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Ammonium polyacrylate adsorption on "aluminium hydroxides and oxyhydroxide" coated silicon nitride powders

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Abstract

Si_3N_4 powders coated with pseudoboehmite, Al hydroxide with a OH/Al mol ratio (R) lower than 3 and bayerite, were prepared from different coating solutions and dispersed in water with an ammonium polyacrylate (NH_4PA) to produce 11.8 vol% slips. The coated powders showed isoelectric points at pH 7, 7.5 and 7.5 close to that of the precipitate coatings of pseudoboehmite, Al hydroxide ($R < 3$) and bayerite, respectively, indicating that the surface coverages were almost complete. The bayerite coated powders had the lowest specific surface area values. The coatings on Si_3N_4 particles were shown to improve the adsorption of NH_4PA dispersant on Si_3N_4. The maximum adsorption of the polyelectrolyte at pH 9.5 increased from 0.01 for the uncoated powder to 0.03, 0.055 and 0.08 mg/m^2 for the coated powders with pseudoboehmite, Al hydroxide ($R < 3$) and bayerite, respectively.

Keywords: D. Si_3N_4; Pseudoboehmite; Al hydroxide; Ammonium polyacrylate adsorption

1. Introduction

Pressureless sintered silicon nitride is an example of a multicomponent system since sintering agents are required to give a liquid phase during densification.

Colloidal processing of ceramic slurries is widely used in the industry to avoid heterogeneities and to improve the final properties of the product [1]. The dispersion of Si_3N_4 particles is a critical step in the colloidal processing of the powder. Ceramic slips can be stabilized electrosterically by adsorption of polyelectrolyte additives such as ammonium polyacrylate (NH_4PA) [2]. However, a surface treatment of the Si_3N_4 powder is necessary to enhance the specific adsorption of the NH_4PA [3,4].

To help the dispersion of the silicon nitride powder with NH_4PA dispersant, three surface modifications were attempted. The approach that we took was to coat the silicon nitride with three different aluminium precipitation products. These precipitate coatings can be transformed to alumina on heating, which is one of the sintering aids for silicon nitride. It would be desirable that the surface coating could also be a sintering aid as well, so that it not only improves the dispersion behaviour of silicon nitride but also has the potential to act as a sintering aid.

Besides the adsorption behaviour of the coated powders, another important aspect to be considered in the colloidal processing of the powders is the specific surface area of the coated powders. Powders with low specific surface area and good adsorption behaviour of the deflocculant are desirable since they will produce slips with low viscosity values and high green densities during consolidation. Therefore, the purpose of this study was to evaluate the influence of the different Al precipitate coatings on the specific surface area of the Si_3N_4 powders and on the amount of NH_4PA adsorbed for 11.8 vol% aqueous Si_3N_4 slips. The adsorption isotherms of the uncoated and coated powders at pH 9.5 were determined.

2. Experimental procedure

2.1. Materials

A commercial α-Si_3N_4 powder (SN-E10, UBE Industries, Japan) was used in this work. The mean particle diameter and the specific surface area were 0.6 μm and 10 m^2/g, respectively.

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Three different solutions were used to coat the Si_3N_4 particles, $AlCl_3$ solution, Al_{13} polymer solution and commercial polymer solution. The Al_{13} polymer solution was prepared by adding NaOH very slowly to an $AlCl_3$ solution for a NaOH/Al mol ratio of 2.1. This solution contains mainly partially neutralized $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{+7}$ polymers and only trace amounts of monomeric Al^{+3} $(Al(H_2O)_6^{+3})$ [5]. The commercial polymer solution was obtained by dilution of a concentrate commercial solution (6.0 M) (Tort Valls S.A., Argentine). This solution is principally composed of platy-gibbsite fragment species and higher amounts of monomeric Al^{+3} than the Al_{13} polymer solution [5]. The gibbsite fragment species are Al polynuclear species partially neutralized with similar basicity to the Al_{13} polymer but different structure [5]. The Al concentration of the solutions was 0.02 M.

2.2. Coating method

The Si_3N_4 powder was dispersed in deionized water at about pH 10 to form a 9.4 vol% (25 wt%) slurry and ultrasonicated for 10 min to break down agglomerates. Then, 25 ml of the coating solution was added while the slurry was stirred, and the pH adjusted at 9 by additions of NH_3 (25%). This process was repeated several times to produce Si_3N_4 particles coated with various amounts of Al. The pH 9 was maintained during the additions. The suspension of the coated particles was centrifuged. The solid was then recovered, washed with distilled water and dried at 100°C.

The Al concentration of the coatings is expressed in this paper as the equivalent concentration of Al_2O_3. Si_3N_4 powders coated with an equivalent concentration of 1, 2, 3 and 4 wt% Al_2O_3 were prepared using the different coating solutions.

2.3. Powder characterization

The Al precipitation products obtained from the $AlCl_3$, commercial polymer and Al_{13} polymer solutions were called A, B and C, respectively. The as-received and the coated Si_3N_4 powders with an equivalent concentration of 3 wt% Al_2O_3 were characterized by Fourier transform infrared (FTIR) analysis (Bruker IFS 66, Germany). The coated Si_3N_4 powders (3 wt% Al_2O_3) were also characterized by differential thermal (DTA) and thermal gravimetric analysis (TG) (Model STA 409, Netzsch Inc., Germany) at a heating rate of 10°C/min in a N_2 atmosphere.

