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Effects of liquid medium and ball-milling on the surface group and aqueous dispersibility of Si_3N_4 powder

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Abstract

Influences of liquid medium and ball-milling process on the particle surface group and aqueous dispersibility of silicon nitride powder were investigated in this paper. After ball-milling in different liquids, the particle surface group and aqueous dispersibility of silicon nitride powder have different alternations. For the powders treated with identical ball-milling process in different liquids, the subsequent calcination in static air recoveries the same surface characteristics and hence the same aqueous dispersibility. Ball-milling process has significant effect on the particle surface group and its aqueous dispersibility. Under conditions of high weight ratio of milling-balls to powders and large rotary speed, the reaction of ruptured Si–O–Si surface groups with ethanol is dominant and the large amount of Si–O–C–R structures depresses its aqueous dispersibility remarkably.

Keywords: Dispersion; Milling; Si_3N_4; Suspensions

1. Introduction

Si_3N_4 ceramics are regarded as a kind of suitable structural material for their excellent mechanical properties at room and elevated temperatures. However, there are still some problems, such as stability and machining cost, urgently to be solved. In situ consolidation colloidal forming process developed in recent years, such as gel-casting and direct coagulation casting (DCC),[1,2] of which homogeneous slurries with high solids loading above 50 vol.% are necessary, is an effective method to resolve these problems.

Lots of studies have involved rheological property and colloidal behavior of silicon nitride suspensions, [3–15] and high concentrated aqueous suspensions with solid loading above 50 vol.% has been prepared.[16–19] Though particle surface characteristics is the intrinsic essential factor determining the aqueous dispersibility of silicon nitride powders, and it is strongly depends on the different production method and the special pulverization process, few investigations focused on the influence of powder surface characteristics on its aqueous dispersibility.[20–23] According to Dai et al., [22,23] particle surface group is one of the crucial factors determining the aqueous dispersibility of silicon nitride powders. As we all know, before shape-forming process, the as-received ceramic powders may be accepted different treatments such as ball-milling in liquid medium and calcination for specific purposes. Influences of these treatments on the particle surface group and hence the aqueous dispersibility are unclear and a clear understanding of the underlying mechanisms that affect the surface group of silicon nitride powders needs to be provided.

The purpose of this report is to investigate the effects of liquid media and ball-milling process on the particle surface group and the aqueous dispersibility of silicon nitride powders.

2. Experimental

The commercial α-Si_3N_4 powder used in this study was made by direct nitridation of Si powder (grade

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Table 1
Powder properties of the as-received silicon nitride product

Chemical composition						Specific surface area (m^2/g)	α Phase (%)
N (%)	O (%)	C (%)	Fe (ppm)	Al (ppm)	Ca (ppm)		
38.69	1.44	0.20	15	500	61	12.9	91.7

M11, H. C. Starck, Berlin, FRG) and powder properties of the as-received product was shown in Table 1. The liquid media used to modify the particle surface group of silicon nitride powder are de-ionized water (about 18×10^6 Ω), analytically pure ethanol and isopropanol, respectively.

To study the influence of liquid media on particle surface group and aqueous dispersibility, the silicon nitride powder was treated as follows. Mixtures of the as-received silicon nitride powders with different liquids (100 g: 200 ml) were ball-milled for 3 days at the rotary speed of 100 rev/min, then dried at 100 °C for 5 days. The weight ratio of ZrO_2 milling-balls to silicon nitride powder is 1:1.

In order to compare influence of ball-milling process on the particle surface group and aqueous dispersibility, for the mixture with ethanol as liquid medium, the weight ratio of milling-balls to silicon nitride powder and the rotary speed are increased to 3:1 and 400 rev/min, respectively. Other parameters such as ratio of powder weight to liquid volume and drying process hold invariant.

All the treated powders are divided into two portions: one part is used directly for rheology measurement and DRIFT (diffuse reflectance infrared Fourier transform) spectra test, the other portion is first calcined at 600 °C for 6 h and then received the same examinations. A standard muffle furnace with a temperature controller, the hearth size of which was 25×15×12 cm, was used with an air static atmosphere, and the powder layer was about 10 mm.

