

Influence of Magnesia on Colloidal Processing of Alumina

G. Tari^a, J. M. F. Ferreira^a and O. Lyckfeldt^b

^aDepartment of Ceramics and Glass Engineering, University of Aveiro, 3810 Aveiro, Portugal

^bSwedish Ceramic Institute, Box 5403, S-40229 Goteborg, Sweden

(Received 10 June 1996; revised version received 18 November 1996; accepted 25 November 1996)

Abstract

The effects of magnesia (MgO) on electrophoretic and rheological properties of aqueous alumina suspensions and on the characteristics of the slip cast bodies were evaluated. The influence of the dispersants and slip preparation procedure on all processing steps and on the ultimate properties of the sintered bodies was also discussed.

The electrophoretic measurements showed a significant decrease in zeta potential when MgO was present in Al₂O₃ aqueous suspension. This destabilising effect of MgO was also confirmed by rheological measurements which showed an increase in viscosity and pseudoplastic behaviour of the slips. In slip casting, the destabilising effect was expressed by a decrease in green body density. Nevertheless, the relative density of the sintered bodies initially increased, reaching a maximum (99.7%) for 0.02 wt% MgO but decreased again with further additions. The results obtained showed that the optimal amount of magnesia resulted from its beneficial effect on densification of alumina, and from its detrimental influence in slip stability and packing behaviour of suspended particles.

The slip preparation procedure also affected the ultimate properties of MgO-doped alumina. Namely, the dispersant used, and the order in which the powders were added to the dispersant solution determine the degree of uniformity of the MgO distribution in the mixture, resulting in different packing densities in both green and sintered states. The highest sintered density was obtained when magnesia was the first component added to the solution of the most efficient dispersant used. Considering the observed results, an optimised route for the slip preparation was established. Copyright © 1997 Elsevier Science Limited.

1 Introduction

Ceramic processing based on powder technology includes many steps from preparation of raw

materials to sintering of shaped components. Each step is, in different ways, crucial for the ultimate material properties. In liquid based forming of ceramics such as slip casting or pressure slip casting the slip preparation, slip stabilisation and casting are processing steps which in an integrated way influence the final result regarding material homogeneity, density and mechanical strength. Generally, an effective breakdown of particle agglomerates in the preparation of the powder suspension, an effective stabilisation of the particles and optimised casting conditions will favour the sintering and consequently, the ultimate properties of the ceramic material.

Alumina is one of the most investigated ceramic materials owing to its wide use in the electroceramic field as well as a structural ceramic, sometimes mixed with other materials in composites. Commercially available alumina powders usually contain some impurities that affect the ultimate material properties. Most of these impurities are not soluble in alumina and, at high temperature, form a thin liquid phase around the alumina particles that leads to abnormal grain growth. Hence, in monolithic alumina, some type of additive is used to enhance the sintering process and/or inhibit abnormal grain growth during sintering since large grains will decrease the mechanical strength. There exist many possible additives, mainly metal oxides which, with various efficiencies, act as sintering aids and grain growth inhibitors. One of the most used and also one of the most effective is magnesia (MgO). Because of its efficiency, very small amounts of MgO are needed for good densification and to limit abnormal grain growth during sintering of alumina.^{1–3}

The role of magnesia in alumina was recently summarised by Bennison and Harmer⁴ in a historical review on the subject. However, most of the studies done so far have been focused on understanding the microstructural effect of MgO in the sintering process, such as an inhibitor of abnormal grain

growth, using various microscopic techniques. There are very few works which consider other processing effects of MgO, for example in slip rheology or the forming process, which also will have a significant impact on the ultimate microstructure of alumina.

An important factor to consider when using MgO in the processing of alumina is its special chemical and surface charge properties. One disadvantage is the strongly basic nature of MgO displayed by a very high isoelectric point (pH 10.5–12). This gives rise to difficulties in accurately dispersing and stabilising MgO particles using conventional dispersants such as polyelectrolytes. Further, MgO has a high solubility in acidic and neutral conditions which make it impossible to use pure electrostatic stabilisation at low pH which is otherwise a common way to stabilise alumina particles.

The aim of this work was to evaluate the effects of MgO additions to alumina slips on the whole processing route from slip preparation to casting and sintering. Basically, the effects of two different dispersants and three different slip preparation routes on slip rheology and surface charge characteristics were examined. Two dispersants, one polycarboxylic acid (expected to give electrosteric stabilisation) and one sulfonic acid (expected to work mainly through an electrostatic stabilisation), were tested to evaluate the best stabilisation mechanisms for the $\text{Al}_2\text{O}_3/\text{MgO}$ system.

2 Experimental Procedure

2.1. Materials

Two commercial powders were used in this study: alumina (A16 SG, Alcoa Chemicals, USA) with a BET specific surface area of $11 \text{ m}^2/\text{g}$ and magnesia (Analytical grade, Merck, Germany) with a BET specific surface area of $30 \text{ m}^2/\text{g}$. Table 1 reports the chemical analysis of both powders as furnished by the suppliers.

