Deposition of colloidal sintering-aid particles on silicon nitride

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Abstract—The deposition of alumina (Al_2O_3) and yttria (Y_2O_3) particles on silicon nitride (Si_3N_4) by electrostatic and electrosteric interactions was studied using acoustophoretic measurements. The characteristics of Si_3N_4 , Al_2O_3 , and Y_2O_3 powders in an aqueous environment were studied by measuring the electrokinetic sonic amplitude (ESA), and appropriate conditions for deposition by adsorption were identified. The deposition of Al_2O_3 , Y_2O_3 , and $Y(NO_3)_3$ on Si_3N_4 particles was conducted at different pH values where these chemically dissimilar particles exhibit electrical charges of opposite sign. The deposition studies indicated that the particle size has a strong effect on the amount of coating on Si_3N_4 particles. The presence of polyacrylic acid as an electrosteric stabilizer for Si_3N_4 had no measurable effect on Al_2O_3 adsorption. The shift of the isoelectric point of Si_3N_4 with Al_2O_3 showed that the total quantity of Al_2O_3 adsorbed on Si_3N_4 . Bremsstrahlungexcited Auger electron spectroscopy (AES) results showed that the as-received Si_3N_4 powder has a native oxide film of 8.9 Å. The presence and relative differences in the surface composition of coated particles were established using X-ray photoelectron spectroscopy (XPS).

Keywords: Colloidal chemistry; silicon nitride powder; sintering-aids addition; surface chemistry: electroacoustics of suspensions; deposition by adsorption.

1. INTRODUCTION

Silicon nitride is one of the important classes of structural materials with a combination of excellent mechanical, thermal, and chemical properties for applications at room and high temperatures. The performance of these materials is highly dependent on the grain boundary chemistry which is determined, among other parameters, by the distribution of sintering aids such as oxides of Y, Al, Ce, and Mg. Colloidal processing of silicon nitride powders offers a promising approach to enhance the homogeneous distribution of sintering aids because particles can be dispersed more uniformly in wet form than in dry form [1]. Moreover, preparation of powders as colloidal suspensions facilitates slip and pressure casting for shape-forming.

The primary methods of densification of silicon nitride are hot-isostatic pressing, hot pressing, high-pressure sintering, and pressureless sintering. Silicon nitrides of different properties can be produced by varying the amount (2-10%) by



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weight) and chemical composition of the sintering aids, and the method of densification. In particular, in the case of pressureless-sintered silicon nitride, a number of sintering aids are added to provide a suitable amount of liquid phase at sintering temperatures. It is in this context that the method of addition of sintering aids becomes an important parameter. Among the methods of sintering aids addition, mixing during ball milling is the most common. However, this method suffers from inadequacies such as inhomogeneous distribution, unwanted size reduction, and undesirable surface-chemical changes of the powder [2].

Chemical techniques appear to provide an improvement in homogeneity, but suffer from various deficiencies. Some examples of the chemical techniques and proposed mechanisms are described below:

(1) Alkoxide hydrolysis [3], e.g.

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$$Al(OC_4H_9)_3 \xrightarrow{H_2O} Al(OH)_3 \xrightarrow{Heat} Al_2O_3$$

Increased uniformity of the sintering aid is achieved, but the cost of raw materials is excessively high.

(2) Metal hydroxide precipitation [4], e.g.

$$Al(NO_3)_3 \xrightarrow{OH^-} Al(OH)_3 \xrightarrow{Heat} Al_2O_3.$$

Although uniformity is enhanced, the green body undergoes excessive shrink-age.

(3) Adsorption of metal-organic surfactants [5], e.g.



Availability of specific surfactants and removal of carbon are some concerns. (4) Electrostatic adsorption from a sol [6],

 $Si_3N_4 + Y_2O_3(colloid) \rightarrow [Si(hydroxyl group)]_{surface}^- \cdot [Y(hydroxyl group)]_{surface}^+$

Adsorption of net positively charged hydroxylated Y_2O_3 colloids takes place on a net negatively charged particle of Si_3N_4 . The surface of Si_3N_4 is assumed to be hydroxylated in an aqueous environment.

