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Forming processes of strontium barium niobate ceramics

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In forming strontium barium niobate (SBN) ceramics, two methods (pressure filtration and slip casting) were employed to investigate the consolidation behaviour. The zeta potentials were measured to understand the interparticle forces of SBN powders. It was found that the zeta potentials of SBN powders were negative above pH 2.2. Several experiments have been conducted to investigate the effect of pH on the rheological behaviour of SBN slurries with 20 vol% solids loading. The rheological behaviour of the slurries SBN with 20 vol% solids loading at pH 11.5 is shear thinning. It is suggested that the increase of the flow rate of the fluid might have the advantages to enhance the packing density and prevent fine particles from clogging in pressure filtration and slip casting. Two different moulds i.e. plaster and alumina have been used to investigate the effect of pore morphology of the moulds on the cake microstructures. A uniform microstructure of cast cake was formed for using an alumina mould and significant contamination was observed in using a plaster mould.

1. Introduction

Strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ ($0.25 < x < 0.75$) has a tungsten bronze type of structure [1] and its physical properties vary with its composition [2, 3]. The solid solutions are of importance in many technological applications such as electro-optic [4, 5], pyroelectric [3, 6], piezoelectric [7] and photorefractive devices [8, 9].

Single crystals of varying chemical compositions of strontium barium niobate (SBN) have been extensively studied [1, 3–6, 10–15]. However, there are still several restrictions in their applications; therefore, ceramic SBN has received attention because of the advantages of ease of fabrication, large size, complex shape and stress resistance. For optical applications, ceramics should be manufactured to achieve nearly theoretical density.

Colloidal methods have been considered to have the potential to produce more reliable ceramic materials and offer the possibility of producing complex shapes. Agglomeration could be avoided by directly casting into a shape from the slurry state (i.e. without drying first) and this mitigates the formation of large pores. Pressure filtration [16–19] and slip casting [20–24] have recently received a lot of attention. They are essentially similar and differ only in the way of dewatering, i.e. the removal of the liquid from the slurry is achieved for pressure filtration by applying an external pressure and for slip casting by the capillary force.

These two methods have been intensively studied but it was found that mass segregation and fine-particle clogging could be adverse to the packing density and microstructure of the cakes [18, 25]. In this paper, the effects of pressure filtration with and without drains (Fig. 1) and pore morphology of the moulds on the green structures of cakes of SBN were investigated. (Note that "drains" refer to the placement of tissue under the filter medium to adsorb the water similar to in the casting mould).

2. Experimental procedure

High purity powders $SrCO_3^*$, $BaCO_3^\dagger$, and $Nb_2O_5^\ddagger$ in a molar ratio of 1 : 1 : 2 were mixed in a jar made of Nylon 6 for 24 h. After mixing, the mixed powders were dried and calcined at 1150 °C for 4 h to form a single-phase SBN50. Slurries containing 20 and 33% volume fraction SBN50 powders were prepared to investigate the optimal grinding efficiency.

Slurries containing 20 vol% SBN50 powders were used for the studies of the rheological behaviour as well as consolidation. Microelectrophoretic mobility and the viscosity of SBN50 powders as a function of pH were measured using zeta meter and a viscometer. Analytical grade HNO_3 and NH_4OH solutions were used for pH adjustments. On the basis of the results of zeta potential and viscosity at different pH (Figs 2 and 3), the slurries at pH 11.5 could be considered to be well dispersed. The dispersed slurries at pH 11.5 have been used to study the rheological behaviour i.e. viscosity versus shear rate and consolidation using two methods: pressure filtration and slip casting. The pressure filtration design is shown schematically in Fig. 1, in which the filter medium with the drains was used to investigate the influence of the residual fluid and fluid

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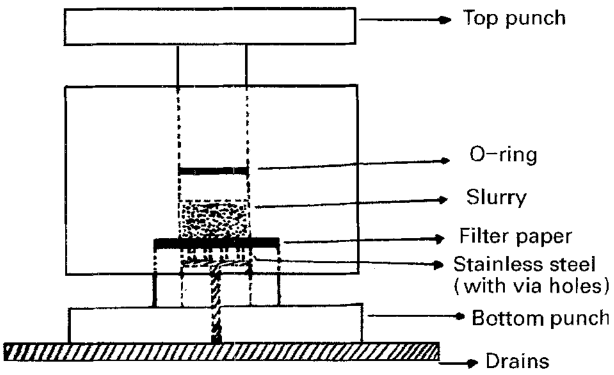

Figure 1 Schematic diagram of the pressure filtration device with drains.