2.4. Specific surface area and zeta potential determinations

The specific surface area of the as-received and coated Si_3N_4 powders was measured by single-point BET (Micromeritics Accusorb).

The electrophoretic mobilities of the as-received and the coated Si_3N_4 powders with an equivalent concentration of 3 wt% Al_2O_3 was measured in a Penkem Laser Zee Meter 501, USA and converted into zeta potentials according to Smoluchowski's equation. For each determination, 0.05 g of sample were dispersed in 100 ml of 10^{-2} M NaCl solution and the slurry stirred magnetically for 10 min before the measurements were carried out. To generate zeta potential versus pH curves and from them the isoelectric point (IEP), the pH of the slurry was adjusted using dilute HCl and NaOH solutions.

2.5. Slip preparation

Slips with a solid loading of 11.8 vol% (30 wt%) were prepared. A commercial ammonium polyacrylate solution (Dolapix CE 64, Zschimmer & Schwarz) with 36.5% by weight of ammonium polyacrylate was used as the deflocculant. The pH of the suspension was adjusted with ammonia (25%). Slips of coated and uncoated Si_3N_4 powders with various amounts of deflocculant were prepared by suspending particles in deionized water via 20 min of ultrasound. The pH was adjusted at 9.5.

2.6. Ammonium polyacrylate adsorption measurements

In order to determine the amount of ammonium polyacrylate adsorbed, slips were centrifuged for 30 min at 2500 rpm and washed once with distilled water. Afterwards, the solid was dried at 100°C and analyzed by thermal gravimetric analysis (TG) at a heating rate of 10°C/min in a N_2 atmosphere.

The TG curves of the Si_3N_4 powders coated with A, B and C will be shown in Section 3.1. The TG data of the Si_3N_4 powders coated with A and B with NH_4PA adsorbed showed a three-step pyrolysis, and a four-step pyrolysis was found for the Si_3N_4 powder coated with C with NH_4PA adsorbed. The final weight loss in a temperature range of 400–600°C for Si_3N_4 powders coated with A, 300–600°C for Si_3N_4 powders coated with B and 350–600°C for Si_3N_4 powders coated with C, was due to the decomposition of ammonium polyacrylate and was used to determine the amount of NH_4PA adsorbed on the samples.

3. Results and discussion

3.1. Powder characterization

Fig. 1 shows the FTIR spectra of the as-received Si_3N_4 powder and Si_3N_4 powders coated with the Al precipitation products obtained from the different coating solutions in the range of 3000–4000 cm^{-1}. The as-received

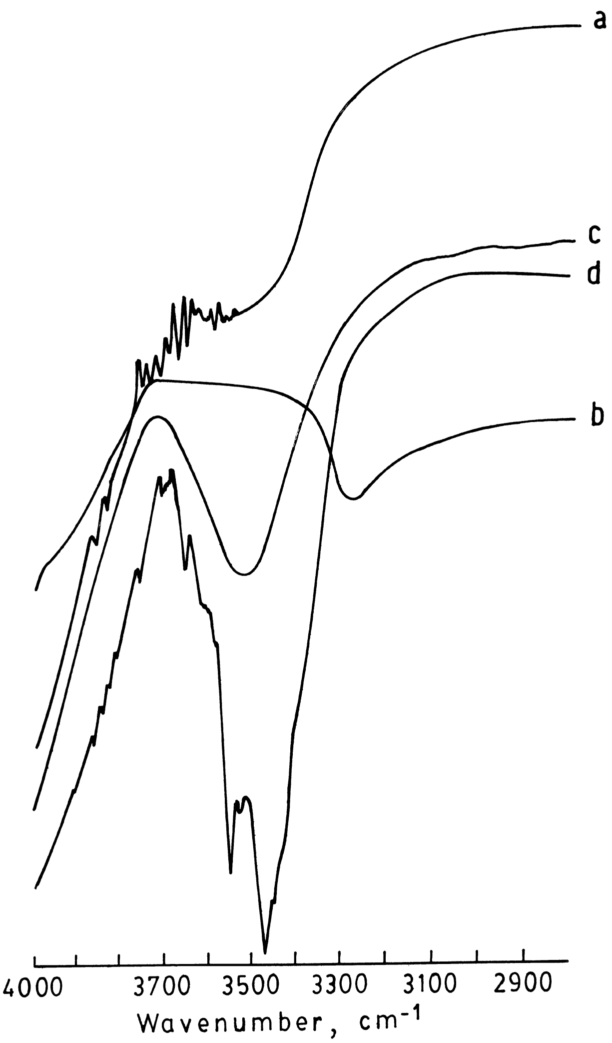

Fig. 1. FTIR spectra of different Si_3N_4 powders: (a) as-received, (b) coated with A, (c) coated with B, (d) coated with C.

Si_3N_4 powder did not show any band in this region (Fig. 1a), however, bands appeared in the spectra of the coated powders (Fig. 1b, c and d).

