

Evaluation of Oxygen Content on Silicon Nitride Powder Surface from the Measurement of the Isoelectric Point

Peter Greil

Technische Universität Hamburg-Harburg, Arbeitsbereich Technische Keramik, Hamburg, FRG

Ralf Nitzsche, Hannelore Friedrich & Waldemar Hermel

Zentralinstitut für Festkörperphysik und Werkstofforschung der Akademie der Wissenschaften, Dresden, FRG

(Received 23 October 1990; revised version received 9 January 1991; accepted 11 January 1991)

Abstract

The oxygen content associated to the surface of silicon nitride powder particles was characterized using a method which is based on the measurement of the specific surface area and the isoelectric point in aqueous solution. From the dissociation model of hydrolyzed surface groups a linear dependence between the fraction of silanol groups (SiOH) and the pH of the isoelectric point is predicted, which was confirmed by electrophoretic measurements of various commercial silicon nitride powders. The proposed method provides rapid information on the particle surface composition, which is of particular relevance for colloidal processing of silicon nitride powders.

Der mit der Oberfläche von Si_3N_4 -Pulvern korrelierte Sauerstoffgehalt dieser Pulver wurde mittels eines Verfahrens bestimmt, das auf der Messung der spezifischen Oberfläche und des isoelektrischen Punktes in wässriger Lösung beruht. Aus dem Dissoziationsmodell hydrolysierter Gruppen an der Oberfläche läßt sich eine lineare Abhängigkeit zwischen dem Anteil der Silanol-Gruppen (SiOH) und dem pH-Wert des isoelektrischen Punktes ableiten. Diese Überlegung konnte durch Elektrophoremessungen an verschiedenen kommerziellen Si_3N_4 -Pulvern bestätigt werden. Dieses Verfahren erlaubt rasche Rückschlüsse über die Zusammensetzung der Teilchenoberfläche, was speziell bei einer kolloidalen Verfahrenstechnik im Fall von Si_3N_4 -Pulvern von Bedeutung ist.

On a caractérisé la teneur en oxygène présent à la surface de poudres de nitrure de silicium par une

méthode basée sur la mesure de la surface spécifique et du point isoélectrique dans des solutions aqueuses. A partir du modèle de dissociation des groupes de surface hydrolysés, on peut prévoir une dépendance linéaire entre le taux de groupes silanol (SiOH) et le pH du point isoélectrique; ceci a été confirmé par des mesures électrophorétiques effectuées sur différentes poudres commerciales de nitrure de silicium. La méthode proposée permet l'accès rapide à des informations relatives à la composition surfacique des particules, ce qui est d'un grand intérêt dans le cas du traitement colloïdal des poudres de nitrure de silicium.

1 Introduction

Increasing interest in high-temperature resistant silicon nitride ceramics for various structural applications has led to efforts in the development of improved silicon nitride powders. Silicon nitride powders of high purity, small and homogeneous grain size are mainly produced by nitridation of fine silicon powder, carbothermal reduction of silica powder or gel and subsequent nitridation, gas-phase reaction of silanes with ammonia and thermal decomposition of silicon diimide.^{1–3} Because of the higher free energy of formation of silica, silicon nitride will always be oxidized to silica or oxynitride in the presence of an oxygen or water-containing atmosphere, even though the reaction kinetics will be extremely slow at room temperature.⁴ Thus, commercial silicon nitride powders always contain an oxygen content typically between 1 and 2.5 wt%.⁵ The lowest oxygen contents were observed in powders which were chemically purified by acid

leaching, as, for example, with hydrofluorine acid, whereas the higher contents occur in as-synthesized powders and in powders of high specific surface area. The sensitivity of the total oxygen content on surface purification treatment and specific surface area clearly indicates that the particle surface will be preferentially oxidized when exposed to an oxidizing environment during post-fabrication processing.

Various techniques have been used to characterize the structure and composition of the powder particle surface such as IR, TEM, XPS, AES and SIMS.⁵⁻⁹ From the experimental analyses a typical thickness of the oxidic surface layer on several commercial silicon nitride powders of approximately 3–5 nm was deduced.⁶ Significantly smaller values of 0.1–0.7 nm, however, were evaluated from a combination of bulk chemical analysis with surface-sensitive XPS measurements.⁵ From controlled oxidation experiments of clean CVD-silicon nitride films the XPS analyses showed the oxidized layer had a composition of a 'graded' oxynitride layer with the elemental concentration of oxygen decreasing steadily with the distance from the surface.¹⁰ Thus, the discrepancies in defining a 'thickness' of the oxide surface layer may be related to the lack of any sharp phase boundaries separating a silica-like outer surface shell from a silicon oxynitride-like inner shell and from the bulk (Fig. 1).

