

# Effects of Surface Purification on the Properties of Aqueous Silicon Nitride Suspensions

Heinz Stadelmann, Günter Petzow

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften,  
Pulvermetallurgisches Laboratorium, Heisenbergstraße 5, D-7000 Stuttgart 80, FRG

&

Peter Greil

Technische Universität Hamburg–Harburg, Arbeitsbereich Technische Keramik,  
Harburger Schloßstraße 20, D-2100 Hamburg 90, FRG

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## Abstract

*The dispersion properties of submicron silicon nitride powder in aqueous solution may significantly be improved by surface purification. IR-spectroscopy of vacuum-treated and acid-leached powder shows that physically adsorbed hydroxide (water) and ammonia groups may easily be desorbed, whereas chemically bounded silanol groups and silylamines remain on the surface. While at pH 11 the as-received powder forms a flocculated suspension with a solid concentration of 43 vol%, the purified powder results in a well deflocculated slip with Newtonian flow behavior. The aggregates formed upon dewatering are of much higher strength from the as-received compared to the purified powder, which may be related to a nitrogen and hydrogen bridging mechanism, respectively. Thus, the relative increase of the silanol site density by surface purification may be used to further improve the colloidal processing and shaping properties of submicron silicon nitride powders.*

*Die Dispergierungseigenschaften von submicronen Siliziumnitridpulvern in wässrigen Lösungen können durch Oberflächenreinigung entscheidend verbessert werden. IR-Spektren von vakuum- und säurebehandelten Pulvern zeigen, daß physikalisch adsorbierte Hydroxide (Wasser) und Ammoniakgruppen einfach desorbiert werden können. Dagegen verbleiben chemisch gebundene Silanol-Gruppen und Silylamine auf den Oberflächen. Während bei Ph 11 das unbehandelte Pulver eine flockulierte Suspension mit einem*

*Feststoffgehalt von 43 vol% bildet, resultiert aus dem gereinigten Pulver ein gut deflockulierter Schlicker mit Newtonschem Verhalten. Die während des Entwässerns gebildeten Aggregate sind erheblich fester beim unbehandelten Pulver als beim nachgereinigten Pulver. Das kann im ersten Fall auf einen Stickstoff- und im zweiten Fall auf einen Wasserstoff-Brückenmechanismus zurückgeführt werden. Der relative Anstieg der chemisorbierten Silanolgruppensdichte durch eine Oberflächenreinigung kann für eine weitere Verbesserung des kolloidalen Processing und der Formgebungseigenschaften von submicronen Siliziumnitridpulvern verwendet werden.*

*L'aptitude à la dispersion d'une poudre de nitrure de silicium submicronique en suspension aqueuse peut être notablement améliorée au moyen d'une purification de la surface. La spectroscopie IR d'une poudre traitée dans le vide et lessivée à l'acide montre que les groupes ammoniacques et hydroxydes (eau) physisorbés peuvent être désorbés facilement alors que les groupes silanols et silylamines chimisorbés restent liés à la surface. Alors qu'à pH 11 la poudre non traitée forme une suspension flocculée à un taux de solide de 43% volumiques, la poudre purifiée donne une barbotine bien défloculée à comportement rhéologique Newtonien. Les agrégats formés lors de la déshydratation présentent une cohésion beaucoup plus grande dans le cas des poudres non traitées (cohésion due au pontage azote) que dans celui des poudres purifiées (pontage hydrogène). Ainsi, l'augmentation relative de la densité de sites silanols lors de la*

*purification de surface pourrait être utilisée pour améliorer le traitement colloïdal et la mise en forme des poudres submicroniques de nitrure de silicium.*

## 1 Introduction

Silicon nitride based ceramics are of high potential for various high-temperature/high-stress applications such as in heat engines and gas turbines. Defect-controlled colloidal processing of submicron silicon nitride powders of high purity has become a key aspect in producing high strength and reliable components.<sup>1,2</sup> Colloidal consolidation techniques such as slip casting, vacuum and pressure filtration, extrusion, high-pressure extrusion and centrifugal casting of highly concentrated powder suspensions gain in significance as shaping and forming techniques for high-density green compacts with complex shape.<sup>3,4</sup> Green compacts with uniform microstructure and high packing density may exhibit improved sintering properties, resulting in silicon nitride materials with reduced property scattering and better performance.

Generally, surface-related phenomena such as agglomeration, adsorption of impurities and particle flocculation in suspensions exert an increasing influence with decreasing particle size and increasing purity. Hence, advanced powder processing needs to control the major chemical and physical interactions between the particle and its liquid environment. Thus, surface chemistry, solution chemistry and reactions between the particle surface and the solution (and dissolved components) have to be analyzed for each particular ceramic system in order to obtain well stabilized suspensions with high solid concentrations.

