

The surface characteristics of polyacrylamide-coated silicon carbide powder used in the preparation of highly concentrated ceramics suspensions

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Polyacrylamide (PAAM) coating layer was formed by chemical methods on the SiC powder surface. The surface characteristics of polyacrylamide (PAAM)-coated silicon carbide (SiC) powder were analyzed. The carbonyl band of amide and NH_2 deformation absorbing band existed at 1638 cm^{-1} , 1619 cm^{-1} in the Fourier Transform Infrared Spectra (IR).

Transmission electron microscopy (TEM) showed clearly the powder was coated by an organic compound layer which was PAAM judged by the reaction. The result of Differential Scanning Thermal Analyses (DSC) and Thermogravimetric (TG) showed the oxidizing decomposition temperature of PAAM was 411.9°C . The coating layer changed the surface characteristics of the SiC powder. At $\text{pH} = 5$, the suspensions of homogeneity and stability with 55 vol% solid content was prepared. © 2003 Kluwer Academic Publishers

1. Introduction

Preparation of highly concentrated ceramics suspensions of proper rheological property, homogeneity and stability is not only the applied basis of colloidal processing but also one of the ways to effectively control the microstructure of green body so as to reduce the defects inside of the materials and improve the properties and reliance of ceramics materials. Thus, nowadays more and more attention is paid to the study on the highly concentrated ceramics suspensions [1–4].

The formation of the highly concentrated ceramics suspensions is concerned with the surface characteristics of the powders [5]. The results indicate that proper surface characteristics can improve the stability, dispersion capability, and rheological property and increase the solid content of the suspensions. How to improve the surface characteristics of the powders has been one of the important research directions to prepare highly concentrated ceramics suspensions.

Silicon Carbide is one of the important ceramics materials that is widely used for structural application at high temperature [6]. At present, one of the problems to be solved in preparing the highly concentrated SiC

ceramics suspensions is the improvement of the surface characteristics of powders. The previous researches have been focused on two aspects [7, 8]. One is to erase the high valence anti-charge by rolling and acid washing [9–14]. Thus, the repulsive force between particles has been diminished, the particles dispersion capability has been enhanced, and the solids content has been increased. However, the disadvantage of this methods lies in its low efficiency and time-consumption; For the other, the SiC powder is coated with Aluminum Oxide [15] (Al_2O_3); thus, the powder behaves in a manner similar to Al_2O_3 , and then by selecting proper dispersants, the highly concentrated SiC ceramics suspensions is prepared. However, it is difficult to obtain the completed coating layer by such method.

In the paper, different method compared to the above is proposed. The APS (short for “3-aminopropyltriethoxysilane”) layer has been produced on the SiC powder surface by the reaction between APS and hydroxyl of the powder surface. Then, Acrylamide (AAM) has been grafted from the APS-coated surface by using of a redox system consisting of ceric ion and reducing groups on the surface. Finally, the PAAM coating layer

