羟基化对 Si₃N₄ 粉体水相分散性的影响

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摘要: 通过施加硝酸有效地使氮化硅(Si₃N₄)粉末的表面羟基化,以改善在水性介质中的分散性。与天然粉末相比,羟基化粉末在水性介质中产生更稳定的胶体分散。傅里叶变换红外光谱和 X 射线光电子能谱结果表明,随着羟基改性,Si₃N₄ 粉末的羟基含量显著增加。这有助于防止 Si₃N₄ 粉末在水性介质中聚集。 此外, 热重分析表明羟基化 Si₃N₄ 粉末的羟基含量比天然粉末高68.8%。Si₃N₄ 粉末的表面亲水性通过羟基改性而增强,并且粉末分散性随着羟基含量的增加而提高。

Effects of Hydroxyl Groups on Dispersibility of Silicon Nitride Powder in Aqueous Media

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Abstract: The surface of silicon nitride (Si₃N₄) powder was efficiently hydroxylated via application of nitric acid to improve dispersibility in aqueous media. Hydroxylated powder results in more stable colloidal dispersion in aqueous media compared to native powder. Results of Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy show that hydroxyl group content of Si₃N₄ powder significantly increased with hydroxyl modification. This is helpful in preventing Si₃N₄ powder from aggregating in aqueous media. In addition, thermogravimetric analysis indicates that hydroxyl group content of hydroxylated Si₃N₄ powder was 68.8% higher than that of native powder. Furthermore, surface hydrophilicity of Si₃N₄ powder is enhanced with hydroxyl modification, and powder dispersibility is improved with an increase in hydroxyl content.

Keywords: silicon nitride; hydroxylation; surface modification; dispersibility

0　Introduction

Silicon nitride (Si₃N₄) is an important structural ceramic material and is widely used in many fields because of its high strength, high hardness, high temperature resistance, good wear resistance, thermal shock resistance, oxidation resistance, and other excellent properties[1-3]. It has been shown that Si₃N₄ powder is a release agent for inhibiting oxygen diffusion from quartz crucible to polysilicon ingot in production of polysilicon ingot[4-5]. Si₃N₄ ceramics can be used in extreme environments of turbine engine

components and high-speed ceramic bearing materials[6-9]. Si_3N_4 coating can be used as an anti-oxidation coating to enhance service performance of high temperature alloy products and as an anti-corrosion coating to extend service life of alloys used in the ocean. With the development of 3D printing technology, high-performance Si_3N_4 powder has been used in the medical field as human bone and teeth[10].

High-performance Si_3N_4 powder has high purity, fine particle size, and good dispersivity. In particular, dispersion of ultra-fine powder is a key factor in restricting performance of products and downstream applications. However, Si_3N_4 powder has a strong tendency to agglomerate because of its high surface energy. Improving the dispersion stability of Si_3N_4 powder has become a hot issue in Si_3N_4 research[11]. Thus far, research on Si_3N_4 dispersion has mainly been focused on organic media, and the primary ways to modify Si_3N_4 powder include small molecular coupling agents, macromolecular coupling agents, and surface modification via grafting polymer chains[12-15].

Although research on dispersion of Si_3N_4 powder in organic media is advanced, the increasing need for green production and the strict requirements of environmental problems caused by organic solvents cannot be ignored. Dispersion of Si_3N_4 powder in aqueous media has received considerable attention because of significant environmental protection and cost savings. At present, study of Si_3N_4 powder dispersion in aqueous media as mainly focuses on modification using different dispersants. Lü et al.[16] studied the effects of the amount of dispersant and pH value on dispersion of Si_3N_4 powder in aqueous media using polyethylene glycol (PEG) as a dispersant and reported that the optimum conditions for nano-Si_3N_4 dispersion were pH 9.5~10 with an addition of 0.5% PEG. Paik et al.[17] investigated the interaction of dispersant and binder on the surface of Si_3N_4 particles. They prepared a Si_3N_4 aqueous suspension with good dispersion using PMAA as dispersant and PVA as binder. Larrz et al.[18] studied the mechanism of cationic polyelectrolyte for improving Si_3N_4 powder dispersion in aqueous media and confirmed that the improvement of Si_3N_4 powder dispersibility using cationic polyelectrolyte is based on electrostatic stabilization and that cationic polyelectrolyte has better dispersion effects under alkaline conditions. Although the above study achieved better dispersion, the organic dispersant and ionized metal ions in the dispersion process have adverse effects on properties of Si_3N_4 powder. Therefore, because of the surface properties of Si_3N_4 powder, it is necessary to develop a new surface modification method.

