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The Effect of Alcohol Treatment on the Rheology of Si_3N_4

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Abstract

Slip casting of Si_3N_4 requires well-dispersed low viscosity suspensions. Two alternative procedures have been applied: (a) premixing by attritor milling in isopropanol, drying followed by the final slip preparation with deflocculant and water in a ball mill (batch A) and (b) suspending the powder in water using a deflocculant and mixing milling in a continuous attritor-like mill (batch B). Both batches were identical with respect to the starting powder, additives and the solid content. Astonishingly, the rheology was found to be quite different. Batch A had a strong tendency to Bingham behaviour whereas batch B showed a clear Newtonian shear curve. The differences are attributed to a reaction of the alcohol used (isopropanol) in batch A with the powder surfaces forming stable surface groups. The most probable configuration is a silyl ester Si–O–C–R, shielding the active sites against the coupling of the deflocculants. Burn-out experiments revealed that temperatures of 500°C are necessary to remove these surface groups. After this treatment the powders could be suspended giving the same shear curve as batch B.

Der Schlickerguß von Si_3N_4 erfordert die Beherrschung von niedrigviskosen Suspensionen. Zu deren Herstellung wurden alternativ zwei Routen beschritten: (a) Vormahlen der Pulvermischung in Isopropanol, Trocknung und anschließende Suspensionsherstellung mit Wasser und einem Verflüssiger in einer Kugelmühle (Charge A) und (b) Dispergierung des Schlickers mit Verflüssiger in Wasser und Mischmahlung in einem kontinuierlich arbeitenden Attritor (Charge B). Beide Chargen wurden aus den identischen Ausgangspulvern mit gleichem Festoffgehalt und gleichen Additiven hergestellt. Dennoch mußten beträchtliche Unterschiede bezüglich der Rheologie festgestellt werden. Charge A hatte eine ausgeprägte Bingham-Fließgrenze, während Charge B ein Newtonsches Fließverhalten aufwies. Die unterschiedlichen rheologischen Eigenschaften werden auf die Reaktion des Isopropanols mit den Pulveroberflächen in Charge A zurückgeführt. Als wahrscheinlichste Konfiguration wird ein Silylester Si–O–C–R angesehen, der die aktiven Zentren gegen den Verflüssiger abschirmt. Es mußten Temperaturen von 500°C angewendet werden, um die Pulveroberflächen zu reinigen. Danach ergab sich ein Fließverhalten wie bei Charge B.

Le coulage en barbotine de Si_3N_4 nécessite des suspensions bien dispersées et de faible viscosité. Deux processus ont été testés: (a) prémélange par attrition dans l'isopropanol, suivi d'un séchage et d'une préparation finale de la barbotine au broyeur à boulets, dans l'eau et avec un défloculant (batch A); (b) dispersion de la poudre dans l'eau avec un défloculant et mélange-broyage dans un attriteur en continu (batch B). Ces deux batches sont identiques en ce qui concerne la matière première, les additifs et la teneur en matière sèche. Etonnement, la rhéologie est tout-à-fait différente. Le batch A présente une tendance sévère à un comportement de type Bingham, tandis que le batch B montre une courbe de cisaillement type Newton. Les différences sont attribuées à la réaction préalable dans le batch A de l'alcool utilisé (isopropanol) avec la surface des poudres formant des groupements superficiels stables. La configuration la plus probable est un silylester Si–O–C–R, protégeant les sites actifs de l'action des défloculants. Des essais de calcination ont montré que des températures de l'ordre de 500°C sont nécessaires pour éliminer ces groupements superficiels. Après un tel traitement, le poudres en suspension présentent un comportement rhéologique identique au batch B.

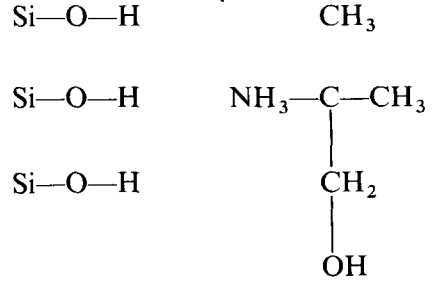
1 Introduction

Si_3N_4 is applied to various structural applications such as cutting tools and engine components.[1–4]

The geometry of most components is fairly complex and the machining costs in the as-sintered (hard) state are very high. Thus, a near net shape forming technique is required. For many reasons slip casting or, as an alternative, pressure filtration is of interest.

