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Technical report

Influence of Network Structure on Abnormally High Viscosity of Mixed Slurries of Silicon Carbide Nanopowder and Polycarbosilane

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Silicon carbide powder, polycarbosilane (PCS) and xylene mixed slurries were prepared for viscosity measurement and microstructure observation. Absolute slurry viscosity and shear rate dependence of viscosity were investigated at various SiC concentrations and particle sizes. Temperature dependence of viscosity was also investigated. As the primary particle size in powders decreases, viscosity increases relatively at a low SiC concentration. Microstructure observation on diluted slurries revealed the existence of secondary particles composed with primary nanoparticles and network formation by physically or chemically contacted secondary particles. Some of the microstructure changes with shearing was consistent with a strong shear thinning phenomenon of slurry viscosity. [Received September 25, 2007; Accepted October 18, 2007]

Key-words : *Silicon carbide, Precursor method, Powder, Slurry, Viscosity, Shear thinning, Ceramic matrix composite*

1. Introduction

Precursor method for covalent bond ceramic synthesis has wide application for producing unique shape ceramic materials (fiber,[1)-5)] coating,[6)-8)] minute MEMS parts,[9)-12)] porous materials[13)-15)] and source of ceramic matrix in CMC[16)-18)]) by the use of polymer nature in melting or solution states. In such uses, the combination of ceramic powders with polymer precursors is essential technology, because pure precursors are usually fragile in a raw state, which tend to cause cracks by volume shrinkage during pyrolysis. Ceramic powders compounded with polymer precursors can simply reduce such volume shrinkage. In addition, the possible network by particle contacts in compounds is expected to be effective for holding complex shapes of formed materials during pyrolysis. In recent years, chemical reactions between powders and the surrounding matrix has also been investigated to compensate for volume shrinkage during pyrolysis. Such filler effects on material preparation were termed "active filler".[19)] In any case, small size particles are favorable not to prevent formability of precursor polymers. It is critically important how much inorganic content can be combined with the precursor without increasing viscosity.

We have investigated the viscosity of silicon carbide nanopowder–polycarbosilane mixtures and observed abnormally high viscosity with a strong shear thinning effect in some cases.[20)] In this article, some noteworthy characters of such powder–precursor systems, including size dependence and temperature dependence, are reported. In addition, the possible reason of abnormally high viscosity is described on the basis of direct optical observation of the slurry microstructure.

2. Experimental procedure

4 kinds of silicon carbide (Greendensic GC #2500 (averaged size of 10 μm) [Showa Denko], Ultrafine (averaged size of 270 nm), [Ibiden] 50 nm SiC (averaged size of 50 nm) [Nanostructure & Amorphous Materials], 20 nm SiC (averaged size of 20 nm) [Nanostructure & Amorphous Materials]) were prepared for slurry mixing (**Fig. 1**). Polycarbosilane (Nippon Carbon, Japan) and xylene (Wako Chemicals) were also prepared. After dissolution of PCS in xylene, SiC particles were added in the solution step by step. After stirring for 15 minutes, ultrasonic treatment was performed. A high power ultrasonic treatment (Model 4021, Kaijo, 200 kHz, 5 mm distance between slurry container and oscillator) was additionally performed in some cases to obtain strong dispersion on the slurries. In the case of 20 nm SiC slurries, 1 hour of ball-milling (Planetary micro mill pulverisette 7, FRITSCH, with Alumina balls of 10 mm and 5 mm) was also performed to break the microstructure of slurries. Viscosity measurement was carried out by Multivisco (Fungilab, S.A) with a Head-R and a LCP adopter in a range of 278–298 K.

Some of the slurries were diluted and inserted between glass plates to observe its microstructure by an optical microscope (Olympus BX60).

3. Results and discussion

Figure 2 shows results of viscosity measurement on slurry containing GC SiC. The measured viscosity increases as the SiC concentration increases. The viscosity usually does not show shear rate dependence. At a 40 mass% SiC concentration, however, the viscosity shows a small increase with a lowering shear rate below 10 s^{-1}.