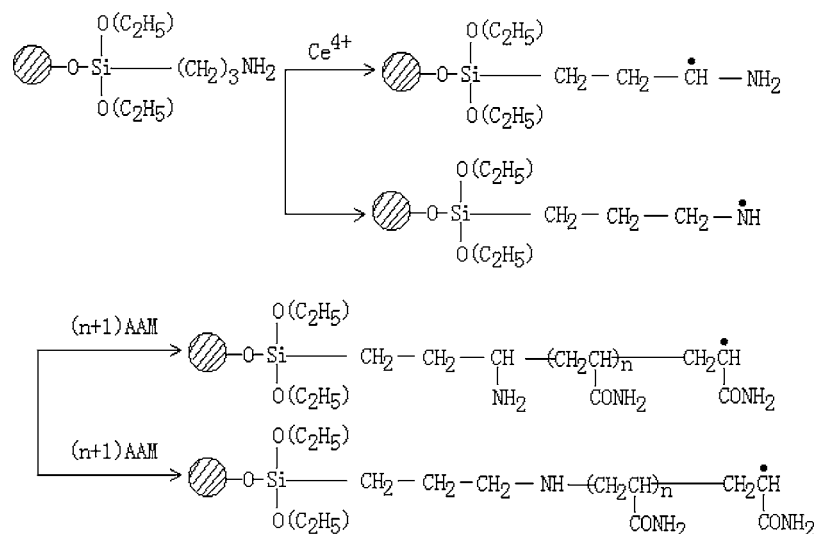


Figure 1 The chart of PAAM-coated SiC powder.

has been formed [16–20], as shown in Fig. 1 (See, P10: Fig. 1. The chart of PAAM-coated SiC powder). The surface characteristics of PAAM-coated SiC powder and its application in preparing the highly concentrated ceramics suspensions have been mainly studied.

2. Experiment

2.1. Raw material

SiC powder (Rs07, HuaMei Grinding Material and Apparatus Company, China) were used. The powder characteristics are shown in Table I (See, P11: Table I. The physical and chemical characteristics of SiC powder). AAM (Tianjin Da Mao Chemical Instrument Company, China) and APS (Wuhan University Chemical & New Material Company Limited, China) were analytical-grade. pH value was adjusted by analytical-grade HCl and NaOH (1 mol/ml). The water was distilled.

2.2. Process

Into a flask that contained 100 g of SiC, 200 ml of 5% toluene solution of APS was added. The mixture was refluxed in a stream of nitrogen for 5 h. After the reaction, the SiC was extracted and dried for 24 h in vacuo at 110°C.

Into the same flask, some of APS-coated SiC powder and aqueous solution of AAM were added. After deaeration of the mixture by bubbling nitrogen, 1 ml solutions of ceric ammonium nitrate in 1 mol·dm⁻³ nitric acid were added. The process was conducted at 30°C with dry nitrogen stirring. After the reaction, the reaction mixture was filtrated and the product was dried in vacuo at 45°C. Then PAAM-coated SiC powders were obtained.

TABLE I The physical and chemical characteristics of SiC powder

Raw material	d_{50} (μm)	Special		SiC (wt%)	Free Si (wt%)	O (wt%)	Free C (wt%)	Fe ₂ O ₃ (wt%)
		area (m ² ·g ⁻¹)						
Fine SiC powder	1.2	4.19	>98	0.45	0.49	0.66	<0.5	

2.3. Measurements

2.3.1. Measurement of fourier transform infrared spectra

The Fourier Transform Infrared Spectra was used to characterize the surface state of uncoated and coated SiC powder. To record the infrared spectra, the powders were compacted with KBr. For comparison, the PAAM-coated SiC powders that had been dipped into the water and the organic solute agent, respectively, were also measured.

2.3.2. Measurement of Zeta potential

ZetaPals instrument (Brookfield, Britain) was used to measure the Zeta potential of powder surface. Using the distilled water as solvent, 0.4 mg/ml SiC suspensions were prepared and then ultrasonicated and stirred for 15 min prior to the measurement to ensure that only the single particles were measured; pH value was adjusted by using analytical-grade HCl, NaOH and was demarcated by using PXS-5 digital acidity indicator at 25°C. The average value of the three points in each measurement was recorded.

2.3.3. Measurement of stability

Stability was measured by sediment experiment, which was performed by dispersing 16.89 g SiC powders in 100 ml distilled water, using calibrated glass cylinders with scale. The upper of cylinder was sealed by plastic film to ensure minimum evapour, the suspensions were ultrasonicated and stirred for 30 min and allowed to stand undisturbed for several days. Time and sediment height were recorded. The stability varies with the change of the relative height of the sediment, the ratio of the height of opacitus suspensions to the total height of suspensions. The higher the height value was, the better the stability was.

