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Colloidal behaviour of mullite powders produced by combustion synthesis

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Abstract

The combustion synthesis method is very attractive to produce homogeneous powders of pure or mixed oxidic ceramics without further thermal treatment. Previous work reports the synthesis of monophasic mullite powders by a suspension combustion process using two combustions aids, ammonium nitrate and hydrogen peroxide, and an excess of colloidal silica suspension.

The combustion synthesis leads to coarse, agglomerated powders that must be crushed. The effect of attrition milling on both particle size and morphology was studied. Aqueous suspensions of the milled powders were prepared using two dispersants: citric acid and a polyacrylic acid-based polyelectrolyte. The stability of the powders was studied by measuring the zeta potential. The effect of the dispersants on the rheological behaviour of concentrated suspensions was also studied. The sintered densities and the microstructures of specimens obtained by slip casting were studied, demonstrating that mullite powders obtained by a single step combustion process can be processed through conventional shaping routes.

Keywords: Powders-chemical preparation; Suspensions; Mullite; Combustion synthesis

1. Introduction

The study of mullite has focused on its excellent refractory properties. In the last decades mullite has received great attention in electronic, optical, and high-temperature structural applications due to its good mechanical properties at high temperature, chemical stability, low thermal expansion coefficient, low dielectric constant, etc.[1,2]

In order to control the properties of mullite and mullite composites it is necessary to control the synthesis and the earlier processing steps to determine their effect on the microstructure of the final bodies and thus, the corresponding behavioural properties.[2,3]

Different routes of synthesis have been devoted toward preparation of mullite powders with fine particles and high reactivity. One of them is the combustion method. It consists on the mixing of reagents that oxidize easily, such as nitrates, and an organic fuel, acting as a reducing agent. An external heat supply is needed to promote the ignition of the mixture leading to a self-sustaining and exothermic redox reaction. Mullite powders have been synthesised in a single step process without further thermal treatment.[4–7]

Previous works[7,8] reported the combustion synthesis of mullite adding ammonium nitrate as a combustion aid and using the stoichiometric ratio of Al to Si. The presence of unreacted α-alumina was observed in those powders so that an excess of silica was necessary to obtain monophasic mullite. Similarly, the present work studies the effect of an excess of silica for powders synthesised with H_2O_2 as combustion aid, as compared to those synthesised with ammonium nitrate.

Colloidal processing routes have been successfully used to produce green bodies with defect-free, homogeneous microstructures. In colloidal processing it is essential to control the particle size and stability of the particles against settling, which determine the rheological properties of the suspensions and therefore, on the properties of the green bodies and the sintered compacts.[8–10]

The aim of the present work was to study the stability and rheological properties of mullite powders synthesized by a combustion method using colloidal silica in excess of 20 mol% over the stoichiometric ratio and using two different combustion aids, i.e. ammonium nitrate and hydrogen peroxide. Due

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to the coarse particle size of as-synthesised powders, they were attrition milled before the colloidal characterization.

2. Experimental

2.1. Combustion synthesis

$Al(NO_3)_3 \cdot 9H_2O$ (analytical-reagent grade, Panreac, Spain) was used as an Al source for the synthesis of mullite. Si was incorporated using a colloidal silica suspension (LEVASIL VP AC 4051, Bayer, Germany), which was supplied as an aqueous suspension with 20 wt.% solids, pH 3, a specific surface area of 200 m^2/g, and an average particle size of 15 nm. In order to obtain monophasic mullite mixtures were always prepared with 20 mol% in excess of silica over the stoichiometric ratio. As a fuel urea (analytical-reagent grade, Panreac, Spain) was employed. As combustion aids, NH_4NO_3 and H_2O_2 (analytical-reagent grade, Panreac, Spain) were tested to obtain the crystalline mullite. Hence, two different powders were synthesised, both with an excess of SiO_2 of 20 mole% over the stoichiometric, the difference being the substance used as combustion aid. Powders prepared with ammonium nitrate and hydrogen peroxide as combustion aids were labeled as M1 and M2, respectively.

