Journal of the European Ceramic Society 7 (1991) 361-368

Surface Modification and Dispersion of Silicon Nitride and Silicon Carbide Powders

E. Lidén,[a] L. Bergström,[b] M. Persson[a] & R. Carlsson[a]

[a] Swedish Ceramic Institute, Box 5403, S-402 29 Göteborg, Sweden
[b] Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden

(Received 3 November 1990; revised version received 7 January 1991; accepted 11 January 1991)

Abstract

A surface modification technique using controlled hydrolysis and polymerization of Al-alkoxide is presented. It was found by measuring the electrokinetic behaviour and the adsorption properties that a minimum amount of about 0·5 mg Al/m^2 was necessary to give SiC and Si_3N_4 powders alumina-like surface properties. This permanent surface coating improved the dispersability of Si_3N_4 in cyclohexane using a commercial dispersant with an acidic headgroup.

Es wird ein Verfahren vorgestellt, das auf einer kontrollierten Hydrolyse und Polymerisation von Al-Alkoxid basiert und die Veränderung von Oberflächen ermöglicht. Durch Messung des elektrokinetischen Verhaltens und der Adsorptionseigenschaften hat sich gezeigt, daß circa 0·5 mg Al/m^2 nötig sind, damit sich SiC-und Si_3N_4-Pulver, oberflächlich wie Al_2O_3 verhalten. Diese dauerhafte Beschichtung der Oberfläche verbesserte die Dispersionseigenschaften von Si_3N_4 in Cyclohexan, wobei ein übliches Dispersionsmittel mit einer saueren funktionellen Gruppe verwendet wurde.

On présente ici une technique de modification de surface faisant appel à l'hydrolyse contrôlee et à la polymérisation de l'alcoolate d'Al. Par mesure du comportement électrocinétique et des propriétés d'adsorption, on a établi qu'une teneur minimale de de composé (environ 0·5 mg Al/m^2) était nécessaire pour donner à des poudres de SiC et de Si_3N_4 des propriétés de surface semblables à celles de l'alumine. Ce recouvrement surfaçique permanent améliore la dispersabilité du Si_3N_4 dans le cyclohexane en présence d'un dispersant commercial possédant des groupes acides.

1 Introduction

In order to disperse a powder in water the surface charge properties of the powder have to be controlled. Knowledge about the surface charge behaviour is essential when choosing the mechanism (electrostatic or steric) to obtain a dispersion with good colloidal stability. When, for instance, electrostatic stabilization is used, the pH range in which the particles have a high surface charge, which will give a high repulsion and good stabilization, has to be known. Steric or electrosteric stabilization requires strongly attached and dense layers of polymer or polyelectrolyte on the powder surfaces. The adsorption of these additives is to a large extent determined by the surface properties and charge behaviour of the powder.

However, it is well known that the surface charge properties of different ceramic powders vary with the type of powder and in some cases even with the producer. It has been shown that silicon nitride powders obtained from different manufacturers can have quite different electrophoretic mobilities and stability regions.[1] The isoelectric point of silicon nitride can vary between $pH_{iep} = 3$ and 9. As an example, electrophoretic mobilities of one silicon carbide powder (UF 15, Lonza Werke FRG) as well as three different silicon nitride powders are shown in Fig. 1. The silicon carbide powder surface consists of an oxide film and the surface can be considered as acidic due to Si—OH groups. On the other hand, it has been found that the particle surface of silicon nitride consists of both acidic (Si—OH) and basic (Si_2—NH) groups.[2] It is the ratio between these acidic and basic groups which determines the charge behaviour of the silicon nitride powders and hence the isoelectric point. A high amount of silanol

Journal of the European Ceramic Society 0955-2219/91/$3.50

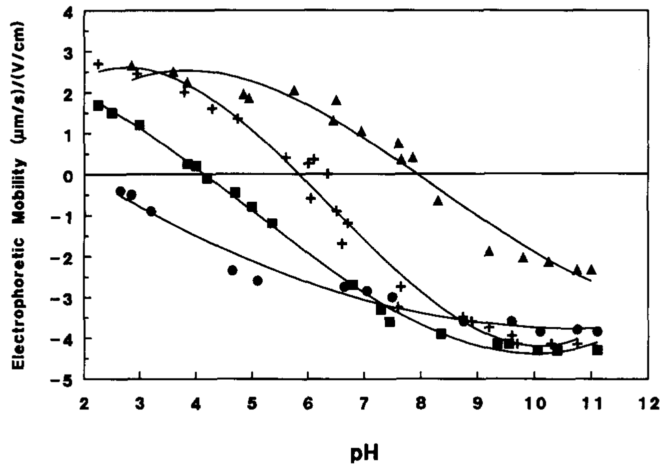

Fig. 1. Electrophoretic mobilities versus pH of pure Si_3N_4 (■, Kema-Nord P95; +, UBE E-10; ▲, LC 10) and SiC (●, Lonza UF 15) in water. $pH_{iep} \approx 2$ for α-SiC and varies between $pH_{iep} = 4{\cdot}2$ and $pH_{iep} \approx 8$ for different Si_3N_4 powders.

groups shifts the pH_{iep} to low pH values and a high amount of amine groups shifts the isoelectric point to high pH values.

