

Colloidal Filtration of Silicon Nitride Aqueous Slips. Part I: Optimization of the Slip parameters

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Abstract

The slip parameters for the manufacture of dense, pressureless sintered silicon nitride by colloidal forming methods, such as slip or pressure casting, are studied. This work focuses the optimization of the rheological behaviour of the slip considering different kinds and concentrations of dispersants and it has been stated that the electrostatic stabilizing mechanism is essential. The best rheological conditions are achieved with tetramethylammonium hydroxide (TMAH) or any strong base (as NaOH), but the use of TMAH limits the progressive oxidation of the particles suspended in water by action of a partially oxidized protective screen. The study has been made with Al₂O₃ and Y₂O₃ as sintering aids, in concentrations of 3 and 6 wt% each. An optimum pH for dispersing has been located at 11.3 ± 0.2, where neither yield point nor thixotropy are found for 65 wt% slips. Different homogenizing techniques are used and compared, such as strong mechanical agitation, centrifugal milling or mixing in a rotatory bottle with nylon balls. Since the starting silicon nitride powder is submicronic, no milling is required, but a long homogenization time is convenient to assure an equilibrium state at the particles surface. © 1998 Published by Elsevier Science Limited.

Introduction

Silicon nitride has attracted an increasing interest in the development of structural ceramics due to its high performance in high temperature engineering applications,^{1,2} where a low amount of glassy phase is a basic requirement and, consequently,

only a low amount of sintering aids can be accepted. For such cases, many works dealing with the production of dense bodies by pressure sintering methods have been reported, mainly using hot pressing (HP), hot isostatic pressing (HIP) and gas pressure sintering (GPS).³⁻⁵ However, these methods are too expensive to consider an easy exploitation and, in the case of HP, the limitations in the shape are an additional problem. This has led to a search for cheaper fabrication methods by pressureless sintering. However, an important limitation in the obtention of dense, cost-effective Si₃N₄ parts by pressureless sintering is related to the lack of an adequate control of the several processing steps to assure a high reliability and good homogeneity in the final properties.

Colloidal processing techniques are commonly accepted to provide a powerful route to improve the reliability of ceramic materials.⁶ This is an attractive route to process Si₃N₄ which provides different possibilities to obtain pieces with complex shapes, for example by slip casting or pressure slip casting. However the preparation of a well dispersed, uniform and concentrated slip of a submicronic Si₃N₄ powder with the corresponding sintering additives is considered a critical step in those colloidal forming techniques.

Many authors have studied the colloidal behaviour of silicon nitride slips, either in water or in organic media.⁷⁻¹⁰ Similar powders behave differently depending on many processing parameters. The powder fabrication method determines the specific surface area, the morphology and particle size distribution, the oxygen content, and the amount of carbon and metallic impurities in the powder, which have an important effect on green densification and sintering behaviour and hence, in the final thermomechanical properties. Further forming or other processing steps (energy of mixing or milling and its vehicle, shaping from

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slips, and particularly in water, etc) can influence all these parameters. Previous works have reported that the isoelectric point of silicon nitride can change from 3 to 9^{7,11-13} depending on the different species which can form on the particle surface. It is generally accepted that some dissolution of Si₃N₄ particles takes place under any pH conditions because of the reactions with H⁺ and OH⁻ to form siloxane and/or silazane species. This can modify the stability conditions of the slip. The pH control becomes important because it is also related to the formation of oxidized species. The oxygen at the surface will represent a serious problem during sintering. Some authors have treated the starting powders to reduce the oxygen concentration.¹⁴⁻¹⁶

In contrast to the significant amount of information about electrophoretic and colloidal properties, the study of forming operations from concentrated slips requires more attention. Some papers describe the characteristics of low concentrated slips (in the range of 50 wt%) but for casting operations higher solid loadings are preferred. Olgnon *et al.*¹⁷ studied concentrated Si₃N₄ slips, showing that the rheological behaviour was complex and non-Newtonian. They suggested that viscosity was a function of shear rate because during shearing the agglomerates were broken down, but a reagglomeration of the particles occurred again for decreasing shear rates. On the other hand, the possible effects of the oxidic sintering aids must be considered since they contribute to increasing the complexity of the system in terms of homogeneity and presence of oxidized species at the particle surface.

The aim of this work is to present a systematic study of the rheological behaviour of concentrated aqueous silicon nitride slips optimizing the conditions for further casting operations. The influence of the different parameters involved in the slip preparation, such as the type and concentration of deflocculant, the pH, the solid loading, the homogenizing procedure and the effect of sintering aids, are discussed. In a second part the casting kinetics and the green characteristics of both slip cast and pressure cast bodies will be studied and related to the rheological studies shown here.

Experimental

Powder characterization

A commercial silicon nitride powder was used (Hermann C. Starck, LC12SX, Germany). Pressureless sintering of silicon nitride is usually performed by means of a liquid phase, which is provided introducing sintering additives, mostly

oxides. In this work, commercially available European powders of Al₂O₃ (Condea HPA05, Germany) and Y₂O₃ (Mandoval, UK) were used. The main characteristics of the starting powders are summarized in Table 1. The particle size distribution was measured with a laser particle size analyser (Coulter LS130, USA). Specific surface area was measured by single point N₂ adsorption method (Monosorb, Quantachrome, USA) and the total oxygen content by the inert gas fusion technique (LECO, EF400, USA). As observed in Table 1, the starting Y₂O₃ powder is coarser, with a mean particle size of 3.5 μm, four times higher than the other powders. This higher particle size can produce heterogeneities in the distribution of Y₂O₃ in the green body, and could produce density gradients. However, its much lower price justify the selection of this powder. Therefore, part of the starting Y₂O₃ powder was attrition milled in aqueous media using silicon nitride balls. The resulting particle size distribution after different milling times is plotted in Fig. 1. A mean particle size of 0.8 μm (similar to that of silicon nitride) is obtained after 8 h milling.

The oxidation state at the particle surface was evaluated using the X-ray photoelectronic spectroscopy with a Fisons ESCALAB MkII electron spectrometer employing MgK_α X-rays (photon energy, $h\nu=1253.6\text{eV}$), and an electron takeoff angle of 45°. The base pressure of the spectrometer

Table 1. Characteristics of the starting powders

Powder	Si ₃ N ₄	Al ₂ O ₃	Y ₂ O ₃
Impurities (wt%)	C=0.18; O=2.04 Ca, Al<0.01	<0.01	<0.01
Specific surface area (m ² g ⁻¹)	18	9.5	6.9
Mean particle size (μm)	0.7	0.4	3.5

