Influence of Particle Size Distribution on Colloidal Processing of Alumina

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Abstract

Two commercial alumina powders with different particle size distribution (PSD) shapes were blended in different proportions, and the rheological behaviour of the aqueous slurries was analysed. Slip casting experiments were performed in order to correlate the flow properties of the alumina slips with the green density. It was observed that the coarser alumina powder component which exhibits a bimodal PSD near to that predicted by the Furnas model, leads to slips with lower viscosity and green compacts with higher density. In order to reduce particle segregation phenomena and further increase the packing density of green compacts, the solid volume fraction of the bimodal powder with the highest packing ability was increased and maximised. Suspensions with a total solids loading as high as 70 vol% could be achieved by using a polyelectrolyte dispersant and milling to deagglomerate the powders. The results obtained show that the green density in the slip cast body continuously increases with increased solids loading, reaching a maximum value of about 78% of the theoretical density. © 1997 Elsevier Science Limited.

1 Introduction

The strength of a ceramic material is mainly limited by the presence of various types of defects. These defects can arise from agglomerates present in the early stages of the processing which may lead to packing inhomogeneity during the forming process. The number and size of these agglomerates can be partially reduced by dispersing particles in a liquid medium, using the so-called colloidal processing route.[1,2] Since the liquid phase has to be removed during consolidation and drying,

an optimisation of the processing implies the utilisation of stable and deagglomerated slips containing a minimum amount of liquid and avoiding particle segregation phenomena.

In order to maximise the solid volume fraction of a casting slip it is necessary to adapt the particle surface chemistry and optimise the particle size distribution (PSD). Previous theoretical[3–6] and experimental works[7–10] have demonstrated that appropriate size distributions of the particles in suspension promote the particle packing in the cast body and, hence, increase the apparent density in the green state. In particular, Ferreira *et al.*[9] and Taruta *et al.*[10] have shown for SiC and Al_2O_3, respectively, that it is possible to obtain high density slip cast bodies by using bimodal PSDs in which fine and coarse powders are combined in an appropriate proportion and size ratio.

The purpose of the present work was to study the influence of PSD on the colloidal processing of alumina. The total solid loading of the dispersed alumina slips was maximised and their rheological properties were correlated to the packing ability during slip casting.

2 Experimental Procedure

2.1 Materials
Two commercial alumina powders (Alcoa Chemicals, USA) with different average particle size and PSD were used in this study: a finer A16 SG with a BET specific surface area of $11 m_2 g^{-1}$ and a coarser CT530 SG with a BET specific surface area of $5 m_2 g^{-1}$. The PSD of each powder and blends, measured by X-ray sedimentation (SediGraph 5100 V3.02, Micromeritics Instr. Corp., USA) is shown in Fig. 1 where it is possible to see that the size range of both alumina powders is between 0.1 and $10 \mu m$, hence within the typical colloidal size range. Further, the PSD of alumina CT530 is

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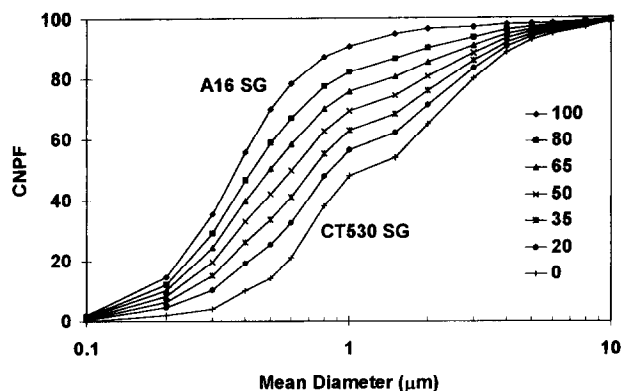*To whom correspondence should be addressed.

Fig. 1. Cumulative number percent finer than curves (CNPF) of the starting fine (A16 SG) and coarse (CT530 SG) alumina powders and their two-component formulation. The label indicates the proportion of fine powder into the mixture.

essentially bimodal, whereas the alumina A16 is characterised by a continuos PSD.

The dispersant used was a polyacrylic acid (Dolapix CE 64, Hans Barnstorf & C., Germany) expected to act by a combination of steric and electrostatic interaction. In a previous work[11] with pure alumina suspension, it was shown that Dolapix enables the preparation of lower viscous slips compared with Tiron, a very powerful dispersant for alumina[12] which acts mainly through an electrostatic mechanism. The difference in viscosity level was attributed to lower interaction size of the alumina particles dispersed with Dolapix, owing to its lower electrostatic contribution to stabilisation. Hence, for preparing suspensions with high solid volume fraction, it seems reasonable to utilise a dispersant that can adequately stabilise the alumina particles without significantly increasing their effective volume in suspension.

