Dispersibility of SiC Whiskers in Several Organic Solvents

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As fundamental research to raise the strength and fracture toughness of ceramics, the dispersibility of SiC whiskers, W (A) and carbon-coated SiC whiskers, W (AC), was studied. In eight organic solvents, 1l. of ethanol, 2-propanol, and mixtures of these were selected as media to study the dispersibility of SiC whiskers. The dispersibility was evaluated by measuring the zeta potential and sedimentation velocity. Ethanol and 2-propanol were selected from these media, and the dispersibility was studied in detail. The electric charge of W (A) was positive in ethanol and negative in 2-propanol. On the other hand, the charge of W (AC) was negative in both solvents. The charge of their whiskers was a minimum (negative) by the addition of 0.001–0.002 g/l dispersant for W (A) and 0.0002–0.001 g/l for W (AC). The dispersibility of W (AC) was worse than that of W (A) in ethanol. The dispersibility of both SiC whiskers was improved by the addition of the dispersant to ethanol and 2-propanol. It was estimated that the dispersibility of W (A) and W (AC) is considerably affected by the charge of the polymer used as a dispersant.

Key-words: Dispersibility, SiC whisker, Organic solvent, Ethanol, 2-propanol, Zeta potential, Sedimentation

1. Introduction
Ceramics have numerous advantages such as a high melting point, high strength at high temperature, high abrasion resistance, high erosion resistance, high corrosion resistance and they are lightweight. Therefore, ceramics have potential for use as new mechanical and structural materials. However, there exists a disadvantage in that the fracture toughness of ceramics is small in comparison with metals, which restricts the applied field magnitudes. Therefore, improvement of the mechanical properties of ceramics has been attempted by the addition of SiC whiskers.

It is important for SiC whiskers to exhibit good dispersibility in a ceramic matrix in order to improve the mechanical properties. If the whisker dispersibility is poor, the mechanical properties of a composite material are adversely affected because the addition of these whiskers leads to the introduction of defects. Therefore, as a first step, it is essential that the dispersibility of SiC whiskers and matrix ceramic particles in a solvent used in a wet mixing process is good. Furthermore, it is important to establish a technology to dry the mixed powder while maintaining good dispersibility of SiC whiskers and ceramic particles in the solvent. Dispersibility of ceramic particles has been already studied in aqueous solutions of which the pH was adjusted or to which an organic dispersant was added.

In this study, we use organic solvents as media to disperse SiC whiskers and accumulate basic data in order to select the best mixing medium from amongst those organic solvents. Furthermore, it was examined in detail whether dispersibility was further increased with adding dispersant to the selected solvents. The dispersibility of SiC whiskers in solvents was evaluated by measuring the zeta potential and a sedimentation velocity.

2. Experimental procedure
The SiC whiskers used in this study were of two types; one with an average diameter of 0.4 μm and a length of 30 μm (W (A)) and the other was a carbon-coated whisker of average diameter of 0.5 μm and length of 35 μm (W (AC)). Both SiC whiskers are commercially available (manufactured by Tokai Carbon Co., Ltd.). Eight organic materials were used as solvents, and the dispersant was provided as an ethanol solution containing 10 mass% of a styrene-halfester of maleic acid copolymer.

In order to characterize the dispersant, the chemical shifts of proton 1H and carbon 13C NMR spectra were recorded on a nuclear magnetic resonance spectrometer (NMR) (JEOL, JNM-A500 and JNM-FX60) and an infrared adsorption spectrum on an infrared spectrometer (IR) (JEOL, JIR-5500). On the other hand, the characterization of the SiC whisker was performed by X-ray diffraction analysis (JEOL, XRD–3500) and X-ray photon spectroscopy (XPS) (JEOL, JPD–905X).

The zeta potential value of the SiC whisker in organic solvents was measured with an electrophoresis type zeta potential measurement device (Rank Brother Co., Mark II). A small amount of SiC whiskers were dispersed in the solvents and their mobility under various applied voltages were observed by means of an optical microscope. The zeta potential was calculated from the mobility and applied voltage. In addition, the concentration of the dispersant in this measurement was indicated by the weight (g) of the dispersant in solvents of 1 l.

A messcylinder of 20 ml was used for a sedimentation experiment. The concentration of the SiC whisker in the solvents was 0.5 vol1%. The solvent containing the whiskers was left standing after vigorous stirring using an ultrasonic equipment, and the height of the interfaces between the sediment layer and the cloudy liquid as well as between two cloudy layers of different concentrations was measured as a function of time after standing. In addition, the concentration of the dispersant in this sedimentation measurement was indicated by mass% of the dispersant with respect to the whiskers.