The use of high solid content suspensions with low viscosity and a tailored flow behaviour are prerequisites for a successful casting. The reaction between the powder surfaces and the deflocculant is of great importance for the slip properties. Thus, the surface composition of the matrix powder is of deciding importance for the stabilization of slips. A receptive Si_3N_4 surface composition requires the presence of polar groups such as SiO_2 and SiOH.[2,3,5] The electron pairs of the oxygen are considered to be the active sites. Thus, commercial powders are engineered to have a fairly high oxygen content of 1·5–2·1 wt% for a submicron powder. The oxygen is required for enrichment at the powder particle surface.

For Si_3N_4 various deflocculants are commonly available combining the effects of steric and electrostatic stabilization. Chemically they are either polyacrylates or amines. At low pH values a positive surface charge will enable the coupling of Si_3N_4 with the COOH groups of the polyacrylates. For this type of deflocculation the pH must be adjusted by the addition of acid. The other group of deflocculants is designed to work at a high pH. The Si_3N_4 surface charge is then negative. The coupling group of the deflocculant should have a positive charge. This can be established by either amino groups, phosphorus-containing groups or by alkali-containing groups. Because of chemical compatibility amino groups are preferred. In this work an aminoalkanol deflocculant (Zschimmer and Schwarz, Produkt KV5088, Lahnstein, Germany)[6] was used. Using combined elementary analysis and IR and NMR spectrometry the deflocculant was identified as 2-amino-2-methylpropanol. The NH_2 groups will hydrolyse to form an NH_3 group with a positive charge at the nitrogen ion. The configuration at the powder surface can be described as follows:



Si_3N_4 surface deflocculant

Owing to the hydrolysis of the amino group a high pH value of the solution will be established. From the practical point of view this is a great advantage because no further additions for setting the pH are required. In the experiment with a solid content of 50 to 70 wt% the pH value was automatically adjusted in the range of 10·5 to 11.

2 Experimental

2.1 Processing

Si_3N_4 powder with an oxygen content of 1·86 wt% (LC 12 S, H. C. Starck, Goslar, Germany) was used as matrix material and Al_2O_3 (AKP 30, Sumitomo, Düsseldorf, Germany) and Y_2O_3 (grade fine, H. C. Starck, Goslar, Germany) were used as sinter additives. The standard additive composition for these experiments was 2 wt% Al_2O_3 and 6 wt% Y_2O_3. The suspensions were prepared by the addition of 1 wt% KV5088 deflocculant (90% of 2-amino-2-methyl-propanol in aqueous dilution; compare to Section 1) calculated on the basis of the solid content. The solid content of the suspensions was kept constant at 70 wt%.

The powder characteristics are compared in Table 1. Starting from these powders two processing procedures were compared (Table 2).

Batch A was attrition milled in isopropanol (Si_3N_4 milling balls) at a speed of 3·6 m/s for 4 h for homogenization of the additives and then dried at 70°C for 20 h. This powder was then used for slip preparation. An amount 1 wt% of deflocculant was added and the slip was dispersed in a ball mill (polyethylene lining, 1 h milling time, aqueous system).

In order to investigate the effects of surface adsorption parts of the alcohol-milled powders were guided to further experiments. Small batches of this powder were heated under vacuum at 210°C, 350°C and 550°C and the volatile substances were collected in a cooling trap for gas chromatography/mass spectrometry (GC/MS) investigations. The remaining powders were investigated concerning C and H_2O content and furthermore used for slip preparation applying the identical condition as for the starting material.

Batch B was prepared using a continuously working pearl mill. The slip composition (powder, water and deflocculant) was suspended by overnight stirring and then simultaneously homogenized and ground by attrition milling. Batches of 4 litres volume and 60 wt% solid content were processed by cyclic milling (variations from 2 to 8 cycles, typically 4 cycles).

The rheology of the slips was then characterized by a rotation viscosimeter (Haake viscosimeter RV 12, Karlsruhe, Germany) at 25°C. A measuring cell for low viscosities was used (type NV).