Yet another method of addition of sintering aids is the controlled deposition by adsorption of fine (submicrometer) particles on coarse particles [7–9]. In this paper, the term adsorption is used in a slightly unconventional way to refer to surface interaction between fine and coarse particles. The purpose of this study was

to examine the adsorption of Y_2O_3 and different sizes of Al_2O_3 particles on Si_3N_4 particles aided by electrostatic and electrosteric interactions. The adsorption process was studied with the help of acoustophoretic mobility measurements. In addition, Si_3N_4 particles containing adsorbed layers of Al_2O_3 and Y_2O_3 were characterized by XPS.

2. EXPERIMENTAL

One Si₃N₄ powder from (SN E-03] Ube Industries* $(d_{50} = 1.1 \,\mu\text{m}$ and specific surface area = $3.1 \,\text{m}^2/\text{g}$) and two Al₂O₃ powders of different size distributions were used for the present studies. The first Al₂O₃ powder, AKP-50 (referred to as A in the text), from Sumitomo Electric Co., had a mean diameter of $d_{50} = 0.2 \,\mu\text{m}$ and a specific surface area of $10.6 \,\text{m}^2/\text{g}$. The second Al₂O₃ powder, Dispal-180 (referred to as B in the text), from Vista Chemical Co., had a mean diameter of $d_{50} = 40 \,\text{nm}$ and a specific surface area of $147 \,\text{m}^2/\text{g}$. The Y₂O₃ powder was obtained from Unocal Molycorp ($d_{50} = 0.46 \,\mu\text{m}$, specific surface area = $23.6 \,\text{m}^2/\text{g}$). The chemical purity of all oxide powders was specified to exceed 99.99%. A polyacrylic acid (PAA) of molecular weight 5000 from Aldrich Chemicals was used as a dispersant.

Samples were prepared for XPS analysis by sprinkling the powder on adhesive tapes so as to achieve uniform and complete coverage, and XPS data were obtained with a modified AEI ES-100 photoelectron spectrometer.

The uniformity of the distribution of Al_2O_3 and Y_2O_3 particles in Si_3N_4 suspensions was enhanced by obtaining as complete a dispersion as possible. The controlled deposition by adsorption technique consisted of the following steps:

- (a) deagglomeration of Si₃N₄, Al₂O₃, or Y₂O₃ powder at a predetermined pH in aqueous environment using an ultrasonic probe;
- (b) measurement of the settling behavior to ensure the absence of settling;
- (c) stabilization of Si_3N_4 , Al_2O_3 , or Y_2O_3 particles by pH control. The pH selected for stabilization was sufficiently remote from the isoelectric point, pH_{iep} , to impart a high surface charge;
- (d) charge enhancement by adsorption of PAA (molecular weight 5000) on Si_3N_4 particles, again at a pH sufficiently remote from the apparent pH_{iep} of the $Si_3N_4 + PAA$ system;
- (e) charge enhancement on Al₂O₃ or Y₂O₃ particles prior to their mixing with Si₃N₄ by pH control only; and
- (f) finally, Si_3N_4 suspensions were mixed with those of Al_2O_3 or Y_2O_3 to enable their deposition by adsorption on the Si_3N_4 particles.

Distilled water and analytical grade NH_4OH (0.1 N) or HNO_3 (0.01 N) were used for the slurry preparation. Deagglomeration by ultrasonics was carried out using a probe of 19 mm diameter at a power output of 40 W per 100 ml slurry. The primary method used for the study of the adsorption of either PAA or Al_2O_3 and Y_2O_3 particles on Si_3N_4 was the ESA measurement. All ESA measurements were carried out without the addition of a supporting electrolyte at a solids concentra-

^{*} Certain tradenames and company products are mentioned in the text in order to adequately specify the experimental procedure, materials, and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

tion of 6.3% by weight for Si_3N_4 and 1.2% by weight for Al_2O_3 and Y_2O_3 . In dilute suspensions, similar to those used in this study, dynamic mobility as measured by the ESA is proportional to electrophoretic mobility. Hence, the ESA values were used to calculate zeta potentials [10].