Figure 3(a) shows the shear rate dependence of viscosities of 4 kinds of slurries with different SiC powders. As the primary SiC particle size decreases, the viscosity tends to increase even at low SiC concentrations. In cases of ultrafine and 50 nm SiC, increase in the slurry viscosity is observed at low shear rates, while such increases are not remarkable at a high shear rate beyond 10 s^{-1}. In the case of the 20 nm slurry, however, measured viscosity monotonously increases as the shear rate decreases. There is almost linear log–log relationship between viscosity and shear rate. A calculated slope between log (shear rate) and log (viscosity) is –0.89 at a shear rate range of 1–500 s^{-1}.

When PCS content is lowered to 3.4 mass%, shear rate dependence becomes mild. The viscosity, however, mainly depends on the absolute SiC content, not on the PCS content. A calculated slope between log (shear rate) and log (viscosi-

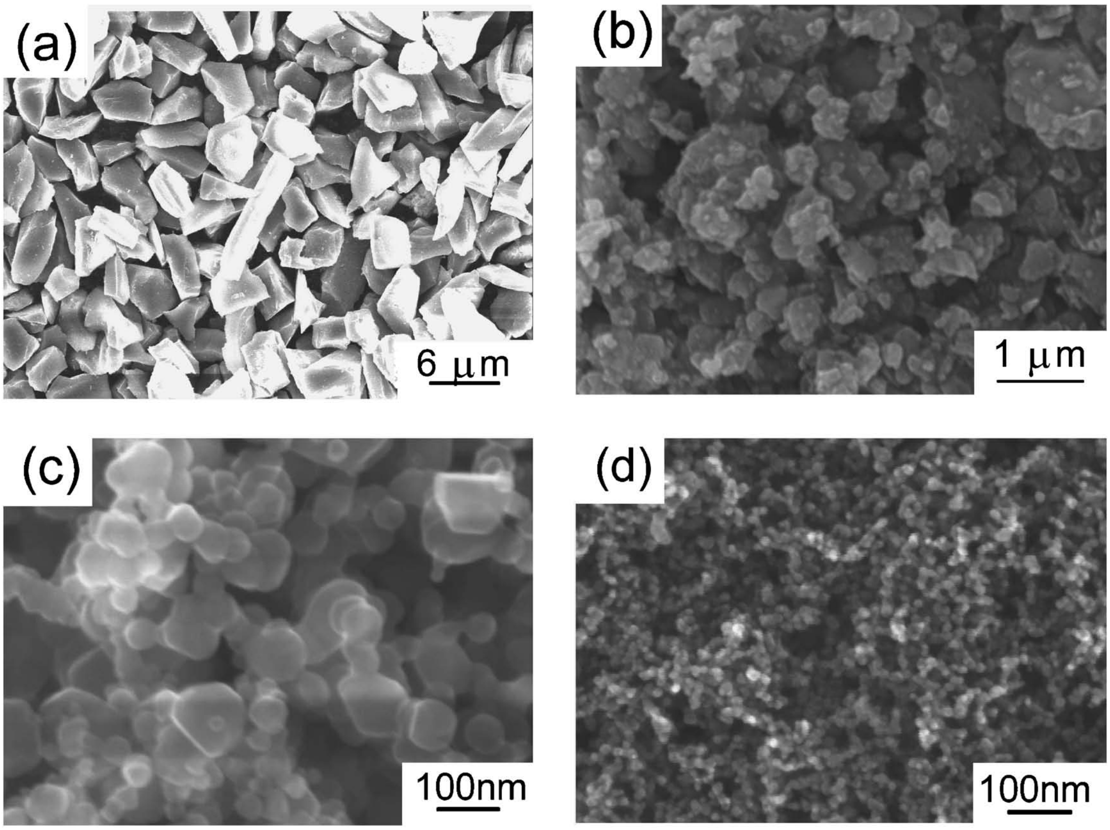

Fig. 1. SEM images of starting SiC particles; (a) GC SiC (b) Ultrafine, (c) 50 nm SiC, (d) 20 nm SiC.