Table 1. Impurities in Si_3N_4 and in sinter additives

Powder type	*Fe* (*ppm*)	*Al* (*ppm*)	*C* (*wt%*)	*O* (*wt%*)
Si_3N_4, LC 12S H.C. Starck, batch 148/88	90	380	0·19	1·98
Y_2O_3, H. C. Starck, batch 10/89	n.d.	n.d.	0·13	n.d.
Al_2O_3, Sumitomo, batch HB-9301	8	n.d.	n.d.	n.d.

Table 2. Flow diagram of the Si_3N_4 processing

Batch A *Conventional route*	*Batch B* *Single-step route*
Homogenization of the additives in isopropanol	Homogenization + preparation of the dispersion by cycling milling
↓	↓
Drying at 75°C	↓
↓	↓
Sieving	↓
↓	↓
Preparation of the dispersion	↓
↓	↓
↓	↓
Casting	

2.2 Determination of carbon

For the determination of carbon the sample is slowly heated in an oxygen stream in a quartz-tube furnace from 100°C to about 1000°C at a rate of about 50 K/min (CWA 5003, Rosemount, Analysentechnik, Hanau, Germany). In this method the C contribution bound as SiC (which might be present in the starting powder or which might form during the burn-out process) is not quantitatively decomposable at the applied temperatures. In order to reach a perfect decomposition of the carbidic bound C a higher temperature had to be applied. Thus a second combustion method was used in which the samples were heated by HF-field induction (maximum temperature = 2500°C). The powder samples were additionally admixed with metallic additives for perfect decomposition; hence, streaming O_2 gas was used (Leco CS-244, Leco Instrumente, Kirchheim, Germany). In this technique the full carbon content could be quantitatively determined.

2.3 Measurement of volatile species (GC/MS)

In the burn-out process various volatile species were expected to leave the sample. The condensable parts were collected in a liquid N_2-cooled trap and subsequently analysed by a gas chromatograph coupled to a mass spectrometer. The system consisted of an HP 5890 Series III GC equipped with a separation column (ultra 2, 50 m, 0·2 mm in diameter, with a 0·33 μm filling consisting of 5% diphenyl- and 95% dimethylpolysiloxane) and an MSD HP 5970 detector (Hewlett-Packard, Karlsruhe, Germany). The injected volume was 2 μl and a temperature programme from 80 to 280°C was applied.

3 Results and Discussion

3.1 Differences in rheological behaviour

Two methods of slip preparation are compared (Table 2). Both suspensions are made from the same additives, the same solid and deflocculant content. Nevertheless, significant differences in viscosity were observed. Figure 1 (curve A) shows a shear curve with pronounced Bingham behaviour and a medium apparent viscosity. In contrast, slip B exhibits a Newtonian-type shear rate at a low viscosity (curve B). The two curves also vary considerably in spite of both suspensions being planned to have the same average composition. The detailed investigations showed that several parameters were found to be different.

The applied milling procedures had a considerably different energy input because of the duration

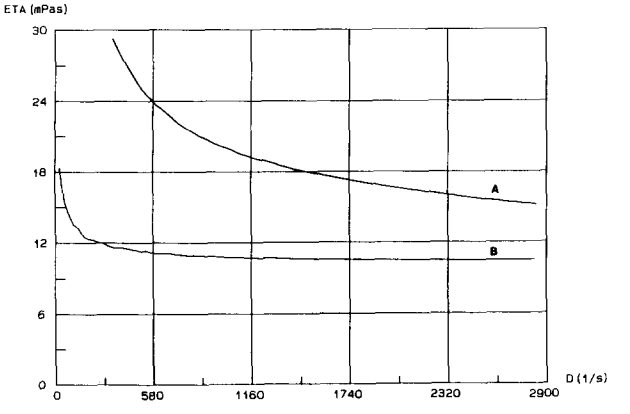


Fig. 1. Viscosity versus shear rate plot for batch A (see curve A) and batch B (see curve B) suspensions. Batch A suspension shows a pronounced Bingham behaviour.