Due to the differences in surface properties it is often necessary to use a certain dispersing agent for each separate powder. When producing multicomponent ceramics where more than one kind of ceramic powder has to be dispersed, there can be difficulties in obtaining high stability and homogeneity of the system due to heterocoagulation and competitive adsorption.

One way to control the charge behaviour is to modify the particle surfaces of the powder. In this paper a surface modification technique is described using Al-alkoxide.[3,4] The addition of alkoxides to ceramic powders has recently been studied by several different authors. In most cases alkoxides have been used to prepare composite powders with uniform composition[5-8] or to homogeneously disperse small amounts of sintering agents in a ceramic system.[9-11] Due to their ability to form strong covalent bonds with the particle surfaces, metal alkoxides have also been used as coupling agents when dispersing ceramic powders in non-aqueous media.[12,13] In this paper the use of alkoxide coating is only reported as a tool for changing the charge and adsorption behaviour of ceramic powders.

To take advantage of the surface modification technique it is important that the amount of adsorbed Al-alkoxide is minimized, since the goal is to change the surface charge behaviour without increasing the specific surface area or changing the morphology of the powder too much. As controlled hydrolysis of alkoxides results in porous gels, coating of the particles by this technique will always give an increase in the specific surface area. Very high specific surface areas will give problems during the dispersing and forming steps, especially when complex-shaped components with high and uniform green densities are to be produced. In this study the modification of the ceramic powders are optimized by controlling the hydrolysis and polymerization reactions of the alkoxide molecules. The change in surface charge behaviour as well as adsorption behaviour of the modified powder is examined.

2 Experimental

2.1 Ceramic powder

A silicon nitride powder, SN-E10, manufactured by UBE Industries, Japan and a silicon carbide powder, Carbogran, UF-15, manufactured by Lonza Werke, FRG, were used in the study. The specific surface areas of the powders were measured by a single-point BET method (Flowsorb II 2300, Micromeritics, USA) to $9{\cdot}8\,m^2/g$ for the silicon nitride powder and $15{\cdot}0\,m^2/g$ for the silicon carbide powder. The isoelectric points were measured for the silicon nitride powder to $pH_{iep} = 6{\cdot}2$ and for silicon carbide to $pH_{iep} = 3{\cdot}8$.

2.2 Surface modification

The alkoxide used to modify the powder surfaces was aluminium tri-isopropoxide ($Al(OC_3H_7)_3$; Merck-Schuchardt, FRG), here referred to as Al-alkoxide. This compound is very sensitive to hydrolysis. Since any small amount of water will cause uncontrolled hydrolysis reactions of the alkoxide molecules, the experiments were performed in dry N_2 atmosphere in a glove box and the Al-alkoxide was vacuum distilled prior to use. The solvent, *n*-hexane, was dried by using molecular sieves and the powders were dried at 140°C in air for 12 h. Controlled conditions were used to avoid the formation of isolated Al hydroxide precipitates and Al hydroxide-bonded agglomerates. The goal was to change the surface behaviour of the ceramic powder to an 'alumina-like' surface with the minimum amount of alkoxide.

Ceramic powder (40 g) was dispersed in 500 ml *n*-hexane, using a high-shear mixer to break up hard agglomerates. Then 6 wt% distilled Al-alkoxide (equivalent to 0·8 wt% Al) diluted in hexane was slowly added to the suspensions during stirring. It was very obvious that a reaction between the alkoxide molecules and the particle surface took place. The hydrophilic particles obtained a hydrophobic surface when the alkoxide was added and the particles were wetted and deflocculated in the organic media. After 1 h of mixing, 0, 0·45, 1 and 5 mol deionized water (diluted in 2-propanol) per mol alkoxide was added dropwise to the stirred alkoxide/powder suspensions. After a total blending time of 3 h the excess, non-reacted alkoxide was removed by repeatedly centrifuging and decanting in pure hexane. The hexane was finally evaporated and the powder was dried at 130°C for 10 h. Additional experiments with no water added were performed at higher temperature (50°C) to study if this increased the reactivity of the alkoxide.

2.3 Electrophoretic mobility

Electrophoretic measurements were used to determine the change in the isoelectric point of the modified powders. This microelectrophoresis technique (Zetasizer Mk II, Malvern Instruments, UK) uses the dopplershift in the laser light scattering from the particles to obtain a mobility spectrum. NaCl was used to keep constant ionic strength of 0·01 M and pH was adjusted with HCl and NaOH. All measurements were made at 20°C. The modified powders were only dispersed in distilled water for 20 min before measurements. This relatively short dispersing time was chosen to be sure that a change in the surface charge properties of silicon nitride was not due to a reduced amount of silanol groups from the particle surface. It has earlier been shown by Bergström & Bostedt[2] that by ageing silicon nitride powders in water for an extended period of time (several weeks) soluble silica can be leached from the powder, thus resulting in a change of the amount of silanol groups and the isoelectric point.