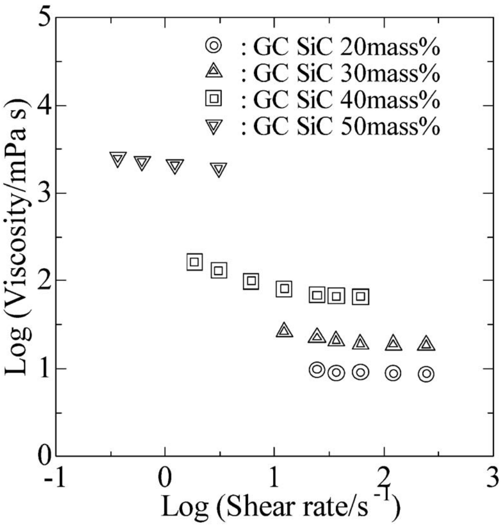

Fig. 2. Viscosity of GC SiC slurries with various SiC concentrations (PCS: 27 mass% and residual xylene).

ty) is −0.68 in this case (Fig. 3(b)). In order to destroy possible particle networks, a ball-milling procedure was applied on the 20 nm SiC slurry sample. A calculated slope in this case is −0.58 at shear rate range of 1–500 s^{-1} (Fig. 3(b)).

Figure 4 shows temperature dependence of slurry viscosities. The results of the GC SiC and 50 nm SiC slurries are usual. As the temperature decreases, the measured viscosity increases. It is natural because the volume shrinkage of PCS-xylene media is expected to be far larger than that of solid SiC. A decrease in particle distance is sufficient to cause viscosity increases.

In the case of the 20 nm SiC slurry, however, viscosity behavior is almost independent of temperature. Even a small decrease in viscosity is observed by lowering the experimental temperature. It is an abnormal phenomenon. Perhaps, viscosity of the 20 nm SiC slurry has originated from the SiC network structure, which is not changed by temperature. In any case, there is no remarkable hysteresis in viscosity. It suggests that shear rate dependence of viscosity is not a transient phenomenon. This is a kind of shear thinning effect corresponding to a stationary state in deformed slurries.[21),22)]

Figure 5 shows the microstructure of diluted slurries of ultrafine. Secondary particles (aggregates of the primary particles) with Brownian motion were observed in PCS-xylene media. Physical contacts between particles, however, sometimes restrict the Brownian motion of drifted particles and large size islands are formed. Ultrasonic treatment is effective to reduce a number of such islands. Once formed, the size of the islands grows with time, if the system is not stirred or vibrated again.

In the case of GC SiC, the observed structure in the slurry was usual and common, which shows morphology of primary particles (averaged size of 10 μm). In the case of 50 nm SiC slurries, the Brownian motion of each particle was too rapid to determine the size of the isolated particles. The slurry usually showed a turbid appearance by transmitted light with averaged effect of rapid Brownian motion. The secondary particle size (aggregate of primary particles) was undoubtedly larger than 50 nm.[20)] However, it was impossible to determine the absolute size of the drifted particles by optics.

Figure 6 shows the microstructure of 20 nm SiC slurries.