Hydroxyl is a strongly polar group, and thus, a substance that contains a large amount of hydroxyl groups has good compatibility with polar solvents according to the principle of similarity and intermiscibility. A water film can be formed via interactions between Si_3N_4 powder and water molecules when the powder is modified with hydroxyl groups. Additionally, modified Si_3N_4 powder has good wettability in aqueous media, which can improve its dispersion[19], and surface water film has a certain steric hindrance that helps prevent agglomeration of Si_3N_4 powder[20-21]. Therefore, it is possible to prepare hydroxyl-modified Si_3N_4 powder with good dispersion in aqueous media. In this paper, the preparation process and structural characteristics of hydroxylated Si_3N_4 powder were investigated. In addition, dispersion of Si_3N_4 powder in aqueous media was characterized.

1 Experimental

1.1 Materials and procedures

Regents included Si_3N_4 (commercially available), nitric acid (commercially available), and deionized water. All reagents were analytical grade and used as received without further purification.

Si_3N_4 powder was dried at 110 ℃ in a vacuum oven for 24 h to remove adsorbed moisture from the surface before surface modification. Native Si_3N_4 (1 g) was dispersed in 50 mL of deionized water using ultrasonic-assisted stirring. The dispersion was then transferred into a 200 mL flask, and 50 mL of nitric acid (85%~88%) was added. The mixture was refluxed at 140 ℃ for 6 h. After reaction, modified Si_3N_4 powder was separated via filtration and was washed

three times with deionized water and then dried at 110 ℃ for 8 h in a vacuum oven.
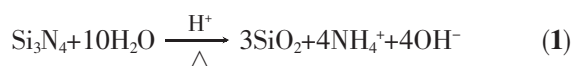
1.2　Characterization of the Si₃N₄ powder

Surface functional groups of modified Si₃N₄ powder were tested using Fourier transform infrared spectroscopy (FTIR, IRPrestige-21, Shimadzu, Japan) with a step size of 2 cm⁻¹. The chemical composition of Si₃N₄ and binding energies of various elements were characterized using X-ray photoelectron spectroscopy (XPS, Escalab 250XI, Thermo Fisher Scientific, America) with a step size of 0.05 eV. Thermogravimetric (TG, Setsys Evolution 18, Setaram, Caluire, France) analysis was performed under a nitrogen atmosphere with a heating rate of 10 ℃·min⁻¹ from 50 to 600 ℃. X-ray diffraction (XRD) patterns of samples were obtained on a D8 Focus with Cu $K\alpha$ radiation (λ=0.154 178 nm) at 200 kV and 50 mA with a graphite monochromator(10°~80°). Particle sizes of the samples were examined using a laser particle size analyzer (90Plus/BI-MAS, Brookhaven, America). Morphologies of Si₃N₄ powder before and after hydroxylation were characterized using scanning electron microscopy (SEM, S-4800, Hitachi, Japan) at 15 kV accelerating voltage. The particle settling process of the above Si₃N₄ powder in deionized water was monitored using ultraviolet-visible spectrophotometry (UV-Vis, TU19, Puxi Instrument, Beijing, China).

Dispersibility experiments were performed in colorimetric tubes. Briefly, 0.1 g of Si₃N₄ powder (with and without hydroxylation) as dispersed in 150 mL of deionized water using ultrasonic-assisted stirring at room temperature. Then, 25 mL of suspension was transferred into a colorimetric tube. Si₃N₄ powder dispersibility was estimated using sedimentation differences with a specific time.

