Ceramics International 25 (1999) 577–580

CERAMICS INTERNATIONAL

Influence of particle size and particle size distribution on drying-shrinkage behaviour of alumina slip cast bodies

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Received 7 January 1998; received in revised form 4 April 1998; accepted 18 September 1998

Abstract

This paper focuses on the possibility of characterising slip cast bodies microstructures through their behaviour during drying, by using the Bigot's curves. The Bigot's curves are normally used as routine control in traditional clay-based ceramic production (tiles, sanitary wares, earthenware, etc.) for testing the sensitivity of clays and pastes to drying. In order to test the validity and usefulness of the Bigot's curves to characterise wet porous structures as that obtained by slip casting, "tailored" alumina slip cast bodies, prepared from suspensions having different mean particle sizes (PSs) and particle size distributions (PSDs), were used. The results showed that a decrease of the mean PS leads to an increase of the shear-thinning behaviour in the low shear rate range due to the predominance of the surface forces, relative to the hydrodynamic forces. In the slip cast bodies, a diminution of the mean PS leads to an overall decrease of green density and to an increase of both Critical Moisture Content (CMC) and total shrinkage in the first stage of the drying process. Regarding the effect of the PSD shape, alumina CT530 characterised by a bimodal PSD, gave slips with lower viscosity and denser slip cast bodies, compared with the other aluminas characterised by a continuous PSD. Accordingly, the Bigot's curves showed a decreasing trend of CMC and total shrinkage. Overall, this work demonstrates that the use of Bigot's curves can be extended to the advanced ceramic field, as an important tool for characterisation of slip cast bodies, including the wet state, giving complementary information in respect of Hg porosimetry or density.

Keywords: A. Slip casting; Particle packing; Rheology; Colloidal processing

1. Introduction

Process control is becoming a key concept in managing the fabrication process to prevent errors and problems rather than relying on post-process activities, such as inspection and sorting out defective products [1]. In the specific domain of ceramic processing, the experimental methods normally used to characterise green microstructures are: (i) density, by Archimedes immersion method; (ii) open porosity, by Hg porosimetry; (iii) qualitative analysis, by electron microscopy [2]. Moreover, there exist other capillary phenomenon than Hg intrusion porosimetry, that are pore-size related and can be used to characterise porous materials, for instance the interaction between wetting fluid and packed particles during drying [3]. A slip cast body after de-moulding, indeed, can be thought of as a porous structure saturated with liquid. Hence, the drying of this saturated body can be connected with the porous structure of the material [4].

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The aim of this work was to design different porous structures of slip cast bodies by manipulating PS and PSD of the starting powders and evaluate the efficacy of the drying-shrinkage behaviour, as given by the Bigot's curves [5] to characterise them.

2. Experimental procedure

2.1. Materials, slip preparation and characterisation

Four commercial alumina powders (Alcoa Chemicals, USA) with different average particle sizes and PSDs were used in this study: A16 SG, CT2000 SG, CT1200 SG and CT530 SG. BET specific surface area (Quantasorb, Quantacrome, USA) and X-ray sedimentation (SediGraph 5100, Micrometrics, USA) were used to characterise the powders after milling.

Alumina suspensions at 30 vol% solid loading were prepared at pH 4 by adding the required amounts of HCl (37 wt% R.G., Riedel-de Haen, Germany). The alumina powders were first added to the acid solution

0272-8842/99/$ - see front matter
PII: S0272-8842(98)00068-6

and stirred for 30 min under pH controlled conditions. De-agglomeration was then completed by ball milling for 24 h. During the milling step, the pH was regularly checked and HCl was added to set the acidity of the medium at pH 4. Following this, a de-airing step was performed for a further 24 h by rolling the slips in the milling container without balls.

Steady shear measurements were carried out with a rotational CS rheometer (Carri-med 500 CSL, UK) at 20°C in the shear rate range approx. 0.5–550 s^{-1}. The configuration system used was double concentric cylinders with 1 mm gap. Pre-shearing was performed at the highest shear rate for 1 min followed by a rest of 2 min to transmit the same rheological history to all suspensions being tested.

2.2. Green body preparation and characterisation

Solid cast bars (l = 110 mm, trapezoidal section area [15.(15 + 17)/2] mm^2) were obtained by conventional slip casting in suitable plaster mould. Just after de-moulding, two pieces of 40 mm were cut, weighed and carefully placed in the barelatographe (Adamel Lhomargy, France) for the simultaneous measurement of shrinkage and weight loss. The natural drying (at room temperature) of the samples was recorded for 24 h and, after that, the drying was completed in an oven at 120°C. The weight and length of the wholly dried samples were then measured and used as reference for plotting the Bigot's curves. A linear regression of the data in the first stage of drying was used to determine the Critical Moisture Content (CMC), given by the intercept of the curve with the humidity axis, in the constant-rate period.