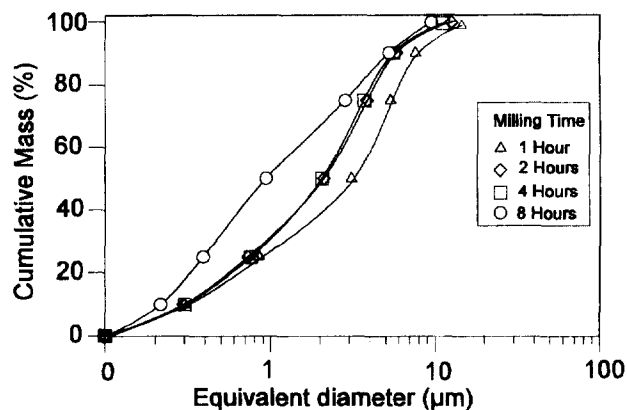


Fig. 1. Particle size distribution of Y₂O₃ after different milling times.

was typically 10^{-9} mbar. The X-ray gun was operated at 12 kV and 10 mA, corresponding to a power of 120 W. A survey spectrum (50–1150 eV) was recorded for each sample (single scan) followed by Si2p, N1s, O1s and C1s regions where appropriate (60 scans). The analyser was operated in fixed analyser transmission (FAT) mode with a pass energy of 50 eV (survey spectrum) and 20 eV (individual peaks). Atomic percentage values were calculated from the peak areas using sensitivity factors provided with the data system and background subtraction. The accuracy of the XPS quantitative analysis, as derived for duplicate analysis, was within $\pm 4\%$. Spectra were corrected for sample charging by referencing photoelectron peaks to C–C/C–H at 284.9 eV. The precision in the binding energy of the XPS lines, obtained as average of at least two measurements, was estimated as ± 0.1 eV.

The colloidal stability of the starting materials was studied in terms of zeta potential to determine the corresponding isoelectric points (i.e.p.). A laser Doppler (D.E.L.S.A. 441, Coulter, USA) equipment was used. For these measurements, aqueous slurries were prepared by mechanical stirring of 15 mg of powder with the addition of electrolyte solution ($\text{NaCl } 10^{-2} \text{ M}$) up to a volume of 100 ml. The pH values were adjusted adding HCl or NaOH and maintaining the slurries in agitation with an orbital stirrer for 24 h to ensure complete stabilization. The pH was measured again before measurements.

Slip formulation

Deflocculation studies on silicon nitride aqueous slips were performed testing different kinds and concentrations of deflocculants. A number of polyelectrolytes were tested, as well as strong bases, trying to stabilize the concentrated slips by means of both electrosteric and electrostatic mechanisms. NaOH and tetramethylammonium hydroxide (TMAH) were tested as strong bases and were found to be very effective, being selected for further experiments.

High solid loading slips (up to 70 wt%) were prepared. Facing forming and sintering steps, compositions including sintering aids were studied. The studied compositions were labelled as SN1, consisting only on Si_3N_4 , SN2, including 3 wt% of each oxide, and SN3, including 6 wt% of each oxide. These are reported compositions for sintered silicon nitride (SSN). The total content of oxidic additives is 0, 6 and 12 wt%, high enough to evaluate the possible effects of the additives along the different processing steps. Better compositions could be selected to enhance some properties in the sintered compact, but the aim here is to control the

slip and the influence of sintering aids. If this objective is achieved, the composition can be easily modified as desired.

Slips containing only one of the additives were also considered for comparison purposes. These compositions were labelled as SN6A and SN6Y and contain 6 wt% of only Al_2O_3 and Y_2O_3 , respectively.

Homogenization of the slips

For rheological and forming studies, concentrated slips of the considered compositions were prepared according to different homogenization routes, as follows:

Route A

High speed mixing. Strong shear is produced mechanically. This energetic mixing produces a heating effect that limits the use of this technique to short times. In this work a mixing time of 3 min was fixed. On the other hand, the strong agitation promotes the formation of big air bubbles that should be removed. The fresh slips prepared by this route were maintained at low stirring at least for 30 min to remove those bubbles. A Silverson L2R (UK) machine was used.

Route B

Ball milling. A plastic bottle with nylon balls was used as ball mill. With this method, no milling takes place and the possible contamination (carbon) is negligible considering the low energy of the mixing and the organic character of the deflocculant TMAH. Homogenizing times from 1 to 48 h were studied measuring the rheological behaviour in order to fix the optimum mixing time.

Route C

Centrifugal milling. This homogenizing route is more energetic and can produce some milling effect due to shear and impact forces. Since no milling is required and long milling times can produce significant contamination, the centrifugal mill was limited to a maximum time of 30 min.

Route D

Attrition milling. Only for comparison purposes the attrition milling for 2 h was also considered. This route produces an effective milling of particles that can modify their surface state. The milling time was 2 h.

The rheological behaviour of concentrated slips was studied using a rotational viscometer with concentric cylinders (distance between cylinders 1.74 mm) at a constant temperature of 25°C. The flow curves were obtained increasing the shear rate from 0 to 1000 s^{-1} in 2 min (up-curve) maintaining

1 min at this shear rate and decreasing again to 0 s^{-1} in other 2 min (down-curve). Since conventional control rate viscometers cannot measure the yield point, this was estimated considering the viscosity and the shear stress measured at a shear rate of 10 s^{-1} . The time dependency of the slips was evaluated as the difference in viscosity between the up-curve and the down-curve at a fixed shear rate of 500 s^{-1} .

The optimization of the slip properties for subsequent colloidal forming steps was made considering the type and concentration of deflocculant, the pH, the solid content, the effect of sintering aids and the homogenization conditions.

Results and Discussion

Surface chemistry

The electrical charges providing electrostatic stabilization in aqueous suspensions arise from surface dissolution of the particles promoting the development of a double layer. The strong surface reactions of Si_3N_4 with H^+ and OH^- in water involve different kinds of interactions, such as the formation of silica and silanols, ammonia and amine-related reactions, and dissolution and readsorption of impurities.¹² The dominant species resulting from these reactions are SiOH_2^+ and Si_2NH_2^+ for pHs lower than the i.e.p., and SiO^- and Si_2N^- for pHs higher than the i.e.p.

Figure 2 shows the variation of zeta potential with pH for the starting silicon nitride. The i.e.p. is located at pH 8.5, which suggests a relatively low oxidation degree.⁷ However, XPS analysis reveals that both Si2p and N1s peaks can be split into doublets. Figure 3(a) and (b) show the Si2p and the N1s peaks as registered and after deconvolution.

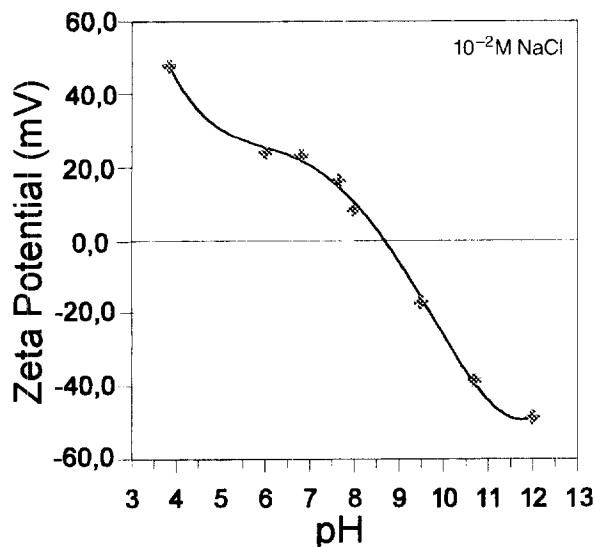


Fig. 2. Zeta potential of the Si_3N_4 as a function of pH.

