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Optimizing the rheological behavior of silicon nitride aqueous suspensions

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Abstract

This work focuses on the optimization of the rheological behaviors of the Si_3N_4 aqueous suspensions by changing the kind and concentration of dispersant, pH value of dispersing medium and other process parameters. Zeta potentials, sedimentation and rheological behavior measurements have been carried out to prepare a well dispersed, uniform and concentrated Si_3N_4 aqueous suspension. The isoelectric point of Si_3N_4 powders is at the pH value of 4.2 and the value of Zeta potential is up to its maximum near pH 11. A good agreement between sedimentation and electrophoresis tests is found which identifies the optimum pH value for promising dispersion. Na_2SiO_3 is an efficient dispersant which increases Zeta potentials in magnitude and improves the fluidity of Si_3N_4 suspensions effectively. The optimum concentration of dispersant is in the range of 1.0 to 1.2 wt%, which is independent on the solids volume fraction of slips. A ball milling of 8 h helps to improve the fluidity of suspensions while longer milling is detrimental.

Keywords: A. Suspensions; D. Si_3N_4; Rheological behavior

1. Introduction

Colloidal processing techniques is commonly accepted as a powerful route to improve the homogeneity and reliability of Si_3N_4 ceramic components with complex shapes [1,2]. For this purpose, Si_3N_4 powder should be dispersed effectively in liquid medium to form a desirable suspension with the lowest viscosity and highest solids content.

The dispersion of colloidal particles in an aqueous media by electrostatic repulsion and/or steric hindrance has been investigated extensively [3]. The former mechanism is managed by both attractive and repulsive forces between powder particles. The net effect of these forces determines the state of dispersions. In the latter case, the colloidal stability is achieved by steric hindrance among colloidal particles. Most often, the colloidal dispersion can be obtained by electrosteric mechanism [4–7]. However, according to the basic principles of direct coagulation casting [8], a stabilized suspension induced only by electrostatic mechanism is desirable. In general, an electrostatic stabilization of suspensions can be achieved by manipulating electrostatic charges on the particle surface by controlling pH and/or adding a dispersant into the suspension [9].

The present work focuses on the optimization of the rheological behavior of the Si_3N_4 aqueous suspensions by changing the kinds and concentrations of dispersant, pH value of dispersing medium and other process parameters. Various methods are used to characterize the dispersing behaviors of suspensions. The Zeta potentials of the starting materials are studied by measuring the electrophoretic mobilities in dilute powder dispersions. The colloidal stability is determined by sedimentation tests and the fluidity of the slip is monitored by rheological behavior measurements. Additionally, the influence of ball milling on the fluidity of Si_3N_4 suspensions is also investigated.

2. Experimental

The powders used were Si_3N_4 (Starck LC-12, Germany) with an average particle size of 0.60 μm and a BET specific surface area of 21.0 $m^2 \cdot g^{-1}$. An inorganic compound, Na_2SiO_3 (purity 99.8%, Shanghai Puqiao Chemical Plant), was used as dispersant for the present study.

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Samples for Zeta potential measurements were prepared at a solids concentration of 1.0 wt% in deionized water, 10^{-3} M NaCl electrolyte, and dispersed for 10 min using a ultrasonic probe. After dispersing, the solution was allowed to sediment for 30 min and the agglomerates were removed. Taking the effects of aging conditions of Si_3N_4 solutions on the Zeta potential measurements into account [10,11], an extra aging of 60 min was necessary before measurement to obtain parallel results. The measurements were performed at 25°C on Zetasizer 4 (Malvern, UK) which uses the Doppler shift resulting from laser light scatter from the particles to obtain a mobility spectrum. To determine the Zeta potential as a function of pH, the 10^{-2} N HCl and 10^{-2} N NaOH solutions were used to adjust pH to the desired values.