The amounts of reacted Al-alkoxide were measured by X-ray fluorescence analysis and the specific areas of the modified Si_3N_4 powder were measured using a single-point BET method.

Leaching and ageing experiments of the surface modified powders were performed to examine the resistance of the surface coating. Surface-modified Si_3N_4 was leached in distilled water for 16 h and the amount of dissolved Al was analysed. The electrophoretic mobility of the same powder was examined after different times of ageing.

2.4 Adsorption measurements and dispersion tests

The ability of the powder surface to interact specifically with functional groups through acidic and basic sites was estimated by determining the adsorption capacity of benzoic acid and benzylamine in cyclohexane. This solvent was chosen because it can be assumed that it will interact with the powder surface or with the probe molecules only through dispersion forces so that it will not affect the adsorption capacity differently for different probes.

The ceramic powder, vacuum-dried over phosphorous pentoxide at room temperature, was mixed with dried cyclohexane containing small amounts of probe molecule. The sample was equilibrated for 16 h and the amount adsorbed was calculated from the remaining probe concentration in the supernatant. The experiments were performed at room temperature.

The dispersion effect of one polymeric dispersant was studied by settling experiments in cyclohexane. Suspensions containing about 6 vol.% dried powder were prepared by sonication (Soniprep 150, MSE Instruments, UK) for 10 min. The suspensions were poured into graduated tubes and left for four weeks. The final sediment volume was measured and the relative sediment densities calculated. A commercially available polymeric dispersant (Hypermer KD 4, ICI Chemicals, UK) was used with an acidic head-group and a polyester-type stabilizing moiety.[14]

3 Results

3.1 Surface modification

Mixing the ceramic powder (SiC or Si_3N_4) with Al-alkoxide with no water present results in a coverage of about 0·12 mg Al/m^2 particle surface. Even with excess of alkoxide present or at a higher reaction temperature more Al-alkoxide was not adsorbed on the particle surfaces. Since the amount of reacted alkoxide was the same on the two powders, this indicates that the silicon nitride and silicon carbide powders have the same amount of surface active sites on the particle surface, probably silanol (Si—OH) groups. The electrophoretic measurements showed that this amount of Al-alkoxide was not enough to change the surface charge characteristics of the powders to an 'alumina-like' behaviour. This means that a complete coverage was not obtained. More probably a patchwise coverage was achieved in these experiments. It has to be noted that the alkoxide molecules are never in the monomeric state. Freshly distilled aluminium isopropoxide is for instance in a trimeric form and changes to a tetrameric form after being aged for a few weeks.[15] In this study the structure of aluminium isopropoxide in *n*-hexane was not examined but other authors[16] have found that Al isopropoxide in aliphatic alcohols (organosols) consists of aggregates of amorphous monohydroxide with primary spherical particles, 2–3 nm in size.

By starting the hydrolysis reactions (adding water)

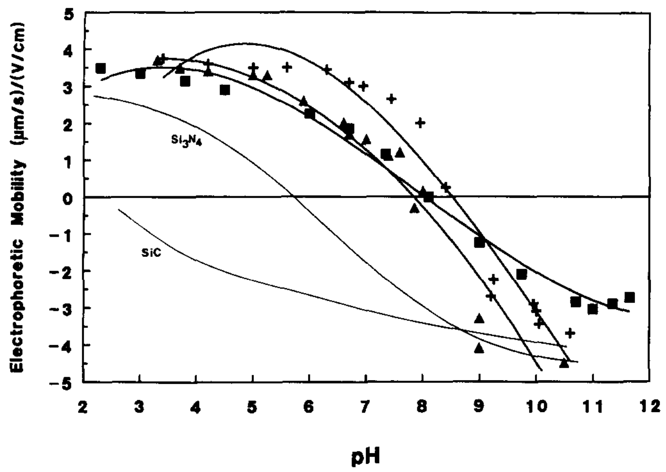

Fig. 2. Electrophoretic mobilities of surface-modified SiC (▲) and Si_3N_4 (+) compared to pure Al_2O_3 (■). 1×10^{-2} M NaCl used as an indifferent electrolyte. Note the similarity in electrokinetic behaviour and pH_{iep} for the surface-modified powders and Al_2O_3.

