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Dispersing SiC powder and improving its rheological behaviour

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Abstract

The surface properties of silicon carbide powder was investigated by zeta potential measurements and compared with silicon oxide powder. The quantitative adsorption behaviour of polyethylene imine onto silicon carbide powder in aqueous solution is measured with UV adsorption spectrum at three pH ranges. In acid and neutral pH ranges, the adsorption isotherms belong to Langmuir type and reach the maximum value around 0.038 mg/m^2. In basic range, the adsorption amount is more than 10 times that in the low pH range, as high as 0.456 mg/m^2. The FTIR spectra are presented to verify this adsorption. Improved rheological properties of slurries are obtained through addition of PEI. An optimum amount of dispersant is given as 1.0 dwb% when the solid content is kept as 40 vol%. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Adsorption; Dispersion; Polyethylene imine; Rheology; SiC

1. Introduction

Silicon carbide is currently used in a number of industrial applications such as heat engine, gas turbines and high temperature energy conversion systems.[1,2] However, an important aspect of the fabrication sequence, which can improve subsequent sintering and final properties of bodies, is the achievement of a homogenous structure and good packing of powders at the consolidation stage of the green body. Increasing attention is, therefore, directed on the colloidal processing method, which may result in a more homogenous green microstructure.[3,4] In order to disperse a powder in water, the surface charge properties of the powder have to be controlled. [5] Knowledge about the surface characteristics is essential when choosing the mechanism to obtain dispersion with good colloidal stability. [6] When, for instance, electrostatic stabilization is used, the pH range in which the particles have a high surface charge, which will give a high repulsion and good stabilization, has to be known. Steric or electrosteric stabilization requires strongly attached and dense layers of polymer or polyelectrolyte on the powder surfaces. However, it is well known that the surface charge properties of different ceramic powders vary with the type of powder and in some cases even with the producer [7]. Due to the differences in surface properties, it is often necessary to use a certain dispersing agent for each separate powder. Polyethylene imine (PEI) is a common used dispersant in ceramic colloidal process. It is positively charged in a low pH range and provides a steric repulsion force via its branch. Previous employment of PEI as a dispersant was applied to hematite, [8] silica, α-SiC [9] and zirconia [10] in a pH range lower than pK_a of PEI. In this paper, the adsorption behaviour of PEI at three different pH ranges were studied and compared. Two different adsorption mechanisms are proposed to explain the differences. The dispersion of SiC with polyethylene imine has been investigated as an improved method to obtain stable and high solid content slurries.

2. Materials and methods

Silicon carbide is purchased in China with mean particle size as 0.88 μm and BET surface area as 10 m^2/g. Powder SiO$_2$ was provided by Zhoushan Nanostructure Materials Company of China with particle size of 20 nm. Solutions of hydrochloride acid and sodium hydroxide were used to adjust the pH values. A solution

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of sodium chloride was used to adjust the ionic strength of suspensions in electrophoretic experiments. All reagents were of analytical grade. Polyethylene imine (PEI) with a molecular weight of 50,000 was purchased from BDH laboratory suppliers, England. The 50 wt.% PEI (claimed by the producer) aqueous solution was diluted and adjusted with HNO_3 or NaOH to a certain pH value.

Electrophoretic mobility of SiC particles as function of pH was determined on Zeta Plus (Brook Heaven Instrument Corporation, NY, USA) and converted into zeta potential by the Smoluchowski equation. The 0.01 vol.% SiC, SiO_2 suspensions were regulated by HCl and NaOH to fixed pH value and ultrasonicated for 5 min prior to zeta potential analysis. Stock SiC suspensions of 5 wt.% solid loading were prepared with the fixed amount of PEI solution and ball milled for 24 h. Particles and supernatant were separated by centrifugation at 3000 rpm for 60 min. The remaining PEI concentration is determined by UV-vis spectrophotometer (UV-1602PC, Japan) at the wavelength of 250 nm. The adsorbance versus concentration plots followed in an identical Beer's law curve. The error for the adsorption results is estimated not exceed 0.5%, which mainly comes from the signal's drift and noise from the instrument. Adsorption measurements were made at room temperature at three different pH values, pH 3.57, 6.61 and 11.10. The concentration of PEI adsorbed on SiC was then calculated by detracting the left in supernatant from the added amount.

Rheological characteristics were determined using cylindrical measuring system on rotational viscosimeter (Model Rheomat 260, Mettler Torledo AG, Switzerland). Measurements were performed at a temperature of 25°C. To eliminate artifacts from different treatments during the filling procedure, the samples were presheared for 3 min, followed by 5 min at rest. All the suspensions used for the rheological studies were prepared as volume percent. The concentrations of the dispersant expressed as the dry weight percentage of the powder basis (dwb%).

