Journal of the European Ceramic Society **17** (1997) 327–331
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0955-2219/97/$17.00

PII: S0955-2219(96)00142-2

Influence of Slip Rheology on Pressure Casting of Alumina

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(Received 15 September 1995; revised version received 15 July 1996; accepted 22 July 1996)

Abstract

Pressure slip casting has been developed more intensively since it can produce near net-shaped green bodies with shorter processing cycles. As with the other colloidal forming techniques, the preparation and control of stable, well-dispersed ceramic slips is considered a key parameter. In this study a series of alumina slips containing different kinds of dispersants including potential determining ions, counterions or electrosteric forms, were prepared. According to the shear stress/shear rate relationships, the slips were found to behave very differently, showing Newtonian, plastic, pseudoplastic or thixotropic behaviour. The slips were cast at a pressure of 3·4 MPa and the highest densities were obtained if Newtonian slips without or with only slight thixotropy were cast. The cast bodies produced with slips of plastic and/or strongly thixotropic behaviour did not reach the required density nor wet cast consistency. © 1996 Elsevier Science Limited.

1 Introduction

Colloidal forming techniques have attracted the interest of scientists and engineers for the shaping of defect-free ceramic parts with high and uniform density. In addition to slip casting on gypsum moulds, different slip forming methods are being developed. For thin and thick films one can apply tape casting, dip coating or electrodeposition methods. However, for thick pieces, traditional slip casting has serious limitations relating to the maximum thickness which can be obtained in the cast. For this reason, pressure slip casting (PSC) has received attention due to the possibility of attaining such thick bodies, up to 50 mm.[1-3] Furthermore, this technique allows increased production ratio of complex shapes by decreasing the shaping times by up to an order of magnitude which leads to an important reduction in the fabrication costs.

The full exploitation of the pressure casting shaping technique is strongly influenced by two key parameters: the slip preparation and properties and the press design, in which the mould properties and the characteristics of the press, must be taken into account. However, although the importance of preparing a well-dispersed slip has been repeatedly stated, inadequate information has been obtained to prepare slips of optimal rheological behaviour.

The aim of this work is to correlate the state of deflocculation and the rheological properties of the slip to the pressure casting parameters. Alumina slips have been prepared at different dispersion conditions, changing the chemical nature of the dispersants, their relative concentration and consequently the rheological flow curves. The slips were all pressure cast under constant pressure. The casting curves obtained and the characteristics of the cast bodies are correlated with the rheological parameters.

2 Theoretical Background

The stabilization of a suspension can be provided by different mechanisms, chiefly the following:

(1) electrostatic repulsion, as the result of the development of an electrical double layer around the particles when immersed in a polar liquid;
(2) polymeric stabilization, related to the adsorption of macromolecules onto the particle surface, providing a steric hindrance; and
(3) the combination of these two mechanisms, resulting in the electrosteric mechanism, in which there is an anchored polymer providing the steric hindrance and an electrostatic contribution that can be due to a net charge on the particle surface and/or the presence of charges associated with the anchored polymer.

In aqueous media, the stabilization of a slip has always an electrostatic component, since water is a polar liquid. For this reason the most usual mechanisms for the stabilization of aqueous slips are the electrostatic and the electrosteric. The electrostatic stabilization can be achieved by means of:

(1) Potential determining ions (P.D.I.): in aqueous slips these ions are H^+ and OH^-, i.e. the control of pH.
(2) Counterions: the salts of monovalent ions are very good dispersants for ceramics, since the flocculation value decreases inversely with the charge of the cation. The most common dispersants for ceramics include silicates, carbonates and polyphosphates of a monovalent ion, such as sodium or ammonium.

The best electrosteric stabilization occurs through the use of polyelectrolytes. In this case the steric stabilization prevents contact of particles in the primary minimum in the potential energy curve while at longer distances the electrostatic repulsion is responsible for the stabilization.

Three rheological models are commonly used to represent the behaviour of slips:

(1) Newtonian, in which the shear stress (τ) is proportional to shear rate ($\dot{\gamma}$) where the constant of proportionality is the viscosity (η), such that $\tau = \eta \cdot \dot{\gamma}$.
(2) Plastic Bingham flow, in which $\tau = \tau_0 + \eta \cdot \dot{\gamma}$, where the viscosity is constant above a yield stress.
(3) Casson model, in which $(\tau)^{1/2} - (\tau_0)^{1/2} = (\eta\ \dot{\gamma})^{1/2}$, corresponding to plastic behaviour where the viscosity changes with the shear rate above a yield.

Moreover, most of the ceramic slips exhibit a time dependence of viscosity (thixotropy) that must be taken into account when discussing the rheological behaviour.