an increased amount of Al-alkoxide was bound to the powder surfaces and the surface properties of silicon nitride and silicon carbide were changed. In Fig. 2 the electrophoretic mobilities of pure as well as modified (0·5 mg Al/m^2) Si_3N_4 and SiC are seen. The electrophoretic mobility of pure Al_2O_3 is also shown in the figure and as can be seen the modified powders have a very similar electrokinetic behaviour. Figure 3 shows how the adsorbed amount of Al on silicon nitride and silicon carbide is increased when more water is added. This increase is probably due to hydrolysis and polymerization of the alkoxide molecules. The reactions involve several steps. Firstly an initial surface layer is formed by chemical adsorption and then the amount of reacted alkoxide is increased by starting the hydrolysis, as shown in Fig. 4. Hydrolysis reactions upon water additions link the alkoxide molecules by a polymerization type of sol–gel reaction. The adsorption reaction and the hydrolysis can be described according to Ref. 12:

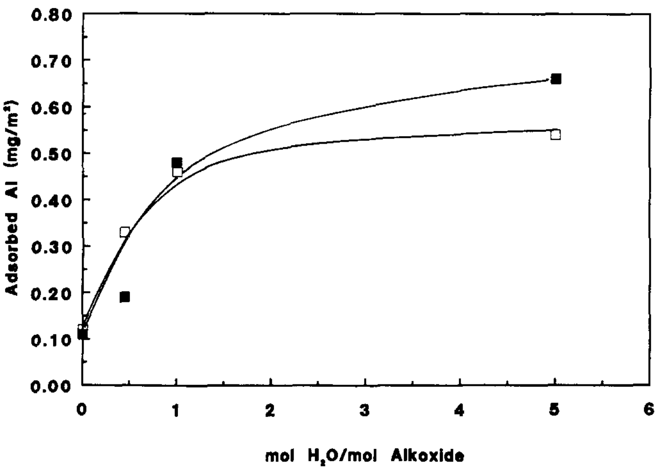

Fig. 3. Adsorbed amount of Al versus molar ratio H_2O/alkoxide on Si_3N_4 (■) and SiC (□). 6 wt% Al-alkoxide (equivalent to 0·8 wt% Al) added to all powders before the water amount was added.

Chemical adsorption:

$$\equiv Si—OH + RO—Al(OR)_2 \longrightarrow \equiv Si—O—Al(OR)_2 + ROH \quad (1)$$

Hydrolysis:

$$\equiv Si—O—Al(OR)_2 + RO—Al(OR)_2 \xrightarrow{H_2O} \equiv Si—O—Al(OR)_2 + HO—Al(OR)_2 \quad (2)$$

$$\equiv Si—O—Al(OR)_2 + HO—Al(OR)_2 \longrightarrow \equiv Si—O—Al(OR)—O—Al(OR)_2 + ROH$$

When more Al is bound to the particle surfaces, the isoelectric point is moved to a higher pH and at the same time the specific surface areas of the coated powders increase, as can be seen in Fig. 5. The results show that about 0·5 mg Al/m^2 is required to modify the silicon nitride and silicon carbide powders. Since the increase in specific surface area is substantial, it indicates that the surface coating consists of a porous layer. The increase in specific surface area would have been much higher if the excess of non-reacted alkoxide had not been removed before drying.

Leaching and ageing experiments of surface-modified Si_3N_4 and SiC with 0·5 mg Al/m^2 show that the solubility of the coating in water is very low, typically below 1 ppm Al at neutral pH. This agrees well with the solubility of $Al(OH)_3(s)$ calculated from equilibrium constants.[17] Furthermore, subjecting a surface-modified Si_3N_4 powder to different conditioning times does not result in any major change in the electrokinetic behaviour (Fig. 6). Thus, the surface coating can be treated as permanent with a low solubility.

3.2 Adsorption behaviour and dispersion tests

The adsorption data for α-Al_2O_3, Si_3N_4 and Al-modified Si_3N_4 (0·5 mg Al/m^2) is shown in Fig. 7.

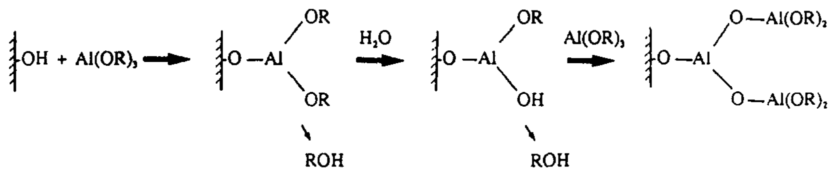

Fig. 4. Schematic drawing of the surface reaction.

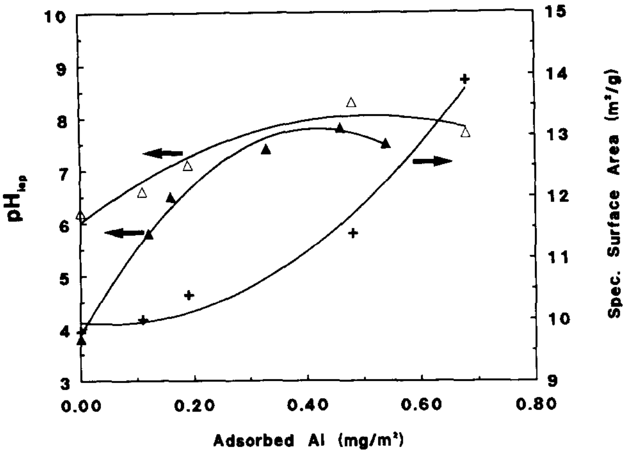

Fig. 5. pH$_{iep}$ and specific surface area (SSA) versus adsorbed amount of Al for Si_3N_4 (△, pH$_{iep}$; +, SSA) and SiC (▲, pH$_{iep}$ only).