Table 3. Characteristics and experimental parameters of batch A and batch B powders

	Batch A	*Batch B*
Powder characteristics before slip preparation		
Particle size (μm)	0·4	0·4
Carbon content[a] (wt%)	0·43	0·14
Milling conditions		
Effective milling volume (ml)	500	150
Effective milling time (min)	240	12
Oxygen uptake during milling (wt%)	1·0	0·1
Slip conditions		
Solid content (wt%)	60	60
Minimum deflocculant concentration (wt%)	1	4

[a] Batch A powder: after attrition milling in isopropanol; batch B powder: as received.

time and the rotor speed. The effective milling time is calculated using the equation:

$$t_{eff} = t_{total} \times V_{eff}/V_{slip}$$

with

t_{eff} = effective milling

t_{total} = total milling time

V_{eff} = effective volume of the mill

and

V_{slip} = volume of the processed slip

For the applied conditions in batch B t_{eff} was found to be as low as 12 min at 10 m/s rotor speed. For batch A, applying batch milling the ratio V_{eff}/V_{slip} equals 1, i.e. the total milling time and the effective milling time are becoming identical. Thus, t_{eff} for batch A is 240 min (at 3·6 m/s). The long milling time is responsible for the high oxygen uptake of 1 wt% compared to only 0·1 wt% in batch B (Table 3). However, the different oxygen content of the two Si_3N_4 powders should not create difficulties in deflocculation, because the applied aminoalkanol couples at high pH values at which both types of powder have strong negative surface charge and oxidic anchor groups present at the surface.

The minimum concentration of aminoalkanol required for complete deflocculation was higher in batch B (minimum viscosity at 4 wt% in batch B compared to 1 wt% in batch A. This behaviour can be attributed to Y^{3+} ions dissolved in slip B. In this slip 350 ppm of Y^{3+} was measured. Further experiments with additions of Y^{3+}-containing solutions also showed a negative effect on the deflocculation. It is believed that the Y^{3+} ions couple with the OH group of the deflocculant which causes the flocculation of the slip. Therefore a higher amount (4 wt%) of deflocculant was needed for compensation. Furthermore the residual alcohol content contains OH groups, which might couple with the Y^{3+} ions in the slip. The active concentration of Y^{3+} reacting with the deflocculant would then be much lower, which explains the need for less deflocculant (1 wt%).

Neither the difference in oxygen content nor that in Y^{3+} concentration is strong enough to explain the differences in rheology. Thus, further investigations were started.

The lower viscosity of slip B indicates a better deflocculation, the main difference being that batch A involves treatment with isopropanol whereas batch B did not have any contact with alcohol at all. Evidently, powder treatment during slip preparation plays an important role in determining the eventual viscosity of the suspension.

It is believed that powder treatment with isopropanol alters the surface of the particles, so that the reaction between the deflocculant and the surface is somehow influenced. This idea gave the reason for the following investigations.

3.2 Burning out the powder—the effect on viscosity

TGA investigations of isopropanol-treated powder, A, were carried out in order to investigate the effect of alcohol treatments in a process. There is a weight loss of 1·0% in the temperature regime up to 650°C depicted by the lower curve in Fig. 2, compared to a

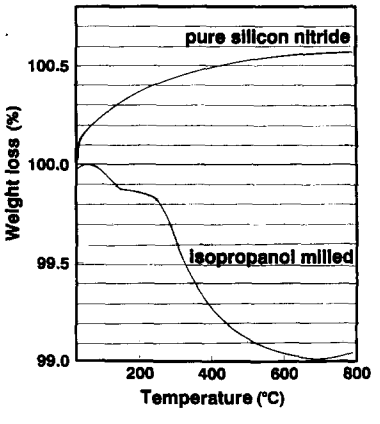


Fig. 2. TGA measurements of a Si_3N_4 powder in the as-received state (curve A) compared to a material which was attrition milled in isopropanol for 4 h at 3·6 m/s (curve B; compare to Table 3).

Table 4. Si_3N_4 treated in isopropanol and subsequently burned out at various temperatures

Treatment	*C content (wt%)*
Not heated (RT)	0·43
Vacuum (210°C)	0·37
Vacuum (350°C)	0·36
550°C	0·14

slight increase for as-received Si_3N_4 (upper curve in Fig. 2).