3. RESULTS AND DISCUSSION

3.1. Al_2O_3 deposition

The ESA values as a function of the suspension pH obtained for Si_3N_4 powder at 6.3 wt% along with those obtained in 100 ppm PAA solution are shown in Fig. 1. While the as-received powder exhibited a pH_{iep} of 5.1, it can be seen that the PAA made the particles more negatively charged; a pH_{iep} of 3.0 was obtained for the $Si_3N_4 + 100$ ppm PAA system. The behavior of Si_3N_4 is known to be affected by the presence of H⁺, OH⁻, and NH₄⁺ species [11], while the PAA-modified surface approaches that of PAA itself. Data obtained for Al_2O_3 , Y_2O_3 , and $Y(NO_3)_3$ in water alone are shown in Fig. 2. The Al_2O_3 powders exhibited a positive ESA



Figure 1. Change in the ESA and pH_{iep} of 6.3 wt% Si₃N₄ and 6.3 wt% Si₃N₄ containing 100 ppm PAA as a function of the suspension pH.

below about pH 8.6. The closeness of the pH_{iep} values (8.6 ± 0.1) of the two Al₂O₃ powders, though manufactured by two different synthesis methods, shows the similarity of their surface chemical behaviors in an aqueous environment. The ESA/zeta potential values of the two powders are different at pH < pH_{iep}, probably due to differences in the concentration of dissolved species resulting from different specific surface areas. While the Y(NO₃)₃ did not show the presence of a pH_{iep}, a pH_{iep} of 10.5 was obtained for Y₂O₃.

The effect of Al_2O_3 on the ESA/zeta potential at pH 5.9 of Si_3N_4 was determined by adding Al_2O_3 in increasing concentrations to the Si_3N_4 suspensions. The results are given in Table 1. The negative values of ESA in the absence and presence of Al_2O_3 -A indicate that very little adsorption of Al_2O_3 -A takes place on Si_3N_4 . On the contrary, Al_2O_3 -B shows a drastic effect on the ESA/zeta potential, with a reversal of ESA at less than 1.5 wt% Al_2O_3 -B, suggesting a



Figure 2. Change in the ESA and pH_{iep} of AKP-50 (Al₂O₃-A), Dispal 180 (Al₂O₃-B), Y₂O₃, and Y(NO₃)₃ as a function of the suspension pH. All powders in suspension were at 1.2 wt%.

marked affinity for the Si_3N_4 surface. The increase of ESA as a function of the Al_2O_3 -B concentration is an indication of increased adsorption of Al_2O_3 . However, the amount of Al_2O_3 -B adsorption appears to reach a plateau between 1.5 and 3 wt% of Al_2O_3 in the bulk phase.

Table 1.

ESA and zeta potential of Si_3N_4 in aqueous suspensions (6.3 wt%) at p	H 5.9±0.1 by
the addition of various concentrations of Al ₂ O ₃ -A or -B powders	

		ESA (mPa	∙M/V)	Zeta potential (mV)	
Si3N4 (wt%)	Al ₂ O ₃ (wt%)	Al ₂ O ₃ -A	Al ₂ O ₃ -B	Al ₂ O ₃ -A	Al ₂ O ₃ -B
100.0	0	0.80	-0.84	-27.0	- 28.4
98.5	1.5	-0.79	+0.38	-25.6	+13.1
97.0	3.0	-0.79	+0.75	-24.8	+25.5
95.5	4.5	-0.73	+0.75	-24.8	+ 25.5
94.0	6.0	-0.62	+0.76	-21.1	+ 25.6

 Si_3N_4 suspensions, equilibrated with different weight concentrations of Al_2O_3 -A or -B at pH 5.9±0.1, were titrated to determine the effective pH_{iep} . Titrations were aimed at testing the presence of an adsorbed layer and to determine whether the particles remained adsorbed even after changing the suspension pH. The data in Fig. 3 for Al_2O_3 -A show no apparent change in the pH_{iep} , whereas for Al_2O_3 -B a shift in pH_{iep} is obtained as a function of the concentration of Al_2O_3 -Pa does not have any measurable affinity for the Si_3N_4 surface, while Al_2O_3 -B exhibits a strong affinity. The differences in the ESA values in Fig. 3 at high pH could have resulted from surface dissolution and/or an increase in ionic strength.