The location of the Si2p peak may change from 99.3 eV for Si (elemental) to 101.4 eV for Si–N bonds and 103.7 eV for Si–O bonds. The location of the peaks at intermediate values of binding energy (BE) reveals that both silazane and siloxane species are present at the powder surface. Table 2 shows the obtained BE values, suggesting that the powder has a representative amount of Si₂–NH and Si–NH₂ groups, in good agreement with the determined i.e.p.

The zeta potential of the sintering aids must be also considered for the preparation of stable slips of sinterable silicon nitride. Figure 4 shows the zeta potential versus pH curves of the starting Al_2O_3 and Y_2O_3 powders and corresponding to the milled Y_2O_3 powder. The i.e.p. of Al_2O_3 occurs at pH 9.1, in good agreement with other reported values for pure alumina. The i.e.p. of the starting Y_2O_3 powder is located at pH 8.5, slightly lower than expected.¹⁸ This may be due to the agglomeration state of this coarse powder, whose i.e.p. after milling shifts up to pH 9.

Since all the powders have a quite similar i.e.p. value (8.5 to 9.1) it is expected that well-dispersed slips could be prepared at basic pH conditions. Acidic media cannot be used because it could promote the surface oxidation of Si_3N_4 particles.

Selection of deflocculants

Different commercial polyelectrolytes were tested in order to provide electrosteric stabilization to the slip. Table 3 summarizes in a qualitative way the behaviour of slips prepared at different conditions using different deflocculants. In each case the deflocculant was added progressively up to the values reported in the table, where fluidity was enhanced, but no measurements of viscosity were made because of the general poor aspect of the slips. The qualitative behaviour of slips prepared with strong bases (NaOH and TMAH) is also included. In this case fluid slips could be obtained and were further characterized, as reported below. According to this Table, some polyelectrolytes could be used for the preparation of stable slips with solid contents up to 50 wt%. However, for casting operations, higher solid loads are desirable. Stable slips with solid loadings of 65 wt% can be only prepared using the strong bases, that is by means of a pure electrostatic stabilizing mechanism.

Effect of pH and solid contents on the rheology

Figure 5 shows the flow curves of silicon nitride slips with a solid content of 60 wt% deflocculated with NaOH and with TMAH at pH values of 10.5 and 11.5, respectively. The viscosities obtained by dispersing with NaOH are even lower than those

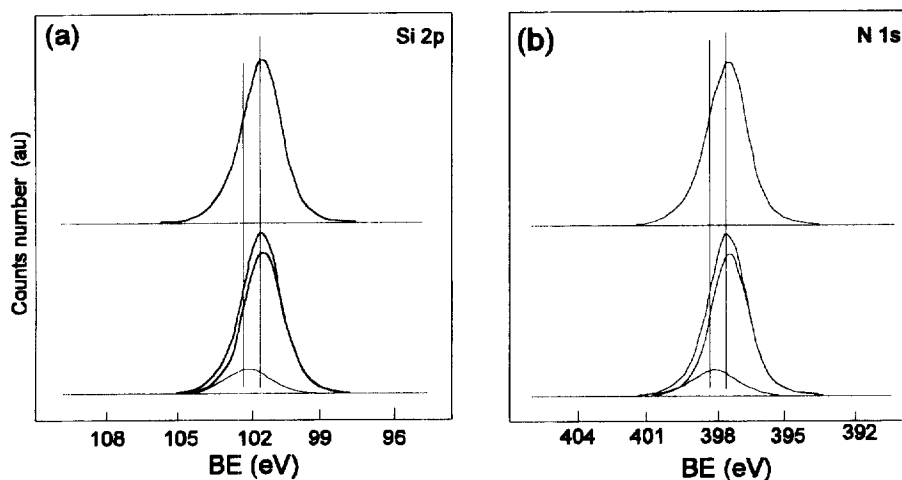


Fig. 3. Core level spectra for the Si_3N_4 powder as registered and after curve fitting to two components (nitride and oxynitride) for (a) Si2p peak and (b) N1s peak.

Table 2. Assignment of the XPS peaks of silicon nitride and surface concentration of the elements

Peak	BE (eV)	Percentage	Species	Atomic ratio
Si2p	101.6	72	Si_3N_4	28
Si2p	102.6	28	SiO_xN_y	11
N1s	397.6	80	Si_3N_4	41
N1s	398.6	20	SiON(H)	10
O1s	532.7	—	SiON(H)	—

obtained with TMAH, thus confirming that a high pH is the key parameter responsible for the effective dispersion. However, the use of NaOH must be avoided because it is a strong glass former at low sintering temperatures in the presence of silica, which has a deleterious effect on the properties of the sintered compact. No more NaOH was added because at pH 10.5 the viscosity was very low.

Using TMAH as deflocculant the resulting flow curve is strongly dependent on pH. Figure 6 shows the flow curves of SN1 slips at different pHs and

65 wt% solids. Some rheological parameters, such as the viscosity, the shear stress at 10 s^{-1} and the thixotropy are summarized in Table 4. A small variation of pH produces a strong variation in the viscosity, which presents a minimum value for pH 11.5. Lower pH values result in increased viscosities, probably due to the lower surface potential. At pH 11 the slip behaves according to a plastic flow with a high yield point, whereas at pH 11.5 the flow curve can be fitted to a Newtonian model. Higher pHs slightly increase the viscosity, which can be related to an increase in the ionic strength.

The optimum solid content was fixed from the flow curves of SN1 slips prepared by shearing (route A) deflocculated with either NaOH or TMAH at pH values where a minimum viscosity was obtained (10.5 and 11.5, respectively). Figure 7 plots the viscosity values at different solid contents of the slip at a shear rate of 100 s^{-1} . Comparing the curves obtained with TMAH and with NaOH, it can be seen that NaOH gives always lower viscosities

