Journal of the European Ceramic Society 16 (1996) 671–678

0955-2219(95)00172-7
0955-2219/96/$15.00

Surface Charge and Viscosity of Mixed Si_3N_4–Y_2O_3 Suspensions Containing Lignosulphonate

Heidi Fagerholm,[a] Leena-Sisko Johansson,[b] Mats Graeffe[a] & Jarl B. Rosenholm[a]

[a]Åbo Akademi University, Department of Physical Chemistry, Porthansgatan 3–5, FIN–20500 Åbo, Finland
[b]Materials Research Centre, University of Turku, ElectroCity 4D, FIN–20520 Turku, Finland

(Received 20 June 1994; revised version received 31 August 1995; accepted 9 September 1995)

Abstract

We have studied the surface charge and the dispersion behavior of silicon nitride–yttrium oxide–lignosulfonate powder dispersions, prior to sintering. In our previous study we reported on the effect of pH on the adsorption of yttria (Y_2O_3) and lignosulfonate (LS) on the surface of silicon nitride (Si_3N_4) powder. The adsorption was studied by particle size measurements, scanning electron microscopy, X-ray photoelectron spectroscopy (ESCA) and carbon analyses. In this study, we report the results from the electrophoretic mobility and surface charge determinations and viscosity measurements of the slip. The viscosity measurements were performed as a function of the LS concentration added in the dispersion. This was done in order to determine the optimum concentration of lignosulfonate added in the dispersion, i.e. the concentration which would result in the lowest viscosity for the highest possible dry content of the slip. The surface charge was determined via potentiometric titrations and by measuring the electrophoretic mobility.

Introduction

Silicon nitride based ceramics have great potential for high-temperature, high-stress applications. In order to obtain defect-free ceramic bodies it is of importance to avoid aggregation of the dispersed powder and to be able to sinter the green body at sufficiently low temperatures.[1]

In our previous publication[2] we reported on the effect of pH on the adsorption of yttria (Y_2O_3) and lignosulfonate (LS) on the surface of silicon nitride (Si_3N_4) powder. In this paper we report on the suspension properties of Si_3N_4 matrix with an addition of sintering agent, yttria.

Electrophoretic mobility measurements were used to determine the change in the surface charge on the interface of the silicon nitride and yttria particles after conditioning in aqueous solutions of pH 7 and pH 10. Potentiometric titrations of the Si_3N_4–Y_2O_3–LS system were performed to quantify the surface charge and determine the isoelectric point (IEP) and to investigate if any specifically adsorbed positive or negative surface groups were present.

The viscosity of the slip was studied as a function of the concentration of lignosulfonate added to the dispersion. This is to obtain the lowest viscosity/highest dry content of the powder in the slip. In general the homogeneity and viscosity of the slip relate to the sintering properties of the green body.

Experimental

Raw materials

The silicon nitride powder (SN E-10) used in this study was supplied by Ube Industries, Yamaguchi, Japan. According to the manufacturer, the specific surface area was 10 $m^2\ g^{-1}$ and the particle size ~0·4 μm. The yttrium oxide powder (grade fine) was supplied by H. C. Starck, Berlin, Germany. The BET specific surface area according to the manufacturer was 13·7 $m^2\ g^{-1}$. The particle size distribution was given to be $X_{90} < 2{\cdot}5$ μm, $X_{50} <$ 0·8 μm and $X_{10} < 0{\cdot}35$ μm. The lignosulfonate used was Wargonin extra (calcium–sodium lignosulfonate) supplied by Lignotech Sweden.

The powders were used without further purification. The water used was distilled and purified with a Milli Q system to obtain a minimum resistivity of 18 $M\Omega\ cm^{-1}$.

Sample preparation

The list of samples is given in Table 1. The samples contained silicon nitride, yttrium oxide and/or lignosulfonate. The amount of the sintering agent, Y_2O_3, was kept at a constant level of 5 wt% and the concentration of the dispersing agent added to the solution was 0·05, 0·5 or 2·0 wt% for the electrophoretic mobility measurements. Viscosity was

Table 1. List of the samples. All samples except pure lignosulfonate specimen were treated in solutions of pH 7 and pH 10

Si_3N_4
Y_2O_3
Lignosulfonate (LS)
Si_3N_4 + 5 wt% Y_2O_3
Si_3N_4 + 5 wt% Y_2O_3 + 0·05 wt% LS
Si_3N_4 + 5 wt% Y_2O_3 + 0·5 wt% LS
Si_3N_4 + 5 wt% Y_2O_3 + 2·0 wt% LS

determined against the concentration of LS added to the dispersion, the amount of LS added being in the range 0·05–1 wt%. Percentage additives were calculated for the dry content of the slip. All samples were prepared by first adding the lignosulfonate powder (when used) in Milli Q purified water, then adding Y_2O_3 and finally Si_3N_4.

The pH 7 was chosen in order to obtain countercharged particle surfaces, thus ensuring an electrostatic adsorption of Y_2O_3 on the surface of Si_3N_4.[3] This pH is close to the natural pH of the slurry, and, according to Lidén *et al.*,[3] the colloidal yttria particles are stable and positively charged only in the pH range close to pH 7. However, the solubility of yttria at pH 7 might cause problems in the interpretation of the surface charge measurements.[4] According to the literature,[5] yttria is insoluble in bases and soluble in acids, and the solubility of yttria into cold water is 0·0018 g dm^{-3} (ie. 18 ppm). In our experiments the solubility of yttria into water was still insignificant at pH 7 (100 ppm). We did not measure the solubility of yttrium in aqueous silicon nitride dispersions but Rosenholm *et al.*[6] have reported that in aqueous ZrO_2 dispersions stabilized with 3 mol% Y_2O_3, the solubility of yttrium was at its minimum at a pH range of 6–7·5.