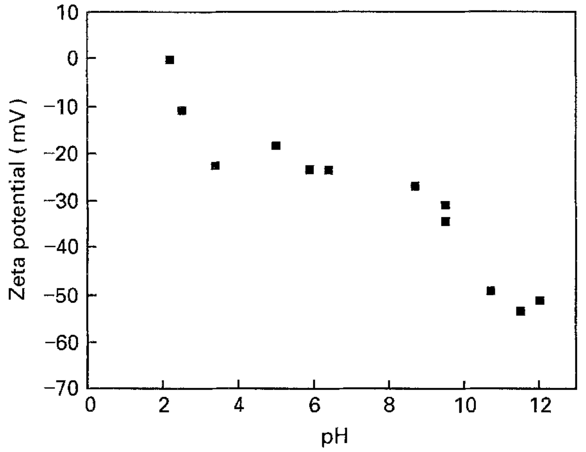

Figure 2 The effect of pH on the zeta potentials of the SBN powders.

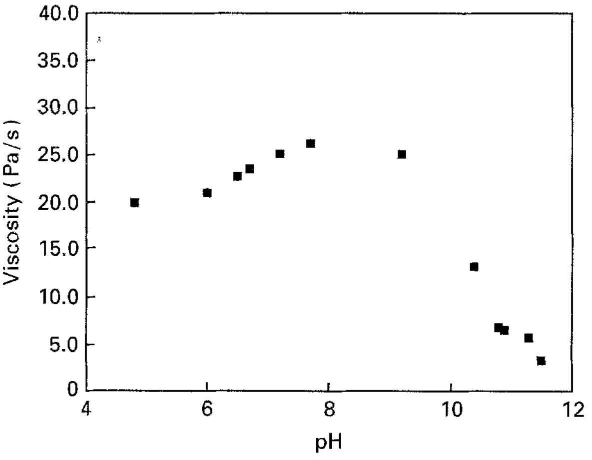

Figure 3 The effect of pH on the rheology behaviour of the SBN slurry with 20 vol % solids loading at shear rate of 76.8 s^{-1}.

flow on the cake microstructures. Two kinds of moulds, plaster and alumina, were selected to investigate the pore morphology of the moulds on the casting time and cake microstructures during slip casting. The slip-casting process was analysed in one dimension. The plaster mould was cast in a plaster/water ratio of 1, and the alumina mould was prepared by sintering a cast alumina plate at 1000 °C without soaking.

X-ray diffraction was used to examine the phases of the calcined powders and sintered bodies. The densities of the bodies formed by pressure filtration or slip casting were measured by the geometrical method. Mercury intrusion porosimetry was used to characterize pore morphology. Scanning electron microscopy (SEM) was employed to examine the microstructures of the green and sintered bodies. Energy dispersive spectroscopy (EDS) was employed to detect the contamination of the cast cakes.

3. Results and discussion

3.1. The effect of milling on the particle morphology of SBN ceramics

The formation mechanism of SBN has been proposed in a previous work [26]. It was found that the calcination conditions for completely forming a single-phase SBN were 1150 °C for 2 h. However, the particles were heavily aggregated and had a broad distribution. Therefore, wet milling has been conducted to reduce the particle size and aggregation. The influence of the physicochemical environment on wet milling has been critically reviewed [27]. While there is no unique relationship between viscosity and efficiency of grinding, it was shown [27] that decrease of suspension viscosity and degree of flocculation might enhance the reduction of the particle size during wet milling. In this study, two different solids loading of slurries have been selected to investigate their effect on the particle size reduction for different milling times. Fig. 4 shows that particles have been substantially reduced within 5 h of milling for these two slurries. For the slurry with 20 vol % solids loading, the particle size was still reduced for milling times longer than 15 h, but for the slurry with 33 vol % solids loading, the particle size was not reduced, apparently, for milling times longer than 5 h.