The spectra of the Si_3N_4 powder coated with A (Fig. 1b) was made from a broad band centered at about 3300 cm^{-1}. Pseudoboehmite shows two OH stretching bands in the region studied at 3300 and 3100 cm^{-1} [5]. The very broad band centered at 3300 cm^{-1} might indicate the presence of a poorly crystallized pseudoboehmite. Thus, this coated powder had a pseudoboehmite-like surface.

The spectra of the Si_3N_4 powder coated with B (Fig. 1c) showed a very broad OH stretching band centered at 3500 cm^{-1}. Bottero et al. [6] prepared samples of aluminium hydroxide with a OH/Al mol ratio (R) from 2.5 to 3 by partial hydrolisis of a $AlCl_3$ solution with NaOH solution. Their FTIR results showed that the spectra of samples with $R < 3$ were similar and made from a band centered at 3500 cm^{-1}. Hsu [5] found that the molar ratio of OH^- to Al^{+3} is a significant factor in preparing gels from chloride solutions. When the ratio was not over 2.75, the products were amorphous, and remains so far for at least 6 months. Thus, the observation of the broad band at 3500 cm^{-1} could be considered as evidence for the presence of an amorphous Al hydroxide with a OH/Al mole ratio lower than 3 on the Si_3N_4 powder surface.

Well resoluted bands at 3652, 3621, 3548, 3527, 3464, 3440 and 3390 cm^{-1} for the Si_3N_4 powder coated with C (Fig. 1d) indicated the presence of a well-crystallized precipitation product on the Si_3N_4 particle surface. Each of the polymorphs of $Al(OH)_3$ (gibbsite, bayerite and nordstrandite) have a series of characteristic OH-stretching bands in the IR region [5]. The OH-stretching frequencies reported for well-crystalized gibbsite are at 3623, 3527, 3460, 3396 and 3384 cm^{-1} [5]. Bayerite shows four OH-stretching bands at 3653, 3550, 3463 and 3435 cm^{-1} [5]. Consequently, the bands found for the Si_3N_4 powder coated with C was an evidence for the presence of bayerite and well-crystallized gibbsite. Morever, the relative intensity of the bands indicated that this coated Si_3N_4 powder had a bayerite-like surface with a small amount of gibbsite-like structure.

The DTA and TG analysis strengthened the findings of FTIR analysis. Fig. 2a, b and c shows the DTA, TG and DTG curves of the Si_3N_4 powders coated with A, B and C, respectively. The TG and DTG curves of the Si_3N_4 powder coated with A (Fig. 2a) showed a two-step pyrolysis. The first weight loss (20–150°C) was attributed to the removal of free water. Then, a continuous weight loss of chemically bound water was observed from 150 to 450°C. According to the TG results the DTA curve showed a peak at 84.4°C due to absorbed water and a broad endothermic centered at 350°C which indicated the presence of a significant amount of strongly bound water molecules. The endothermic peak at 523°C represented the dehydration of boehmite.

Violante and Huang [7] noted that the amount of chemically bound water was important for very small crystals of pseudoboehmite. This was due to its crystal structure. Pseudoboehmite is essentially poorly crystallized boehmite frequently referred to as gelatinous boehmite that consists of very small crystals of the same atomic arrangement as boehmite at short distance, but a large excess of water is situated between the elemental units [5].

The curves for the Si_3N_4 powder coated with B (Fig. 2b) showed an endothermic peak at 74.2°C which represented the removal of free water up to 150°C and a small endothermic peak at 219°C attributed to the transformation of noncrystalline Al hydroxide to Al_2O_3 with the corresponding water weight loss. This was in agreement with the reported TG and DTA behaviour of noncrystalline Al hydroxide which yield endothermic peaks at temperatures slightly above 200°C lower than that observed for crystalline $Al(OH)_3$ [5]. This was a