The dispersants used were Dolapix CE 64 (Zschimmer & Schwarz, Germany) based on a polycarboxylic acid that imparts stability by electrosteric interaction⁵ and 4,5-dihydroxy-1,3-benzenedisulfonic acid, (Tiron, Aldrich-Chemie, Germany) that imparts stability preferentially by electrostatic interactions.⁶

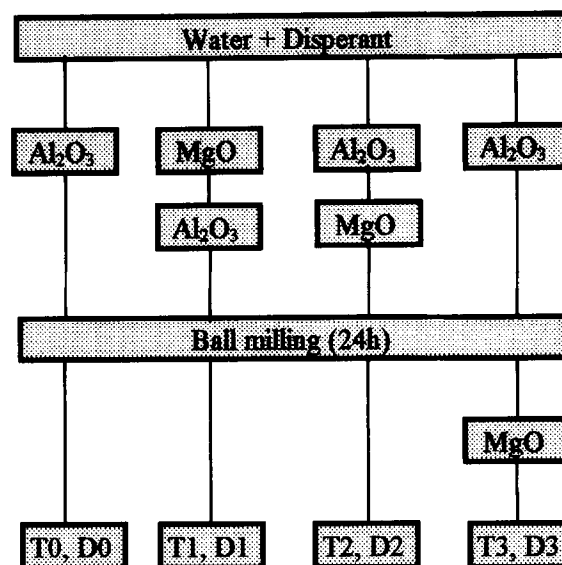


Fig. 1. Samples description (T = Tiron, D = Dolapix CE64).

2.2 Slip preparation

A first set of experiments, aimed to establish the best way to prepare MgO-doped alumina slips, was carried out by using suspensions with a constant solid loading of 40 vol% without or with MgO powder addition (0.10 wt% based on alumina). The amounts of Tiron (0.25 wt%) and Dolapix CE 64 (0.45 wt%) were determined in a pre-study carried out with pure alumina suspensions. These values correspond to the optimised amount of each dispersant that gave the most stable and low-viscosity aqueous alumina suspension.

Basically, each slip was prepared by first mixing dispersant and water. Then, while stirring, the powders were added and the resulting suspension was kept stirred for 30 min more. Deagglomeration and homogenisation was performed by ball milling in a plastic container for 24 h with Al_2O_3 cylindrical grinding media. After milling, the slip was conditioned for 24 h, by rolling in milling containers without balls, to stabilise its properties.

In order to analyse the effects of MgO additions on slip preparation procedure, eight samples were prepared (see Fig. 1). In six of the samples MgO powders were mixed with Al_2O_3 in three different ways, using both dispersants.

The optimised slip preparation procedure was then chosen to evaluate the effects of different amounts of magnesia on alumina slip properties, the subsequent influence on slip casting and on the green and sintered body densities achieved.

Table 1. Chemical analysis reported by the manufacturer of the Al_2O_3 and MgO powders used

	Al_2O_3	MgO	Na_2O	CaO	SiO_2	CO_3^{2-}	Fe_2O_3
Alumina, Alcoa, A16 SG, (wt%)	99.9	0.01	0.05	0.02	0.02	—	0.01
Magnesia, Merck, (wt%)	—	min 97	—	0.03	—	1.5	0.005

Alumina suspensions containing five different amounts of magnesia were tested. The total solids loading, ϕ , of the earlier slips was 40 vol% ($\text{Al}_2\text{O}_3 + \text{MgO}$), except for the composition with the highest MgO content (0.5 wt%) where ϕ had to be lowered to 25 vol% owing to a remarkable increase in slip viscosity caused by the additive.

2.3 Slip characterisation

2.3.1 Electrophoresis measurement

The electrophoretic analysis was carried out with a Malvern Zetasizer 4 (Malvern Instruments Ltd, UK). This instrument uses a photon-correlation spectroscopy technique that enables particle size and zeta potential measurements. The zeta potential was detected from the motion of particles caused by an external electric field applied to the sample. Measuring the rate of motion (electrophoretic mobility) and using the Smoluchowski equation, the zeta potential of the particles was determined.⁷

The analysed suspensions were very dilute (< 0.01 wt%). The solvent used was an aqueous electrolyte solution (0.001 M KCl) and the pH adjustment was done with aqueous solutions of HCl or NaOH. The pH was measured with a pH meter (Corning 240), calibrated with buffer solutions (pH 7 and 10, Merck, Germany).

2.3.2 Rheological measurements

Rheological measurements were done with a rotational controlled stress Rheometer (Carrimed 500 CSL), immediately after the 24 h slip conditioning at a controlled temperature of 20°C. The measuring configuration adopted was a concentric coaxial cylinder and steady shear measurements were performed determining the equilibrium viscosity (maximum equilibrium time 5 min) at several shear rates from about 0.5 s⁻¹ up to 550 s⁻¹. Before starting a measurement, pre-shearing was performed at high shear rate in order to transmit the same rheological history to all the suspensions being tested.

2.4 Green and sintered body characterisation

Cylindrical discs (diameter = 28 mm, thickness c.10 mm) were prepared by unidirectional slip casting on a plaster plate and used for the density measurements both in green and sintered state. The samples were sintered at 1600°C for 4 h (from 20°C until 1580°C at 5°C/min and from 1580°C until 1600°C at 1°C/min).

The density was measured by the Hg immersion method. Before measurement the green bodies were dried at 120°C in a stove for at least 24 h,

whereas the sintered samples were dried in a stove at 120°C for 1 h in order to eliminate superficial humidity.

3 Results and Discussion

The presentation of the results is focused on the following four points: (i) the general MgO effect on aqueous alumina suspensions, (ii) the effect of the dispersant in $\text{Al}_2\text{O}_3/\text{MgO}$ suspensions, (iii) the effect of the slip preparation route on the final material and (iv) the effect of different amounts of additive on colloidal processing of alumina.

The first point was evaluated by comparing the results of samples T0 and T1, and D0 and D1. The evaluation of the second point was conducted by comparing the result of the samples T and D. For the evaluation of the slip preparation route the results of the samples T1–T3 and D1–D3 were compared. Finally, following the best slip preparation procedure, the effect of different amounts of additive on colloidal processing of alumina was evaluated by comparing samples containing: 0 (T0), 0.02, 0.05, 0.1 (T1), 0.2 and 0.5 wt% of MgO.

