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Ceramics International 28 (2002) 747–754

CERAMICS
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Effect of pretreatment on rheological properties of silicon carbide aqueous suspension

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Received 6 July 2001; received in revised form 31 October 2001; accepted 19 December 2001

Abstract

The effect of surface treatments, including leaching with acid solution, base solution and deionized water, on flow properties of SiC aqueous slurry has been studied. The SiC powder was well dispersed irrespective of the surface treatment. However, the viscosity was affected by the surface treatment. Base leaching exhibits a distinctly lower viscosity. The reason for the leach effect was discussed. Calcination of SiC powders at 550 °C is observed to effectively reduce the viscosity of the SiC slurry. But further increase of the calcination temperature will be deleterious to the rheologic properties. The hydration of amorphous SiO_2 on the SiC surface is used to clarify the phenomenon. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Suspension; B. Surface; D. SiC; FT-IR

1. Introduction

For an advanced ceramic material, attainment of a well mixed, uniform green body with a high density, minimum density variation and homogenous pore size distribution is the most important aspect in its production. Many efforts have been made to optimize the processing route. It seems that colloidal processing is one of the most important ways to obtain a uniformly consolidated compact and components with complex shape [1].

Many kinds of novel colloidal processings have emerged in recent years, e.g. gel casting, freezing forming, temperature induced gelation (TIG), and direct coagulation casting (DCC) [2]. The major difference between them is the intrinsic mechanism for the formation of a green body. Gel casting is based on polymerization of a monomer dissolved in the medium. In freezing forming, shape forming is based on the rapid solidification of a solvent carrier. In TIG, temperature is changed to cause gelation of the sterically stabilized suspension to form a green body. DCC utilizes the destabilization of electrostatically stabilized suspension through enzyme catalyzed and time-delayed reaction in the suspension to flocculate the concentrated slurry. Although the physical or chemical process responsible for consolidation of slurry differs greatly, all methods mentioned above require a well-dispersed suspension of high solids loading with reasonably low viscosity to facilitate the mold-filling process.

As a covalent ceramic material, silicon carbide (SiC) has been widely used for high temperature structural application. At the same time, its excellent combination of thermal properties (low coefficient of thermal expansion, high thermal conductivity), availability and cost have also made it an arresting class of candidate as reinforcement for high volume fraction metal matrix composite (MMC) [3]. Colloidal techniques have been tried on SiC ceramics [4] and many influencing factors on the rheological behavior of SiC slurry were investigated, such as the slurry structure, pH value, addition of dispersant [5–7]. The results show the potentialities of colloidal technique suitable for fabricating advanced SiC components with complex geometry.

When the variables including particle size distribution, particle shape, and solid loading are kept constant, the rhelogical behavior of concentrated suspension of ceramic particles is merely influenced by the magnitude of interparticle forces, which is determined by the surface chemistry of particles. Liden et al. [8] used hydrolysis reaction to deposit Al-alkoxide on the SiC powders, and found that the surface modification drastically improved the dispersability in cyclohexane. Yang

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PII: S0272-8842(02)00038-X

et al. [9] used a sol-gel approach to make the boehmite layer on SiC powders. The results showed that the gelation, consolidation and rheological properties were all improved to a certain extent.

The objective of the present study is to construct a direct relationship between different kinds of surface leaching processes and rheological properties in aqueous suspension. We also made great efforts to clarify the relationship that exists between the surface chemistry and their rheological behavior by oxidizing SiC powders at different temperatures.

2. Experiment procedure

ß-SiC powders, manufactured by Sanxin Industries, China, were used in the study. The specific surface area of the powder was measured by a single point BET method (Masterisizer 2000, Malvern Instrument Ltd., UK) to be 6.5 m^2/g and the $d_{(0.1)}$, $d_{(0.5)}$ and $d_{(0.9)}$ are 0.366, 1.627 and 3. 896 μm, respectively. A chemical composition of the powder that has been used is given in Table 1.