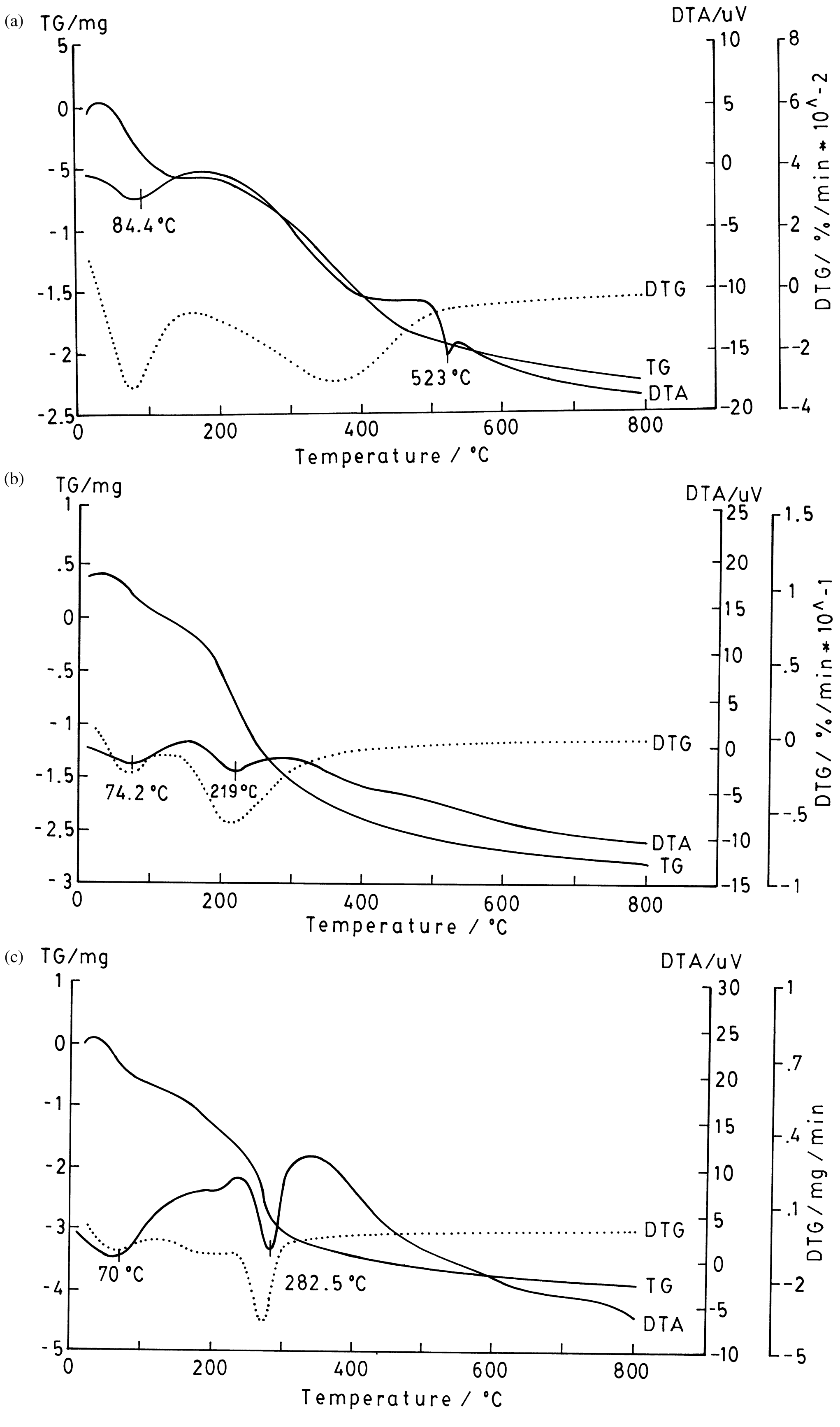

Fig. 2. DTA, TG and DTG curves of different Si_3N_4 powders: (a) coated with A, (b) coated with B, (c) coated with C.

consequence of the smaller particle size and greater reactivity of the amorphous compound.

The curves for the Si_3N_4 powder coated with C (Fig. 2c) showed a peak at 70°C due to the loss of absorbed water and an endothermic peak at 282.5°C attributed to the dehydration of bayerite. Several researchers [5,8] reported that fine bayerite yields an endothermic peak at a temperature slightly lower than 300°C. The TG curve showed that bayerite lost the majority of its water in a temperature range from 220 to 350°C.

The water weight loss in the temperature range from 150–600°C was 1.474, 2.001 and 2.898 mg for the Si_3N_4 powder coated with pseudoboehmite, Al hydroxide ($R < 3$) and bayerite, respectively (Fig. 2). This increase in the water weight loss was a consequence of the coating crystal structure. Crystalline $Al(OH)_3$ is composed of Al^{+3} hexagonal rings; in the interior hexagonal rings, each Al^{+3} shares six OH^- with three other Al^{+3}, and each OH^- is bridged between two Al^{+3} (Al-OH-Al linkage). At the edge, however, each Al^{+3} shares only four OH^- with two other Al^{+3}, and the other two coordination sites are occupied by one OH^- and one H_2O molecule, neither is bridged between Al^{+3} [5]. Less OH^- bonded to each Al^{+3} was expected for Al hydroxide with a OH/Al mol ratio lower than 3.

On the contrary, pseudoboehmite is composed of OH–Al–O chains with Al–O–Al linkage (oxo linkage). Thus, part of the Al–OH–Al linkage of Al hydroxides was transformed into oxo linkage in the pseudoboehmite structure, with the corresponding loss of water. Consequently, the water weight loss for the transformation from pseudoboehmite to Al_2O_3 was lower than that observed for Al hydroxides.

The results showed that when coated Si_3N_4 powders were prepared from $AlCl_3$ solutions, the Al was precipitated as pseudoboehmite, indicating that the monomeric Al^{+3} species were only partially neutralized at pH 9. However, coated Si_3N_4 powders prepared from Al_{13} polymer solutions produced an Al trihydroxide coating on the Si_3N_4 particle surfaces. This could be expected since the Al_{13} polymer solutions contained partially neutralized $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{+7}$ polymers which were completely neutralized when the pH of the solution was increased up to 9, and the Al_{13} rapidly converted to $Al(OH)_3$. Bottero et al. [6] studied the transformation from Al_{13} units to homogeneous octahedral domains such as that of crystalline Al trihydroxides. Their results showed that for OH/Al mol ratio of 3 the crystalline organization of bayerite was obtained.

