.3 μm, much lower than that achieved with the other sintering treatments. From this microstructure, it is expected that mullite-based materials with superior thermo-mechanical response can be obtained. It is also remarkable that the maximum temperature of sintering was 1550 °C, lower than that commonly used for sintering mullite by means of powder processing techniques.

4. Conclusions

Dense mullite compacts with dispersed alumina have been produced by slip casting. Alumina powders were dispersed in a commercial colloidal silica suspension with nanosize silica. The preparation of concentrated suspensions of the mixture was performed by ultrasounds probe. This allows an effective dispersion of the particles but also an increase of viscosity on ageing because a heating effect. Rheological studies allowed to optimise the dispersing conditions with 0.2–0.3 wt.% citric acid, thus preventing ageing. Slip casting leads to green compacts with high relative densities (>68% of TD) which demonstrated that well-dispersed suspensions were achieved. Sintering studies indicate that better sintering behaviour is reached using a heating schedule with a plateau after the temperature of maximum sintering rate (i.e. 1330 °C) and maximum heating temperature of 1550 °C for 2 h, relatively low as compared with conventional sintering treatments for powder processing of mullite.

Acknowledgement

This work has been supported by CICYT (Spain, contract N° MAT2003-836).

References

[1] S. Somiya, R.F. Davies, J.A. Pask (Eds.), Mullite and Mullite Matrix Composites, Vol. 6, Ceramic Transactions, The American Ceramic Society, Westerville, OH, USA, 1990.

[2] I.A. Aksay, D.M. Dabbs, M. Sarikaya, Mullite for structural, electronic, and optical applications, J. Am. Ceram. Soc. 74 (10) (1991) 2343–2358.

[3] M.D. Sacks, H.W. Lee, J.A. Pask, A review of powder preparation methods and densification procedures for fabricating high density mullite, in: S. Somiya, R.F. Davies, J.A. Pask (Eds.), Mullite and Mullite Matrix Composites, Vol. 6, Ceramic Transactions, American Ceramic Society, Westerville, OH, USA, 1990, pp. 167–207.

[4] M.D. Sacks, M. Bozkurt, G.W. Scheiffele, Fabrication of mullite-matrix composites by transient viscous sintering of composite powders, J. Am. Ceram. Soc. 74 (10) (1991) 2428–2437.

[5] B. Sonupaslak, Sol–gel processing of infrared transparent mullite, Adv. Ceram. Mater. 3 (3) (1988) 263–267.

[6] L.C. De Jonghe, M.N. Rahaman, C.H. Hsheh, Transient stresses in bimodal compacts during sintering, Acta Metal. Mater. 34 (7) (1986) 1467–1471.

[7] P.C. Hidber, T.J. Graule, L.J. Gauckler, Citric acid-A dispersant for aqueous alumina suspensions, J. Am. Ceram. Soc. 79 (7) (1996) 1857–1867.

[8] M.I. Nieto, G. Urretavizcaya, A.L. Cavalieri, P. Pena, Structural changes in colloidal and polymeric aluminosilicate gels with mullite composition, Br. Ceram. Trans. 97 (1) (1998) 17–23.

[9] M.I. Osendi, C. Baudín, S. de Aza, Mullite materials from a 3:2 alumina–silica gel. Part II: micro structural evolution, J. Eur. Ceram. Soc. 10 (1992) 399–403.