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Surface characteristics and aqueous dispersibility of commercial silicon nitride powders: Effects of acid leaching, surface hydrolysis, and thermal oxidation

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Abstract

Four types of commercial silicon nitride (Si_3N_4) powders with poor dispersibilities have been studied, and influences of acid leaching, surface hydrolysis, and thermal oxidation on the aqueous dispersibilities for the powders have been investigated systematically, in conjunction with their DRIFT spectra and soluble counterions. Soluble counterions (especially high-valency counterions) and particle surface groups have proved to be the two crucial factors that determine the aqueous dispersibility of Si_3N_4 powders. A universal modification method involving surface hydrolysis and subsequent thermal oxidation gives the different Si_3N_4 powders similar, and excellent, dispersibilities.

Keywords: Silicon nitride; Slurries; Acid leaching; Surface hydrolysis; Thermal oxidation

1. Introduction

Homogeneous slurries with high solids loading and low viscosity are necessary for the ceramic colloidal forming process, because solids loading highly influences the density, strength, and homogeneity of green bodies. For example, the minimum solids loading of suspensions should be >50 vol% for gelcasting [1,2].

Oxide powders, such as Al_2O_3, of which the solids loading of a practical suspension exceeds 60 vol% [3], are easy to use to prepare concentrated slurries and can adopt these advanced forming techniques directly. However, for non-oxide powders, such as Si_3N_4, because of the more complex characteristics of the particle surfaces, preparation of a highly concentrated suspension is difficult, and the application of gelcasting to Si_3N_4 powders has met some trouble. Although numerous studies have investigated the rheological properties and colloidal behavior of Si_3N_4 suspensions [4–18], and highly concentrated aqueous slurries with solids loading > 50 vol% have been prepared by adopting specific methods [15–18], few of those studies have concerned particle surface differences among Si_3N_4 powders and the influence of particle surface characteristics on the aqueous dispersibility of Si_3N_4. The commercial Si_3N_4 powders used in the studies were all produced by the direct nitridation of silicon powder. In the case of commercial powders produced by the thermal decomposition of a diimide ($Si(NH)_2$) precipitate (representative products of which are manufactured by UBE, Tokyo, Japan), the solids loading of their aqueous slurries has not yet reached 50 vol%. For example, the product graded as UBE SN-E10 was regarded as ‘‘notoriously difficult to disperse at high solids loading’’ by Janney et al. [19], and the maximum content of solids loading for the aqueous suspension of this grade powder is in the preparation of highly concentrated slurries remains uncertain, and a clear understanding of the underlying mechanisms that affect the aqueous dispersibility of Si_3N_4 powders needs to be provided.

The surface characteristics and aqueous dispersibility of commercial Si_3N_4 powders depend strongly on the specific production method and post-treatment processing [20–22].

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Four representative types of commercial Si_3N_4 powders were used in the present investigation. Based on an understanding of the surface characteristics and aqueous dispersibility of the as-received products [22], the effects of powder surface modifications, such as acid cleaning, surface hydrolysis, and thermal oxidation, on the surface characteristics and aqueous dispersibility were studied systematically in this paper. Another object of the present investigation was to develop a universal surface modification method that can give different commercial Si_3N_4 powders similar, excellent aqueous dispersibilities.

2. Experimental procedure

The four types of commercial α-Si_3N_4 powders used in the present study are referred to as FD1, FD2, M11, and UBE, respectively. The powder properties of the as-received products are described elsewhere [22]. To prepare concentrated Si_3N_4 slurries, deionized water ($\sim$18 MΩ cm) was used as the liquid medium, and a 10 wt% solution of tetramethyl ammonium hydroxide (TMAH) was added to adjust the pH values. The apparent viscosity of the suspensions was examined by rheometry (Model MCR300, Physica Messtechnick GmbH, Stuttgart, Germany) at 25 °C. Before viscosity measurement, the suspension was ball-milled for 24 h, with the slurry pH maintained at 11.5 ± 0.3 during the ball-milling process. The analysis methods and instruments used for determining the soluble ions, ion conductivity, and diffuse reflectance infrared Fourier transformation (DRIFT) spectra of the Si_3N_4 powders are given in references [20,22].

The total oxygen content of the powders was determined by the inert-gas-fusion method, using an O/N determinator (Model TC-436, LECO, St. Joseph, MI). To determine the bulk oxygen content, the powders were leached in 5% HF (1 g Si_3N_4:10 mL 5% HF) for 1 h, to remove the surface oxygen. (A systematic investigation of surface oxygen elimination in Si_3N_4 powder by HF leaching is also described elsewhere [23].) The surface oxygen content was obtained from the difference between the total and the bulk oxygen contents.