The as-received powders were subjected to various pretreatment strategies, which include washing the powders in pure deionized water, in acidic solution (pH 2) and in 2 wt.% $(NH_4)_2CO_3$ solution. In order to remove foreign ions thoroughly, the leached powders were repeatedly rinsed with deionized water until no change in conductivity was detected. The SiC powders leached with base solution were then calcined in air for 1 h at different temperatures: 250, 400, 550, 850 and 1000 °C respectively in order to change the surface chemistry of the powder. A muffle furnace with a temperature controller was used with a static air atmosphere.

Suspensions containing a certain amount of SiC powders and deionized water were prepared. The suspensions were then blended thoroughly by ball milling for 10 h using SiC spherical grinding media. The pH value of the suspensions was adjusted to 10.0 by the addition of 25% tetrapropyl ammoniuin hydroxides (TMAH Shanghai Chemical Plant, China).

A strain-controlled rheometer (4ARES-9a, Rheometric Scientific Inc. USA) was used to measure the rheological properties of the SiC suspensions at room temperature. Couette (cup diameter: 36.8 mm; bob diameter: 35.0 mm; bob length: 37.37 mm) was used for all these measurements. The samples were protected from drying by the addition of a thin layer of paraffin oil on top. To avoid undesired influences from different mechanical histories, fresh samples were homogenized by pre-shearing at an identical rate of 100 s^{-1} for 1 min and left standing for an additional 2 min prior to measurement. Three types of rheological measurements were carried out. Steady rate sweep measurements were used to characterize the general flow behavior with shear rates ranging from 10^{-2} to 300 s^{-1}. The other two kinds of oscillatory measurements—a strain sweep measurement from 10^{-2} to 20% at 1 Hz and a frequency sweep measurement from 0.2 to 100 Hz—were also used to obtain information on the viscoelastic behavior of suspensions.

Table 1
Chemical composition (wt.%) of SiC powder[a]

SiC	Free carbon	Oxygen	Calcium	Aluminum	Magnesium	Iron	Sodium
98	0.2	0.9	0.05	0.05	0.04	0.03	0.04

[a] As given by the supplier.

Samples for Zeta potential measurement were prepared at solids concentration of 0.5 wt.% in deionized water, 10^{-3} M NaCI electrolyte, and dispersed for 10 min using an ultrasonic probe. After dispersing, the solution was allowed to sediment for 20 min and the agglomerates were removed. The measurements were performed on BI-ZetaPlus (Brookhaven Instruments Corp., USA) which uses the Doppler shift resulting from laser light scatter from the particles to obtain a mobility spectrum. The 10^{-2} N HCI and 10^{-2} N NaOH solution were used to adjust pH to the desired values.

Diffused reflectance infrared Fourier transform (DRIFT) spectrometry is a method for measuring the infrared spectra of powdered samples. A Bruker Spectrometer (Equinqx55, Germany), operated in the diffused reflectance mode, was used here. The spectral measurement in the 400–4000 cm^{-1} region was made at 4 cm^{-1} resolution with the use of 120 scans. To measure the DRIFT spectra, 20 mg SiC was mixed with 370 mg KBr powders. The mixture of about 180 mg was transferred to a 10 mm diameter cup without compression and then was leveled.

3. Results and discussion

3.1. Effect of surface treatment on the rheological properties

Fig. 1 is a steady strain rate sweep measurement for as-received and three kinds of leached powders. The ordinate represents the viscosity η. It is quite evident that the rheological behavior improved efficiently. The viscosity of leached SiC suspension at any shear rate was lower than that of the as-received suspension. All of these suspensions are characterized by shear-thinning behavior. The as-received suspension shows a pronounced shear-thickening trend. Leaching of the powder eliminates the shear-thickening behavior within the scope of measurement and these suspensions display a Newtonian plateau at intermediate shear rates between 100 and 250 s^{-1}.