Viscosity of slurry increases with increase of the solids loading and it has been shown [27] that the viscosity decreases with increase in milling time, but in general, viscosity seems not to be decreased significantly for milling times longer than 5 h. Therefore, while the ineffective particle size reduction might not be caused by the viscosity *per se*, it was found that because of too high a viscosity, more powder accumulated at the place in the jar where the balls could not collide, which in turn reduces the grinding efficiency. As observed in Fig. 4, the particle size was not reduced significantly for milling times longer than 15 h, therefore, in order to reduce the contamination during the comminution process, a milling time of 15 h was selected for the wet milling process in this study. Fig. 5 shows the SEM observation of the particle morphology of the slurry with 20 vol % solids loading milled for 15 h. As can be seen in the figure, part of the particles are still heavily aggregated and the distribution seems to be bimodal.

3.2. Rheology of slurry (or slip)

The flocculated concentration has a great influence on the packing of a slurry. Thus, it is important to understand the interparticle forces of colloidal suspensions.

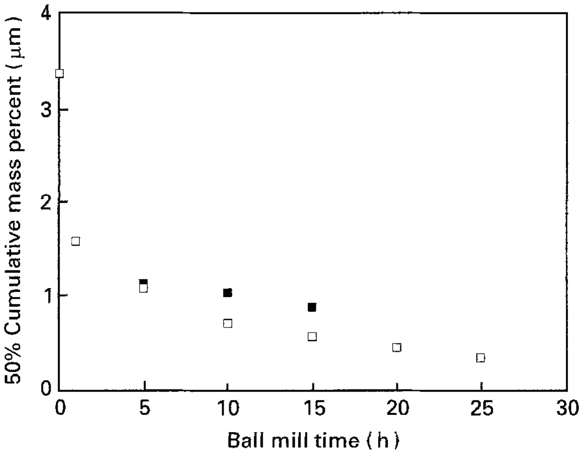

Figure 4 The effect of milling time on the particle size during wet milling with different solids loadings; (a) 22 vol % (□); (b) 33 vol % (■).

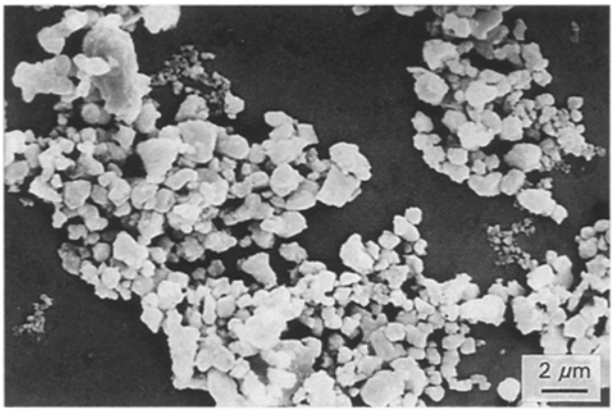

Figure 5 SEM observations of the particle morphology of the slurry with 20 vol % solids loading milled for 15 h.

3.2.1. Zeta potentials of SBN50 powders at different pH values

Fig. 2 shows the effect of pH on the zeta potential of dilute SBN50 suspensions. As can be seen in Fig. 2, the zeta potentials are all negative above pH 2.2; pH 2.2 is the point of zero charge (PZC) for the SBN powders studied. The zeta potential of the SBN powders became more negative in the range of pH values from 2.2 to 3.5 and pH > 9 but remained constant from pH 3.5 to pH 9. These data suggest that when the pH is > 11, where the zeta potentials are around -50 mV, the suspensions are stable and the particles possess the largest repulsive interparticle forces.