A rather complex picture of the interfacial chemistry of silicon nitride powder in aqueous suspensions was analyzed by various surface-sensitive experimental techniques such as ESCA, IR spectroscopy, electrophoretic measurements, surface charge and leaching experiments.<sup>5-10</sup> A variety of surface-active species, such as Si-OH, Si<sub>2</sub>-NH and Si-NH<sub>2</sub>, could be identified as intermediate reaction products of the hydrolysis of the thermodynamically unstable silicon nitride. Chemisorbed silanol Si-OH and Si-NH groups and physisorbed water and ammonia dominate the solid-liquid interactions and thus the colloidal stabilization behavior.

In aqueous silicon nitride suspensions an electrical double layer may provide sufficient repulsive forces between equally charged particles to stabilize

the powder against rapid flocculation. The formation of the surface charge primarily depends on the pH (dissociation of the surface groups) but is strongly influenced by additional chemical and physical surface reactions; hydrolysis, adsorption of hydrolysis products, polyelectrolytic surfactants, electrolytes and interactions with sintering additives.<sup>7,10-13</sup> The generation of surface charge on silicon nitride particles dispersed in aqueous solutions is mainly attributed to the formation of silanol groups Si-OH which react to positively charged Si-OH<sub>2</sub><sup>+</sup> and negatively charged Si-O<sup>-</sup> at low and high pH, respectively. Generally, slip preparation at high pH > 8 is preferred, because higher (negative) surface charges are developed, the adsorption of anionic surfactants is enhanced and the concentration of positive counterions (commonly Y<sup>3+</sup>, Mg<sup>2+</sup>, etc.) by dissociation of hydrolyzed sintering additives is low.<sup>12,13</sup>

The aim of the present work is to analyze the effect of physical and chemical surface treatments of a submicron silicon nitride powder on its electrostatic stabilization mechanism in water suspensions. The removal of physisorbed and chemisorbed surface impurities by vacuum treatment and acid leaching is expected to change the surface composition by increasing the silanol site density after controlled hydrolysis of the purified powder. Thus, surface charging and specific adsorption of polyelectrolytes may be further optimized in aqueous silicon nitride slips which will be used for colloidal filtration techniques.

## 2 Basic Understanding

The effect of surface purification on the dispersability of silicon nitride powders in aqueous solution may be divided into three major effects which will be discussed in what follows: (i) the wetting behavior of the dried powder by the solution; (ii) the stabilization against rapid flocculation after wetting, and (iii) the coagulation of primary particles, either by controlled flocculation in solution or by uncontrolled agglomeration when the liquid is separated from the solid upon drying. Although, from the physical point of view, this separation into subsequent processes may not be correct, the consideration of specific processes may help to characterize the major effects which powder pretreatment may exert on important technical steps for the development of optimized slip systems.

### 2.1 Wetting

Stabilization of deflocculated suspensions will only

be possible after complete wetting of the silicon nitride particles by the aqueous solution. As the polyelectrolytic deflocculant is dissolved in water, the liquid works as a vehicle to transport the surfactant to the particle surface. Thus, specific adsorption may also occur only when the powder surface is completely covered by the liquid, which makes the wetting at the solid-liquid interface a maximum. When the solid-air interface is replaced by the solid-liquid interface the change of the free energy is given by the total work,  $W$ , for all wetting processes, i.e. adhesion, immersion and spreading:<sup>14</sup>

$$W = (\gamma_{sl} - \gamma_{sv}) = -\gamma_{lv} \cos \theta \quad (1)$$

$\gamma$  represents the interface energy with  $s$ ,  $l$  and  $v$  denoting the solid, liquid and vapor phases, respectively. At equilibrium force balance the wetting angle  $\theta$  is expressed by the Young equation:<sup>15</sup>

$$\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \quad (2)$$

The wetting angle at the solid-liquid contact point should be  $\theta \rightarrow 0$  for spontaneous wetting to occur, whereas non-wetting results when  $\theta > 90^\circ$ . Thus, an increase in  $\gamma_{sv}$  and a decrease in  $\gamma_{sl}$  by changing the surface chemistry of the solid phase will result in a reduction of  $\theta$ , and hence wetting will be improved. Pre-oxidation or purification treatment of the silicon nitride powder is expected to influence the interface energies between the solid phase and other phases, i.e.  $\gamma_{sv}$  and  $\gamma_{sl}$ , while the surface tension of the liquid,  $\gamma_{lv}$ , will remain unaffected ( $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ ,  $78.2 \times 10^{-3}$  ( $78.2 \text{ ergs cm}^{-2}$ )). A silica-covered silicon surface is known to be only poorly wetted by water,<sup>16-18</sup> whereas the wetting behavior is significantly improved on hydrated silica surfaces.<sup>18</sup>