3.1 Slip characterisation

3.1.1 Electrophoresis

Figure 2 shows zeta-potential curves for alumina and magnesia powders without any dispersant added. The isoelectric points (IEP) are located at pH 8.1 for Al_2O_3 and at pH 10.8 for MgO which is in agreement with the pH range reported in the literature.⁸ In the case of MgO it was not possible to measure the electrophoretic mobility at pH values lower than pH 8.5 owing to the increasing solubility of this oxide with decreasing pH.⁹ Because of this reaction between the solid particles and the liquid medium the ionic strength should increase continuously with time at a given pH. This increase might be responsible for the low and almost constant zeta potential values observed in

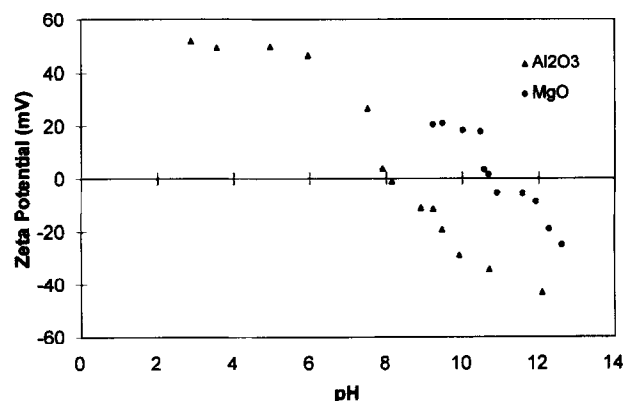


Fig. 2. Zeta potential curves for MgO and Al_2O_3 powders.

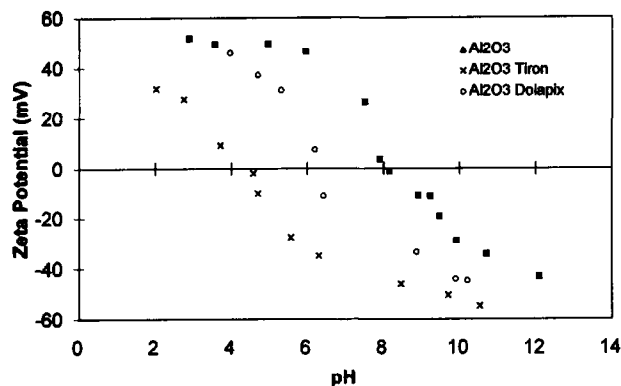


Fig. 3. Effect of the dispersants on zeta potential curves for Al_2O_3 powder particles.

the pH range 8.5–10.5. When decreasing the pH in this region the electric double layer will be compressed by the increased ionic strength compensating the higher surface-charge density. Although these results should be regarded with caution they indicate clearly that the use of a pure electrostatic stabilisation mechanism could only be possible for pH values above 12.5. However, such high pH will be very aggressive to plaster moulds as well as human skin. For lower pH values the opposite signs of surface charges on particles of individual oxides or an insufficient negative charge density on MgO particle surfaces will most likely lead to a hetero-coagulation phenomenon.^{10–13} Strong enough repulsive forces in this pH range can only be developed by using surface active agents or defloculants.

The effects of Dolapix and Tiron on the electrophoretic behaviour of alumina and magnesia particles are shown in Figs 3 and 4, respectively, as a function of pH. For comparison, the curves without dispersant are also presented. It can be seen that the addition of dispersants causes significant changes in surface charge properties of both oxides. The IEP of the bare particles, as well as all the initial curves, were shifted in the acidic direction. In the case of alumina, the displacement of the IEP was almost two pH units with Dolapix,

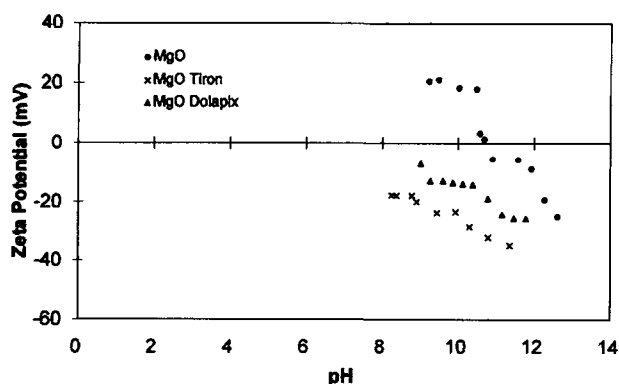


Fig. 4. Effect of the dispersants on zeta potential curves for MgO powder particles.

and more than three pH units with Tiron. Further, the negative zeta potentials increase in the basic pH region and the positive values in the acidic pH region decrease. These effects were more pronounced when Tiron was used. In the case of magnesia the effects of the dispersants on the surface charge properties were similar to those observed with alumina. The presence of the dispersants also enabled electrophoretic measurements further in the acidic direction, suggesting that the solubility of the MgO particles might have been diminished by formation of some type of complex on the surfaces (see Ref. 14). Again, this effect as well as the electrostatic charging was stronger when Tiron was used. However, independently of the dispersant used, colloidal instability and almost complete dissolution of the MgO occurred before any isoelectric points could be detected. Zeta potential measurements were interrupted when the intensity detected by the photomultiplier decreased to about 25% of the maximum counting rate observed at higher pH values, since reliable reading was impossible.