2.3.4. Measurement of solids content

10 g distilled water was balanced exactly and then SiC powder was added into the water gradually. According to the different amounts of powders, the

suspensions with different solid content were obtained, and the equation is $\text{vol}\% = (m_{\text{powder}}/\rho_{\text{powder}}) * 100\% / (m_{\text{powder}}/\rho_{\text{powder}} + m_{\text{water}}/\rho_{\text{water}})$. In this paper, the highest solids content of suspensions refers to the solid content value from the time of adding powders into the distilled water to that of the formed suspensions could not flow.

2.3.5. Analysis of particle size

The particle size of the uncoated and coated SiC powders was examined by laser particles size instrument (Marlven, Britain) to ensure the flocculation state of uncoated and coated SiC powder.

2.3.6. Observation of dispersion

Dispersion of uncoated and PAAM-coated SiC powders in the distilled water was observed by Transmission electron microscopy (TEM, JEM-100CX) and the coating state on the powder surface was also observed with it.

2.3.7. Analysis of TG-DSC

PAAM-coated SiC powder was measured by TG and DSC (STA 449C, Jupiter, German nachi), which was conducted in air atmosphere at a heating rate of 10°C/min.

2.3.8. Measurement of viscosity and rheological property

The viscosity and rheological property were examined by NXS-11A rotation viscometer at constant temperature (25°C). The shear rate was increased from 5.6 rpm to 360 rpm, with each shear rate keeping for 1 min and viscosity being recorded; then the shear rate was decreased from 360 rpm to 5.6 rpm, with each shear rate keeping for 1 min and viscosity being recorded again.

3. Results and discussion

3.1. IR of PAAM-coated SiC powder

IR of uncoated, APS-coated and PAAM-coated SiC powders are showed in Fig. 2 (See, P12: Fig. 2. The IR of uncoated SiC, APS-coated SiC and PAAM-coated SiC powder). According to the chart, for the uncoated SiC powder, its curve smoothes between 1404 cm^{-1} –939 cm^{-1} and no other absorbing band exists; whereas for the APS-coated SiC powders, apparent absorbing band appears on the curve when the wave-number is between 1404 cm^{-1} –939 cm^{-1} . It is certified that 1089 cm^{-1} is the Si–O vibration characteristics peak [21] which indicates the presence of APS on the SiC powder surface. For the curve of uncoated SiC powder, the strength of silanol absorbing band at 939 cm^{-1} is strong, while for the APS-coated SiC powder, the curve becomes smooth at 939 cm^{-1} and the strength of absorbing band decreases, the reason of which is the reaction between APS and –OH site causes the elimination of the silanol of SiC powder surface in part. IR of PAAM-coated SiC powder is different from that of the uncoated SiC powder but similar to that of APS-coated SiC powder. At 1089 cm^{-1} , the Si–O absorbing band exists, which indicates that the structure of coating APS is not destroyed by coating PAAM and that PAAM is grafted at the end of APS. In the characteristic absorbing band of amide [21], the carbonyl band of amide is close to 1640 cm^{-1} and NH_2 deformation absorbing band is close to 1620 cm^{-1} . For the IR curve of PAAM-coated SiC powder, the absorbing band exists at 1638 cm^{-1} , 1619 cm^{-1} , which indicates there exists amide group in the coating layer. Identified from the raw materials and reaction processing, it is PAAM.

