

# Processing of Concentrated Aqueous Si<sub>3</sub>N<sub>4</sub> Slips Stabilized with Tetramethylammonium Hydroxide

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The optimization of the dispersion of 43 vol% aqueous Si<sub>3</sub>N<sub>4</sub>/sintering aid slurries with tetramethylammonium hydroxide to achieve high packing slipcast compacts and subsequent high sintered densities was investigated. Slips containing 43 vol% solids were obtained by dispersing most of the solid (35 vol%) at high pH values (9.7 to 12.3) with different amounts of tetramethylammonium hydroxide and with subsequent addition of the remaining solid up to 43 vol%. The influence of pH on the viscosity and on the amount of tetramethylammonium ions adsorbed, and in solution, of 43 vol% slips was studied. The minimum viscosity was observed in the 9.7 to 10.2 pH range. This pH range seemed to be an intermediate situation between high ionic strength (pH higher than 10.2) and low electrostatic repulsion (pH lower than 9.7). The maximum sintered density at 1650 °C, 97.5% of theoretical density (TD), was obtained from bars of green density, 55.6% TD, prepared from slips with the minimum viscosity (44 mPa/s).

**Keywords** processing, Si<sub>3</sub>N<sub>4</sub>, slips

## 1. Introduction

Silicon nitride materials have received a great deal of interest for structural applications because of their high strength, high thermal shock resistance, and good oxidation resistance. Silicon nitride structural components are fabricated by liquid phase sintering of powder compacts composed of a mixture of silicon nitride powder and sintering aid powders (typically Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>) (Ref 1).

The production of ceramic monoliths from micrometer-sized powders requires an initial consolidation to shape the final piece (Ref 2). Slip casting is a suitable consolidation process to obtain materials with high green densities and microstructural homogeneity, allowing the manufacture of components with complex shapes (Ref 3).

The goal of dispersion in this process is to achieve a high loading of solids with a high degree of dispersion. In general, suspensions can be dispersed by electrostatic, steric, or electrosteric stabilization mechanisms (Ref 4). Albano and Garrido (Ref 5) have previously studied the electrosteric stabilization of concentrated aqueous Si<sub>3</sub>N<sub>4</sub> and Si<sub>3</sub>N<sub>4</sub>/sintering aid slips by addition of a dispersant such as ammonium polyacrylate. In this work, an electrostatic stabilization mechanism was chosen to obtain dispersion in the colloidal state.

The tetramethylammonium hydroxide (TMAH) provides high pH values and is highly volatile, so it is eliminated from the green compact on heating.

Castanho and Moreno (Ref 6) showed that well dispersed concentrated aqueous Si<sub>3</sub>N<sub>4</sub> slips could be obtained in the pH range of 11 to 12 with the addition of TMAH. In order to achieve high green densities by slip casting, it was observed that well deflocculated slips with a content of solids as high as

possible, 43 vol%, must be prepared. However, a great amount of TMAH must be added to prepare 43 vol% solid slurries at pH values of 11 to 12. This results in a high viscosity and does not permit deagglomeration of the powder in an attrition mill. At pH values lower than 11, the viscosity of 43 vol% solid slips is also high. Therefore, a procedure for producing stable 43 vol% aqueous slips was investigated. This process consisted of dispersing most of the solid, 35 vol%, at high pH values with different amounts of TMAH, and with subsequent addition of the remaining solid up to 43 vol% without additional TMAH.

In this work the optimization of the dispersion of 43 vol% aqueous Si<sub>3</sub>N<sub>4</sub>/sintering aid slurries was investigated. The influence of pH on the viscosity and on the amount of [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ions adsorbed and in solution of 43 vol% slips was studied. Finally, the microstructure of green cast samples and the sintered density were studied and related to the degree of 43 vol% slip dispersion.

## 2. Experimental Procedure

### 2.1 Materials

A commercial  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder (SN-E10, UBE Industries, Japan) was used in this study. The mean particle diameter and the specific surface area taken from the manufacturer specifications were 0.6  $\mu$ m and 10 m<sup>2</sup>/g, respectively. A mixture of 6 wt% Y<sub>2</sub>O<sub>3</sub> (Molycorp, USA) and 4 wt% Al<sub>2</sub>O<sub>3</sub> (A-16 SG, ALCOA, Pittsburg, PA) was used as a sintering aid.