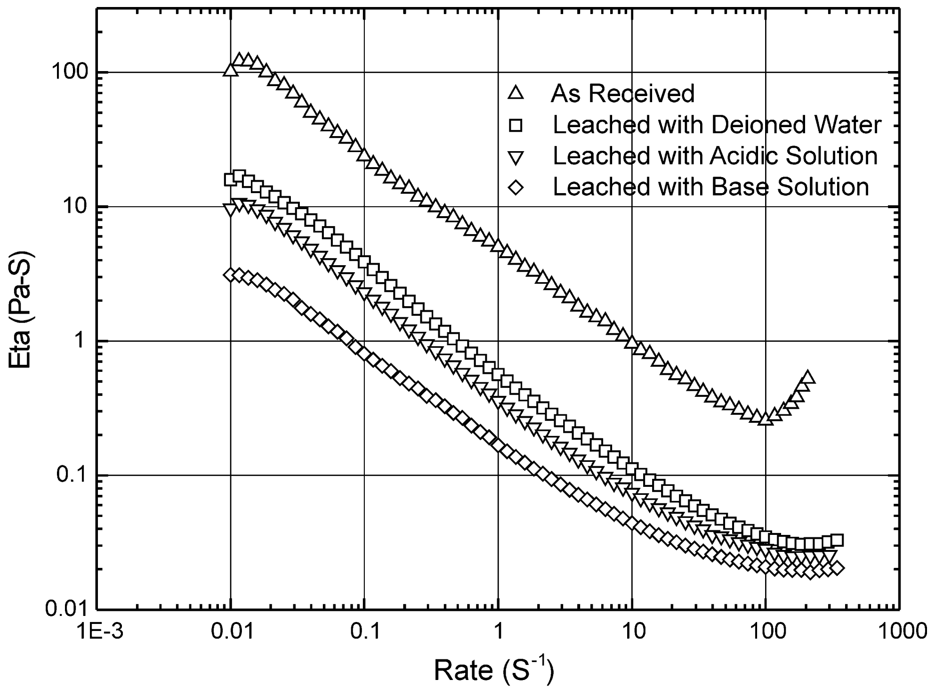

Fig. 1. Steady shear viscosity for leached and as-received SiC suspension at pH 10 and 38 vol.% solid.

Concentrated colloidal suspensions commonly display viscoelastic behavior, which can be characterized by oscillatory techniques. During oscillation measurements, a frequency-dependent shear stress or strain is applied to a suspension, and the shear moduli are obtained, The complex shear modulus (G^*) has a real and an imaginary component as given by

$$G^* = G' + iG''$$

G', which is proportional to the elastic modulus of suspensions, is a measure of elastically stored energy through particle–particle interaction while G'', which is proportional to suspension viscosity, characterizes dissipated energy through particle–medium or medium–medium interactions. Fig. 2 shows the effect of strain amplitude γ on the storage modulus G' of concentrated silicon carbide suspensions. At small strain amplitude, the suspensions are in the linear region where G' is constant with respect to γ, indicating the onset of the liquid-like behavior at higher strain amplitude. The storage modulus in the linear region may be extrapolated from the constant G' value at small strain amplitudes, which we designate as G_o'. We refer to the largest strain amplitude below which the suspensions show a linear viscoelastic response as the limit of linearity, γ_o. From Fig. 2 we can see that leaching of the powders results in a substantial decrease of G' from 10^2 to 10° pa and γ_o is found to increase from 0.2% for the as-received SiC suspension to 2% for the base leached suspension. γ_o increases with a decreasing G_o'.

Fig. 3 shows the frequency sweep of the different suspensions. All measurements were performed at low strain amplitude, $\gamma < \gamma_o$, where the viscoelastic response is linear and the storage modules G' can be obtained directly. It can be seen from Fig. 3 that the SiC suspensions change from being a strong elastic behavior for the as-received SiC suspension to displaying predominantly viscous for the base leached SiC suspension.