PAAM-coated SiC powder is dipped respectively into the water and the organic agent for 24 h and then it is dried. The IR is shown in Fig. 3 (See, P13: Fig. 3. The IR of PAAM-coated SiC and PAAM-coated SiC dipped in water or organic solvent). After being dipped in water and organic agent, IR of PAAM-coated SiC

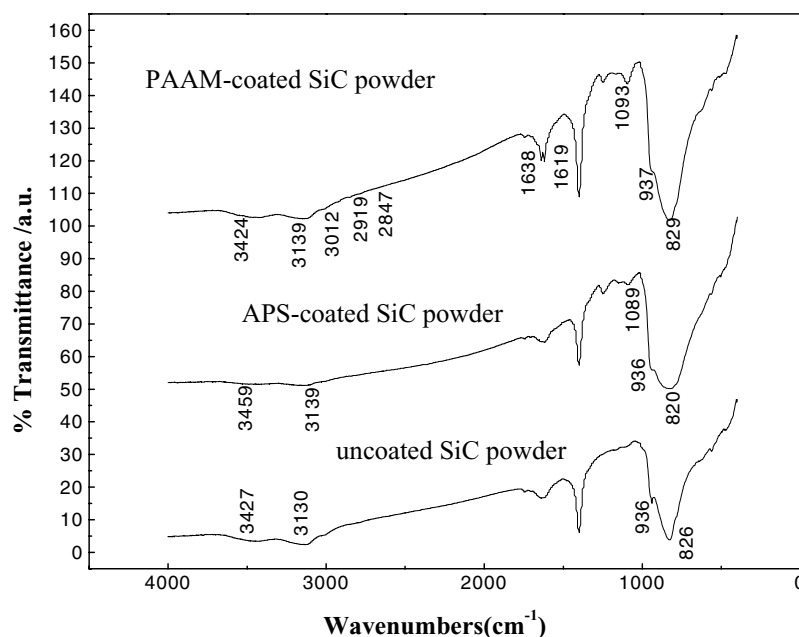


Figure 2 The IR of uncoated SiC, APS-coated SiC and PAAM-coated SiC powder.

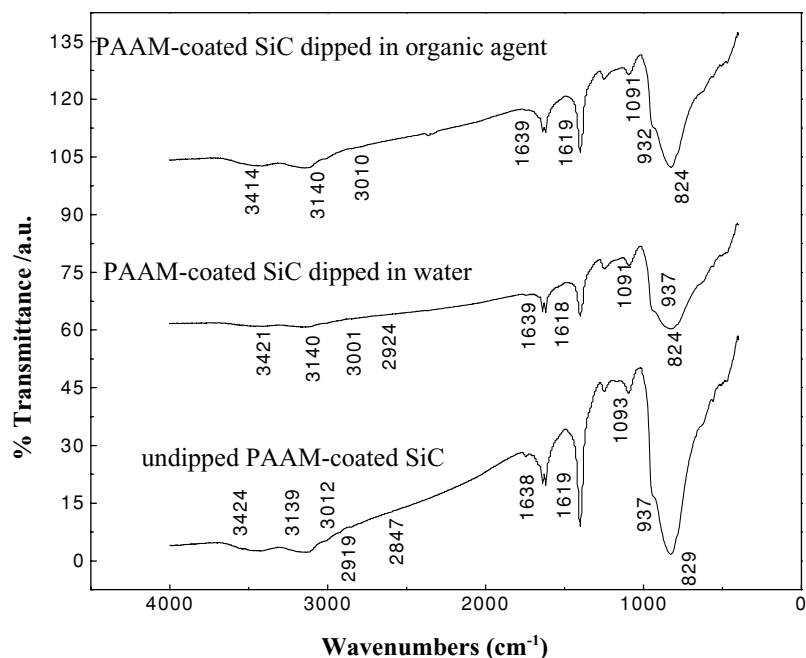


Figure 3 The IR of PAAM-coated SiC and PAAM-coated SiC dipped in water or organic solvent.

powder does not change notably, and all the characteristic absorbing bands exist, which indicates that the combination is close between the coating layer and SiC powder surface and that the combination force is strong. It can be certified that the formation of PAAM coating layer has been grafted via chemical reaction.