The pH 10 was chosen for our experiments, since pH 9–10 is typically used in processing of silicon nitride powders.[7] The pH of the respective slurries was adjusted using 0·1 M HCl or NaOH (Merck titrisols).

Sample preparation for electrophoretic mobility measurements

The dispersion was prepared by first adjusting the pH of the water. The dispersions were processed in an ultrasonic stirrer, after which the pH of the dispersion was readjusted. The dispersion was allowed to equilibrate for 24 h under stirring to ensure a sufficient conditioning time. The concentration of each slurry was about 20 wt%.

Prior to the measurements the pH of the dispersions was readjusted once more, after which the dispersion was centrifuged (3000 rev min^{-1}, 30 min) and separated from the supernatant. The dispersion was then diluted according to the requirements of the instrument manufacturer.

Sample preparation for surface charge measurements

Samples were prepared by adding 40 ml of the electrolyte (NaCl) to a preweighted amount of powder. This addition resulted in a suspension containing 15–21 m^2 powder. The suspensions were dispersed by an ultrasonic device and then allowed to equilibrate for about 20 h in a sealed container in normal atmosphere under stirring.

The supernatants used as blanks were obtained by centrifuging identically prepared suspensions at 3500 rev min^{-1} for 3 h. The supernatant was filtrated through a 0·22 μm Millipore filter paper before the titration.

Sample preparation for viscosity measurements

The viscosity was measured on dispersions containing 20–34 vol% powder. The measurements at the native pH of the slurry (close to pH 7) were made on freshly made slips, after 15 min treatment with an ultrasonic rod (model 450 Sonifer® Branson). The conditioned slips were prepared by allowing the powder dispersion to condition for 24 h. The alkaline slips were prepared by adding 5 ml 0·1 M NaOH in water; measurement of the pH of the slip after conditioning revealed a value of ~10–11. For the slips at conditioned native pH, the pH measured after conditioning was ~7–8.

Electrophoretic mobility

The electrophoretic mobility measurements were carried out using a Zetasizer IIc instrument from Malvern Instruments. The results of the measurements are reported as electrophoretic mobility since the size/diffuse layer thickness ratio is outside both the Huckel and the Smoluchovski limits and the transformation to zeta potential is not at all straightforward.

Surface charge

The surface charge density was determined using the method first developed by Parks and de Bruyn.[8] A Titrino 702 titroprocessor (from Metrohm) was used for potentiometric titrations. We measured the surface charge density as a function of pH, using HCl, NaOH and three different electrolyte concentrations.

Both the electrolytes used in the suspensions and the supernatants of the suspensions were used as blanks. Differences between titrations can be expected depending on whether the electrolyte or supernatant is used as a blank, since a larger amount of titrant is required for neutralizing the ions leached into the supernatant.

Titrations were conducted between pH 3 and 11. The dispersion rate for the titrate was 0·02 ml min^{-1} which gave a titration rate of 4 to 8 pH units per hour.

The surface charge as a function of pH was determined from the net adsorption densities (Γ/mol cm^{-2}) by

$$\sigma_0 = F(\Gamma_{H^+} - \Gamma_{OH^-}) = \frac{F}{s}[(n_{H^+} - n_{OH^-}) - (n^b_{H^+} - n^b_{OH^-})]$$

where n_{H^+} and n_{OH^-} are the total number of moles H^+ and OH^- added to the suspension, $n^b_{H^+}$ and $n^b_{OH^-}$ are the number of moles added to the blank to give the same pH, s is the available surface area and F is the Faraday constant.

According to Gibb and Koopal,[9] the surface charge of the oxides and their mixtures as a function of pH in various electrolyte concentrations and the isoelectric points (IEPs) can be determined via potentiometric titrations. According to Lyklema,[10] the presence of specifically adsorbed cations or anions may be observed from shifts of the common intersection point (cip) of the potentiometric titration curves measured in various electrolyte concentrations. For an inert electrolyte, in absence of specific adsorption cip may be identified as the point of zero charge (PZC). The electrolyte used in our experiments was, according to Bergström and Pugh,[11] found to be inert for silicon nitride.

Viscosity

The shear stress and viscosity measurements were made using a Bohlin VOR Rheometer System

Results and Discussion

Electrophoretic mobility

Results from the electrophoretic determinations are given in Fig. 1.

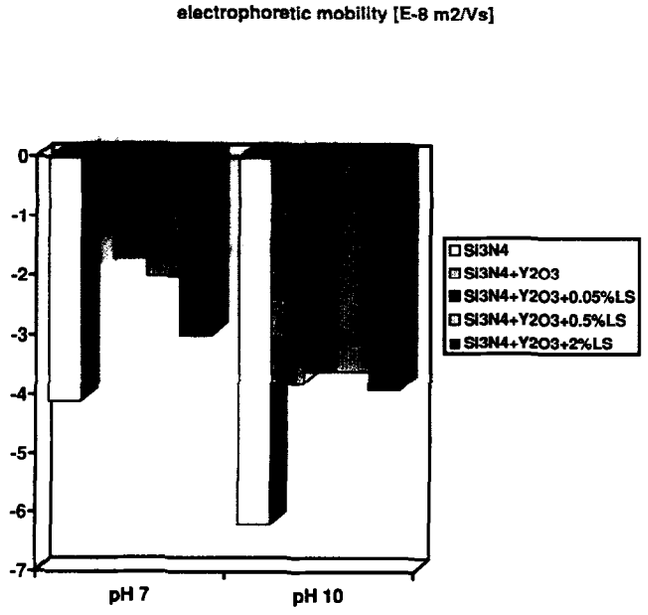


Fig. 1. Si_3N_4 + Y_2O_3 + lignosulfonate.