The relative density and pore size distributions of the dried slip cast samples were measured by Archimedes immersion method and Hg intrusion porosimetry (Pore-Sizer 9320, Micromeritics, USA), respectively. The high-pressure part of each experiment was carried out using the automatic mode with an equilibration time of 10 s at each point (55 points, from approx. 0.1 up to 200 MPa). The surface tension and contact angle adopted were 48.5 10^{-2} N/m and 130°, respectively.

3. Results and discussion

Since the development of the cake takes place directly from the ceramic powder suspension, there exists a close relationship between the properties of the suspended particles, rheological behaviour and slip casting performance in terms of packing density and homogeneity [6]. The main factors controlling the properties of the suspensions and the structure of slip cast bodies are PS and PSD [7], particle shape [7], solid loading [8] and the interaction forces between the suspended particles [9]. In the experimental conditions used in this work (fixed solid loading and very well dispersed slurries), particle packing ability is mostly size-related.

Fig. 1 shows the cumulative PSD curves of the alumina powders used. The size of all powders is within 0.1–10 μm, hence included in the typical colloidal size range. Further, the PSD of alumina CT530 is essentially bimodal, whereas the other aluminas were characterised by continuous PSDs.

The rheological behaviours of these powders in suspension are reported in Fig. 2. It can be seen that the equilibrium viscosity gradually increases with decreasing PS, with the highest values being observed in the case of A16, the finest powder tested. Further, Fig. 2 shows that A16 slip is shear-thinning over the whole shear rates range, whereas the coarser ones are shear-thinning only at low shear rates, becoming progressively shear-thickening as the shear rate increases.

The 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 and so, the surface forces dominate the particulate system. As the shear rate increases, the flocs and floc network break down, the entrapped liquid is released 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

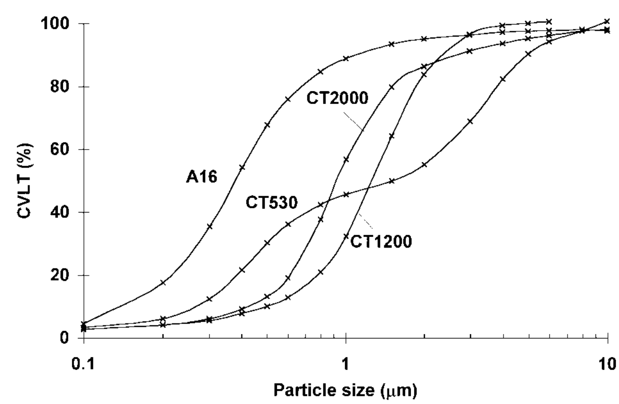

Fig. 1. Particle size distributions of the starting alumina powders.

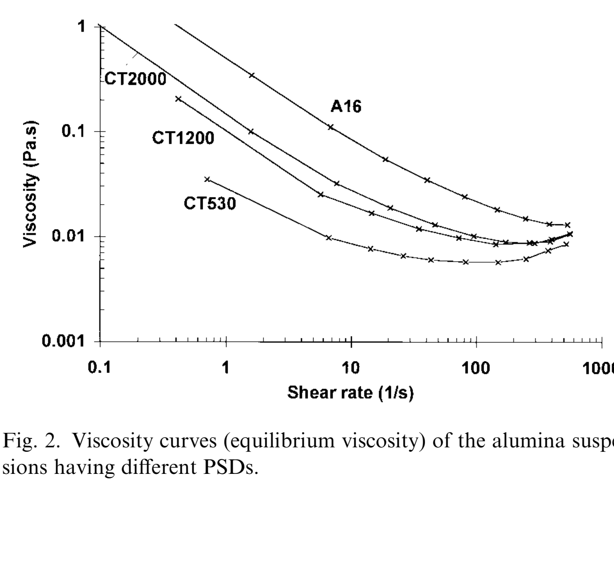

Fig. 2. Viscosity curves (equilibrium viscosity) of the alumina suspensions having different PSDs.

higher specific surface area and to a predominant role of the surface forces. The agitation action can gradually break down this structure by overcoming the attractive energy corresponding to the secondary minimum of the total interaction energy curve, according to the classical DLVO theory, and thus the viscosity of the suspension decreases. At high shear rates, the importance of the hydrodynamic interactions between particles increases. When PS increases, they can even become dominant tending to individualise the particles. Furthermore, for such particles to slide over each other they have to increase their average separation distance, especially when coarser particles are present. This causes an apparent increase of the volume of the system. As a consequence, part of the water already available for flowing are immobilised in the interstices, resulting in an overall increase of viscosity, i.e. shear-thickening, as in the case of aluminas CT2000, CT1200 and CT530. Similar dependencies of the flow behaviour on the PS and PSD have been reported by Barnes [10] and Bergström [6], among many others.