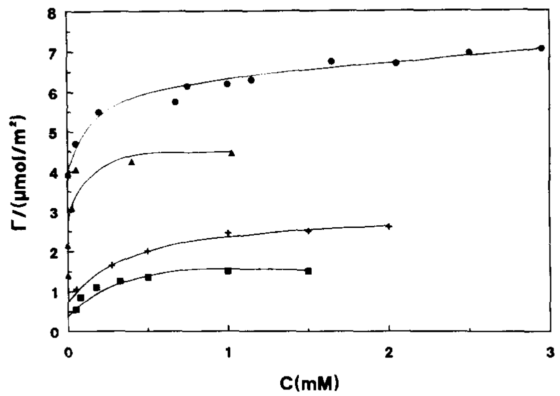

Fig. 7. Adsorption isotherms of benzoic acid on α-Al_2O_3 (●), Si_3N_4 (■) and Al-modified (0·5 mg Al/m²) Si_3N_4 (▲). The isotherm of benzylamine on Si_3N_4 (+) is also included. The adsorbed amount (Γ) per m² on dried powder is plotted versus the equilibrium concentration in the solution.

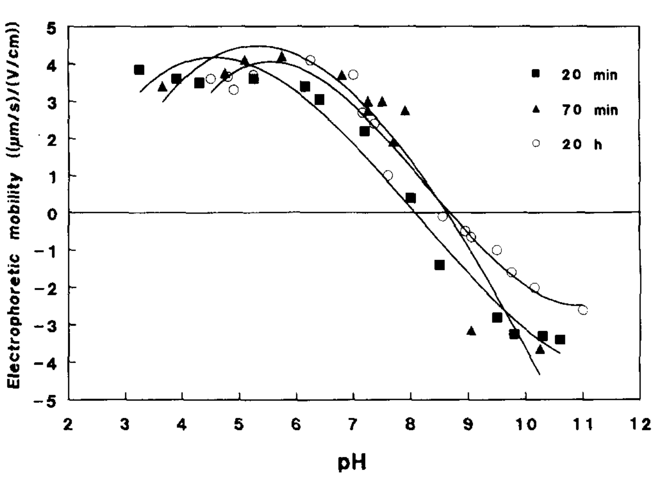

Fig. 6. Electrophoretic mobility versus pH at different conditioning times for surface modified Si_3N_4 (0·5 mg Al/m²). ■, 20 min; ▲, 70 min; ○, 20 h.

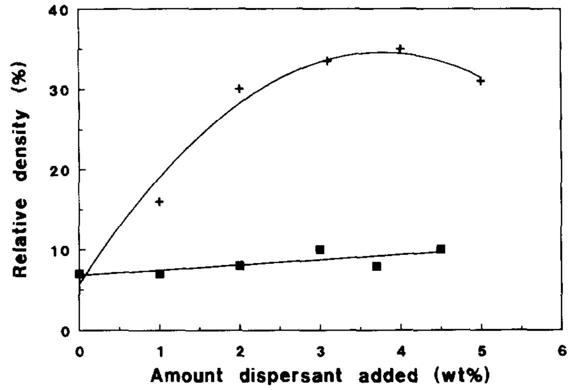

Fig. 8. Sediment densities versus amount of polymeric dispersant KD 4 added for pure Si_3N_4 (■, UBE E-10) and Al-modified Si_3N_4 (+, 0·5 mg Al/m²).

The results indicate distinct differences in the affinity between benzoic acid and the specific surface groups on the different powders. The basic Al—OH groups on the α-Al_2O_3 surface show a high affinity for the carboxylic acid group in benzoic acid, while the affinity for the acidic Si—OH, which dominates the surface chemistry of this Si_3N_4 powder, is substantially lower. Benzylamine, with basic head-group, shows a stronger interaction with the silanol groups.[14] However, by modifying the Si_3N_4 surface with a layer of hydrolysed Al-alkoxide, the affinity to benzoic acid increased drastically. The maximum adsorption (Γ_{max}) increases from 1·6 μmol/m² (Si_3N_4) to ~4·6 μmol/m² (Al-modified Si_3N_4). Although the surface modification does not raise Γ_{max} for benzoic acid to the same level as for α-Al_2O_3, the surface modification certainly changes the adsorption behaviour to more 'alumina like'. In Fig. 8 the relative sediment density versus the amount of polymeric dispersant is shown. The results show striking differences between pure and Al-modified Si_3N_4 (0·5 mg Al/m²). With the polymeric dispersant chosen high sediment densities, indicating good colloidal stability, were obtained for the Al-modified Si_3N_4 in cyclohexane, while the pure Si_3N_4 powder showed low sediment densities, indicating a strongly flocculated suspension. The structure of the dispersant KD 4 has been discussed in an earlier study,[14] where it was assumed to be consisting mainly of a non-polar carbon chain with a carboxylic acid head-group. The difference in dispersion properties can thus be referred to the difference in affinity of the powder surface to the carboxylic head-group.