3.2.2. Rheological behaviour of SBN50 slurries

As discussed in Section 1, the slurry of 20 vol % solids loading has better grinding efficiency and was selected for the study of rheology behaviour. Fig. 3 shows the effect of pH on the slurry viscosity at a shear rate of 76.8 s^{-1}. As observed in the figure, when the pH is between 4 and 9, the viscosity of the slurry is essentially constant. The slightly increased viscosity might arise from the dilution of the slurry concentration by adding HNO_3 to adjust pH because the pH of SBN slurry is 9.2. When pH > 9, the viscosity of the slurry reduces sharply. This behaviour is consistent with that of the zeta potential, thus, the decrease of the slurry viscosity at pH > 9 would be attributed to the deflocculation of the particles because of the repulsive forces. Fig. 6 shows the viscosity versus shear rate curve for the SBN50 slurries at pH 11.5. As can be seen in the figure, the rheological behaviour of the slurry was shear thinning at all shear rates. It has been pointed out [28] that shear thinning can be a characteristic of a flocculated slurry because liquid is immobilized in the interparticulate void space of the flocs and floc networks at low shear rates, but flocs and floc networks would be broken down and the entrapped liquid is released with increasing shear rate. This suggests that the slurry of SBN50 powders at pH 11.5 might be not fully deflocculated.

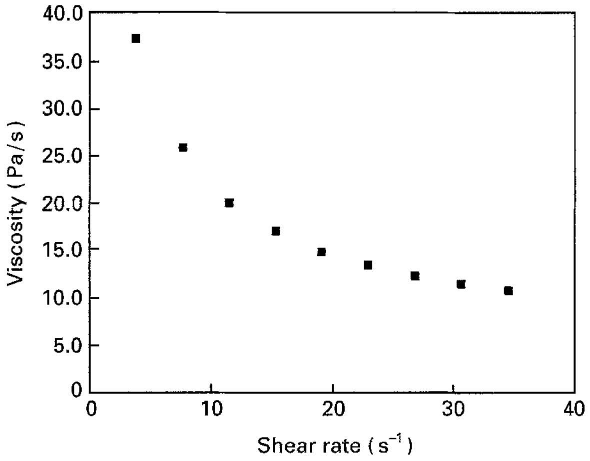

Figure 6 Viscosity versus shear rate curve of the SBN slurry with 20 vol % solids loading at pH 11.5.

3.2.3. Pressure filtration of SBN50 slurries

It has been reported [17] that the packing density of the dispersed slurry is independent of applied pressure, but flocculated slurries show a pressure dependence of particle packing. Moreover, it was also shown [16] that upon unloading, fluid might re-enter the consolidated body and cause its expansion, which could promote crack extension. As mentioned in Section 2, although the slurry of SBN50 powders is not highly dispersed, they can still be considered to be well dispersed. Fig. 7 shows the compaction behaviour of SBN50 slurry with and without the drains during pressure filtration. As can be seen in this figure, when the pressure < 100 MPa, the compaction appeared to be pressure independent, but when the pressure was in the range 100–170 MPa, green density increases rapidly with increasing pressure. The latter seems to be related to the fracture of the aggregates leading to continued sliding and rearrangement similar to the index of the fracture stress of the particle in compacting dry powders. At pressures higher than 170 MPa, the green density ceases to increase. However, it is quite interesting to understand the reasons why the

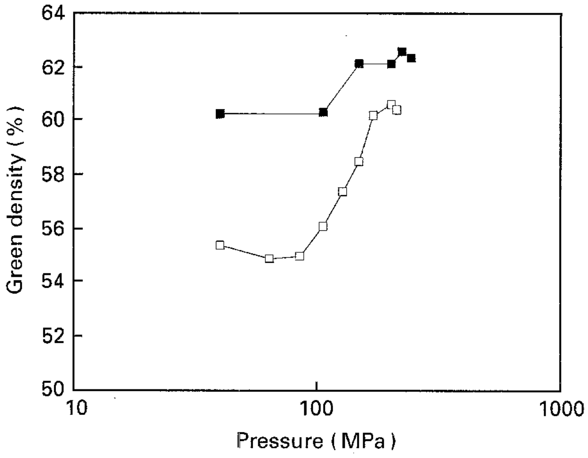

Figure 7 Green density of the SBN slurry with 20 vol % solids loading by filtration at different applied pressures with (■) and without (□) drains.

green density increases more for the filtration with the drains. It was found that the bottom layer of the consolidated bodies seem to be wet and soft when compacted without the drains. This phenomenon might be related to the fluid re-enter as reported by Lange and Miller [16]. When the consolidated bodies were sintered the density variation was quite apparent as shown in Fig. 8. The bottom layer of the sintered body seems not to be densified.