### 2.2 Slip Preparation

Slips with two different solids loading, 35 and 43 vol%, were prepared. A commercial tetramethylammonium hydroxide solution (Fluka AG, CH-9470 Bucks) was used to adjust the pH.

Aqueous slips were prepared by deagglomeration of the powder in an attrition mill using 1.6 mm diameter alumina balls

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at different pH values. The various pH values were obtained by adding different amounts of tetramethylammonium hydroxide.

To prepare 35 vol% slips, distilled water with the amount of TMAH adjusted at a desired value was added to the attrition mill, and then the powder up to 35 vol% solid was added. To prepare 43 vol% slips, the rest of the solid (difference between 43 and 35 vol%) was added in portions to the suspensions without additional TMAH. The slips were allowed to equilibrate in a plastic flask for a few minutes before the pH was measured.

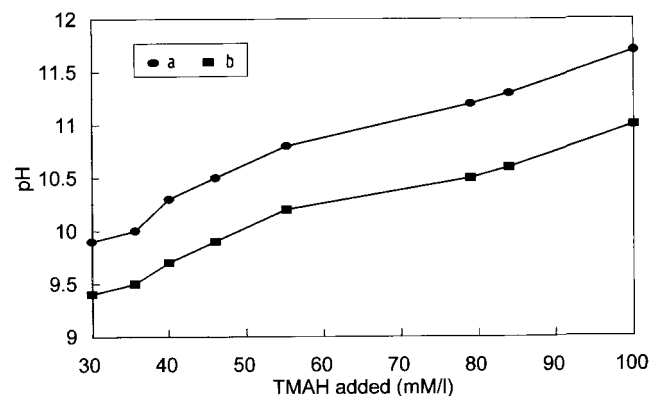
### 2.3 Viscosity Measurements

Slip rheological properties were determined using a concentric cylinder viscometer (Haake RV3, Germany) at 25 °C. The apparent viscosity was calculated as the ratio between the shear stress and the shear rate at 175 s<sup>-1</sup>.

### 2.4 Adsorption Measurements of Tetramethylammonium Ion

In order to determine the amount of tetramethylammonium ion adsorbed, slips were centrifuged for 30 min at 2500 rpm, and the solid was washed twice with distilled water to remove any [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ion not adsorbed on the powder surface. Thus, this procedure removed any free [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ion in the suspension, and only those ions that were strongly adsorbed remained bound. Afterward, the solid was dried at 100 °C and analyzed by thermal gravimetric analysis (TGA) (Model STA 409, Netzsch Inc., Germany) at a heating rate of 10 °C/min in N<sub>2</sub> atmosphere. The TGA data showed a water weight loss at temperatures near 100 °C and a weight loss due to the tetramethylammonium decomposition at a temperature range from 250 to 500 °C. This weight loss was used to determine the amount of tetramethylammonium ion adsorbed on each sample. Although the adsorption data obtained with this technique were semiquantitative, they provided a relative measure of the amount of [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ions adsorbed on the samples.

The amount of tetramethylammonium ion in solution for each sample was taken as the difference between the amount added and the amount adsorbed.



**Fig. 1** pH versus amount of tetramethylammonium hydroxide (TMAH) added for slips with different loading of solids. (a) 35 vol%. (b) 43 vol%

### 2.5 Slip Casting and Characterization of Green Samples

Slips were cast in plaster molds into bars with dimensions of 6 by 1.24 by 1.24 cm. The consolidated bars were removed from the mold after 1 h and dried slowly in air for 24 h at room temperature, 4 h at 60 °C, and 24 h at 100 °C.

Green densities were calculated after measuring dimensions and the weight of dried bars. The pore size distribution of green samples was measured using mercury porosimetry (Porosimeter 2000 Carlo Erba, Italy).

### 2.6 Sintering and Characterization of Sintered Samples

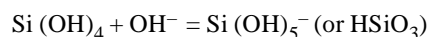
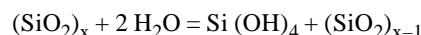
Green bars were embedded in a powder bed consisting of 50 wt% Si<sub>3</sub>N<sub>4</sub>, 45 wt% BN, and 5 wt% sintering additives. They were sintered in a N<sub>2</sub> atmosphere of 0.1 MPa at 1650 °C for 3 h using heating rates of 2 °C/min up to 800 °C and 5 °C/min up to 1650 °C. The N<sub>2</sub> flow rate was 0.5 L/min. The bulk density of the sintered bars was determined by water immersion (standard method ASTM C 20).