The liquid medium to prepare aqueous suspensions was de-ionized water, and tetramethyl ammonium hydroxide $(CH_3)_4NOH$ is added as dispersant to break up agglomerate of silicon nitride powders. After ball-milled 24 h, the slurries holding pH at 11.5±0.3 were measured by a rotating viscometer (model NXS-11, ChengDu Instruments Plant, China) to determine their rheological properties.

The diffuse reflectance infrared Fourier transformation (DRIFT) spectra were recorded using a Nicolet 750 Fourier transformation spectrometer (8 cm^{-1} resolution, 64 scans, mirror face of the specimen cup as background). All the silicon nitride powders were measured as undiluted state.

3. Results and discussion

3.1. *Effect of liquid media*

DRIFT spectra of the as-received and liquid-treated silicon nitride powders are shown in Fig. 1. According to Refs.7, 24–26 the wide peak from 3200 to 3500 cm^{-1} corresponds to amine structures (Si_2–NH and Si–NH_2) on the particle surface, while the peak at 3740 cm^{-1} is due to isolated Si–OH surface group. In the range of 800–1500 cm^{-1}, previous investigations of DRIFT spectra for undiluted silicon nitride samples have shown [26–28] that the strong sharp peak at about 1200 cm^{-1} is due to anti-symmetry stretching vibration of siloxane Si–O–Si surface group. It can be seen from Fig. 1a that the amine structures (3200–3500 cm^{-1}) have obscure change and the weak peak corresponding to isolated Si–OH group disappeared after liquid-treatment. For powders ball-milled in ethanol and isopropanol (referred to M11–ethanol and M11–isopropanol, respectively), there are

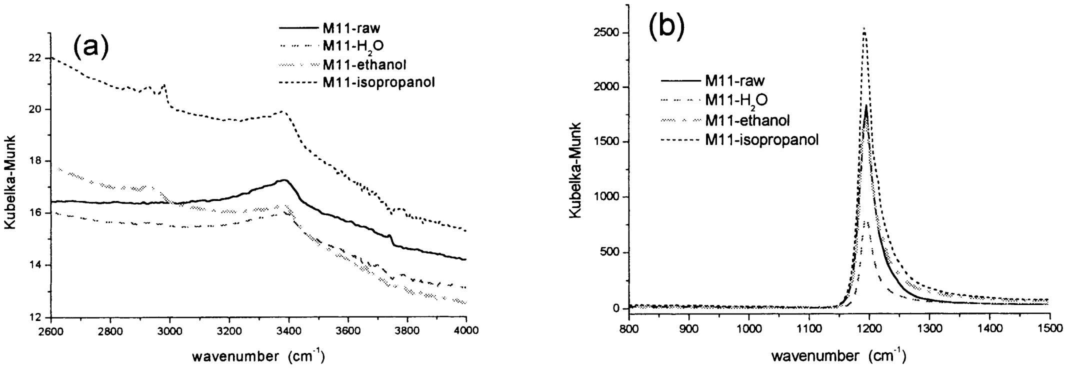

Fig. 1. DRIFT spectra of the silicon nitride powders ball-milled in different liquids: (a) 4000–2600 cm^{-1}; (b) 1500–800 cm^{-1}.

three peaks emerged during 2800–3000 cm^{-1}, which correspond to the stretching vibration of C–H bonding,[24] while these peaks are nonexistent in DRIFT spectrum of sample treated in de-ionized water (referred to M11–H_2O). In comparison to powder M11–ethanol, the C–H peak of powder M11–isopropanol is more intensive. During the wave number range of 800–1500 cm^{-1} (Fig. 1b), compared to the as-received powder (referred to M11-raw), the peak intensity of Si–O–Si group for powder M11–H_2O decreases and that of sample M11–isopropanol increases, while the peak intensity of M11–ethanol keeps invariant.