3 Experimental

The experimental work was performed using a 99·5% α-Al_2O_3 (A16SG, Alcoa Inc. USA) with a specific surface area of 9·7 m^2/g (measured by one-point BET method) and a mean particle size of 0·4 μm (measured with a laser particle size analyzer, Laser Coulter LS 130, USA).

In the present work different Al_2O_3 slips have been prepared using the following dispersants:

(1) As PDI dispersant HCl was used to modify the pH.
(2) As a counterion sodium hexametaphosphate (NaHMP) was used.
(3) To provide the electrosteric stabilizing mechanism three different polyelectrolytes were used:
    (i) a polycarbonic acid salt (Dolapix PC33);
    (ii) a carbonic acid ester (Dolapix ET85);
    (iii) a carbonic acid (Dolapix CE64).

All of them are manufactured by Zschimmer-Schwarz (Germany) as synthetic polyelectrolytes free from alkalis.

Aqueous slips with different concentrations of each of the dispersing agents were prepared maintaining the solid content of the slip constant at 33 vol% (66·2 wt%). Homogeneous slips were prepared by a ball mill equipped with zirconia jar and balls.

Rheological measurements were carried out using a concentric cylinders rotational viscometer with a cylinder distance of 1·74 mm (Haake, Rotovisco RV20, Germany). The temperature was maintained constant at 25°C. The shear stress (τ) versus shear rate ($\dot{\gamma}$) curves were determined for all the slips prepared. The resulting curves were fitted with different theoretical models to find the best correlation. The thixotropy was evaluated from the viscosity after maintaining the slip at a shear rate of 500 s^{-1} for 1 min.

Pressure casting experiments were performed using an hydraulic press equipped with pressure and linear displacement transducers that allow the continuous monitoring of the cast body thickness, via a mass balance of the slip and the cast body. The applied pressure was maintained at 3·4 MPa.

4 Results and Discussion

4.1 Rheological measurements

As reported in other papers for similar Al_2O_3 powders, the isoelectric point of the powder used in this work occurs at pH 9.[4] Thus, the stabilization of the slip by means of P.D.I. was best performed at pH 4 to 5, where high zeta potential values are obtained.

The variation of viscosity with the addition of HCl was measured and a minimum viscosity value was obtained at pH 4. Figure 1 shows the shear stress versus shear rate curves of Al_2O_3 slips at different pH values. At pH 4 the flow curves could be fitted with a Newtonian model. However, at pH 5·7 the best fit corresponds to a Bingham plastic flow, with a yield value of $\tau_0 = 1{\cdot}7$ Pa. The pH-dispersed slips show a slight time-dependent behaviour in all cases, this dependency increasing with pH.

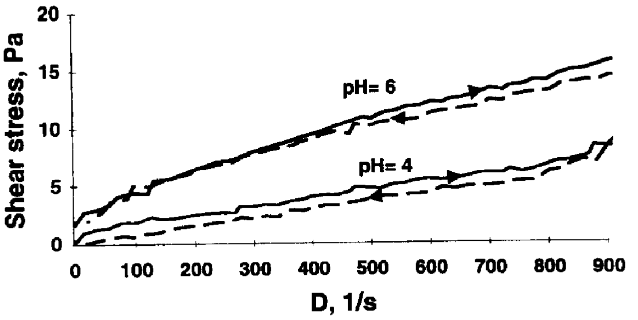

Fig. 1. Flow curves of alumina slips in function of pH value.

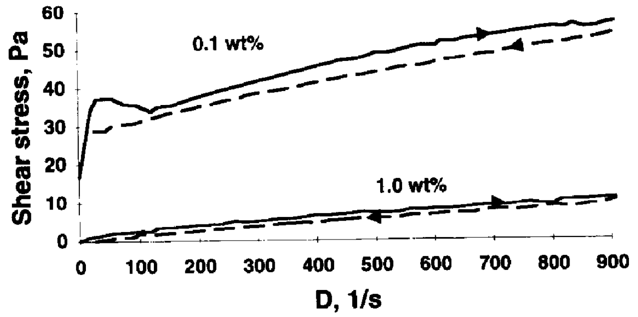

Fig. 2. Flow curves of alumina slips containing NaHMP.

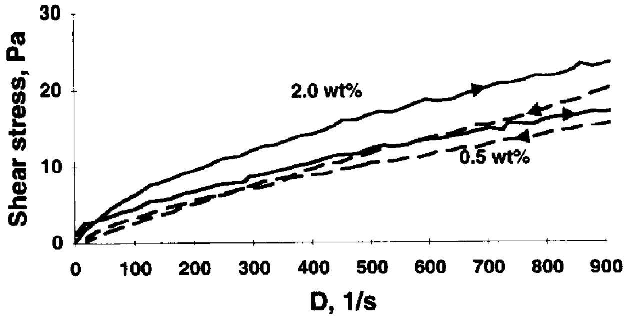

Fig. 3. Flow curves of alumina slips dispersed with polycarbonic acid salt.