A series of 5 vol% Si_3N_4 suspensions with different pH values were prepared for setting test, which were then ultrasonicated and stirred for at least 30 min. 25 ml of each resultant suspension was poured into graduated test tube which were then sealed for determination the variation of relative sedimentation height (RSH) versus setting time at various intervals. In this study, the RSH is defined as the ratio of the dispersion height to the total suspension height, in which the dispersion height is referred to the distance between the dispersion/supernatant interface and the bottom of the tube, including the height of any sediment.

The suspensions containing 24 vol% of Si_3N_4 powder, deionized water, and 0.1–1.6 wt% dispersant (based on the weight of the Si_3N_4 powder) were prepared. The suspensions were blended thoroughly by ball milling (Si_3N_4 balls) for 8 h. The rheological behaviors of Si_3N_4 suspensions were characterized in steady shear mode with a couette (cup radius: 34.0 mm, bob radius: 32.0 mm, bob length: 33.3 mm) on Rheometeric Fluid Spectrometer II (RFS II).

3. Results and discussion

The Zeta potential of powder has an important effect on the state of particulate dispersion in suspensions during colloidal processing. A zero Zeta potential is defined as isoelectric point (IEP) which is the indicative of uncharged (electrical neutrality) particle surface (balancing of positive and negative sites) that leads to the flocculation of particles in suspension. Higher Zeta potential value means a higher charge density on the particle surface which develops a good colloidal stability due to the generation of strongly electrical double-layer repulsive force between equally charged particles. It has been found that the Zeta potential derived successfully represents the electrostatic interaction between particles in the dispersion [10]. Therefore, it is vital to determine the IEP of powder so that a pH region can be defined in which a promising dispersion will be easily attained.

Fig. 1 shows the Zeta potential of Si_3N_4 particles at various dispersant additions as a function of pH. In the case of Si_3N_4 suspensions without dispersant addition, the IEP of Si_3N_4 particles is at the pH of 4.2. Above this value, it exhibits a negative Zeta potential that gradually increases in magnitude with pH value of the dispersing medium. At pH values above 10.5, the Zeta potential approaches a maximum. The introduction of dispersant results in a higher negative Zeta potential and shifts the IEP from 4.2 to 2.8. It seems that the changes of Zeta potentials and IEP of Si_3N_4 particles are caused by the increasing of the charging density of particles which, in turn, is caused by the adsorption of negatively charged anion groups of dispersant on the surface of Si_3N_4 particles. Although the IEP of Si_3N_4 particles has shifted after the addition of dispersant, the pH value corresponding to the maximum Zeta potential is still near pH 11. Therefore, it is expected that the optimum fluidity of Si_3N_4 suspension will be achieved at pH 11.

In addition to Zeta potential, the influence of the acidity in medium on the stability of Si_3N_4 dispersion can be shown by sedimentation tests. Fig. 2 gives the dispersion behavior of Si_3N_4 suspensions against pH after setting for 1 h and 1 week, respectively. Evidently,

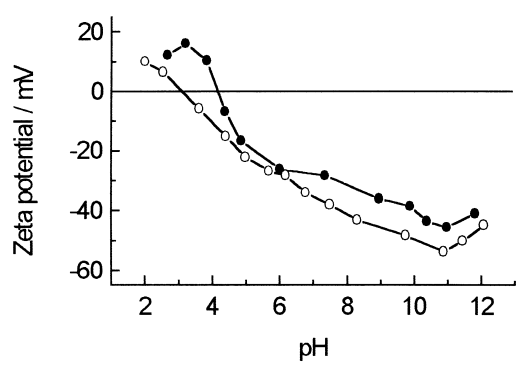

Fig. 1. Zeta potential as a function of pH for Si_3N_4 particles at various dispersant additions (●) 0.0wt%; (○) 0.25wt%.