3.2. TEM analyses of PAAM-coated SiC powder

TEM photographs of uncoated and PAAM-coated SiC powders are showed in Fig. 4 (See, P14: Fig. 4. The TEM of uncoated SiC powder) and Fig. 5 (See, P15: Fig. 5. The TEM of PAAM-coated SiC powder). At the same magnification, there is a slight layer on the surface of PAAM-coated SiC powders, whereas the light layer does not exist on the surface of uncoated SiC powder which indicates that the surface characteristics of powder has been changed. Seeing from another point of view, the coating layer is formed on the surface. The

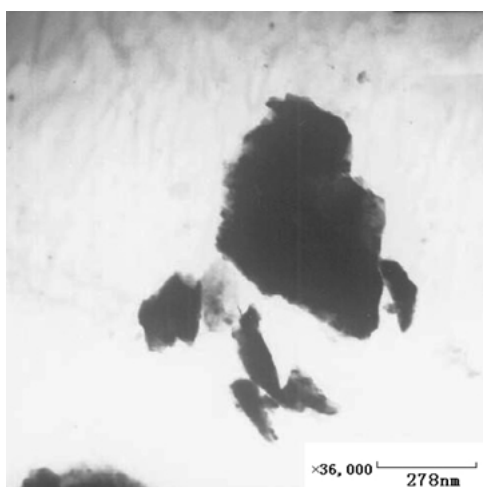


Figure 4 The TEM of uncoated SiC powder.

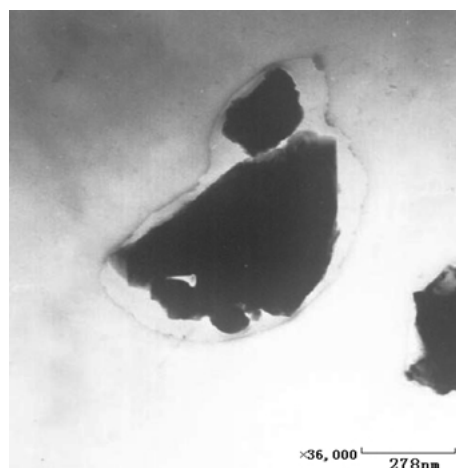


Figure 5 The TEM of PAAM-coated SiC powder.

shape of the coating layer is similar to that of the powder. Except for the edges and corners, the thickness of the coating layer is even of 55 nm and about 1/10 of particle size. The coating layer was transparent and homogeneous and the outline is clear. The reasons for the transparency of the coating layer in TEM photograph may be that the layer forms a net structure and electron can transmit the layer and thus make it transparent.

3.3. Thermal analysis of PAAM-coated SiC powder

As shown in Fig. 6 (See, P16: Fig. 6. The TG-DSC analysis of PAAM-coated SiC powder), the clear exothermic peak exists at 221.1°C, 441.9°C and is accompanied with the changing of the mass, which indicates there is organic compound on the surface of the SiC powder. As temperature increases, the coating organic compound is oxidized and decomposed under the air atmosphere. The oxidizing process of organic substance is exothermic and accompanied with the weightlessness

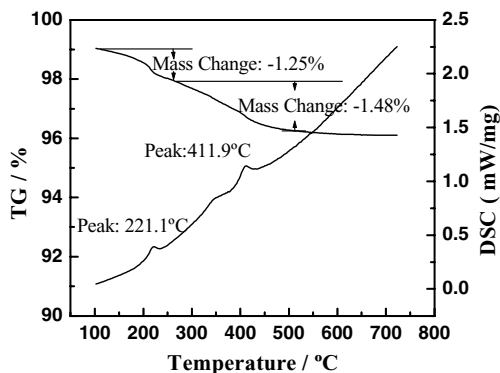


Figure 6 The TG-DSC analysis of PAAM-coated SiC powder.

resulting from CO_2 volatilizing, which causes two exothermic peaks on the DSC curve and two points which indicate weightlessness on the TG curve. According to the data [21], the decomposing temperature of PAAM is about 410°C corresponding to 411.9°C in the experiment. Another exothermic peak at 221.1°C is the oxidizing decomposition temperature of APS.