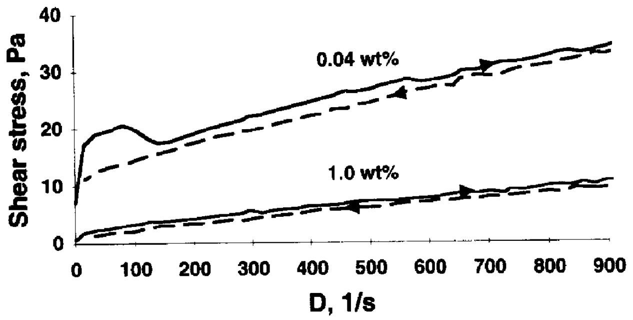

Fig. 4. Flow curves of alumina slips dispersed with carbonic acid ester.

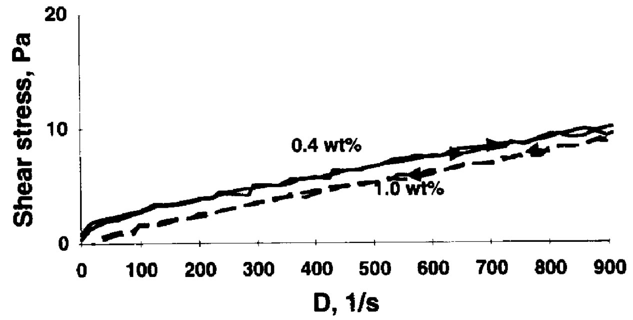

Fig. 5. Flow curves of alumina slips dispersed with carbonic acid.

In the case of the dispersion by counterions (NaHMP) different rheological models can fit the data depending on the dispersant content (Fig. 2). The flow curve has been measured for a broad range from 0·04 to 1·0 wt% of dispersant. For a low dispersant content the slip behaved as Bingham plastic, with a high yield point (τ_0 = 7·1 Pa) and a small time dependency. For higher concentrations of dispersant the slip was nearly Newtonian (the yield point tends to disappear). An excess of dispersant (1 wt%) produced deviations from Newtonian to plastic flow, with a low yield point (τ_0 = 0·6 Pa). Thus, it is possible to change the rheological behaviour by changing the concentration of dispersant.

The rheological behaviour of slips dispersed with polyelectrolytes is shown in Figs 3–5. In the case of polycarbonic acid salt relatively high contents were needed to provide the required stability. In the case of low dispersant contents, such as 0·5 wt%, the slip showed plastic nature with a small yield point (1·1 Pa). At higher dispersant contents, such 2 wt%, the viscosity increased but the yield decreased. In all cases there was some thixotropy which increased with the dispersant content.

In the case of carbonic acid ester a concentration of 0·1 wt% provided a high viscosity and a high yield point (τ_0 = 16·9 Pa) with a Bingham behaviour and significant time dependency. When increasing the dispersant concentration the yield value and the viscosity decreased as well as the magnitude of the time dependence. For 1 wt% (the best dispersing conditions for this dispersant) the yield value was low (0·9 Pa) but a thixotropic behaviour was still evident. From the general point of view the carbonic acid ester gave too high viscosities and broad thixotropic cycles, seriously hindering the casting process.

The alumina slips dispersed with 0·2–0·4 wt% carbonic acid behaved as nearly Newtonian fluids with yield values decreasing from 2·9 to 0·8 Pa. For higher dispersant contents, such as 1 wt%, the yield point decreased. However, a slight time dependency is observed in all cases.

The rheological behaviour of the prepared slips is summarised in Table 1.

4.2. Pressure casting

The casting curves for the slips listed in Table 1 are shown in Figs 6 and 7. These figures show the relationship between cast thickness and time. The parameters relevant to the pressure casting,

Table 1. Characteristics of 33 vol% alumina slips with different dispersants

Dispersant	*HCl*		*NaHMP*		*Polycarbonic acid salt*		*Carbonic acid ester*		*Carbonic acid*	
Conc. (wt%)			*0·04*	*1·0*	*0·5*	*2*	*0·1*	*1·0*	*0·4*	*1·0*
pH	*4*	*5·8*								
τ_r,[a] at 0·7 s^{-1} (Pa)	0·11	1·7	7·1	0·63	1·13	0·09	16·9	0·87	0·76	0·37
Flow curve type[b]	N	P	T/P	N/t	PP/t	PP/T	P/T	PP/T	N/t	N/t
$\Delta\tau$[c] (Pa)	0·8	0·6	2·24	1·07	1·8	4·8	5·04	2·71	1·35	1·32

[a] Considered as the shear stress nearest to the yield point.
[b] N-Newtonian, P-Plastic, PP-Pseudoplastic, T-Thixotropic, t-Slightly thixotropic.
[c] Shear stress difference between increasing and decreasing flow curves at 500 s^{-1}.