The electrophoretic behaviours of the oxide particles observed in this work are closely related with the ability of the dispersant molecules to adsorb on the solid surfaces, which in turn depends on factors such as pH, ionic strength, molecular weight, adsorption behaviour, nature, number and steric arrangement of the functional groups.^{5,6,14–16} For the alumina particles, this dependence has been clearly shown by Kummert and Stumm¹⁴ and by Graule *et al.*^{5,6,15,16} who correlated the efficiency of organic dispersants with their molecular structure. Low molecular weight aromatic^{5,14,15} and aliphatic acids^{6,14,15} were used as model compounds which were adsorbed on particle surfaces as single or multiple charged ions. Maximum adsorption densities were observed in the pH range of the pKa values of the dissociable groups, according to a ligand-exchange model (see Ref. 6). For compounds based on the benzene molecule they concluded that their efficiency as defloculants was enhanced when two or more hydroxyl groups in the ortho-position were used as adsorbing (anchor) groups and when other functional groups were arranged in the meta-position, relative to the hydroxyl groups. This arrangement is favourable since repulsive electrostatic interactions between the charging groups are avoided and the alumina surface is highly negatively charged. Tiron fulfils all these specifications and was pointed out as a very effective defloculant for aqueous alumina suspension.⁶ In agreement with these findings, our results show that Tiron is more effective as surface charge modifier than Dolapix for both oxides used and can be concluded to be

Table 2. pH of concentrated and diluted slurries and zeta potential of the suspended particles

	0.25 wt% Tiron				0.45 wt% Dolapix CE 64			
	T0	T1	T2	T3	D0	D1	D2	D3
pH of the slips	10.1	10.4	10.4	10.4	9.9	10.3	10.3	10.2
pH after dilution	8.0	8.1	7.9	7.9	8.1	8.3	8.7	8.2
ζ (mV)	-50.7	-34.1	-31.6	-30.2	-44.4	-25.2	-23.3	-24.6

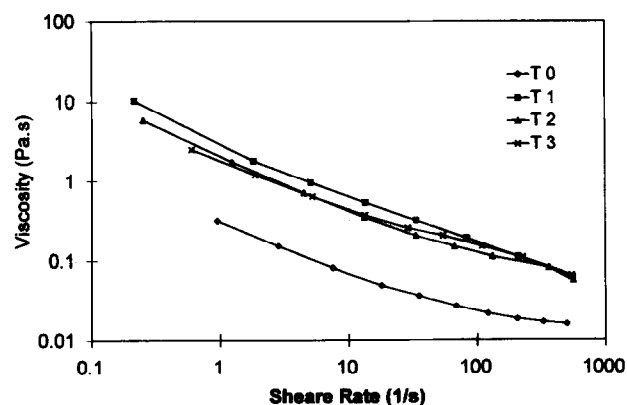
so also for the mixed system. This is also confirmed by the single point measurements displayed in Table 2, conducted with the different dispersants and slip preparation routes. Note here that in the concentrated slurries the pH obtained with the two dispersants without any adjustments is in the range of 10.2–10.4 for a fixed amount of MgO (0.1 wt%) and changes between 10 and 11.4 when the additive varies from 0 to 0.5 wt%. On dilution with electrolyte (0.001 M KCl) for zeta potential measurements, the basic character of the suspensions decreased about 2–3 pH units and for that containing MgO it was also time-dependent. For the slurries containing 0.1 wt% MgO, the average measured values immediately after dilution were roughly pH 8 and pH 8.4 when the dispersant used was Tiron or Dolapix, respectively. This instability in pH might be mainly due to the dissolution process experienced by the MgO particles and in a lower degree, to small differences in solids content. Hence, the measured values should be regarded with caution. Nevertheless, they indicate that the differences in zeta potential observed using the two dispersants cannot be attributed to different extensions of the proton association–dissociation reactions between surface particles and the surrounding solution, but rather to specific interaction between dispersant molecules and oxide surfaces and the resulting surface-charge density.

Table 2 also shows that for the binary system the zeta potential was somewhat higher when route 1 was followed. When MgO particles are first added to the dispersant solution, the abundant dissociated multiple charged ions or polyelectrolyte chains adsorb at the solid/liquid interface, increasing the negative surface charge, and push the IEP of the magnesia particles close to that of the bare alumina particles. In these conditions the introduction of Al₂O₃ does not cause strong electrostatic attractions between particles of different materials and enables a homogeneous distribution of both powders to be achieved. When solid components are added in a reverse order (route 2) the suspended alumina particles acquire a high negative surface charge at the pH of the suspension (pH ≈ 10.1, see Table 2) where MgO particles exhibit a net positive surface charge. So, strong

electrostatic attractions between different particle materials should occur in these conditions leading to a hetero-coagulation process. Further, the alumina is the major component of the system (99.9 wt%). This fact combined with the high affinity of the dispersants to the alumina surface^{5,6,14–16} means that a solution will become almost completely depleted of absorbing species when MgO is added. Hence, MgO particles must compete with alumina particles to share the dispersant molecules and change their surface charge properties to avoid flocculation effects. The distribution of the dispersant among different particle materials needs time, especially in a hetero-coagulated suspension, and a degree of homogenisation as high as that obtained when magnesia is the first component added (route 1) will probably never be achieved. As expected the result was even worse when route 3 was followed since in this case no effective homogenisation procedure was used after MgO addition.

3.1.2 Rheology

The rheological behaviours of suspensions, expressed by viscosity curves as a function of shear rate are shown in Figs 5 and 6, for the slips dispersed with Tiron and Dolapix, respectively. All suspensions displayed typical pseudoplastic character. However, this shear-thinning behaviour is stronger and the viscosity level is higher for the slips with MgO. These effects are consistent with electrophoretic results in that the strong repulsive interaction forces between alumina particles were

**Fig. 5.** Viscosity curves (equilibrium viscosity) for suspensions dispersed with Tiron.

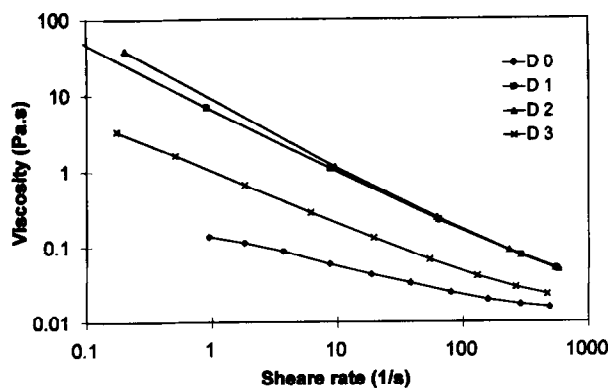


Fig. 6. Viscosity curves (equilibrium viscosity) for suspensions dispersed with Dolapix.

