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Pressure Filtration of Si_3N_4

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Abstract

Pressure filtration is receiving increasing scientific and technological interest as a promising forming technique in the field of technical oxide and non-oxide ceramics. In this study various aspects of pressure slip casting of Si_3N_4 *were examined; in particular, slip behaviour, casting curves at different pressures (up to 10 MPa) and physical and microstructural characteristics of pressureless-sintered cast bodies. The rheological parameters of silicon nitride slips containing up to 6 wt% of yttria and alumina as sintering aids have been optimized for a high solids loading of 36 vol%. Pressure-cast samples reach a density of 56·7% of theoretical, while sintering at a temperature of 1750°C under nitrogen flow results in a density higher than 96% of theoretical. The microstructure of the samples was characterized by high homogeneity, confirming the auspices expected from the studied forming technique. © 1996 Elsevier Science Limited.*

1 Introduction

Non-oxide ceramics are of great interest for structural and heat engine applications due to their excellent thermomechanical properties. However, their controlled production on a large scale has still important limitations owing to the lack of reliability of the final products. For this reason, colloidal forming methods have undergone a long period of development to enhance the reproducibility of the products.

In this context, pressure slip casting is increasingly being considered as a production method for the large-scale fabrication of complex-shaped ceramics.[1,2] From a technological point of view, thickness control in pressure casting is one of the most critical parameters to be taken into account. It has been proved that a high casting rate is easily achievable in this process, but much more research must be done in relation to the process parameters, such as the effect of applied pressure on the wall formation rate and on the characteristics of the green and the sintered bodies.

The aim of this work was to study the kinetics of pressure casting of silicon nitride slips as a function of the applied pressure, as well as the density and microstructural properties of the materials obtained. Slip casting was also conducted as a reference for this study.

2 Experimental

The following starting powders were used in this work:

(1) α-Silicon nitride (Hermann C. Stark, Germany), with a mean particle size (d_{50}) of 0·8 μm and a specific surface area (S_s) of 18 $m^2\ g^{-1}$.
(2) Yttrium oxide (Mandoval, UK), high purity with d_{50} = 3·5 μm and S_s = 6·9 $m^2\ g^{-1}$.
(3) Aluminium oxide (Condea HPA 05, Germany), high purity, d_{50} = 0·4 μm and S_s = 9·5 $m^2\ g^{-1}$.

On the basis of preliminary experiments,[3,4] the rheological behaviour of pure Si_3N_4 slips has been studied as well as the effect of oxide additives on the flow curves. In this work pure Si_3N_4 is denoted as SN1, while silicon nitride with 3 wt% Y_2O_3 and 3 wt% Al_2O_3 is denoted SN2. In all cases the slips were deflocculated with tetramethylammonium hydroxide (TMAH) and the solid content of the slips was 65 wt% (i.e. 36·9 vol% for SN1 and 36·4 vol% for SN2). The slips were homogenized in a rotating plastic bottle with nylon balls for 24 h. The effects of pH and mixing time on the rheological behaviour have been followed.

The rheological measurements were performed with a rotational viscometer (Haake, model Rotovisco RV20, Germany) at a constant temperature of 25°C. Pressure casting experiments were

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done using a laboratory press (Gabbrielli, Italy) equipped with displacement and pressure transducers and computerized data acquisition system. The pressures of 1·7, 3·4, 6·3 and 10·8 MPa were selected. Slip casting experiments on gypsum were also performed for comparison purposes.

The green densities of the cast bodies were measured by Archimedes' method in mercury. The silicon nitride samples were sintered at 1750°C/2h under a flow of nitrogen. The sintered sample surfaces were examined by optical microscopy on polished areas. The final density was measured by the immersion method in water.