A reference solution was prepared on the basis of the stoichiometric molar ratio Al_2O_3/SiO_2 (3:2), 30 mole of urea and 5 mole of the combustion aid (either NH_4NO_3 or H_2O_2). Reagents supplied in the solid state such as aluminium nitrate, urea and ammonium nitrate (when this was the combustion aid) were dissolved in deionised water with a resistivity greater than 18 MΩ cm, produced by a Milli-Q Plus pure water generating system from Millipore (USA). Then, the liquid reagents were added, i.e. the colloidal silica suspension, and H_2O_2 when this was the combustion aid. The powders studied in this work resulted by mixing the product of the reactions carried out at least three times in order to ensure that the combustion reaction leads to reliable results.

The experimental procedure for the synthesis was explained in detail in previous works.[6,7] The combustion powders calcined at 1400 °C were characterized by X-ray diffraction (D5000, Siemens, Germany) to determine the crystalline phases. The morphology of the as-prepared combustion reaction powders was observed by scanning electron microscopy, SEM (DSM 950, Zeiss, Germany) and field emission microscopy, FEM (Hitachi S-4700 type I, Japan).

2.2. Milling

The as-synthesised powders had irregular morphology and a coarse particle size due to the high temperature reached during ignition. Thus, a reduction of particle size was necessary for further processing. The synthesised powders were attrition milled in isopropanol using alumina balls. The effect of milling was studied by controlling the average size every hour from 1 h to 8 h. The particle size distributions were measured using a laser diffraction analyser (Mastersizer S, Malvern, UK). The crystalline phases were determined by X-ray diffraction and the morphology of the particles was observed by SEM and FEM.

2.3. Colloidal behaviour

The stability of the milled powders was studied as a function of pH through zeta potential measurements that were performed using the Laser Doppler Electrophoresis technique (Zetasizer NanoZS, Malvern, UK). The samples were prepared to a solids content of 0.1 g/l in a solution of KCl 10^{-2} M, to maintain a constant ionic strength. Suspensions were stirred for 20 h prior to measurements in order to reach surface equilibrium.

Two dispersants were selected: Citric acid (PROBUS, Spain) and an ammonium salt of a polyacrylic acid (PAA, Duramax D3005, Rohm and Haas, PA, USA). This polyelectrolyte is an emulsion prepared to a concentration of 35 wt.% of active matter and has pH = 7–8 and density of 1.16 g/cm^3. Zeta potential measurements were performed for different dispersant contents in order to determine the influence of these dispersants in the stability.

Concentrated suspension of both mullite powders (M1 and M2) were prepared to a solids loading of 40 vol.% adding the optimised content of dispersant according to zeta potential measurements. Homogenisation was carried out by 6 h ball milling using alumina jar and balls. The rheological behaviour of these suspensions was studied using a rheometer (RS50, Haake, Thermo Electron Co., Germany) with a double-cone/plate sensor configuration (DC60/2°).

Optimised suspensions were slip cast into plaster of Paris moulds. Cast green densities were determined by Archimedes'method in mercury after drying for 48 h at room temperature. The green bodies were sintered at 1600 °C/2 h. Sintered densities were measured by immersion in water. The phases present in the sintered bodies were also analysed by XRD and the microstructures were observed by SEM.

3. Results and discussion

3.1. Combustion synthesis

Fig. 1 shows the XRD spectra of the powders obtained employing ammonium nitrate and H_2O_2 as combustion aids and 20 wt.% of silica excess over the stoichiometric after a thermal treatment at 1400 °C for 1 h. At these conditions monophasic mullite is practically the unique phase obtained for any of the combustion aids used. Some differences in peak broadening and intensity are appreciated between M1 and M2 powders due to the different features involved in the combustion process, as it will be discussed later.

