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Effect of Slurry Structure on the Slip Casting of Silicon Carbide Powders

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Abstract

Silicon carbide powders of two different particle size distributions were dispersed in water at various pH values. The structure of particle aggregates in the resulting suspensions was determined by rheological techniques, particle size analysis, and electrophoretic mobility. Samples were prepared by slip casting of the suspensions in moulds of plaster of Paris.

Relative green density and water content of the bodies were measured and a good correlation between the properties of slip-cast bodies and the structure of initial suspensions was observed.

Zwei Siliziumcarbidpulver mit unterschiedlichen Korngrößenverteilungen wurden in Wasser bei verschiedenen pH-Werten dispergiert. Die Struktur der Agglomerate in dem entstandenen Schlicker wurde mit rheologischen Methoden, Korngrößenanalyse und elektrophoretischer Mobilitätsmessung bestimmt. Die Proben wurden durch Schlickerguß in Gipsformen hergestellt.

Bei der Bestimmung der relativen Gründichten und der Wassergehalte der Formkörper wurde eine gute Korrelation zwischen den Eigenschaften der Grünkörper und der Beschaffenheit des Schlickers beobachtet.

Des poudres de carbure de silicium avec deux dimensions différentes de particules ont été dispersées dans de l'eau à différentes valeurs de pH. La structure des agrégats dans les suspensions obtenues a été déterminée par des techniques rhéologiques, et une analyse de la taille des particules et de la mobilité éléctrophorétique. Les échantillons ont été préparés par slip casting des suspensions dans des moules de plâtre de Paris.

La densité brute et la proportion d'eau dans les échantillons ont été mesurées, et une bonne corrélation entre les propriétés des composés obtenus par slip casting et la structure des suspensions initiales a été observée.

1 Introduction

Silicon carbide is being considered for its great potential as a structural material for various applications: diesel engines,[1] gas turbines,[2,3] industrial heat exchangers and high-temperature energy conversion systems.[4] Sintered SiC exhibits high hardness and strength over a broad range of temperatures, excellent erosion and oxidation resistance, and good thermal stress resistance.[4–6] However, an important aspect of the fabrication sequence which can improve subsequent sintering and final properties of bodies, is the achievement of a homogeneous structure and a good packing of powders at the consolidation stage of the green body. Inhomogeneities in green bodies, such as pores and agglomerates with different density from the matrix, affect the ability to reach high final packing densities. An agglomerate with higher green density than the matrix will sinter better and shrink more than the surrounding matrix, leading to microstructures with dense areas surrounded by large cracks that will have a detrimental effect on the strength of the material.[7] Similar effects of agglomeration on the sintered microstructures have been reported for other materials.[8,9] Colloidal consolidation techniques can, therefore, be used to obtain homogeneous, high-density green compacts.[10]

The literature concerning slip casting of silicon carbide is not extensive. As referred to by Rado,[11] successful casting slips of SiC and other non-oxide materials was first explored in a German patent in

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1936.[12] More recently, stabilization and colloidal processing of SiC has been studied in aqueous[13–18] and nonaqueous solvents.[19,20] Degtyareva and coworkers[13,14] studied the influence of pH and added clay and silicon on the properties of SiC slips and castings. Person *et al.*[15,16] and Rizzo *et al.*[18] have discussed the stabilization of SiC suspensions and the sintering of cast bodies. The effect of applied pressure on some properties of SiC specimens was also evaluated by Rogers[17] in aqueous medium and by Haggerty *et al.*[19] and Okuyama *et al.*[20] in nonaqueous medium.

The aim of the present work was to evaluate the influence of pH on the rheological behaviour, suspension stability and slip casting performance of two α-SiC powders with different particle size distributions.

2 Experimental

2.1 Materials and reagents

The raw materials were two commercially available SiC powders, NF0 and NF1 (Elektroschmelzwerk, Kempten, FRG). The mean diameters, as given by the manufacturer, are 1·2 and 2·8 μm, respectively.

Solutions of hydrochloric acid and sodium hydroxide were used to adjust the pH values. A solution of sodium chloride was used to adjust the ionic strength of suspensions in electrophoretic experiments. All reagents were p.a. grade (Merck Portuguesa Lda, Portugal).

2.2 Techniques

The suspensions were prepared by first adding the powders to distilled water and hand stirring, followed by ultrasonication for 10 min. The pH was then adjusted to the required values and ultrasonication allowed for more than 10 min. The solid content of suspensions was limited to about 0·01 wt% in electrophoretic measurements and particle size analysis; and to 62·5 wt% in rheological and slip casting experiments, because of their high viscosity at and near the isoelectric point.