2.2 Slip preparation and characterisation

The effect of PSD on colloidal processing of alumina was investigated by blending the two alumina powders in seven different proportions. The approach that was followed in this work to study the influence of the particle size distribution on the colloidal processing of alumina was to gradually vary the shape of the PSD from a continuous distribution to a bimodal one by increasing the proportions of alumina CT530 in the mixture. All these slips were prepared with a total solids loading of 40 vol% (A16 + CT530). The amounts of dispersant added to reach the most stable and low-viscosity aqueous alumina suspensions were 0·45 wt% and 0.35 wt% for A16 and CT530, respectively. For the other five slips, the amount of dispersant was calculated by using the rule of mixtures. Additional slips with alumina CT530 SG at 65 and 70 vol% and with alumina A16 SG at 60 vol%, were also prepared. For each solids loading

tested, at least five slips were prepared in order to determine the optimal amount of dispersant to give the lowest viscosity, but the minimum amount did not differ from the values found for the previous slips at 40 vol%.

The slips were prepared by first dissolving the dispersant in distilled water. Then, while stirring, the alumina powder was added. In the blended slips the finer alumina A16 was introduced before the coarser CT530. The resulting suspensions were additionally stirred for 30 min. Deagglomeration and homogenisation were performed by ball milling in a plastic container for 24 h using Al_2O_3 cylindrical grinding media with various sizes. After milling, the slip was conditioned for 24 h, by rolling in milling containers without balls, prior to further experiments.

The slurries were characterised by means of rheological measurements. These were performed with a rotational controlled stress Rheometer (Carri-med 500 CSL, UK), immediately after the 24 h slip conditioning at a strictly constant temperature (20°C). The measuring configuration adopted was a concentric coaxial cylinder and both steady shear and stress sweep measurements were performed from about $0·5\,s^{-1}$ until $550\,s^{-1}$. Before starting with the measurement, pre-shearing was performed at a high shear rate for 1 min, followed by a rest of 2 min in order to give the same rheological history to all the suspensions being tested.

2.3 Green body preparation and characterisation

Three cylindrical samples ($\varnothing = 28\,mm$) were obtained by unidirectional slip casting in plastic rings placed on an adsorbent plaster plate. The so-obtained green bodies were characterised by density and pore size measurements. The densities were measured by the Archimede's immersion method with a Hg balance, whereas the pore size distribution was measured with a Hg intrusion porosimeter (PoreSizer 9320, Micromeritics, USA). The high pressure part of each Hg porosimetry experiment was carried out using the automatic mode with an equilibration time of 10 s at each point. Before measurements, the samples were completely dried in a stove at 120°C for 24 h.

3 Results and Discussion

3.1 Rheology

The effect of the PSD on the equilibrium viscosity of the slips with a constant solid loading of 40 vol% is shown in Fig. 2. It can be seen that the slips containing high proportions of the coarser CT530 alumina powder show lower viscosity values. The equilibrium viscosity gradually increased as
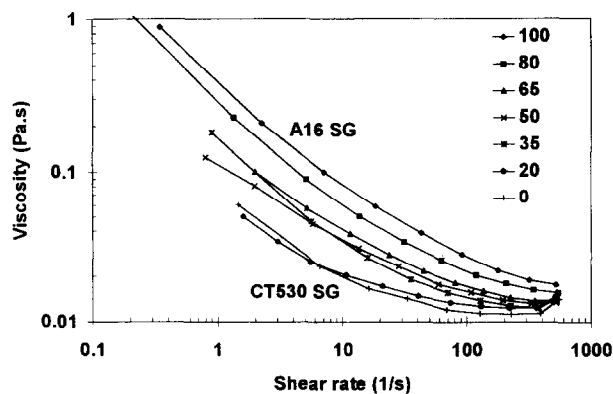
Fig. 2. Viscosity curves (equilibrium viscosity) for two-component alumina suspensions at 40 vol%. The label indicates the proportion of fine powder into the mixture.

the CT530 was replaced by A16, reaching a maximum when only the finer powder was present. From Fig. 2, it is possible to observe that the slips with a quantity of finer powder lower than 50 wt%, were initially shear thinning, reaching a minimum viscosity and then displaying a slightly shear thickening behaviour at higher shear rates. For the slips containing more than 50 wt% of finer alumina powder, shear thinning behaviour was observed over the whole shear rates range. This shear thinning behaviour is usually associated with the slurry structure. At low shear rate, liquid is immobilised in void spaces within flocs and the floc network. As the shear rate is increased, the flocs and floc network break down and the entrapped liquid is released[13] and a more ordered structure in the flow direction is formed.