Fig. 2 shows SEM pictures of powders synthesised with both combustion aids NH_4NO_3 (a) and H_2O_2 (b). Pictures of Fig. 2c and d show the high magnification microstructure of powders M1 and M2 as observed by FEM. Regarding the general microstructure a porous structure with plate-like powder morphology is observed in both samples, typical of a combustion process, in which hard agglomerates are present due to the high temperatures achieved in the process that promote

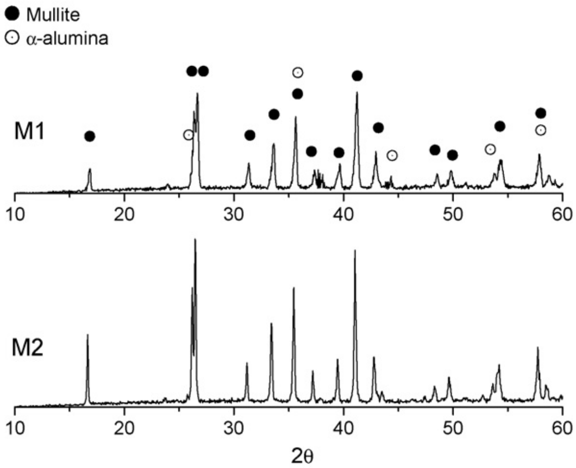

Fig. 1. XRD spectra of the synthesised powders obtained with 20 wt.% of silica in excess over the stoichiometric using ammonium nitrate (M1) or hydrogen peroxide (M2) as combustion aids. Powders were thermally treated at 1400 °C/1 h.

the formation of sintering necks. The FEM pictures demonstrate that these coarse agglomerates are formed by nanometer sized particles and a high remaining porosity is present inside those agglomerates.

Measurements of particle size distribution show a broad distribution with coarse mean diameters of 90–110 μm (Fig. 3). The differences in the particle size are related to the temperatures achieved in the combustion synthesis, which is higher for the reaction with H_2O_2 as described elsewhere.[7] This may be correlated with the differences in the crystallinity between both powders, also.

3.2. Milling

Attrition milling was carried out in order to reduce the large particle sizes obtained in the combustion process. The study was performed for the two considered powders: M1 and M2. Fig. 4 shows the evolution of the mean particle size as a function of milling time. The milling seems to be very effective for low times, the mean particle size decreasing from 90 to 15 μm for M1 and from 110 to 20 μm for M2 during the first hour of