The acid cleaning procedure was as follows: the mixture of as-received Si_3N_4 powders with 5% HCl (100 g:200 mL) was put into a ball-milling jar (without milling balls) and trundled for the first 24 h. The mixture then was centrifuged, the supernatant was removed, and fresh acid was added to the jar, after which the suspension was trundled for another 24 h. That whole process was repeated three times more. Finally, the acid-cleaned powder was leached with deionized water four or five times, to remove residual acid, and then dried.

For the particle surface hydrolysis process, the ratio of Si_3N_4 powder to deionized water and TMAH was 100 g:60 mL:10 mL; the weight ratio of powder to zirconia milling balls was 1:1.5. The mixtures were ball-milled for 48 h at a rotary speed of 200 rotations per minute and then dried at 150 °C.

For thermal oxidation treatment, the Si_3N_4 powders were calcined in air at 600 °C for 6 h. A standard muffle furnace with a temperature controller was used in a static air atmosphere. The depth of the powder layer was $\sim$10 mm.

3. Results and discussion

3.1. Effects of acid cleaning and thermal oxidation

Fig. 1 shows the slurry rheological properties of the acid-cleaned and/or thermal-oxidized powders. ‘‘Raw’’, ‘‘W’’, and ‘‘O’’ represent the as-received, acid-washed (cleaned), and thermal-oxidized Si_3N_4 powders, respectively, and ‘‘WO’’ represents the acid-washed and then thermal-oxidized powder. Fig. 1(a) shows that acid cleaning remarkably improved the aqueous dispersibility of powder FD1. Although direct thermal oxidation improved dispersibility, the effect was inferior to that produced by acid cleaning. Post-thermal oxidation after acid cleaning further improved the aqueous dispersibility of powder FD1. For powder FD2 (Fig. 1(b)), acid cleaning increased the solids loading from 35 to 40 vol% under similar viscosity conditions. Thermal oxidation was superior to acid leaching for powder FD2. For example, the viscosity of the 40 vol% suspensions of powder FD2-O was dramatically lower than that of FD2-W, and the slurry showed near-Newtonian liquid behavior, with the viscosity remaining invariant as the shearing rate increased. As shown in Fig. 1(c), thermal oxidation also notably improved the aqueous dispersibility of powder M11. However, for powder UBE, thermal oxidation decreased dispersibility instead of improving it, as shown in Fig. 1(d); the aqueous dispersibility of powders UBE-W and UBE-WO improved somewhat, but not significantly.

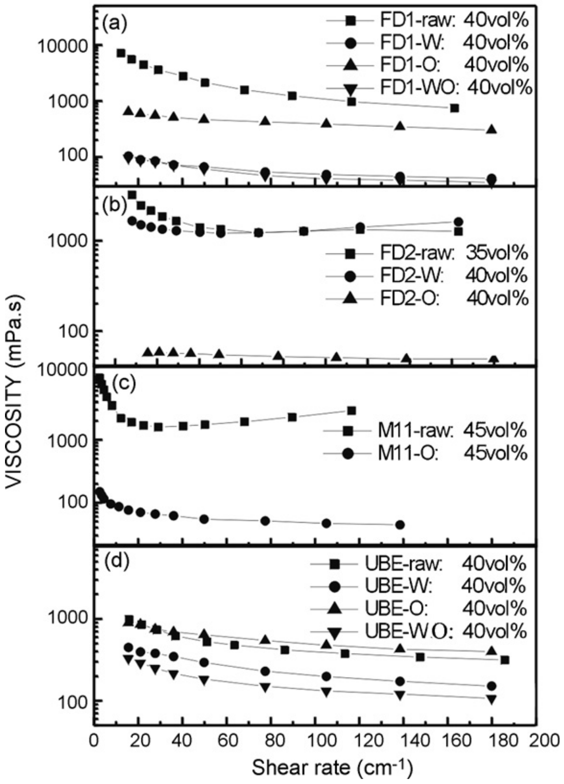

Fig. 1. Effects of acid-cleaning and thermal oxidation on aqueous dispersibility of silicon nitride powders; (a) FD1; (b) FD2; (c) M11; (d) UBE (*raw* represent the as-received powder; O: thermal oxidation; W: acid-cleaning; WO: acid-cleaning and then thermal oxidation).

