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Ceramics International 25 (1999) 13–18

CERAMICS
INTERNATIONAL

Dispersion of concentrated aqueous Si_3N_4–Y_2O_3–Al_2O_3 slips with tetramethylammonium hydroxide

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Received 12 June 1997; accepted 2 September 1997

Abstract

The influence of pH and sintering aid powders on the viscosity and on the amount of tetramethylammonium ions adsorbed of 35Vol% aqueous Si_3N_4 slips were determined. The as-received Si_3N_4 powder was used. A mixture of 6 wt% Y_2O_3 and 4 wt% Al_2O_3 was used as sintering aid. Aqueous slips were prepared at different pH values in a range of 9.7 to 12.3 in an attrition mill. Tetramethylammonium hydroxide was used to adjust the pH. The viscosity of Si_3N_4 slips increased with increasing pH at the pH range studied. The sintering aid powders had a positive effect on the dispersion of the Si_3N_4 powder at pH higher than 10.3 since a greater degree of dispersion could be obtained. The lowest viscosity value (30 mPa.s) could be achieved from Si_3N_4/sintering aid slips at pH 10.5. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

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1. Introduction

Silicon nitride structural components are fabricated by liquid phase sintering of powder compacts composed of a mixture of the silicon nitride powder and sintering aid powders (typically Al_2O_3 and Y_2O_3) [1].

The production of ceramic monoliths from micrometer-sized powders requires an initial consolidation to shape the final piece [2]. It is commonly accepted that colloidal processing techniques provide a powerful route to improve the reliability of ceramic materials [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 [3].

The state of dispersion and rheology of the suspension determine the green and sintered density of the ceramic product. In order to achieve high green densities by slip casting, well deflocculated slips with a high content of solids must be prepared. However, the preparation of a well dispersed, concentrated slip of a submicronic Si_3N_4 powder with the corresponding sintering aid additives is considered as a critical step in slip casting [4].

In general, ceramic slips can be stabilized by addition of an appropriate dispersant such as polyelectrolytes [5]. Albano and Garrido [6] have previously studied the processing of concentrated aqueous Si_3N_4 and Si_3N_4/sintering aid slips with ammonium polyacrylate. The results demonstrated that a preoxidation treatment of the as-received Si_3N_4 powder was required to obtain well dispersed concentrated slips [6]. However, the introduction of oxygen on the powder surface may be detrimental for the mechanical properties of sintered silicon nitride [7].

Castanho and Moreno [8] showed that well dispersed concentrated slips prepared from the as-received Si_3N_4 powder, without any surface treatment, could be obtained at pH 11–12 with the addition of tetramethylammonium hydroxide (TMAH). This strong alkali provides high pH values and is eliminated from the green compact on heating [9].

The TMAH is successfully used to obtain concentrated aqueous Si_3N_4 slips; [8,9] however, the properties of the slip depend on the starting powder and more information is required on the stabilization effect of the TMAH and on the influence of the sintering aid powders on the slip rheology. Therefore, this work was undertaken to study the influence of pH and sintering aid powders on the degree of dispersion, measured by the viscosity, of 35 vol% aqueous Si_3N_4 slips.

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PII: S0272-8842(97)00078-3

2. Experimental procedure

2.1. Materials

A commercial α-Si_3N_4 powder (SN-E10, UBE Industries, Japan) was used in this study. The mean particle diameter and the specific surface area were 0.6 μm and $10\,m^2\,g^{-1}$, respectively. A mixture of 6 wt% Y_2O_3 (Molycorp, USA) and 4 wt% Al_2O_3 (A-16 SG, ALCOA, Pittsburg, PA) was used as sintering aid.

2.2. Powder characterization

The as-received powder was characterized by Fourier transform infrared (FTIR) analysis (Bruker IFS 66, Germany) in the diffuse reflectance mode.