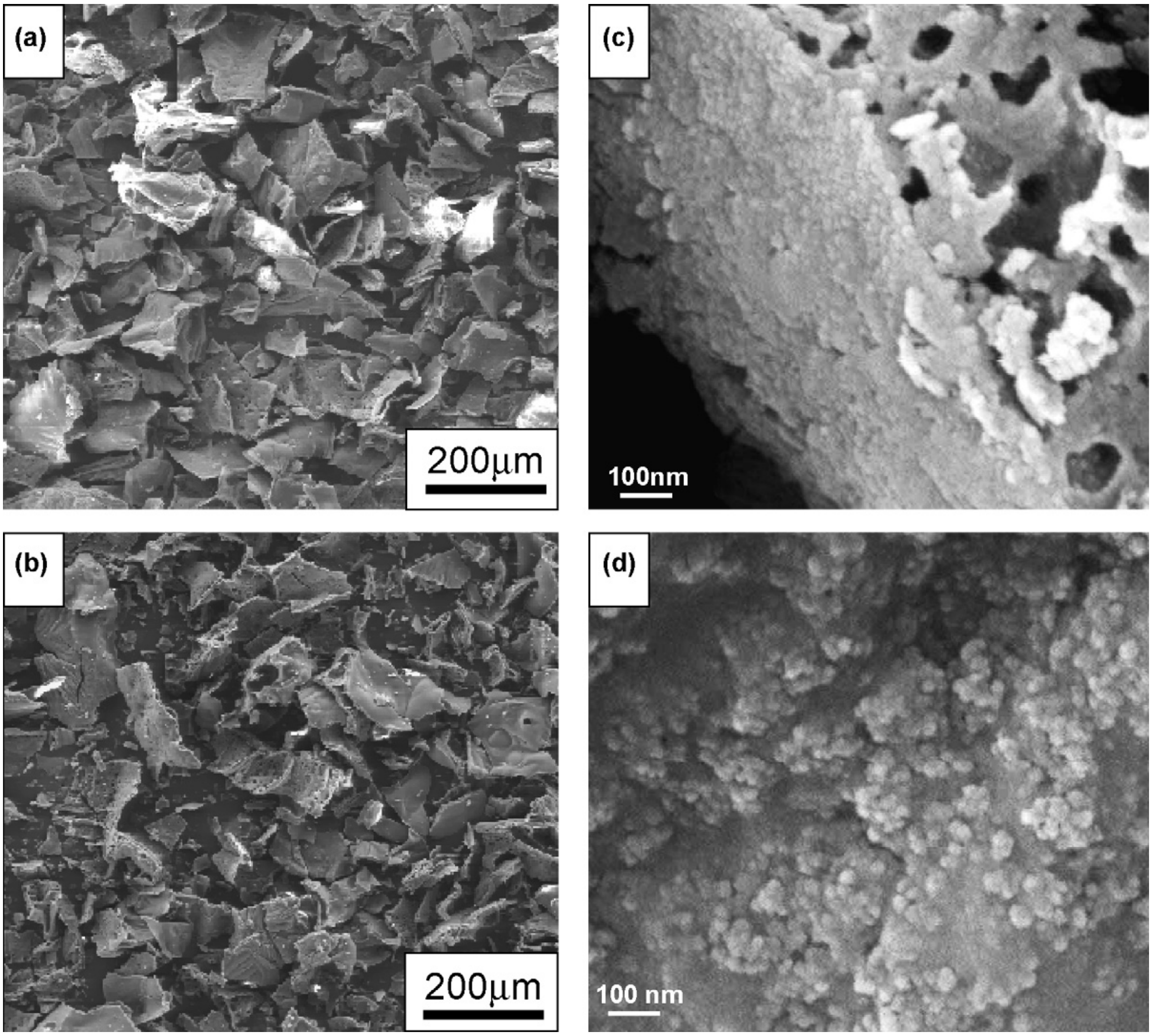

Fig. 2. SEM (a and b) and high magnification FEM (c and d) pictures of as-synthesised M1 (a and c) and M2 (b and d) powders.

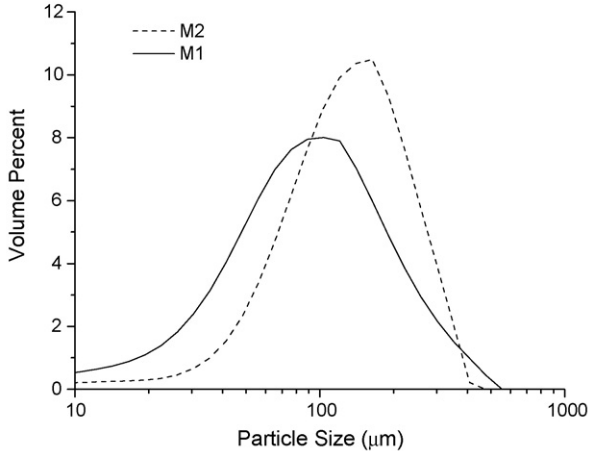

Fig. 3. Particle size distributions of as-synthesised M1 and M2 powders.

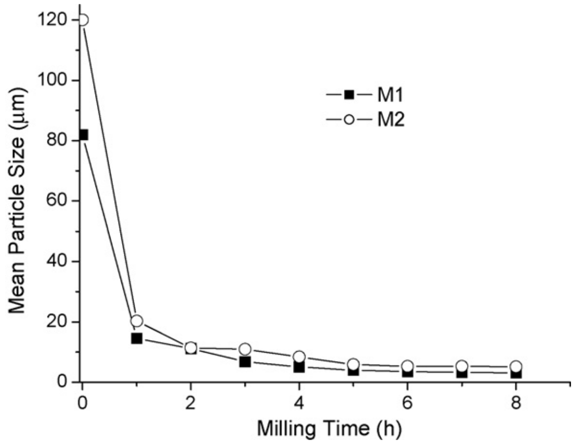

Fig. 4. Evolution of the mean particle size with milling time for both M1 and M2 powders.

milling. The minimum sizes are achieved after 8 h of milling: 3.2 and 5.2 μm for M1 and M2, respectively, although no effective milling occurs above 5 h. Longer times lead to re-agglomeration of new created surfaces and average sizes tend to increase again.