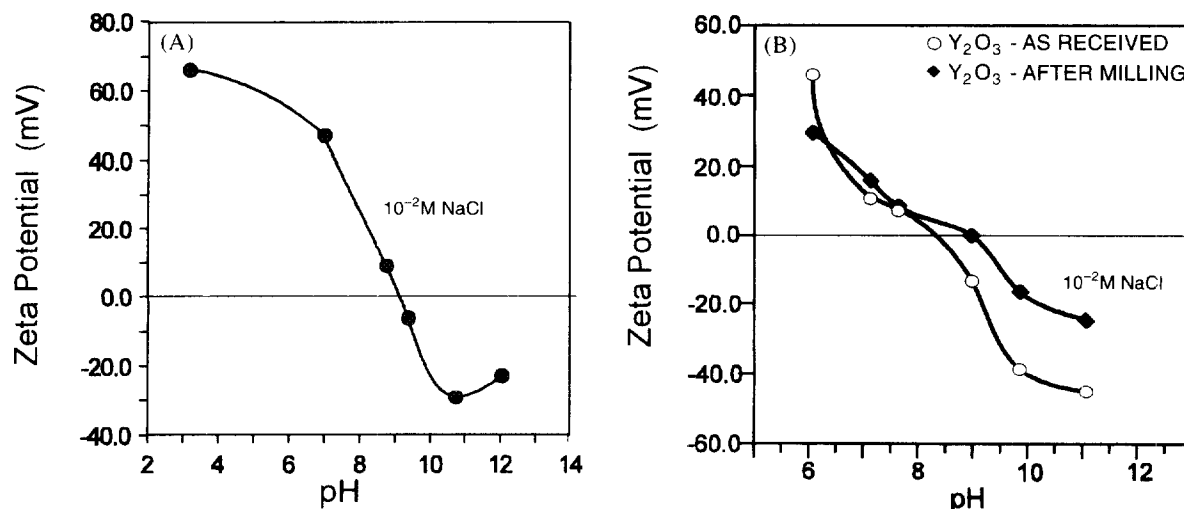


Fig. 4. Zeta potential (ζ) versus pH for Al_2O_3 (A) and for Y_2O_3 , as received and after milling (B).

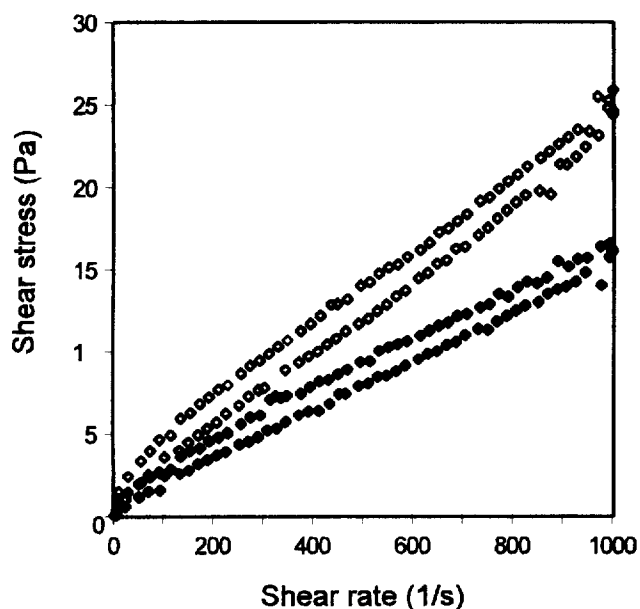
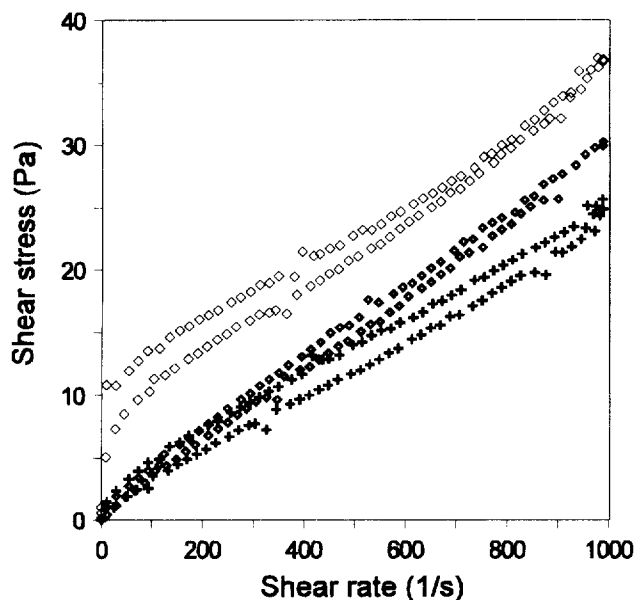
Table 3. Dispersion behaviour of Si_3N_4 with different dispersants

Dispersant	Conc. (% wt)	Suspending liquid	pH	Maximum solids (wt%)	Estimated viscosity	Observations
DOLAPIX PC-33*	1	H ₂ O	8.4	33.2	High	After 3h mixing
	2	H ₂ O	9.4	33.5	Very high	
DARVAN C†	1	H ₂ O	7.5	48	High	—
	2	H ₂ O	9	45	Very high	—
KV5080*	0.5	H ₂ O	7.2	28.1	High	—
KV5088*	0.5	H ₂ O	10	44.8	High	—
KV9021*	2	Ethanol	—	50	Very high	12h ball milling
KV9027*	2	Ethanol	—	50	Very high	
TMAH‡	≥1	H ₂ O	11–12.5	70	Low–Very low	—
NaOH	—	H ₂ O	11	70	Low–Very low	—

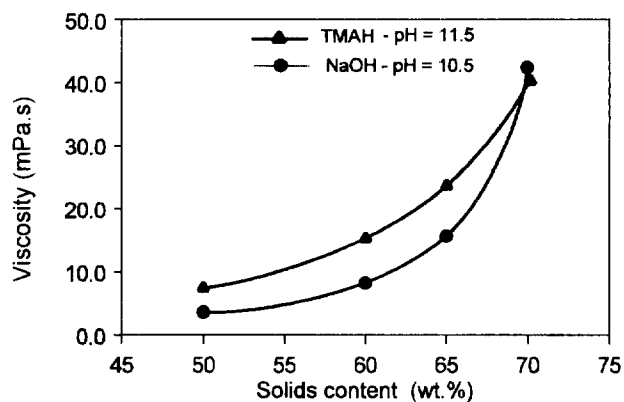
*Zschimmer-Schwarz, Germany.

†Vanderbilt, USA.

‡Aldrich, UK.

**Fig. 5.** Flow curves of Si_3N_4 slips (60 wt%) deflocculated with TMAH (\diamond) and NaOH (\blacklozenge).**Fig. 6.** Flow curves of Si_3N_4 slips (solids content 65 wt%), at pH = 11.1 (\diamond); 11.5 (+) and 12.4 (\circ).**Table 4.** Rheological parameters of Si_3N_4 suspensions with 65 wt% solids using TMAH as deflocculant

pH	τ at 10 s^{-1} (Pa)	η at 100 s^{-1} (mPa s)	η at 500 s^{-1} (mPa s)	$\Delta\tau$ at 500 s^{-1} (Pa)
11.0	10.8	145	45.7	1.6
11.5	1.5	42.3	28.2	2.3
12.4	1.0	42.4	31.8	1.2

**Fig. 7.** Viscosity of Si_3N_4 slips deflocculated with TMAH and NaOH as a function of solids content (shear rate 100 s^{-1}).

demonstrating, even when a lower pH is reached, its dispersing efficiency. The viscosity of 70 wt% solids is relatively high for a good control of casting (82.3 and 83.6 mPa s for TMAH and NaOH, respectively at a shear rate of 100 s^{-1}) and presented some thixotropic hysteresis cycle. Consequently, the slips containing 65 wt% were selected as the most adequate for subsequent forming operations, because they did not present thixotropy and the viscosity was reduced to 28.8 and 42.3 mPa s at the same shear rate.