While the fluid re-enter might cause the flaws at the bottom layer of the consolidated layer, the density variation should be developed by another factor. It should be pointed out that because the applied pressures were > 60 MPa, it seems that at this stage, the top punch should have met the consolidated layer. Therefore, the gradient in the net pressure might dissipate to the applied pressure [17]. However, inferring from the pressure independence, the difference of the green densities for filtration with and without drains could have developed before the top punch met the consolidated layer. In general, the resistance of the filter medium is negligible. However, in this study, the resistance of the filter medium (filter paper and stainless steel mesh) seems to be significant because higher applied pressure is needed. Thus, the system with drains could increase the permeability of the filter medium, which in turn would increase the flow rate. The flowing liquid would exert a cumulative drag on the cake resulting in a compressive pressure on the particles [24] and enhance the sliding and rearrangement of the particle packing at the consolidated layer, which would increase the packing density. This suggestion was also supported by the change of the mould during slip casting (see Section 3.2.4.). It should be noted that this case is different from the flocculated slurry with a faster filtration rate due to the density gradient in the consolidating layer. While the drains could increase the green density, the clogging of fine particles in the cake bottom using such a broad particle distribution can not be dismissed. As observed in Fig. 9, many fine particles fill the pores between the larger particles at the bottom layer of the cake.

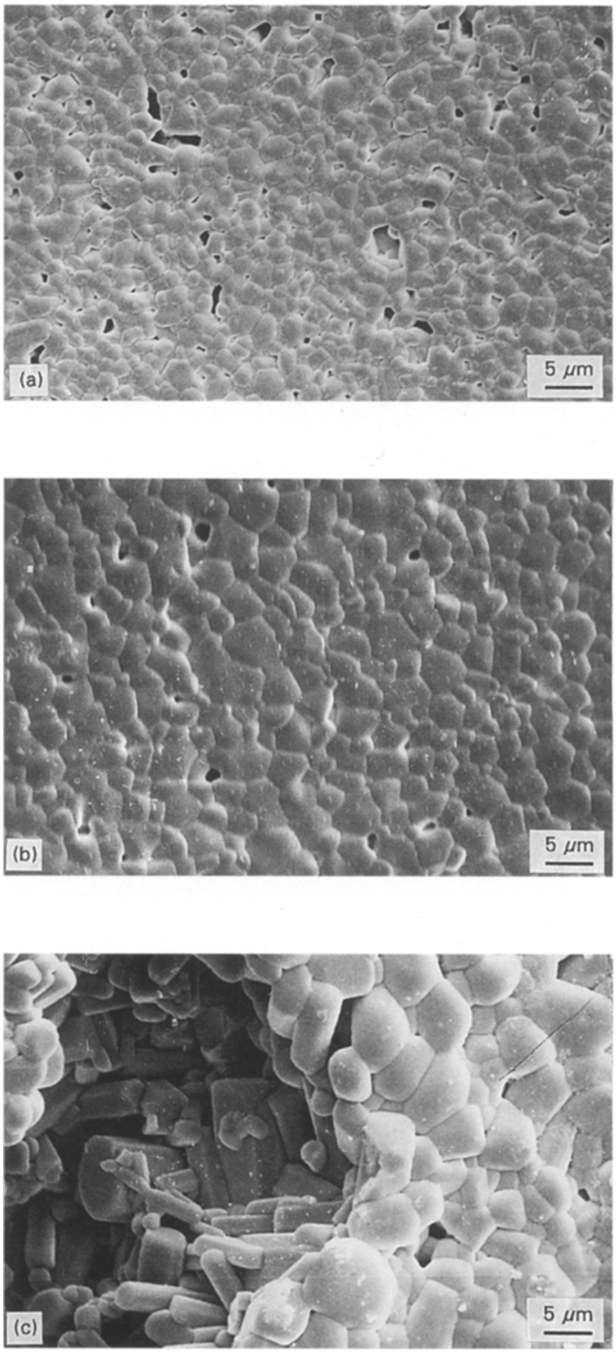

Figure 8 SEM observations of the sintered body whose green body was pressure-filtrated without drains; (a) upper layer; (b) middle layer; (c) bottom layer.