Thus it may be justifiable to assume that an increase of the silanol site density on the powder surface may primarily decrease  $\gamma_{sl}$ , which leads to a reduction of the wetting angle and hence better wetting behavior. The influence of the SiOH surface concentration  $C_{\text{SiOH}}^s$  may be expressed in a similar way to the effect of surface adsorbents on the energy  $\gamma_{sl}^0$  in solid-liquid systems:<sup>15</sup>

$$\gamma_{sl} = \gamma_{sl}^0 - \pi \quad (3)$$

In a first approximation the factor  $\pi$ , by which the initial interface energy is reduced, may be expressed as a linear function of the silanol site concentration on the surface:

$$\pi = m C_{\text{SiOH}}^s \quad (4)$$

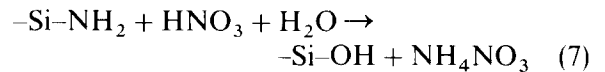
where the proportionality factor  $m$  is a function of  $RT$  and the surface activity of the silanol groups. For

the case of purification treatment, only the excess of silanol sites as compared to the unpurified powder has to be considered, so that eqn (3) may be written as:

$$\gamma_{sl} = \gamma_{sl}^0(\text{Si}_3\text{N}_4) - n(C_{\text{SiOH}}^s)_{\text{init.}} - m(C_{\text{SiOH}}^s)_{\text{purif.}} \quad (5)$$

$$\gamma_{sl} = \gamma_{sl}^0(\text{Si}_3\text{N}_4) - m^* \Delta C_{\text{SiOH}}^s \quad (6)$$

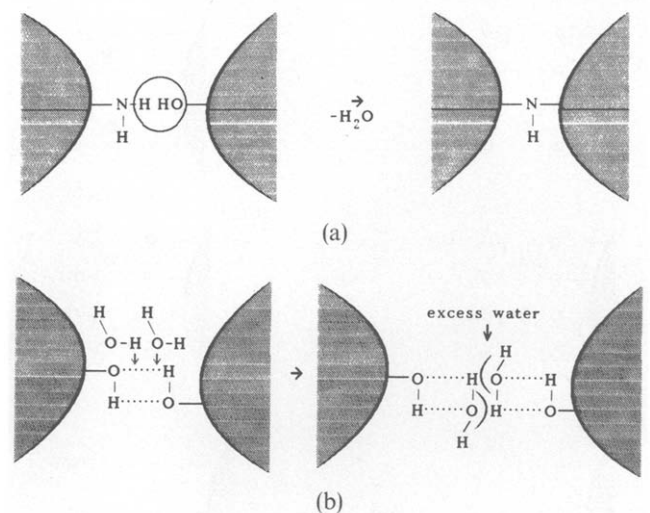
$\Delta C_{\text{SiOH}}^s$  is assumed to be increased by the acid leaching, which primarily results in an exchange of surface-adsorbed (chemically) less acidic amino (and  $\text{Si}_2\text{-NH}$  in chemically bridged agglomerates; Fig. 1(a)) by silanol groups:



The tendency to form hydrogen bridges to saturate the free valencies of surface silanol sites<sup>18</sup> to decrease the solid-liquid interface energy is achieved by silanol-water bridges, whereas the solid-solid interface energy decreases by the formation of silanol-silanol bridges (Fig. 1(b)). Because of the large excess of water the formation of silanol-water bridges is believed to be the dominating mechanism. Thus, as the total free energy of the system can be minimized by forming silanol-water bridges, wetting occurs.

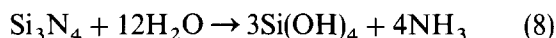
## 2.2 Stabilization after wetting

After complete wetting of the powder surface, a hydrolysis reaction commences. The powder-water reaction will be dominated by two major hydrolysis reactions that may occur on fresh particle surfaces,

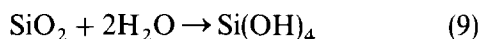


**Fig. 1.** Schematic model of particle bridging in aggregates formed by silicon nitride powders which have been in contact with water: (a) a nitrogen-bridged 'hard' agglomerate; (b) a hydrogen-bridged 'soft' aggregate which may easily be redispersed by water.

i.e.  $\text{Si}_3\text{N}_4$ , and on oxidized or aged powder surfaces.  
i.e.  $\text{SiO}_2$ :

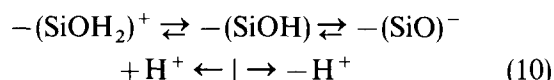


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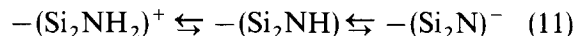


Both reactions result in the formation of surface silanol groups, Si-OH, and the hydrolysis of fresh  $\text{Si}_3\text{N}_4$  surfaces, in addition in the formation of ammonia. While both equations (eqns (8) and (9)) describe the overall hydrolysis reactions which may occur at nm-sized particles only, the hydrolysis of larger particles only proceeds in a surface layer. Thus, the hydrolysis products dissolved in the solution may be physically or chemically adsorbed on the particle surfaces. The potential surface reactions which finally may result in SiOH,  $\text{Si}_2\text{NH}$  and  $\text{SiNH}_2$  surface groups are shown in Fig. 2. From diffuse reflectance infrared spectroscopy of laser synthesized high purity silicon nitride powder an amino nature of untreated surfaces was concluded, with a predominance of silazane,  $\text{Si}_2\text{NH}$ , over silylamine,  $\text{SiNH}_2$ , species.<sup>8</sup> In the case of leached powder those hydrolysis reactions already take place during the controlled hydrolysis (Fig. 2, eqn (7)), resulting in a pure SiOH surface. Hence, the completely silanolated surface of the leached powder shows no further hydrolysis reactions, and the dissolved or adsorbed hydrolysis products described in eqns (8) and (9) are absent when dispersing and stabilizing leached powder. Electrostatic stabilization by formation of a high surface charge may then be explained by the dissociation of