The oxidic surface composition strongly influences the colloidal dispersion behavior of silicon nitride in aqueous suspensions.¹¹ Highly concentrated, low viscosity powder suspensions, however, are of increasing importance for defect-controlled processing and shaping techniques such as colloidal pressing and filtration, slip casting, etc.¹² The objective of the present paper is to describe a potential method for estimating the oxygen content which may be attributed to the surface of the silicon nitride particles from measurements of the specific surface area, S_v , and the pH of the isoelectric point, pH_{iep} , in aqueous solution. Both variables are of particular significance for the colloidal properties

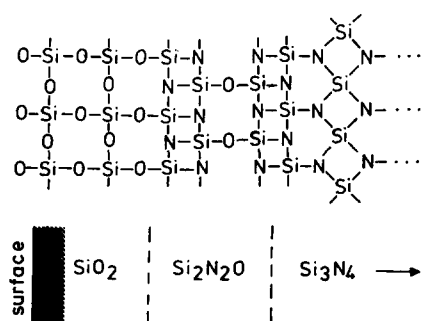


Fig. 1. Scheme of compositional gradient from the surface to the bulk of oxygen containing silicon nitride particles.

of silicon nitride during processing in aqueous solution. Various techniques such as electrophoresis or acoustophoresis can be applied to find the pH_{iep} without requiring as strict assumptions for the double layer extension and the retardation correction function as for calculation of the zeta potential.¹³ Thus, the proposed method is believed to provide rapid information on relevant processing properties of silicon nitride powders.

2 Experimental

A variety of commercial silicon nitride powders (Table 1) were reviewed for their oxygen content and examined for their isoelectric point. The powders were synthesized according to the major production routes, i.e. direct nitridation of silicon, carbothermal reduction of silica and subsequent nitridation, chemical vapor deposition of silanes and thermal decomposition of silicon diimides (for details see Refs 5 and 14). As-received powders as well as powders which were milled in a jet mill under nitrogen, in a ball mill with water or ethanol and subsequently leached in diluted hydrofluoric acid were examined.

The specific surface area of the powders was determined by the three-point BET method. Data on the total oxygen content of the silicon nitride powders were taken from the literature,⁵ where the oxygen content was determined by the inert gas fusion technique.¹⁵ Data for the surface oxygen concentration were taken from results of XPS measurements where the O 1s, N 1s and Si 2p signals were analyzed. From the peak intensities an equivalent thickness of the surface layer assuming SiO_2 or $\text{Si}_2\text{N}_2\text{O}$ composition was calculated and compared to the surface layer thickness derived from the total oxygen content as determined from bulk chemical analysis.⁵

Various techniques can be used to determine the pH of the isoelectric point. Earlier measurements have shown that K^+ and Cl^- ions behave as indifferent electrolytes for Si_3N_4 , so that KOH and HCl can be used to adjust pH.¹⁶ Thus, the point of zero charge, where the fraction of positively charged equals that of negatively charged surface groups, can be expressed by the isoelectric point,¹³ which can be measured by electrophoretic or acoustophoretic techniques.¹⁷ A zeta potential meter (MV 870, Ingenjörfirman REPAP, Stockholm, Sweden) was used to determine the isoelectric points from the zeta potential—pH relationship at 298 K. The electric field strength was 15 V/cm and only very diluted