3. Results and discussion

3.1. The electrophoretic properties of silicon carbide powders

Fig. 1 shows the relationship of the Zeta potential as function of pH. The isoelectric point (IEP) of SiC and SiO_2 is almost overlapped at pH 2. After being washed by 5% HF for several days, the IEP of the powder SiC moved to 4.7. Table 1 shows the chemical analysis result of the main components in SiC powder. We can infer that powder SiC has an oxide layer on the surface. After washing with HF, the oxide layer on the SiC was dissolved, the content of oxygen is lowered.

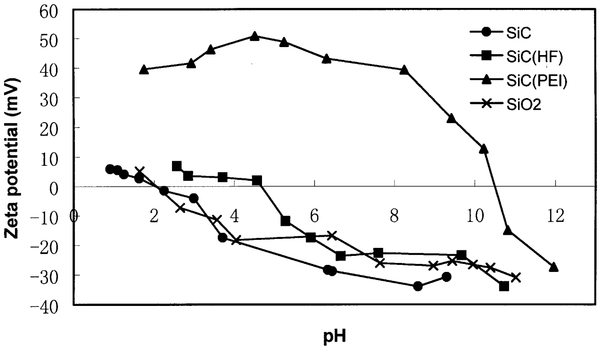


Fig. 1. The isoelectric points of powders SiC, SiO_2, SiC (washed by HF), SiC (with PEI-H^+).

Table 1
The main components of SiC powder before and after washing with HF

Main components (%)	SiC	SiC (washed with HF)
C	28.73	28.54
O	0.84	0.29
Si	69.38	69.57

The surface charge of SiC is negative when pH is higher than 2. Polyethylene imine, ionized by addition of a strong acid possessed positive charge and could be adsorbed onto SiC powder surface by electrostatic adsorption. When PEI-H^+($pH = 3.57$) is added into the suspension, the surface charge then becomes positive and the isoelectric point of SiC is moved to pH 10.5.

3.2. Adsorption studies

Fig. 2 shows the adsorption isotherms of PEI on silicon carbide powder at pH 3.57 and 6.61 respectively. The amount of PEI adsorbed on silicon carbide is dependent on the overall dispersant concentration. For the two measured pH values, the adsorption curves attained saturation with increasing addition of PEI. At pH 3.57,

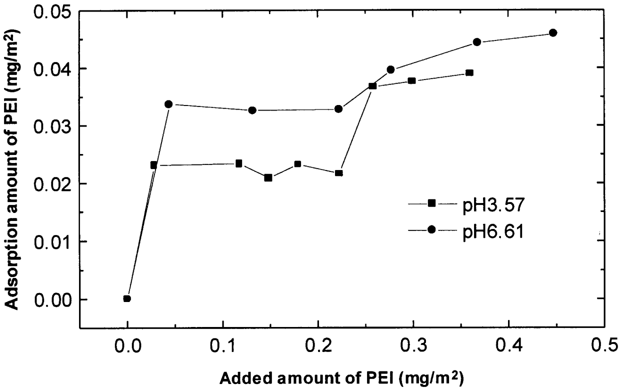


Fig. 2. Adsorption amount of PEI at pH 3.57, 6.61 versus the total added amount PEI.

the saturation adsorption value is approximately 0.038 mg/m^2, whereas at pH 6.61, the saturation adsorption value is about 0.046 mg/m^2.

Fig. 3 is the adsorption isotherm of PEI onto SiC at pH 11.10. The amount of PEI adsorbed increased sharply at low concentration and then attained saturation with increasing concentration followed by a little decrease. The maximum amount of adsorption value is about 0.456 mg/m^2, almost 10 times compared to that of the acid and neutral pH range. The difference observed in adsorption isotherms in acid and basic pH range can be associated with different mechanisms and the configuration change of PEI. At acid and neutral pH range, SiC particles are negatively charged and PEI is positively charged. The adsorption mechanism of PEI on solid surfaces seems to be mainly by electrostatic interaction. The relatively lower adsorption value indicates the flattening form of PEI. Very similar results were obtained in previous study for Fe_2O_3 and SiO_2.[8,9] At pH 11.10, SiC particles are negatively charged, while PEI molecules are neutral, the adsorption is mainly occurred via hydrogen bonding.

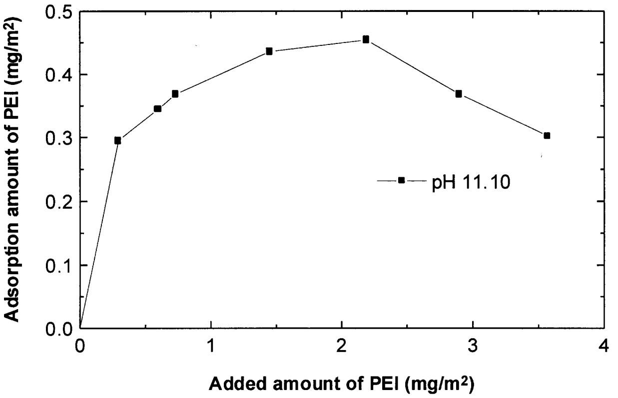


Fig. 3. Adsorption amount of PEI at pH 11.10 versus the total added amount PEI.