The electrophoretic mobility was measured at room temperature using a microscope-type electrophoresis equipment (Mark II, Rank Brothers, Cambridge, UK) with a planar silica glass cell and blacked platinum electrodes. The ionic strength of the liquid medium was adjusted to 0·001 M NaCl.

The floc size distributions (FSDs) of the finer powder were determined by using a photosedimentometer (Lumosed-Retsch, F. Kurt Retsch, FRG) at various pH values.

The rheological properties of suspensions were evaluated with a cone-plate viscosimeter (Ferranti-Shirley, Ferranti Ltd, Manchester, UK) coupled to a personal computer by means of an analog and digital I/O board (Data Translation Inc., Harboro, MA, USA, DT2805). The flow curves (yield stress versus shear rate) were built up by collecting 1000 points in both branches (up and down). Shear rate varied from 0 to 1176·8 s^{-1} in a sweep time of 10 s. The pseudoplastic behaviour observed was analysed under the Bingham approximation using the linear part (intermediate 900 points) of the down curve. The plastic viscosity and yield stress were calculated from the slope and the intercept of the straight line with the shear stress axis respectively.

In slip casting experiments, care was taken to avoid air entrapment that could cause casting defects. Green bodies were prepared by pouring the suspensions into plaster moulds with a plaster : water ratio of 1:25, to form solid samples 15 × 15 × 100 mm; samples were unmoulded as soon as casting was completed. Samples were then weighed, dried in an oven at 110°C for 24 h and then reweighed. The green density was measured in a mercury balance[21] using two pieces from each sample.

3 Results and Discussion

3.1 Electrophoretic measurements

The electrophoretic mobility (epm) of NF0 and NF1 particles was measured to determine how the interface potential changes with pH of suspensions. The results are shown in Fig. 1. The isoelectric points (ieps) of both powders at pH ≈ 2 are in good agreement with other values reported in the

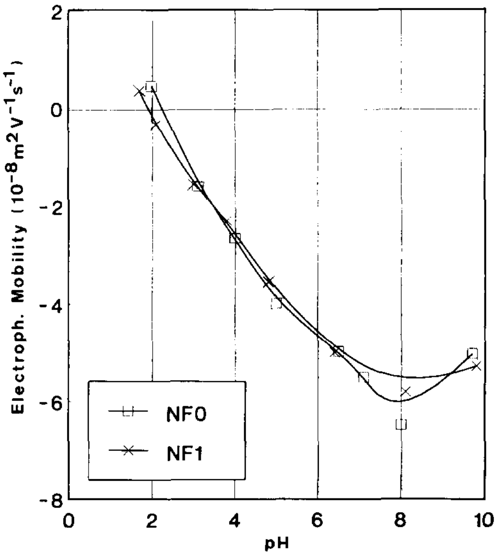

Fig. 1. The effect of pH on the electrophoretic mobility (0·001 M NaCl).

literature.[18,22,23] The surfaces of SiC particles are usually covered by a thin film of silica. When this film grows, the iep will reach a value near that of the silica (pH 2–3·7).[24] In the present case, the SiC particles behaved as if they were covered by a SiO_2 film. As the pH is changed from the iep by addition of acid or base, the zeta potential will increase. The increase in zeta potential (or electrophoretic mobility) will be limited when maximum adsorption of potential determining ion on the particle surface is reached. This seems to occur at pH $\approx$ 8. Further increase in pH only increases the charge in the liquid phase and reduces the potential difference between the surface and liquid, resulting in an upward trend of this curve for pH values greater than 8. The curves show a similar trend, which is not surprising, since the powders are different fractions of the same material. The major observed difference was at pH $\approx$ 8, where particles must exist as individuals, which might be due to an increased suspension effect resultant from the higher surface/volume ratio of finer particles.[25,26] This effect, due to the existence of fixed charges on the particle surfaces and to the presence of counter-ions that compensate that charge, is expected to increase with decreasing particle size. According to Chernoberezhskii,[27] the suspension effect is inversely proportional to the particle radius.