2　Results and discussion

2.1　Hydroxylation mechanism of Si₃N₄ powder

Si₃N₄ powder has high surface activity. It undergoes the following process in acidic aqueous solution[22-23]:

$$Si_3N_4 + 10H_2O \xrightarrow[\triangle]{H^+} 3SiO_2 + 4NH_4^+ + 4OH^- \tag{1}$$

As shown in reaction (**1**), Si₃N₄ powder is partially hydrolyzed in aqueous solution. As a result, a thin layer of silicon oxide film is uniformly coated on the powder surface. The hydrolysis reaction proceeds in the positive direction, and this promotes formation of silicon oxide film in acidic conditions. The newly formed silicon oxide film has many coordination defects, especially on its surface, where dangling silicon bonds have a tendency to capture negative charges to maintain charge balance. During hydroxylation, charge transfer takes place between dangling silicon bonds and water molecules, and this causes water molecules to dissociate at the end of dangling silicon bonds. Thus, Si-OH groups form on the surface of the silicon oxide film[24-25]. The hydroxylation reaction of Si₃N₄ powder is shown in Fig.1.
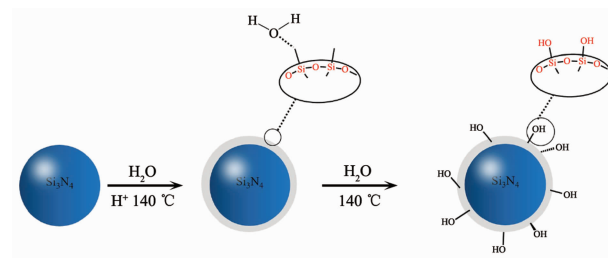

Fig.1　Schematic illustration of hydroxylation reaction of silicon nitride powder

2.2　Surface structure characterization

To characterize differences in surface functional groups of Si₃N₄ powder before and after hydroxylation, FTIR spectra were recorded and the results are presented in Fig.2. Native Si₃N₄ powder has three distinct absorption peaks. Absorption peaks at 1 631 and 3 441 cm⁻¹ are attributed, respectively, to bending and stretching vibrations for hydroxyl groups of surface-adsorbed water molecules[26]. The absorption peak at 1 383 cm⁻¹ corresponds to the bending vibration of Si-OH[27]. Ultrafine Si₃N₄ powder has high activity, and thus it reacts slowly with water vapor in the air. As a result, the surface region of commercial Si₃N₄ powder has a spot of Si-OH groups. As shown in Fig.2 (b), the absorption peak at 1 383 cm⁻¹ becomes stronger after hydroxylation, and this indicates that hydroxylation causes Si₃N₄ powder to produce more
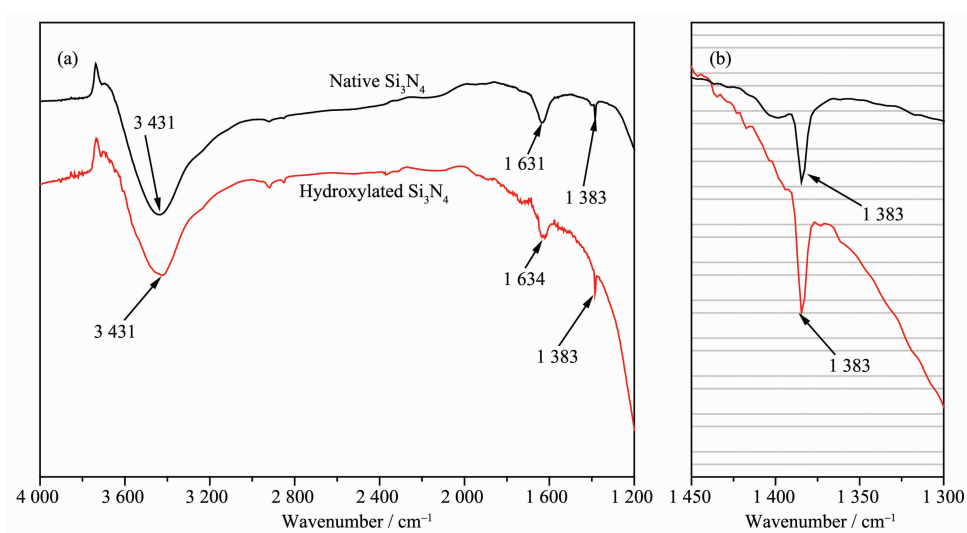
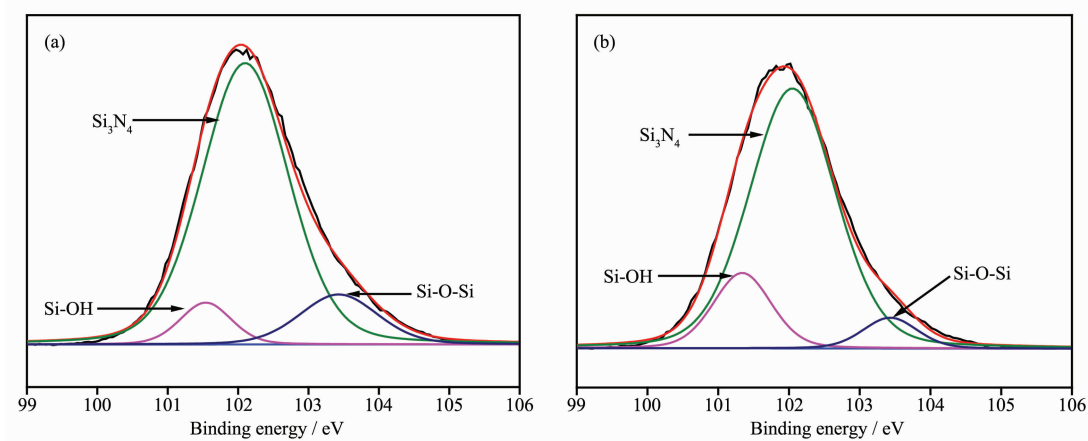Fig.2　FTIR spectra of native Si_3N_4 powder and hydroxylated Si_3N_4 powder