the surface groups in dependence on the pH in aqueous solutions:<sup>19</sup>



and



The effective surface charge,  $\sigma_0$ , depends on the surface excess,  $\Gamma$ , of the protonated or deprotonated surface groups, and on the Faraday constant,  $F$ :<sup>19</sup>

$$\begin{aligned} \sigma_0 = F[ &(\Gamma_{(\text{SiOH}_2)^+} - \Gamma_{(\text{SiO})^-}) \\ &+ (\Gamma_{(\text{Si}_2\text{NH}_2)^+} - \Gamma_{(\text{Si}_2\text{N})^-})] \end{aligned} \quad (12)$$

With  $\Gamma_{(\text{SiOH}_2)^+} = K_a C_{\text{SiOH}} C_{\text{H}^+}$  and  $\Gamma_{(\text{SiO})^-} = K_b C_{\text{SiOH}} C_{\text{OH}^-}$  in aqueous solution and the equivalent expressions for  $\text{Si}_2\text{NH}$ , eqn (1) can be written:

$$\begin{aligned} \sigma_0 = F[ &C_{\text{SiOH}}(K_a^1 C_{\text{H}^+} - K_b^1 C_{\text{OH}^-}) \\ &+ C_{\text{Si}_2\text{NH}}(K_a^2 C_{\text{H}^+} - K_b^2 C_{\text{OH}^-})] \end{aligned} \quad (13)$$

Equation (13) directly relates the surface charge to the silanol and silazane site concentrations and to the relevant dissociation constants. The  $\text{Si}_2\text{NH}$  groups are basic, with a  $\text{p}K_b$  of approximately 5, so that they can easily be protonated to positively charged  $\text{Si}_2\text{NH}_2^+$ , whereas the SiOH groups are slightly acidic with a  $\text{p}K_a$  of approximately 7<sup>20</sup> and therefore will be less protonated at the same pH. This explains the significant differences of the zeta potentials between the untreated and acid leached powders. The higher value of the zeta potential of the untreated powder at low pH corresponds to a higher concentration of surface ammonium groups. At  $\text{pH} > \text{iep}$  the acidic silanol groups can easily be deprotonated to negatively charged  $\text{SiO}^-$ , even by a weak base such as ammonia. For the formation of negatively charged amides such as  $-\text{NH}^-$ , however, a much stronger base would be necessary. Thus, the effective negative charge of the  $\text{Si}_3\text{N}_4$  powder at  $\text{pH} > 5$  can mainly be attributed to the dissociation of silanol groups according to eqn (10), whereas the positive charges at  $\text{pH} < 3$  are dominated by the formation of positively charged ammonium groups such as  $-\text{NH}_3^+$ . Zeta potentials at  $\text{pH} 1.5$  of +40 mV and 11 of -48 mV, respectively, for the as-received powder, but +25 mV and -56 mV for the acid-leached powder, prove that the removal of chemically adsorbed NH species increases the negative surface charge at high pH. The shift of the isoelectric point of the acid leached powder from  $\text{pH} 4.5$  to 3.2 also indicates the formation of a more acidic surface due to the higher concentration of silanol groups on the surface.

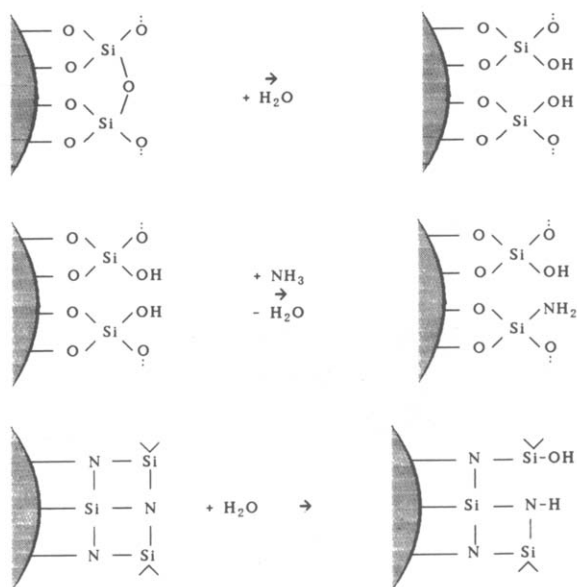


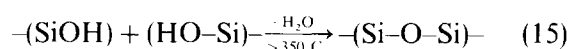
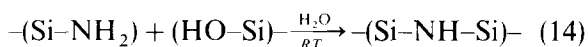
Fig. 2. Potential reactions on the surface of silicon nitride powder in contact with water.