3.2 Floc size distributions

The floc size distributions (FSDs) of NF0 are shown in Fig. 2. The floc size (FS) is larger and FSD is broader at the iep where electrical double layer repulsions are absent and the van der Waals attractions dominate. Due to Brownian movements particles collide and form aggregates which grow heavy and sink. The variation of the pH away from the iep results in the development of charge on the surface of the particles, and repulsive double layer forces arise between them, reducing their collision efficiency.[28] Consequently, the FS will decrease. These results are as expected, according to the DLVO theory of colloid stability,[29,30] which is able to predict the stability of colloids in polar liquids by considering the balance between electrical double layer repulsions and van der Waals attractions.

The finest and narrowest FSD observed at pH 8 is in good agreement with epm results and was assumed as the particle size distribution (PSD) of the powder. With $\approx$83% of its particles having an equivalent spherical diameter (esd) smaller than 0·85 μm, it seems to be much finer than indicated by the manufacturer. This difference can be due to the proximity of the lower limit of Stokes range where the effect of Brownian motion becomes significant and the results given by gravimetric sedimentation will show a wider PSD than is actually present in the submicron fraction.[31] Another inaccuracy source results from the time dependence of FS which could not be evaluated with this technique. Light scattering techniques have been used to study the kinetics of Brownian coagulation.[32–34] Agrawal[34] studied the kinetics of flocculation of alumina particles in dilute suspensions and found a rapid growth in the FS at pH near the iep, whereas at pH away from the iep there was little or no growth.

3.3 Rheology

The Bingham yield stress and plastic viscosity of suspensions containing 62·5 wt% solids are reported in Fig. 3 as a function of pH. These curves show a

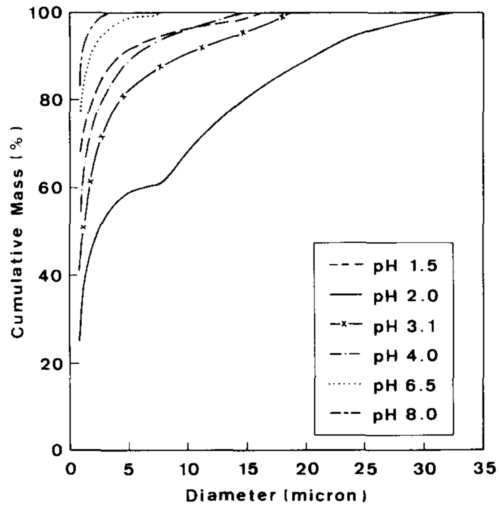

Fig. 2. The effect of pH on the floc size distributions of the finer powder, NF0.

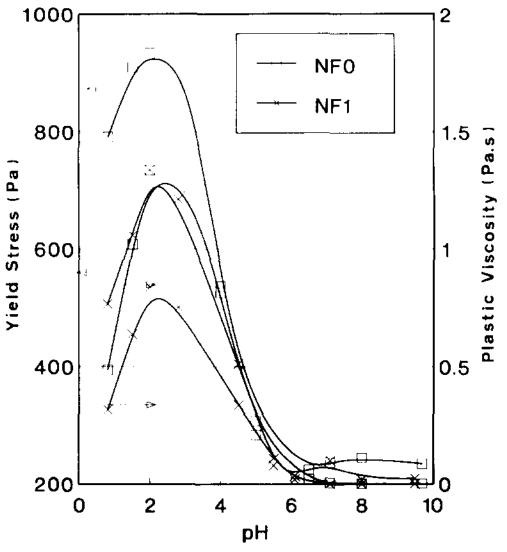

Fig. 3. The effect of pH on the yield stress and plastic viscosity (62·5 wt% solids).

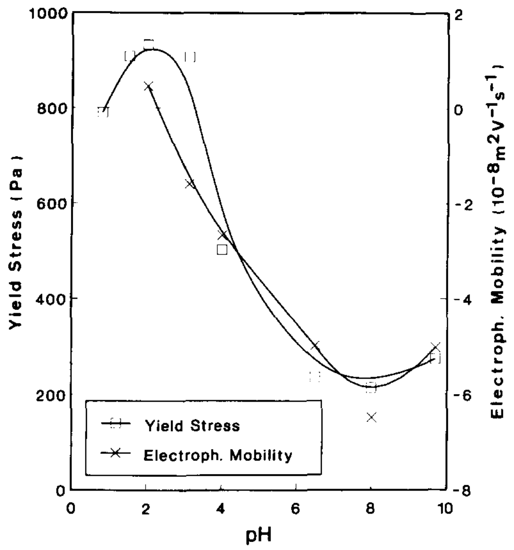

Fig. 4. Relationship between yield stress and electrophoretic mobility of the finer powder particles.