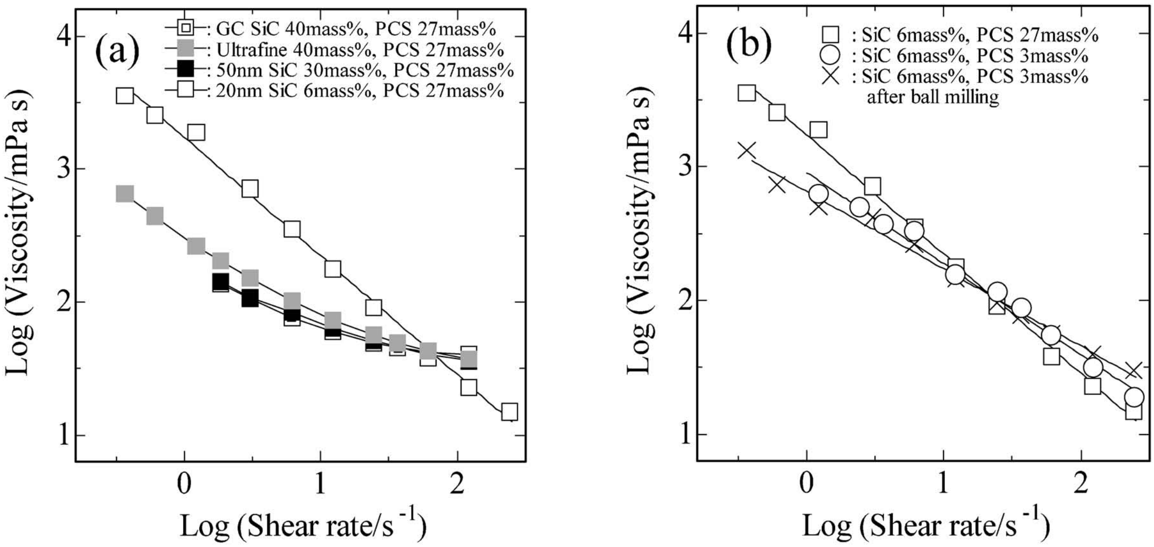

Fig. 3. Viscosity of slurries; (a) GC SiC (SiC 40 mass%), Ultrafine (SiC 40 mass%), 50 nm SiC (SiC 30 mass%) and 20 nm SiC (SiC 6 mass%), (b) 20 nm SiC (SiC 6 mass%, PCS 3 mass%) before and after ball milling.

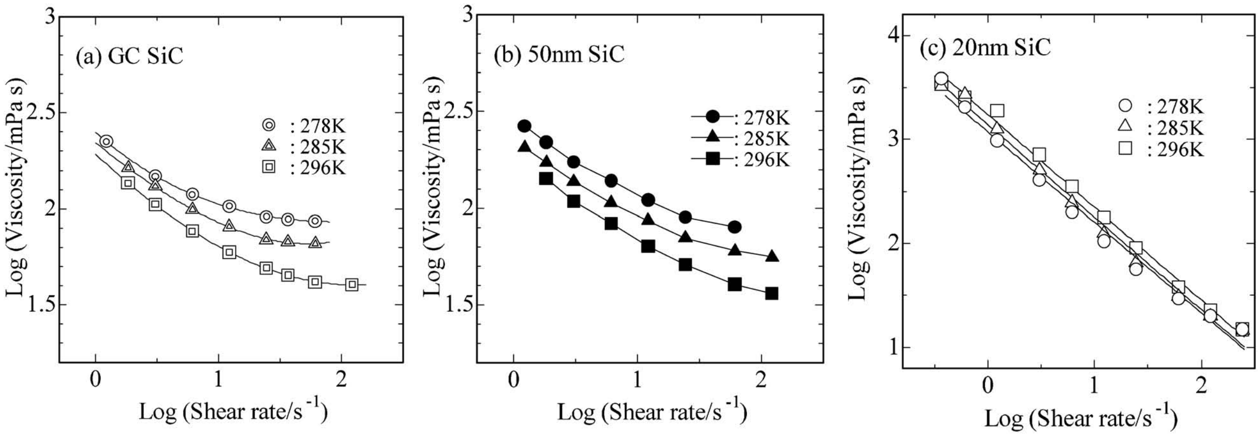

Fig. 4. Temperature dependence of various SiC slurries (PCS 27 mass%); (a) GC SiC (SiC 40 mass%), (b) 50 nm SiC (SiC 30 mass%), (c) 20 nm SiC (SiC 6 mass%).