Effect of the mixing procedure on the rheology

Once the critical role of pH was established, a complete characterization of the slips was made considering the possible effects of the different

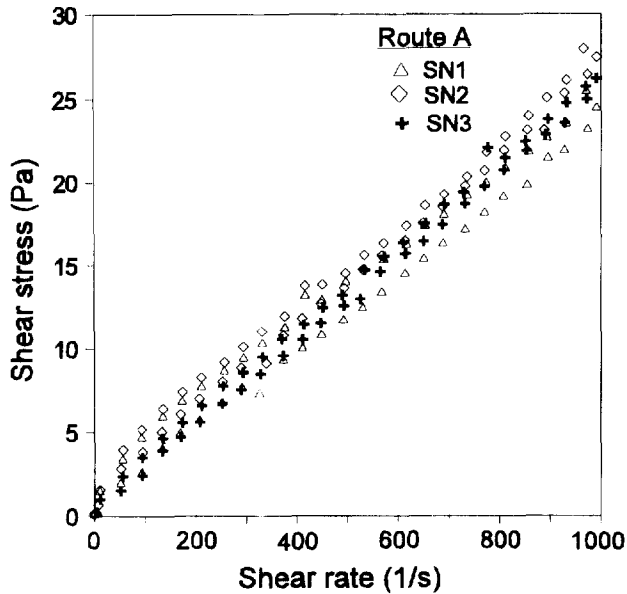


Fig. 8. Rheological behaviour of 65 wt% solid content slips of the three studied compositions at $\text{pH} = 11.3 \pm 0.1$ prepared with TMAH according to mixing route A.

homogenizing procedures on the rheology for all three considered compositions. In all cases the solid content was maintained at 65 wt% and the pH at 11.3 ± 0.2 . This solids content corresponds to volume fractions of 36.8, 36.3 and 35.8% for compositions SN1, SN2 and SN3, respectively. Figure 8 shows the flow curves obtained for the three compositions prepared according to the mixing route A (shearing). As observed in the figure, quite similar behaviour is obtained in all cases, thus showing that the addition of sintering aids practically does not modify the rheology of the major component (silicon nitride), which always controls the slip behaviour. The viscosity is nearly the same, but there is a small tendency to decrease the thixotropy when increasing the content of additives. This can be related to the lower volume content of solids when the concentration of additives increases.

In the case of routes A and C the mixing time is limited to avoid other problems, such as heating, bubbles, contamination, etc. However, route B does not have these limitations. Prior to the comparison of the rheological behaviour with the other methods, the optimum homogenization time must be also defined. Figure 9 plots the resulting viscosity of SN1 slips as a function of the homogenization time. As observed, there is a mixing time of 24 h in which the viscosity decreases (25 mPa s at 500 s^{-1}), while a prolonged mixing for one week leads to slightly higher viscosities. Thus, a mixing time of 24 h has been fixed for the preparation of slips according to this route.

The flow curves of slips prepared according to optimized mixing routes B and C were also determined for the three compositions, as plotted in

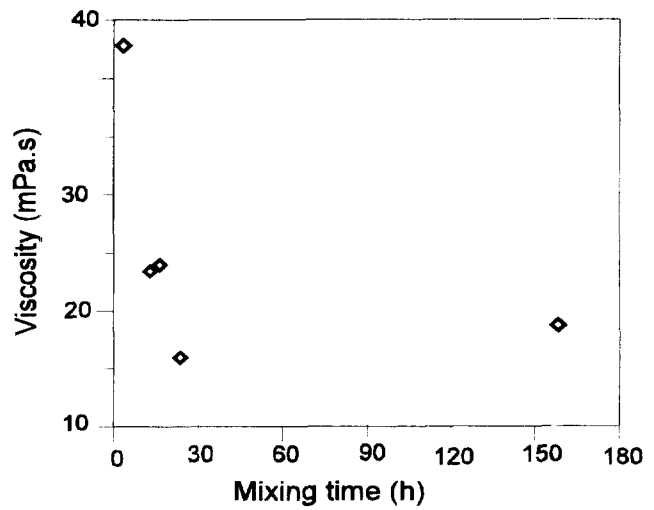


Fig. 9. Viscosity of SN1 slips as a function of the homogenization time (at 500 s^{-1}).

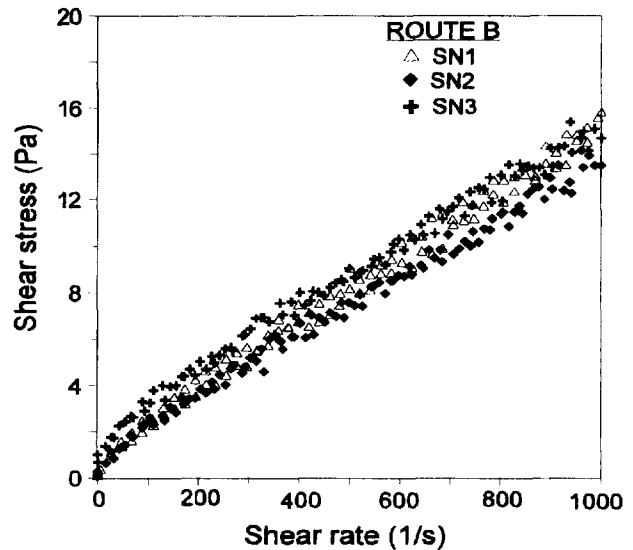


Fig. 10. Flow curves of 65 wt% solid content slips of the three studied compositions at $\text{pH} = 11.3 \pm 0.1$ prepared according to mixing route B.