Si_3N_4–lignosulfonate

The Si_3N_4 slip conditioned at pH 7 showed a clearly negative electrophoretic mobility which was not significantly changed in samples with an increasing addition of LS in the dispersion. The slip conditioned at pH 10 showed an enhanced negative electrophoretic mobility. As in the case of pH 7, treatment with an increasing amount of LS at pH 10 also resulted in no significant change in the electrophoretic mobility.

Si_3N_4–Y_2O_3–lignosulfonate

The results from the electrophoretic mobility measurements are given in Fig. 1. An addition of yttria in the Si_3N_4 matrix at pH 7 resulted in a less negative electrophoretic mobility of the powder particles in the suspension, compared with that of pure Si_3N_4. This was expected as yttria is known to have a positive surface charge at pH 7 and also is expected to adsorb on the silicon nitride surface covering the Si_3N_4 particles. An increasing addition of lignosulfonate in the Si_3N_4–Y_2O_3 matrix was detected as an increasing negative electrophoretic mobility of the particles. However, this was detected only at pH 7, as increasing the amount of LS added to the slip at pH 10 did not change the electrophoretic mobility of Si_3N_4–Y_2O_3–LS particles. Thus these results support the previous assumption that lignosulfonate does not cover the Si_3N_4–Y_2O_3 particles.[2]

Surface charge

Native pH of the slips

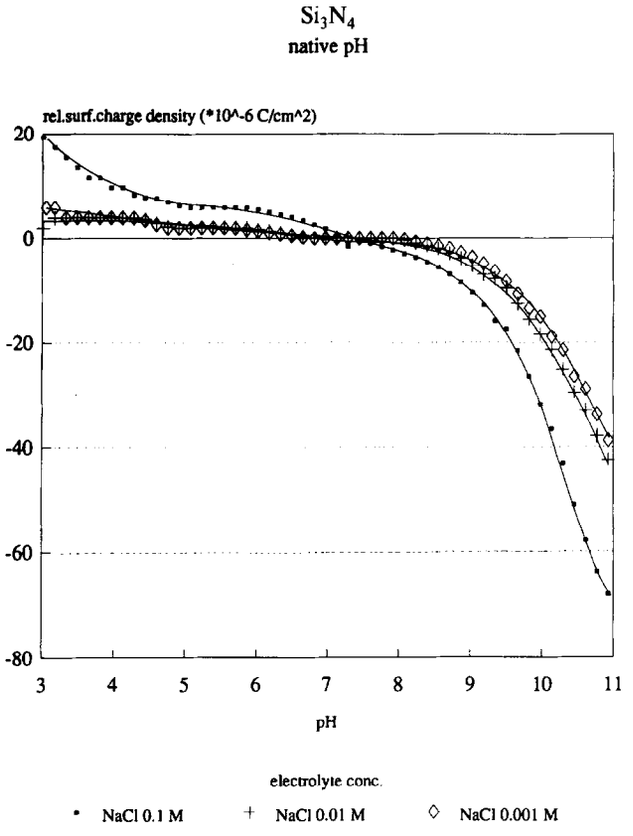
Results from surface charge measurements of Si_3N_4 and Si_3N_4–Y_2O_3 are shown in Fig. 2. Our titration curves for Si_3N_4 showed decreased relative surface charge densities when supernatant was used as blank at pH values > 8. This is in agreement with the results reported by Bergström and Pugh, although in our experiments the decrease was smaller. The difference in Si_3N_4 titration curves (electrolyte vs. supernatant) was explained to be due to a large amount of titratable species leached from the powder surface.

The isoelectric point (IEP) for the Si_3N_4 suspensions was determined to be at pH 7·2 when using either electrolyte or supernatant as blank, indicating no leaching of titratable ions. Since the common intersection point of titration curves (cip) was also at pH 7·2, no specific adsorption was observed and cip coincides with PZC.