4 Discussions

In eqns (1) and (2) the reactions of the alkoxide molecules were described by a polymerization-type of a sol–gel reaction. Through this reaction a porous gel is assumed to be formed on the powder surface by subsequent adsorption and hydrolysis. However, another possible reaction route is that the alkoxide molecules hydrolyse in solution upon addition of water. As the molecular weight of the hydrolysed polymer grows it becomes more and more unstable in the poor solvent hexane and finally collapses to form a precursor particle, which could be described as a nucleus. If there is an attractive interaction between the nuclei and the powder surface, the nuclei are probably irreversibly adsorbed on the powder surface. Look *et al.*[18] have studied the precipitation of uniform particles by hydrolysis and condensation of silicon and titanium alkoxides. They suggest that the primary growth mechanism is aggregation of small nuclei formed in solution and not by molecular addition to the solid phase. This proposed mechanism was supported by the porosity of the final solids and the presence of small subunits within the final particles. By using classical nucleation theory they calculated nuclei radii for both alkoxides as around 2–2·5 nm. Thus, a multiple-step reaction may be a more probable picture of the formation of the porous coating on the ceramic powder surface. The reaction starts with chemical adsorption of a monolayer of the alkoxide followed by addition of further alkoxide molecules on this monolayer upon hydrolysis together with adsorption of the small hydrolysed alkoxide nuclei formed in solution. This picture of the coating can explain the increase in specific surface area detected already at rather 'thin' surface coatings. In Fig. 6 the increase in pH_{iep} of both SiC and S_3N_4 is plotted versus the amount of Al adsorbed. The results for Si_3N_4 show a gradual increase in pH_{iep} from 6·2 to a maximum around 8·2 at a coverage of 0·48 mg Al/m^2. Similar results were obtained for SiC which, however, start at a lower pH_{iep} ($pH_{iep} = 3{\cdot}8$). Thus, it is assumed that an 'alumina-like' surface charge behaviour, i.e. a $pH_{iep} > 8$, needs a coverage around 0·5 mg Al/m^2. Assuming a uniform surface layer this amount is equivalent to about 10 Al atoms/nm^2, which, if each Al atom is assumed to be associated with an $Al(OH)_3(s)$ molecule, certainly represents a multilayer. However, using the proposed model of the layer formation above, the amount of Al needed for 'alumina-like' charge behaviour can be associated with the formation of a layer of adsorbed hydrolysed nuclei, i.e. a porous layer, several nm thick. The change in pH_{iep} during the formation of the coating can be described by the dissociation reaction of the surface groups. For Si_3N_4 and SiC the main surface group is Si—OH, described by:

$$\text{Si—OH}_2^+ \rightleftarrows \text{Si—OH} + \text{H}_s^+ \qquad (3)$$

$$\text{Si—OH} \rightleftarrows \text{Si—O}^- + \text{H}_s^+ \qquad (4)$$

For Si_3N_4, the existence of an additional basic amino group has been suggested:[2]

$$\text{Si}_2\text{NH}_2^+ \rightleftarrows \text{Si}_2\text{—NH} + \text{H}_s^+ \qquad (5)$$

The relative amount of these groups on the surface and the equilibrium constants for each reaction determine the isoelectric point of the powder. However, with the formation of an $Al(OH)_3$ layer on the surface, Al—OH groups start to dominate the charge behaviour. The dissociation can be described by:

$$\text{Al—OH}_2^+ \rightleftarrows \text{Al—OH} + \text{H}_s^+ \qquad (6)$$

$$\text{Al—OH} \rightleftarrows \text{Al—O}^- + \text{H}_s^+ \qquad (7)$$

As the equilibrium constants for eqns (6) and (7) are much higher than for eqns (3) and (4)[19] the pH_{iep} is shifted to higher values with an increase in the number of Al—OH groups on the surface. Thus, by coating the surface with a more or less continuous layer of $Al(OH)_3$ the silanol and amino groups of the native surface are buried and the AlOH groups on the coating are exposed at the solid–liquid interface. However, there is also another possible mechanism for the increase in isoelectric point which has been proposed.[9]

By adsorption of hydrolysed cations such as $Al(H_2O)_6^{3+}$ the surface charge behaviour is changed according to:

$$\text{Si—O}^- + \text{Al}^{3+} \rightleftarrows \text{Si—O—Al}^{2+} \qquad (8)$$

$$\text{Si—O}^-\text{AlOH}^{2+} \rightleftarrows \text{Si—O—AlOH}^+ \qquad (9)$$

James & Healey[20] have described a model for this type of specific adsorption. Their model was also used in an earlier study on the uptake of Mg(II) on α-SiC and α-Al_2O_3.[21] However, one important feature of the adsorption–desorption and precipitation reactions is that they are reversible on a rather short time scale and that strongly hydrolysed cations such as Al^{3+} show a weak adsorption.