## 3. Results and Discussion

### 3.1 Viscosity and Amount of Tetramethylammonium Ion Adsorbed and in Solution versus pH for 35 and 43 vol% Slips

The isoelectric point (IEP) of the Si<sub>3</sub>N<sub>4</sub> powder was at about pH 6 (Ref 7). At pH values higher than the IEP, the zeta potential had negative values and increased with an increase in pH in the range from 6 to 12.

Albano and Garrido (Ref 7) demonstrated recently that the tetramethylammonium ion was adsorbed specifically on the Si<sub>3</sub>N<sub>4</sub> powder surface because it increased the IEP from pH 6 (10<sup>-2</sup> M NaCl) to 7 (10<sup>-2</sup> M (CH<sub>3</sub>)<sub>4</sub>NCl). The silanol groups are the sites on the Si<sub>3</sub>N<sub>4</sub> powder at which adsorption occurs. Ionic attraction between [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ions and Si<sup>-</sup> groups exists (Ref 8). However, at pH of >9, the silica dissolves according to the following reactions:



generating soluble silicate (HSiO<sub>3</sub><sup>-</sup>) ions (Ref 9). The solubility of SiO<sub>2</sub> increases with an increase in pH. Therefore, the adsorption of [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ions on the Si<sub>3</sub>N<sub>4</sub> powder was very low at pH higher than 9 due to the dissolution of the silica layer on the powder surface (Ref 7).

The IEP of the Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> powder was found to be around 10.3 (Ref 10) and 8 (Ref 11), respectively.

Albano and Garrido (Ref 7) found that the [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ions were adsorbed on the sintering aid particles in the 9.5 to 12.5 pH range. The adsorption occurred at the negative sites of the Al<sub>2</sub>O<sub>3</sub> powder surface at that pH range and on the Y<sub>2</sub>O<sub>3</sub> powder surface at a pH of 10.3 to 12.5, where its zeta potential had negative values. However the amount of [(CH<sub>3</sub>)<sub>4</sub>N]<sup>+</sup> ions adsorbed was very low; consequently substantial modifications

of the interfacial charge properties of the powders were not expected (Ref 7).

Figure 1 shows the pH as a function of the amount of TMAH added for 35 and 43 vol% solid slurries. At a pH higher than 10.5, the amount of TMAH added to reach the same pH values was about twice higher for the 43 vol% solid slurries. The pH of 35 vol% slips increased from 9.7 to 11.7, with increasing concentration of TMAH from 30 to 100 mM/L. At the same concentration range of TMAH, the pH values of 43 vol% slips increased from 9.3 to 11.

Figures 2(a) and (b) show the amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions adsorbed and the amount in solution versus pH, respectively, for 35 and 43 vol% slips. The amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions adsorbed for 35 vol% slips increased with increasing pH from 9.7 to 10.5 and then decreased upon further increasing of pH up to 12.3 (Fig. 2a). At pH of <10.3, the  $\text{Y}_2\text{O}_3$  particles were positively charged, and the  $[(\text{CH}_3)_4\text{N}]^+$  ions were only adsorbed at the negative ( $-\text{Al}-\text{O}^-$ ) sites of the  $\text{Al}_2\text{O}_3$  powder surface (Ref 12). At pH higher than 10.3, the  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  powders were both negatively charged, and the negative surface sites of the

powders increased with increasing pH; therefore, a greater adsorption was expected. However, the amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions adsorbed decreased.

The amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions in solution for 35 vol% slips showed a minimum at pH 10.5 (Fig. 2b) where the  $[(\text{CH}_3)_4\text{N}]^+$  ion adsorption has its maximum (Fig. 2a). A decrease in the amount of counterions in solution up to pH 10.5 was found, followed by an important increase from 20 to 100 mM/L with further increasing of pH up to 12.3 (Fig. 2b). This significant increase in the concentration of counterions in solution was attributed to a combination of two effects: the great amount of TMAH added to reach pH values higher than 10.5 (Fig. 1) and the decrease in the amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions adsorbed at those pH values.

The surface solubility of  $\text{Al}_2\text{O}_3$  increased at pH of >10.5, as was mentioned by Yariv and Cross (Ref 13), generating soluble  $\text{Al}(\text{OH})_4^-$  ions. However,  $\text{Al}(\text{OH})_4^-$  ions were not detected in the solution by colorimetric analysis (aluminon method) (Ref 14).