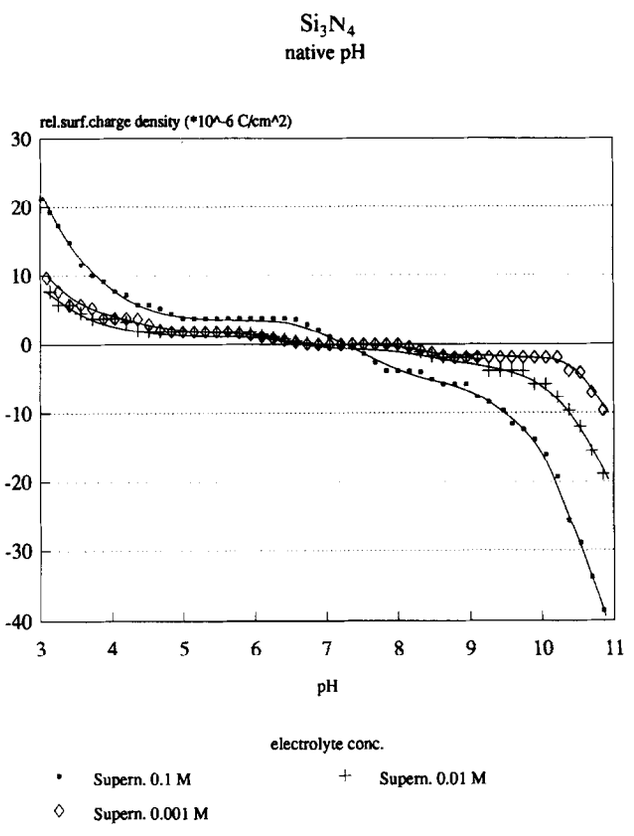
An addition of 5 wt% Y_2O_3 in the Si_3N_4 matrix resulted in more positive surface charge densities than those of Si_3N_4. This could be explained by the electrostatic adsorption of positive yttria particles on negative silicon nitride particles, as shown

by electrophoretic mobility measurements. Moreover, the titration curves of Si_3N_4–Y_2O_3 were less dependent on the blank used than the titration curves of Si_3N_4. This would indicate that less titratable ions were leached out from Si_3N_4–Y_2O_3.

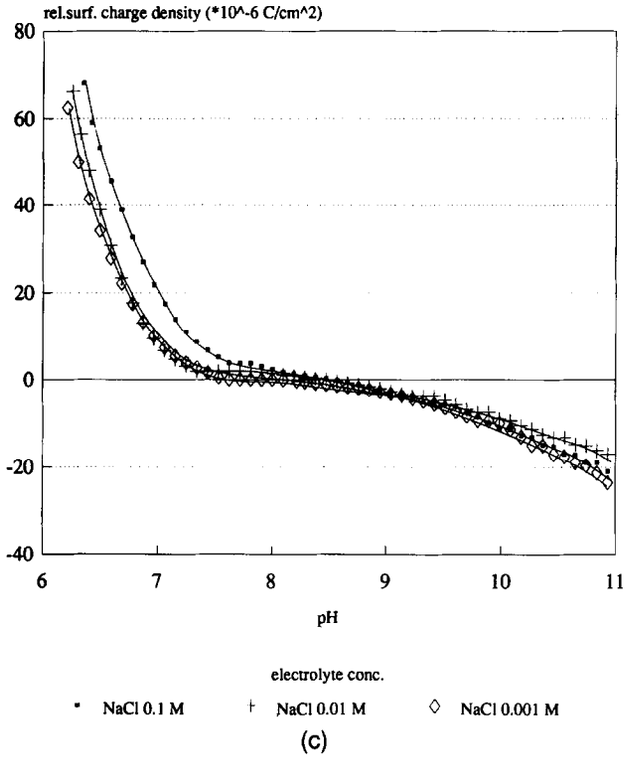
A shift in the IEP value of Si_3N_4–Y_2O_3 from 8·4 to 9·2 was detected when the ions leached from the powder were taken into account, i.e. by using the supernatant as a blank. In addition, the cip value differed slightly from the IEP value suggesting



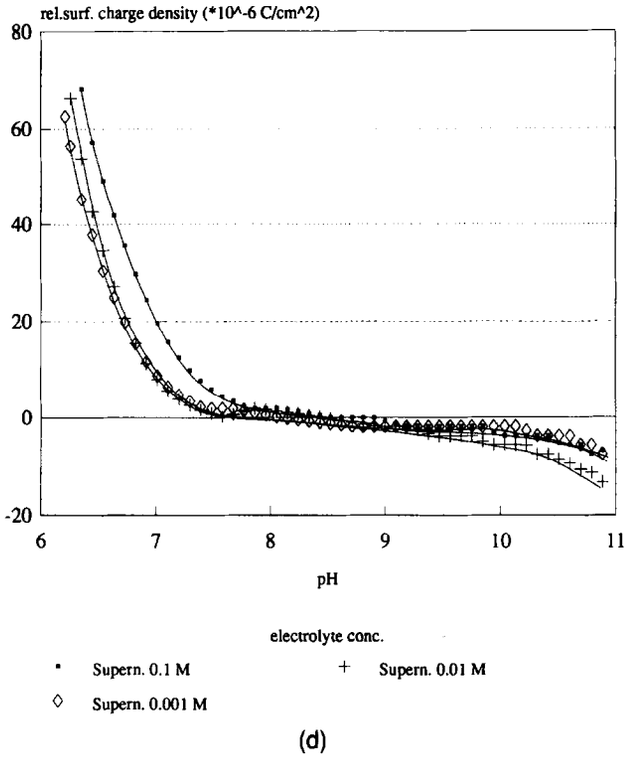
(a)



(b)



(c)



(d)

Fig. 2. Surface charge of (a) Si_3N_4 using pure electrolyte as blank; (b) Si_3N_4 using supernatant as blank; (c) Si_3N_4–Y_2O_3 using pure electrolyte as blank; (d) Si_3N_4–Y_2O_3 using supernatant as blank.

a specific adsorption of cations, presumably ammonia. According to Pollinger,[12] the IEP value for Y_2O_3 appears at pH 9·25. Thus, our results support the assumption of yttria particles covering the silicon nitride particles, preventing the leaching of ions from Si_3N_4 matrix. This explains why the Si_3N_4–Y_2O_3 system behaves rather like pure yttria when the supernatant is used as blank. On the other hand, when the electrolyte was used as blank the IEP value of Si_3N_4–Y_2O_3 was closer to that of pure Si_3N_4 (8·4).