Table 1 Commercial silicon nitride powders considered in this work

Number	Powder	Method	Number	Powder	Method
1	H-1, H.C. Starck, FRG	A	16	SN-9FW, Denka, Japan	A
2	H-2, H.C. Starck, FRG	A	17	Grade 1001, Anzon, UK	A
3	S-1, H.C. Starck, FRG	A	18	P-95, KemaNord, Sweden	A
4	LC-10, H.C. Starck, FRG	A	19	S-1, Nippon Koukan, Japan	A
5	LC-10 N, H.C. Starck, FRG	A	20	S-2, Nippon Koukan, Japan	A
6	LC-12, H.C. Starck, FRG	A	21	S-3, Nippon Koukan, Japan	A
7	LC-12S, H.C. Starck, FRG	A	22	A-200, Toshiba Ceram., Japan	B
8	LC-12N, H.C. Starck, FRG	A	23	TC-2, Sumitomo Chem., Japan	B
9	SN-GX, Denka, Japan	A	24	SN-502, GTE Sylvania, US	C
10	SN-G2, Denka, Japan	A	25	TS-7, Toso, Japan	C
11	SN-GD, Denka, Japan	A	26	TS-8, Toso, Japan	C
12	SN-6, Denka, Japan	A	27	SN-E10, UBE Ind., Japan	D
13	SN-6S, Denka, Japan	A	28	KSN-10, Sinetsu Chem., Japan	A
14	SN-7, Denka, Japan	A	29	KSN-100, Sinetsu Chem., Japan	D
15	SN-9S, Denka, Japan	A			

A: Nitridation of silicon: $3\text{Si} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4$.

B: Carbothermal reduction: $3\text{SiO}_2 + 6\text{C} + 2\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 + 6\text{CO}$.

C: Gas-phase reaction: $3\text{SiCl}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{HCl}$
 $3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2$.

D: Thermal decomposition: $3\text{Si}(\text{NH})_2 \rightarrow \text{Si}_3\text{N}_4 + 2\text{NH}_3$.

suspensions with solid fractions <0.001 vol.% were used. The constant background electrolyte concentration was 0.001 m/liter of KCl. pH was adjusted by adding HCl, NaOH or NH_3 solution and the pH was measured with a pH-meter (MV 870 VEB Präcitronik, Dresden, FRG). Prior to the measurement the suspensions were ultrasonicated for 5 min. In addition, the isoelectric point was determined from acoustophoretic measurements (PEN KEM 7000, Bedford Hills, NY, USA) using concentrated suspensions up to 5 vol.%.¹⁶

3 Results and Discussion

3.1 Specific surface area and oxygen content

Figure 2 summarizes a variety of commercial silicon nitride powders representing the total oxygen content versus the specific area. A general trend of increasing oxygen content with increasing surface area may be recognized in Fig. 2, which indicates a preferential surface oxidation in ultrafine powders. The total oxygen content, $C_{\text{O}}^{\text{tot}}$, of a silicon nitride powder is composed of the oxygen dissolved in the bulk, C_{O}^{b} , and the oxygen associated to the surface, C_{O}^{s} , by

$$C_{\text{O}}^{\text{tot}} = C_{\text{O}}^{\text{b}} + C_{\text{O}}^{\text{s}} \quad (1)$$

Assuming the oxygen content in the bulk corresponds only to the temperature-dependent solubility limit of O in $\alpha\text{-Si}_3\text{N}_4$, C_{O}^{b} should remain constant with increasing specific surface area, S_V , whereas C_{O}^{s} will be a function of S_V . From the extrapolation of

the data to a surface area of zero, a solubility range C_{O}^{b} of 0.6 to 0.9 wt% for oxygen in bulk material of α -silicon nitride is obtained. From XPS measurements a solution limit of 0.8 ± 0.2 wt% was deduced for α -silicon nitride fabricated at approximately 1400°C .⁵ Previously, α -silicon nitride was considered to be an oxygen-stabilized silicon nitride modification with a composition of $\text{Si}_{23}\text{N}_{30}\text{O}$ which would correspond to a solubility limit of 0.9 wt%.^{18,19} Subsequent investigations, however, proved the α -modification to be stable also in the total absence of oxygen.²⁰

The surface oxygen content may be derived from the difference between the total volume of a spherical

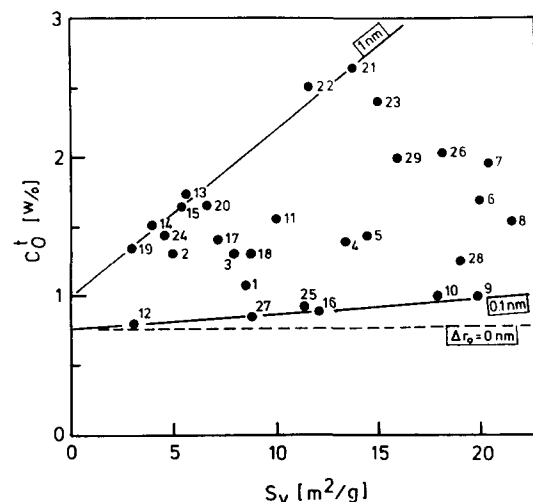


Fig. 2. Oxygen content and specific surface area of various commercial silicon nitride powders (Table 1). Δr_0 for a SiO_2 -like surface layer.