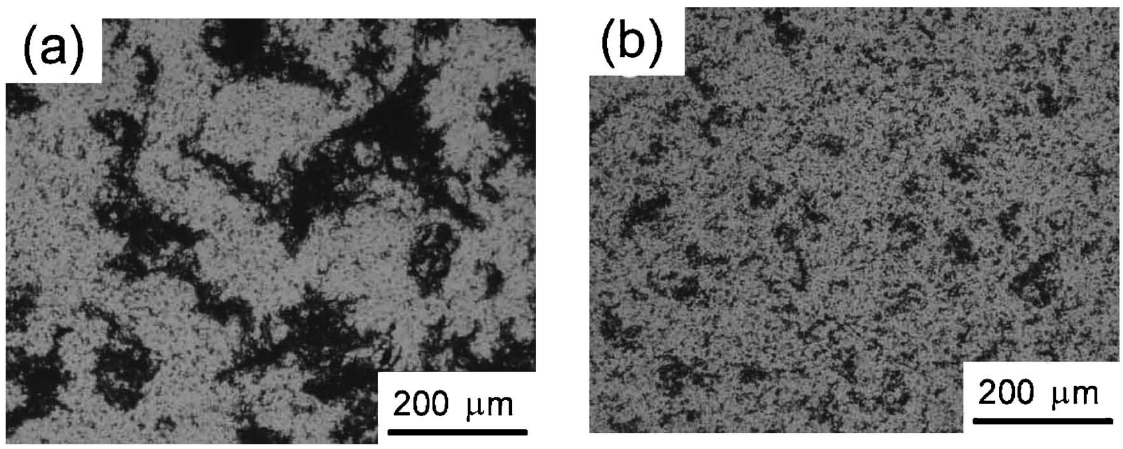

Fig. 5. Optical micrographs with transmitted light of diluted ultrafine slurries (SiC 1 mass%, PCS 0.9 mass%); (a) Ordinary dispersion, (b) After high power ultrasonic treatment.

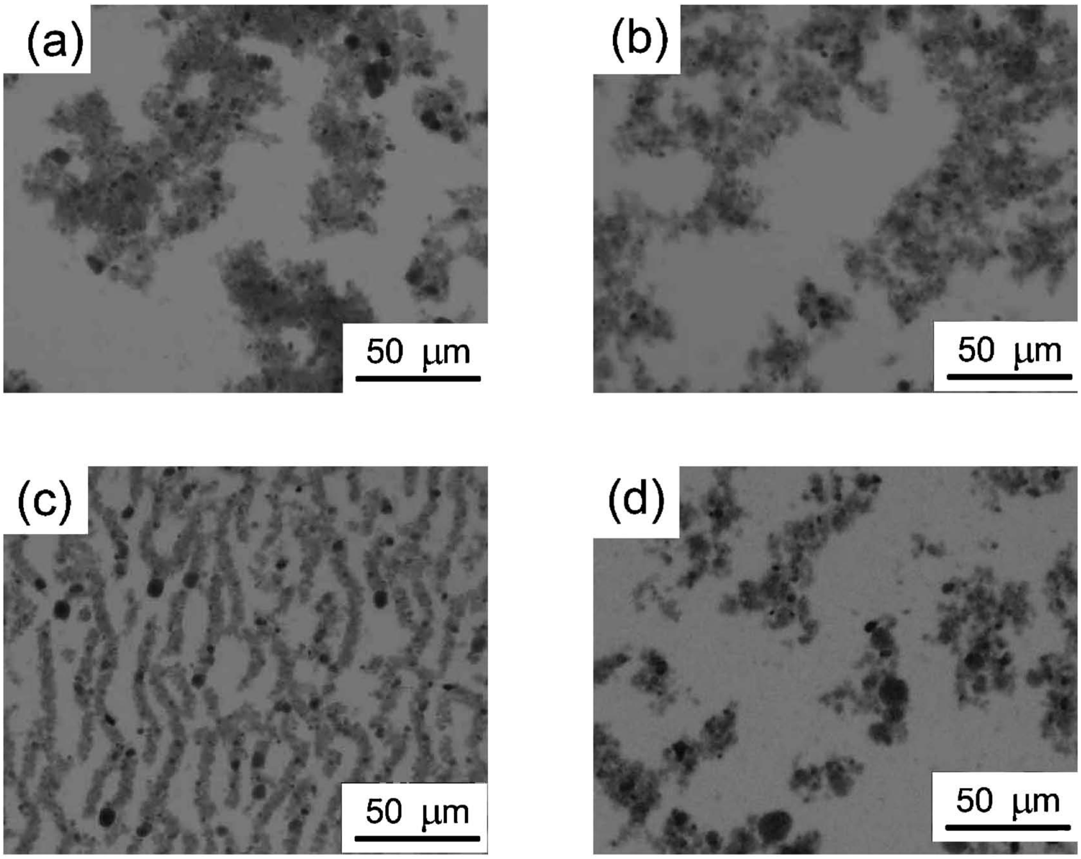

Fig. 6. Optical micrographs with transmitted light of diluted 20 nm slurries (SiC 1 mass%, PCS 0.5 mass%); (a) Ordinary dispersion, (b) After high power ultrasonic treatment. (c) Shear orientation, (d) After ball-milling.