Slip conditioned at pH 7

Results from surface charge measurements of Si_3N_4 and Si_3N_4–Y_2O_3 conditioned at pH ≈ 7 are shown in Fig. 3. Titrations for pH conditioned slips were performed only using the supernatant as blank, thus taking the titratable leached species into account. The ionic strengths referred here are given as the original ionic strengths for the pure electrolyte, although they will be changed during the conditioning due to the leaching of ions from the matrix into the supernatant.

For pure Si_3N_4 the cip and IEP appeared at about pH 7, suggesting no specific adsorption of ions. Thus the cip can be identified as PZC. This is in agreement with the surface charge measurements of the non-conditioned slip, since the native pH of the slip is at about pH 7.

Once again, an addition of 5 wt% Y_2O_3 in the Si_3N_4 matrix resulted in more positive surface charge densities than those of pure Si_3N_4. This was explained by the electrostatic adsorption of the positive yttria particles covering the negative silicon nitride particles. However, the surface charge densities of the Si_3N_4–Y_2O_3 suspension conditioned at pH 7 were slightly less positive than the ones for the non-conditioned slip. A shift in the IEP value from 9·2 to 8 was detected as a result of the conditioning. The cip was also shifted from 8·5 to 7·3. This supports again our assumption of specific adsorption of cations.

Slip conditioned at pH 10

Results from surface charge measurements of Si_3N_4 and Si_3N_4–Y_2O_3 conditioned at pH ≈ 10 are shown in Fig. 4. For pure Si_3N_4 conditioned at pH 10, the IEP appears at about pH 10 and the cip at pH close to 11. This could be due to the dissociation of silicon nitride in strong alkaline solutions which drastically increases the solubility of Si from Si_3N_4 matrix in the suspension.

An addition of 5 wt% Y_2O_3 in the Si_3N_4 matrix and conditioning of the suspension at pH 10 resulted in an IEP at pH 7·2, which is similar to the IEP of pure Si_3N_4. According to these results yttria does not adsorb colloidally on Si_3N_4 particles. Neither does it cover the silicon nitride particles in slips conditioned at pH 10 as suggested in Part 1 of this study. The common intersection of electrolyte