3. Results and discussion
3.1 Characterization of dispersant and SiC whisker
Chemical shift of proton 1H and carbon 13C NMR signals for the dispersant are listed in Table 1. The basic structures assigned to each chemical shift along with the proton...
ratios are also shown in Table 1.

Figure 1 shows an infrared absorption spectrum for the dispersant. Broad absorption at 3000-3100 cm⁻¹ and 2500-2700 cm⁻¹ shows the existence of a carboxylic group and the absorption at 1720-1740 cm⁻¹ shows that a part of the carboxyl group was esterified. A sharp signal in the neighborhood of 2940 cm⁻¹ corresponds to an aliphatic series, and that at 730-770 cm⁻¹ and 690-710 cm⁻¹ to a monosubstituted aromatic ring.

It is estimated from the analyses of NMR and IR spectra that the dispersant consists of the main chain of aliphatic series which have a phenyl group, carboxyl group and ester group as side-chains. If the dispersant consisted of styrene halfester of maleic acid copolymer, it is estimated that the ratio of styrene to maleic acid was 35:65 from the proton ratio shown in Table 1.

SiC whisker as observed from X-ray diffraction pattern is a β-type crystal well developed in the c-axis direction. X-ray photoelectron spectra of the SiC whisker as-obtained and annealed at 800°C in air for 1h are shown in Fig. 2. Peaks were observed only at around 101 eV for the as-obtained SiC whisker, and at around 101 and 103 eV for the oxidized SiC whisker. The peak at around 101 eV corresponds to Si-C binding energy and that at around 103 eV to Si-O binding energy. That is, it was evident that the surface of the as-obtained SiC whisker was not oxidized and was smooth.

3.2 Zeta potential of SiC whisker

Figure 3 shows the zeta potentials of SiC whisker W (A) and carbon-coated whisker W (AC) in several organic solvents. The SiC whisker in ethanol showed a positive charge of 23 mV. However, the charges in 1-propanol and 1-butanol were negative values of -21 and -36 mV, respectively. If the solvent turned into 2-propanol of an isomer from 1-propanol, the negative charge increased slightly from -23 to -29 mV. That is, as the length of aliphatic chain in alcohol increased from 1-propanol to 1-butanol, the negative charges of the SiC whisker increased and the charge in 2-propanol was intermediate between those of 1-propanol and 1-butanol. On the other hand, the charge of the carbon coated SiC whisker showed a negative value of -30 mV in ethanol. If the solvent changed from ethanol to 1-propanol and 1-butanol, their negative charges increased to -41 and -50 mV, respectively. The whiskers in 2-propanol showed the largest value of negative charge of -60 mV in all four kinds of solvents.

Ethanol and 2-propanol were selected from the four kinds of solvents, and the effect of the added dispersant content on the zeta-potential of the SiC whisker and carbon-coated SiC whisker in these solvents were shown in Fig. 4. Figure 4(a) shows the relation between zeta potentials and dispersant contents for SiC whisker W(A). A zeta potential of W(A) whisker showed a positive charge of 23 mV in ethanol and a negative charge of -29 mV in 2-propanol. The value of the positive charge in ethanol decreased by adding a dispersant and the electric charge became zero at the addition of 0.0001-0.0002 g/l. Furthermore, the charge became negative by adding more dispersant and showed the minimum value of -42 mV at 0.001 g/l in ethanol. On the other hand, the amount of the negative charge in 2-propanol slightly increased with increasing dispersant content.
and became a minimum value of \(-43\, \text{mV}\) at the addition of 0.002 g/l dispersant. However, the amount of their negative charges adversely decreased by the addition of more dispersant than the contents showing minimum zeta potentials in both ethanol and 2-propanol.

Figure 4 (b) shows the relation between zeta potentials and dispersant contents for the carbomcoated SiC whisker W (AC). The zeta potential of W (AC) shows negative charges of \(-30\, \text{mV}\) in ethanol and \(-60\, \text{mV}\) in 2-propanol. The quantity of the negative charges increased with increasing dispersant contents, and the zeta potential had the minimum values of \(-69\, \text{mV}\) at the addition of 0.001 g/l in ethanol and \(-71\, \text{mV}\) at 0.0002 g/l in 2-propanol. However, upon the addition of more dispersant, the amount of their negative charges decreased adversely. In addition, the pH of the solvents remained almost unchanged by the addition of the dispersant.