The more pronounced shear thinning character of alumina A16 can be attributed to its higher specific surface area. The effective volume of one particle is given by the sum of the bulk particle plus the thickness of the adsorbed or solvated layer. For a given solids loading, the number of suspended particles is considerably higher for A16. Hence, for the same solids loading, the effective volume fraction should be higher in the case of alumina A16, compared with CT530. These factors explain why the finer alumina powder A16 was more difficult to disperse than the coarser CT530. At rest, the structure of the suspension is determined by Brownian motions and the interaction forces between particles, as described by the well known DLVO theory.[14] The equilibrium separation distance between particles corresponds to the secondary minimum in the total interaction energy curve. At low shear rate the superficial forces still dominate the particulate system. However, the agitation action can gradually break down this structure by overcoming the attractive energy corresponding to the secondary minimum and thus the viscosity of the suspension decreases. At high shear rates, the

hydrodynamic interactions between particles become dominant. The number of collisions per unit time increases. On the other hand, for particles to slide over each other they have to increase their average separation distance, especially at high solids loading and when coarse particles are present. This causes an apparent increase in solid volume fraction which is responsible for the increased viscosity,[15] i.e. shear thickening, which tends to be more pronounced when the amount of CT530 increases. The same trend exhibited by the equilibrium viscosity was also observed with the yield point and plastic viscosity, as reported in Fig. 3. By increasing the proportion of finer alumina powder in the mixture, the yield point and plastic viscosity continuously increase, reaching maximum values when only A16 was present.

The effect of solids loading on slip rheology is reported in Fig. 4 and shows the success of using CT530. With this powder it was possible to reach a solid loading at 70 vol%, compared to 60 vol% obtained with A16 resulting in a similar viscosity level. This difference should be related both to the different shapes of their PSDs as well as specific surface areas, confirming the strong influence that these factors have on the ability to reach high solids volume fractions, as described above. Hence, it is possible to prepare low viscosity and highly concentrated suspensions by using a powder with an appropriate bimodal PSD.

As observed for 40 vol%, the alumina CT530 also exhibits a similar rheological behaviour at higher solids loadings (65 and 70 vol%) characterised by an initial shear thinning followed by a shear thickening behaviour, occuring above a certain shear rate. From Fig. 4, it can also be observed that the viscosity as well as the severity of the shear thickening tends to increase with increasing particle concentration, as expected.[16,17]

3.2 Slip casting

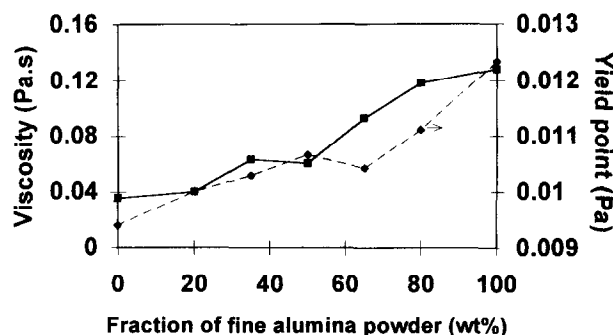The results of the slip casting experiments performed with 40 vol% solids loaded slurries are

Fig. 3. Bingham (apparent) yield stress and plastic viscosity of the two-component alumina suspensions versus the fraction of the fine powder into the mixture.
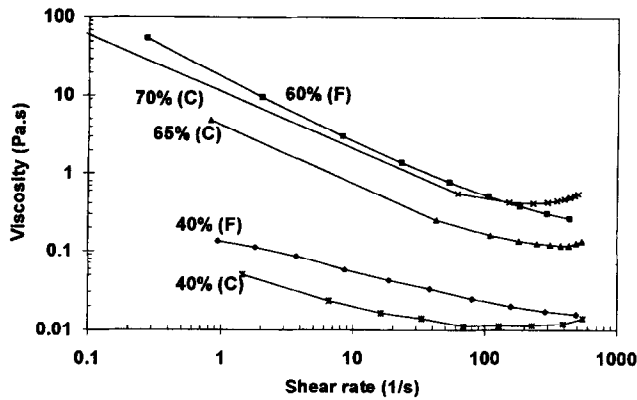
Fig. 4. Viscosity curves (equilibrium viscosity) for coarser (CT530 SG) and finer (A16 SG) alumina suspensions at various solid loadings.

reported in Table 1. It can be seen that the green density continuously decreases with increasing amounts of finer alumina, reaching a maximum when only CT530 was present. These results were further confirmed by Hg porosimetry, as reported in Fig. 5, in which the total pore volume continuously decreases with increasing amounts of alumina CT530 in the mixture. Compared to sample with only the finer powder, the blends display narrower pore size distributions. However, a comparison between them clearly show a broadening trend with increasing proportions of alumina CT530. This indicates that at this solid loading segregation phenomena are occurring[9] and point out the need to increase the solid volume fraction.