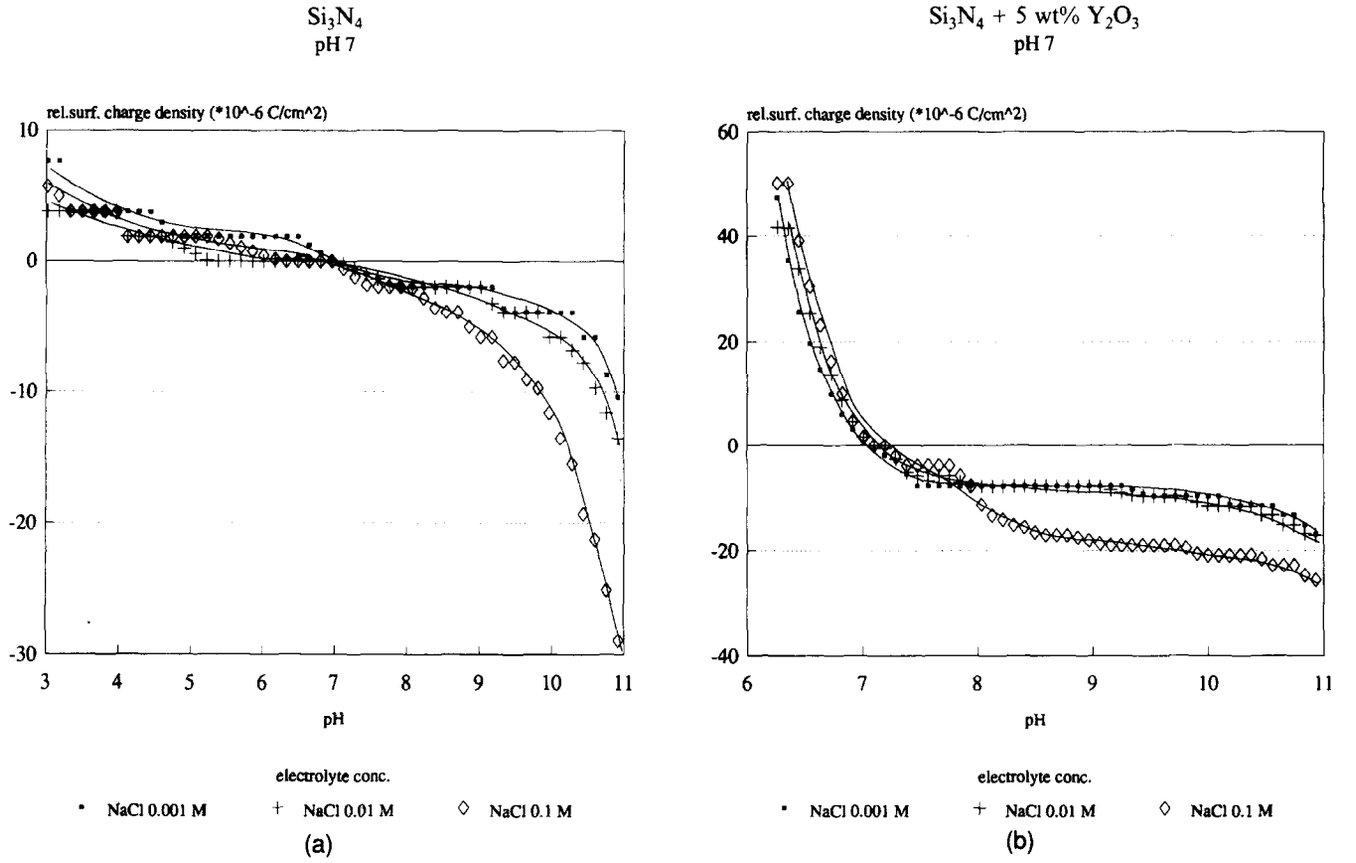


Fig. 3. Surface charge of (a) Si_3N_4 using supernatant as blank; (b) Si_3N_4–Y_2O_3 using supernatant as blank.

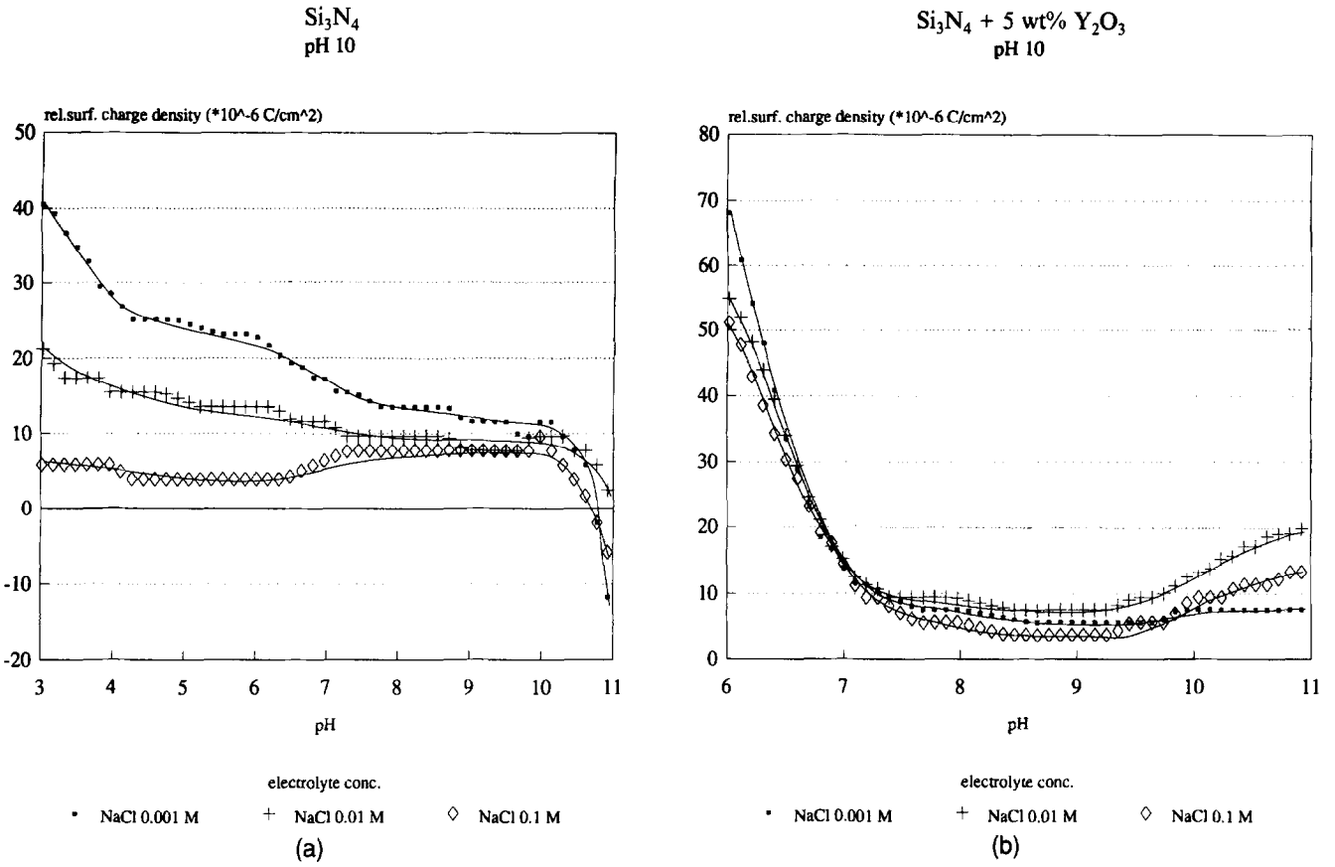


Fig. 4. Surface charge of (a) Si_3N_4 using supernatant as blank; (b) Si_3N_4-Y_2O_3 using supernatant as blank.

curves for the Si_3N_4–Y_2O_3 slip conditioned at pH 10 was never reached. However, the addition of yttria in the Si_3N_4 matrix caused a clear change in the surface charge density towards more positive values.

Viscosity

The results from viscosity measurements are shown in Figs 5 (for Si_3N_4 + LS slip) and 6 (for Si_3N_4 + Y_2O_3 + LS slip). The viscosity of the slips was measured for freshly made slips (native pH) and for slips that had been conditioned in solutions of about pH 7 and in alkaline solution of pH 10–11 for 24 h.