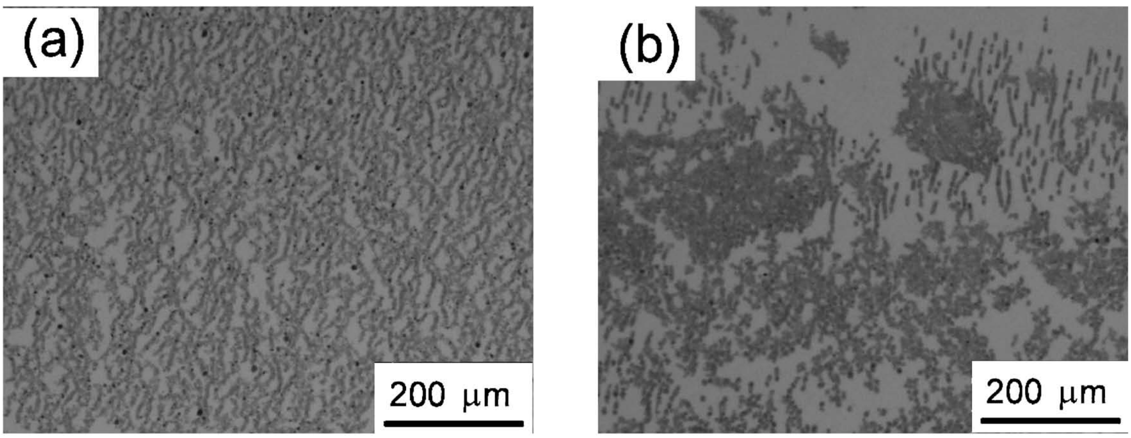

Fig. 7. Effect of shear on diluted 20 nm SiC slurry structures (SiC 1 mass%); (a) PCS 0.5 mass%, (b) Without PCS.

There are no isolated particles with Brownian motion. Balky 2 μm particles connected with each other was observed. These particles are partly transparent to light and occupied a large area in spite of the small SiC concentration. Ultrasonic treatment partly deconstructs the connection between 2 μm particles. After applying shear on glass plates, such network-like structures change their morphology to a chain-like oriented structure. The oriented direction is perpendicular to the shear strain. It may suggest an introduced rotation of micro chains composed of secondary particles in the PCS-xylene media. Ball-milling is effective to deconstruct not only connections between secondary particles, but also 2 μm particles itself. However, there are no small particles showing Brownian motion. The ball-milling effect is not sufficient to obtain a wholly dispersed structure.

Figure 7 shows the effect of PCS existence on an oriented microstructure. Even without PCS, some short chains are observed after shear application. Long chain structure is, however, absent.

The kind of interaction, which contributes to such a chain-like structure formation, is not clear at present. Since SiC crystallites exists as nano size branches in the 20 nm SiC powder, physical hooks of such nano size branches at the surface of the secondary particles may originate strong connections of the secondary particles. On the other hand, it is well known that the surface of SiC particles possess a complex chemical nature.[23] When surface is covered by oxide, the hydrogen bond interaction is possible by the effect of Si–OH groups. When the surface is covered by carbon, the hydrophobic interaction is possible in an aqueous medium. Sometimes, even the co-existence of an oxide layer and carbon layer can be observed. Of course, such chemical nature of the particle surface influences the PCS adsorption. These issues are, however, beyond the region of this technical report.

4. Summary

In cases of slurries with SiC particles of micrometer sizes, the viscosity suddenly jumps up at high SiC concentration. In these cases, shear rate dependence of apparent viscosity is small at any SiC concentration. As the primary particle size decreases, the measured viscosity increases at the same SiC concentration. Shear rate dependence is sometimes observed at a high SiC concentration with low shear rates. Slurry with 20 nm SiC, however, shows abnormally high viscosity even at low SiC concentrations. The apparent viscosity depends on the shear rate at the wide rate region, called the "shear thinning effect". The optical microscope observation on the diluted slurry shows the existence of secondary particles (aggregates of primary particles) in PCS-xylene media. As the size of the primary particle size decreases, the secondary particle size usually decreases. In the case of slurry with 20 nm SiC, however, quite balky secondary particles forming a complex network structure are observed. There are no isolated particles with a Brownian motion. After applying shear on the slurry between glass plates, chain-like orientation of secondary particles perpendicular to the shear direction is observed. Physical contacts between secondary particles possibly contribute to the observed microstructure and measured high viscosity.

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