2.3. Zeta potential determinations

The electrophoretic mobility was measured (Penkem Laser Zee Meter 501, USA) and used to calculate zeta potential according to Smoluchowski's equation. Electrophoretic measurements were used to determine the isoelectric point (IEP) of the Si_3N_4 powder in 10^{-2} M NaCl and 10^{-2} M $(CH_3)_4NCl$ aqueous solutions. For each determination, 0.05 g of sample were dispersed in 100 ml of 10^{-2} M NaCl or $(CH_3)_4NCl$ solutions and the slurry stirred magnetically for 10 min before the measurements were carried out. The pH of the slurry was adjusted using dilute HCl and NaOH solutions to generate zeta potential vs pH curves and from them the IEP.

2.4. Slip preparation

Slips with a solid content of 35 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 at different pH values in a range of 9.7 to 12.3. This pH range was obtained by adding different amounts of tetramethylammonium hydroxide.

The powder was added in two portions to the suspensions. The milling time was half an hour, by this time the whole amount of powder was present in the suspension. Then the slip was allowed to equilibrate for 1 min before the pH was measured.

2.5. 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 $175\,s^{-1}$.

2.6. 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 washed twice with distilled water. Afterwards, the solid was dried at 100°C and analized by thermal gravimetric analysis (TGA) (Model STA 409, Netzsch Inc., Germany) at a heating rate of $10°C\,min^{-1}$ in N_2 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.

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

2.7. Soluble silica measurements

The slips were centrifuged for 1 h at 3000 rpm and the supernatant was drawn-off. The pH of the supernatant of Si_3N_4 slips was shifted up to 6 to coagulate the remaining Si_3N_4 particles. KCl was added to the supernatant of Si_3N_4/sintering aid slips to coagulate the remaining Si_3N_4/sintering aid particles. Then, the clear supernatant of each slip was analyzed colorimetrically with the formation of a silicomolybdate acid complex (Standard Method IRAM 41318).

3. Results and discussion

3.1. Powder characterization

Fig. 1 shows the FTIR spectra of the as-received Si_3N_4 powder in the range of 3000–4000 cm^{-1}. Two peaks were found: one peak at $3750\,cm^{-1}$ due to silanol bonding and another one from 3000 to $3400\,cm^{-1}$ which corresponds to the amine structure [10]. This characterization of the Si_3N_4 powder surface was in agreement with Liu et al. [11] who reported that the Si_3N_4 surface consisted of silanol (Si–OH) and amine (=N–H) functional groups.

3.2. Zeta potential vs pH curves

Fig. 2 shows the zeta potential vs pH curves of the Si_3N_4 powder in 10^{-2} M NaCl and 10^{-2} M $(CH_3)_4NCl$ aqueous solutions. The measurements were performed in two different media of the same ionic strength: an inert electrolyte, NaCl, which does not adsorb specifically on the particles [12] and $(CH_3)_4NCl$ which has the same cation as the hydroxide used in the slip preparation and in a similar concentration.

The IEP in 10^{-2} M NaCl solution was at about pH 6 (Fig. 2(a)). This was in agreement with the reported electroacoustic behaviour of this Si_3N_4 powder [11,12]. At pH values higher than the IEP, the zeta potential had negative values and increased with an increase in pH in the pH range from 6 to 12.

The IEP in 10^{-2} M $(CH_3)_4NCl$ solution was at about pH 7 (Fig. 2(b)). The increase in the IEP with respect to that determined in NaCl solution (pH_{IEP} 6) indicated that the tetramethylammonium ion was adsorbed specifically on the Si_3N_4 particles.

The zeta potential of the powder in $(CH_3)_4NCl$ solution had lower negative values than those in NaCl solution in the pH range from 7 to 10. Thus, the adsorbed $[(CH_3)_4N]^+$ ions decreased the negative charge of the Si_3N_4 powder at alkaline pH range. However, at pH range from 10 to 12 the powder had the same zeta potential values in both electrolytes. This adsorption behaviour at pH 10–12 will be explained in Section 3.3.