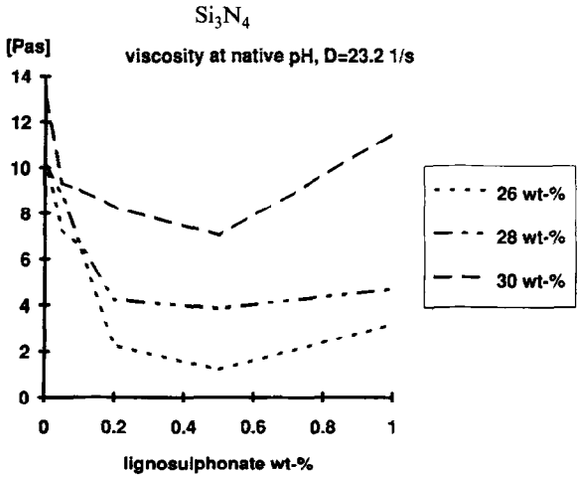


Fig. 5. Viscosity of Si_3N_4–LS slip at native pH.

The results from the viscosity measurements at a shear rate of about 23 s^{-1} for the Si_3N_4 slips at the native pH are presented in Fig. 5. The lowest viscosity for the slips appeared to be at ~ 0·4 wt% addition of LS.

The results from similar viscosity measurements for the Si_3N_4–Y_2O_3 slips at three different pH treatments (native, conditioned at pH 8 and pH 10–11) are presented in Fig. 6. The viscosities of the non-conditioned slip and the slip conditioned at pH 8 were found to be similar, and the lowest viscosity was achieved with an addition of 0·5 wt% LS. The viscosity of the Si_3N_4–Y_2O_3 slip conditioned at pH 10–11 was markedly lower. Also, the viscosity behaviour of this slip was different: the lowest viscosity was achieved with an addition of 0·05–0·2 wt% LS. This is in good accordance with the results for silicon nitride powders with a specific surface area of 11 m^2 g^{-1} reported by Rabinovich *et. al.*[13]

Since the optimal slip casting properties are achieved by using proper conditioning with minimum amount of dispersing agent, to ensure the best slip casting properties an LS addition of ~ 0·2 wt% is required for the Si_3N_4–Y_2O_3 slip.

Unfortunately we were unable to record the viscosity for the slips without LS addition due to problems with dispersability of the powders.

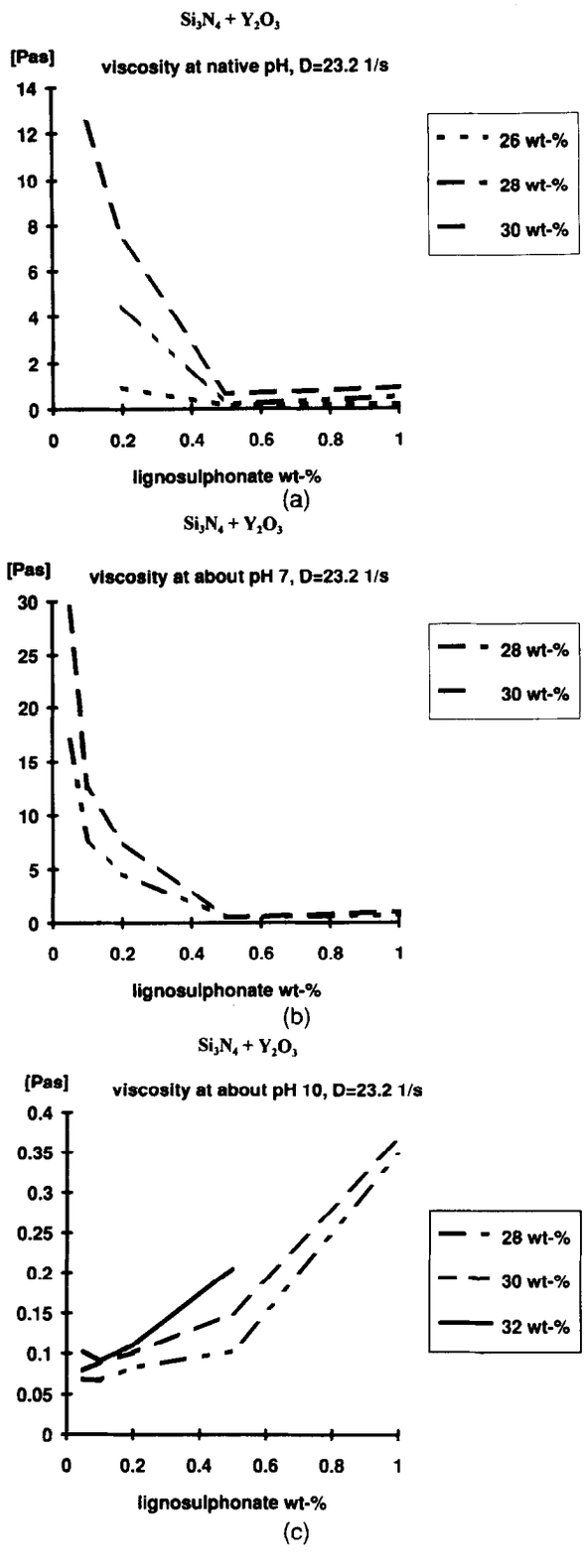


Fig. 6. Viscosity of (a) Si_3N_4–Y_2O_3–LS slip at native pH; (b) Si_3N_4–LS slip conditioned at pH 7–8; (c) Si_3N_4–LS slip conditioned at pH 10–11.