3.4. Zeta potential of coated SiC powder

Zeta potential of uncoated and coated SiC powders is showed in Fig. 7 (See, P17: Fig. 7. The relationship curve of pH value vs. Zeta potential). As shown in the chart, Zeta potential of two SiC powders are different. It indicates that each powder has different surface characteristics. The isoelectric point (IEP) of uncoated powder is close to $\text{pH} = 3$, basically, the higher the Zeta potential is, the higher the absolute value of Zeta potential is, at $\text{pH} = 8$, Zeta potential is -35 mV . Considering electrostatic, uncoated SiC powder can be easily dispersed under basic condition. IEP of the coated powders is shifted, when IEP of PAAM-coated SiC powder is close to $\text{pH} = 7$ and the higher Zeta-potential is under the acid condition; at $\text{pH} = 2$, Zeta potential is about 50 mV . Hence, the surface characteristics of coated SiC powders are different from that of the uncoated SiC powder and this has manifested the properties of the coating layer.

3.5. Stability of SiC suspensions

As shown in Fig. 8 (See, P18: Fig. 8. Stability of uncoated SiC powder with different pH value), the vari-

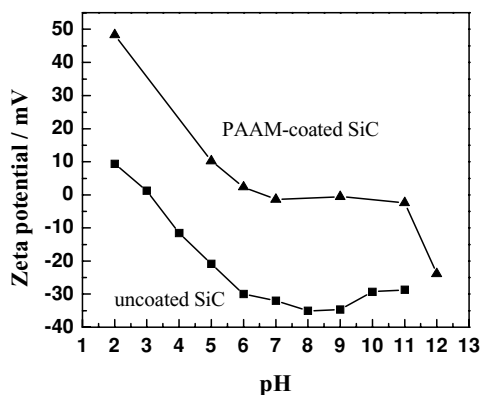


Figure 7 The relationship curve of pH value vs. Zeta potential.

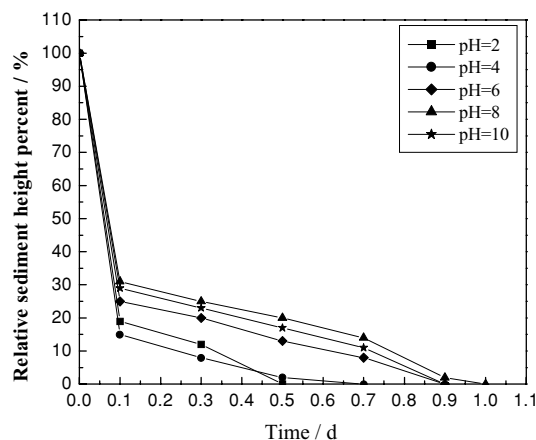


Figure 8 Stability of uncoated SiC powder with different pH value.

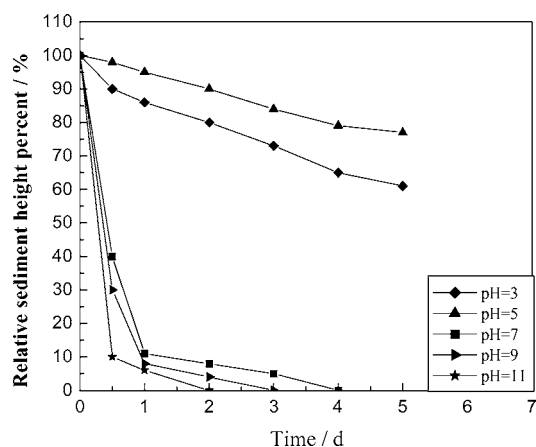


Figure 9 Stability of PAAM-coated SiC powder with different pH value.

ation of pH value has an effect on the stability of the suspensions. For uncoated SiC powder, the stability of suspensions is better at $\text{pH} = 8$ compared with that at other pH values, which indicated that the uncoated SiC powder is easily dispersed under the basic condition. For the PAAM-coated SiC powder, the stability of suspensions is better under the acid condition than under the basic condition. At $\text{pH} = 5$, the stability of suspensions with PAAM-coated SiC powder is optimum. When $\text{pH} = 3$, the stability becomes slightly worse; whereas when $\text{pH} > 7$, the stability of powder decreases sharply and serious flocculation occurred to the suspensions.