As for silicon nitride powders, leaching of the powders with deionized [10] or acidic aqueous solution [11] both resulted in a decrease in suspension viscosity. But the mechanism put forward by the authors for the leaching effect was inconsistent. Based on the research of Bergström and Bostedt [12], Liu et al. [11] attributed the decrease of viscosity to the reduction of the amount of silanol groups on the powder surface. They thought that too many silanol groups on untreated powder surfaces could result in multi-molecular adsorbed layers, which would increase the efficient solid volume fraction and decrease the fluidity. While the density of surface silanol groups was reduced by leaching, mono-molecular layers would be formed on SiC surfaces and the improved fluidity was observed. However, because the difference of zeta potential between the as-received and the leached powder was found to be very small, which indicates that there is no significant difference of silanol group quantity on the as-received and the leached powder surface, Larrz et al. [10] attributed the improvement of the rheological properties to the dissolution of the surface oxide layer and the change of some physical properties, such as surface roughness and size distribution.

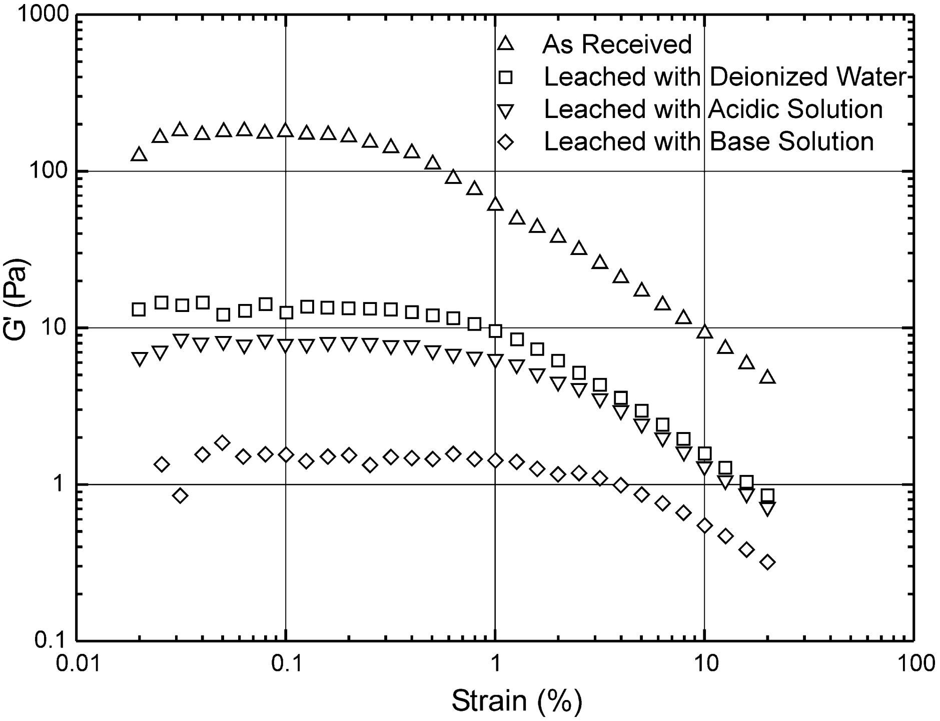

Fig. 2. Storage modulus as a function of strain amplitude for SiC suspension at pH 10 and 38 vol.% solid.