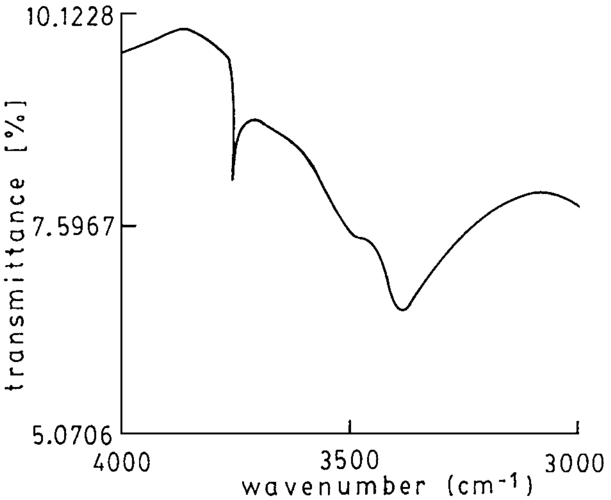

Fig. 1. FTIR spectra of the as-received Si_3N_4 powder.

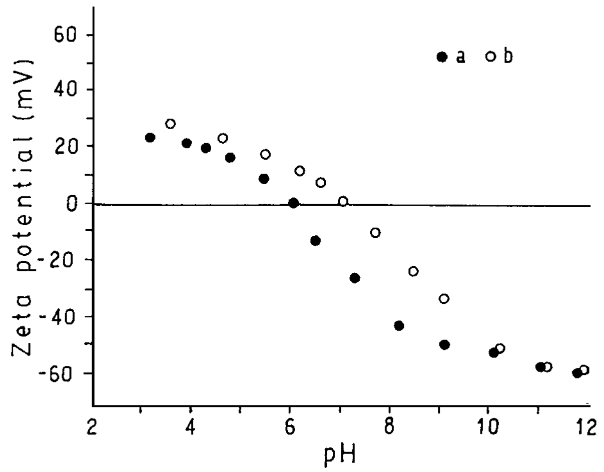

Fig. 2. Zeta potential vs pH curves of the Si_3N_4 powder in different solutions: (a) 10^{-2} M NaCl; (b) 10^{-2} M $(CH_3)_4NCl$.

3.3. *Viscosity, amount of tetramethylammonium ion adsorbed and amount of species in solution vs pH*

Fig. 3(a) and (b) show the viscosity as a function of pH for 35 vol% Si_3N_4 and 35 vol% Si_3N_4/sintering aid slips, respectively. The Si_3N_4 powder could be dispersed only at pH ≥ 9.7 in the pH range investigated (Fig. 3(a)). The slip viscosity increased with an increase in pH. A minor increase in viscosity up to pH 11.2 was found followed by a greater increase with further increasing of pH up to 12.2.

The zeta potential measurements (Fig. 2) suggested that the most stable dispersions of the powder should occur at pH near 12 where the powder had the maximum negative surface charge; however, well dispersed slips at that pH could not be obtained. Well deflocculated slips of the Si_3N_4 powder could be formed over a pH range of 9.7 to 11.2. Thus, the dispersion of the Si_3N_4 powder in suspension was not determined by the magnitude of the powder surface charge. Fig. 4 shows the amount of $[(CH_3)_4N]^+$ ions adsorbed and the amount in solution versus pH for 35 vol% slips. The amount of $[(CH_3)_4N]+$ ions adsorbed on the Si_3N_4 powder (Fig. 4(a)) was negligible at the pH range studied and adsorption was not detected at pH$\geq$11.

The silanol groups are the sites on the Si_3N_4 surface at which adsorption occurs. Ionic atraction between $[(CH_3)_4N]^+$ ions and Si-O$^-$ groups exists [13]. However, at pH > 9 the silica dissolves according to the following reactions:

$$(SiO_2)_x + 2H_2O = Si(OH)_4 + (SiO_2)_{x-1}$$

$$Si(OH)_4 + OH^- = Si(OH)_5^- (\text{or } HSiO_3)$$

generating soluble silicate ($HSiO_3^-$) ions [14]. The solubility of SiO_2 increases with an increase in pH and at pH

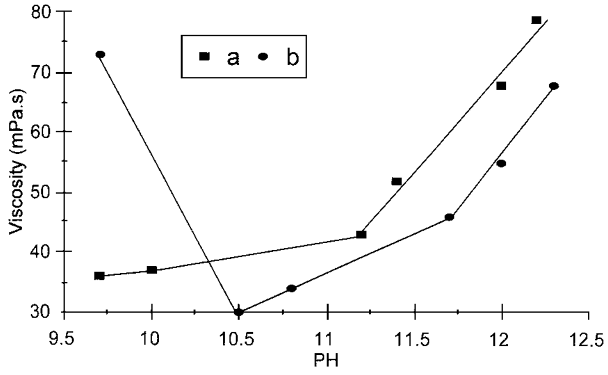

Fig. 3. Viscosity as a function of pH for different 35 vol% slips: (a) Si_3N_4 slips, (b) Si_3N_4/sintering aid slips.