Experiments were conducted in which aqueous supernatants from 3 and 6 wt% Al_2O_3 -B were mixed with Si_3N_4 at pH 5.9±0.1 to determine the cause of the shift





Figure 3. Comparison of the ESA and pH_{iep} vs. the suspension pH for Si₃N₄ and Si₃N₄ containing 6 wt% concentration of Al₂O₃-A.



Figure 4. Comparison of the ESA and pH_{iep} vs. the suspension pH of Si₃N₄ and Si₃N₄ containing 1.5, 3.0, and 6 wt% concentrations of Al₂O₃-B.

in the pH_{iep} of Si_3N_4 due to Al_2O_3 . The ESA measurements were conducted with these supernatants to determine whether dissolved species from Al_2O_3 suspensions could be affecting the pH_{iep} . The data in Fig. 5 show that the pH_{iep} of Si_3N_4 was affected by the supernatant of Al_2O_3 -B. ESA values of Si_3N_4 equilibrated with supernatants of 6 wt% Al_2O_3 -B at four pH values are also shown in Fig. 5. By comparing the data in Figs 4 and 5, it be can seen that the shift in pH_{iep} due to the supernatant is small compared with that in the presence of 6 wt% Al_2O_3 -B. In addition, the pH_{iep} values of supernatants prepared at different pHs indicate that titration of the suspensions has not influenced the adsorption process. The differences in the ESA values of the two sets of data at 6 wt% Al_2O_3 -B are attributed to the difference in solids concentration of the suspensions.



Figure 5. ESA of Si_3N_4 suspensions in the presence of supernatant (SUPT.) from Al_2O_3 -B in aqueous environment at pH 5.8.

Polyelectrolytes are commonly used to prepare stable suspensions of Si_3N_4 . In this study, polyacrylic acid (PAA) of molecular weight 5000 was used to disperse the Si_3N_4 powder at pH 5.9±0.2. Suspensions containing different concentrations of Al_2O_3 -A or -B were added to these dispersions. The ESA/zeta potential data in Table 2 indicate that no coating of Al_2O_3 -A has taken place, where Al_2O_3 -B

Table 2. ESA, zeta potential, and conductivity of aqueous suspensions of Si_3N_4 (6.3 wt%) containing 100 ppm PAA at pH 5.9±0.2 to which various concentrations of Al_2O_3 -A or -B were added

ESA		ESA (mP	a·M/V)	Zeta potential (mV)		Conductivity (μ S/cm ²)	
Si3N4 (wt%)	Al ₂ O ₃ (wt%)	Al ₂ O ₃ -A	Al ₂ O ₃ -B	Al ₂ O ₃ -A	Al ₂ O ₃ -B	Al ₂ O ₃ -A	Al ₂ O ₃ -B
100.0	0	- 1.56	- 1.58	53.7	54.0	71	55
98.5	1.5	-1.54	-0.35	- 53.3	-11.9	73	95
97.0	3.0	-1.53	-0.07	- 52.9	-2.2	73	134
95.5	4.5	-1.51	+0.39	- 52.2	+13.2	72	161
94.0	6.0	-1.51	+0.58	- 52.0	+ 19.9	69	169

appears to have formed a coating on Si_3N_4 . It is to be noted that there is a major difference between the data obtained for Al_2O_3 -B coating in the presence and absence of PAA in terms of the concentration of Al_2O_3 at which the ESA sign reversal takes place. In the presence of PAA, the reversal took place between 3.0 and 4.5 wt% addition of Al_2O_3 -B whereas in the absence of PAA (Table 1), the reversal took place between 0 and 1.5 wt%. This behavior is possibly due to the presence of unadsorbed PAA in the bulk phase which is likely to adsorb on the Al_2O_3 particles and increase their negative charge. As shown in Fig. 6, even at pH 4.0 only a minor fraction of the PAA is adsorbed on Si_3N_4 . At pH 10.0, PAA shows practically no adsorption on Si_3N_4 . Although the Si_3N_4 surface has become strongly negatively charged in the presence of PAA, its effect on increasing the deposition of Al_2O_3 is not obvious. Adsorption of Al_2O_3 -B on Si_3N_4 with a PAA adsorbed layer resulted in a considerable pH_{iep} shift to 5.2 (Fig. 7). However, the pH_{iep} obtained is not close to that of Al_2O_3 -B (8.6) or to that of the Si_3N_4 +6 wt% Al_2O_3 -B system (8.0) in Fig. 4.