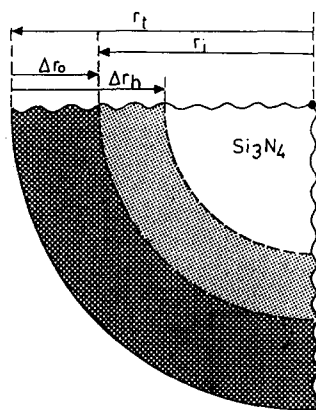


Fig. 3. Surface layer structure model of a silicon nitride particle (Δr_o and $\Delta r_h \ll r_i$).

particle with radius r_t and the volume of a surface oxide layer free particle of radius r_i by

$$C_O^s = K \frac{\rho_{\text{SiO}_2}}{\rho_{\text{Si}_3\text{N}_4}} \left[1 - \left(\frac{r_i}{r_t} \right)^3 \right] \quad (2)$$

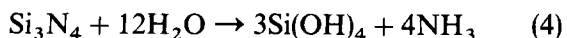
where $\rho_{\text{Si}_3\text{N}_4}$ is the density of $\alpha\text{-Si}_3\text{N}_4$ ($3.21 \times 10^6 \text{ g/m}^3$), ρ_{SiO_2} is the density of the surface oxide layer composition, e.g. SiO_2 (cristobalite, $2.32 \times 10^6 \text{ g/m}^3$), and K a factor to convert wt% oxygen into wt% SiO_2 ($K = 53.27$). Introducing a hypothetical surface oxide layer thickness, Δr_o ($= r_t - r_i$; see Fig. 3) and expressing r_t in terms of the specific surface area S_V ($= 3/(r_t \rho_{\text{Si}_3\text{N}_4})$) for $\Delta r_o \ll r_i$) finally results in the following expression for the surface oxygen content:

$$C_O^s = 38.5 \left[1 - \left(1 - \frac{\rho_{\text{Si}_3\text{N}_4}}{3} \Delta r_o S_V \right)^3 \right] \quad (3)$$

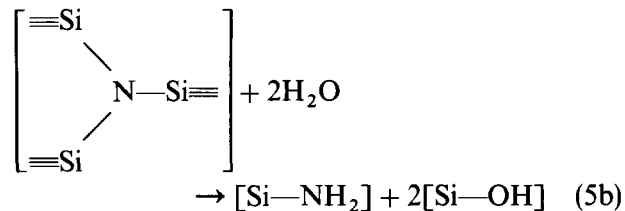
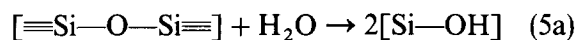
where the dimensions for Δr_o and S_V are given in m and m^2/g , respectively. Equation (1) can be used to compare the experimental data given in Fig. 2 with calculated data according to eqn (1) ($C_O^s \approx 0.8 \text{ wt}\%$) and eqn (3) ($\Delta r_o \approx 0.1\text{--}1.0 \text{ nm}$). As may be seen the majority of the experimental data lie within the boundary curves for $\Delta r_o = 0.1$ and 1.0 nm for a silica-like surface ($\approx \frac{1}{3}$ to 4 monolayers). Similar results for the surface oxide layer thickness have been obtained from XPS measurements where, for a variety of commercial silicon nitride powders, a surface oxide layer thickness between 0.1 and 0.7 nm was derived.⁵ A significantly larger thickness of $\Delta r_o = 0.3$ to 3 nm is deduced when a surface composition corresponding to $\text{Si}_2\text{N}_2\text{O}$ is assumed.