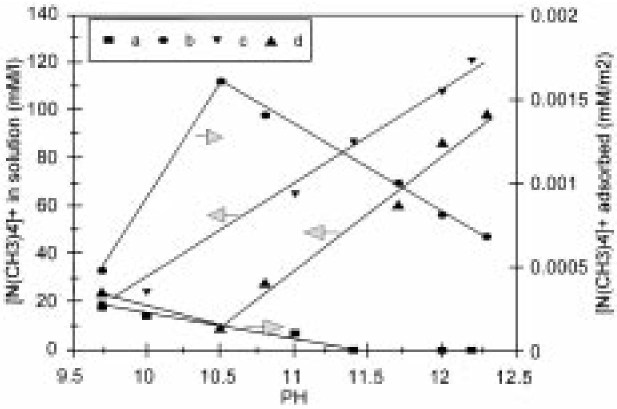

Fig. 4. Amount of $[(CH_3)_4N]^+$ ions adsorbed and amount of $[(CH_3)_4N]^+$ ions in solution versus pH for different 35 vol% slips: (a) and (c) Si_3N_4 slips, (b) and (d) Si_3N_4/sintering aid slips.

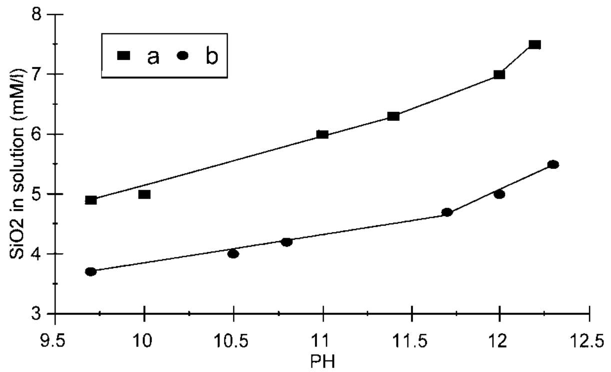

Fig. 5. Amount of SiO_2 in solution as a function of pH for different 35 vol% slips: (a) Si_3N_4 slips, (b) Si_3N_4/sintering aid slips.

higher than 10.7 the SiO_2 is completely dissolved. Thus, the $HSiO_3^-$ ions are present in increasing amounts as the pH is raised, especially above pH 9 [14].

Fig. 5(a) and (b) show the amount of soluble SiO_2 as a function of pH for 35 vol% Si_3N_4 and 35 vol% Si_3N_4/sintering aid slips, respectively. The amount of soluble SiO_2 in Si_3N_4 slips increased slightly with an increase in pH in the range from 9.7 to 12.2 (Fig. 5(a)). Therefore, the negligible adsorption of the $[(CH_3)_4N]^+$ ions on the Si_3N_4 powder at the pH range studied was due to the dissolution of the SiO_2 layer on the powder surface.

The similarity found between the zeta potential values of the powder in NaCl and $(CH_3)_4NCl$ solutions at pH 10–12 (Fig. 2) was consistent with the low adsorption of the $[(CH_3)_4N]^+$ ions at those pH values.

As the $[(CH_3)_4N]^+$ ions adsorption on the Si_3N_4 powder was very low, an appreciable equilibrium concentration of $[(CH_3)_4N]^+$ ions in solution existed at all the pH values studied. The amount of $[(CH_3)_4N]^+$ ions in solution increased with increasing pH (Fig. 4(c)). Therefore a decrease of the particle mobility at high pH values was expected with increasing the ionic strength of the solution.