Silicate ions produced by the dissolution of the  $\text{SiO}_2$  on the  $\text{Si}_3\text{N}_4$  powder surface were detected in the solution by colorimetric analysis (standard method IRAM 41318). The amount of soluble silica had a maximum value of 5 mM/L at pH 12.3. As the concentration of  $[(\text{CH}_3)_4\text{N}]^+$  ions was about 4 to 20 times higher than the concentration of  $\text{HSiO}_3^-$  ions, the counterions contributed mainly to increase the ionic strength of the solution.

Several researchers demonstrated the influence of the electrolyte concentration on the zeta potential of oxide powders (Ref 15). An increase in the electrolyte concentration increased the ionic strength of the solution with decreasing the zeta potential of the powders, especially at low and high pH values. Therefore, the significant increase in the amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions in solution for 35 vol% slips at pH higher than 10.5 (Fig. 2b) produced a decrease in the negative zeta potential of the sintering aid powders. This reduced the electrostatic attraction between the negative powder surfaces and the  $[(\text{CH}_3)_4\text{N}]^+$  cations, thereby decreasing the amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions adsorbed.

The increase in the volume percent of solids up to 43 vol% shifted the adsorption maximum to pH 10.2. At low additions of TMAH (<55 mM/L, pH <10.2) the increase of the pH produced an increase in the negative surface charge of the powders and in the amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions adsorbed (Fig. 2a). A great amount of TMAH was added (>55 mM/L) to reach pH values higher than 10.2 (Fig. 1). This produced an increase in the amount of counterions in solution (high ionic strength), resulting in a decrease in the amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions adsorbed (Fig. 2a and b).

Figure 3 shows the viscosity as a function of pH for 35 and 43 vol%  $\text{Si}_3\text{N}_4$ /sintering aid slips, (a) and (b) curves, respectively. The viscosity of 35 vol% slips was high at pH <10.3. Upon further increase of the pH to 10.5, the slip could be effectively dispersed; then the viscosity increased at pH values higher than 10.5.

As was previously mentioned, the adsorption of the  $[(\text{CH}_3)_4\text{N}]^+$  ions on the  $\text{Si}_3\text{N}_4$  powder was very low in the pH range of 9.5 to 12.3 due to the dissolution of the  $\text{SiO}_2$  layer on the powder surface (Ref 7). This behavior was supported by

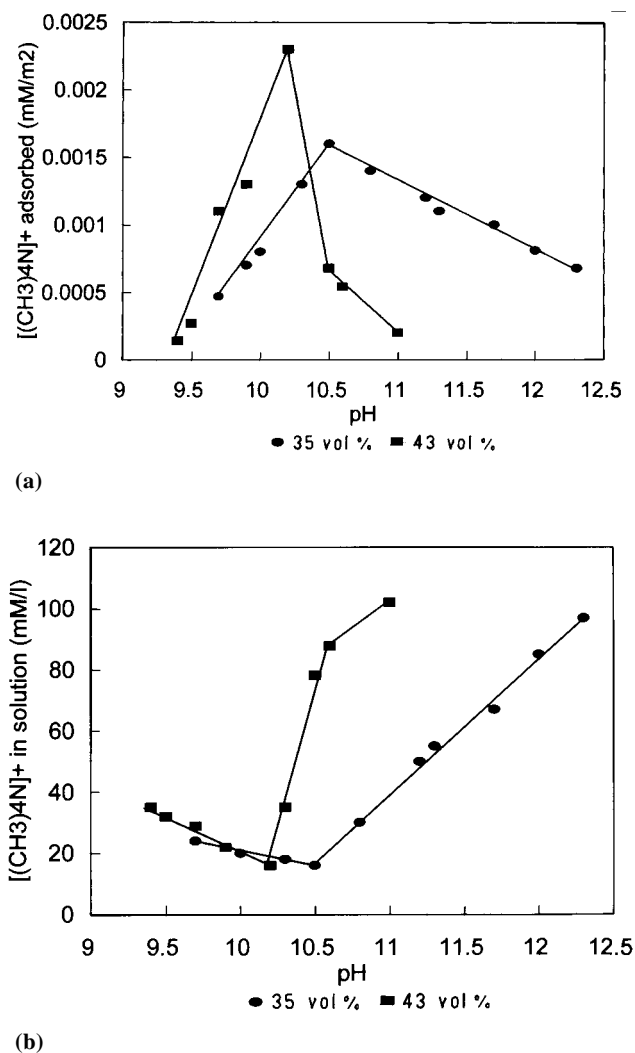
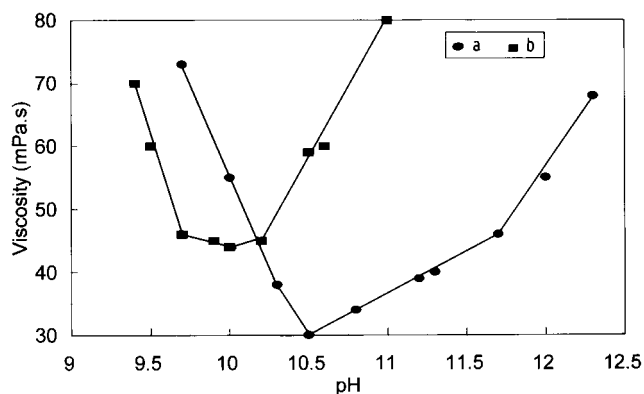