The density and CMC values and the porosimetry data of slip cast bodies are reported in Table 1. It can be noticed that, for the continuous PSDs, the green density continuously increases with the coarsening of alumina powder. This can be attributed to an enlargement of PSD (Fig. 1) (Ref. [7] and references therein). As expected, the green density increased when the bimodal PSD alumina powder (CT530) was used [11], reaching a maximum value of 68.3%. These results match very well with the rheological measurements. In fact, the viscosity level of the suspensions gradually decreases with increasing particle size, reaching a minimum in the case of alumina CT530, due to a more efficient particle packing even in suspension. The porosity data are roughly consistent with density and CMC trends. However, there exits a discrepancy between total pore volume and green density in the case of the compact prepared from A16. This probably derives from its lower pore sizes and/or incomplete Hg intrusion.

Fig. 3 shows that the drying-shrinkage behaviour is strongly dependent on particle size and PSD of the starting powders, since these parameters determine the porous structure of the alumina slip cast bodies. A hydrated layer surrounds solid particles in a wet body.

Table 1
BET specific surface areas (Quantasorb, Quantacrome, USA) of the starting alumina powders, density, main porosity data of the slip cast bodies and CMC

	A16 SG	CT2000 SG	CT1200 SG	CT530 SG
BET (m^2/g)	10	5	4	5
TD (%)	62.1	63.8	65.9	68.3
Pore volume (ml/g)	0.147	0.143	0.122	0.113
Mean pore diameter (μm)	0.065	0.161	0.183	0.058
CMC (%)	14.5	13.9	12.1	9.5

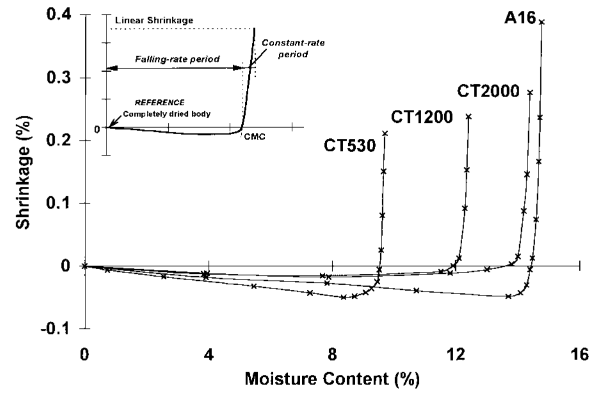

Fig. 3. Drying-shrinkage behaviour (Bigot's curves) of the slip cast bodies. Inserted, there is a schematic representation of the main features of Bigot's curves.

The gradually disappearing of this layer leads to a mutual approach of particles during the first stage of the drying, i.e. the observed shrinkage of the body. At the low concentration of the starting suspension used in this work, the extent of the shrinkage can be mainly attributed to the specific surface area of the starting powders and so, size-related. In fact, the number of hydrated layers per unit length increases as particle size decreases. Accordingly, for monomodal powders, shrinkage decreases from the samples prepared with A16 to CT1200 (Fig. 3). Powders CT2000 and CT530 have equal BET surface areas, but the shrinkage is slightly lower in the case of the bimodal powder. This might derive from the higher packing density and lower moisture content of this sample after de-moulding.

Regarding the evolution of the CMC, it steadily decreases when the packing ability of the particles increases, due to a lower volume of water in the interstices of the wet compacts. Accordingly, the lowest CMC occurs in the case of the bimodal powder CT530.

4. Summary and conclusions

Three main conclusions can be drawn from this work:

- With continuous PSDs, a decrease of particle size gives rise to an increasing importance of the surface forces with respect to the gravitational/hydrodynamic ones. This favours floc formation and less efficient particle packing both in suspension and in the slip cast bodies. The amount of water associated with surface of particles also increases. Consequently, the drying-shrinkage is influenced by the mean particle size with (i) an increase of shrinkage, due to an increased number of hydrated layers per unit length as PS decreases and (ii) a decrease of the CMC when the particle packing ability increases.

- Alumina CT530, characterised by a bimodal PSD, leads to more efficient particle packing, both in suspension and in the slip cast body, compared with the other powders. This enables the obtaining of slips with lower viscosity and green bodies with higher density, compared with the other aluminas characterised by more continuous PSDs. Accordingly, drying-shrinkage behaviour of CT530 shows the lowest values of CMC and shrinkage in the first stage of drying.
- Considering the consistency between the information given by the Bigot's curves, density and porosimetry, the former method represents a very simple and interesting technique to characterise the porous structures of slip cast bodies. Furthermore, Bigot's curves also enable the identification of the most critical drying steps where the kinetics of the drying process can be kept under control.

Acknowledgements

The authors acknowledge FCT (Portuguese Foundation for Science and Technology) for the financial support and for the fellowship grant in the frame of Praxis XXI programme.

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