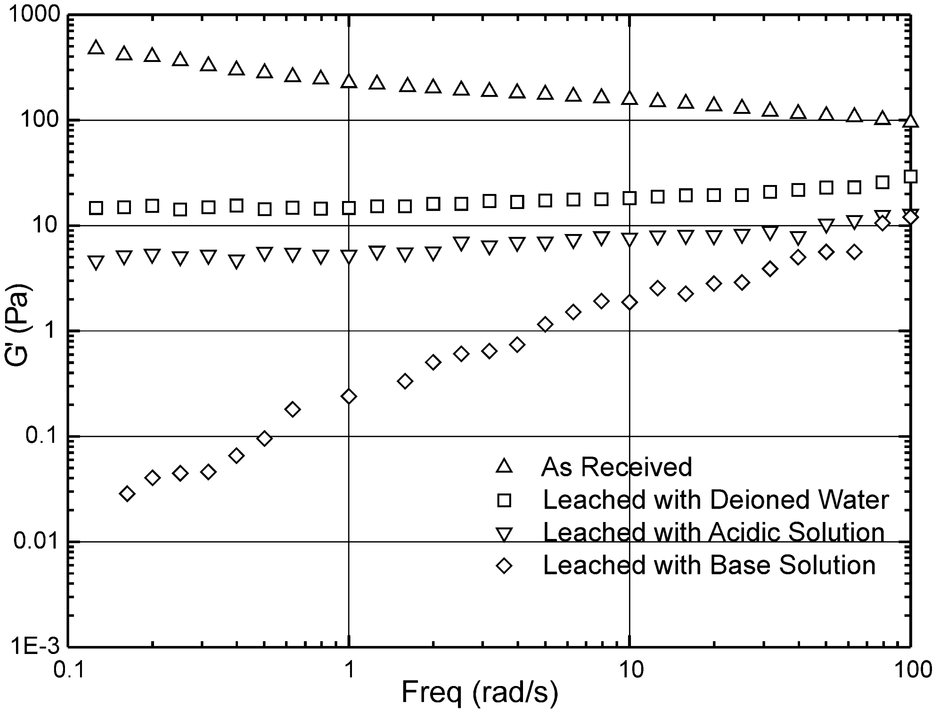

Fig. 3. Storage modules as a function of radian frequency for SiC suspension at pH 10 and 38 vol.% solid.

Few works have been done on the relationship between leaching of the SiC powder and the viscosity of their slurry. By comparing the titration curves for the well washed SiC powder (in deionized water and acidified electrolyte solution) and for the as-received powder, Whitman [13] concluded that the washing would not change the surface chemistry of the SiC powder. In our experiment, the DRIFT spectra of the as-received and various leached powders did not exhibit distinct difference and no peak at 3750 cm^{-1} due to the silanol group

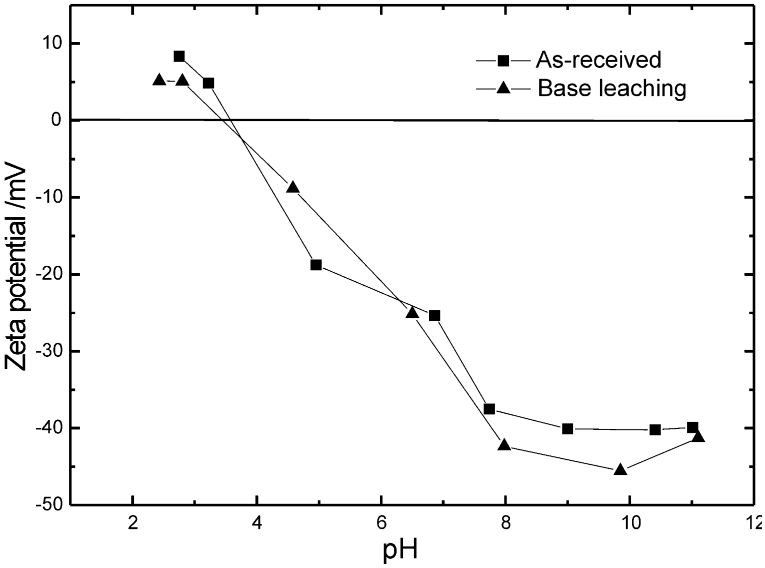

Fig. 4. Effect of base leaching on Zeta-potential of SiC powder.

were found in the spectra. By XPS and SIMS, Rahaman [14] pointed out that apart from oxygen, which exists mainly as a Si–O band, sodium, iron, fluorine, carbon and chlorine were the major impurities on the SiC powder surface. Chemical data of the powder used here also confirm the conclusion. So we propose that the reason for the improvement of rheological properties is that leaching effectively decreases the quantities of the surface impurity such as Na, Fe, F, C, Cl etc.