The hydrolyzed silica surfaces are known to exhibit a better adsorption behavior<sup>18,20,21</sup> of anionic surfactants at high pH. Because of the acidic character of the functional groups (polyacrylic acid) of the polyacrylate they will dissociate into COO<sup>-</sup> groups at high pH.<sup>22,23</sup> Depending on the pH and the dissociation constant of the polyacrylic acid, the polymer surface charge may vary from neutral to highly negative.<sup>24</sup> Thus, the silanol-rich surface is able to adsorb the negatively charged polyacrylates, resulting in a zeta potential increase from -56 to -70 mV.

Although polyelectrolyte stabilization can exist with low levels of electrostatic repulsion, it is necessary that an appreciable zeta potential is present on the particles. From results obtained for polyacrylate adsorption on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles at pH above the zero point of charge at pH 8.5–9, an additive effect between the negatively charged polyacrylate and the negative surface was found, which yields a larger zeta potential than expected from the amount of polyacrylate adsorbed.<sup>22,23</sup> Thus, the actual zeta potential built up on the particles due to polyacrylate adsorption is a function of the amount of polyacrylate adsorbed, the fraction of polyelectrolyte dissociation, and the surface charge of the base particle.

### 2.3 Agglomeration behavior

As the surface chemistry dominates the formation of agglomerates, the amine-free hydroxylated surface of the acid-leached powder exhibits a completely different agglomeration behavior as compared to the silica-like powder surface, where the chemically adsorbed ammonia derivatives are still attached to the surface. Those amino groups are supposed to cause the formation of hard agglomerates, because of the possible reaction between silanol and amino groups of different particles (Fig. 1(a)). While the nitrogen-bridging may take place at low temperatures,<sup>25</sup> the reaction between silanol surface groups takes place above 350°C to form oxygen-bridged particles:<sup>18,20,25</sup>



Both the nitrogen- and oxygen-bridged silicon nitride particles are attached by chemical bonds, which result in much higher cohesion strength as compared to hydrogen-bridged particles (due to the differences in bond strengths<sup>26</sup>). The amino group free surfaces of the acid-leached powder only form hydrogen-bridged agglomerates upon drying at

temperatures below 200°C. In Fig. 1(b) are shown the surface reactions that may take place when water is added to those purified powders. The agglomerates formed by hydrogen-bridge bonding are easy to break and to redisperse in water, by formation of a thin aqueous inter-particle layer.<sup>27</sup> Thus, no attrition of the starting powder will be necessary to break down agglomerates to prepare low viscosity and highly concentrated slips.

## 3 Experimental Procedure

Since an SiOH-rich surface should exhibit superior suspensibility behavior, the as-received powder was leached<sup>10</sup> with dilute HNO<sub>3</sub> in order to form a silanolated surface. The effects of that leaching on the surface chemistry, suspension stability and the particle packing are investigated by IR spectroscopy, zeta potential measurements, rotation viscosimetry and SEM.

### 3.1 Powder processing

High-purity  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> powder (LC 12, H.C. Starck, Berlin, FRG) was subjected to vacuum treatment and chemical leaching in aqueous electrolyte solutions in order to remove physisorbed and chemisorbed impurities from the powder surface. The powder composition data and the specific surface area are summarized in Table 1. The silicon nitride powder contained a total oxygen content of 1.7 wt% (after leaching) as determined with an oxygen–nitrogen gas analyzer (TC 436, Leco, St Joseph, Michigan, USA). Slightly lower values of approximately 1.5 wt% have been reported from the same powder, where a ratio of 3 to 7 by weight was estimated from XPS measurements and bulk chemical analysis for oxygen on the surface and in the bulk.<sup>28</sup>

Powder batches of 400 g were heated to 200°C in an argon atmosphere and then evaporated to a residual pressure of 10<sup>-6</sup> MPa. Subsequently, the powder was dispersed in 1.5 liters of 0.1 M KNO<sub>3</sub> solution, which was set to pH 2–3 by HNO<sub>3</sub>. For

**Table 1.** Chemical composition of the silicon nitride powder

Element	Wt%
N	38.57
O	1.35
C	0.18
Fe	0.01
Al	0.05
Ca	0.005
$\alpha/\beta$	> 18
$S_r$	20.3 m <sup>2</sup> g <sup>-1</sup>

deglomeration the powder was treated for 1 h in an ultrasonic bath. The powder was separated from the electrolyte solution with a Büchner funnel using a Blauband filter. The filter cake was washed with  $4 \times 0.5$  liter  $0.1 \text{ M KNO}_3$  solution at pH 3 to remove any chemisorbed hydrolysis products from the surface. Finally, the powder was again dispersed in  $0.5$  liter of double-distilled water adjusted to pH 3 ( $\text{HNO}_3$ ) and ultrasonically treated for 20 min. After filtration the powder was again washed with distilled water at pH 3 and dried at  $180^\circ\text{C}$ . The dried powder was sieved with a  $160 \mu\text{m}$  mesh and then exposed to an argon atmosphere at  $10^{-6} \text{ MPa}$  at  $200^\circ\text{C}$  in order to remove traces of moisture. The powder was stored under argon to prevent rehydrolysis.