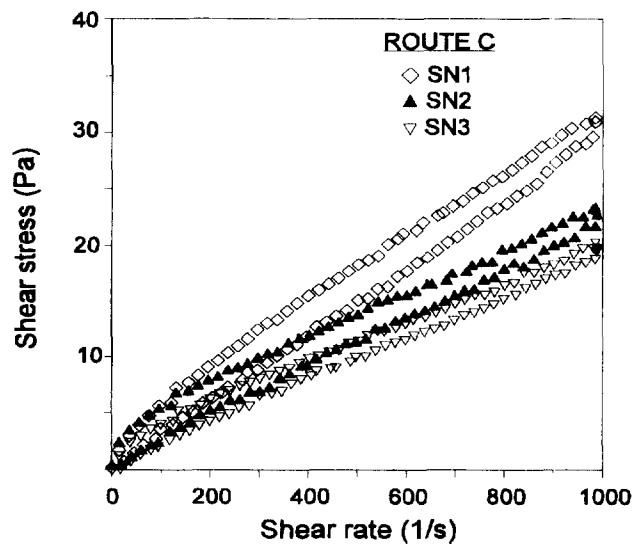


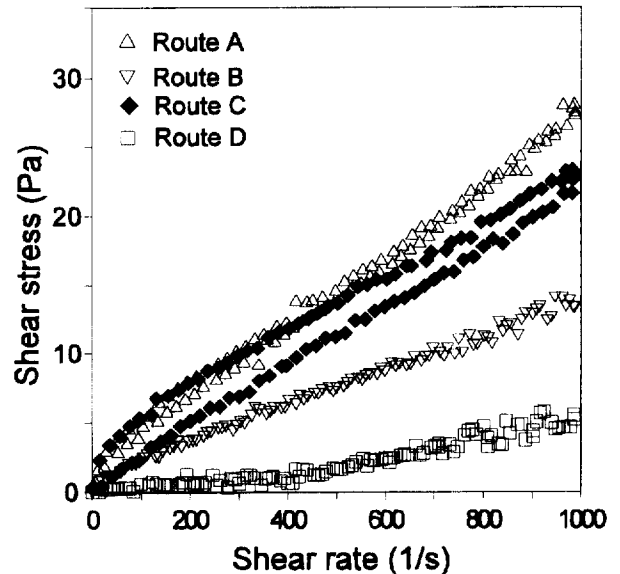
Fig. 11. Flow curves of 65 wt% solid content slips of the three studied compositions at $\text{pH} = 11.3 \pm 0.1$ prepared according to mixing route C.

Table 5. Optimized conditions for the preparation of Si_3N_4 based suspensions

Parameters		Optimized values
Additives		3 %wt Al_2O_3 + 3 %wt Y_2O_3 ; 6 %wt Al_2O_3 + 6 %wt Y_2O_3
Dispersant:	Type	TMAH (strong base)
	Concentration	Up to pH = 11.5
Solids content:	Mass	65 wt%
	Volume	SN = 36.8%
		SN3A3Y = 36.3%
	SN6A6Y = 35.8%	
Mixing equipment		Ball mill (plastic jar)
Time of mixing		24 h
Rheological behaviour		Newtonian
Viscosity (at 500 s^{-1})		< 30 mPa s
Yield point		No
Tixotropy (at 500 s^{-1})		< 1 Pa

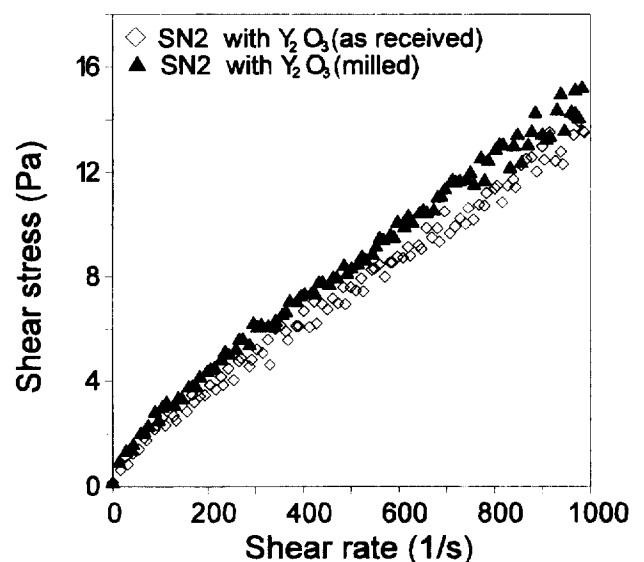
Figs 10 and 11, respectively. In the case of route B the flow curves are very similar also for the different compositions, confirming the efficiency of this homogenization route. In the case of route C the slip SN1 is quite different to those including sintering aids and has a higher viscosity, specially at shear rates higher than 200 s^{-1} . This can be related to the stronger mixing energy, allowing some milling of particles and the creation of new surfaces difficulting stabilization and pH shifts down. In the slips SN2 and SN3 the presence of oxides seems to promote deflocculant adsorption and helps to maintain the initial pH.

Table 5 shows the rheological parameters of the considered slips. Generally speaking, the sintering aids do not modify the rheology, but the comparison of the curves obtained by different mixing routes for one composition reveals significant differences in the rheology. Figure 12 plots the flow curves of the composition SN2 prepared according to the different procedures. Route A is based in a strong mechanical agitation in a short time and introduces a big number of air bubbles, which remain occluded in the bulk of the slip, even after 30 min low speed agitation. The viscosity in this case is higher than in the case of route B, as expected. However, route C results in the highest viscosities. This can be due to different reasons: first, many bubbles are also retained in this case due to the high speed movement of the mill, producing impact of the balls; second, the centrifugal mill is fabricated from ZrO_2 , which can introduce important contamination levels. In the same figure, the flow curve obtained by route D (attrition milling) is also plotted. This method provides the lowest viscosity, but the rheological behaviour is dilatant, with a significant increased slope for a shear rate of 400 s^{-1} . The dilatancy has been

**Fig. 12.** Flow curves of 65 wt% slips with SN2 composition prepared according to mixing routes A, B, C and D.

demonstrated to be rather inconvenient for casting operations, specially for pressure casting,¹⁹ because it seriously difficults the handling of the as-cast piece, which could flow when is being removed from the mould. When compared to method B, this route does not produce benefits from a rheological point of view, but the use of attrition milling difficults slip preparation, increases processing costs and can introduce significant contamination levels.

According to these results, route B is clearly the most adequate for the preparation of stable and well-dispersed slips of the selected Si_3N_4 powder, since effective milling is not required. The longer homogenizing time allows to reach an equilibrium at the particle surface and a better adsorption of the deflocculant. After arriving at this conclusion, the only possible parameter to be considered for

**Fig. 13.** Flow curves with SN2 compositions, using both as-received and milled Y_2O_3 .

the obtention of uniform casts is the coarse particle size of the starting yttria powder. Slips of compositions SN2 and SN3 have been prepared in the optimized conditions (route B, 24h) using the attrition milled yttria powder. The rheology of the slips containing the milled Y_2O_3 is quite similar to that corresponding to the compositions prepared with the starting one. To illustrate this, Fig. 13 shows the flow curves of SN2 slips prepared with both powders. The curve for the milled Y_2O_3 shows slightly higher viscosity, probably due to the higher specific surface area.

As a consequence of these data, the best way to produce highly loaded (65 wt%) aqueous slips of silicon nitride alone or including the sintering aids is the use of TMAH up to a pH 11.5 by a low energy milling during a long time enough to reach an equilibrium at the surface of the suspended particles. The slip obtained under these conditions presents a Newtonian behaviour, with a thixotropy value at 500 s^{-1} lower than 1 Pa and apparent viscosity lower than 25 mPa.s. These optimized slips do not reveal the existence of a yield value.

The deflocculation mechanism

As reported below, the optimum conditions for the preparation of the slips are a high pH value by action of a strong base. TMAH and NaOH have been considered although the introduction of Na^+ is not convenient because it forms low viscosity liquids during sintering. However, the rheological behavior is also good for casting. In previous works,^{20,21} it has been stated using the XPS analysis that green bodies obtained by aqueous slip casting using TMAH as deflocculant did not have a higher oxidation degree than other samples prepared by isostatic pressing using alcohol as homogenizing media. Another objective here is to compare the surface state behaviour of silicon nitride bodies processed in water using either TMAH or NaOH as pH adjuster.