Milled powders of M1 and M2 have specific surface areas of 11.3 and 29.1 m^2/g, respectively. The relatively large values are related to the irregular morphology and the presence of pores trapped inside the particles. Unexpectedly, a larger value is obtained for M2 although this powder achieves a higher temperature during the combustion process. This difference is related to the larger volume of gases involved during the ignition.[6,7]

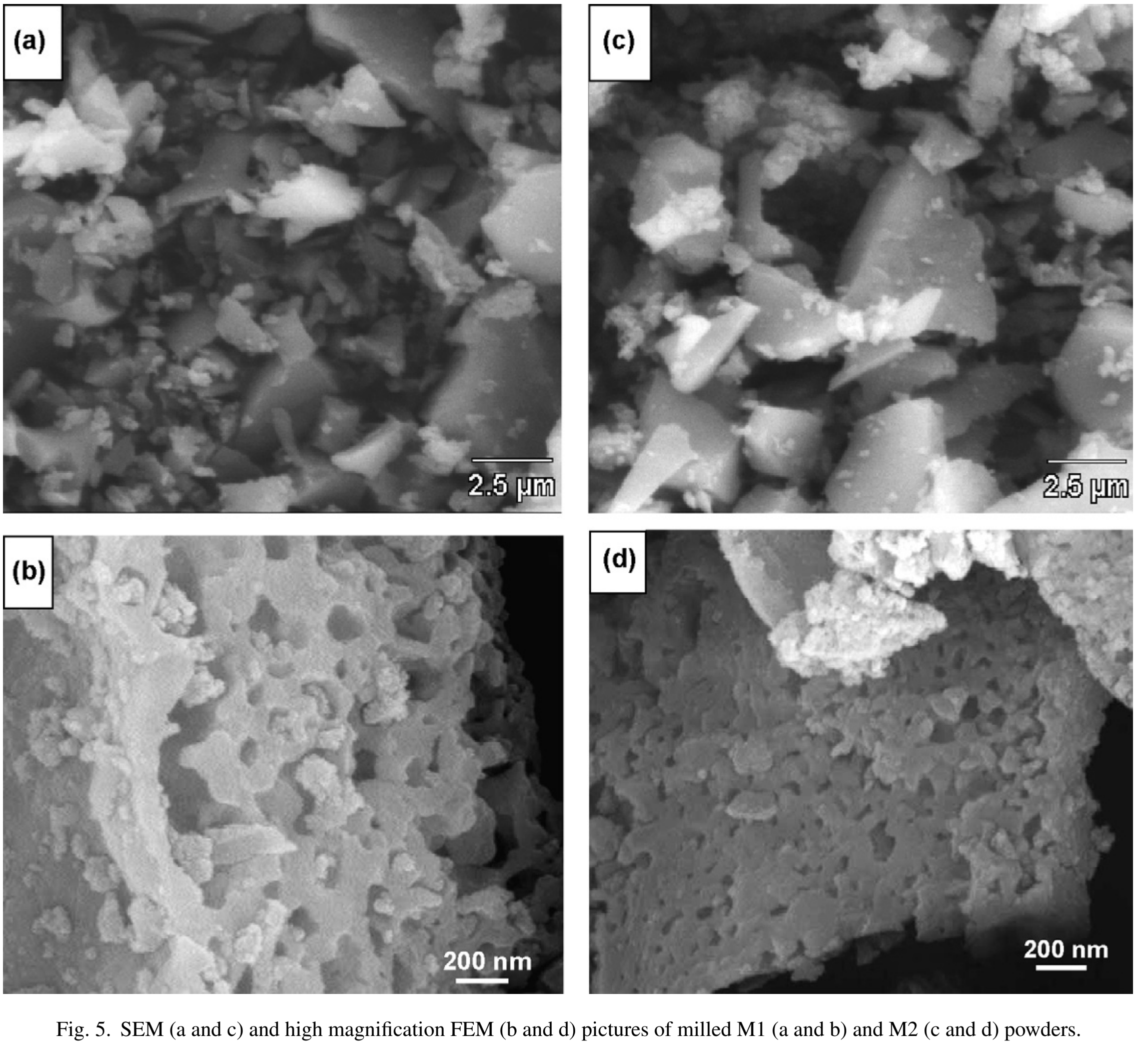

Fig. 5. SEM (a and c) and high magnification FEM (b and d) pictures of milled M1 (a and b) and M2 (c and d) powders.