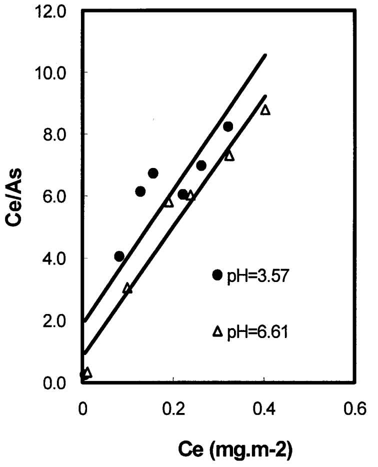


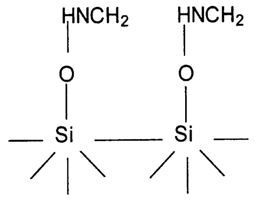
Fig. 4. Replot of Fig. 2 according to Langmuir equation.

Fig. 4 is reanalysed from Fig. 2 using the langmuir monolayer adsorption equation:

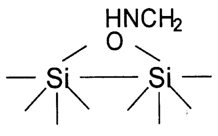
$$\frac{Ce}{As} = \frac{Ce}{Cm} + \frac{K}{Cm} \qquad (1)$$

The data are also plotted as Ce/As, versus Ce, where Ce is the equilibrium concentration of PEI in solution, As is the adsorbance of PEI and Cm the monolayer adsorbance of PEI, K is the constant. Straight lines are observed, which indicated that these isotherms are of langmuir monolayer type adsorption. Because the slope of these straight lines represent the reciprocal of the monolayer adsorption of PEI, the results in Fig. 4 indicate that the amount of monolayer PEI adsorption does not change much with the two pH values. The values of Cm is 0.033 mg/m^2 at pH 3.57 and 0.040 mg/m^2 at pH 6.61.

Fig. 5 is the adsorption isotherm of powder SiC washed by HF at pH 6.61. Almost no adsorption amount of PEI can be detected. After being washed by acid HF, the surface layer of SiO_2 has been dissolved. These results indicate that the adsorption of PEI onto SiC surface is mainly by the adsorption onto the surface layer of SiO_2 via electrostatic interaction. Two types of the possible hydrogen bonding can be described as follows, via hydrogen bonding with free surface silanol (1) or siloxane (2).



(1)



(2)

The FTIR spectra of silicon carbide powder with and without PEI at three different pH ranges are presented

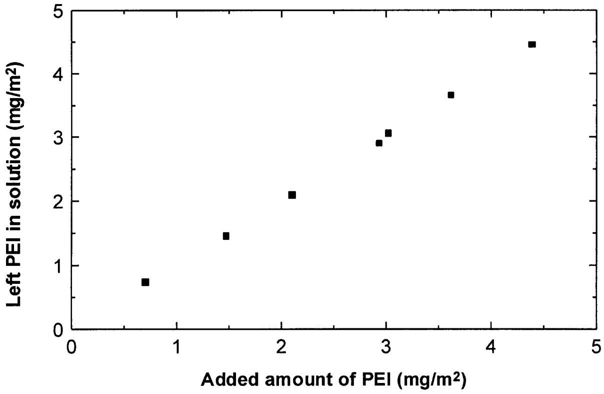


Fig. 5. Adsorption amount of PEI on SiC powder washed by HF at pH 6.61.

in Fig. 6. Curve 1 is the spectrum of PEI-H^+ at pH 3.57. Infrared band at 688 cm^{-1} is related with the asymmetric vibration mode of –NH and at 1637.5 cm^{-1} related with the C–N stretching mode. Bands at 2110 and 2357.5 cm^{-1} are characteristic of the symmetric and asymmetric vibration of–NH_2^+. Curve 2 is the IR spectrum of silicon carbide powder. The bands at 810 and 912.5 cm^{-1} are associated with the Si–C vibration. Curves 3, 4 and 5 correspond with the silicon carbide powder adsorbed PEI at pH values of 3.57, 6.61 and 11.10 respectively. Several major differences are observed when comparing the infrared spectra of the pure PEI-H^+ and silicon carbide powder. Bands at 2110 and 2357.5 cm^{-1} are totally disappeared after adsorption onto the SiC powder. The band at 810 cm^{-1} of SiC moved to 835 cm^{-1} after adsorption, which verifies the interaction between the silicon carbide powder and the –NH group. The interaction can be carried out via electrostatic force in acid and neutral pH range or through the hydrogen bonding at basic pH range. The weaker intensity of peak 1635.7 cm^{-1} in curve 1 after adsorption is another proof that there must have some interaction between the silicon carbide powder and PEI. A new peak at 1380 cm^{-1}, which related with the NH_2^+ vibration appeared at pH 3.57 and 6.61in curve 3 and 4. The FTIR spectra strongly support the surface reaction at the PEI and SiC powder interface after adsorption.