In addition, the burn-out of the alcohol was monitored by C determination. In the C analyser samples (powders) are heated and the C-containing species leaving the specimen are oxidized to CO_2 and detected by IR spectroscopy (CO_2 mode). Samples burned out at 210°C and 350°C showed an almost equally high C content compared to the alcohol-treated starting material. For samples burned out at 550°C a comparably low value was observed, indicating a complete removal of the hydrocarbons (Table 4). Figure 3 shows the evolution of CO_2 and H_2O at 450°C for the attrition-milled powder and those burnt out at temperatures less than 450°C; these peaks disappear for the powder burned out at 550°C. The simultaneous evaporation of CO_2 and H_2O indicates the presence of a hydrocarbon. The high temperature of 450°C supposes a strong bonding which cannot be explained only by adsorption.

In order to obtain more detailed information as to how the alcohol had altered the powder surface, the burned out powders were used to prepare slips. The suspension made of the original alcohol-treated powder and the powders burned out at 210°C and 350°C exhibited the same Bingham-like flow behaviour (Fig. 4). However, the slip prepared from the powder burned out at 550°C exhibited an almost Newtonian behaviour, which compares very well with slips prepared from powder which had had no contact with alcohol at all (batch B).

In a further experiment the condensable species burned out of the powders were collected in a cooling

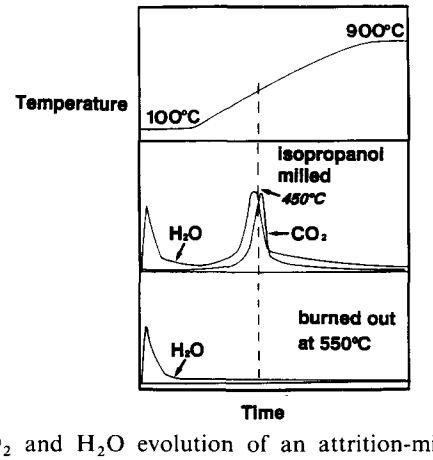


Fig. 3. CO_2 and H_2O evolution of an attrition-milled (isopropanol) powder compared to a material burned out at 550°C.

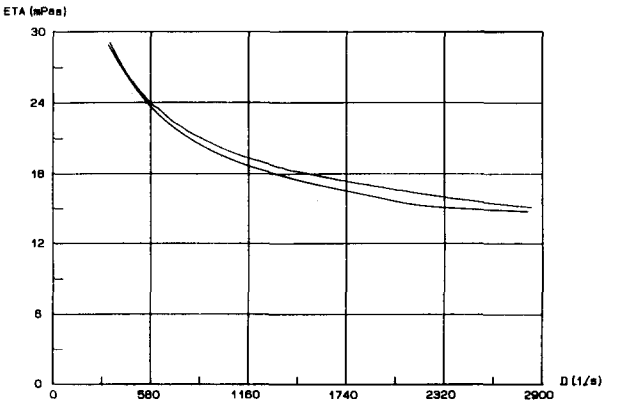


Fig. 4. Viscosity versus shear rate plot of slips which were made powders burned out at 210°C and 350°C respectively. These curves coincide with the original curve of batch A slip as depicted in Fig. 1.

trip and analysed by GC/MS. The chromatogram shows (Fig. 5) isopropanol as the most significant peak and in addition a variety of aliphatic (linear and cyclic) and aromatic compounds, a great part of them with N and O as heteroatoms. At a burn-out temperature of 350°C a significantly higher amount of cyclic compounds compared to 210°C can be observed. The formation of heterocyclic compounds at the applied temperatures of 210°C and 350°C is, however, very unlikely, but the crack products of alcohol, deflocculants and their intrinsic contaminants might occur. As the powders have been attrition milled in polyamide containers, crack products of polyamide have to be taken into account. For this process the formation of various organic compounds remains to be clarified by further experiments. The overlapping of different decomposition (cracking) reactions is reducing the possibility of interpretation of the measurements, hence, clean specimens with only Si_3N_4 and alcohol in contact have to be prepared for more significant GC/MS results.