The commercial polymer solution contains gibbsite fragment species with its Al^{+3} ions distributed in hexagonal rings connected by OH^- bridges and higher amounts of monomeric Al^{+3} than the Al_{13} polymer solution [5], and a total neutralization of the Al species could not be reached at pH 9, resulting in a coating of Al hydroxide with a OH/Al mol ratio lower than 3.

3.2. Specific surface area of the powders

Fig. 3 shows the specific surface area of the coated Si_3N_4 powders with various Al concentrations expressed as alumina percentages. The specific surface area of bayerite coated powders (Fig. 3a) increased from 10 m^2/g for the uncoated powder to 13 m^2/g for the 1 wt% Al_2O_3 coated powder. It was kept constant with increasing the Al_2O_3 content of the coated powders from 1 to 3 wt% and then increased by further increasing the Al_2O_3 concentration up to 4 wt%.

The Al hydroxide ($R < 3$) and pseudoboehmite coated powders showed an alumina concentration dependency of the specific surface area markedly different to that of the bayerite coated powders. The specific surface area of Si_3N_4 powders coated with Al hydroxide ($R < 3$) and pseudoboehmite continuously increased with increasing the Al_2O_3 content up to 18 and 23 m^2/g for 4 wt% Al_2O_3, respectively.

The increase in the surface area was due to the high specific surface area of the Al precipitates. However, bayerite coated powders showed lower specific surface area values for Al_2O_3 concentrations higher than 1 wt%. This was attributed to the small particle size and consequently high specific surface area of noncrystalline compounds such as pseudoboehmite and Al hydroxide ($R < 3$). According to Bottero et al. [6] much denser aggregates with closer structure were found with increasing the OH/Al mol ratio of the Al hydroxides from 2.5 to 3.

Since pressureless sintering of Si_3N_4 requires the addition of about 3 wt% Al_2O_3, coated powders with an equivalent concentration of 3 wt% Al_2O_3 can be used for the processing of concentrated aqueous slips with NH_4PA. As the specific surface area of the bayerite coated powder was the lowest, lower viscosity values and higher green densities during consolidation would be expected.

Besides the specific surface area other important aspects to be considered in the colloidal processing of the powders are the surface charge of the coated Si_3N_4 powders and their dispersion with NH_4PA. Therefore, coated Si_3N_4 powders with an equivalent concentration of 3 wt% Al_2O_3 were chosen to study the electrophoretic mobilities and the adsorption behaviour of aqueous slurries with NH_4PA.

3.3. Zeta potential versus pH curves

Fig. 4 shows the zeta potential versus pH curves of the as-received and coated Si_3N_4 powders with an equivalent concentration of 3 wt% Al_2O_3. An IEP at pH 5.2 was found for the as-received Si_3N_4 powder. This IEP value was in agreement with that previously reported for this Si_3N_4 powder [9]. As shown in Fig. 4, the coatings on the Si_3N_4 powder shifted the IEP value to higher pHs.

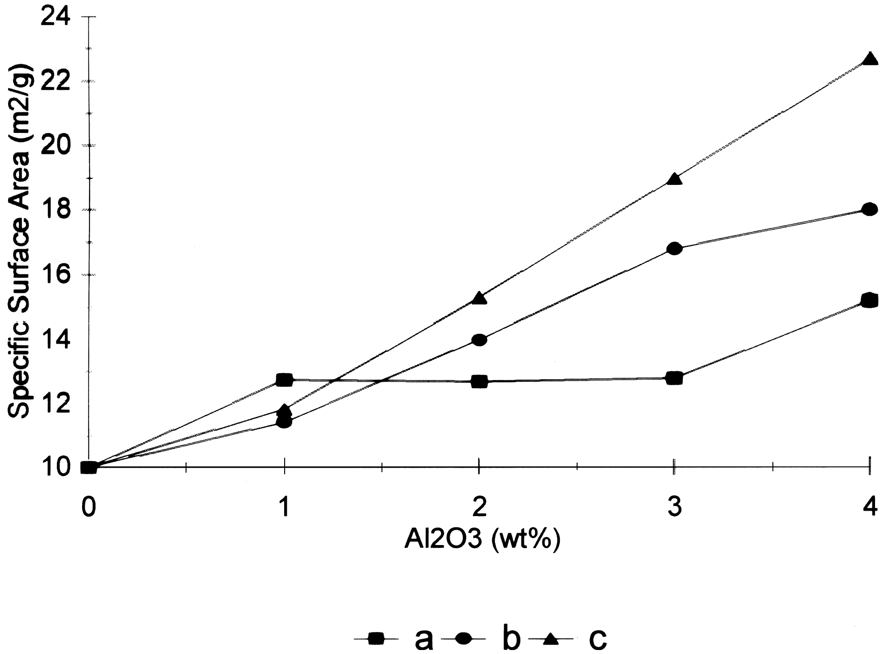

Fig. 3. Specific surface area of Si_3N_4 powders coated with different aluminium precipitation products: (a) bayerite, (b) aluminium hydroxide ($R < 3$), (c) pseudoboehmite, with various aluminium concentrations expressed as alumina percentages.