In Fig. 5 the morphology of the milled powders obtained by scanning electron microscopy can be seen (Fig. 5a and c). Milling leads to irregular shaped particles, most of them keeping the high aspect ratio observed in the as-synthesised powders. Higher magnification pictures taken by FEM (Fig. 5b and d for M1 and M2) are helpful to resolve the microstructure of the mullite agglomerates, as well as the inner porosity. Similar microstructures have been described elsewhere for the solution combustion synthesis of Al_2O_3–ZrO_2 nanocomposites.[11] The evolution of grain size of mullite is related to the temperature achieved in the process. Schmücker et al.[12] have studied the evolution of grain growth in mullite fibres, demonstrating that it follows a simple empirical law with an exponent that is remarkably small below 1600 °C (1/*n*–1/12), while above 1600 °C grain growth exponents reach typical values of ∼1/3, thus leading to fast and oriented grain growth that lead to acicular grain shapes. The combustion processes described in the present work occur at temperatures well below 1600 °C, where grain size evolution should be still slow and particle size would be controlled.

3.3. *Colloidal behaviour*

Once the synthesised powders were milled, their colloidal behaviour was studied. Fig. 6 shows the evolution of zeta potential with pH for milled M1 and M2 powders. Both powders have a similar behaviour, the isoelectric point (iep) occurring near pH ∼6, in good agreement with that reported elsewhere.[8,9,13] The differences in the experimental values obtained for both powders seem not to be significant enough to take conclusions, although the small decrease in the iep of powders obtained with ammonium nitrate could indicate that some specific adsorption of the anion may occur.

The absolute values of zeta potential are very high in the basic pH region (pH 9–11) indicating a good stability. However the particle size is still too coarse to avoid sedimentation with time. For this reason the effect of dispersants on the stability needs to be studied. For this purpose two dispersant were tested: citric acid and a PAA type polyelectrolyte. The zeta potential values (Fig. 7a and b) reveal that in the absence of polyelectrolyte both powders have positively charged surfaces, because the suspensions pH is 5.5, just below the iep according to Fig. 6. When the dispersants are added the zeta potentials become negative due to their anionic nature. However, there are important differences in the behaviour of both M1 and M2 powders, probably related to the different particle size. In general, the finer powder M1 (Fig. 7a) cannot stabilise with citric acid since zeta potential values maintain near to zero for up to 1 wt.% citric acid and thus the suspension should spontaneously coagulate. When using the polyelectrolyte a concentration of 0.8 wt.% gives a reasonably high zeta potential (absolute value of ∼30 mV), i.e., good stability. In the case of powder M2 (Fig. 7b), the coarser size makes it to settle more easily and higher concentration of deflocculant

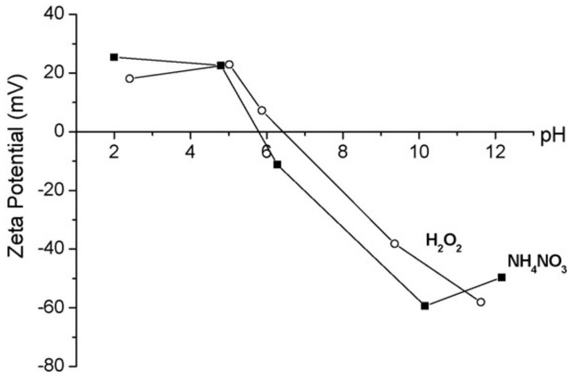

Fig. 6. Evolution of zeta potential with pH for attrition milled powders M1 (a) and M2 (b).