3.2.4. Slip casting of SBN50 slips

The dewatering of the slip casting is due to the capillary action of the pores in the mould. Moreover, it has been reported [21] that the mould permeability would be proportional to the square of the pore diameter. Thus, the suction pressure and permeability should be related to the mould density. However, it was shown [23] that the mould density has no effect on the proportionality constant $F (F = L^2/t)$ and green density of the cake. In this study, it was found that the pore morphology of the mould had a significant influence on the cake density and microstructure. Fig. 10 shows the surface microstructures and pore size distributions of plaster and alumina moulds. As can be seen

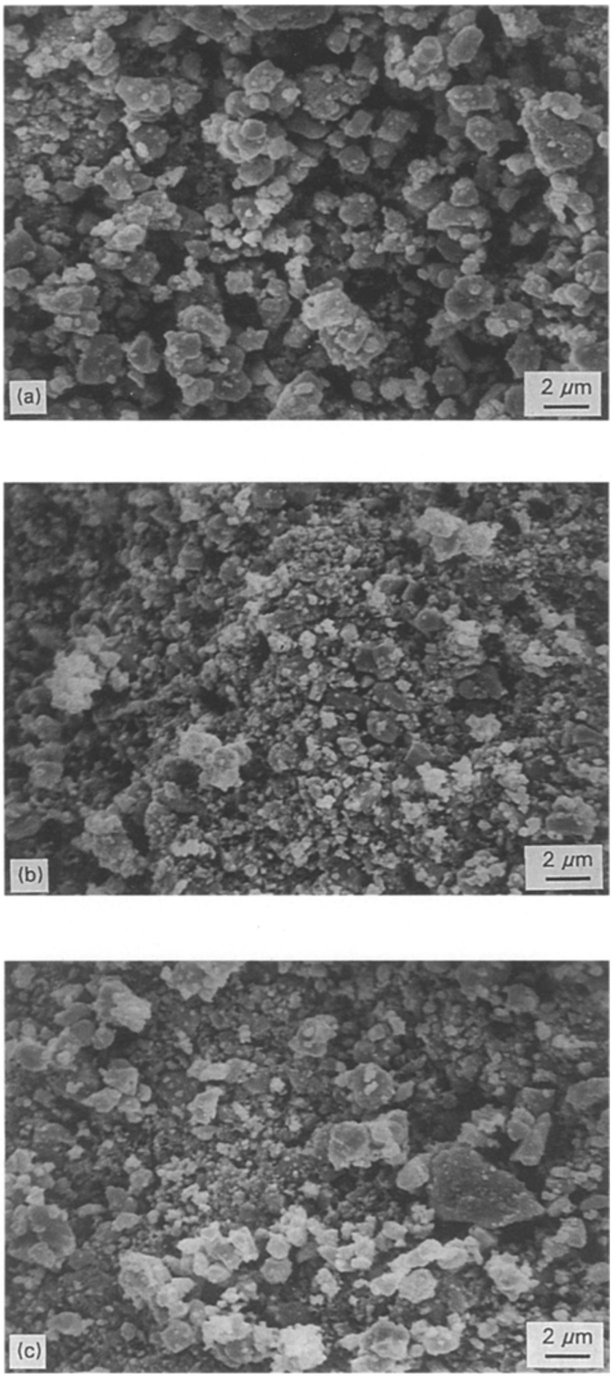

Figure 9 The SEM observations of the green body by pressure filtration with drains; (a) upper layer; (b) middle layer; (c) bottom layer.