3 Results and Discussion

According to the isoelectric points of Si_3N_4 (occurring at pH = 8[5]) and of the additives (up to pH = 10 for yttria), basic pH conditions are required to prepare a well-dispersed slip. The rheological behaviour of Si_3N_4 aqueous slips is strongly influenced by the pH. Acidic pH is not useful since, at pH values lower than the corresponding isoelectric point, the formation of protonated species such as $SiOH_2^+$ and $Si_2NH_2^+$ is promoted[6,7] and higher surface oxidation of the silicon nitride takes place. In the basic range of pH it has been found that very slight pH variations result in large differences in the viscosity values and in the model applicable to the flow curve. Thus, the pH is a main factor to be controlled.

In order to prepare Si_3N_4 slips with high solids content, different dispersants were taken into consideration. Tetramethylammonium hydroxide was the one chosen because this is the only one allowing the preparation of low viscosity slips with up to 70 wt% solids. However, to provide better rheological control, all the slips studied in this work were prepared with a solids content of 65 wt%.

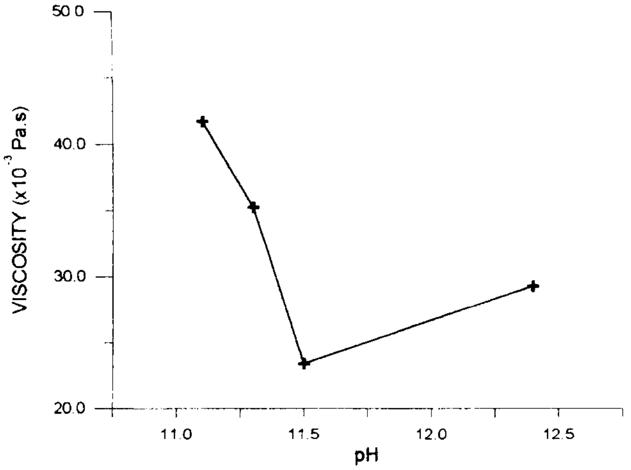

Fig. 1. Effect of pH on the viscosity of Si_3N_4 slips (at 500 s^{-1}).

Figure 1 shows the variation of the apparent viscosity (at a shear rate of 500 s^{-1}) with pH for basic conditions. As observed, the pH must be at least 11·3 since even at a slightly lower value, such as 11·0, the viscosity increases and a time dependence also appears. For this reason all the slips were prepared at the same pH value of 11·3 ± 0·1 in order to ensure consistent rheological properties.

As pointed out before,[5] the addition of sintering additives does not modify the rheological behaviour of the slips, since their content is relatively low. Thus it has been observed that the variation of viscosity versus pH or mixing time is similar for compositions SN1 and SN2. Homogenization of both slips requires some time to reach equilibrium conditions at the particle surfaces. It has been observed that a minimum viscosity is obtained after a mixing time of 24 h. Further mixing times tend to increase the viscosity values slightly. The variation of viscosity as a function of the homogenizing time is presented in Fig. 2.

Figure 3 shows the casting rate curves of composition SN2 obtained by slip casting and pressure casting (at a pressure of 6·3 MPa). Slip casting experiments show that the casting rate decreases when sintering additives are present in the slip. It is important to note that high cast thicknesses cannot be achieved by slip casting on plaster moulds: the SN2 slip produces a cast thickness of 4 mm after about 1000 s, but after this point increased casting time does not increase the thickness significantly. The pressure casting rate is much higher than that corresponding to slip casting, reducing the shaping time by up to one order of magnitude.

The thickness formation rate in pressure casting depends directly on the applied pressure. Figure 4 shows the thickness growth, after reaching the constant pressure, of SN2 slips at different applied