maximum at pH ≈ 2, which corresponds to the iep of the powder surfaces. As was discussed previously, flocculation promoted by van der Waals attractions will be maximum at the iep where the long-range electrostatic repulsive forces are absent and where the FS also reaches a maximum. As the pH is changed from the iep by addition of acid or base, the zeta potential will increase, the number of flocs and FS will decrease, resulting in lower viscosity and yield stress values. An increased degree of flocculation results in a larger number of flocs with lower density and higher interstitial pore space occupied by the liquid phase.[35] The amount of liquid between the flow unities is lessened and an increase in viscosity and yield stress is expected.

The comparison between the yield stress and either the electrokinetic behaviour (Fig. 4), or FS,

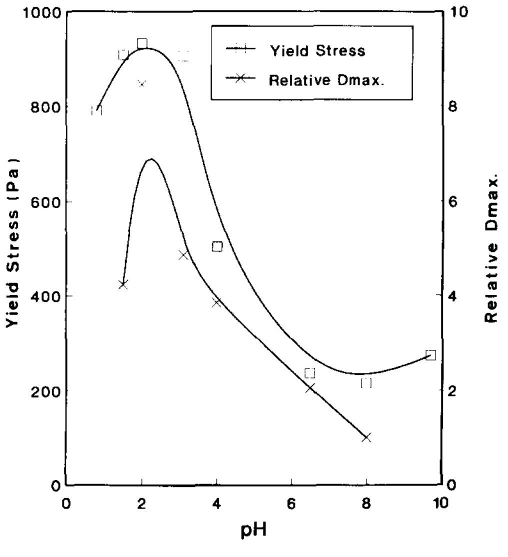

Fig. 5. Relationship between yield stress and relative maximum floc diameter.

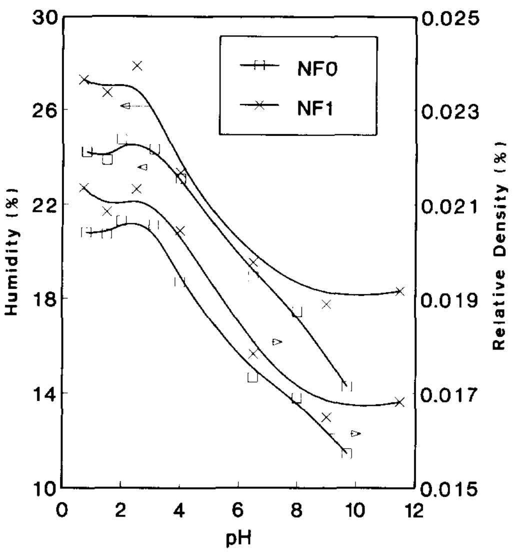

Fig. 6. The effect of pH on the green properties of the slip cast bodies for suspensions containing 62·5 wt% of each powder.

expressed as the relative maximum diameter (Relative Dmax., Fig. 5) of the NF0 suspensions, shows that they are intimately related.

The lower values of the rheological parameters presented by NF1 can be attributed to its higher particle size and lower surface area.[36]

3.4 Casting

The green density and the water content of the samples after unmoulding are presented in Fig. 6. It can be seen that the density is at a minimum at or near the iep and increases when pH is varied by addition of acid or base. In the basic region, values as high as 63·62% and 60·62% could be achieved with the finer and the coarser powders, respectively. As expected, humidity after mould release shows an inverse trend.

There are good correlations between the rheological properties of the suspensions and the electrokinetic behaviour of the dispersed particles, the size of the flow unities, and the properties of the formed bodies, and also between the green density and the water content after unmoulding. These correlations allow a good relationship to be established between the structure of particles in suspension and that of the slip cast bodies, and allow determination of the optimum degree of deflocculation.

The modification of the structure of particles in suspension by changing the pH and increasing the potential determining ion adsorbed on its surface might be the factor responsible for the greater density of the cast samples obtained from less viscous suspensions. In fact, it has been suggested[35] that increased deflocculation leads to the decrease in the number of flocs and an increase in its density. If the structure of particles in suspension is transmitted to the solid wall being formed near the surface of the mould, as proposed for clay[37,38] and oxide systems,[39] then a less porous, denser body should result, as seems to be the case.