3.3 Sedimentation of SiC whisker

Figure 5 shows the results of the sedimentation test performed on the SiC whisker in eight kinds of organic solvents. As observed in Figs. 5 (a) and (b), the sedimentation velocity of the SiC whisker in the absence of a dispersant was the slowest in acetone and the whisker was stable for 20 min. The whisker in benzene was stable for 0.1 min and that in hexane suddenly sedimentated after agitating-standing. Sedimentation velocity in four kinds of alcohol was intermediate between those in acetone and toluene. The velocity was the fastest in ethanol and decreased in the sequence of 1-propanol, 1-butanol and 2-propanol. That is, the longer the length of the chains from ethanol to 1-propanol and 1-butanol, the slower the sedimentation velocity. The sedimentation velocity in 2-propanol, an isomer of 1-propanol, was slower than in the three other kinds of alcohol. That is, it can be concluded that the dispersibility of the SiC whisker is the best in 2-propanol among the four kinds of alcohol considered in this study.

The floatation time of the SiC whisker in four kinds of alcohol increased by the addition of a dispersant. The effect was significant in ethanol and slight in 1-butanol. The effect in 2-propanol was intermediate between those in ethanol and 1-butanol. On the other hand, as observed in Figs. 5 (c) and (d), sedimentation velocity of the SiC whisker in acetone, benzene and hexane was not affected by the addition of a dispersant. However, it was adversely affected by the addition of the dispersant to toluene as solvent.

Figure 6 shows the result of the sedimentation test carried out on the carbon-coated SiC whisker in eight kinds of organic solvents. In the absence of a dispersant, sedimentation of the SiC whisker occurred immediately in all eight kinds of organic solvents as shown in Figs. 6 (a) and (b).

However, the floatation time of the carbon-coated SiC whisker increased by the addition of only 0.5 % dispersant to ethanol and 2-propanol in the eight kinds of organic solvents. That is, it became apparent that the dispersibility of the carbon-coated SiC whisker was improved by the addition of the dispersant to ethanol and 2-propanol.

Next, the sedimentation of the SiC whisker and carbon-coated SiC whisker in ethanol and 2-propanol, and the accumulation at the bottom were observed in detail. Figure 7 shows the sedimentation of the SiC whisker W (A) in ethanol. Figure 7 (a) shows the resultant sedimentation in ethanol in the absence of a dispersant and the floatation layer was stable for 1 min after agitating-standing. However, the floatation layer began to divide into a bottom dense layer and a top diluted layer after 1 min, and the bottom layer descended rapidly after around 20 min. After about 100 min, the top layer was separated into 2 levels of which the bottom layer descended. In the case of a settling time of more than around 2000 min, the top layer was separated and the third sedimentation occurred, too. The concentration of the dispersed whiskers in the top layer decreased whenever such sedimentation was repeated. Hereafter, the first, second and third sedimentation layers are denoted as Height 1, Height 2 and Height 3, respectively, in Fig. 7 and Fig. 8.
Figure 7 (b) shows the result of the sedimentation test for the solution containing 0.5 mass% dispersant. The phenomenon similar to the first sedimentation in Fig. 7 (a) was not observed. However, at the settling times of about 100 and 2000 min, phenomena similar to the second and third sedimentation, respectively, in Fig. 7 (a) were observed. The concentration of dispersed particles in the top layer became gradually thin by repeating sedimentation. However, even upon keeping the solution undistributed for 7 d, it remained cloudy.

Figure 7 (c) shows the result of the sedimentation test for the solution containing 2.5 mass% dispersant. The sedimentation situation was similar to that which occurred upon the addition of 0.5 mass% dispersant. However, the sedimentation velocity upon the addition of 2.5 mass% dispersant decreased in comparison with that of 0.5% addition. The sediment layers of W (A) formed by the addition of 0.5 and 2.5 mass% dispersant became more dense than that formed in the absence of a dispersant. The density of the sediment layer at the bottom of a messcylinder reflects the dispersibility of whisker particles in the solvent. A high density of the sediment layer corresponds to good dispersibility. That is, the dispersibility of the W (A) whisker in ethanol increased with increasing dispersant and was improved by adding over 0.5 mass% dispersant.

Figure 8 shows the results of the sedimentation test for a SiC whisker W (A) in 2-propanol. The manner of the sedimentation and the density of sediment layer in 2-propanol were similar to those in ethanol. However, as apparent from the comparison between Fig. 8 and Fig. 7, the floating time of the whiskers in 2-propanol became larger than that in ethanol. It is concluded that whisker dispersibility in 2-propanol is better than that in ethanol.