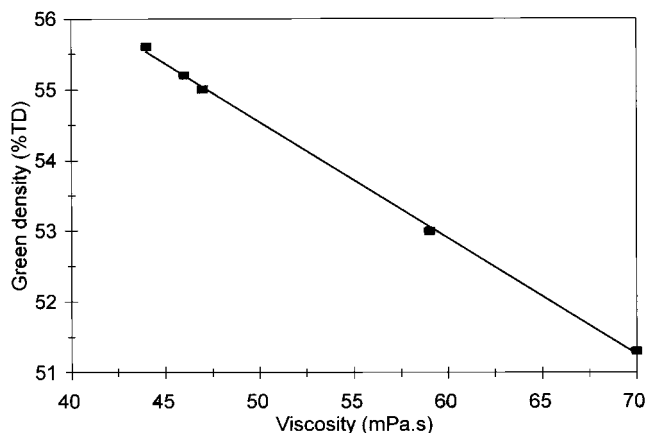
Fig. 2 Amount of  $[(\text{CH}_3)_4\text{N}]^+$  ions. (a) Adsorbed. (b) In solution versus pH for slips with different loading of solids

zeta potential versus pH measurements of 0.16 vol% slips of the  $\text{Si}_3\text{N}_4$  powder in  $10^{-2}$  M NaCl and  $10^{-2}$  M  $(\text{CH}_3)_4\text{NCl}$  aqueous solutions (Ref 7). The zeta potential of the powder in  $(\text{CH}_3)_4\text{NCl}$  solution had lower negative values than those in NaCl solution in the pH range from 7 to 9.5. However, at a pH of 9.5 to 12.3, the powder had the same negative zeta potential values in both electrolytes, indicating that the  $[(\text{CH}_3)_4\text{N}]^+$  ions were not adsorbed at that pH range.

The zeta potential values of the  $\text{Si}_3\text{N}_4$  powder in  $10^{-2}$  M  $(\text{CH}_3)_4\text{NCl}$  aqueous solution increased from  $-50$  mV at pH 9.5 to  $-55$  mV at pH 10.5 (Ref 7). Therefore, low viscosity values for 35 vol% aqueous  $\text{Si}_3\text{N}_4$  slips with TMAH could be prepared (35 mPa/s at a pH of 9.7, 38 mPa/s at a pH of 10.1) (Ref 7). However, the viscosity of 35 vol%  $\text{Si}_3\text{N}_4$ /sintering aid aqueous slips with TMAH was very high at pH values lower than 10.3 (Fig. 3a). This behavior could be explained considering that the  $\text{Y}_2\text{O}_3$  powder had the opposite sign zeta potential (positive) with respect to  $\text{Si}_3\text{N}_4$  powder up to pH 10.3, and heterocoagulation may have occurred, decreasing the negative surface charge of the  $\text{Si}_3\text{N}_4$  powder and consequently the electrostatic repulsion between particles. The authors have previously observed this behavior for 32 vol% slurries of the same system at pH <10.3 adjusted with  $\text{NH}_4\text{OH}$  (Ref 5). Pollinger et al. (Ref 10) studied the effect of 5 wt%  $\text{Y}_2\text{O}_3$  (IEP = 9.25) additions to