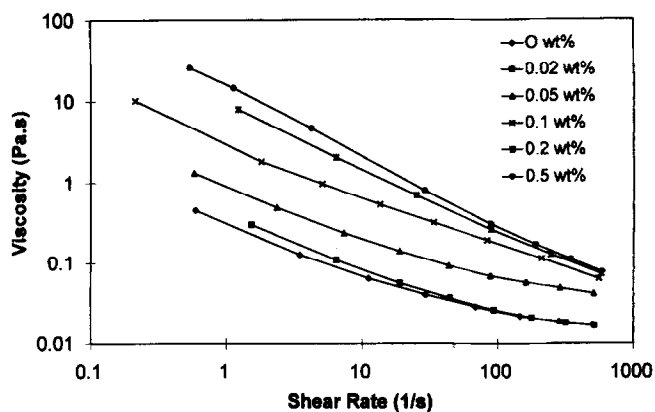


Fig. 7. Viscosity curves (equilibrium viscosity) for Al_2O_3 slips at various amounts of MgO.

disturbed by the presence of magnesia. The detrimental effect of the additive on slip stability can arise from the relatively low charge density on the magnesia particle surfaces and from an increased ionic strength (compressed double layer) due to partial dissolution of this oxide, or adsorption of $\text{Mg}(\text{II})$ ions onto the alumina surface.⁹

Figures 5 and 6 also allow comparison between the effects of the dispersants on flow properties of Al_2O_3 and $\text{Al}_2\text{O}_3/\text{MgO}$ suspensions. Both are very effective in dispersing alumina, but Dolapix gives lower viscosities than Tiron, especially at lower shear rates. So, from the rheological point of view one could be tempted to choose Dolapix as the best deflocculant for alumina and attribute its dispersing efficiency to a steric contribution, since its ability to change the surface charge is lower than that of Tiron. However, another completely different interpretation can also be given for the same rheological results using the concepts of hard size and interaction size.^{9,17} The calculated volume fraction corresponds to the solid loading of the slurry. The thickness of the hydrated, adsorbed, or electrical double layers around the particle powders is not taken into account. However, collisions between particles do not necessarily involve hard-wall contact but could be mediated by interparticle forces, namely electrostatic repulsive forces which are stronger in the presence of Tiron. The interparticle separation at which they may begin to 'feel' each other's presence depends on the range of surface forces. Thus each particle may be thought of as having an interaction size (effective diameter) which is something like its diameter plus twice the range of total surface force. The distinction between hard size and interaction size becomes important when high solid loadings and/or small particles are used.^{18,19}

The effect of dispersants with a low molecular weight such as Tiron is mainly based on the charging of the surface particles, thereby increasing the repulsive double layer forces. The steric

hindrance caused by the adsorption of these small molecules is believed to be insignificant except at very small particle/particle separations and/or for low surface potentials.^{15,16} Nevertheless, the range of the repulsive interparticle forces should be longer when Tiron is used to disperse alumina as compared to Dolapix. The same holds for the binary system where Tiron gives lower viscosities than Dolapix. These results are in agreement with the electrophoretic measurements, in which the particles dispersed with Tiron had higher zeta potentials than when dispersed with Dolapix. Hence, the steric contribution to the interparticle potential expected by the polyelectrolyte-based dispersant can be concluded to be negligible.

The rheological measurements also show differences caused by the slip preparation route. Route 1 (samples T1, D1) gives slips with higher viscosity than routes 2 and 3. This could be explained by a more homogeneous distribution of MgO particles which also might result in a more homogeneous hetero-coagulation. With routes 2 and 3, MgO was not so well distributed and parts of the suspensions might exist where the flocculation effect of MgO was less pronounced. This trend was confirmed by the lower viscosities observed when route 3 is followed and Dolapix, the less efficient dispersant, is used.

The rheological results expressed by equilibrium viscosity, for suspensions with various MgO contents are presented in Fig. 7. From the viscosity curves it can be seen that all suspensions exhibit typical shear thinning behaviour with a relatively weak deviation from Newtonian behaviour for the slurries with no, or a small amount of MgO. These suspensions also showed a low degree of time-dependency. However, both shear thinning and thixotropic characteristics of the suspensions gradually increase with increasing amounts of MgO. From Fig. 7 it can be also observed that the equilibrium viscosity always increases with increasing MgO content, even for the suspension containing

Table 3. Density of the green bodies (the samples T0 and T1 are without and with 0.1 wt% of MgO, respectively)

	0.25 wt% Tiron								0.45 wt% Dolapix CE 64			
	T0	T1	T2	T3	Amount of MgO				D0	D1	D2	D3
					0.02	0.05	0.2	0.5*				
Density (g/cm ³)	2.63	2.25	2.26	2.25	2.48	2.36	2.17	1.99	2.57	2.12	2.18	2.35
TD(%)	66.1	56.5	56.8	56.5	62.3	59.3	54.5	50.0	64.6	53.3	54.7	59.0

*($\phi = 25\%$).

0.5 wt% MgO that has a total solid loading of only 25 vol%, compared with 40 vol% in the other suspensions.