4 Conclusions

The data and discussion in this paper enable the following conclusions to be drawn:

(1) It is possible to obtain relatively high density silicon carbide bodies by slip casting as a basis for the production of SiC ceramics.
(2) To achieve this goal, strong repulsive interparticle potentials are required, which can be controlled by suspension pH.
(3) The use of a finer powder resulted in higher density samples.
(4) There are good intercorrelations between the electrophoretic mobility, floc size, plastic viscosity and yield stress, green density and humidity after unmoulding of cast bodies.
(5) It appears that there is a good agreement between the suspension behaviour and earlier models relating the interparticle forces to the suspension rheology and elastic modulus.[35]

References

1. Broussaud, D., Wicker, A. & Magnet, J. L., Introduction of sintered α-SiC in diesel engines: Example of a French experiment. In *Brit. Ceram. Soc. Proc. of Special Ceramics*, Vol. 7, ed. D. Taylor & P. Popper. 1981, p. 19.
2. Storm, R. S., Ohnsorg, R. W. & Frechette, F. J., Fabrication of injection molded sintered alpha SiC turbine components. *J. Eng. Power*, **104** (1982) 601.
3. Carruthers, W. D. & Smyth, J. R., Ceramic component development for the AGT101 gas turbine engine. *Ceram. Eng. Sci. Proc.*, **5** (1984) 350.
4. Norton/TRW Ceramics, Rapports sur l'utilisation de céramiques dans les moteurs. *L'industrie Céramique* (821/11) (1987) 717.
5. Kawakubo, T., Hirayama, H. & Goto, A., Corrosion behavior of ceramics in 290°C pure water. *J. Soc. Mater. Sci. Jpn*, **38** (1989) 300.
6. Kraft, E. H. & Coppola, J. A., In *Ceramics for High Performance Applications—II*, ed. J. J. Burke, E. N. Lenoe & R. N. Katz. Brook Hill Publishing Co., Chestnut Hill, MA, 1978.
7. Carlström, E., Tjernlund, A. K., Hermansson, L. & Carlsson, R., Influence of powder and green compact characteristics on microstructure of sintered alpha-SiC. In *Proc. Brit. Ceram. Soc.*, ed. D. Taylor, 1983. p. 89.
8. Blanchard-Ardid, C. R. & Page, R. A., The effect of ultrasonic treatments on the particle size distributions and microstructure of a slipcast Al_2O_3. In *Ceram. Trans.*, Vol. 1-B, ed. G. L. Messing, E. R. Fuller, Jr & H. Hausner. 1988, p. 724 (and references therein).
9. Schilling, C. H. & Aksay, I. A., Gamma-ray attenuation analysis of particle structure evolution during powder consolidation. In *Ceram. Trans.*, Vol. 1-B, ed. G. L. Messing, E. R. Fuller, Jr & H. Hausner. 1988, p. 800 (and references therein).
10. Aksay, I. A., Principles of ceramic shape-forming with powder systems. In *Ceram. Trans.*, Vol. 1-B, ed. G. L. Messing, E. R. Fuller, Jr. & H. Hausner. 1988, p. 663.
11. Rado, P., Slip casting of non-clay materials. *Trans. J. Brit. Ceram. Soc.*, **73** (1974) 291.
12. Reichman, R., Method of fabrication of sintered bodies especially hollow shapes of high refractory metals. German Patent, 627980, 26 March 1936.
13. Degtyareva, E. V., Kainarskii, I. S. & Safronova, I. P., The rheological and technological properties of silicon carbide suspensions. *Ognewpory*, **27** (1974).
14. Safronova, I. P., Degtyareva, E. V. & Kainarskii, I. S., The rheological and technological properties of silicon carbide slips and castings containing added silicon and clay. *Refractories*, **16** (1975) 45.
15. Person, M. *et al.*, Steric stabilization of silicon carbide slips. In *High Tech Ceramics*, ed. P. Vincenzini. Elsevier Science Publishers, Amsterdam, 1987, p. 623.
16. Person, M., Hermansson, L. & Carlsson, R., Some aspects of slip casting of silicon nitride and silicon carbide. In *Ceramic Powders*, ed. P. Vincenzini. Elsevier Science Publishers, Amsterdam, 1983, p. 735.
17. Rogers, M. G., High-pressure slip casting of silicon carbide. In *Proc. Brit. Ceram. Res. Assoc., Special Ceramics*, Vol. 5, ed. P. Popper. 1970, p. 87.
18. Rizzo, C., De Angelis, B. A., Ferretti, R. & Howlett, S. P., Slip casting of α-silicon carbide. In Paper presented at 7th *CIMTEC*, Montecatini Terme, Italy, 1990, p. 1095.
19. Haggerty, J. S. *et al.*, Processing and properties of reaction bonded silicon nitride and silicon carbide made from laser synthesized powders. In *Ceram. Trans.*, Vol. 1-B, ed. G. L. Messing, E. R. Fuller, Jr & H. Hausner. 1988, p. 1059.
20. Okuyama, M., Garvey, G. J., Ring, T. A. & Haggerty, J. S., Dispersions of silicon carbide powders in non-aqueous solvents. *J. Am. Ceram. Soc.*, **72** (1989) 1918.
21. Ashworth, D. R., A method of determining the bulk density of ceramics. *J. Brit. Ceram. Soc.*, **6** (1969) 70.
22. Almeida, J. C. M., Sacramento, J. M. G., Correia, R. N., Fonseca, A. T. & Baptista, J. L., Dispersions and packing of mixtures of Si_3N_4 powders with SiC whiskers. In *Proc. Brit. Ceram. Proc.*, ed. R. W. Davidge & D. P. Thompson. 1990, p. 179.
23. Crimp, M. J. & Piller, R. C., Dispersions of SiC whiskers in a Si_3N_4 matrix using pH control. In *Proc. Brit. Ceram. Proc.*, ed. R. W. Davidge & D. P. Thompson. 1990, p. 199.
24. Hunter, R. J., *Zeta Potential in Colloid Science. Principles and Applications.* Academic Press, London, 1981.
25. Wiegner, G., Über Wasserstoff- und Hydroxylionen in den Ionenschwärmen um suspendierte Teilchen und dispergierte Ultramikronen. *Kolloid Z.*, **51** (1930) 49.
26. Pallman, H., Die Wasserstoffaktivität in Dispersionen und Kolloiddispersen Systemen. *Kolloid Beih.*, **30** (1930) 334.
27. Chernoberezhskii, Yu. M., The suspension effect. In *Surface and Colloid Sciences*, Vol. 12, ed. E. Matijevic. Plenum Press, New York and London, 1982, p. 359.
28. François, R. J., Growth kinetics of hydroxide flocs. *J. Am. Water Work Assoc.*, **80** (1988) 92.
29. Derjaguin, B. V. & Landau, L. D., Theory of stability of highly charged lyophobic sols and adhesion of highly charged particles in solutions of electrolytes, *Acta Physicochim., URSS*, **14** (1941) 633.
30. Verwey, J. W. & Overbeek, J. Th. G., *Theory of Stability of Lyophobic Colloids.* Elsevier Science Publishers, Amsterdam, 1948.
31. Cooper, J. J., Particle size measurements. *Ceram. Eng. Sci. Proc.*, **12** (1991) 133.