**Fig. 3** Viscosity as a function of pH for slips with different loading of solids. (a) 35 vol%. (b) 43 vol%



**Fig. 4** Green density (% of theoretical density) of cast samples versus viscosity of 43 vol% slips

$\text{Si}_3\text{N}_4$  (IEP = 4) for 37.7 vol% aqueous suspensions at pH 8.5 to 10.5 by zeta potential and viscosity measurements. Their results showed that at pH values lower than the IEP of the  $\text{Y}_2\text{O}_3$ , a small decrease in the zeta potential with respect to that of the  $\text{Si}_3\text{N}_4$  powder, due to heterocoagulation between  $\text{Y}_2\text{O}_3$  and  $\text{Si}_3\text{N}_4$  particles, resulted in a significant increase in the slip viscosity. Thus, at high solids content the viscosity was very sensitive to small changes in zeta potential (Ref 10).

At pH values higher than 10.3, the  $\text{Y}_2\text{O}_3$  powder moved through its IEP and became negatively charged, the same charge sign as the  $\text{Si}_3\text{N}_4$  powder; so mutual repulsion then occurred. The minimum viscosity was observed at pH 10.5 where electrostatic repulsion between particles occurred and the amount of counterions in solution was minimal (Fig. 2b).

The electrophoretic mobility of diluted (0.16 vol%) aqueous slips of the  $\text{Si}_3\text{N}_4$  powder in  $10^{-2}$  M  $(\text{CH}_3)_4\text{NCl}$  increased with an increase in pH in the range from 10.5 to 12.3 (Ref 7); however at that pH range the viscosity of concentrated (35 vol%) slips increased (Fig. 3a). This was produced by the increase of the amount of counterions in solution at a 10.5 to 12.3 pH range (Fig. 2b), which had a detrimental effect on the slip viscosity as the ionic strength of the solution was increased. At high ionic strength ( $>10^{-2}$  M), a decrease in the particle mobility was observed (Ref 16) due to the large compression of the double layer reducing the electrostatic repulsion between particles.

As the volume percent of solids increased from 35 to 43 vol%, the magnitude of the slip viscosity also increased, whereas the effective pH range became lower and smaller (Fig. 3).

The slip viscosity increased with increasing the content of solids due to hydrodynamic interactions. In addition, Pollinger et al. (Ref 10) studied the effect of  $\text{Si}_3\text{N}_4$  slip solids content on the zeta potential measured by the acoustophoresis technique at pH 10. Their results showed that the zeta potential decreased from  $-50$  mV for 10 vol% solids content to  $-25$  mV for 45 vol% solids content, and the slip viscosity increased from 5 to 110 mPa/s in that range of solids content. Therefore, in addition to hydrodynamic interactions, lower electrostatic repulsion between particles could be expected at higher solids content.

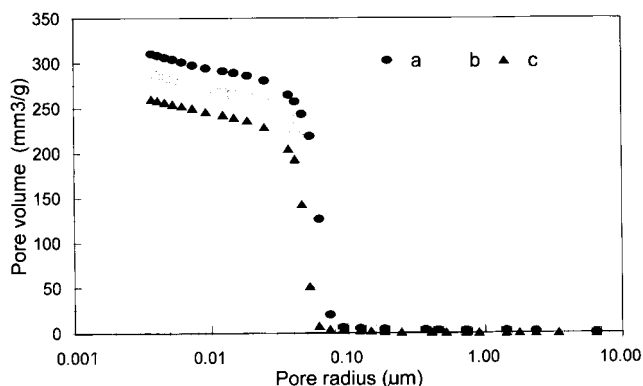
The decrease in the zeta potential of the  $\text{Si}_3\text{N}_4$  powder with increasing the ionic strength of the solution has been well studied and understood (Ref 10, 16). The great amount of counterions in solution for 43 vol% slips at pH >10.2 (Fig. 2b) contributed to a decrease in the particle mobility with increasing ionic strength of the solution, reducing the electrostatic repulsion between particles. Therefore, the important increase in the slip viscosity at pH >10.2 (Fig. 3b) was attributed to the high ionic strength of the solution.

At pH <9.7 the slips were flocculated due to the low electrostatic repulsion between particles.