For the two powders, as shown in Fig. 9 (See, P19: Fig. 9. Stability of PAAM-coated SiC powder with different pH value), under the optimum condition of stability, the sediment of uncoated powder is fast, the percentage of the relative sediment height is $< 80\%$ in 1 h. Then the velocity of the sediment decreases and the sediment is completed nearly within a day, whereas the PAAM-coated SiC powders are very stable and the velocity of sediment is slow. In 5 days, the percentage of the relative sediment height is still about 80% .

3.6. The particle size analysis of uncoated and coated SiC powder

Larger surface effect and surface energy make the fine SiC powder ($1.2\ \mu\text{m}$) agglomerate easily, which usually

TABLE II The particle size analysis of uncoated and PAAM-coated SiC powder

Particle size	d_{50} (μ)	d_{10} (μm)	d_{90} (μm)
Uncoated SiC powder	1.74	0.63	5.45
PAAM-coated SiC powder	1.18	0.59	3.98

leads to the increase of the particle size. As shown in Table II (See, P20: Table II. The particle size analysis of uncoated and PAAM-coated SiC powder), for the uncoated SiC powder, $d_{50} = 1.7 \mu\text{m}$ (bigger than $1.2 \mu\text{m}$ in Table I), whereas for the PAAM-coated SiC powder, $d_{50} = 1.18 \mu\text{m}$, whose size is smaller. It has indicated that the extent of agglomeration decreases while the capability of dispersion is improved by coating PAAM on the surface of SiC powder. In addition, to some extent, the results of particle size measurement also indicate that most of the SiC powders are not linked though AAM has been grafted and polymerized on the surface. That is, the PAAM layer might be formed on the surface of single SiC powder. Hence, it has improved the capability of dispersion and has offered the condition of preparing highly concentrated ceramics suspensions.

3.7. Dispersion of PAAM-coated SiC powders

Proper dispersion is one of the conditions to control the agglomeration of powder and to increase the solid content of suspensions [22–25]. As shown in Fig. 10 (See, P21: Fig. 10. The TEM of uncoated SiC powder), Fig. 11 (See, P22: Fig. 11. The TEM of PAAM-coated SiC powder), in the same scope, for uncoated SiC powder, the agglomeration of powder is serious and the dispersion is heterogeneous, whereas for PAAM-coated SiC powder the fine particle increases and the powders are dispersed homogeneously. So, the purpose of dispersion is realized by using PAAM-coated SiC powders.

3.8. Solids content of uncoated and PAAM-coated ceramics suspensions

As shown in Fig. 12 (See, P23: Fig. 12. The relationship between the viscosity of suspensions and shear

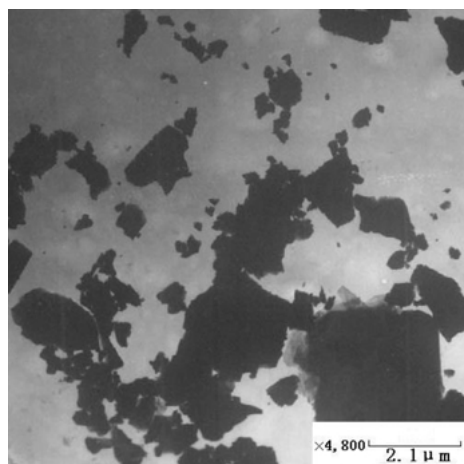


Figure 10 The TEM of uncoated SiC powder.