3.3 Casting

The effect of alcohol adsorption on the Si_3N_4 surfaces was found to influence the casting behaviour. The surface ester resulted in an incomplete deflocculation and Bingham flow behaviour (batch A as prepared; batch A/210°C and batch A/350°C burned out). The casting rate of these suspensions was found to be fast (Fig. 6), but at the expense of a low green density (52%). Batch B slips (or material burned out at 550°C) showed a sluggish body formation but an improved green density (60% TD). These facts can be understood in the way that an incomplete dispersion (batch A) results in agglomerate formation in the suspension which causes low density green bodies with a wide pore size distribution. In contrast, a complete dispersion (batch B) leads to a high green density and a narrow pore size distribution (Fig. 7).

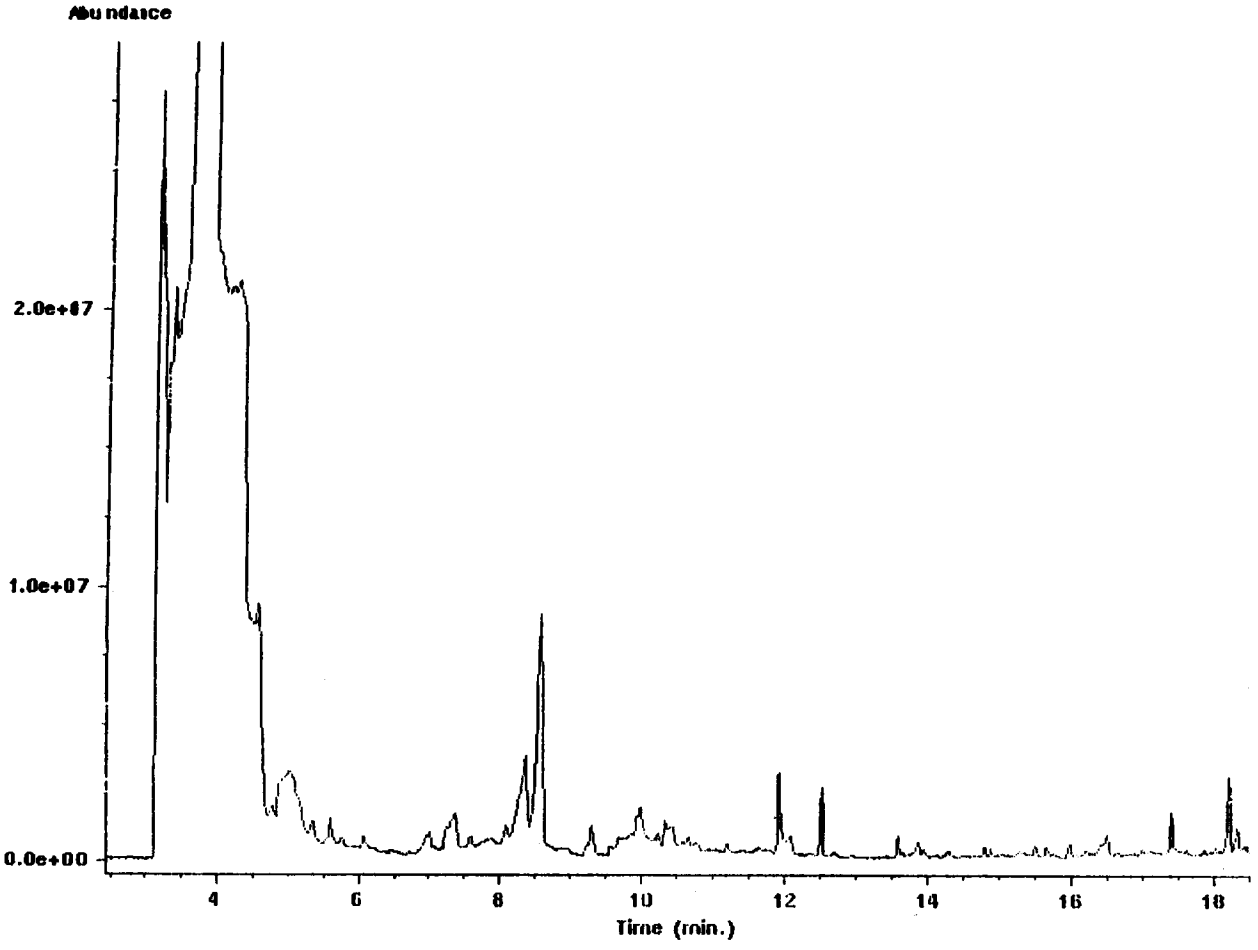


Fig. 5. Gas chromatogram showing isopropanol as the major outgasing species.