3.3. Rheological behavior

The absolute value of zeta potential is above 30 mV when pH is higher than 8. From the viewpoint of electrostatic mechanism, it is possible to obtain stable slurries of silicon carbide powder by adjusting pH. In fact, the suspensions formed by silicon carbide powder has very poor rheological properties, it cannot flow even when the solid content is only 30 vol.% at any pH values. Dispersant PEI-H^+(pH = 3.57) is added into slurry to improve its rheological properties. The effect of shear rate on the relative viscosity of the ceramic dispersion in presence of PEI-H^+ is shown in Fig. 7. The addition of PEI-H^+ improved much of the flowability of the slurry. The viscosity of 30vol% content is only 10.3 mPas when the shear rate is 20 s^{-1}. When the volume fraction is raised as high as 40 vol.%, three of these suspensions display a shear thinning behaviour with a drop of one order of magnitude of the viscosity from low shear rate to high shear rate. This shear-thinning phenomenon can be related to a change of the colloidal stability. The addition of dispersant PEI-H^+ can effectively improve the flowability of SiC slurry. There exists an optimum amount of dispersant. From Fig. 7, for the solid content as 40 vol.%, the optimum amount of dispersant is 1.0 dwb%.

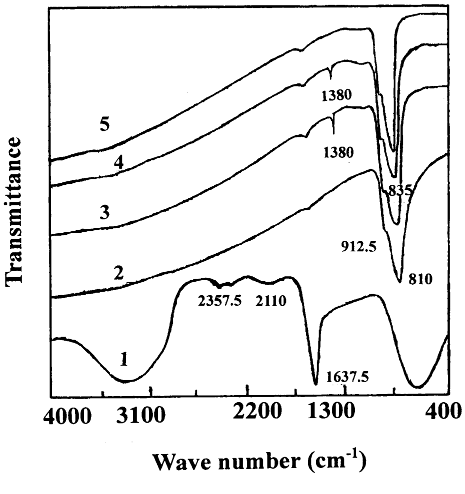


Fig. 6. FTIR spectra of PEI, SiC and adsorbent at different pH range. Curve-1, PEI at pH 3.57; curve-2, SiC powder; curve-3, SiC-PEI adsorbent at pH 3.57; curve-4, SiC-PEI adsorbent at pH 6.61; curve-5, SiC-PEI adsorbent at pH 11.10.

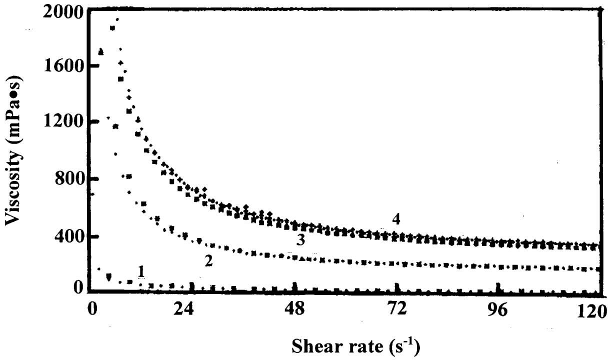


Fig. 7. The relationship of viscosity and shear rate of slurries formed by powder SiC in the presence of PEI at pH 3.57. Curve-1, 30 vol.%, 0.5 dwb%PEI; curve-2, 40 vol.%, 1.0 dwb%PEI; curve-3, 40 vol.%, 1.5 dwb%PEI; curve-4, 40 vol.%, 2.5 dwb%PEI.

4. Summary

The surface chemistry of silicon carbide powder was characterised via electrophoretic properties and chemical analysis. The adsorption behaviour of PEI onto SiC is strongly dependent on pH. At acid or neutral pH range, the adsorption amount is of low value 0.038 mg/m^2, while at high pH range, the total adsorption amount has been raised 10 times, 0.46 mg/m^2. The adsorption occurred via the electrostatic interaction between the negative powder surface and positive charge of PEI at acid or neutral pH range. Hydrogen bonding interaction of nonelectrostatic nature accounts for the driving force of adsorption in high pH range. The adsorption of PEI onto SiC powder is carried out through the oxide silica layer of SiC powder. The addition of PEI onto SiC can raise its solid content from 30 to 40 vol.%, and the optimum amount is 1.0 dwb% for 40 vol.% content.

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