RESIDUAL POLYMER CONC., ppm

Figure 6. Isotherms of PAA adsorption on Si_3N_4 at three pH values of the suspension



Figure 7. Shift in the pH_{iep} of Si₃N₄ containing PAA in the presence of 6 wt% Al₂O₃-B.

The conductivity of suspensions as a function of the particle concentration showed no variation for Al_2O_3 -A (Table 2); however, the conductivity increased steadily with the addition of Al_2O_3 -B powder. This could be an effect of surface

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dissolution and/or a change of ionic composition as a result of interaction between Al_2O_3 -B, PAA, and the bulk phase.

3.2. Y_2O_3 and $Y(NO_3)_3$ deposition

The ESA, zeta potentials, and conductivity of Si_3N_4 suspensions containing various concentrations of Y_2O_3 or $Y(NO_3)_3$ at pH 7.3±0.2 are shown in Table 3. The shift in ESA/zeta potentials is more gradual for Y_2O_3 than it is for $Y(NO_3)_3$, indicating that deposition by adsorption of Y_2O_3 on Si_3N_4 is weaker than it is for the adsorption of the latter. The relatively small increase in the conductivity of $Si_3N_4-Y_2O_3$ suspensions as a function of the Y_2O_3 concentration is an indication that surface dissolution of Y_2O_3 particles is not significant. Adsorption of $Y(NO_3)_3$ is known to take place via its hydroxylation and formation of a positively charged surface that interacts with the negatively charged hydroxylated surface of silicon nitride [1, 4]. The fine nature as well as the high charge on the $Y(NO_3)_3$ surface could be responsible for the observed high adsorption on Si_3N_4 .

Little deposition of Y_2O_3 on Si_3N_4 was found, as suggested by a relatively slow decrease of the ESA/zeta potential as a function of the Y_2O_3 concentration in the PAA-containing Si_3N_4 suspensions (Table 4). Most of the observed adsorption of

Table 3.

ESA, zeta potential, and conductivity of aqueous suspensions of Si_3N_4 (6.3 wt%) at pH 7.3±0.2 by the addition of various concentrations of Y_2O_3 or $Y(NO_3)_3$

		ESA (mPa·M/V) Zeta pot		tential (mV)	Conductivity (μ S/cm ²)		
Si ₃ N ₄ (wt%)	Y_2O_3 or $Y(NO_3)_3$ (wt%)	Y ₂ O ₃	Y(NO ₃) ₃	Y ₂ O ₃	Y(NO ₃) ₃	Y ₂ O ₃	Y(NO ₃) ₃
100.0 98.5 97.0	0.0 1.5 3.0	-1.67 -0.43 -0.15	- 1.62 + 1.39 + 1.17	-56.0 -14.3 -5.1	- 55.2 + 47.1 + 39.8	66 88 87	37 2650 4800
95.5 94.0	4.5 6.0	-0.05 +0.05	,	-1.5 +1.5		127 127	

Table 4. ESA, zeta potential, and conductivity of aqueous suspensions of Si_3N_4 (6.3 wt%) plus 100 ppm PAA at pH 7.3±0.2 by the addition of various concentrations of Y_2O_3

Si ₃ N ₄ (wt%)	Y2O3 (wt%)	ESA (mPa·M/V)	Zeta potential (mV)	Conductivity (μ S/cm ²)
100.0	0.0	-1.84	-62.8	148
98.5	1.5	-1.32	-45.0	228
97.0	3.0	-1.13	- 38.5	222
95.5	4.5	-1.06	- 36.2	215
94.0	6.0	-1.10	-38.1	215

 Y_2O_3 took place at the first addition of 1.5 wt%. Subsequent addition of Y_2O_3 showed a much smaller change of the ESA/zeta potential. The constant conductivity values suggest no significant adsorption and/or surface dissolution of Y_2O_3 . The interaction between Y_2O_3 and unabsorbed PAA could be playing a role in this case. It is possible that the kinetics of PAA adsorption on Y_2O_3 are faster than those of Y_2O_3 on Si₃N₄, which can cause a decrease of the positively charged surface sites on Y_2O_3 .