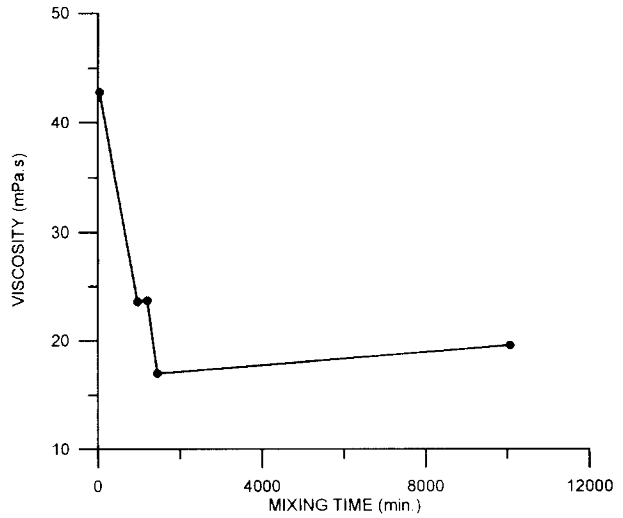

Fig. 2. Effect of mixing time on the viscosity of Si_3N_4 slips (at 500 s^{-1}).

pressures ranging from 1·7 to 10·8 MPa. As observed, the cast thickness increases with pressure for a certain casting time. Nevertheless, another factor to be considered in any casting process, is the formation of the first layer of the cake. In uniaxial pressure filtration this step involves the time needed to increase the pressure from zero to the constant pressure filtration value. In this zone of increasing pressure, it is difficult to control the growth of the first layer of the cake. Figure 5 shows the cast thickness versus casting time of SN2 slips for selected pressures. It is important to note that, disregarding the applied pressure, the first layer of cake has the same thickness (about 1·5 mm) but

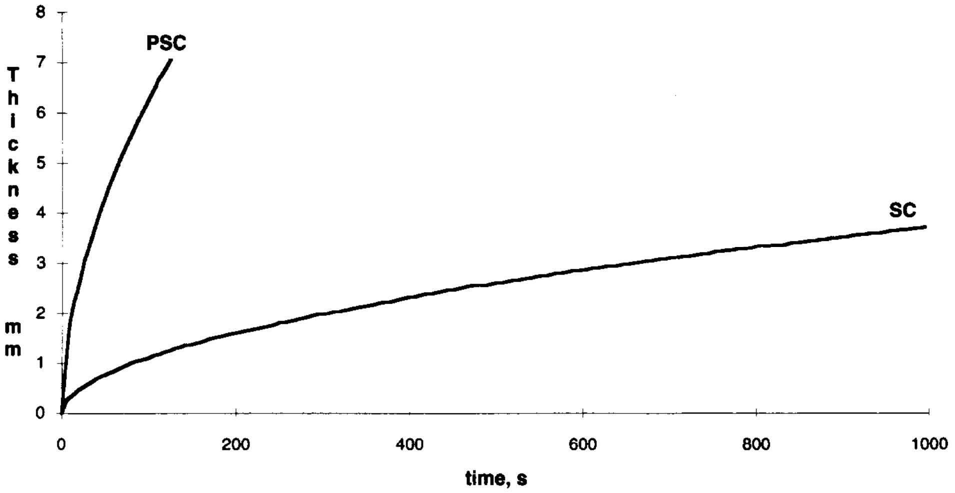

Fig. 3. Casting rate curves of SN2 compositions by pressure casting at 6·3 MPa (PSC) and slip casting (SC).