Table 1
Ionic conductivity and ($Ca^{2+} + Mg^{2+}$) concentration of the supernatants and surface oxygen content of powders after acid-cleaning and thermal oxidation

	Powders										
	FD1			FD2			M11		UBE		
	Raw	W	O	Raw	W	O	Raw	O	Raw	W	O
Ionic conductivity (mS cm^{-1})	0.72	0.19	0.02	0.14	0.18	0.05	0.73	0.04	0.15	0.12	0.01
[$Ca^{2+} + Mg^{2+}$] (mmol/L)	2.07	0.30	0.18	0.61	0.18	0.12	0.26	0.11	0.42	0.27	0.12
Surface oxygen content (mg/m^2)	2.98	3.07	5.97	0.56	0.61	11.9	0.56	0.76	0.47	0.76	1.12

Table 1 summarizes the ion conductivities and ($Ca^{2+} + Mg^{2+}$) concentrations of the supernatants and the surface oxygen content of the powders after acid leaching and thermal oxidation. The high-valency counterions of ($Ca^{2+} + Mg^{2+}$) were removed by acid leaching, especially in the case of powder FD1. The ion conductivity of powder FD1 decreased notably after acid leaching, whereas that of powder UBE decreased somewhat. The increased ion conductivity of powder FD2-W may be attributable to the residual H^+ and Cl^- introduced by acid cleaning. As shown by Table 1, thermal oxidation significantly decreased the ion conductivity and the ($Ca^{2+} + Mg^{2+}$) concentration of these powders. For instance, the soluble NH_4^+ concentration of powder M11 decreased from 6.44 to 0.06 mmol/L after thermal oxidation. Among the as-received powders, the surface oxygen content of powder FD1 was very high, whereas the number of surface oxygen for the other as-received powders was low. The particle surface oxygen concentration increased after acid leaching and thermal oxidation.

The DRIFT spectra of the powders after acid cleaning and thermal oxidation are shown in Fig. 2(a) and (b), respectively. The peak positions corresponding to various surface groups (Si–OH, $SiNH_2$, Si_2NH, Si–O–Si, and C–H) have been shown in a previous report [22]. For powder FD1 in Fig. 2, the DRIFT spectrum of the acid-cleaned sample at 2600–4000 cm^{-1} changes little compared with that of the as-received powder, whereas the number of Si–O–Si groups at ~1190 cm^{-1} decreases somewhat after acid cleaning. Thermal oxidation noticeably changes the DRIFT pattern of powder FD1 at 2600–4000 cm^{-1} and causes the peak position of the Si–O–Si groups to shift to high frequency, whereas the change in the DRIFT spectra of sample FD1-WO is similar to that of sample FD1-O. Fig. 2 shows that the spectra of powder FD2-W at 2600–4000 and 800–1500 cm^{-1} are similar to that of the as-received powder, which implies that the numbers of amine structures, Si–O–C–R groups, and Si–O–Si groups change little after acid cleaning. The DRIFT results for powder FD2-O show that thermal oxidation removes the amine structures and Si–O–C–R groups while it increases the number of Si–O–Si surface groups. The DRIFT spectra of powder M11 show that the amine structures are eliminated after thermal oxidation, but the numbers of Si–O–Si and isolated Si–OH groups have increased at the same time. For powder UBE, the numbers of amine structures and silanol groups for sample UBE-W remain almost the same as those of the as-received powder, but the number of Si–O–Si groups decreases significantly after acid leaching. The DRIFT spectra of powder UBE-O clearly indicate that thermal oxidation eliminates the amine structures and increases the number of isolated Si–OH groups, and that several satellite peaks of the Si–O–Si groups emerge at higher frequencies after thermal oxidation.