According to DLVO theory [1,4], the net force between particles in a suspension is the sum of the van der Waals force and the electrostatic force. The former is insensitive to ionic strength, whereas the latter is repulsive and is screened by counterions so that it depends on ionic strength. The thickness of the double-layer can be used to characterize the magnitude of this repulsive force and it is described by

$$\Lambda = \left(\frac{2000\mathrm{e}^2\mathrm{N_A}I}{\varepsilon_0\varepsilon_\mathrm{r}\mathrm{kT}}\right)^{-1/2} \tag{1}$$

where $\mathrm{N_A}$ is the Avogadro number, ε_0 is the dielectric permittivity of a vacuum, ε_r is the dielectric constant of the solvent, I is the ionic strength and e as well as kT have their usual meaning. Surface impunity on SiC powders will dissolve into suspensions and leads to the increase of ionic strength. The double-layer thickness decreases with increasing ionic strength [Eq. (1)].

Zeta potential derived successfully represents the electrostatic interaction between particles in dispersion. Higher Zeta potential is favorable to develop a good colloidal stability due to the generation of more strongly electrical double-layer repulsive forces between particles. The effect of base leaching on the Zeta potential of SiC is shown in Fig. 4. As can be seen, the isoelectric point (IEP) of SiC particles shifts slightly to the acid region and the Zeta-potential of SiC particles in the alkaline region increases in magnitude to a small extent for the leached powders.

As predicted by DLVO theory, weakly attractive aqueous suspensions will form and suspensions will be rendered unstable and even partially destablized by the increment of ionic strength. From our experimental results (Figs. 1–3), we can see that leaching of the SiC powder with a base solution is a very effective way to decrease the amount of foreign ions, and make the suspension convert from a weak flocculated to a well dispersed one.

3.2. Effect of calcination on the rheological properties

Fig. 5 shows the steady shear behaviors for various kinds of SiC powders which were calcinated at different temperatures. Oxidizing SiC powders at 200 and 400 °C slightly reduced the viscosity, the critical shear rate (r_crit) for the onset of shear thickening changes from 100 s^{-1} for the original powder to 200 s^{-1} for the one oxidized at 400 °C. The thickening effect has a tendency to become less pronounced with the oxidizing temperature. Powders oxidized at 550 °C display the lowest value of viscosity. SiC powders calcinated at 700, 850 and 1000 °C exhibit similar rheological behaviors, but the viscosity increased slightly compared with powders oxidized at 550 °C.

DFTIR spectra of the SiC powders calcinated at different temperatures in the range of 600–4450 cm^{-1} is shown in Fig. 6. The peaks at 897 and 782 cm^{-1} from Si–C vibration are found in all spectra. Bands in the range between 1050 and 1300 cm^{-1} are attributed to Si–O–Si bands and Si–O–C–O bands [15,16], which indicate