As previously investigated,[22,23] the surface oxygen content of the as-received silicon nitride powder is 0.72 wt.%, and there are large amount of Si–O–Si groups on the particles surface, which can be hydrolyzed gradually in aqueous solution as follows:

$$\mathrm{Si-O-Si+2H_2O \longrightarrow 2Si-OH}$$

so the amount of Si–O–Si surface groups will decrease due to the hydrolysis reaction, and it is consistent with observations in the DRIFT spectrum of powder M11–H_2O.

For the powders ball-milled in ethanol and isopropanol, both of which are quite volatilizable, the emergence of C–H bonding implies reaction of the liquids with particles surface. The reaction may occur as follows:

$$\mathrm{Si-O-H + HO-CH_2CH_3 \longrightarrow Si-O-CH_2CH_3 + H_2O}$$
$$\mathrm{Si-OH + HO\text{-}CH(CH_3)_2 \longrightarrow Si-O-CH(CH_3)_2 + H_2O}$$

Amount of the Si–OH groups (isolated and adjacent) decreases and that of the Si–O–Si surface species keeps invariant according to these two reaction equations. Emergence of the C–H bonding and disappearance of the isolated Si–OH groups in their DRIFT spectra lend support to the postulate. This finding is also consistent with the results by Schwelm et al., [20] of which the Si–OH groups at the silicon nitride particle surface react with isopropanol and form esters of Si–O–C–R. Their results also demonstrated that the Si–O–C–R surface groups are very stable and can be burned out at temperatures above 450 °C. The peaks of amine structures for powders M11–ethanol and M11–isopropanol are the same as those for the as-received sample implies that there is no reaction between amine structures and liquids of ethanol and isopropanol. For powder M11–ethanol, amount of the Si–O–Si surface groups keeps the same as that of the as-received powder, which demonstrates that the Si–O–Si groups will not react with ethanol. For sample M11–isopropanol, however, the obvious increase of Si–O–Si amount indicates that there exists other reaction of isopropanol with silicon nitride particle surface. It has been proposed in a previous paper [23] that there is another kind of Si–O bonding (neither Si–O–Si nor Si–OH), which is unstable and easy to form Si–OH groups in aqueous solution, at the amorphous oxygen-rich layer on the silicon nitride powder surface. The long-term ball-milling of silicon nitride powders in isopropanol may cause the following reaction, which increases the amount of Si-O-Si surface groups:

$$\mathrm{2Si-O + Si-H + HO-CH(CH_3)_2}$$
$$\mathrm{\longrightarrow Si-O-Si + Si-O-CH(CH_3)_2 + H_2O}$$

The rheological properties of 40 vol.% aqueous slurries for the as-received and liquid-treated powders are shown in Fig. 2a. In contrast to rheological property of slurry M11-raw, apparent viscosity of slurry M11–H_2O is reduced, while that of slurries M11–ethanol and M11–isopropanol are increased. As mentioned above, hydrophobic Si–O–C–R groups have been formed on particle surface of the powders ball-milled in ethanol and isopropanol. It is this kind of hydrophobic surface group that deteriorates the aqueous dispersibility.[23] For the liquid-treated powders after thermal oxidation at 600 °C for 6 h, as exemplified in Fig. 2b, their 40 vol.% suspensions show the same rheological behaviors. It can be clearly seen from Fig. 3 that DRIFT spectra of these