3.2 Surface charge formation in aqueous solution

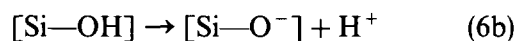
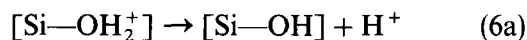
While complete hydrolysis of small silicon nitride particles results in the formation of silicic acid according to



surface hydrolysis of larger particles in aqueous solution results in the formation of a gel layer of thickness Δr_h (Fig. 3) within which oxide $[\equiv\text{Si}-\text{O}-]$ and nitride groups $[\equiv\text{Si}-\text{N}=\equiv]$ are hydrolyzed:



Surface charging of the silicon nitride particles in water may therefore be described by the pH-dependent dissociation reactions of amphoteric silanol $[\text{Si}-\text{OH}]$:²¹



and basic primary amine $[\text{Si}-\text{NH}_2]$ sites:



at the solid-liquid interface.²²⁻²⁵ Depending on the fractional site occupancy of the various surface groups and their pH-dependent dissociation behavior, a wide variation of the isoelectric point (pH_{iep}) was observed in silicon nitride powders ranging from $\text{pH} \approx 2$ to >9 .²⁶⁻²⁹ Figure 4 shows the results of isoelectric point measurements where the surface oxygen content normalized to the specific surface area is given versus the pH_{iep} . The surface oxygen content of the powders was taken from the

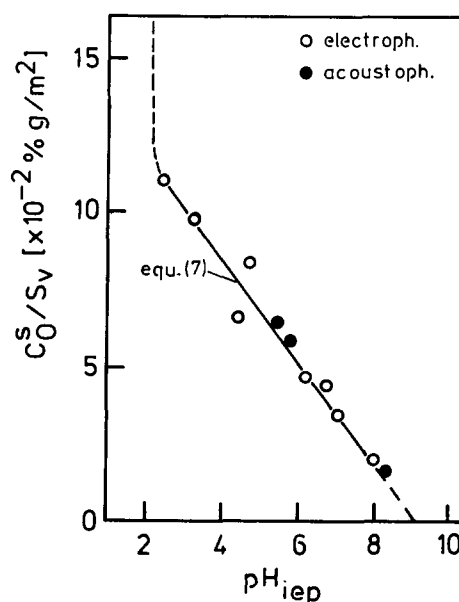


Fig. 4. Surface oxygen content (normalized to the specific surface area), C_O^s/S_V , as a linear function of the pH_{iep} .

data given in Ref. 5. From regression analysis a linear expression may be derived:

$$\frac{C_o^s}{S_v} = 0.0161 (9.3 - \text{pH}_{\text{iep}}) \quad (7)$$

with a correlation coefficient of 0.97. Equation (7) shows that for an oxygen-free nitride surface a pH_{iep} of approximately 9.3 is extrapolated, which may well be explained by the basic dissociation behavior of amine groups as compared to the acidic behavior of silanol groups.²⁵

Using the concept of surface dissociation constants for the potential dissociation reactions³⁰

$$K_+ = \frac{[\text{Si}-\text{XH}][\text{H}^+]_s}{[\text{Si}-\text{XH}_2^+]} \quad (8a)$$

$$K_- = \frac{[\text{Si}-\text{X}^-][\text{H}^+]_s}{[\text{Si}-\text{XH}]} \quad (8b)$$

with $\text{X} = \text{O}$ or NH , respectively, and where the concentration of protons on the particle surface, $[\text{H}^+]_s$, is related to the bulk concentration, $[\text{H}^+]$, by a Boltzmann equation

$$[\text{H}^+]_s = [\text{H}^+] \exp\left[-\frac{q\Psi_o}{kT}\right] \quad (9)$$

the surface potential, Ψ_o , is related to the pH by a Nernst equation^{22,24,31}

$$2.303(\text{pH}_{\text{iep}}^{\text{Si-OH}} - \text{pH}) = \frac{q\Psi_o}{kT} + \frac{1}{2} \ln \left[\frac{[\text{Si}-\text{OH}^+]}{[\text{Si}-\text{O}^-]} \right] \quad (10)$$

Equation (10) provides a relation between charge, q , surface potential, Ψ_o , and pH for the case of a simple amphoteric $\text{Si}-\text{OH}$ site.²⁵ For silicon dioxide $\text{pH}_{\text{iep}}^{\text{Si-OH}}$ values of 1.5–3.5 were found in aqueous solution.^{23,32} Thus, in most of the pH range ($\text{pH} > \text{pH}_{\text{iep}}^{\text{Si-OH}}$) a negatively charged surface will be generated on a hydrolyzed silicon dioxide surface. Also from eqn (8)

$$K^s = \frac{K_+}{K_-} = \frac{[\text{Si}-\text{OH}_2^+][\text{H}^+]_s}{[\text{Si}-\text{OH}]^2} \quad (11)$$

and

$$\Delta \text{p}K^s = \log K^s = \text{p}K_-^s - \text{p}K_+^s \quad (12)$$

which describes the tendency to dissociate for the $\text{Si}-\text{OH}$ sites.²⁴ Similar equations may be generated for the $\text{Si}-\text{NH}_2$ sites. From theoretical calculations as well as experimental results $\Delta \text{p}K^s$ values in the range of 8–10 were reported.^{22,24} For the amine sites $[\text{Si}-\text{NH}_2]$ undergoing reaction (6c) the equilibrium constant is not known directly; however, for organic

amines, $\text{p}K_+^s$ is always close to 10, irrespective of the organic group or the order of amine.²⁵