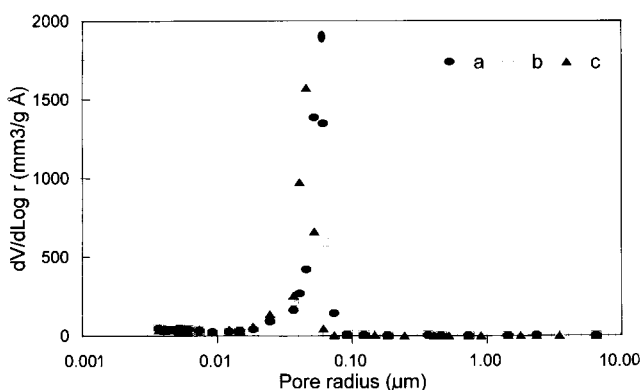
The lowest viscosity values (greater degree of dispersion) of 43 vol% slurries were achieved at a 9.7 to 10.2 pH range (Fig. 3b), which corresponded to a concentration of TMAH added in the range of 40 to 55 mM/L (Fig. 1). This optimum pH range seemed to be an intermediate situation between a high ionic strength (pH higher than 10.2) and a low electrostatic repulsion (pH lower than 9.7).

### 3.2 Green Microstructure and Sintered Density

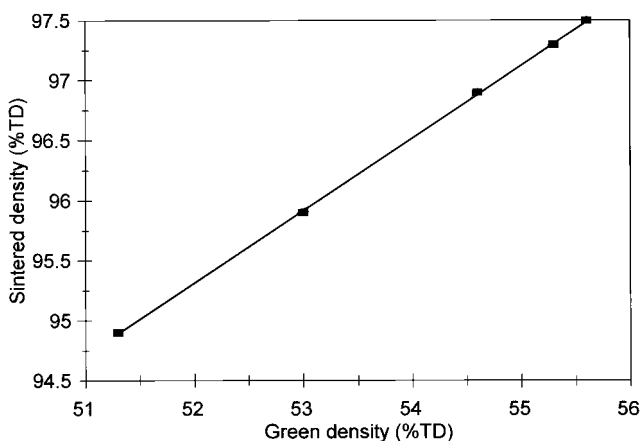
The green density of cast samples was related to the viscosity of 43 vol% slips and to the sintered density. Figure 4 shows the green density of cast bars versus the slip viscosity (at



**Fig. 5** Cumulative micropore volume by mass unit versus pore radius curves of green bars with different green densities (% of theoretical density). (a) 51.3% TD. (b) 53% TD. (c) 55.6% TD



**Fig. 6** Micropore size distribution curves of green bars with different green densities (% of theoretical density). (a) 51.3% TD. (b) 53% TD. (c) 55.6% TD



**Fig. 7** Sintered density (% of theoretical density) at 1650 °C as a function of green density (% of theoretical density) of cast samples

175 s<sup>-1</sup>). Lower viscosities of the slips resulted in higher slip-cast packing density compacts at a given solid loading. A green density of 55.6% of the theoretical density could be achieved from the slip of viscosity 44 mPa/s.

Figures 5 and 6 show the micropore size distributions of green bars with different green densities. Figure 5 shows the cumulative micropore volume by mass unit versus pore radius curves, and Fig. 6 is a representation of the micropore size distribution as  $dV/d\log r$  (differential pore volume) versus pore radius.

All the green bars had a similar narrow micropore size distribution (Fig. 6). As the green density increased from 51.3 to 55.6% TD, the most frequent pore radius decreased from 0.065 to 0.045  $\mu\text{m}$ , and a reduction in the volume of pores with pore radius between 0.05 and 0.1  $\mu\text{m}$  was observed.

A linear correlation between the sintered density and the green density was found (Fig. 7). Green compacts with smaller pore sizes and pore volumes resulted in higher sintered densities. The maximum sintered density at 1650 °C, 97.5% TD, was obtained from the bar of green density, 55.6% TD.

## 4. Conclusions

Slurries containing 43 vol% aqueous  $\text{Si}_3\text{N}_4$ /sintering aid can be obtained with the addition of tetramethylammonium hydroxide. This is accomplished by preparing a stable 35 vol% slip at high pH values with subsequent addition of the remaining solid up to 43 vol%.

Low viscosity values of 43 vol%  $\text{Si}_3\text{N}_4$ /sintering aid slurries are obtained at pH 9.7 to 10.2. At pH lower than 9.7 the viscosity is high due to the low electrostatic repulsion between particles. The increase in viscosity at pH higher than 10.2 is attributed to the increasing ionic strength of the solution.

The maximum sintered density at 1650 °C, 97.5% TD, is obtained from bars of green density, 55.6% TD, prepared from slips having the minimum viscosity (44 mPa/s).

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