in the figure, the surface of the plaster mould is rough and has a lot of large pores and its distribution is bimodal but that of the alumina mould is smooth and has uniform fine spores. The median pore diameter and porosity are 2.023 μm and 41.2% for the plaster mould and 0.0575 μm and 37.62% for the alumina mould, respectively. It was observed that the casting time of a cake using an alumina mould is half that using a plaster mould, as might be expected from the higher suction pressure. Moreover, most cast cakes formed using a plaster mould were laminated because the density variation is quite significant. The green density of the upper layer of the cake is about 46.6% of the theoretical density and that of the bottom layer

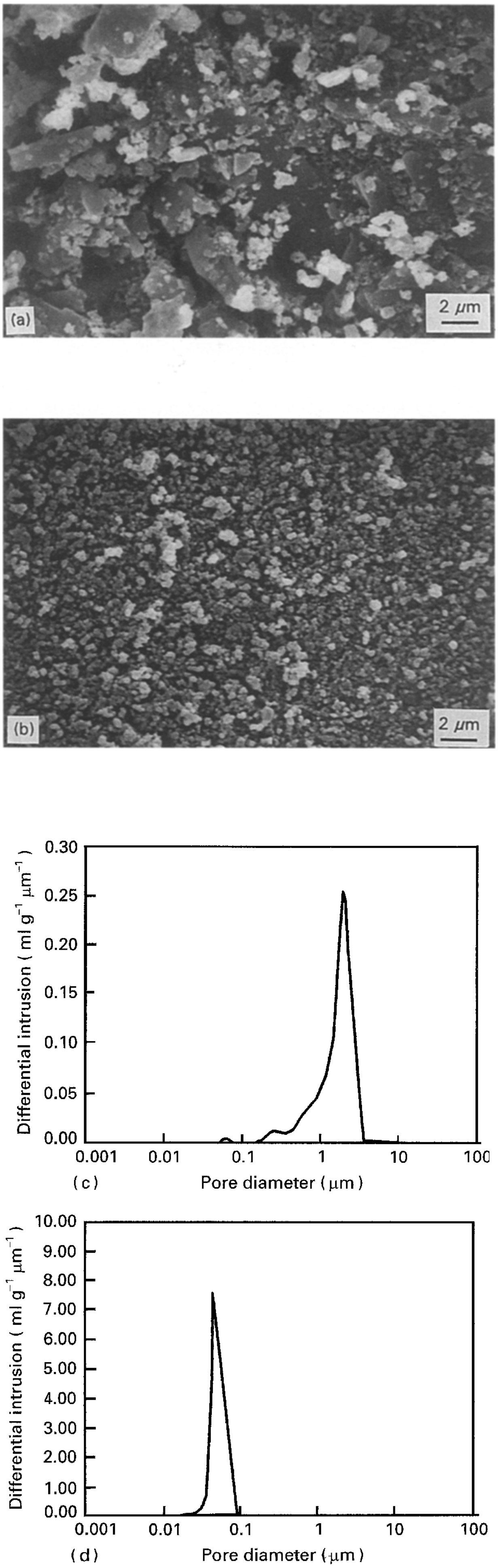

Figure 10 Microstructures and pore size distributions of plaster mould ((a) and (c)) and alumina mould ((b) and (d)), respectively.

is about 56.8% of the theoretical density. For cast cakes using an alumina mould, the density distribution is uniform and density is about 56.7% of the theoretical density.

The density of cast cakes using an alumina mould is nearly the same as the highest density at the bottom layer of the cast cakes using a plaster mould. The alumina mould should produce a higher density in the consolidated layer before the cake is completely formed because the casting time using the plaster mould is longer and more fine particles would fill the pores between larger particles. The shorter casting time implies that the flow rate of the fluid is higher, which would produce rearrangement of the particle packing and increase the packing density in the consolidated layer, as suggested in section 3.2.3. for pressure filtration. Therefore, density variation has been improved using an alumina mould which could be attributed to higher density in the consolidated layer and shorter casting time to prevent clogging with fine particles. Furthermore, the contamination is quite apparent when using a plaster mould because significant calcium lumps were detected at the bottom surface of the cakes. Fig. 11 shows the microstructure of the cake using a plaster mould after sintering. As can be seen in the figure, the final density of the bottom layer of the sintered cakes was lower, although its green density was higher than that of the upper layer of the cakes. It is suggested that the calcium contamination could play an important role in inhibiting densification.