Fig.3　Si2p XPS spectra of native Si_3N_4 powder (a) and hydroxylated Si_3N_4 powder (b)

hydroxyl groups than native powder. In addition, no new absorption peaks appear in the spectrum for hydroxylated Si_3N_4 powder, and this suggests that hydroxylation did not change the surface functional groups of native Si_3N_4 powder and did not adversely affect its intrinsic properties.

　　Fig.3 shows the Si2p XPS spectra of Si_3N_4 powder with and without hydroxylation. It can be seen that hydroxylation did not substantially alter the original binding form of Si in Si_3N_4 powder. Before and after hydroxylation, Si in Si_3N_4 powder had the same three kinds of binding, namely Si_3N_4, Si-OH, and Si-O-Si, and their binding energies are 102.09, 101.34 and 103.37 eV, respectively[28]. Results of further fitting show that the molar ratio of Si-O-Si to Si-OH on the surface of native Si_3N_4 is 0.56:1. However,

after hydroxylation, the molar ratio of Si-O-Si to Si-OH increased to 2.5:1. The results show that hydroxyl content of the Si_3N_4 surface significantly increased after hydroxylation. This is because of interactions between unsaturated bonds of the SiO_2 film on the powder surface and water molecules, which result in the formation of new Si-OH on the surface of the powder, thus increasing Si-OH content on the surface of hydroxylated Si_3N_4 powder.

2.3 TGA characterization

　　Thermogravimetric analysis was used to study weight loss of Si_3N_4 powder with and without hydroxylation to characterize the change in hydroxyl content on the surface of Si_3N_4 powder, and the results are shown in Fig.4. Native Si_3N_4 powder has two distinct weight loss processes. The weight loss before