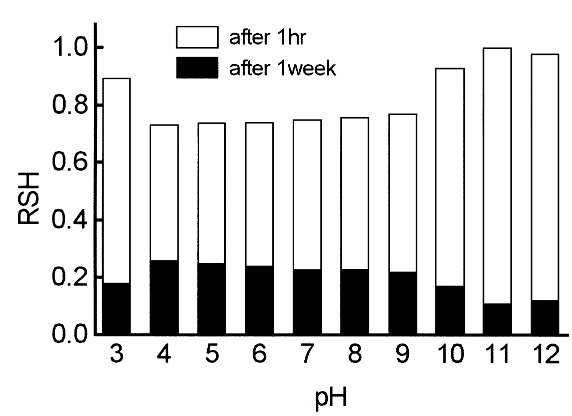

Fig. 2. Sedimentation of 5 vol% Si_3N_4 suspension at various pH values.

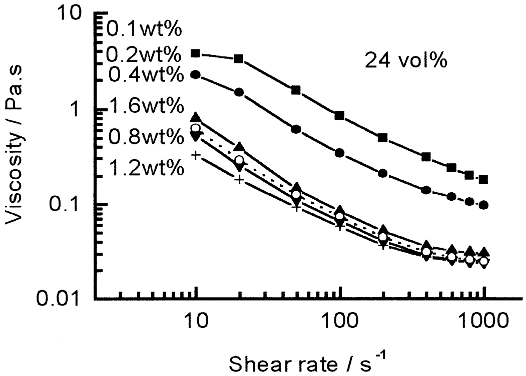

Fig. 3. Influence of dispersant concentrations on the viscosity of 24 vol% Si_3N_4 suspension.

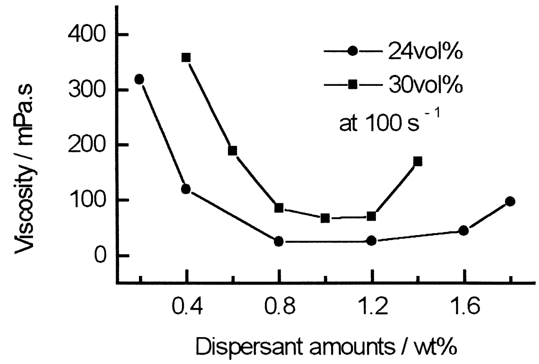

Fig. 4. Viscosity as a function of dispersant concentrations at different solids volume fraction.

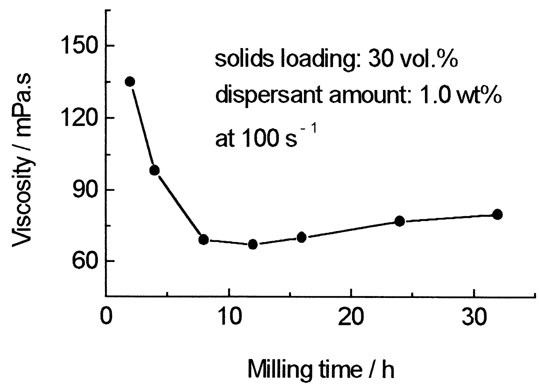

Fig. 5. Influence of ball milling time on the viscosity of 30 vol% Si_3N_4 suspension.

for a shorter time setting, a smaller RSH means a poor dispersion, since flocs have formed and settled. On the contrary, for a longer time setting, a smaller RSH means a good dispersion, since the suspended particles under mutual repulsion have enough time to rearrange so that a dense sediment body produces. It is evident that the results of sedimentation are very consistent with the measurements of Zeta potentials.

In order to prepare a promising powder suspension, dispersant is frequently used [9]. In this work, the dispersant was selected from a number of commercially available dispersants, including sodium citrate, sodium oxalate, sodium silicate, sodium ortho(meta-, hypo-, pyro-)phosphate, PAA, and PMAA. Although PAA or PMAA is usually used as dispersant for Si_3N_4 suspensions [5,6], it is not the optimal one in the present work according to the sedimentation tests. A promising dispersion was prepared by additions of sodium silicate (Na_2SiO_3) which seem to work by the adsorption of anion group SiO_3^{2-} on the surface of particles and thus increases the repulsive force among Si_3N_4 particles.