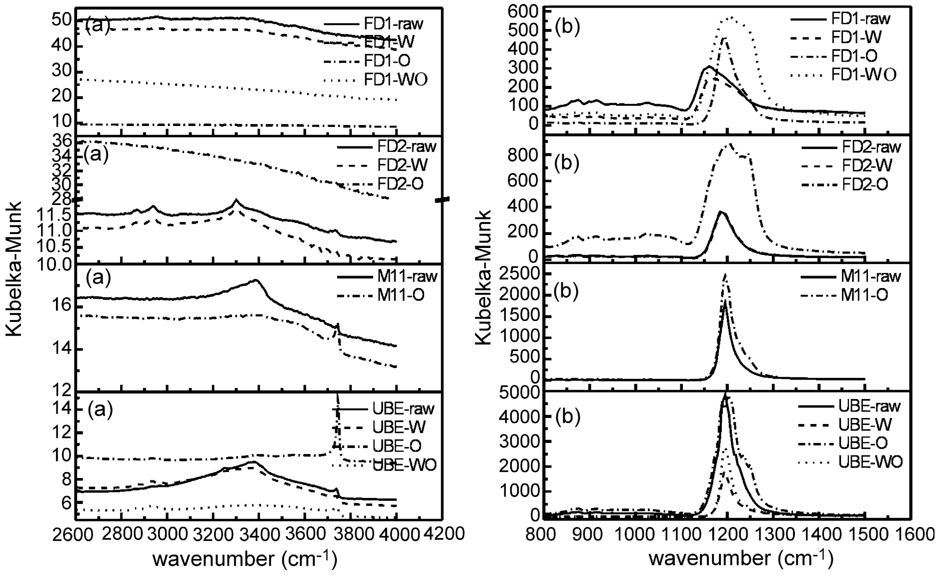

Fig. 2. The DRIFT spectra of powder FD1, FD2, M11 and UBE after acid-cleaning and thermal oxidation: (a) 4000–2600 cm^{-1}; (b) 1500–800cm^{-1}.

According to the Schulze-Hardy rule [24], the critical flocculation concentration (cfc) is in inverse proportion to the sixth power of the counterion valency. Thus, high-valency soluble counterions affect the slurry rheological properties and even take a crucial role in limiting the preparation of highly concentrated aqueous suspensions. Surface charging of the Si_3N_4 particles in aqueous solution is attributed to the dissolution of surface groups [25–27]. From the viewpoint of preparing highly concentrated suspensions, the substitution of Si–OH for other types of surface groups improves the aqueous dispersibility of the Si_3N_4 powders.

According to the present experimental results and previous investigations [21,22], a crucial factor limiting the aqueous dispersibility of powder FD1 is the high-valency counterions of ($Ca^{2+} + Mg^{2+}$), which can be removed almost completely by acid cleaning. However, for powder FD2, the hydrophobic groups of Si–O–C–R on the as-received particle surfaces decrease the aqueous dispersibility, and the effect of thermal oxidation on dispersibility is nearly perfect, whereas the effect of acid leaching is not as satisfactory. For powder M11, the ($Ca^{2+} + Mg^{2+}$) concentration of the supernatant for the as-received sample is very low, and the NH_4^+ content is astonishingly high. The NH_4^+ concentration and ion conductivity are decreased dramatically, and the ($Ca^{2+} + Mg^{2+}$) concentration also is decreased simultaneously. On the other hand, as shown by the DRIFT spectra of powder M11, the number of amine structures decreases after thermal oxidation, while the numbers of Si–O–Si and isolated Si–OH surface groups increase at the same time. These data show conclusively that the remarkable improvement of aqueous dispersibility for powder M11-O results mainly from elimination of the soluble NH_4^+ ions.

For powder UBE, the ion conductivity and ($Ca^{2+} + Mg^{2+}$) concentration are low enough that they cannot be a barrier to preparing highly concentrated aqueous slurries, and numerous amine structures and Si–O–Si groups occur on the particle surfaces. In comparison with the other three types of as-received samples, the as-received UBE powder has an extraordinary number of Si–O–Si surface groups. Although the amine structures are nearly removed, and quite a number of isolated Si–OH groups are formed after thermal oxidation, accompanied by a higher-frequency shift of the Si–O–Si groups and the emergence of several satellite peaks, the aqueous dispersibility of powder UBE is not improved by this treatment. The influence of acid leaching on the amine structures and the Si–OH groups of powder UBE is unclear, but it obviously affects the number of Si–O–Si groups and somewhat improves the aqueous dispersibility of UBE-W. Although acid leaching plus thermal oxidation has a more beneficial effect than acid leaching alone on the aqueous dispersibility of powder UBE, concentrated slurries with solids loading > 50 vol% are impossible to prepare. The effects of acid leaching and oxidation on the rheological properties of powder UBE, and the corresponding DRIFT spectra, indicate that the crucial factor that determines the aqueous dispersibility of the UBE may be the Si–O–Si surface groups.