150 ℃ was attributed to a series of physical processes that happen on the powder surface during heating, such as desorption of water and gases on the powder surface. The weight loss between 150 and 550 ℃ resulted from removal of surface hydroxyl groups, and this was caused by the breaking of Si-OH chemical bonds on the powder surface at high temperature. Hydroxylated Si_3N_4 powder also has two weight loss processes, and the reason for weight loss at temperature lower than 150 ℃ was the same as that for native Si_3N_4 powder. Between 150 and 500 ℃, the thermogravimetric curve presented multiple weight loss steps, and these were caused by constant poly-condensation of hydroxyl groups on the Si_3N_4 powder surface during heating. The final hydroxyl group is volatilized in the form of gaseous water. The weight loss of hydroxylated Si_3N_4 powder was significantly higher than that of native powder over the whole stage, and this was mainly because of the combined action of adsorbed water and hydroxyl groups. The weight loss of Si_3N_4 powder before and after hydroxylation were 0.292% and 0.493%, respectively. The weight loss rate increased 68.8% after hydroxylation (compared with native Si_3N_4 powder), and this means that hydroxyl group content increased 68.8%. Therefore, these results further illustrate that hydroxyl groups were produced on the surface of Si_3N_4 powder after hydroxylation.
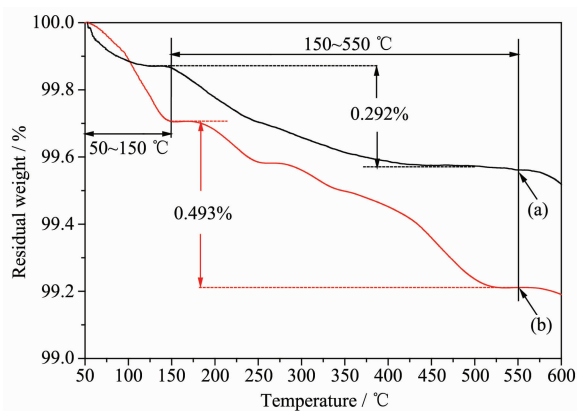
composition changes before and after hydroxylation to verify the effects of hydroxylation on phase composition of Si_3N_4 powder, and the results are shown in Fig.5. It can be deduced that all of the diffraction peaks of native Si_3N_4 powder can be labeled as Si_3N_4. It is mainly composed of α phase with farthing β phase. There are no observable peaks indicating impurities, peak intensity is strong, and the half width is narrow, all of which indicate that the Si_3N_4 powder crystal was better. On the other hand, SiO_2 or other impurity phases were not found in the XRD pattern for Si_3N_4 powder with hydroxylation. Thus, it is proved that the oxide layer produced by surface hydrolysis of Si_3N_4 is an amorphous structure that is extremely thin. In addition, compared with native Si_3N_4 powder, there were no new diffraction peaks in the pattern for hydroxylated powder, and this indicates that hydroxylation did not change the phase composition and had no adverse effects on properties of Si_3N_4 powder.
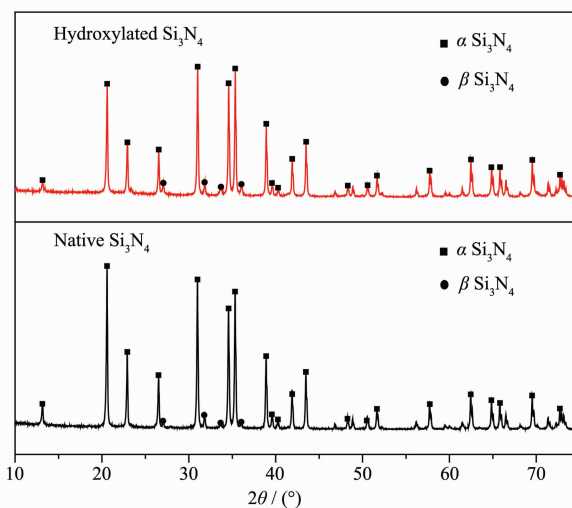

Fig.5　XRD patterns of native Si_3N_4 powder

2.5　Particle size characterization

A laser particle size analyzer was used to measure particle size distribution of Si_3N_4 powder with and without hydroxylation, and the results are shown in Fig.6. The median diameter (d_{50}) of native Si_3N_4 powder is 592.5 nm. This indicates that native Si_3N_4 powder is a typical submicron powder and that it is consistent with requirements for preparation of structural ceramics. The median diameter (d_{50})

Fig.4　TG curves of native Si_3N_4 (a) and hydroxylated Si_3N_4 (b)