Figure 9 shows how the electrokinetic behaviour of α-SiC is changed upon specific adsorption of Al^{3+} cations in an $AlCl_3$-containing solution. Without describing the behaviour too extensively it is interesting to note that the electrokinetic mobility is *negative* at low pH values due to the charge behaviour of the native surface and the weak adsorption of Al^{3+} which dominates in this region. Increasing pH leads to a change in sign of the electrophoretic mobility from negative to positive with a plateau at a high positive mobility around pH = 6. This drastic change in electrokinetic behaviour is caused by the adsorption of the $AlOH^{2+}$ species. A comparison between Fig. 9 and the surface modified SiC powder

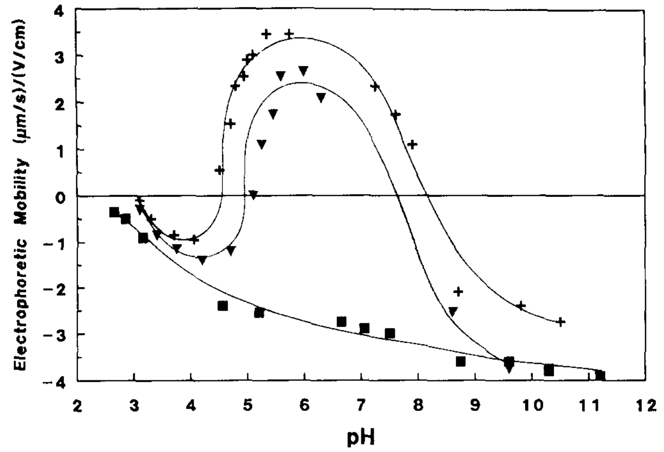

Fig. 9. Electrophoretic mobility versus pH for pure SiC in electrolyte with $AlCl_3$ (▼, 10^{-5}M; +, 10^{-4}M) and without (■).

in Fig. 2 shows a striking difference. While SiC with Al^{3+} cations in solution shows the native SiC surface charge behaviour with *negative* mobilities at low pH, the surface-modified powder shows a stable positive mobility at low pH values, very similar to an Al_2O_3 powder. The results in Fig. 6 also show that there are minor changes in the electrokinetic behaviour of surface-modified Si_3N_4 with time. Thus, it can be concluded that the surface modification by hydrolysis of Al-alkoxide results in a permanent surface layer which shows an electrokinetic behaviour very similar to α-Al_2O_3 when enough Al has been added.

The settling experiments in Fig. 8 showed a dramatic increase in sediment density for the surface-modified Si_3N_4 compared to the pure Si_3N_4 powder for the dispersant used. This was referred to the difference in the surface chemistry of the powders. Although this shows the effect of surface modification, the maximum sediment density was only 35%. Using the same dispersant on a fine α-Al_2O_3 powder resulted in a maximum sediment density of >50%, and using a similar type of surfactant with basic (instead of acidic) head-group on pure Si_3N_4 resulted in a maximum sediment density around 50%.[14] This decrease in maximum sediment density can either be due to incomplete surface coverage of the surfactant or a less optimal particle packing during sedimentation due to the porous surface coating. At this stage no definite answer can be given to this question.

5 Conclusion

In this paper a method to surface modify a ceramic powder surface by using an Al-alkoxide is presented. A model is discussed where the build up of the surface layer is considered to proceed through a multistep reaction. The reaction starts by chemisorption of a monolayer of Al-alkoxide followed by polymerization and hydrolysis both at the surface and in the solution when water is introduced. By controlling the ratio of water to Al-alkoxide and washing away all unreacted Al-alkoxide, the amount of Al present on the powder surface can be controlled. As a rather porous coating is obtained the specific surface area increases with the amount of Al on the surface. It was found that by measuring the electrokinetic behaviour and the adsorption properties an amount of about 0·5 mg Al/m^2 was necessary to give SiC and Si_3N_4 powders alumina-like surface properties. This coating has a very low solubility in water at neutral pH and does not change its properties by ageing. It was found that the surface modification drastically improved the dispersability in cyclohexane using a commercial dispersant with an acidic (carboxylic acid) head-group. This improvement is due to the higher affinity for Al—OH groups than for Si—OH groups of carboxylic acids in cyclohexane.