The rheological results are in close agreement with the electrophoretic measurements. In the absence of magnesia, strong repulsive forces exist between alumina particles owing to the high negative surface charge density given by the adsorbed and dissociated molecules of Tiron⁶ as referred to before. Owing to the strong basic character of MgO, its surface charge density is always lower than in the case of alumina at a given pH value. So, repulsive electrostatic interactions between unlike particles in suspension are weaker than electrostatic interactions between alumina-alumina particles. The solubility of magnesia and the consequent increase in ionic strength and possible adsorption of Mg(II) ions onto the alumina particles' surface further reduces the range of the electrostatic repulsions. The affinity between Al₂O₃-MgO particles will tend to build up a structure within the slurry leading to a hetero-coagulation process.¹⁰⁻¹² The connective network formed can be broken down by shearing. Firth and Hunter²⁰⁻²³ discussed this concept in the context of low solids loadings ($\phi < 0.2$) and flocculated slurries. They suggest that the yield stress and viscosity levels in these systems result from the bond formation between particles when there is no net interparticle repulsion. The bulkiness of the structure formed and the amount of liquid entrapped therein always increases as the repulsive component of the interaction decreases. The hydrodynamic forces exerted by the flow field, break this structure into smaller and smaller flow units releasing the liquid immobilised in the agglomerates and the viscosity decreases. The results show a close relationship between the flow characteristics of the suspensions and zeta potential near the particle surfaces in agreement with the DLVO theory.^{24,25}

3.2 Green body characterisation

The relative density of the slip cast bodies prepared with undoped and MgO-doped alumina is shown in Table 3. In both cases the theoretical

density (TD) was assumed to be that of the pure alumina (3.98 g/cm³). It can be seen that high green packing densities could be achieved in the absence of MgO, 66.1 and 64.6% for samples T0 and D0, respectively. These results show that the highest packing density corresponds to the slurry with the strongest repulsive interparticle forces. Repulsive forces imply the retention of some stabilising medium (the difference between 'interaction size' and 'hard size') which can lubricate the particle 'contacts', enabling particle rearrangement. Furthermore, a homogeneous microstructure will be maintained as each particle tries to remain as far away as possible from all its neighbours.

Addition of magnesia causes a general decrease in green densities which gives additional confirmation about the flocculation effect of MgO. In fact, a linear relationship between the bulkiness of the flocculation and the green density achieved by slip casting has been established before.²⁶ The decrease in green density is about 10% units of the TD when suspensions are dispersed with Tiron, independent of the route used to mix the powder components. With Dolapix the difference is even higher, 12.8% for sample D1 and 11.4% for sample D2, but smaller (7.1%) when suspensions were prepared according to route 3. These results are in close agreement with the electrophoretic and rheological measurements and clearly show that Tiron is the better dispersant. As discussed above, slip preparation route 1 should give the higher degree of homogeneity and higher viscosity, considering the flocculating effect of MgO. When magnesia is added in a reverse order, before (route 2) or after the milling step (route 3) an increasing tendency to form local heterogeneities is expected and the flocculating effect of MgO is not transmitted to the whole suspension. This tendency should be accentuated when the less efficient dispersant is used. Hence, the observed results with lower suspension viscosity and higher cast green density, using Dolapix and route 3, are explained and further confirmed by a less effective sintering which will be shown later (Section 3.3). This situation gives emphasis to the importance of conducting the slip

Table 4. Density of the sintered bodies (the samples T0 and T1 are without and with 0.1 wt% of MgO, respectively)

	0.25 wt% Tiron								0.45 wt% Dolapix CE 64			
	T0	T1	T2	T3	Amount of MgO				D0	D1	D2	D3
					0.02	0.05	0.2	0.5*				
Density (g/cm ³)	3.86	3.88	3.86	3.82	3.97	3.94	3.84	3.83	3.86	3.84	3.80	3.78
TD(%)	97.0	97.5	97.0	96.0	99.7	99.0	96.4	96.2	97.0	96.5	95.5	95.0

*($\phi = 25\%$).

preparation in a proper way in order to avoid local agglomeration between Al₂O₃ and MgO particles and starting by homogeneously distributing the magnesia. To accurately disperse the MgO particles they should be added to the dispersant solution in order to approach the surface charge properties of the alumina. Otherwise, the opposite net-charge on different oxide particles will promote strong local flocculation which gives rise to microstructural heterogeneities.

The relative density of slip cast bodies prepared from suspensions containing different amounts of magnesia is also reported in Table 3. It can be observed that the packing density decreased with increasing amounts of MgO. The strong basic nature of MgO surface particles, their appreciable solubility in water and the low surface charge density developed even in presence of Tiron, a very powerful surface charge modifier, might be the factors responsible for the modification of the structure of particles in suspension and, consequently, in consolidated bodies. It has been suggested that increased flocculation leads to increasing number and bulkiness of flocculations.²⁰⁻²³ Further, a linear relationship between the bulkiness of the flocculation and the green density achieved by slip casting has been established before.²⁶ In agreement, the present results show that the structure of the particles in suspension is transmitted to the solid wall being built up at the plaster mould surface, as was already suggested,²⁶⁻²⁸ and that MgO exerts a detrimental effect on slip casting performance of Al₂O₃ suspensions.

3.3 Sintered body characterisation

Table 4 shows the results of density measurements. The relative density values were calculated assuming that the theoretical density of Al₂O₃ is 3.98 g/cm³. It can be observed that the density of the undoped alumina is quite high (97.0%) and independent of the dispersant used, in close agreement with electrophoretic and rheological results where samples T0 and D0 have the highest zeta potential values and the lowest viscosities. Under these conditions particles are expected to be strongly repulsive, and act as individual flow units

enabling homogeneous and high packing green densities to be achieved in slip casting, and more effective densification during sintering.