### 3.2 IR spectroscopy and zeta potential measurements

The surface composition of the silicon nitride powders was characterized by means of IR spectroscopy. The dried silicon nitride powders were mixed with KBr, pressed into pellets at  $15 \text{ MPa}$ , and investigated in a lattice IR spectrometer (PE 283, Perkin-Elmer, Konstanz, FRG). IR spectra (transmission mode) were recorded for reciprocal wavelengths from  $3000$  to  $4000 \text{ cm}^{-1}$ . In this region, the valency oscillations of the major OH and NH vibrations occur (Table 2).

The zeta potential was calculated from electrophoretic mobility and the Helmholtz–Smoluchowski equation.<sup>15</sup> The mobility measurements were completed in very diluted suspensions with solid concentrations  $< 10^{-4} \text{ wt}\%$ . A laser scattering technique, using the change of the laser interference field by particle oscillation in an electric field, was used to measure mobilities at various pH (Zetasizer II, Malvern, Cambridge, UK). Prior to taking the measurements, the dilute suspensions were ultrasonicated and magnetically stirred to ensure that only singlet particles were measured. At least ten measurements were completed for each sample, resulting in an average standard deviation of  $\pm 15\%$  for the zeta potential, in mV.

**Table 2.** IR absorption bands of OH and NH groups in the range  $3000\text{--}4000 \text{ cm}^{-1}$

Molecular species	Vibrational frequency ( $\text{cm}^{-1}$ )	Ref.
Si–OH (surface)	3 740	20
H <sub>2</sub> O	3 710	29
–OH (free)	3 650–3 590	29
–OH (bridging)	3 600–3 200	29
–OH (crystal water)	3 600–3 100	29
Si <sub>2</sub> –NH, –NH	3 500–3 300	29
–NH <sub>3</sub> <sup>+</sup>	3 130–300	29

### 3.3 Slip casting

Highly concentrated aqueous suspensions were prepared by mixing  $125 \text{ g}$  of purified  $\text{Si}_3\text{N}_4$  powder,  $50 \text{ ml}$  of distilled water,  $0.6 \text{ ml}$  of a polyelectric surfactant (Dolapix PC 33, Zschimmer und Schwarz, Lahnstein, FRG) and  $2 \text{ ml}$  of triethylamine at pH 11 for 1 h in a ball mill. The ball mill was equipped with a polyamid liner and zirconia milling balls. The surfactant was a polyacrylate with  $-\text{COOH}$  groups, which are dissociated at pH 11 to negatively charged  $-\text{COO}^-$ .<sup>22,23</sup>

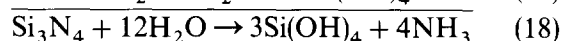
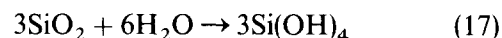
Viscosity measurements were conducted with a rotary viscosimeter (Rotavisco RV 12, Haake, Karlsruhe, FRG) with a sample chamber NVST which allowed shear rate variation from  $1.3$  to  $660 \text{ s}^{-1}$ . To determine the relative magnitude of viscosity and whether the suspensions were flocculated or stabilized, the following rheological measurement method was used. (i) The suspensions were initially sheared at a maximum shear rate of  $660 \text{ s}^{-1}$ . This ensured that permanent particle clusters were dispersed. (ii) The shear rate was decreased stepwise and the shear stress was measured at a constant shear rate after 10 s. (iii) An apparent yield stress was determined from the shear stress–shear rate curves by linear regression in the interval  $40\text{--}180 \text{ s}^{-1}$ .

The highly concentrated slips with a solid to liquid ratio of  $71.5 \text{ wt}\%$  ( $43 \text{ vol}\%$ ) were cast in plaster molds and dried for 3 days in a climate chamber (Labotest-Klimaschrank VLK 07/90, Heraeus-Vötsch, Balingen, FRG). Starting with a humidity of  $90\%$  and a temperature of  $40^\circ\text{C}$ , the humidity was reduced to  $20\%$  at a final temperature of  $70^\circ\text{C}$ . The green density was measured and the cross-sections of cast green microstructures were examined by scanning electron microscopy (SEM). Each cake was broken and then coated with a thin gold layer prior to the examination.

## 4 Results

### 4.1 Surface chemistry

The overall hydrolysis reaction of silicon nitride in the presence of  $\text{H}_2\text{O}$  may be expressed by the following partial reaction equations:



which is confirmed by surface titration studies, in which silanol groups and physisorbed ammonia