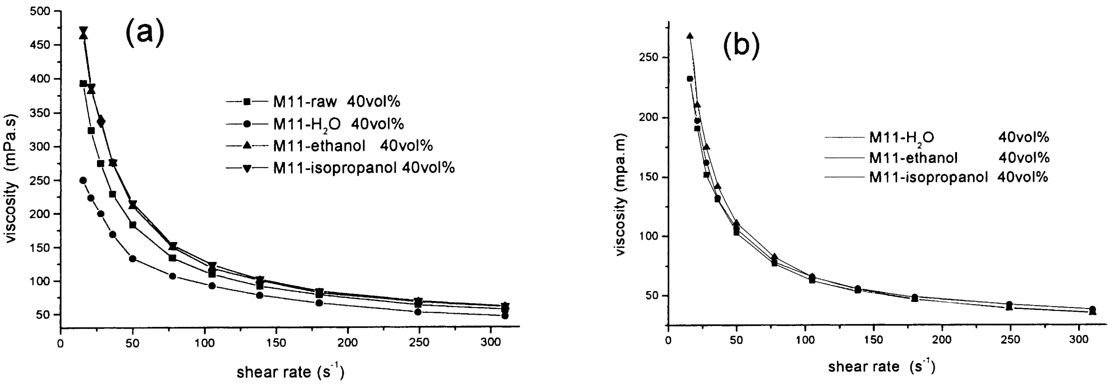

Fig. 2. Slurry rheological properties of the liquids-treated silicon nitride powders: (a) before and (b) after calcination.

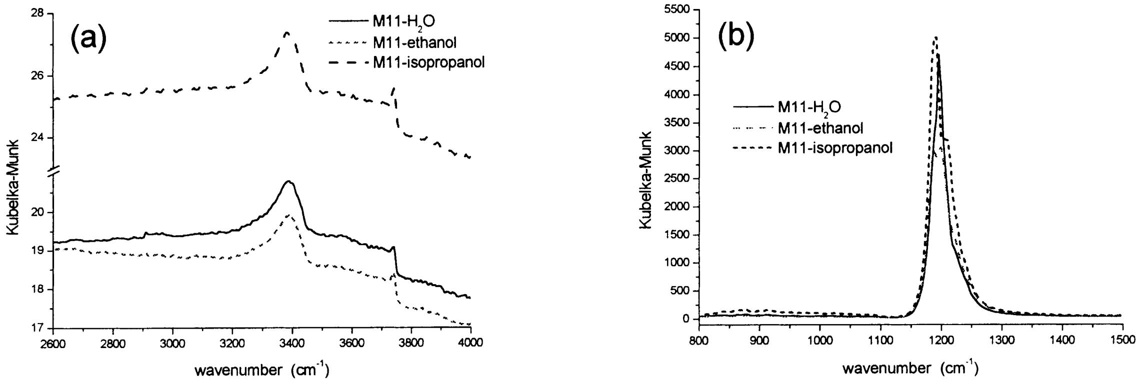

Fig. 3. DRIFT spectra of the liquids-treated silicon nitride powders after calcinations: (a) 4000–2600 cm^{-1} (b) 1500–800 cm^{-1}.

liquid-treated samples are very similar after calcination, which indicates that the hydrophobic Si–O–C–R groups are removed and the surface characteristics of the liquid-treated powders are recovered to identical after calcination.

3.2. *Effect of ball-milling process*

Though aqueous dispersibility of the liquids-treated powders has been modified, the change is not very notable, which may be due to the weak reaction of liquid media with particle surface of silicon nitride powder. To study influence of ball-milling process on the aqueous dispersibility and particle surface group, the weight ratio of milling-balls to powders ball-milled in ethanol increased from 1:1 to 3:1, and the rotary speed was picked up from 100 to 400 rev/min at the same time. The treated samples were referred to M11-11 and M11-34, respectively. As shown in Fig. 4, the DRIFT spectra of powder M11-34 have remarkable difference in comparison to that of sample M11-11. First, amount of the amine structures and C–H bonding increases dramatically, and the peak positions also have deviation (shown in Fig. 4a). Second, peak of the adjacent Si–OH surface groups during 3500–3600 cm^{-1} emerges. Third, amount of the Si–O–Si surface groups decreased obviously and the peak position shifted visibly to lower frequency. Besides the condensation reaction of ethanol with Si–OH surface species to form Si–O–C–R groups, the results are also strong evidence for other reaction with the particle surface, which is related the ball-milling process. For powder M11-34, during ball-milling process, the particle surface bears intensively mechanical impact, which will break the Si–O–Si bonding and cause reaction of ethanol with the ruptured Si–O–Si groups:

$$\mathrm{Si-O-Si + HO-CH_2CH_3}$$

$$\longrightarrow \mathrm{Si-O-CH_2CH_3 + Si-OH}$$

According to this reaction, amount of the Si–O–Si groups decreases, while that of Si–O–C–R and Si–OH group increases at the same time, which is confirmed from the DRIFT spectra of powder M11-34. Further more, peak shift of the Si–O–Si groups from 1190 to 1175 cm^{-1} also demonstrates that there is large tensile stress in the cyclic Si–O–Si structure due to the intensive impact.[23] The DRIFT spectra of powder M11-34 show conclusively that the dominant process during ball-milling is the reaction of ethanol with the ruptured Si–O–Si groups, which generates large amount of Si–O–C–R groups and consumes the Si–O–Si structures obviously.

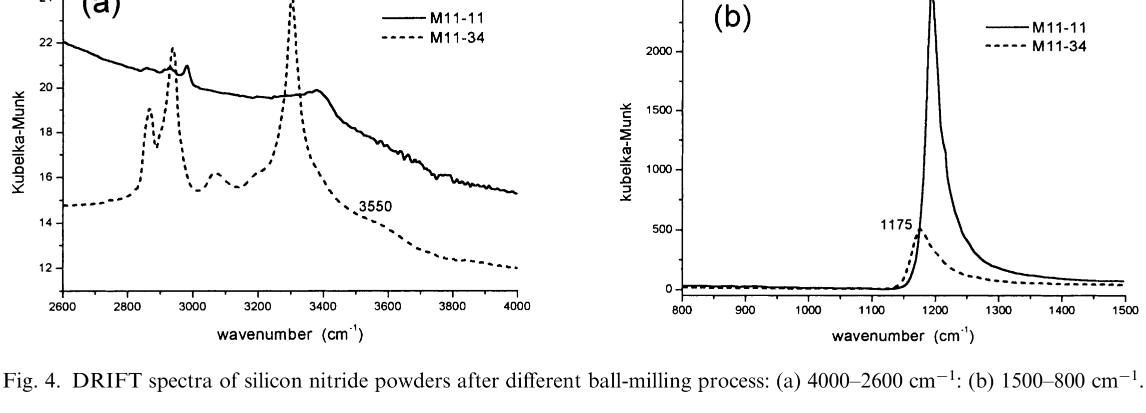

Fig. 4. DRIFT spectra of silicon nitride powders after different ball-milling process: (a) 4000–2600 cm^{-1}: (b) 1500–800 cm^{-1}.

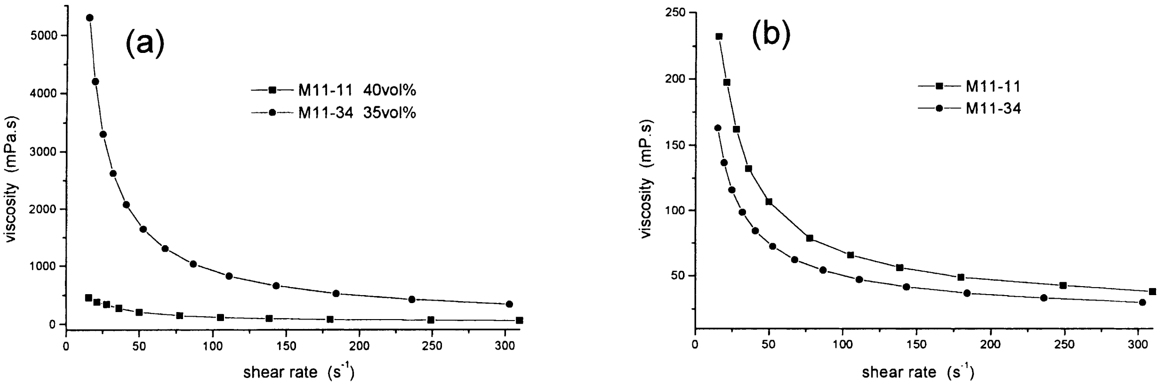

Fig. 5. Slurry rheological properties of powders M11-11and M11-34: (a) before calcinations; (b) after calcinations.