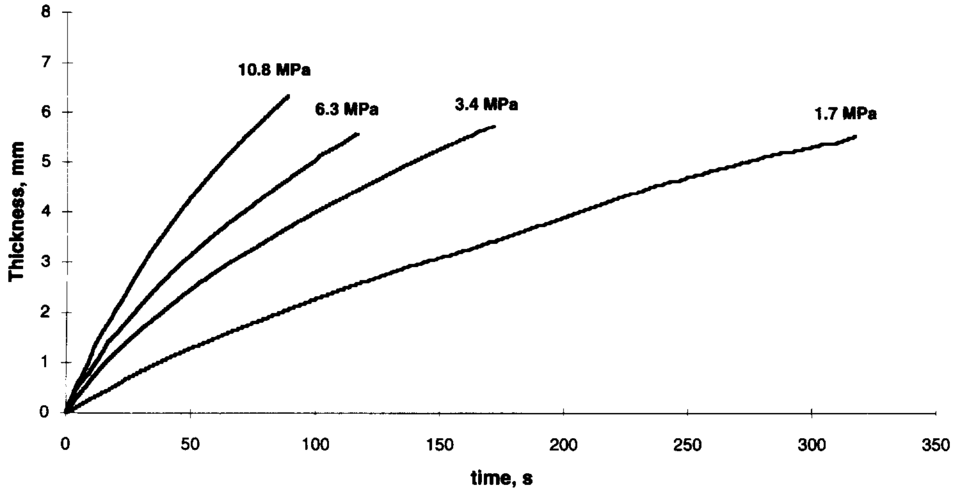

Fig. 4. Pressure casting curves of SN2 compositions at different pressure values after reaching the final constant pressure.

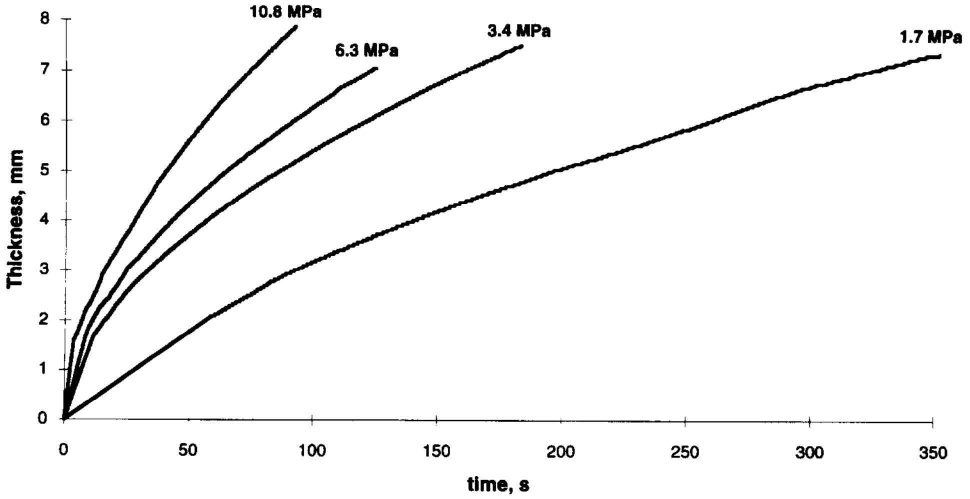

Fig. 5. Total thickness formation rate of SN2 compositions at different pressures.

requires decreasing times to be formed when the pressure increases. This result indicates that, if high thicknesses are required, the casting kinetics depends strongly on the pressure rather than on the characteristics of the cake formed at the first step. All these curves were obtained by pressing slips adjusted to a pH = 11·3, since a slight pH variation strongly modifies the casting curve.

According to these results it is possible to control the casting kinetics, depending on the production requirements, by changing the applied pressure. A cast body of 5 mm is obtained at 1·7 MPa after 300 s, while at 10·8 MPa the same thickness can be obtained after only 70 s.

The green densities of both slip-cast and pressure-cast SN2 bodies at different pressures are given in Table 1. Slip casting gives a slightly higher green density than pressure casting since there is more time, allowing closer packing through rearrangement of the particles. In the pressure-cast samples a similar green density is obtained irrespective of the applied pressure. This is an important result, since a large increase in the casting rate and hence in the shaping cycle does not decrease either the properties of the final product or the process control. Furthermore, after sintering at 1750°C, all the slip- and pressure-cast samples have a similar density of 3·10 to 3·12 g cm^{-3} for SN2 composition. The sintered density depends only on the composition and is strongly influenced by the heating conditions (temperature, time, atmosphere, sintering bed, etc).