Concluding Remarks

The results presented in Parts 1[2] and 2 of this study enable the following conclusions to be made.

Dispersion mechanism

According to the results from X-ray photoelectron spectroscopy (ESCA), particle size and carbon analyses, the dispersion mechanism of LS is dependent on the pH of the slip.

At pH 7 the dispersability of the Si_3N_4–Y_2O_3 powders increased with increasing amount of LS added to the solution, as indicated by the viscosity measurements and particle size analyses. In this case the carbon content of the dried Si_3N_4–Y_2O_3 – LS powder dispersion was also increased and LS was found to adsorb on the Si_3N_4 and Y_2O_3 particle surfaces (ESCA). These results indicate that at pH 7 LS acts as an adsorbing dispersant, suggesting steric stabilization of the suspension.

At pH 10, the viscosity of the Si_3N_4–Y_2O_3–LS powder dispersion was drastically lower than that at pH 7, indicating an enhanced dispersability of the powders. However, now the viscosity of the suspension increased with increasing amount of LS added to the solution, indicating a decrease in dispersability of the powders. ESCA, particle size and carbon analyses indicated that LS was not adsorbed on the Si_3N_4 and Y_2O_3 powder particles, although the carbon content of the matrix still increased slightly with increasing amount of LS added to the solution. According to these results, at pH 10 LS acts as a non-adsorbing, free polymer dispersant in the solution. Thus we propose that the dispersion mechanism of LS at pH 10 is of depletion stabilization.

Colloidal/specific adsorption

The addition order of the powders in water, ie. LS, Y_2O_3 and Si_3N_4, supports the colloidal adsorption of LS on the powder particles especially at pH 7 due to the formation of counter-charged LS and yttria particles. This was confirmed by ESCA results.

Leaching of ions from the matrix in the dispersion was confirmed by the surface charge measurements and specific adsorption of cations at pH 7 is suggested.

Processability

In the colloidal processing of silicon nitride based ceramics, an addition of sintering agents typically in the range of 0·05–2 wt% is required. The typical pH used in processing is pH 9–10. Treatment in the alkaline environment at pH 10 ensures the lowest viscosity values and the smallest particle sizes for the powder dispersion, indicating a good dispersability in water. The dispersion stability found for Si_3N_4–Y_2O_3 powder dispersion treated at pH 10 indicates that the stability is enhanced by small additions of LS although no adsorption of LS was confirmed.

Applicability of methods

Great care must be taken when the results from

'dry' characterization techniques are related to the surface conditions present in a real slurry. Traditional 'wet' methods, such as viscosity, surface charge, electrophoretic mobility and particle size analyses, are considered to represent the prevailing process conditions of (for example) high-performance ceramics in a realistic way. Dry methods, such as ESCA, scanning electron microscopy and carbon analysis, yield information on chemical or structural composition of the dried samples.

In this study we have applied both wet and dry methods in order to understand the observed processing behaviour of silicon nitride based ceramics. Results gained from different methods were found to be in accordance with each other, verifying that dry analyses can be related to the characteristics of the slurry. Due to the complexity of the system studied, the use of several independent characterization techniques proved to be a proper way to extract reliable and complementary information.

Acknowledgements

We wish to thank Ms Kirsi Haapoja and Mr Jukka Kujanpää for assistance with the measurements. Financial support from the Research Councils for Technology and the Natural Sciences of the Academy of Finland is gratefully acknowledged.

References

1. Richerson, D.W. (ed.), *Modern Ceramic Engineering: Properties, processing, and use in design, 2nd edition.* Marcel Dekker Inc., New York, 1992.
2. Fagerholm, H. M., Johansson, L.-S. & Rosenholm, J. B., *J. Eur. Ceram. Soc.*, **14** (1994) 403–9.
3. Lidén, E., Persson, M., Carlström, E. & Carlsson, R., *J. Am. Ceram. Soc.*, **74**(6) (1991) 1335–9.
4. Pugh, R. J. & Bergström, L. (ed.), *Surface and Colloid Chemistry in Advanced Ceramic Processing, Surfactant Series, Vol. 51*, Marcel Dekker, NY, 1994, pp. 99–101.
5. *Handbook of Chemistry and Physics, 60th edition.* CRC Press Inc., Boca Raton, FL, 1981, p. B141.
6. Rosenholm, J., Manelius, F., Fagerholm, H. Grönroos, L. & Byman-Fagerholm, H., *Progr. Colloid Polym. Sci.*, **97** (1994) 51–8.
7. Persson, M., Hermansson, L. & Carlsson, R., *Ceramic Powders,* ed. P.Vincenzini. Elsevier Scientific Publ, Holland, 1983, pp. 735–42.
8. Parks, G. A., & de Bruyn, P. L., *J. Phys. Chem.*, **66** (1962) 967–73.
9. Gibb, A. W. M. & Koopal, L. K., *J. Colloid Interf. Sci.*, **34**(1) (1990) 122–38.
10. Lyklema, J., *J. Colloid Interf. Sci.*, **99**(1) (1984) 109–17.
11. Bergström, L. & Pugh, R. J., *J. Am. Ceram. Soc.*, **72**(1) (1989) 103–9.
12. Pollinger, J. P., *III Int. Symp. on Ceramic Materials & Components for Engines, 1988.* Am. Ceram. Soc., 1989, pp. 369–79.
13. Rabinovich, E. M., Leitner, Sh. & Goldenberg, A., *J. Mater. Sci.*, **17** (1982) 323–8.