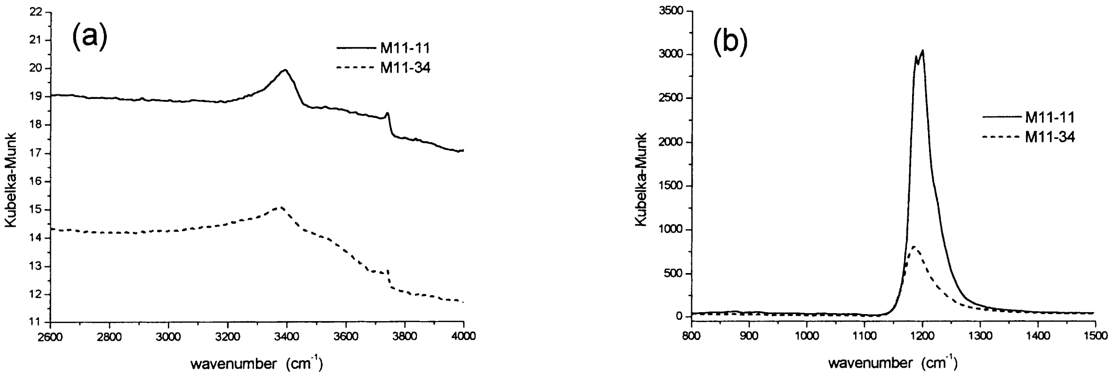

Fig. 6. DRIFT spectra of powders M11-11 and M11-34 after calcinations: (a) 4000–2600 cm^{-1}; (b) 1500–800 cm^{-1}.

The slurry rheological properties of powders M11-11 and M11-34 are plotted in Fig. 5. For the ball-milled powders before calcination (Fig. 5a), the aqueous dispersibility of sample M11-34 is much inferior to that of M11-11, and it is the large amount of hydrophobic Si–O–C–R groups on the particles surface that deteriorates the dispersibility. For the thermal-oxidized powders (Fig. 5b), however, the apparent viscosity of slurry M11-34 is lower than that of slurry M11-11, which is due to the small amount of Si–O–Si groups of sample M11-34 after calcination, as shown in Fig. 6.

4. Conclusions

After ball-milled in different liquids, the particle surface group and aqueous dispersibility of silicon nitride powders have different alternations. For the powder treated in de-ionized water, the aqueous dispersibility has some improvement because of decrease of the Si–O–Si surface groups. For the samples treated in ethanol and isopropanol, the hydrophobic Si–O–C–R groups have been formed on particles surface and deteriorate the aqueous dispersibility. After calcined in static air, the liquids-treated samples with identical ball-milling process recovery the same particle surface characteristics and hence the same aqueous dispersibility.

Ball-milling process has significant effect on the particle surface group and its aqueous dispersibility. Under conditions of small weight ratio of milling-balls to powders (1:1) and low rotary speed (100 rev/min) for sample M11-11, the Si–OH surface groups react with ethanol and form little amount of hydrophobic Si–O–C–R groups. Increasing the weight ratio of milling-balls to powders and the rotary speed to 3:1 and 400 rev/min (sample M11-34), reaction of the ruptured Si–O–Si surface groups with ethanol is dominant and the formation of large amount of Si–O–C–R structures depresses its aqueous dispersibility remarkably. For the two samples ball-milled in ethanol, subsequent calcination eliminates the hydrophobic Si–O–C–R groups and improves their aqueous dispersibility to large degree. For powder M11-34, most amount of Si–O–Si groups have been broken during ball-milling process and not restored after subsequent thermal oxidation, which brings the superior aqueous dispersibility in contrast to that of sample M11-11 after calcination.

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