Silicate ions existed in solution in addition to non-adsorbed $[(CH_3)_4N]^+$ ions. However, the concentration of $[(CH_3)_4N]^+$ ions was about 4 to 16 times higher than the concentration of $HSiO_3^-$ ions (Figs. 4(c) and 5(a)). Consequently, the counterions contributed mainly to increase the ionic strength of the solution with increasing the slip viscosity (Fig. 3(a)).

A greater increase of the slip viscosity was found at $pH > 11.2$ (Fig. 3(a)) where the amount of counterions was higher than $70\,mM^{-1}$ (Fig. 4(c)). Thus, at this concentration of counterions a greater slope of the viscosity vs pH curve occurred.

The IEP of the Y_2O_3 and Al_2O_3 powders was found to be around 10.3 [15] and 8 [16], respectively. At pH higher than the IEP of each powder, the zeta potential had negative values and increased with an increase in pH [15,16].

The viscosity vs pH curve for Si_3N_4/sintering aid slips (Fig. 3(b)) was markedly different from that observed for Si_3N_4 slips at the same pH range (Fig. 3(a)). Thus, the sintering aid powders had a significant influence on the dispersion of the Si_3N_4 powder.

At $pH < 10.3$ the viscosity was high, upon further increase of the pH to 10.5 the slip could be effectively dispersed (Fig. 3(b)). The viscosity increased at pH higher than 10.5, however, the viscosity values at pH 10.3–12.3 were lower than those observed for Si_3N_4 slips at the same pH range (Fig. 3(a) and (b)).

The adsorption of $[(CH_3)_4N]^+$ ions on the Si_3N_4/sintering aid powders was very sensitive to changes in pH and a greater adsorption with respect to the Si_3N_4 powder was found at all pH values (Fig. 4(a) and (b)). Thus, the adsorption of $[(CH_3)_4N]^+$ ions on the sintering aid particles was responsible for the greater adsorption.

The amount of $[(CH_3)_4N]^+$ ions adsorbed increased with increasing pH from 9.7 to 10.5 and then decreased upon further increasing of pH up to 12.3 (Fig. 4(b)). At $pH < 10.3$ the Y_2O_3 particles were positively charged and the $[(CH_3)_4N]^+$ ions were only adsorbed at the negative ($-Al-O^-$) sites of the Al_2O_3 powder surface [17]. At pH higher than 10.3 the Al_2O_3 and Y_2O_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 $[(CH_3)_4N]^+$ ions adsorbed decreased slightly at pH higher than 10.5 (Fig. 4(b)). This behaviour might be produced by an increase of the solubility of Al_2O_3 at pH values > 10.5 as it was mentioned by Yariv [18], reducing the amount of counterions adsorbed on its surface.

The amount of $[(CH_3)_4N]^+$ ions adsorbed on the Si_3N_4/sintering aid powders was low with respect to the amount of TMAH added. Consequently, substantial modifications of the interfacial charge properties of the powders were not expected and an appreciable amount of $[(CH_3)_4N]^+$ ions remained in solution.

The lower equilibrium concentration of $[(CH_3)_4N]^+$ ions in solution for Si_3N_4/sintering aid slips with respect to Si_3N_4 slips at about 9.8–12.3 pH range was consistent with the greater adsorption of counterions on the Si_3N_4/sintering aid powder surface.

The amount of $[(CH_3)_4N]^+$ ions in solution for Si_3N_4/sintering aid slips shows a minimum at pH 10.5 (Fig. 4(d)) where the $[(CH_3)_4N]^+$ ion adsorption has its maximum (Fig. 4(b)). A decrease in the amount of counterions in solution up to pH 10.5 was found followed by an important increase with further increasing of pH up to 12.3 (Fig. 4(d)). Silicate ions produced by the dissolution of the SiO_2 on the Si_3N_4 powder surface were present in the solution (Fig. 5(b)) in addition to $[(CH_3)_4N]^+$ ions. Si_3N_4/sintering aid slips showed a pH dependency on the amount of soluble SiO_2 similar to that of Si_3N_4 slips (Fig. 5(a) and (b)). However, a lower amount of soluble silica in Si_3N_4/sintering aid slips was found due to the lower concentration of Si_3N_4. As the amount of $HSiO_3^-$ ions was very low with respect to the amount of counterions in solution (Figs. 4(d) and 5(b)), the silicate ions had a minor effect on the ionic strength of the solution.