Fig. 3 shows the influence of the concentration of dispersant on the viscosity of 24 vol% Si_3N_4 aqueous suspensions. As can be seen, the viscosity values at any given shear rate decrease with increasing the concentrations of dispersant and reach a minimum at a concentration of 1.2 wt%, further addition of dispersant raises the viscosity of the suspension again. This can be explained as follows: at lower dispersant concentration, the charging density at the surface of Si_3N_4 particles and hence the repulsive potential between particles are low, so the fluidity is bad and the viscosity of the suspension is high. On the contrary, at the regions of higher dispersant concentration, the network developed by the bridging effect retards the sliding of Si_3N_4 particles one over another. So, the increasing of viscosity with further addition of the dispersant at lower shear rate is due to the relatively steady particles network, while the good fluidity of suspension exhibiting at higher shear rate is due to that the network can be broken down by higher shear stress. On the other hand, all of the suspensions are characterized of shear- thinning behaviors in the ranges of the dispersant concentration studied in the present work, indicating that some particle networks are actually developed in suspension.

Fig. 4 illustrates the viscosity of Si_3N_4 suspensions with various dispersant concentrations for different solids content. As is shown, the optimum concentration of dispersant is 1.0∼1.2 wt% (corresponding to 0.48∼0.57 mg·m^{-2}), which is independent on the solids content of slips.

The influence of ball milling on the viscosity of Si_3N_4 slip is shown in Fig. 5. As can be seen, the ball milling effectively improves the fluidity of slip. A milling of 8 hours is appropriate while longer milling is detrimental to obtain higher fluidity.

4. Conclusions

The isoelectric point of Si_3N_4 powders is at the pH value of 4.2 and the value of Zeta potential is up to its maximum near pH = 11. Sedimentation and electrophoresis techniques can be used to identify the optimum pH for dispersing and exhibit good agreement between them. Si_3N_4 is an efficient dispersant which increases Zeta potentials in magnitude and improves the fluidity of Si_3N_4 suspensions effectively. The optimum concentration of dispersant is found in the range of 1.0 to 1.2 wt% and is independent on the solids volume fraction of suspensions. A ball milling of 8 h is appropriate while longer milling is detrimental to obtain higher fluidity.

References

[1] F.F. Lange, Powder processing science and technology for increased reliability, J. Am. Ceram. Soc. 72 (1989) 3–15.

[2] C.P. Cameron, R. Raj, Better sintering through green-state deformation processing, J. Am. Ceram. Soc. 73 (1990) 2032–2037.

[3] J. Theodoor, Overbeek, G. in: R.F. Davis, H. Palmour III, R.L. Porter (Eds.), Emergent Process Methods for High Technology Ceramics, Plenum Press, New York, 1982, pp. 25–44.

[4] L-C Guo, Y. Zhang, N. Uchida, et al., Adsorption effects on the rheological properties of aqueous alumina suspensions with polyelectrolyte, J. Am. Ceram. Soc. 81 (1998) 549–556.

[5] V.A. Hackley, Colloidal processing of silicon nitride with poly-(acrylic acid): II, rheological properties, J. Am. Ceram. Soc. 81 (1998) 2421–2428.

[6] U. Paik, V.A. Hackley, H-W Lee, Dispersant–binder interactions in aqueous silicon nitride suspensions, J. Am. Ceram. Soc. 82 (1999) 833–840.

[7] B.J. Briscoe, A.U. Khan, P.F. Luckham, Optimising the dispersion on an alumina suspension using commercial polyvalent electrolyte dispersants, J. Eur. Ceram. Soc. 18 (1998) 141–147.

[8] T.J. Graule, F.H. Baader, L.F. Gauckler, Shaping of ceramic green compacts direct from suspensions by enzyme catalyzed reactions, Cfi/Ber.DKG 71 (1994) 317–323.

[9] I.A. Akasy, F.F. Lange, B.I. Davic, Uniformity of Al_2O_3-ZrO_2 composites by colloidal filtration, J. Am. Ceram. Soc. 66 (1983) C190–192.

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

[11] L. Bergstrom, E. Bostedt, Surface chemistry of silicon nitride powders: electrokinetic behavior and ESCA studies, Colloids and Surfaces 49 (1990) 183–197.