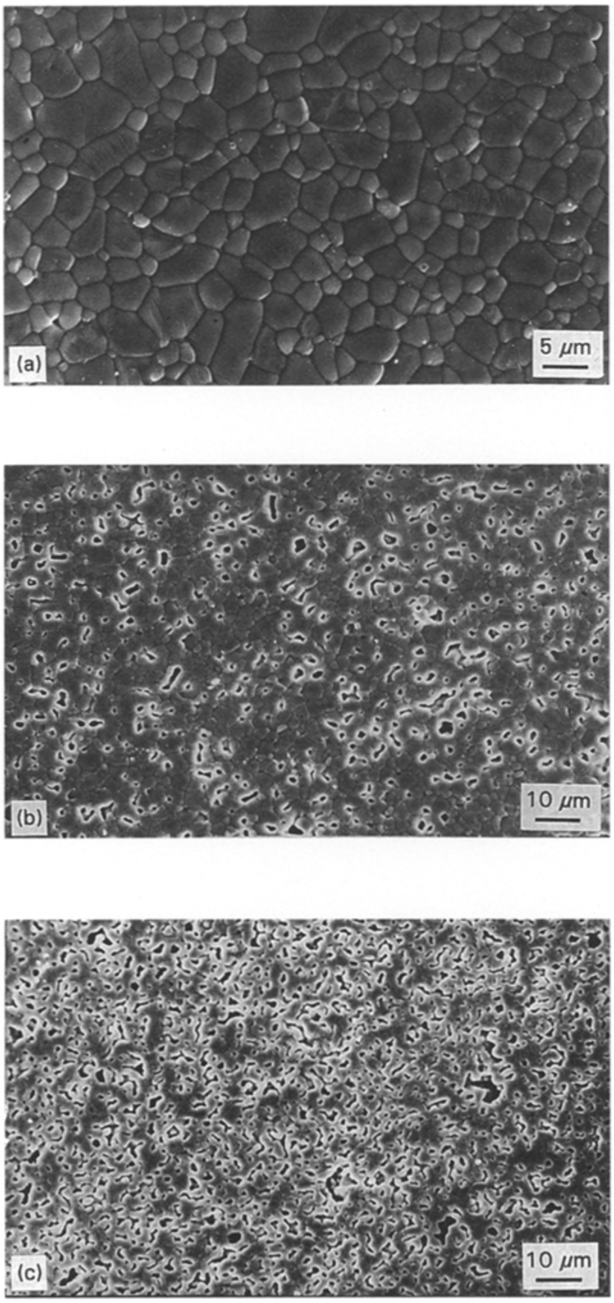

Figure 11 The sintered cake microstructure using a plaster mould for slip casting; (a) upper part; (b) middle part; (c) bottom part.

4. Conclusions

1. The slurries of SBN with 20 vol % solids loading have better grinding efficiency during wet milling.
2. The zeta potentials of SBN powders were negative above pH 2.2. The zeta potentials reduced sharply in the range of pH values from 2.2 to 3.5 and pH > 9 but remained constant from pH 3.5 to pH 9.
3. The viscosity of the slurries of SBN with 20 vol % solids loading is essentially constant when pH is between 4 and 9 but reduces sharply when pH > 9 at shear ate of 76.8 s^{-1}. The rheological behaviour of the slurries of SBN with 20 vol % solids loading at pH 11.5 is shear thinning.
4. For pressure filtration, the filter medium with drains could prevent the residual fluid from re-entering and increase the flow rate of the fluid, which in turn promotes rearrangement of the particle packing and increases the packing density.
5. Pore morphology of the mould has a significant influence on the cake microstructures during slip casting. A uniform pore size distribution and smaller pore size seem to shorten the casting time, which has advantages in preventing clogging with fine particles and enhances the packing density, as suggested for the pressure filtration.
6. The contamination when using a plaster mould is significant and would inhibit densification of SBN ceramics.

Acknowledgements

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