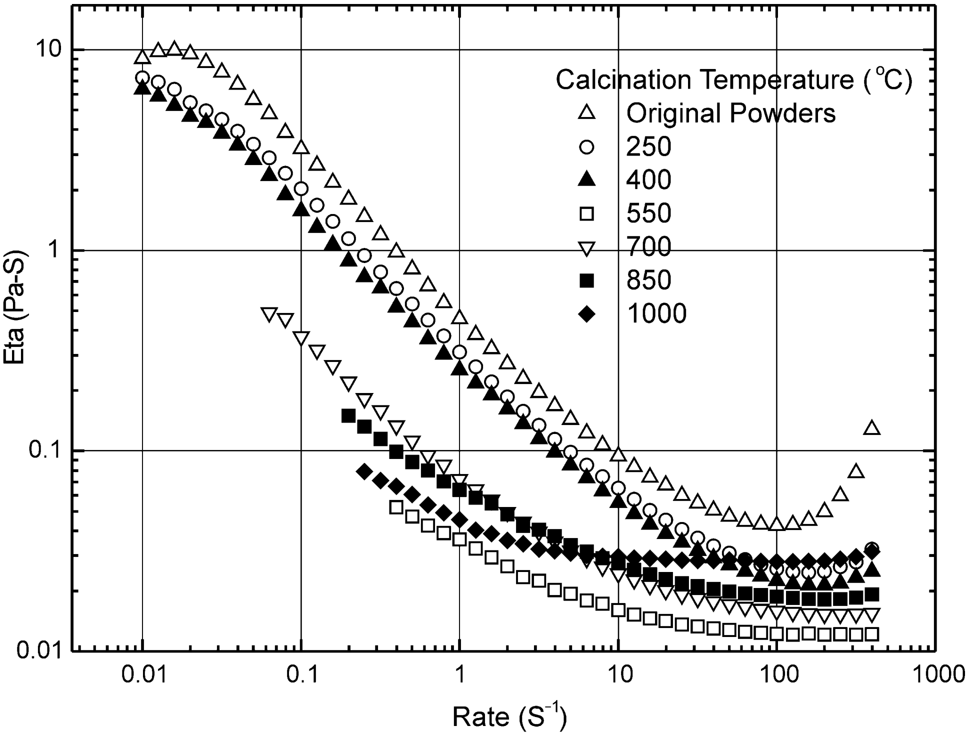

Fig. 5. Steady shear viscosity of aqueous suspensions containing SiC powders calcinated at different temperatures at pH10 and 42 vol.% solid.

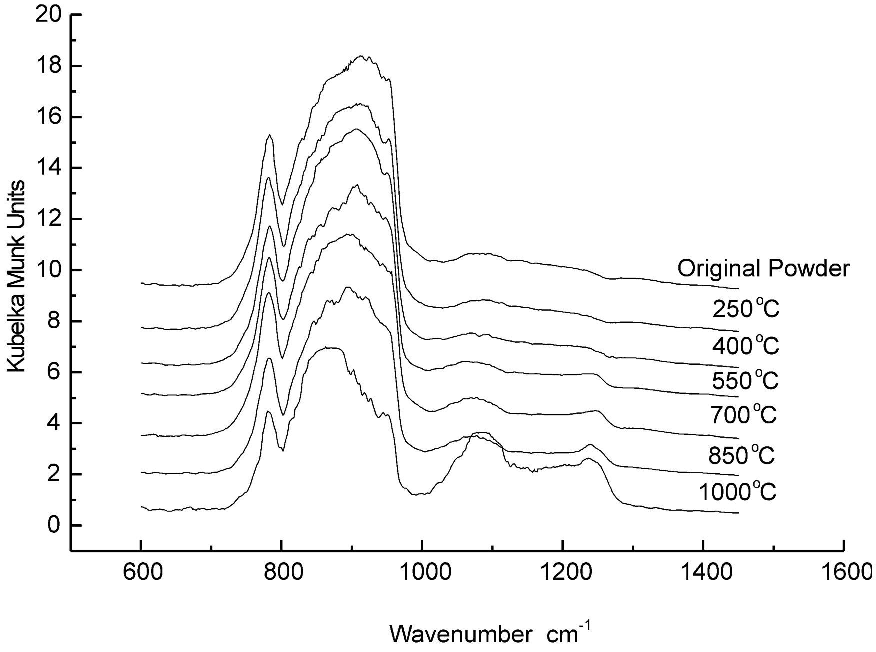

Fig. 6. DRIFT of different SiC powders calcinated at different temperatures.