Although differences in the density have not been detected, the microstructures of the cast samples obtained at different pressures show some peculiarities. The microstructure obtained by optical light microscopy reveals that some segregation of precipitates takes place towards the surface. This fact can be due to two different effects: the possible instability of the oxide additives in the slip or diffusion of the additives during sintering. Further work will be required to determine the possible influence of the process parameters in this segregation effect. The formation of bright precipitates can be observed in the outer part, whereas in the centre of the sintered samples there are no precipitates. In the zones in which precipitation of secondary phases takes place the number of pores is reduced, but the pore size is higher than in the centre of the sample. Figure 6 shows the microstructures corresponding to the centre and one external surface of a pressure-cast sample obtained at 3·4 MPa. The samples have been cut from the cast body at mid-height in the direction perpendicular to the pressing direction.

Table 1. Green and sintered densities (in g cm^{-3}) of slip- and pressure-cast SN2 bodies

	Slip casting	*Pressure casting*			
		1·7 MPa	*3·4 MPa*	*6·8 MPa*	*10·2 MPa*
Green	1·91	1·83	1·80	1·83	1·81
Sintered	3·12	3·10	3·12	3·12	3·10

On the other hand, it can be seen that there is a variation in the pore size distribution with applied pressure: the higher the pressure, the lower is the pore size. Figure 7 shows three micrographs corresponding to the core of samples obtained by pressure casting at 3·4, 6·3 and 10·8 MPa.

According to these results, it seems that there is a barrier to the possible segregation of precipitates since at high pressures the process is much more accelerated. There is a clear diffusion process of the sintering additives to the sample surfaces during sintering which decreases if the forming rate increases. Consequently, higher casting pressures result in higher homogeneity of the sintered compact.

4 Conclusions

The rheology of silicon nitride slips is strongly dependent on pH, which must be controlled within

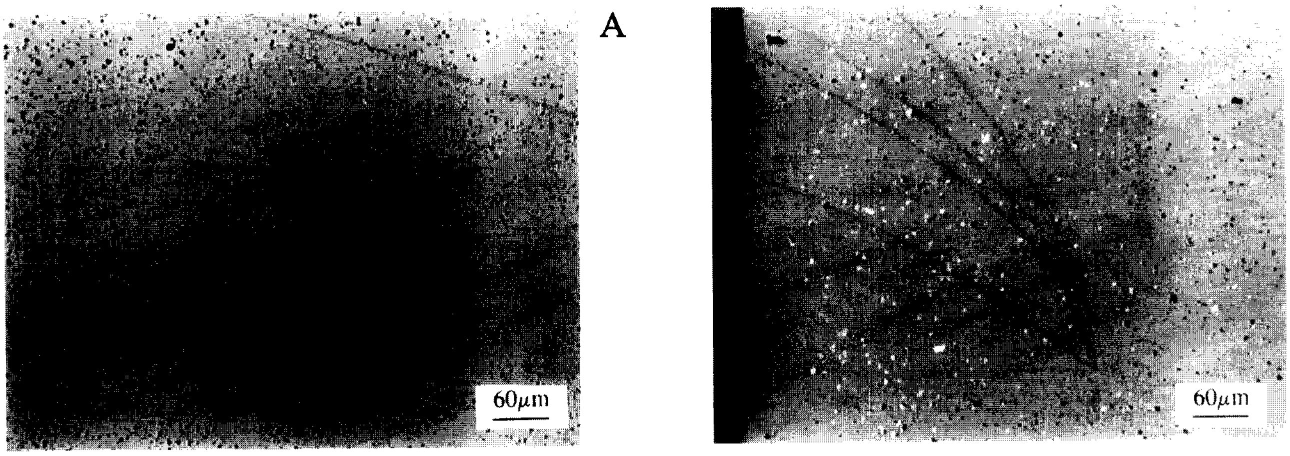

Fig. 6. Optical microstructure of SN2 pressure-cast samples: (A) centre of the sample; (B) surface of the sample.