3.2. Effects of surface hydrolysis and thermal oxidation

Figs. 3 and 4 show the suspension rheological properties of the Si_3N_4 powders after surface hydrolysis alone and surface hydrolysis followed by thermal oxidation, respectively. In the figures, the symbol ‘‘H’’ represents surface hydrolysis, and ‘‘W’’ and ‘‘O’’ indicate acid washing and thermal oxidation, respectively. As shown in Fig. 3, the rheological properties of the 40 vol% suspension of powder FD1-WH are inferior to those of powder FD1-W (Fig. 1). For the 40 vol% suspension of powder FD2, the apparent viscosity of the FD2-H is significantly lower than that of the as-received sample (Fig. 1), and the FD2 powder shows slightly dilatant behavior at a shear rate > 500 s^{-1}. The aqueous dispersibility of powder M11 after surface hydrolysis also shows obvious improvement over that of the as-received sample (a comparison of the rheological curves of the 45 vol% slurries is shown in Figs. 1 and 3). However, the aqueous dispersibility of powder UBE-H is remarkably improved by surface hydrolysis treatment, and the suspension with 45 vol% solids loading has the same rheological properties as those of powder M11-H.

The rheological curves of the 50 vol% slurries of Si_3N_4 powders treated with surface hydrolysis and subsequent thermal oxidation (‘‘HO’’) is plotted in Fig. 4. These results

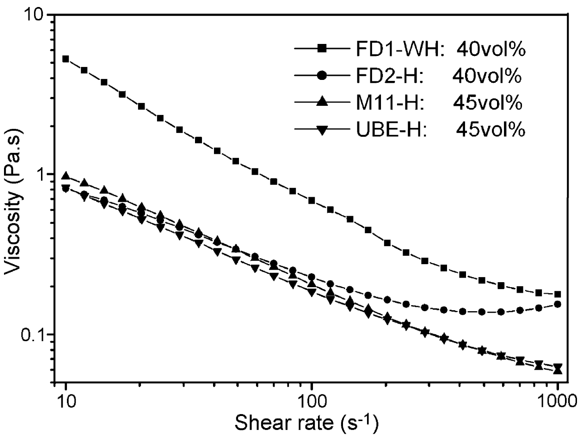

Fig. 3. Rheological properties of silicon nitride powders after surface hydrolysis.

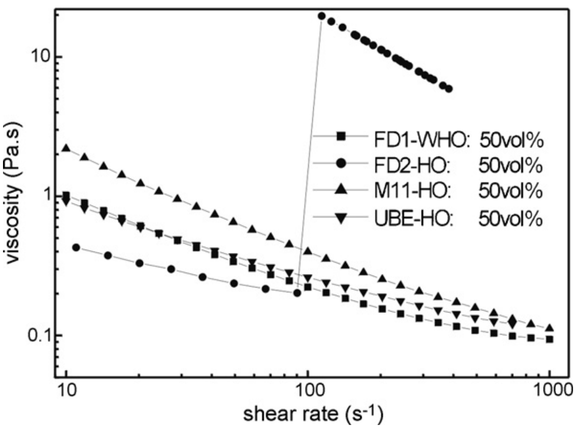

Fig. 4. Rheological properties of 50 vol% suspensions for the silicon nitride powders after surface hydrolysis and subsequent thermal oxidation.

show clearly that the solids loading values of the aqueous suspensions for these HO-treated powders can reach 50 vol%, and the rheological properties of the suspensions (except for that of FD2-HO) are very similar. The apparent viscosities of slurries FD1-WHO, FD2-HO, and UBE-HO are <1 Pa s at a shear rate $> 10\ \mathrm{s}^{-1}$, whereas the rate is $40\ \mathrm{s}^{-1}$ for slurry M11-HO. Slurry FD2-HO shows strong shear-thickening behavior at a shear rate $> 90\ \mathrm{s}^{-1}$, and the shear stress value exceeds the limit of the rheometer. In contrast to the effects of acid leaching, discussed earlier, HO-treatment decreases the aqueous dispersibility of powder FD1-WH, but the dispersibility improves remarkably again after the subsequent thermal oxidation treatment. The most intriguing facet of powder UBE is that the favorable effects of the H- and HO-treatments on the aqueous dispersibility are dramatic, whereas the effects of acid leaching and thermal oxidation alone are insignificant.

Table 2 summarizes the ion conductivities, ($Ca^{2+} + Mg^{2+}$) concentrations, and soluble NH_4^+ contents of the supernatants for the Si_3N_4 powders before and after surface hydrolysis and thermal oxidation and shows their surface oxygen contents. Except for powder M11, the ion conductivity and soluble NH_4^+ concentration of the samples increases significantly after surface hydrolysis, but subsequent thermal oxidation lowers both values for all of the powders. The ion conductivities of the HO-treated samples are nearly the same, and no NH_4^+ ions are detected in the supernatants of powders FD1-WHO and FD2-HO.