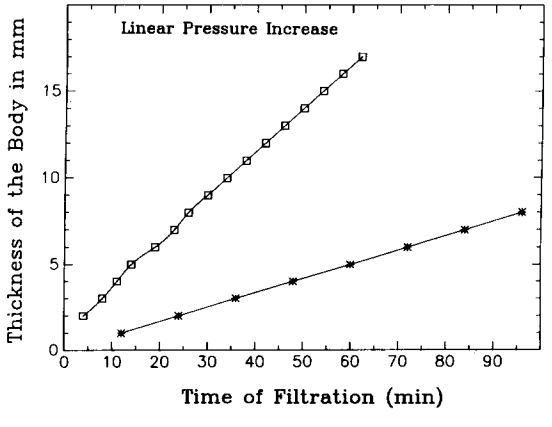


Fig. 6. Thickness of the cast body versus casting time for batch A (□) and batch B (★) slips. The pressure was increased linearly, resulting in a linear increase of body thickness.

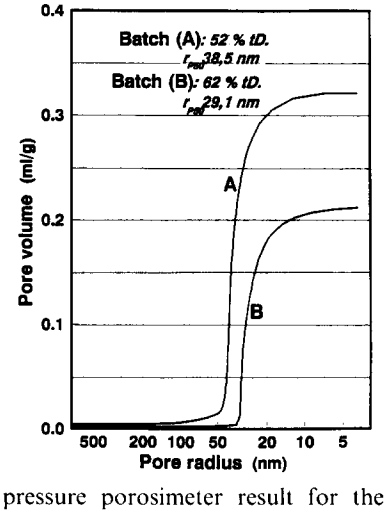


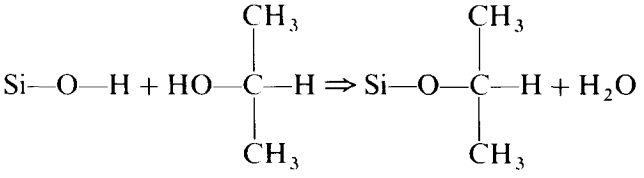
Fig. 7. Hg pressure porosimeter result for the cast bodies (compare to Fig. 6).

4 Discussion and Conclusions

Rabinovich *et al.*[4] have reported differences in slip behaviour of Si_3N_4 with and without alcohol treatment. The suspension made from Si_3N_4 with deflocculant (polyacrylates) and water was found to have the more Newtonian shear curves compared to alcohol-treated powders. There was no further investigation nor explanation.

The results on comparative studies (batch A and B) of two slips with identical chemical average composition and additive content but with difference in the rheological behaviour are considered as a shielding effect of the active site at the Si_3N_4 surface by the formation of stable esters. Temperatures of up to 500°C had to be applied to remove the carbon content from the powder surface. In spite of the low boiling point of alcohols and their high vapour pressure the reaction products at the surface were found to be very stable. The reaction of alcohols with ceramic surfaces has been described in the literature by various authors.[5,7–10] For the

silica–ethanol combination the formation of Si–O–C bonding was proven by IR reflectance measurements (DRIFT) by Scholze[7] and Azrak & Angell.[8] This type of silyl ester was also found for Al_2O_3 and for ZrO_2.[9,10] The existence of such a type of surface ester formation



for Si_3N_4 is very likely. The necessary DRIFT experiments are in progress and will be published later. There is the general difficulty that the IR mode indicating the presence of ester groups overlaps with a background typical for Si_3N_4. The CH_3 groups of the isopropanol are believed to shield the negative charge of the electron pairs at the oxygen ion, which are most likely the active site for deflocculant coupling. The interaction with the positive charge of the aminoalkanol deflocculants is diminished, resulting in a very poor slip stability.

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