When MgO is added, the final sintered density depends on the type of dispersant and slip preparation route. The densification level of the samples with MgO using Tiron as dispersant was always higher than with Dolapix, confirming that Tiron has greater potential to disperse the binary system. The milling action in the slip preparation appears also to be an important factor influencing the final material properties, since the density of the samples steadily decreases from route 1 to 3, contrary to the trend observed in the green state, especially with Dolapix. Obviously, less homogeneously distributed MgO gives a lower degree of flocculation resulting in higher green density, but lower sintered density owing to less favourable sintering properties. However, compared to the pure alumina, only a small gain in degree of densification, was obtained using Tiron and the suspension preparation route 1 (sample T1) in which MgO powder was introduced into the dispersant solution before the Al₂O₃, followed by a milling step.

The influence of the amount of magnesia on TD of sintered bodies is also shown in Table 4. It can be seen that, despite the observed decrease in green density with increasing amounts of MgO, the relative density of the sintered bodies increased initially, reaching a maximum (99.7%) at 0.02 wt% MgO, but decreased with further additions. This maximum in relative density occurs when the concentration of MgO equals that of CaO (see Table 1). These results are in close agreement with the findings of Bae and Baik.² These authors studied the effects of MgO on densification and grain growth of an ultrafine (> 99.999%) alumina in absence of any other impurities, as well as in the presence of various amounts of CaO. The dopants were introduced from aqueous solutions of hydrated calcium nitrate and magnesium acetate tetrahydrate and the doped powders were consolidated by dry pressing techniques. They concluded that MgO addition to ultrapure alumina enhanced both grain growth and densification kinetics. For a given concentration of CaO, at least the same

amount of MgO was necessary to prevent abnormal grain growth and maximise the sintered density. However, despite the higher sintering temperature used (1900°C, compared to 1600°C), the maximum relative density values were considerably lower ($\approx 96\%$) than the almost full density obtained in the present work. Although differences in the physico-chemical characteristics of the starting materials can account for these results, the higher densities achieved in our work can mainly be derived from the efficient consolidation technique used and also from the optimised slip preparation procedure adopted. Consequently, it has been recognised that colloidal methods for treating and consolidating powders offer the potential to produce more reliable structural ceramics.²⁹

Besides the interference that other impurities might have on the role of MgO as a sintering aid of alumina ceramics, which seems still not to be very well understood,^{2,3} the maximum in relative density observed for 0.02 wt% MgO might result from the two contradictory effects of magnesia. Firstly, the reduction of electrostatic repulsive forces with increasing amounts of magnesia enables free particle agglomeration promoted by Van der Waals forces and leads to a continuous lowering of particle packing and to the formation of intra- and inter-agglomerate pores with different size.²⁹ The larger pore sizes formed between agglomerates are stable and can persist during and after the heat treatment determining the densification behaviour and final microstructure of the sintered bodies. On the other hand, the sintered density is higher when using up to 0.1 wt% MgO compared to the pure alumina sample, despite the considerably lower green density. Obviously, MgO has a significant impact on sintering and densification behaviour, also at these higher amounts. This is probably the case at the highest MgO contents (0.2 and 0.5 wt%) where the sintered density still is in the same range as that of pure alumina, considering the much lower green densities for these samples.

4 Summary and Conclusion

MgO additions have been shown to increase the viscosity as well as the degree of pseudoplasticity of alumina slips. This gives a clear indication of a destabilising effect owing to the dissolution of MgO and the consequent increase in ionic strength. The decrease in stability was further confirmed by electrophoretic measurements, in which the zeta potential of the alumina particles was significantly lower with MgO than without. In slip casting, the destabilising effect was expressed by cast bodies with lower densities.

The electrostatic stabilising effect in the $\text{Al}_2\text{O}_3/\text{MgO}$ system given by Tiron is more effective than the electrosteric effect expected from Dolapix. This fact was confirmed in all the steps of the colloidal processing. The slip dispersed with Dolapix showed higher viscosity and lower zeta potential than that with Tiron. Further, the densities of green as well as sintered bodies were lower with Dolapix than with Tiron.

The slip preparation route 1, where the MgO was dispersed before the alumina, was shown to be the most favourable conception since the density of the sintered body obtained with this route was the highest for both dispersants used. Further, the gain in alumina densification with MgO existed only when the slip was prepared with Tiron using route 1.

Finally, the extent of the hetero-flocculation phenomenon caused by addition of magnesia to aqueous alumina suspensions is directly connected to the amount of MgO added. This destabilising effect of MgO caused an increase in equilibrium viscosities as well as in the shear thinning behaviour of alumina slips. The hetero-flocculation effect of MgO particles was also confirmed by the slip casting experiments that clearly showed a continuous decrease in green densities with increasing amounts of MgO. On the other hand, the density of the sintered bodies initially increases by addition of MgO, reaching a maximum (99.7%) for 0.02 wt% MgO and then decreases again with further additions. This maximum in relative density might result from two contradictory effects of magnesia on processing alumina by colloidal techniques: the beneficial effect on densification during sintering, and the deleterious hetero-flocculation effect between different powder components. Consequently, eventual positive effects on the sintering using higher MgO contents, cannot compensate the low green density obtained in slip casting.

To take full advantage of using magnesia as a sintering aid in colloidally processed alumina bodies, its positive influence on densification process needs to be correctly balanced by the negative effect on rheological properties of slips and their ability towards packing.

Acknowledgements

This work was supported by the European Community, CEC Human Capital and Mobility Programme, Contract CHRX-CT94-0574, 'Application of Fundamental Principles of Colloid and Interface Science and Rheology to Ceramic Forming Processes'. The authors also gratefully acknowledge Professor Lennart Begström from Institute of

Surface Chemistry, Stockholm (Sweden) for his helpful discussion.