32. Bowen, M. S., Broide, M. L. & Cohen, R. J., Temporal evolution of the cluster size distribution during Brownian coagulation. *J. Coll. Interf. Sci.*, **105** (1985) 617.
33. Higashitani, K., Kondo, M. & Hatade, S., Effect of particle size on the coagulation rate of ultrafine colloidal particles. *J. Coll. Interf. Sci.*, **142** (1991) 204.
34. Agrawal, D. C., Characterization of dilute ceramic suspensions by photon correlation spectroscopy. *Trans. Ind. Ceram. Soc.*, **47** (1988) 97.
35. Firth, B., Flow properties of coagulated colloidal suspensions. II. Experimental properties of the flow curve parameters. *J. Coll. Interf. Sci.*, **57** (1976) 257.
36. Nienburg, H., Stein, P., Harbach, F. & Boveri, B., Wet chemical forming and characterization of α-alumina ceramics. In *Ceram. Trans.*, Vol. 1-B, ed. G. L. Messing, E. R. Fuller, Jr & H. Hausner. 1988, p. 741.
37. Diz, H. M. M., A influência das characteristicas des moldes de gesso e das suspensões no processo de enchimento por barbotina. *Rev. Soc. Port. Ceram. Vidr.*, **3** (1984) 45.
38. Li Jiaju & Rand, B., Porosity and relative permeability of clay casts determined by application of filtration theory to slip casting kinetics. *Trans. Brit. Ceram. Soc.*, **83** (1984) 186.
39. Diz, H. M. M. & 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 & D. Taylor. 1986, p. 159.