partial oxidation of SiC to amorphous SiO_2. No major difference is found between the spectra of powder oxidized at 250 and 400 °C and the original powder. But when the temperature reached 550 °C, the peaks corresponding to the Si–O bands become increasingly prominent accompanying the decrease of the area under the peaks at 897 cm^{-1}. It is also noticed that the peaks at 897 cm^{-1} slightly shift to lower wavenumbers as the temperature increases. It is suggested that the band shift is related to the incorporation of Si–O bands in the Si–C network.

It is generally considered that the SiC powder surface consists of an oxide film [14] and the major functional group on the surface is probably the silanal group [17].

The surface charging of SiC powder in water is attributed to the dissociation of the silanal group according to the following reaction:

$$[SiOH_2]^+ \xleftarrow{H+} [SiOH] \xrightarrow{OH-} [SiO]^- + H_2O$$

By X-ray proton spectroscopy and electrophoresis measurements, Adar et al. [18] pointed out that Si–O and Si–C were the two kinds of surface sites on SiC powder. Based on the relatively high value of pH_{iep}, the author inferred that the carboxylate group (COO^-) was formed by the reaction between Si–C surface bond and water. Cerovié and Milonjie [19] also made this conclusion by calculating the intrinsic equilibration constant which was obtained by a potentiometric titration method. Silanol groups, which exhibit the characteristic band at 3745 cm^{-1}, is not observed in our experiments. So we assign the surface charging behavior of SiC powders to the hydrolysis of the surface Si–C group with water.

It is noticed that calcination treatment at 550 °C for 1 h improved the rheological properties significantly (see Fig. 5) and the number of Si–O groups increase to a certain extent accompanying the slight decrease of the Si–C groups (Fig. 5). At pH 10, the small amount of SiO_2 dispersed on SiC particle surfaces will dissolve according to the following reaction [20]:

$$SiO_2 + 2H_2O \Longleftrightarrow H_4SiO_4 \tag{2}$$

$$H_4SiO_4 \Longleftrightarrow H^+ + H_3SiO_3^- \tag{3}$$

$$H_3SiO_3^- \Longleftrightarrow H^+ + H_2SiO_3^{2-} \tag{4}$$

$H_3SiO_3^-$ and $H_2SiO_3^{2-}$ will be formed by Eqs. (2) and (3), which will increase the net charge on the SiC particle surface in water by the absorption of these anion groups. Maximum absorption level is obtained for the powder oxidized at 550 °C. As the calcrnated temperature reached 700 °C, the increase of SiO_2 on the SiC surface brings about the increase of ionic strength of the solution, which will compress the diffuse electronic double layer and lead to more viscous suspensions. At higher temperatures, calcination might result in the formation of hard aggregate held together by silica bridges to a certain degree. This can be used to explain the gradual decrease of shear thinning characteristics as calcination temperature increases from 700 to l000 °C (Fig. 5). The elimination of physisorbed or chemisorbed species at 200 and 400 °C contributed to the improvement of rheological performance.

4. Conclusion

The rheological properties of concentrated suspensions of SiC powders washed by different kinds of processes have been investigated. Base leaching processes can be successfully used to optimize the rheological behavior of SiC suspensions. The reduction in viscosity for the suspension with leached powders can be explained by the dissolution of foreign ions on the SiC surface. Consequently, the electrostatic interparticle repulsion is high enough to provide colloidal stability.

By comparing the rheological behavior of SiC powders calcined at different temperatures for 1 h, it was found that the hydration of Si–C bands and Si–O bands both contribute to the surface charging of SiC powder. But excessive hydration of Si–O bands will increase the ionic strength of the solution and decrease the repulsive force among SiC particles. The rheological properties were thus worse accordingly.

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