References

- Lee, W. E. and Rainforth, W. M., Ceramic microstructure — property control by processing. Chapman & Hall, London, 1994.
- Bae, S. I. and Baik, S., Critical concentration of MgO for the prevention of abnormal grain growth in alumina. *J. Am. Ceram. Soc.*, 1994, **77**(10), 2499–2504.
- Handwerker, C. A., Morris, P. A. and Coble, R. L., Effects of chemical inhomogeneities on grain growth and microstructure in Al₂O₃. *J. Am. Ceram. Soc.*, 1989, **72**(1), 130–136.
- Bennison, S. J. and Harmer, M. P., A history of the role of MgO in the sintering of alumina. *Ceramic Transactions*, Vol. 7, *Sintering of advanced ceramics* ed. C. A. Handwerker, J. E. Blendell and W. A. Kaysser. Am. Ceram. Soc. Westerville, OH, 1990.
- Graule, Th., Hidber, P. C., Hofmann, H. and Gauckler L. J., Stabilization of alumina dispersions with carboxylic acids. *Proc. Second European Ceram. Soc. Conf.*, Vol. 1, eds. G. Ziegler and H. Hausner, Augsburg, 1991, pp. 299–305.
- Graule, Th. and Gauckler, L. J., Electrostatic stabilization of aqueous alumina suspensions by substituted phenols. *Proc. Third European Ceram. Soc. Conf.* Vol. 1, eds. P. Duran and J. F. Fernández. Faenza Editrice Ibérica S. L., 1993.
- Hunter, R. J., *Zeta Potential in Colloid Science*. Plenum Press, London, 1982.
- Parks, G. A., The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem. Rev.*, 1965, **65**, 177–198.
- Pugh, R. J. and Bergstrom, L., *Surface and Colloid Chemistry in Advanced Ceramic Processing, Surfactant Science Series, Vol. 51*. Marcel Dekker, New York, 1994.
- Rao, A. S., Effect of pH on the suspension stability of alumina, titania, and their mixtures. *Ceramics International*, 1987, **13**, 233–241.
- Rao, A. S., Electrophoretic mobility of alumina, titania and their mixtures in aqueous dispersions. *Ceramics International*, 1988, **14**, 71–76.
- Rao, A. S., Effect of surface active agents on the electrokinetic and rheological behaviour mobility of alumina and titania slips. *Ceramics International*, 1988, **14**, 141–146.
- Keh, H. J. and Yang, F. R., Particle interactions in electrophoresis III. Axisymmetric motion of multiple spheres. *J. Coll. Interf. Sci.*, 1990, **139**(1), 105–116.
- Kummert, R. and Stumm, W., The surface complexation of organic acids on hydrous γ -Al₂O₃. *J. Coll. Interf. Sci.*, 1980, **75**(2), 373–385.
- Hidber, P. C., Graule, Th. and Gauckler, L. J., Citric acid—a dispersant for aqueous alumina suspensions. *J. Am. Ceram. Soc.* (submitted).
- Hidber, P. C., Graule, Th. and Gauckler, L. J., Influence of the dispersant structure on properties of electrostatically stabilized aqueous alumina suspensions. *J. Am. Ceram. Soc.* (submitted).
- Horn, R. G., Particle interactions in suspension. In *Ceramic Processing*, ed. R. A. Terpstra, P. P. A. C. Tex and A. H. de Vries. Chapman & Hall, London, 1995.
- Higashitani, K., Kondo, M. and Hatade, S., Effect of particle size on coagulation rate of ultrafine colloidal particles. *J. Coll. Interf. Sci.*, 1991, **142**(1), 204–213.
- Ayral, A. and Phalippou, J., Effect of pH on the rheological properties of a silica hydrosol. *J. Europ. Ceram. Soc.*, 1990, **6**, 179–186.
- Firth, B. A. and Hunter, R. J., Flow properties of coagulated colloidal suspensions I. Energy dissipation in the flow units. *J. Coll. Interf. Sci.*, 1976, **57**(2), 248–256.
- Firth, B. A., Flow properties of coagulated colloidal suspensions II. Experimental properties of the flow curve parameters. *J. Coll. Interf. Sci.*, 1976, **57**(2), 257–265.
- Firth, B. A. and Hunter, R. J., Flow properties of coagulated colloidal suspensions III. The elastic flocculation model. *J. Coll. Interf. Sci.*, 1976, **57**(2), 266–275.
- Hunter, R. J., The flow behavior of coagulated colloidal dispersions. *Advances in Colloid and Interface Science*, 1982, **176**, 197–211.
- Derjaguin, B. V. and Landau, L. D., Theory of stability of highly charged lyophobic sols and adhesion of highly charged particles in solutions of electrolytes. *Acta Physico-chim. URSS*, 1941, 633–662.
- Verwey, E. J. W. and Overbeek, J. T. G., Theory of the stability of lyophobic colloids. Elsevier, Amsterdam, 1948.
- Chou, C. C. and Senna, M., Correlation between rheological behavior of aqueous suspension of Al₂O₃ and properties of cast bodies: effects of dispersant and ultrafine powders. *Ceram. Bull.*, 1987, **66**(7), 1129–1133.
- Diz, H. M. M. and Ferreira, J. M. F., Study of the factors influencing the slip casting of mullite-zirconia ceramics. In *Brit. Ceram. Soc. Proc. of Special Ceramics*, Vol. 8, ed. S. P. Howlett and D. Taylor, Stoke-on-Trent, 1986.
- Ferreira, J. M. F. and Diz, H. M. M., Effect of the amount of deflocculant and powder size distribution on the green properties of silicon carbide bodies obtained by slip casting. *J. Hard Mater.*, 1992, **3**(1), 17–27.
- Lange, F. F., Powder processing science and technology for increased reliability. *J. Am. Ceram. Soc.*, 1989, **72**, 3–15.