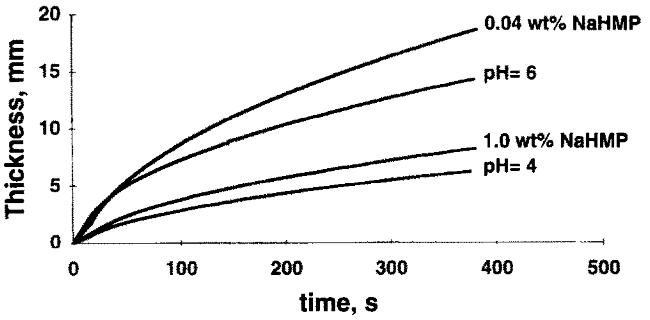

Fig. 6. Casting curves of alumina slips containing inorganic dispersants.

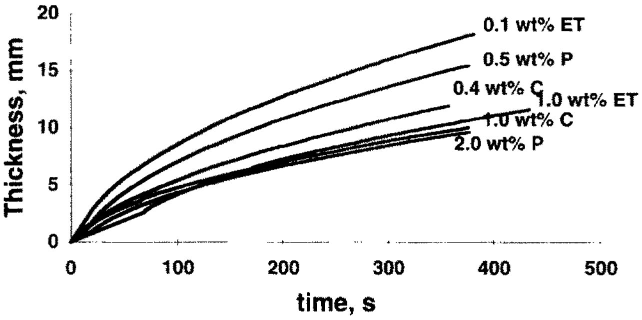

Fig. 7. Casting curves of alumina slips containing organic dispersants.

e.g. the density of the green body, the slip viscosity at two different shear rates and the mean casting rate, represented by the thickness of the casts formed after a casting time of 6 min, are shown in Table 2.

By comparison of the data given in Tables 1 and 2 and in Figs 1–7, one can observe that there is a qualitative relationship among slip parameters, casting rate and density of the formed greens. It is evident that the best dispersing conditions (i.e. the minimum viscosity) provide the slowest casting rates. At these conditions a greater control of the process conditions can be achieved, and hence higher densities are obtained. Furthermore, if the dispersant content is not sufficient to assure a nearly Newtonian behaviour, it is possible to obtain high casting rates, but the density of the cast body decreases.

5 Conclusions

Using the chemically pure and fine-grained alpha-alumina a series of slips containing different dispersants was prepared. The solid content was maintained at 33 vol%, while the dispersants were added in different concentrations. As a potential determining ion dispersant HCl was used while as a counterion sodium hexametaphosphate was added. From possible electrosteric dispersants, polycarbonic acid, polycarbonic acid salt and polycarbonic acid ester were selected for evaluation.

Table 2. Characteristic properties of pressure cast slips and green bodies cast at 3·4 MPa

Dispersant	*Dispersant conc. (wt%) (or pH)*	*Viscosity at 100 s^{-1} (mPa s)*	*Viscosity at 200 s^{-1} (mPa s)*	*Mean casting rate (mm/min)*	*Cast body density (%TD)*
HCl	pH 4	18·2	12·7	1·03	62·8
HCl	pH 5·8	46·6	32·3	2·36	55·5
NaHMP	0·04	195	94·6	3·10	53·0
NaHMP	1·0	32·5	21·2	1·37	59·4
Polycarbonic acid salt	0·5	44·6	33·4	2·50	54·8
Polycarbonic acid salt	2·0	61·9	47·1	1·60	56·8
Carbonic acid ester	0·1	371	187·8	3·02	52·7
Carbonic acid ester	0·2	122·7	70·6	2·90	49·4
Carbonic acid ester	1·0	26·6	18·8	1·90	56·2
Carbonic acid	0·4	28·0	19·2	1·90	53·1
Carbonic acid	1·0	26·6	18·8	1·67	59·0

The rheological measurements showed that the prepared slips behaved very differently depending on the nature and concentration of dispersants covering the broad range of viscosities from 18·2 up to 371 mPa s (at a shear rate of 100 s^{-1}).

The rheological parameters of the slips directly influence the casting rate and some of the properties of the cast bodies. The slips characterised by low viscosities, i.e. high dispersion levels, were pressure cast at the slowest casting rates. This can be related with the fact that the well-dispersed particles pack into a high density structure of limited porosity which decreases the flow rate of slip water. On the other hand, less dispersed slips (if not partially flocculated) show higher viscosities and higher casting rates since their cast bodies are not characterised by an intimately packed structure and, consequently, by a high density.

Low viscosity and low yield point slips are required for a good control of the casting rate and consequent high relative density of the cast bodies. The cast properties depend on the rheological behaviour of the slip rather than on the chemical nature of dispersants.

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