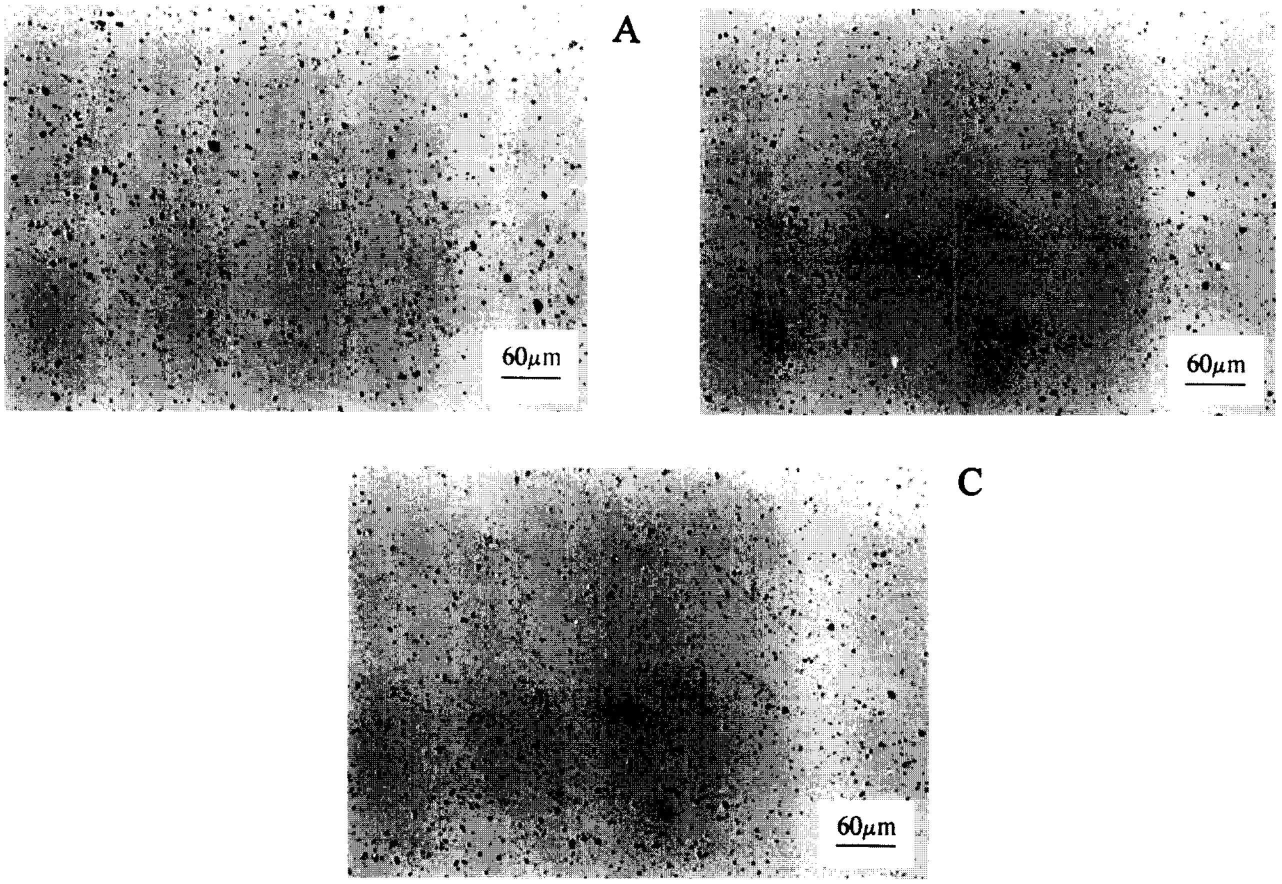

Fig. 7. Optical microstructure of the centre of SN2 pressure-cast samples obtained at 3·4 MPa (A), 6·3 MPa (B) and 10·8 MPa (C).

a narrow margin. No variations in the rheological behaviour have been detected for slips containing up to 12 wt% of oxide additives. A prolonged homogenizing time (24 h) is required to ensure good stability in the slip.

Pressure casting allows thick cast bodies to be obtained within relatively short casting times. The applied pressure strongly affects the casting rates. However, in the range of pressure conditions studied here, no differences in both the green and the sintered densities were found. Microstructural observations reveal the formation of precipitates in the surface of the samples after sintering.

Acknowledgements

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