After the Si_3N_4 powders have been ball-milled 48 h, for surface hydrolysis, and before they are put into the oven to dry at 150 °C, numerous bubbles appear in the suspensions, and an obvious ammonia odor implies that substantive soluble NH_4^+ has been produced during hydrolysis. Because the drying temperature of 150 °C is high enough to volatilize most of the NH_4^+, the NH_4^+ contents of the hydrolyzed and dried powders are not high. For powder M11, the high ion conductivity of the as-received sample results mainly from the high content of soluble NH_4^+, which is almost removed by drying at 150 °C, and the NH_4^+ content, as well as the ion conductivity, decreases remarkably after the drying process that follows hydrolysis. Changes in the soluble ($Ca^{2+} + Mg^{2+}$) concentrations for the various Si_3N_4 powders after surface hydrolysis differ, possibly because the impurities are distributed at the particle surfaces and in the bulk; subsequent thermal oxidation decreases the soluble ($Ca^{2+} + Mg^{2+}$) contents again. Table 2 also shows that the surface oxygen content of all samples increases after surface hydrolysis, especially for powder UBE. Although those values are increased further by subsequent thermal oxidation in the case of powders FD1, FD2, and M11, the surface oxygen content of powder UBE-HO is far lower than that of powder UBE-H. This result implies that most of the surface oxygens of powder UBE-H are unstable (for instance, the hydrated adjacent silanol groups), and that they can be removed from the particle surfaces by thermal oxidation.

The DRIFT spectra of the powders after surface hydrolysis and thermal oxidation are plotted in Fig. 5. During hydrolysis, the oxygen-rich layer on the particle surfaces is first dissolved in an aqueous solution at high pH, and fresh surfaces of Si_3N_4 are exposed. The following reactions then occur:

$$\mathrm{Si_3N} + \mathrm{H_2O} \rightarrow [\mathrm{Si_2NH}] + [\mathrm{Si{-}OH}] \tag{1}$$

$$[\mathrm{Si_2NH}] + \mathrm{H_2O} \rightarrow [\mathrm{Si{-}NH_2}] + [\mathrm{Si{-}OH}] \tag{2}$$

$$[\mathrm{Si{-}NH_2}] + \mathrm{H_2O} \rightarrow [\mathrm{Si{-}OH}] + \mathrm{NH_3} \tag{3}$$

Thus, the numbers of amine structures (Si_2NH and $SiNH_2$), silanol groups (existing as hydrated adjacent Si–OH groups, not as isolated Si–OH), and soluble NH_4^+ groups are increased at the particle surfaces after hydrolysis. The DRIFT spectra of powders FD2-H, M11-H, and UBE-H (Fig. 5(a)) clearly show that the peaks of the amine structures, at $\sim 3300\ \mathrm{cm}^{-1}$, intensify significantly in conjunction with the appearance of the hydrated adjacent Si–OH groups at $3500–3600\ \mathrm{cm}^{-1}$. This conclusion is reconfirmed by the ion chromatographic results (shown in Table 2). For powder FD1-W, which has a very high surface oxygen content (as shown in Table 2), because the main process during hydrolysis is dissolution of the oxygen-rich layer on the particle surface but not hydrolysis of the fresh Si_3N_4 surfaces, the vibration peaks of the amine structures and silanol groups for powder FD1-WH intensify negligibly (as shown in Fig. 5(a)). For the samples after surface hydrolysis, the two peaks at 2860 and $2940\ \mathrm{cm}^{-1}$ in the DRIFT spectra are attributable mainly to C–H bonding of the $(CH_3)_4N^+$ ions. Subsequent thermal oxidation eliminates the C–H bonding almost entirely and decreases the number of amine structures, as well as the appearance of isolated Si–OH groups at $3740\ \mathrm{cm}^{-1}$. The C–H bonding of the samples after surface

Table 2
Ionic conductivity, ($Ca^{2+} + Mg^{2+}$) concentration, soluble NH_4^+ content and surface oxygen content of the powders after surface hydrolysis and thermal oxidation

Powders	Ionic conductivity (mS cm^{-1})	[$Ca^{2+} + Mg^{2+}$] (mmol/L)	NH_4^+ (mmol/L)	Surface oxygen content (mg/m^2)
FD1-W	0.19	0.30	5.34	3.07
FD1-WH	0.34	1.32	5.90	4.61
FD1-WHO	0.06	0.19	–	6.82
FD2-raw	0.14	0.61	1.41	0.56
FD2-H	0.32	0.49	3.45	2.11
FD2-HO	0.08	0.15	–	5.26
M11-raw	0.73	0.42	13.32	0.56
M11-H	0.23	0.59	4.67	5.27
M11-HO	0.07	0.06	0.06	5.52
UBE-raw	0.15	0.26	1.14	0.47
UBE-H	0.27	0.48	3.29	13.70
UBE-HO	0.07	0.16	0.11	1.84