2.4　Phase characterization

XRD analysis was used to study phase

decreased from 592.5 to 454.2 nm after hydroxylation, and the reasons for this are that particle agglomerates break down and dispersibility improves. Water molecules near the surface of hydroxylated Si_3N_4 powder preferentially move toward the hydroxylated surface because of coulomb forces and hydrogen bonding. Interactions between free water molecules and preferential adsorption of water molecules promote water being spread on the surface of Si_3N_4 powder, and thus a water film was uniformly coated on the powder surface. Consequently, hydroxylated Si_3N_4 powder in aqueous media has good wettability and
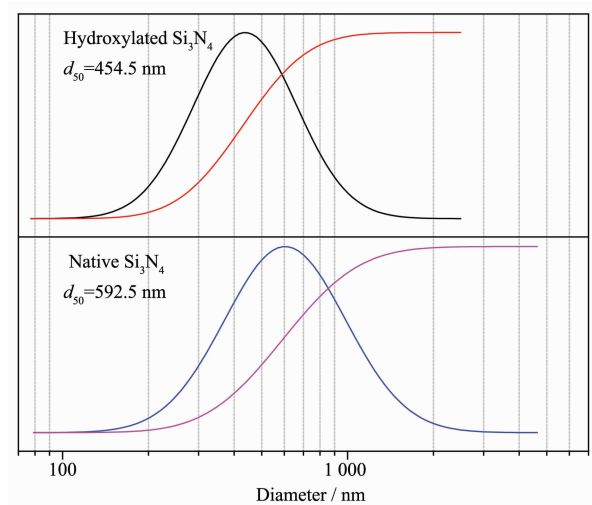

Fig.6   Particle size distribution of native and hydroxylated Si_3N_4 powder

gives rise to homogeneous dispersion[29]. Ren et al.[19] investigated the wetting behavior of the surface of hydroxylated SiO_2 using molecular dynamics simulations, and showed that water clusters have strong interactions with the hydroxylated surface; this makes water molecules preferentially move toward the SiO_2 surface. As such, pre-absorbed water molecules promote adsorption of free water molecules. Finally, water clusters spread completely on the hydroxylated SiO_2 surface. Hydroxylated Si_3N_4 powder preferentially combines with water via hydrogen bonds and results in formation of a solvation layer around each particle. This solvation layer produces repulsive solvation forces that can help prevent Si_3N_4 powder agglomeration[20]. After hydroxylation, dispersibility of Si_3N_4 powder is improved and particle agglomeration is controlled. Therefore, particle size detection is smaller than that of native powder. It can be deduced that hydroxylated Si_3N_4 powder may have better dispersibility than that of native powder in aqueous media.

2.6   Structural and morphology characterization

Fig.7 displays SEM images of Si_3N_4 powder with and without hydroxylation. Obvious aggregation of native Si_3N_4 powder can be seen in Fig.7(a,c), and this aggregation might be ascribed to van der Waals inter-particle attractions among primary particles[30]. Homogeneous dispersion can be observed in the images of
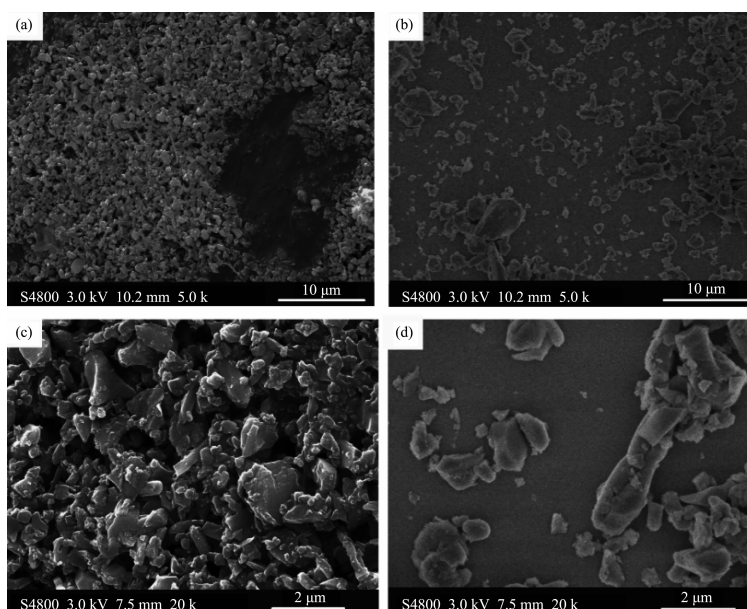

Fig.7   SEM images of native Si_3N_4 (a, c) and hydroxylated Si_3N_4 powder (b, d)

hydroxylated Si_3N_4 powder, as shown in Fig.7(b,d).

Hydroxyl groups on the surface of the powder and hydroxyl groups in water are combined via hydrogen bonding and form a layer of water film. Water film on the surface of the powder has a certain degree of steric hindrance and mutual exclusion. In addition, hydroxylation reduces the surface energy of the powder and effectively reduces agglomeration among the powders. Thus, hydroxyl groups play an important role in dispersion of Si_3N_4 powder. Moreover, it can be presumed that a decrease in particle size of hydroxylated powder (determined using a laser particle size analyzer) was a result of eliminating agglomeration and an increase in dispersibility.