3.3. Y_2O_3 and Al_2O_3 deposition

Sequential adsorption of Y_2O_3 followed by that of Al_2O_3 -B on the Si_3N_4 surface was examined to study the possibility of deposition of two types of sintering-aid particles. Addition of Y_2O_3 caused the ESA values to decrease continuously as a function of the Y_2O_3 concentration (Table 5). However, the sign of the ESA/zeta potentials of the $Si_3N_4 + Y_2O_3 + Al_2O_3$ -B system reversed only after the addition of 1.5 wt% Al_2O_3 -B. These data demonstrate the potential of sequential addition of Al_2O_3 and Y_2O_3 to the Si_3N_4 suspension to obtain a coating.

Table 5.

ESA, zeta potential, and conductivity of aqueous suspensions of Si_3N_4 (6.3 wt%) at pH 7.3±0.1 by the addition of various concentrations of Y_2O_3 , followed by Al_2O_3 -B addition

Si ₃ N ₄ (wt%)	Y ₂ O ₃ (wt%)	Al ₂ O ₃ -B (wt%)	ESA (mPa·M/V)	Zeta potential (mV)	Conductivity (μ S/cm ²)
100.0	0.0	0.0	-1.48	-45.7	40
98.5	1.5	0.0	-0.57	-17.7	56
97.0	3.0	0.0	-0.34	-10.5	58
95.5		1.5	+0.18	+ 6.1	64
94.0		3.0	+0.29	+9.9	74
92.5		4.5	+0.53	+ 16.3	88

The presence of 100 ppm PAA in the Si_3N_4 suspension, prior to Y_2O_3 and Al_2O_3 -B powder addition, showed a trend similar to that described above. As can be seen from Table 6, the magnitude of the ESA/zeta potential shift due to the addition of Y_2O_3 is smaller compared with that due to Al_2O_3 -B. No obvious advantage of addition of PAA to the Si_3N_4 suspension is seen from these data.

3.4. XPS evaluation of deposition

The XPS scans of powder samples in Figs 8a, 8b, 8c, and 8d represent the survey scans of approximately the first 100 Å surface layer of the as-received Si_3N_4 powder and those coated with Al_2O_3 -A, -B, and Y_2O_3 , respectively. As expected, O KLL Auger, O 1s, N 1s, C 1s, Si 2s, and Si 2p XPS peaks were detected for all these samples. In addition, Y 3d was observed for the sample coated with Y_2O_3 (Fig. 8d); Al 2p was detected from samples coated with Al_2O_3 -A and -B (Figs 8b and 8c). Even from these survey scans, one can clearly see that a stronger Al 2p intensity was obtained for the sample coated with Al_2O_3 -B than with Al_2O_3 -A.

The high-resolution C 1s XPS scan of the as-received Si_3N_4 powder is shown in

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Contactor.





Table 6. ESA, zeta potential, and conductivity of aqueous suspensions of Si_3N_4 (6.3 wt%) plus 100 ppm PAA at pH 7.3±0.1 by the addition of various concentrations of Y_2O_3 , followed by Al_2O_3 -B addition

Si3N4 (wt%)	Y2O3 (wt%)	Al ₂ O ₃ -B (wt%)	ESA (mPa·M/V)	Zeta potential (mV)	Conductivity (μ S/cm ²)
100.0	0.0	9.0	-2.13	-71.4	137
98.5	1.5	0.0	-1.65	- 55.2	216
97.0	3.0	0.0	-1.15	- 38.7	228
95.5	<u></u>	1.5	-0.26	-8.6	252
94.0		3.0	+0.10	+3.5	280
92.5		4.5	+0.30	+ 10.0	300

Fig. 9. The photoelectron peak can be deconvoluted into three peaks at binding energies of 288.2, 286.3, and 284.3 eV due to carbon from the surface impurities of C=O, C-O, and CH, respectively, in agreement with reported values [12-14]. The surface compositions in atom % are shown in Table 7 for carbon, silicon, nitrogen, oxygen, yttrium, and aluminum. It is to be noted that in addition to powders, the adhesive tape holding the powder can also contribute to the carbon signal.