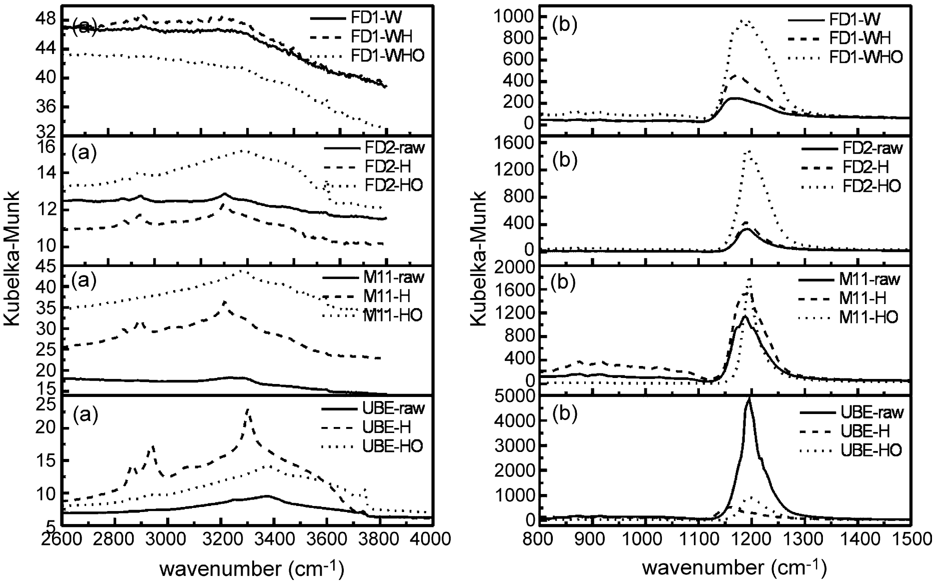

Fig. 5. The DRIFT spectra of powder FD1, FD2, M11 and UBE after surface hydrolysis and thermal oxidation (a)4000–2600 cm^{-1}; (b) 1500–800 cm^{-1}.

hydrolysis results from $(CH_3)_4N^+$ ions, whereas it corresponds to the Si–O–C-R groups for powder FD2-raw.

The DRIFT spectra for the siloxane groups of the samples after surface hydrolysis and thermal oxidation are shown in Fig. 5(b). The number of Si–O–Si groups for powders FD1-W and FD2-raw is small and increases somewhat after hydrolysis, whereas it decreases for powders M11-H and UBE-H. For sample UBE-H, the number of Si–O–Si groups decreases astonishingly, and the peak position clearly shifts to a lower frequency. Subsequent thermal oxidation increases the number of Si–O–Si groups for all of the samples, and the amplitude of increase is higher in powders FD1-WHO and FD2-HO than in samples M11-HO and UBE-HO. As mentioned earlier, the oxygen-rich layer at the Si_3N_4 particle surfaces dissolves first during hydrolysis, and the Si–O–Si groups hydrolyze into Si–OH, as follows:

$$\mathrm{Si-O-Si + H_2O \overset{alkality}{\longrightarrow} 2Si-OH} \tag{4}$$

The Si–OH groups then dissolve into the aqueous solution, and a fresh Si_3N_4 surface is exposed.

In the present study, the hydrolyzed powders were dried directly at 150 °C, without water-cleaning, to remove soluble species formed during hydrolysis, so that the dissolved, oxygen-rich layer was adsorbed onto the particle surfaces again. For the hydrolyzed samples, the oxygen concentration on the particle surfaces increased because of the formation of Si–OH from the Si–O–Si groups, as confirmed by the results shown in Table 2. Especially in the case of sample UBE, because of the extraordinarily large number of Si–O–Si groups, hydrolysis of the siloxane groups was the main process, and hydrated adjacent Si–OH groups were the main products during the hydrolysis treatment, resulting in a high surface oxygen content for powder UBE-H. Subsequent thermal oxidation further increased the surface oxygen contents of all other samples except the UBE-H. The obvious decrease in surface oxygen content for powder UBE-HO implies that dehydration occurred between the hydrated adjacent Si–OH groups and that the anhydrous adjacent and isolated Si–OH groups were formed during thermal oxidation.