2.7　Dispersion characterization

Dispersibility of Si_3N_4 powder with and without hydroxylation is shown in Fig.8. Native Si_3N_4 powder completely precipitated within 4 h, whereas hydroxylated Si_3N_4 powder was a stable colloidal dispersion in aqueous medium. Furthermore, hydroxylated Si_3N_4 powder only precipitated a little after 48 h. The settling process was assessed via ultraviolet-visible spectrophotometry to characterize the dispersibility of Si_3N_4 powder before and after hydroxylation, and the results are shown in Fig.9. Absorbance of native Si_3N_4 powder was the same as the baseline after 4 h, and this indicates that all Si_3N_4 powder settled during this period. Compared with native powder, absorbance of hydroxylated Si_3N_4 powder was just beginning to weaken after 4 h and still maintained a high value 24 h later. This suggests that stability of the Si_3N_4 dispersion improved greatly after hydroxylation. The above phenomenon shows that the increased content of surface hydroxyl groups of Si_3N_4 powder makes it easy for a stable water film to form. As a result, wettability of the powder in water improves, and steric hindrance between particles increases[31]. Hydroxylation has a positive effect on improving the dispersibility of Si_3N_4 powder in aqueous media. It is expected that dispersion of Si_3N_4 powder can be achieved by replacing traditional organic solvent with aqueous solution, and this is of great significance for environmental protection.
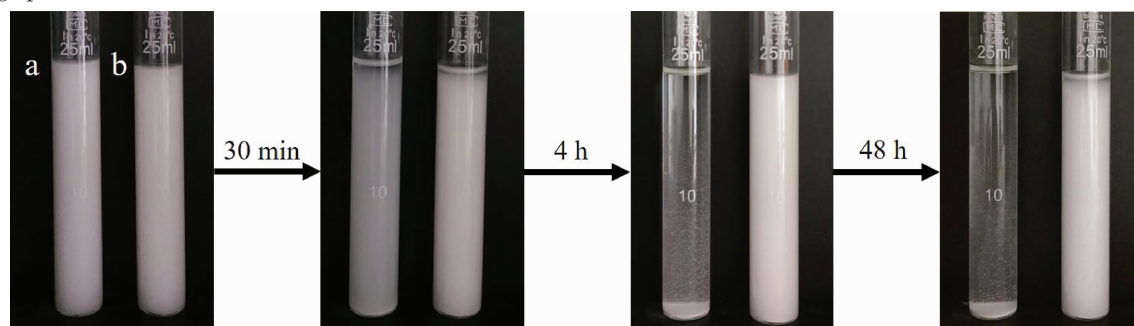

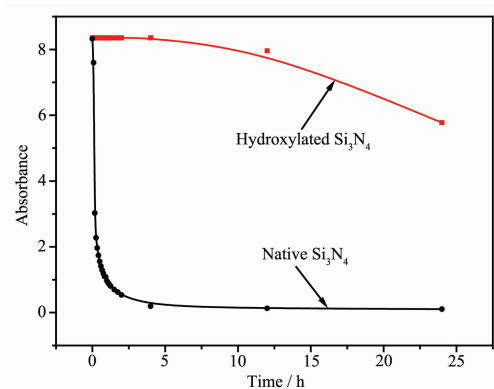Fig.8　Dispersibility of native Si_3N_4 powder (a) and hydroxylated Si_3N_4 powder (b)

Fig.9　Absorbance curve of native Si_3N_4 and hydroxylated Si_3N_4 powder

3　Conclusions

Hydroxylation of Si_3N_4 powder was obtained using nitric acid solution. Si_3N_4 powder was hydrolyzed, and a silicon oxide film formed on its surface in acidic solution. Unsaturated bonds in the silicon oxide film were electronically transferred via water molecules to produce Si-OH on the powder surface with heating. In addition, increased hydroxyl contributes to improving dispersibility of Si_3N_4 powder in aqueous media. Hydroxylation is expected to replace use of organic dispersants for dispersion of Si_3N_4 powder, and this is

important for reducing production costs and for promoting environmental protection during preparation of Si_3N_4 ceramics.

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