The high-resolution Si 2p photoelectron peak is shown in Fig. 10a. The measured binding energy was 102.1 eV for Si₃N₄. However, the line-shape is asymmetric due to the contribution of Si 2p from the surface oxide SiO₂. The binding energy for SiO₂ is only slightly higher than that for the nitride. This observation agrees well with the published data [15]. A better-resolved spectrum of this surface oxide due to Bremsstrahlung-excited Si *KLL* Auger electron peak is shown in Fig. 10b. In this spectrum the kinetic energy difference between the nitride and oxide Auger electrons is 3.4 eV; the peak areas could therefore be calculated. Following the method developed previously [12, 16], the thickness of the native oxide film on Si₃N₄ was calculated to be 8.9 Å.

The O 1s XPS electron binding energy of Al_2O_3 at 531.4 eV is slightly lower than that of SiO₂ (532.8 eV). The measured 532.7 eV binding energy of SiO₂ for the as-received Si_3N_4 agrees well with the reported value (Fig. 11) [17]. With an increase in the amount of coating of Al₂O₃, the line-broadening also increased because of the above difference in the binding energy. As shown in Fig. 11a, a 2.4 eV line-width was obtained at half-maximum intensity for the as-received Si_3N_4 . After coating with Al_2O_3 -A or Y_2O_3 , this line-width increased slightly (Figs 11b and 11d). It is clear from Table 7 that a much thicker coating was obtained by the A1,O₃-B; the line-width of the O 1s XPS peak in this sample hence increased to 3.2 eV. The presence of a thicker coating is also suggested by the higher intensity obtained for Al 2p from the Si_3N_4/Al_2O_3 -B sample (Fig. 12b) than that obtained for the Si_3N_4/Al_2O_3 -A sample (Fig. 12a). The presence of a peak at the binding energy of Al 2p at 74.8 eV is evidence for the presence of Al₂O₃ [13, 16, 17]. The Y_2O_3 coating is also confirmed by the detection of a Y 3d XPS peak with this sample as shown in Fig. 13. In this figure, spin-orbital splitting was observed in the Y 3d photoelectron peak at 159.9 eV and 157.8 eV for $3d_{3/2}$ and $3d_{5/2}$, respectively. The 152.7 eV peak is that of Si 2s from Si₃N₄ [15].



Figure 10. Comparison of high-resolution spectra. (a) Si 2p XPS; (b) Bremsstrahlung-excited Si *KLL* Auger electron peak from the Si₃N₄ powder surface.

$$f_i = \frac{pH_{iep} - (pH_{iep})_2}{(pH_{iep})_1 - (pH_{iep})_2}$$
(3)

In the case of the Al₂O₃-B/SNE-3 Si₃N₄ system, the individual pH_{iep} values were 8.30 [$(pH_{iep})_2$] and 5.10 [$(pH_{iep})_1$], respectively. The value of f_i is calculated from equation (3) by substituting the pH_{iep} values at various concentrations of Al₂O₃-B addition to the bulk phase (see Table 8).

These calculations assume that the Si_3N_4 powder surface has an adsorbed layer of Al_2O_3 , and demonstrate that the surface coverage increases as a function of the % Al_2O_3 present in the bulk phase. However, the surface coverage reaches a maximum value of over 90%, and this coverage is obtained between 1.5 and 3.0 wt% Al_2O_3 in the bulk phase. Complete coverage of the Si_3N_4 surface is probably



Figure 9. High-resolution C 1s XPS scan of an Ube SNE-3 Si₃N₄ powder sample.