3.3 Isoelectric point and surface oxygen content

At the isoelectric point $[\text{H}^+]_s = [\text{H}^+]$ and the number of negatively charged surface sites equals that of positively charged surface sites. From a straightforward analysis of the pH-sensitivity of silicon nitride surfaces used in ion-sensing field effect transistors (ISFET) a non-linear relation between the pH_{iep} and the surface fractions of the $[\text{Si}-\text{OH}]$ sites, v^s , and $[\text{Si}-\text{NH}_2]$ sites, v^A , was derived:²⁵

$$\text{pH}_{\text{iep}} = \text{pH}_{\text{iep}}^{\text{Si-OH}} + \frac{1}{2.303} \sinh^{-1} \left[\frac{\sqrt{K^s} v^A}{2 v^s} \right] \quad (13)$$

The non-linear two-site dissociation model assumes only the outer surface layer to be involved in the dissociation reactions of an amphoteric $[\text{Si}-\text{OH}]$ and a highly basic $[\text{Si}-\text{NH}_2]$ site.

A linear approximation between the pH_{iep} and the surface reaction constants may be derived from eqns (10)–(12):

$$\text{pH}_{\text{iep}} \approx v^s \left[\frac{\Delta \text{p}K^s}{2} + \text{p}K_+^s \right] + v^A \left[\frac{\Delta \text{p}K^A}{2} + \text{p}K_+^A \right] \quad (14)$$

with the fractional site concentrations

$$v^s + v^A = 1 \quad (15)$$

Using the values of $\Delta \text{p}K^s = 8$, $\text{p}K_+^s = -1.8$, $\text{p}K_+^A \approx 10$,^{23,24} and adopting a $\Delta \text{p}K^A$ value of -1.4 as deduced from the maximum pH_{iep} of ≈ 9.3 for a hypothetically oxygen-free surface (Fig. 4), finally a linear relation is obtained to express the fractional silanol site concentration, v^s , as a function of the pH_{iep} of the silicon nitride powder

$$v^s \approx 0.1408 (9.3 - \text{pH}_{\text{iep}}) \quad (16)$$

For $v^s = 1$ eqn (16) yields a $\text{pH}_{\text{iep}}^{\text{Si-OH}}$ of 2.2 which is consistent with the pH_{iep} values of silicon dioxide found in literature.^{23,32} The fractional silanol site concentration, v^s , is given by

$$v^s = \frac{n^s}{N} \quad (17)$$

where N is the total number of dissociating $[\text{Si}-\text{OH}]$ and $[\text{SiNH}_2]$ sites ($N = n^s + n^A$) on the silicon nitride particle surface. Zeta potential measurements of preoxidized silicon nitride powders, however, showed clearly an increase of the amount of zeta potential up to a critical oxide layer thickness Δr_o ,³³ suggesting the hydrolysis reaction affects a surface volume rather than the outer surface layer.

Silicon dioxide films investigated for ISFET application were also found to be sensitive to progressive hydration and ion migration, resulting in hysteresis effects and long-term drifts of the Ψ_0 -pH response.²⁴ Thus, the total number of dissociating sites N in the hydrolyzed gel layer of thickness Δr_h on the particle surface is given by

$$N = \frac{4}{3} \frac{\pi}{\Omega} [3r_t^2 \Delta r_h - 3r_t \Delta r_h^2 + \Delta r_h^3] \quad (18)$$

where Ω is the molecular volume of the dissociating groups. The gel layer thickness Δr_h may be related to the distance from the particle surface up to which H^+ and OH^- ions could penetrate the surface layers and react with the dissociatable Si—XH groups.¹³ Assuming that the hydrolyzed layer thickness will be greater than that present on the particle surface originating from dry oxidation ($\Delta r_h > \Delta r_o$; Fig. 3), and that the hydrolysis will yield constant Δr_h , the oxygen content associated to the surface, C_O^s , may be expressed in terms of v^s by comparing eqns (7) and (18), resulting in