Acknowledgements

The authors wish to thank A. Svensk for help with electrophoretic measurements and B. Engström at KemaNord Industrikemi AB for help with X-ray fluorescence analysis. Finally the authors wish to thank M. Jansson and H. Leandersson for help when preparing the drawings and manuscript. This work was sponsored by the Swedish National Board for Technical Development (STU).

References

1. Bergström, L. & Pugh, R. J., Interfacial characterization of silicon nitride powders. *J. Am. Ceram. Soc.*, **72**(1) (1989) 103–9.
2. Bergström, L. & Bostedt, E., Surface chemistry of silicone nitride powders, elecktrokinetic behaviour and ESCA studies. *Colloids and Surfaces*, **49** (1990) 183–97.
3. Persson, M., Process for surface modification of oxide and non-oxide ceramic raw materials. Swedish Patent SE 8603074-9, 1988.
4. Bostedt, E., Persson, M. & Carlsson, R., Colloidal processing through surface modification. In *Euro-Ceramic, Vol 1; Processing of Ceramics*, ed. G. de With, R. A. Terpstra & R. Metselaar, Elsevier, London, 1989, pp. 1.140–1.144.
5. Fegley, B., White, P. & Bowen, H. K., Preparation of zirconia–alumina powders by zirconium alkoxide hydrolysis. *J. Am. Ceram. Soc.*, **68**(2) (1985) C60–C62.
6. Kishi, K., Umebayashi, S., Tani, E. & Kobayashi, K., Synthesis of β-sialon from Si_3N_4 and aluminium-isopropoxide. *Yogyo-Kyokai-Shi*, **93**(10) (1985) 629–35.
7. Okamura, H., Barringer, E. & Bowen, H. K., Preparation

and sintering of monosized Al_2O_3–TiO_2-composite powders. *J. Am. Ceram. Soc.*, **69**(2) (1986) C22–C24.

8. Kishi, K., Umebayashi, S., Tani, E. & Kobayashi, K., Room temperature strength of β-sialon fabricated from aluminium-iso-propoxide and α-sialon. *Yogyo-Kyokai-Shi*, **94**(1) (1986) 179–92.
9. Kulig, M., Oroschin, W. & Greil, P., Sol–gel coating of silicon nitride with Mg–Al-oxide sintering aid. *J. Eur. Ceram. Soc.*, **5**(4) (1989) 209–17.
10. Takahashi, Y. & Chizaki, J., Titania coatings of alumina powders. *J. Ceram. Soc. Jpn. Inter. Ed.*, **96** (1988) 238–44.
11. Mah, T., Mazdiayasni, K. & Ruh, R., Characterization and properties of hot-pressed Si_3N_4 with Alkoxy-derived CeO_2 or Y_2O_3 as sintering agents. *Ceram. Bull.*, **58**(9) (1979) 840–4.
12. Kishi, K., Umebayashi, S., Pompe, R. & Persson, M., Interaction of aluminium-iso-propoxide solution and Si_3N_4 powder. *J. Ceram. Soc. Jpn. Inter. Ed.*, **96** (1988) 687–9.
13. Landham, R. R., Parish, M. V., Bowen, H. K. & Calvert, P. D., Organotitanate dispersant for $BaTiO_3$ and Al_2O_3. *J. Mater. Sci.*, **22** (1987) 1677–81.
14. Bergström, L. & Lyckfeldt, O., Adsorption behaviour and dispersion of Si_3N_4 powders in non-aqueous media. In *Structural Ceramics: Processing, Microstructure and Properties*, ed. J. J. Bentzer, J. B. Bilde-Sørensen, N. Christiansen, A. Herswell and B. Ralph. Risø National Laboratory, Denmark, 1990, pp. 193–8.
15. Bradley, D. C., Mehrotra, R. C. & Gaur, D. P., *Metal Alkoxides*. Academic Press, London, 1988.
16. Korobova, N. E., Pak, S. & Merkushev, O. M., Study of Aluminium isopropoxide organosols. *Kolloidnyi Zhurnal*, **51**(4) (1989) 770–4.
17. Martel, A. E. & Smith, R. M., *Critical Stability Constants, Vol. 5, Inorganic Complexes*, 1st Suppl. Plenum Press, New York, 1982.
18. Look, J.-L., Bogush, G. H. & Zukoski, C. F., Colloidal interactions during the precipitation of uniform submicrometer particles. *Faraday Discuss. Chem. Soc.*, **90** (1990).
19. Huang, C. P., In *Adsorption of Inorganics at Solid/Liquid Interfaces*, ed. M. A. Andersson & A. J. Rubin. Ann Arbor Science, Ann Arbor, 1981, p. 183.
20. James, R. O. & Healey, T. W., Adsorption of hydrolyzable metal ions at the oxide/water interface. *J. Colloid Interface Sci.*, **40** (1972) 42–80.
21. Pugh, R. J. & Bergström, L., The uptake on Mg(II) on ultrafine α-silicon carbide and α-alumina. *J. Colloid Interface Sci.*, **124** (1988) 570.