High viscosity values at $pH < 10.3$ (Fig. 3(b)) could be expected since the Y_2O_3 powder had the opposite sign zeta potential (positive) with respect to Si_3N_4 and Al_2O_3 powders up to pH 10.3 and hetero-coagulation occurred, decreasing the negative surface charge of the powders [15] and consequently the electrostatic repulsion between particles. At pH values higher than 10.3 the Y_2O_3 powder moved through its IEP and became negatively charged, the same sign charge as the Si_3N_4 and Al_2O_3 powders 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. 4(d)).

The negative zeta potential of the powders increased with an increase in pH in the pH range from 10.5 to 12.3, however the slip viscosity increased (Fig. 3(b)). This was produced by the increase of the amount of counterions in solution at 10.5–12.3 pH range (Fig. 4(d)) which had a detrimental effect on the slip stability as they increased the ionic strength of the solution.

A greater increase of the slip viscosity was observed at $pH > 11.7$ (Fig. 3(b)) where the amount of counterions in solution was about 70 mM litre^{-1} (Fig. 4(d)). This behaviour was also found for Si_3N_4 slips at $pH > 11.2$ (amount of counterions in solution > 70 mM litre^{-1}), Fig. 4(c)). Thus, 70 mM litre^{-1} seemed to be a critical coagulation concentration of counterions for the slips.

The substitution of 10 wt% Si_3N_4 by 6 wt% Y_2O_3 and 4 wt% Al_2O_3 in Si_3N_4/sintering aid slips produced a decrease in the negative surface charge of the powders with respect to Si_3N_4 slips (Al_2O_3 and Y_2O_3 powders have lower zeta potential values at 10.3–12.3 pH range compared with the Si_3N_4 powder) [15]. However, lower viscosity values at 10.3–12.3 pH range could be obtained with Si_3N_4/sintering aid slips due to the lower amount of counterions in solution. Thus, the degree of slip dispersion at high pH values was governed by the amount of free $[(CH_3)_4N]^+$ ions in solution.

The results showed that the sintering aid powders had a positive effect on the dispersion of the Si_3N_4 powder at pH higher than 10.3. The lowest viscosity value (30 mPa.s) of 35 vol% slips could be obtained from Si_3N_4/sintering aid slips at pH 10.5.

4. Conclusions

1. The Si_3N_4 powder can be dispersed at $pH \geq 9.7$. The slip viscosity increases with an increase in pH at 9.7–12.2 pH range. Thus, the dispersion of the Si_3N_4 powder is not determined by the magnitude of the powder surface charge. The increase in the amount of counterions in solution with increasing pH increases the ionic strength of the solution and consequently the slip viscosity.
2. A greater adsorption of the Si_3N_4/sintering aid powders with respect to the Si_3N_4 powder is found at the pH range studied due to the adsorption of tetramethylammonium ions on the sintering aid particles. Therefore, the equilibrium concentration of counterions in solution is lower for Si_3N_4/sintering aid slips.
3. The minimum viscosity for Si_3N_4/sintering aid slips is observed at pH 10.5. At pH lower than 10.3 the viscosity is high since hetero-coagulation occurs. The increase in viscosity at pH higher than 10.5 is attributed to the increasing amount of counterions in solution.
4. The viscosity values of Si_3N_4/sintering aid slips at 10.3–12.3 pH range are lower than those of Si_3N_4 slips due to the lower concentration of counterions in solution.
5. The equilibrium concentration of 70 mM litre^{-1} appears to be a critical coagulation concentration of counterions for Si_3N_4 and Si_3N_4/sintering aid slips. This concentration occurs at pH 11.2 and pH 11.7 for Si_3N_4 and Si_3N_4/sintering aid slips, respectively.
6. The sintering aid powders have a positive effect on the dispersion of the Si_3N_4 powder at pH higher than 10.3 since lower viscosity values of 35 vol% slips can be achieved.

Acknowledgements

The authors thank Dr A.B. Garcia for the electrophoretic mobility measurements.

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