According to [28,29], three main types of the Si–OH groups on precipitated silica surface are twin hydroxy, adjacent hydroxy and isolated hydroxy. These hydroxyl surface groups desorbed below 400 °C can be recovered by adsorbing water, while irreversible dehydration reaction with formation of hydrophobic Si–O–Si groups occurs when temperature beyond 400 °C. When Si_3N_4 powders being heated in air, the postulation that change of Si–OH and Si–O–Si is similar to that of precipitated silica is fair and reasonable. As discussed above, negative charging of silicon nitride particle surface at high pH is attributed to proton-releasing of the Si–OH, Si_2NH and $SiNH_2$ groups, and the Si–OH group is more favorable for negative charging. The Si–O–Si group is hydrophobic and cannot provide proton [30,31], so it is unfavorable for negative charging of silicon nitride particle surface. For aqueous silicon nitride slurries stabilized via electrostatic repulsion, large amount of Si–O–Si groups is harmful to preparation of high concentrated suspensions, and it is the bottleneck for powder UBE-raw to improve its aqueous dispersibility. The amount of Si–O–Si groups of powder UBE decreases dramatically through surface hydrolysis treatment, and the aqueous dispersibility of this powder has remarkable improvement. The subsequent thermal oxidation decreases the ion conductivity and the concentration of high-valency counter-ions of supernatants for the treated powders. For powder FD1-W, the harmful effect of surface hydrolysis on the aqueous dispersibility is due to the increase of (Ca^{2+} + Mg^{2+}) concentration.

The rheological properties of the suspensions of the HO-treated powders with solids loading of 55 vol% are plotted in Fig. 6 after a second HO treatment. Suspensions of powders

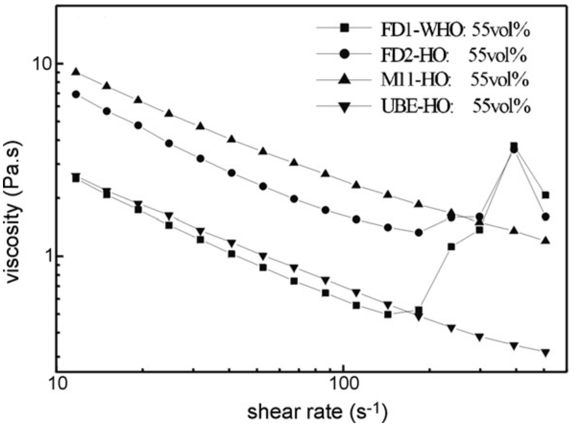

Fig. 6. Rheological properties of 55 vol% suspensions for silicon nitride powders after the *HO*-treatment two times.

FD1 and FD2 show shear-thickening behavior at a shear rate $> 200\ \mathrm{s}^{-1}$, but slurries of powders M11 and UBE behave as pseudoplastic fluids over the whole shear-rate range. The apparent viscosities of suspensions FD1 and UBE are <1 Ps at a shear rate $> 50\ \mathrm{s}^{-1}$.

4. Conclusions

The aqueous dispersibility of the four types of as-received Si_3N_4 powders used in the present study was poor, and highly concentrated suspensions could not be prepared directly from the as-received powders. This study indicates that high-valency counterions of ($Ca^{2+} + Mg^{2+}$) are the crucial factor limiting the dispersibility of powder FD1 and that the problem can be eliminated by acid cleaning. For powder FD2, the barrier to preparing highly concentrated suspension is the large number of hydrophobic Si–O–C–R groups on the particle surfaces, and those groups can be removed by thermal oxidation. For powder M11, the high concentration of soluble NH_4^+ restricts the aqueous dispersibility of the as-received sample, and the NH_4^+ can be removed by thermal oxidation or drying at 150 °C after surface hydrolysis treatment. For the as-received powder UBE, which is notoriously difficult to disperse at high solids loading, hydrophobic Si–O–Si surface groups limits the preparation of highly concentrated slurries, and surface hydrolysis treatment can eliminate these groups and dramatically improve aqueous dispersibility.

Soluble counterions (especially high-valency counterions) and particle surface groups are the two crucial factors that determine the aqueous dispersibility of silicon nitride powders. The process of surface hydrolysis and subsequent thermal oxidation (HO) is a universal method for preparing silicon nitride suspensions with high solids loading. After HO-treatment, the four types of silicon nitride powders used in the present study showed similar, excellent dispersibilities, and the solids loading of their aqueous slurries was >50 vol%. For example, powder UBE SN-E10, which is well-known for its poor dispersibility, exhibited perfect dispersibility after HO-treatment, and the solids loading value of its aqueous suspension reached 55 vol%.

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