Nevertheless, these findings are in close agreement with the previous rheological measurements in which the suspension containing a large amount of alumina CT530 showed lower viscosity values, due to a more efficient particle packing, also in suspension.

To sum up, it seems that the bimodal PSD of alumina CT530 leads to a more efficient particle packing in suspension as well as in green cast bodies. From Fig. 1, it can be observed that the bimodal PSD of CT530 is characterised by a size ratio between average coarse and fine particles size of about 8 and a proportion between fine and coarse particles of approximately 30–70. Both these features of the bimodal PSD of alumina CT530 are in close agreement with the best PSD theoretically predicted by Furnas[3] and experimentally confirmed by other authors.[9,10] The near optimal bimodal PSD of alumina CT530 was disturbed by the introduction of A16, characterised by a high concentration of fine particles. This change in the proportion between coarse and fine particles and the decrease in particle size ratio of coarse to fine powders is the factor responsible for the observed decrease in slip cast bodies density with increasing amount of A16 powder.

The effect of the solids content on green body density is reported in Table 2, showing a significant and continuous increase of density when the solid loading is increased. This improvement in the particle packing can be attributed to a diminution

Table 1. Density of the slip cast bodies obtained by blending the two alumina powders at 40 vol%

	Fraction of fine alumina (wt%)						
	0	20	35	50	65	80	100
Density (g cm^{-3})	2·96	2·89	2·85	2·80	2·72	2·64	2·57
TD (%)	74·4	72·6	71·6	70·4	68·3	66·3	64·6

Table 2. Density and porosity data of the slip cast bodies obtained from alumina CT530 SG at various solids loading

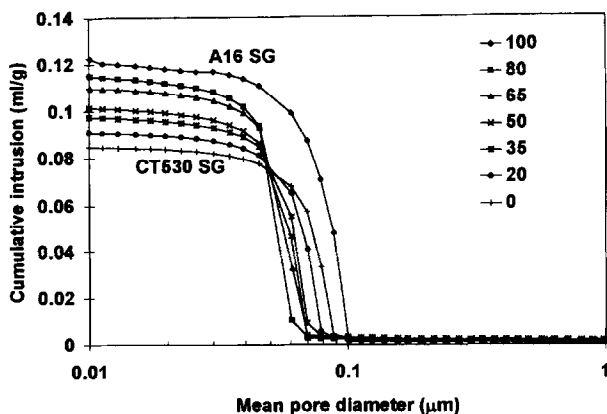|	Solids loading (wt%)		
	40	65	70
Density (g cm^{-3})	2·96	3·03	3·10
TD (%)	74·4	76·1	77·9
Mean pore diameter (nm)	61	53	47

Fig. 5. Pore size distribution of the slip cast bodies obtained from two-component alumina suspensions at 40 vol%. The label indicates the proportion of fine powder into the mixture.
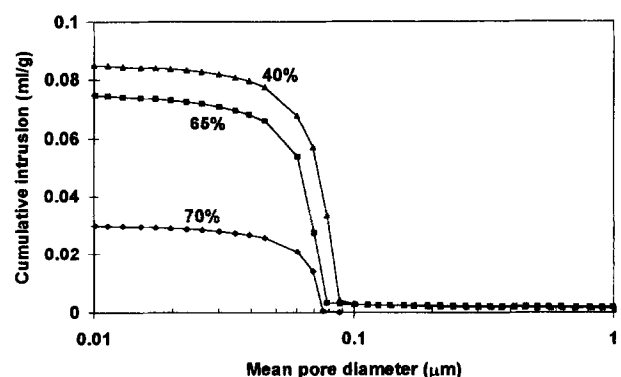

Fig. 6. Pore size distributions of the slip cast bodies obtained from alumina CT530 SG suspensions at various solids loadings.

of segregation phenomena as can be seen in Table 2 with a decrease of mean pore diameter and in Fig. 6 in which pore size distribution became narrower with increasing the solid loading.

4 Conclusion

The results of this study showed that alumina CT530 SG, characterised by a bimodal PSD near to that predicted by the Furnas model, leads to a more close particle packing both in suspension and in the slip cast body. This enables the obtaining of slips with higher solids loading and lower viscosities compared with the slips containing alumina A16 SG, which were characterised by higher concentrations of fine particles and more continuous PSDs. Accordingly, the green compacts obtained with the CT530 SG powder have higher density than those prepared from A16 SG containing blends.

By using the alumina CT530 SG, it was possible to prepare slips with a solid content as high as 70 vol% and obtain slip cast bodies with very high relative density (78%). Beyond the optimal bimodal PSD, these performances in slip casting of alumina can also be attributed to the method adopted to prepare the suspension using electrosteric interaction which enables the powders to be dispersed and stabilised adequately even at high solids loading.

Acknowledgements

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