$$C_O^s = a^* v^s S_v \quad (19)$$

For a dry particle, C_O^s is given by the weight fraction of surface-bonded oxygen

$$C_O^s = \frac{n_{so} M_o}{\rho_{Si_3N_4} \frac{4}{3} \pi r_t^3 A} \quad (20)$$

where M_o is the molecular weight, n_{so} the number of surface-bonded oxygen atoms in a Si_3N_4 particle and A is the Avogadro constant. For the case that a fraction f of n_{so} oxygen atoms will contribute to charge formation upon hydrolysis reaction

$$n^s = f n_{so} \quad (21)$$

an expression for a^* may be derived from eqns (17)–(20):

$$a^* = \frac{\pi M_o}{f \Omega A} \Delta r_h \left[1 - \frac{\Delta r_h}{r_t} + \frac{1}{3} \left(\frac{\Delta r_h}{r_t} \right)^2 \right] \quad (22)$$

a^* corresponds to an activity coefficient which describes the effective depth of the hydrolyzed gel layer as a function of the mean particle radius r_t . a^* will be influenced by the experimental conditions, e.g. the hydrolysis reaction kinetics and the pH at which the Si_3N_4 powder is dispersed in the aqueous solution. Taking $\Omega \approx 2 \times 10^{-30} \text{ m}^3$ ($\approx \frac{1}{4}$ of the SiO_4 tetrahedron volume) and neglecting the polynomial part for small values of Δr_h , eqns (22) and (16) may be suited in eqn (19), finally resulting in

$$\frac{C_O^s}{S_v} \approx 8.35 \times 10^6 \frac{\Delta r_h}{f} (9.3 - \text{pH}_{iep}) \quad (23)$$

Zeta potential measurements of preoxidized silicon nitride powder have shown an increase of the zeta potential with increasing oxygen content of the powder.³³ Above a critical thickness of the silica-like surface layer calculated from the weight gain and mean particle size of approximately 1.5 nm ($\approx \Delta r_h$), however, the zeta potential remained constant and no further dependence on the surface oxygen content was observed. Obviously, above this critical surface oxide layer thickness $\Delta r_o > \Delta r_h$ and the preoxidized silicon nitride powder behaves like a silica particle in aqueous solution. From experimental results (Fig. 4) $a^* \approx 0.114$, which for $\Delta r_h \approx 1.5 \text{ nm}$ results in $f \approx 0.78$. Thus, only a certain portion of the Si—O sites in a surface layer of thickness Δr_h is suggested to dissociate upon hydrolysis and contribute to charge formation. Based on eqn (23) the oxygen content attributed to the surface of Si_3N_4 powders may be estimated from pH_{iep} measurements assuming constant hydrolysis conditions (e.g. temperature, leaching time, pH) and an initial oxide layer thickness which is significantly smaller than the hydrolyzed layer thickness. For such oxide layers, e.g. for oxygen contents attributed to the powder surface below approximately 1 wt%, the pH of the isoelectric point may well be used to estimate the surface oxygen content from electrophoretic measurements.

4 Conclusions

The oxygen content on the surface of Si_3N_4 powder particles severely influences the colloidal properties of Si_3N_4 dispersed in aqueous solution. While a low surface oxygen content (pure nitride surface) results in high pH_{iep} values above 8, preoxidized Si_3N_4 exhibits very low pH_{iep} below 4. The differences in basicity or acidity of amine or silanol groups may be used to characterize the surface-bonded oxygen content which is effective for surface charging and electrostatic stabilization behavior. A linear relationship between the surface oxygen content and the pH_{iep} was predicted by a simple dissociation model approach which could be confirmed by electrophoretic measurements. Although the dissociation of surface-bonded silanol or silazane groups may differ from that of the corresponding acid or base in aqueous solution and the surface composition may be much more complex than assumed, this estimation clearly shows the influence of surface oxygen content on the pH_{iep} . It has been shown that even this simple model whose parameters can be determined from site-dissociation and

double-layer models could fit the experimental data sufficiently. Thus, the proposed method provides rapid information on the particle surface composition which is of particular relevance for colloidal processing of silicon nitride powders.

Acknowledgement

Financial support of Deutsche Forschungsgemeinschaft (DFG, Gr 961/1-1) for part of this work is gratefully acknowledged.

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