were found on the surface of the powder particles.<sup>6,7,10</sup> Thus, physisorbed ammonia and water are assumed to be the major surface adsorbents that may easily be removed by evaporation in vacuum, whereas the chemisorbed silanol groups and amines should remain. These groups may form by subsequent reactions between silica-like surface regions and water, between silanol groups and physisorbed ammonia, or by direct reaction between silicon nitride and an understoichiometric amount of water (Fig. 2). The IR spectra between 3000 and 4000  $\text{cm}^{-1}$  for the as-received and vacuum-treated powders are shown in Fig. 3. While the undisturbed valency oscillations of OH and NH vibrations in water and amines occur at 3710 and 3500–3300  $\text{cm}^{-1}$  (Table 2), respectively, the adsorption bands of the physically adsorbed species are shifted to significantly lower values  $< 3500 \text{ cm}^{-1}$  and the band is broadened by interactions between adsorbed molecules, i.e. hydrogen bridging. The presence of valency oscillations between 3200 and 3600  $\text{cm}^{-1}$  after vacuum treatment, but of lower intensity compared to the as-received powder, is clearly shown in Fig. 3. The desorbed species were caught in a cooling trap during evacuation and identified as water and ammonia. Although a distinction between physisorbed and chemisorbed species is almost impossible by means of IR spectroscopy only, the occurrence of these oscillations may reasonably be attributed to chemisorbed OH and NH groups which have remained on the surface. The significantly lower reciprocal wavelengths as compared to the valency oscillations in free water or ammonia molecules may be explained by the higher polarity of the OH and NH bonds when Si–O or Si–N bonding occurs.

After leaching in an aqueous 0.1 M  $\text{KNO}_3$  solution

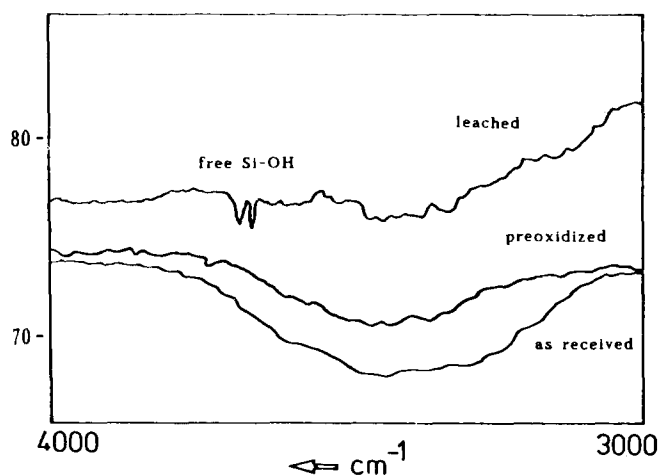


Fig. 3. IR spectra of the as-received, preoxidized and acid-leached powders, respectively, in the range 3000–4000  $\text{cm}^{-1}$  (transmission mode).

at pH 3, however, the IR spectra of the dried powder reveals no adsorption band between 3500 and 3200  $\text{cm}^{-1}$ , which definitely shows the absence of NH vibrations. Only two distinct signals occur at 3670 and 3690  $\text{cm}^{-1}$ , which are characteristic for valency vibration bands of free silanol groups on silica surfaces.<sup>20</sup> The sharp signals indicate no significant interactions between silanol groups, which would be expected for undisturbed silanol groups present on the particle surfaces.

#### 4.2 Suspension stability

Generally, in electrostatically stabilized systems such as aqueous silicon nitride suspensions, stability versus rapid flocculation will increase with increasing zeta potential.<sup>3</sup> The results of zeta potential measurements of the as-received and of the purified powder (vacuum-treated and acid-leached) are shown in Fig. 4. Maximum zeta potentials of the as-received powder are found at pH 2, +40 mV, and pH 10, –48 mV, with an isoelectric point at pH 4.5. The purified silicon nitride powder shows the maxima of the zeta potential at pH 1.1 with +23 mV and at pH 11.5 with –57 mV, with an isoelectric point at pH 3.2. Earlier measurements of zeta potentials of pre-oxidized silicon nitride powder also showed a shift of the isoelectric point to lower pH with increasing oxygen content on the particle surface.<sup>12</sup> Thus, the shift of the isoelectric point to lower pH may indicate an increase of the silanol site density (acidic Si–OH groups) in the purified as compared to the as-received powder.

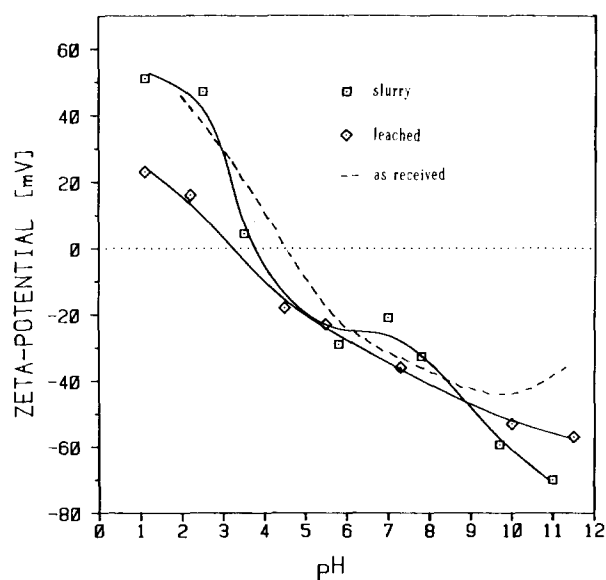


Fig. 4. Zeta potential measurements in aqueous solutions with solid concentrations of  $10^{-4}$  wt%. The pH was adjusted with HCl and NaOH.