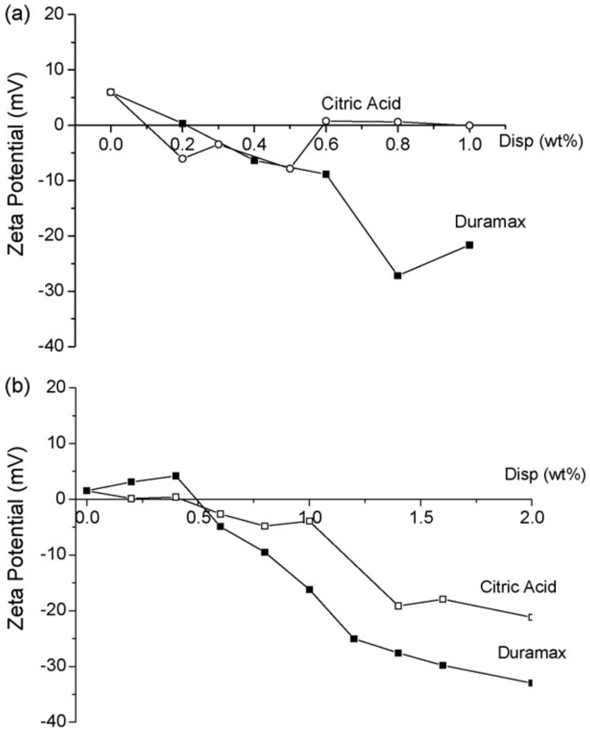

Fig. 7. Variation of the zeta potential versus the concentration of deflocculants for milled powders M1 (a) and M2 (b).

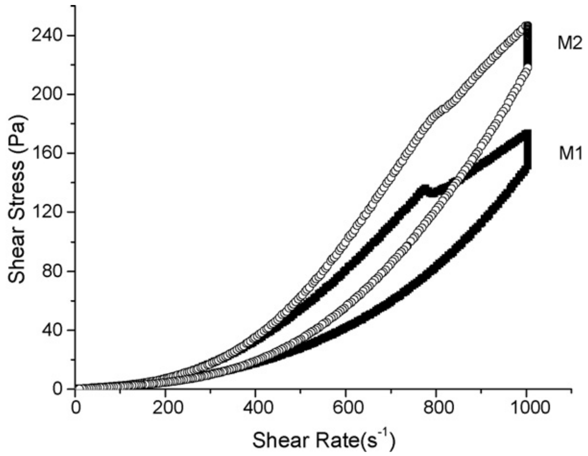

Fig. 8. Flow curves of 40 vol.% suspensions of M1 and M2 powders prepared adding 0.8 and 1.2 wt.% of polyelectrolyte, respectively.

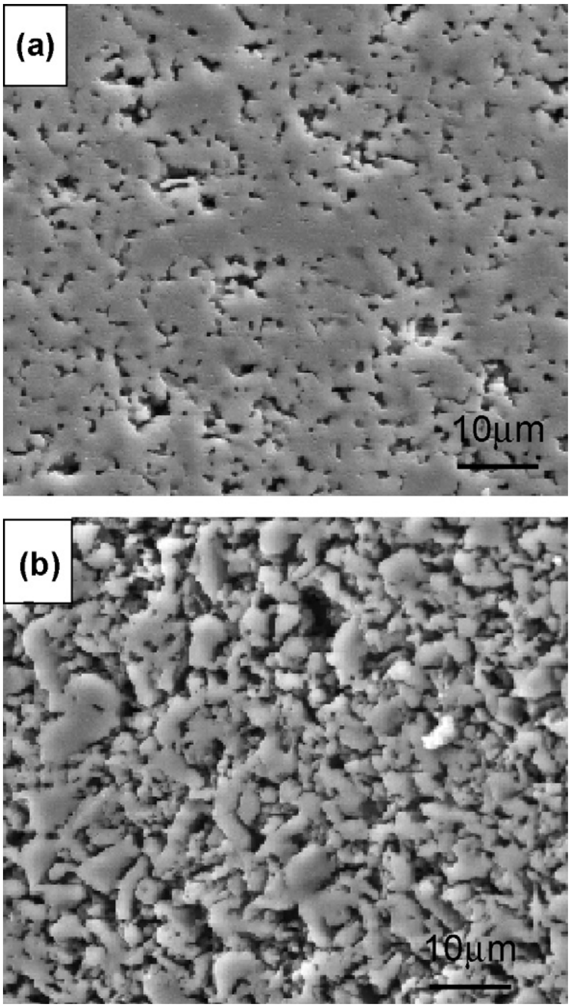

Fig. 9. SEM microstructures of slip cast specimens sintered at 1600 °C/2 h of M1 (a) and M2 (b).

is required to provide stabilisation. Whereas for M1 powder the maximum zeta potential is reached with 0.8 wt.% PAA, the zeta potential of M2 continuously changes up to 2 wt.%. Considering the surface areas of the powders, when 0.8 and 2 wt.% are added for M1 and M2, respectively, the amount of polyelectrolyte adsorbed per unit area is roughly the same, 0.7 mg/m^2. The optimum dispersant content was fixed to 0.8 and 1.2 wt.% for powders M1 and M2, respectively, which led to absolute values of zeta potential of −30 mV.