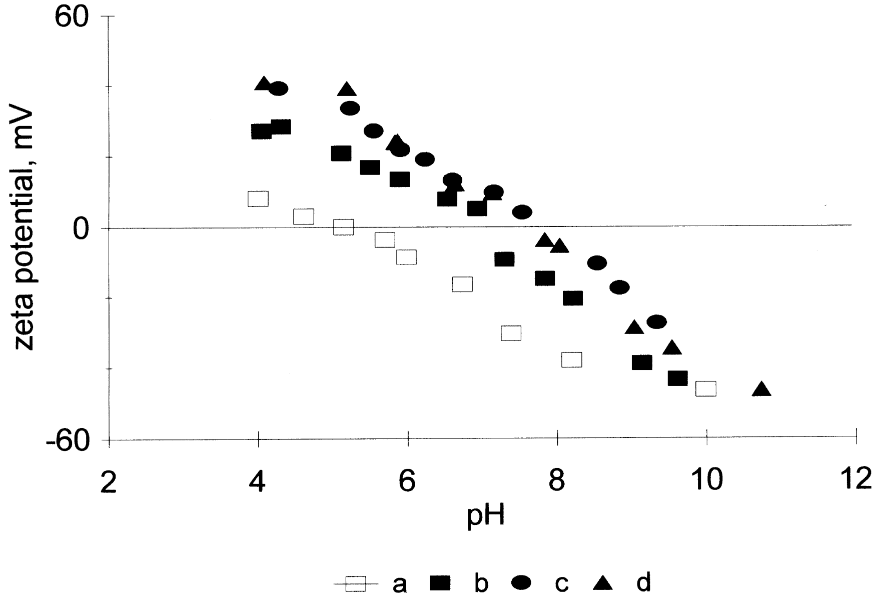

Fig. 4. Zeta potential versus pH curves of different Si_3N_4 powders: (a) as-received, (b) pseudoboehmite coated, (c) aluminium hydroxide ($R < 3$) coated, (d) bayerite coated.

The IEP of boehmite was found to be around 9 [10]. The pseudoboehmite coated Si_3N_4 powder showed an IEP at pH 7 indicating a high surface coverage. However, potential zeta values were difficult to obtain at low and high pH range probably due to dissolution of the pseudoboehmite surface layer on the Si_3N_4 particles.

The reported isoelectric point for Al hydroxides ranged from pH 7.5 to 9.2 [5], similar to that of Al_2O_3. IEPs at pH 7.5 were found for both the coated powders with Al hydroxide ($R < 3$) and bayerite. This clearly showed that the coatings were successful since the IEP of the coated powders changed from that of Si_3N_4 nearly that of Al hydroxides.

The negative zeta potential values of the coated powders increased monotonically with the suspension pH without reaching a plateau, evidencing that the particle surface charge was formed by the adsorption of ions from the solution. This effect was also noticeable in the positive zeta potential, the difference being that in this case the zeta potential value decreased with increasing pH.

The presence of (-Al–OH) groups as terminal sites on the surface of the coated powders can explain this behaviour. Al hydroxides and oxhydroxides have reactive surface Al–OH; although Al oxhydroxides contain Al–O in the structure, their surface Al–O should convert to Al–OH when immersed in water [5]. The reactive surface Al–OH are amphoteric in character [11], therefore, they can adsorb either H^+ or OH^- from the solution to produce dominant positive (-Al–OH_2^+) or negative (-Al–O^-) surface sites below and above the IEP of the coated powders, respectively.

At the pH studied (9.5) the zeta potential value of the uncoated powder was −44 mV and that of the coated powders with Al hydroxide ($R < 3$) and bayerite was -31 and -36 mV, respectively. The increase in the negative zeta potential values of the coated powders from -31 to -36 mV clearly showed that the bayerite coated powder had more Al–OH surface sites than the Al hydroxide ($R < 3$) and pseudoboehmite coated powders, which developed negative surface charge (-Al–O^-) at pH 9.5.

3.4. *Amount of NH_4PA adsorbed*

Fig. 5 shows the amount of NH_4PA adsorbed as a function of the amount of NH_4PA solution added (dry weight basis of powder) at pH 9.5 for the uncoated and coated powders with an equivalent concentration of 3 wt% Al_2O_3. The diagonal line represented the adsorption behaviour that would occur if 100% of the NH_4PA added was adsorbed.

We have previously characterized the as-received Si_3N_4 powder surface by FTIR analysis in the diffuse reflectance mode [4]. These results indicated that the Si_3N_4 surface consisted mainly of amine (=N–H) groups with very few silanol (Si–OH) functional groups. The ammonium polyacrylate dissociation according to the reaction

$$RCOONH_4 = RCOO^- + NH_4^+$$

begins at pH > 3.5; at pH values ⩾8.5 the polymer charge is negative with the fraction dissociated (α) approaching 1 [2]. The $RCOO^-$ groups of the deflocculant are adsorbed at the silanol sites of the Si_3N_4 powder surface [4]. As the Si_3N_4 powder has very few silanol reactive groups towards the deflocculant, a very low adsorption of NH_4PA on the as-received Si_3N_4 powder was found (Fig. 5a).