The XPS analysis of the starting powder shows that around 10% of the surface atoms are oxidized in the form of oxynitrides. The XPS analysis of green cast samples obtained from slips dispersed with one of these mentioned dispersants reveals noticeable differences between them. Figures 14 and 15 show the Si2p and N1s peaks of XPS analysis made on the greens prepared with NaOH, just as registered and after peak splitting. In the samples deflocculated with TMAH a major contribution of Si-N bonds and smaller peaks for the oxidized species are found. However, the signals obtained for slip cast samples deflocculated with NaOH are inverted, showing a higher contribution of the oxidized form. The location in the spectra of the different contributions of the Si2p and N1s

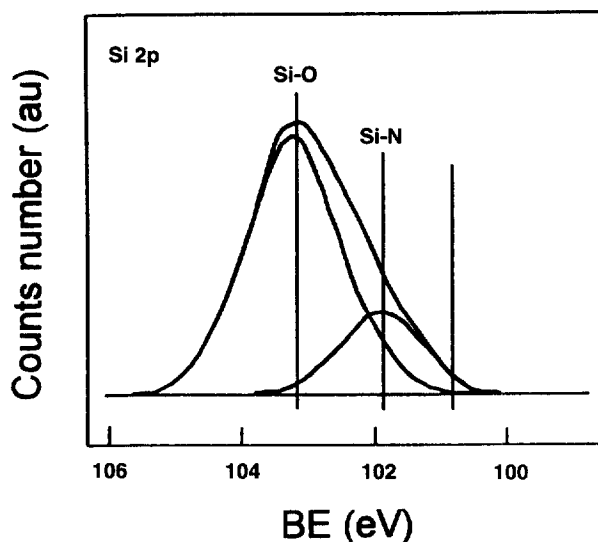


Fig. 14. Si2p peak of SN2 samples deflocculated with NaOH.

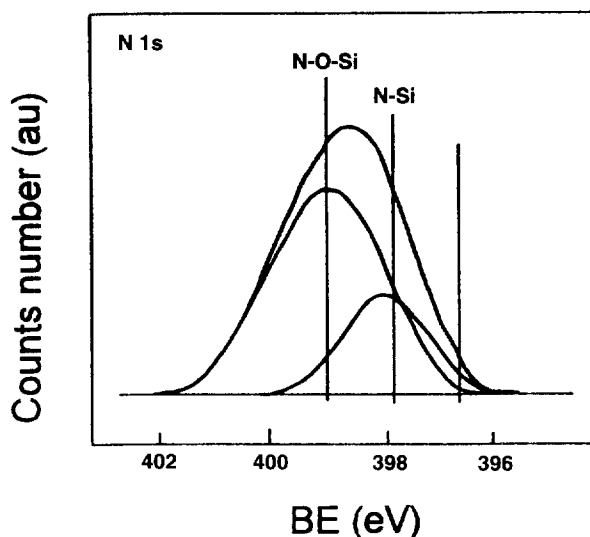


Fig. 15. N1s peak of SN2 samples deflocculated with NaOH.

Table 6. Binding energy of Si2p and N1s peaks of TMAH-treated and NaOH-treated samples in the XPS spectra

Sample	Si2p (eV)	N1s (eV)
TMAH-treated	101.6 (65)	397.5 (87)
	102.3 (35)	398.5 (13)
NaOH-treated	101.9 (29)	397.6 (26)
	103.2 (71)	398.6 (74)

peaks for both samples is reported in Table 6. This surprising result suggests that aqueous slip casting promotes a rapid oxidation of silicon nitride, as usually thought. However, the use of TMAH promotes a partially oxidized layer which protects the particle surface against a further progressive oxidation. In order to demonstrate the protective screen effect of TMAH, the surface of the starting powder and that of the powder obtained from a slip deflocculated with TMAH were analyzed by high resolution transmission electron microscopy (HRTEM).

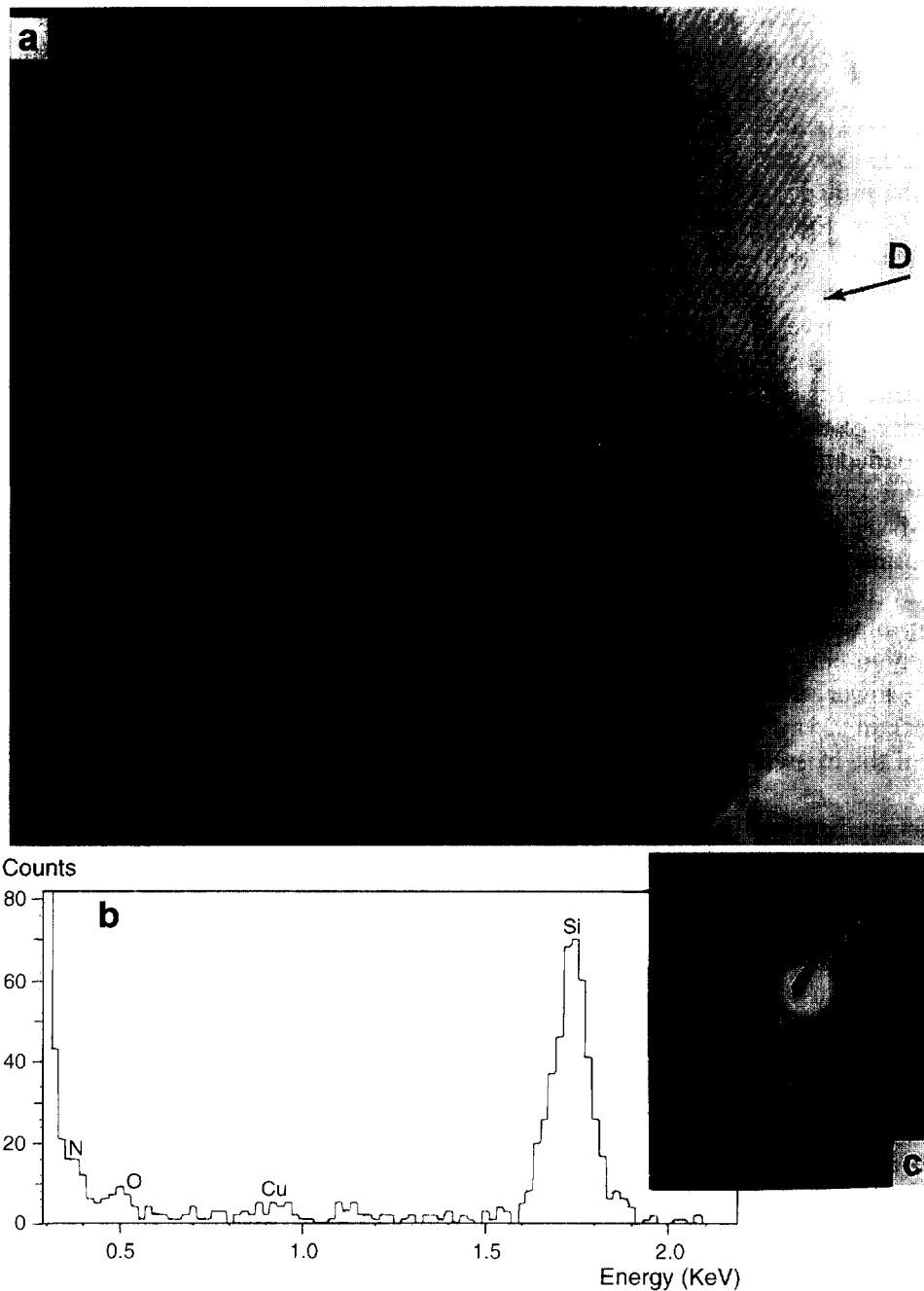


Fig. 16. Microstructure (a) and microanalysis by EDX (b) and DAS (c) in the region D, obtained by HRTEM for the as-received powder.