	Composition (atom %)						
Powder	С	0	N	Si	Aì	v	
Si ₃ N ₄	29.7	23.3	24.5	22.5			
Si ₃ N ₄ /Al ₂ O ₃ -A	43.9	25.4	12.8	14.6	3.2		
Si ₃ N ₄ /Al ₂ O ₃ -B	42.1	35.0	5.4	6.2	11.3		
Si ₃ N ₄ /PAA/Al ₂ O ₃ -B	36.6	32.0	10.3	11.0	8.2		
Si_1N_4/Y_2O_3	33.2	24.6	20:0	20.9		1.4	

Table 7. Surface composition by XPS of Si_3N_4 coated with Al_2O_3 and Y_2O_3

3.5. Surface coverage calculation from pH_{iep} data

Assuming that the point of zero charge (PZC) for these solids is identical to the pH_{iep} , the ESA data were used to calculate the surface composition of Si₃N₄ with adsorbed Al₂O₃-B. Based on Yoon *et al.* [18, 19], the effective isoelectric point of the Al₂O₃ adsorbed on Si₃N₄ is represented by

$$\mathbf{pH}_{iep} = \sum_{i=1}^{2} f_i(\mathbf{pH}_{iep})_i, \qquad (1)$$

where $(pH_{iep})_i$ is the pH_{iep} of component *i* in the adsorbed system, and f_i is the fraction of surface covered by the *i*th component.

$$pH_{iep} = f_i(pH_{iep})_1 + (1 - f_i)(pH_{iep})_2.$$
 (2)

By solving this equation for f_i ,

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Figure 12. Al 2p XP spectrum from the Si_3N_4 powder surface; (a) coated with Al_2O_3 -A and (b) coated with Al_2O_3 -B.

continue to adsorb sintering-aid particles. Even after an adsorbed layer of sintering-aid particles is formed, it is important that the Si_3N_4 particles retain sufficient electrostatic charges for interparticle repulsion. Currently, the ESA technique is not capable of studying this parameter. Secondly, the morphology of coated particles is an important parameter in the shape-forming of green ceramics using these suspensions. High-resolution SEM of coated particles will be able to provide this information. Some of these studies are in progress to develop the necessary data.

4. CONCLUSIONS

The results of ESA, adsorption, and XPS measurements of the Si_3N_4 suspensions and powders containing alumina and yttria particulates suggest the following:

(1) A coating of sintering-aid particles can be formed based on electrostatic and

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limited either by the availability of negatively charged surface sites, and/or by the masking of surface sites by Al_2O_3 particles that are already adsorbed.

In this paper we have described a method for coating colloidal-sized sinteringaid particles on micrometer-sized Si_3N_4 particles by a process largely based on electrostatic and electrosteric adsorption interactions. The ESA technique was used to characterize the coated particles, and the presence and extent of coating were examined by XPS. Although these results clearly demonstrate the feasibility and potential of this coating process, a number of questions remain. First of all, a need exists to examine the degree of dispersion of the Si_3N_4 particles as they





Figure 13. Y 3d and Si 2s XP spectra from a Si₃N₄ sample coated with Y₂O₃

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	п.	

Wt% Al ₂ O ₃ -B in bulk phase	pH _{iep}	f_1 , fractional surface not covered	f_2 , fractional surface covered
1.5	7.2	0.66	0.34
3.0	8.1	0.06	0.94
6.0	8.0	0.09	0.91

electrosteric interactions. Coating formation is dependent primarily on the charge difference between chemically dissimilar particles. The effectiveness of coating was found to increase as a function of the decrease in the particle size of Al_2O_3 . Large particles (0.2 μ m) of Al_2O_3 -A produced a very small amount of coating on Si₃N₄. The coating effectiveness with small particles (40 nm) of Al_2O_3 -B was significantly higher. The maximum surface coverage that can be achieved by this method appears to be in the range of 90%. A limited amount of data on the effect of the presence of PAA in the Si₃N₄ suspensions showed no improvement in the adsorption of either Al_2O_3 or Y_2O_3 due to PAA.

(2) The presence of a coating was confirmed by the measurement of highresolution XPS, which showed that the thickness of the Al_2O_3 -B coating on the Si₃N₄ particles was larger than that of the Al_2O_3 -A coating. Using Bremsstrahlung-excited Si *KLL* Auger electron spectroscopy, the thickness of the native oxide layer on Si₃N₄ was calculated. This oxide film on the Si₃N₄ surface may play an important role in the adsorption process. The evaluation of the surface composition of coated Si₃N₄ particles by XPS demonstrated that the concentration of Al was highest on the Al₂O₃-B-coated Si₃N₄.

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