The coatings on the Si_3N_4 powder resulted in greater adsorption of NH_4PA dispersant (Fig. 5). The greater adsorption of NH_4PA on the coated powders could be attributed to the high affinity of the polyelectrolyte to the Al_2O_3-like surface. An acid-base reaction can occur between hydroxyl groups on alumina and –COOH groups on the NH_4PA chains [12]. However, the coated

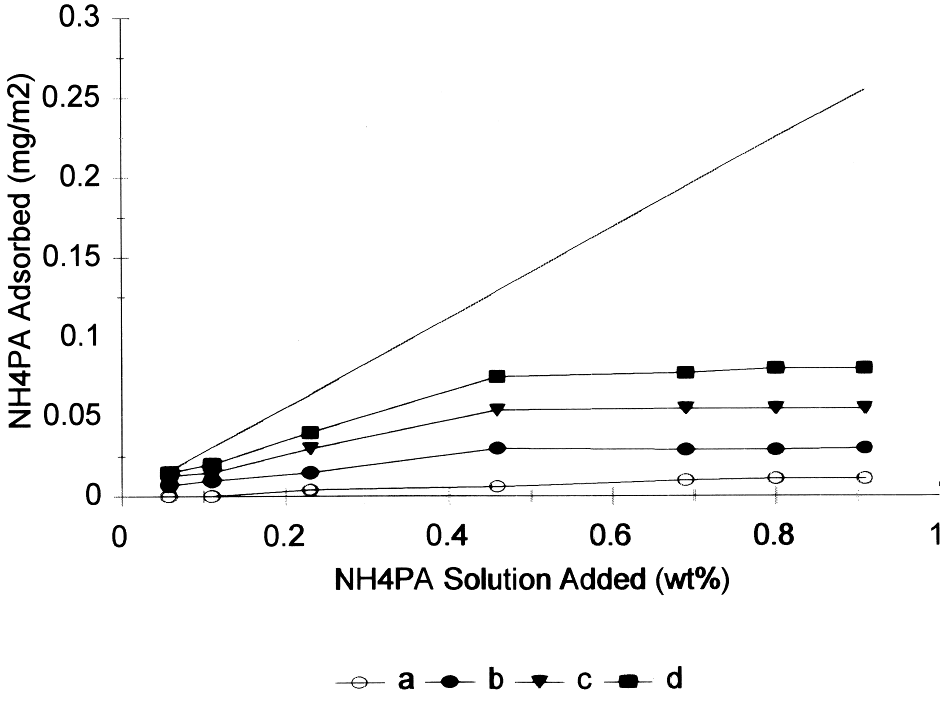

Fig. 5. Amount of ammonium polyacrylate (NH_4PA) adsorbed as a function of the amount of NH_4PA solution added at pH 9.5 for different Si_3N_4 powders: (a) as-received, (b) pseudoboehmite coated, (c) aluminium hydroxide ($R < 3$) coated, (d) bayerite coated. The diagonal line represents 100% of ammonium polyacrylate adsorption.

powders had different adsorption values. The maximum adsorption at pH 9.5 increased from 0.01 mg/m^2 for the uncoated powder to 0.03, 0.055 and 0.08 mg/m^2 for the coated powders with pseudoboehmite, Al hydroxide ($R < 3$) and bayerite, respectively.

Since the bayerite coated powder had the highest negative zeta potential value at pH 9.5 (Fig. 4), an unfavorable electrostatic interaction between the $RCOO^-$ groups of the deflocculant and the coated Si_3N_4 particles was expected. However, this powder showed the maximum NH_4PA adsorption. This indicated that the adsorption behaviour of the coated powders was basically controlled by the precipitate coating structure. In Al hydroxides and oxyhydroxides, a large portion of the surface OH^- are linked between Al^{+3} ions similar to the interior of the structure, and therefore, are inactive [5]. Only the OH^- at the broken edge that is linked to one Al is reactive [5]. Different structures such as bayerite, Al hydroxide ($R < 3$) and pseudoboehmite had different portions of reactive and inactive surfaces. The zeta potential results demonstrated that the bayerite coated powder had a larger portion of reactive surface Al–OH than Al hydroxide ($R < 3$) coated powders did. And the Al hydroxide ($R < 3$) coated powder had even more reactive surface Al–OH groups than the pseudoboehmite one. Therefore, a greater adsorption of bayerite and a lower adsorption of pseudoboehmite coated powders could be expected since the respective coatings had different amounts of reactive OH^- at which the deflocculant could be adsorbed.

The adsorption curves of the coated powders were similar. The amount of NH_4PA adsorbed increased with increasing amounts of NH_4PA solution added up to reaching an adsorption plateau at 0.46 wt% of NH_4PA solution added. This plateau corresponded to the adsorption saturation limit of the polyelectrolyte on the coated powders at pH 9.5.