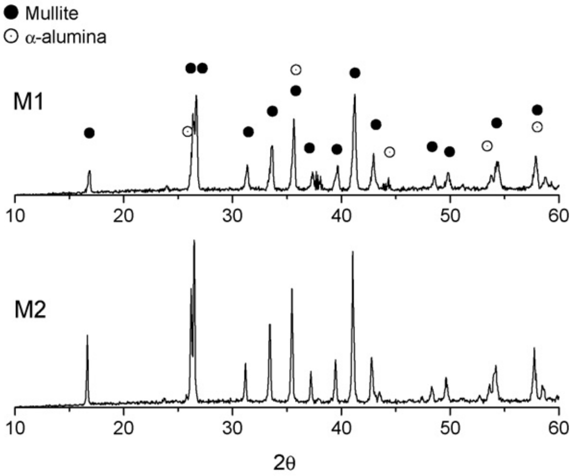

Fig. 10. XRD spectra of bodies obtained from milled powders M1 and M2, sintered at 1600 °C/2 h.

Concentrated suspensions of powders M1 and M2 were prepared to a solids content of 40 vol.% adding the optimum concentration of polyelectrolyte in each case. Concentrated suspensions were homogenised by ball milling for 6 h. Fig. 8 shows the flow curves of 40 vol.% suspensions of milled powders M1 and M2. Both suspensions have a strong shear thickening behaviour and a large thixotropy. This effect is related to the morphology of the particles synthesised via combustion. The plate-like appearance of the particles leads to card-house structures.[14] The higher shear stress (i.e. viscosity) obtained in the case of powder M2 is probably related to its larger particle size.

Green bodies were obtained by casting the suspensions into a plaster mould. The green densities are the same for suspensions M1 and M2, i.e. 1.57 g/cm^3 (54%), although some differences are found in the sintered densities, 2.95 g/cm^3 (93%) and 2.85 g/cm^3 (90%) for powders M1 and M2 due to the different particle size. Fig. 9 shows the SEM microstructures of sintered specimens. It can be observed that the M2 bodies show a less developed structure than M1 bodies. The larger particle size retards the formation of the sintering necks, therefore the microstructure presents high remaining porosity and low sintered densities. The XRD characterisation of the sintered specimens reveals that only mullite phase is detected for compacts obtained with any of the synthesised powders, either M1 or M2 (Fig. 10).

4. Conclusions

In conclusion, mullite powders have been obtained by a single step suspension combustion process using ammonium nitrate (M1) and hydrogen peroxide (M2) as combustion aids. The addition of 20 mol% of silica in excess has been necessary to synthesise nearly monophasic mullite.

The particle size of the as-synthesised powders was as high as 90 and 110 μm for powders M1 and M2, respetively, due to the high temperature reached on ignition. Hence a conminution process was necessary to facilitate powder processing. Particle size was reduced down to 3 and 5 μm for M1 and M2, after ≥6 h attrition milling.

Mullite compacts have been produced by slip casting. Zeta potential studies allowed to fix the optimum dispersing conditions at 0.8 and 1.2 wt.% of amonium polyacrylate for powders M1 and M2, respectively. Concentrated suspensions can be prepared to 40 vol.% solids although a strong shear thickening behaviour was obtained in the high shear region as a consequence of the plate-like morphology of the particles. Slip casting leads to green and sintered compacts with lower relative densities compared with those obtained elsewhere as a consequence of the large particle size. In spite of the relatively low densities, which could be improved by controlling milling, it has been demonstrated that mullite rich powders can be prepared in a single synthesis step and that can be processed by conventional colloidal routes.

Acknowledgements

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