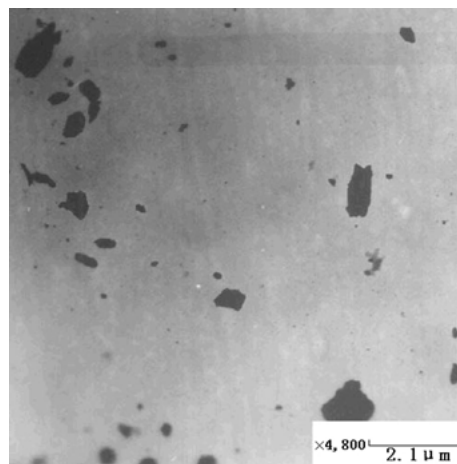


Figure 11 The TEM of PAAM-coated SiC powder.

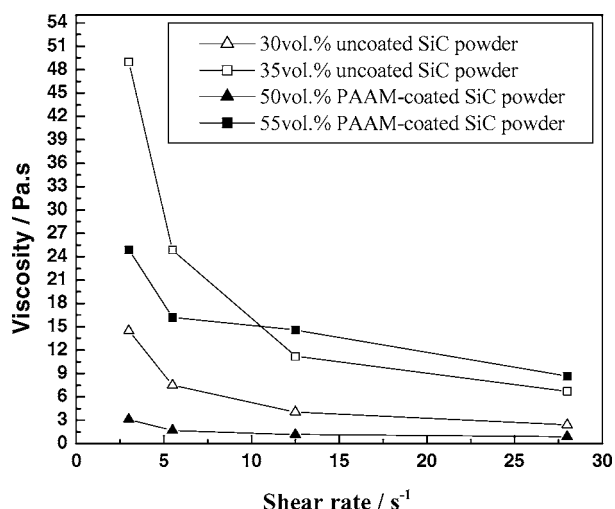


Figure 12 The relationship between the viscosity of suspensions and shear rate.

rate), the rheological property of suspensions prepared by PAAM-coated SiC powder is similar to that prepared by uncoated SiC powder. Two suspensions are shearing thinning. As for PAAM-coated SiC powder, the viscosity of 50 vol% suspensions was $<1 \text{ Pa}\cdot\text{s}$ when the shear rate is $>5 \text{ s}^{-1}$, whose viscosity value is less than that of 30 vol% suspensions prepared by uncoated SiC powder. The highest solid content of suspensions prepared by uncoated SiC powder is 35 vol% and at this time the suspension has bad rheological property. Whereas the highest solid content of suspensions with proper rheological property prepared by PAAM-coated SiC was obtained at $\text{pH} = 5$ and the value is 55 vol% which has increased by 57.14% compared to that of uncoated SiC powders. Thus, PAAM-coated SiC powder can achieve the purpose of increasing the solid content and reducing the water content. Maintained under the condition of $\text{pH} < 7$, PAAM-coated SiC suspensions all have relatively high solid content except for the change of the rheological capability; at $\text{pH} = 5$, the rheological property is proper; at $\text{pH} = 2, 3$, the suspensions can only flow under the condition of lower solid content compared to that when $\text{pH} = 5$ and the rheological property decreases compared to that when $\text{pH} = 5$. When $\text{pH} > 7$, the suspensions lose the rheological property

and flocculate partly. The formation of highly concentrated SiC ceramics suspensions is related to the PAAM coated on the surface of SiC powders.

4. Conclusion

The experimental results indicate that the PAAM coating layer is formed on the surface of APS-processed SiC powder by using a redox system consisting of ceric ion and reducing groups ($-\text{NH}_2$). The formed layer affects obviously the surface characteristics, the stability of SiC powder and the Zeta-potential as well. The solid content of suspensions increases and varies as pH value changes. Under the basic condition, the suspensions flocculate easily, whereas the homogeneous and stable suspensions with high solid content and proper rheological property are obtained under the acid condition.

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