Figures 16 and 17 show the microstructure, the X-ray microanalysis and the selected area diffraction spectra obtained for both samples. In the starting powder, the existence of a layer surrounding the particle surface can be observed. The EDX of this area reveals the presence of O, N and Si, that is, oxidized species, which is in good agreement with the XPS analysis. In the case of the powder suspended with TMAH this layer is not appreciable and the EDX spectrum only detects the presence of N and Si. This demonstrates the lower oxidation degree of the TMAH-treated powder or, at least, that oxynitride species are formed, thus preventing a stronger oxidation to silica.

From the XPS data shown here and the HRTEM observations it can be concluded that TMAH forms a partially oxidized layer in which oxynitrides are present. However, this layer acts as a protective screen avoiding further oxidation to silica, as it was suggested in previous works.^{20,21} This can explain the unexpected low oxidation of slip cast samples in comparison with those obtained by other non-aqueous processing routes, such as isostatic pressing of powders previously homogenized in alcohol, in which the oxygen content at the surface was expected to be markedly lower. This provides also well-founded expectations of obtaining dense silicon nitride parts by a

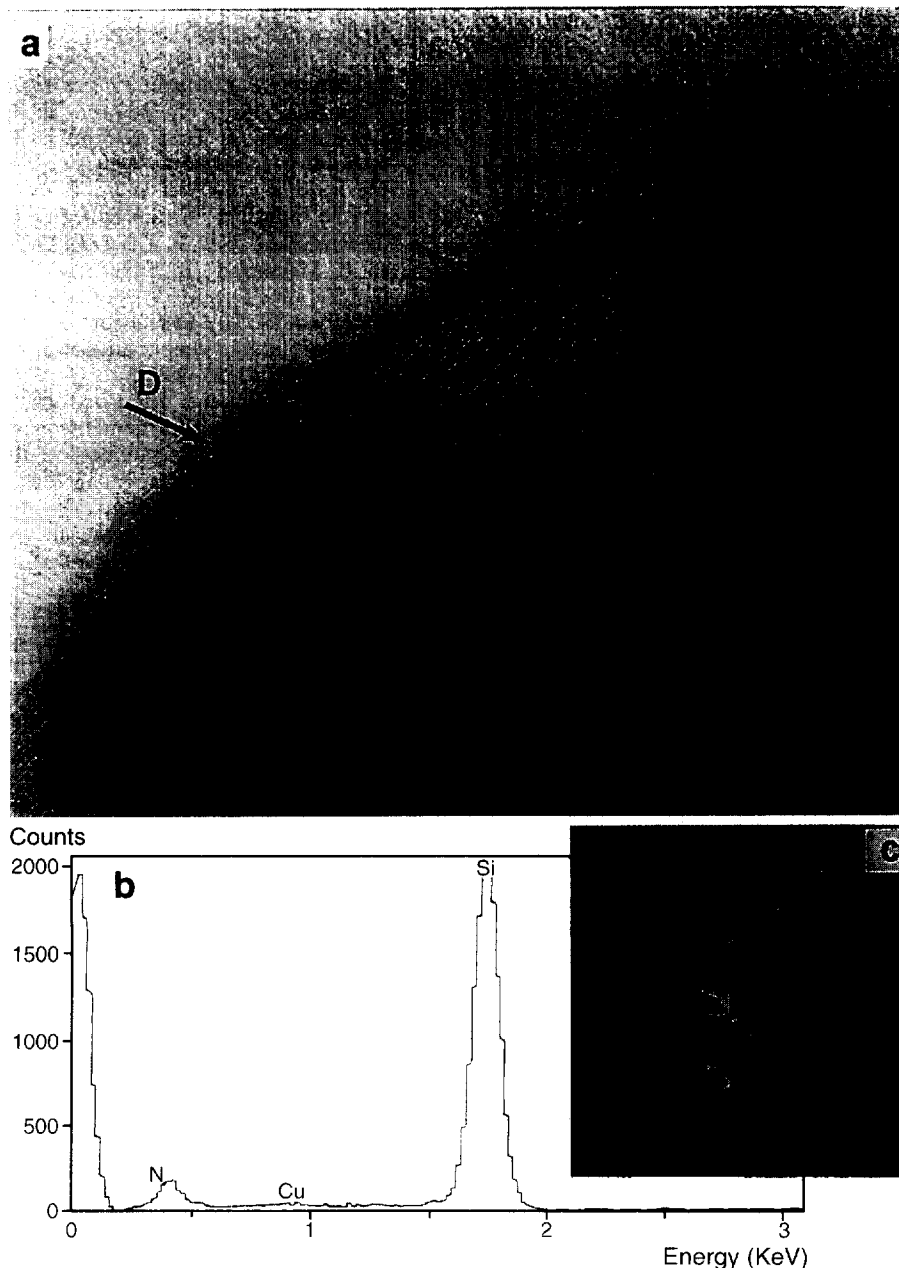


Fig. 17. Microstructure (a) and microanalysis by EDX (b) and DAS (c) in the region D, obtained by HRTEM for the powder treated with TMAH.

simple processing route as slip casting in water, without increased surface oxidation.

Conclusions

Aqueous suspensions of silicon nitride can be prepared at solid contents of 65–70 wt% maintaining a good stability and very low viscosities for casting. When Al_2O_3 and Y_2O_3 are introduced as sintering aids, the isoelectric points are in the same pH range (8–9), and the mixture can be effectively dispersed at basic conditions using strong bases. However, the use of normal bases contributes significantly to the surface oxidation. In this work it is stated that TMAH is useful because it forms a partially oxi-

dize layer with Si–O–N species which acts as a protective screen onto the silicon nitride particles thus diffculting a further oxidation.

The effect of pH is critical on the slip rheology. A small variation in the optimal pH (established at 11.3 ± 0.2) can produce important deviations on the almost Newtonian behaviour of the slip, and can produce not only an increase in the viscosity but also some time dependency. On the other hand, the evaluation of different homogenizing procedures reveals that, since submicronic powders are used, no milling is required, but a relatively long time is desirable to achieve the adequate equilibrium at the surface.

The addition of oxidic sintering aids practically does not modify the rheological behaviour of the major phase, if this is well-dispersed.

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