The curves of the coated Si_3N_4 powders did not follow the 100% adsorption line, thus the adsorption plateau was reached with an appreciable amount of NH_4PA remaining in solution. This adsorption behaviour is not of the "high-affinity type" [2]. In general, for high-affinity adsorption, the isotherm usually has a very steep onset at low concentrations and no appreciable free polymer remains in the suspension until the adsorption attains saturation [2]. Obviously, the non-high-affinity adsorption in the present condition was mainly due to the unfavorable electrostatic forces between NH_4PA-adsorbed coated Si_3N_4 particles and the polymer remaining in solution. At pH 9.5 both were negatively charged (see Section 3.3 and 3.4).

The results showed that the lowest specific surface area values and the greatest adsorption of NH_4PA dispersant at the pH investigated could be obtained with bayerite coated Si_3N_4 powders. Therefore, this powder can be used for the processing of concentrated aqueous slips with NH_4PA.

4. Conclusions

Si_3N_4 powders coated with various amounts of pseudoboehmite, Al hydroxide with a OH/Al mole ratio lower than 3 ($R < 3$) and bayerite, expressed as alumina percentages, were prepared by adding $AlCl_3$, commercial polymer and Al_{13} polymer solutions, respectively, to a well dispersed Si_3N_4 slurry and adjusting the pH at 9 with NH_3. Bayerite coated powders had the lowest specific surface area values for Al_2O_3 concentrations higher than 1 wt%. The isoelectric point of the coated powders changed from that of Si_3N_4 close to that of the precipitate coatings, indicating that the surface coverages were almost complete.

The as-received and coated Si_3N_4 powders were dispersed in water with NH_4PA (PA = polyacrylate) to produce 11.8 vol% slips. The coatings on the Si_3N_4 powder resulted in significantly greater adsorption of NH_4PA dispersant due to the high affinity of the polyelectrolyte to the Al_2O_3-like surface. The maximum adsorption at pH 9.5 increased from 0.01 mg/m^2 for the uncoated powder to 0.03, 0.055 and 0.08 mg/m^2 for the coated powders with pseudoboehmite, Al hydroxide ($R < 3$) and bayerite, respectively. The bayerite coating had more reactive OH^- at which the deflocculant could be adsorbed resulting in a greater adsorption of the NH_4PA. The adsorption behaviour of the coated powders at pH 9.5 was not of the "high-affinity type" since the adsorption plateau was reached with an appreciable amount of NH_4PA remaining in solution.

The lowest specific surface area values and the greatest adsorption of NH_4PA dispersant could be obtained with bayerite coated Si_3N_4 powders. Therefore, the bayerite coated powder with an equivalent concentration of 3 wt% Al_2O_3 can be used for the processing of concentrated aqueous slips with NH_4PA.

References

[1] C. Olagnon, D. McGarry, E. Nagy, The effect of slip casting parameters on the sintering and final properties of Si_3N_4, Br. Ceram. Trans. J. 88 (3) (1989) 75–78.

[2] J. Cesarano III, I.A. Aksay, Stability of aqueous α-Al_2O_3 suspensions with poly(methacrylic acid) polyelectrolyte, J. Am. Ceram. Soc. 71 (4) (1988) 250–255.

[3] M.J. Hoffman, A. Naget, P. Greil, G. Petgow, Slip casting of SiC-whisker-reinforced Si_3N_4, J. Am. Ceram. Soc. 72 (5) (1989) 765–769.

[4] M.P. Albano, L.B. Garrido, Processing of concentrated aqueous silicon nitride slips by slip casting, J. Am. Ceram. Soc. 81 (4) (1998) 837–844.

[5] P.H. Hsu, Minerals in soil environments, 2nd Edition, Soil Science Society of America, Madison, WI, 1989, pp. 331–378.

[6] J.Y. Bottero, M. Axelos, D. Tchoubar, J.M. Cases, J.J. Fripiat, F. Fiessingers, Mechanism of formation of aluminum trihydroxide from Keggin Al_{13} polymers, J. Colloid Interface Sci. 117 (1) (1987) 47–57.

[7] A. Violante, P.M. Huang, Formation mechanism of aluminum hydroxide polymorphs, Clays and Clay Minerals 41 (5) (1993) 590–597.

[8] R.C. Mackenzi, in: R.C. Mackenzi (Ed.), Soils Differential Thermal Analysis, Vol. 2, Academic Press, New York, 1972, pp. 267–297.

[9] L. Bergstrom, R.L. Pugh, Interfacial characterization of silicon nitride powders, J. Am. Ceram. Soc. 72 (1) (1989) 103–109.

[10] Wei-Heng Shih, Leh-Lii Pwu, Ampere A. Tseng, Boehmite coating as a consolidation and forming aid in aqueous silicon nitride processing, J. Am. Ceram. Soc. 78 (5) (1995) 1252–1260.

[11] E.P. Luther, F.F. Lange, D.S. Pearson, "Alumina" surface modification of silicon nitride for colloidal processing, J. Am. Ceram. Soc. 78 (8) (1995) 2009–2014.

[12] C.M. Incorvati, D.H. Lee, J.S. Reed, R.H. Condrate Sr, Obtaining dispersible bayer-process aluminas in water, Am. Ceram. Soc. Bull. 76 (9) (1997) 65–68.