### 4.3 Slip casting

Fully stabilized suspensions are necessary to achieve high solid concentrations  $>35$  vol% with low viscosity ( $<100$  mPa s) for slip casting. The shear stress–shear rate curves (flow curves) of highly concentrated silicon nitride slips with 37 and 43 vol% of solid phase are shown in Fig. 5. While the less concentrated silicon nitride slips were prepared from a pre-oxidized silicon nitride powder (8h,  $550^{\circ}\text{C}$ , in air),<sup>12</sup> the silicon nitride powder purified by the above-mentioned procedure was used for the more highly concentrated slip. The as-received, untreated powder clearly shows a high flow stress of 60 Pa, which indicates that the powder is partly or fully flocculated.<sup>12</sup> However, the two slips with the pretreated powders exhibit a Newtonian flow behavior with a linear shear stress–shear rate dependence and only a very low extrapolated flow stress of approximately 2–5 Pa. The flow curves of the two slips prepared from the pre-oxidized and purified (vacuum-treated and acid-leached) powders, respectively, are almost identical, showing a very low viscosity. From the slope of the flow curves a viscosity of 25–30 mPa s was calculated, which remained constant with time.

The highly concentrated (43 vol%) slip with the purified silicon nitride powder was consolidated by solid casting into plaster of Paris molds. After drying in the climate chamber to a residual humidity of  $<1$  wt% a fractional density of 66% was measured for the green compacts. The micro-

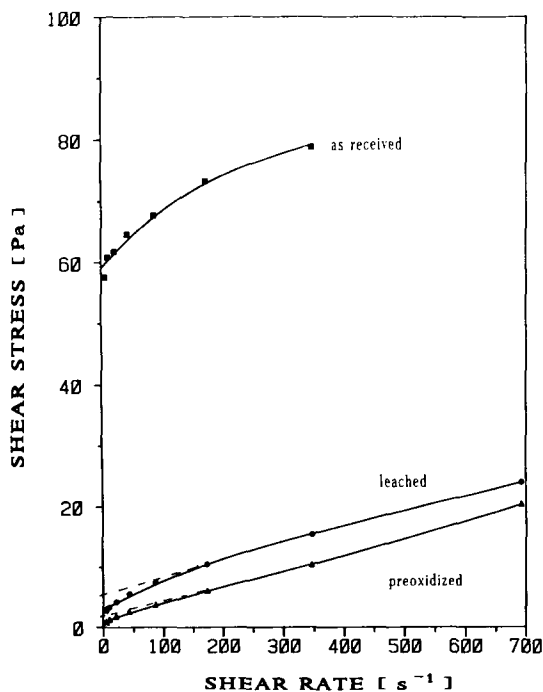


Fig. 5. Shear rate – shear stress curves of the three different powder suspensions with solid concentrations of 37 (pre-oxidized) and 43 (leached) vol%.

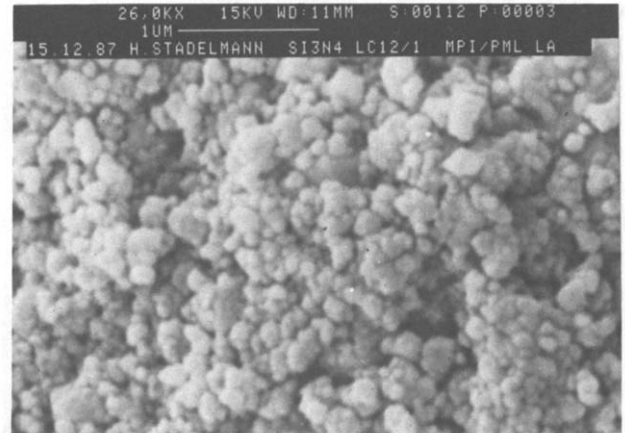


Fig. 6. SEM micrograph of a fracture surface of a green compact prepared by slip casting of the leached powder.

structure of the cast compacts was examined to qualitatively observe what effect the powder purification had on the particle packing. An SEM micrograph of a fracture surface of the cast green compact is shown in Fig. 6. The silicon nitride particles are very homogeneously packed, without any features that would indicate agglomerated secondary particles.

## 5 Conclusions

Colloidal processing of silicon nitride powders in aqueous solutions is dominated by the hydrolysis reactions. Depending on the pH and electrolyte content, complex interactions occur at the solid–liquid interface, including adsorption and desorption of reaction products and surface-active defloculants. While the desorption of physisorbed species such as free water and ammonia may easily be achieved by evacuation, chemisorbed species such as silanol, silazane or silylamine require substitution reactions to change their surface concentrations. Leaching in  $\text{HNO}_3$  was shown to increase the silanol site density, which results in a significant increase of the negative surface charge at high pH. Secondly, the zeta potential increases because of the absence of basic hydrolysis products, since they are removed by this leaching before the powder is dispersed and because of the passivation towards rehydrolysis. The vacuum-treated and acid-leached powders displayed a better rheological and flocculation behavior compared to the as-received powder. Thus, surface-treated (activated) silicon nitride powders will be of particular interest to improve colloidal processing techniques for the manufacturing of defect-optimized silicon nitride engineering ceramics.



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