Figure 9 shows the results of the sedimentation test for a carbon-coated SiC whisker W (AC) in ethanol and 2-propanol. Figure 9 (a) is the result in ethanol. The nature of sedimentation was markedly different from that of the SiC whisker W (A), and the dispersing whiskers were sedimented immediately after standing. The experimental results in the case of the addition of 0.5 and 2.5 mass% dispersants are also shown in Fig. 9. The sedimentation velocity of W (AC) in ethanol decreased with the addition of 0.5 mass% dispersant and the suspension was not sedimented till after 30 s of agitating-standing. However, the whiskers were rapidly sedimentated after the lapse of 30 s. The sedimentation velocity decreased with the addition of 2.5 mass% dispersant and whisker stability in ethanol was extended up to 1 min. That is, the dispersibility of W (AC) in ethanol was improved by the addition of the dispersant.

Figure 9 (b) shows the result in the case of 2-propanol. The manner of sedimentation is similar to that in ethanol. As apparent in the comparison between Fig. 9 (a) and Fig. 9 (b), the floating time of particles in 2-propanol was slightly more than that in ethanol. The manner of sedimentation of W (AC) in both ethanol and 2-propanol was markedly different from that of W (A). The solution remaining after the sedimentation was colorless and transparent, while the solution remaining in the case of the W (A) whisker was cloudy even after standing for 7 d. On the other hand, the sediment layer at the bottom of a messcylinder was loosely accumulated. The thickness of the sediment layer decreased upon the addition of the dispersant, but was still thicker than that in W (A) even after the addition of 2.5 mass% dispersant. It can be concluded that the dispersibility of the carbon-coated SiC whisker W (AC) is extremely poor in both ethanol and 2-propanol in comparison with that of the SiC whisker W (A). However, the dispersibility was slightly improved by dispersant addition. Furthermore, the
dispersibility of W(AC) in 2-propanol was slightly better than that in ethanol.

3.4 Aggregation and dispersion of SiC whisker in solvent

The samples for SEM observation were collected from the remaining solution immediately after the start of the sedimentation test and after standing for 7 d in ethanol containing W(A) whiskers, after which they were dried. Figure 10 shows the SEM photographs. It was observed that the number of whiskers which cohered in solution decreased as the sedimentation was repeated. However, long whiskers remained in the solution even after standing for 7 d. It is estimated that some whiskers begin to cohere immediately after agitating-standing in the case of Fig. 7(a) in the absence of a dispersant, and the sedimentation begins in turn from aggregates containing a certain number of whiskers.

The number of cohering whiskers in the solution decreases immediately after the first sedimentation. However, the agglomeration proceeds with the lapse of time, and the whiskers in the residual solution were sedimentated again by aggregating to a certain amount. On the other hand, the number of cohering whiskers in the solution decreased with the addition of a dispersant even during the early stage when whisker concentration is high because the addition of dispersant into the solvent interferes with whisker cohesion.

As shown in Fig. 4, the electric charge in the minimum zeta potential for the carbon-coated SiC whisker W(AC) is -69 mV in ethanol, and became larger than the electric charge (-42 mV) for the SiC whisker W(A). If the electrostatic repulsion is responsible for the dispersibility, it is estimated that the dispersibility of W(AC) in ethanol becomes more significant than that of W(A) because the electrostatic repulsive force of W(AC) in the ethanol becomes larger than that of W(A). However, the dispersibility of W(AC) becomes remarkably worse than that of W(A) as opposed to that expected from the comparison between Fig. 4(a) and Fig. 4(b). It is considered that the dispersibility of SiC whiskers in solvents was significantly affected by other more remarkable effects than by the electrostatic repulsion force. The steric hindrance of the polymer is considered as the possible effect responsible for enhancing the dispersibility.

On summarizing the results of zeta potential measurements and sedimentation tests, we note that the dispersibility of SiC whisker W(A) in ethanol and 2-propanol was poor, and that of the carbon-coated SiC whisker W(AC) was extremely poor. The dispersibility of W(A) and W(AC) whiskers in 2-propanol was better than that in ethanol. On the other hand, the dispersibility of W(A) and W(AC) whiskers was improved by the addition of a dispersant. It is considered that the improvement of the dispersibility was mainly due to the steric hindrance of the polymer and to a small extent due to the electrostatic repulsion.

4. Conclusions

The dispersibility of SiC whiskers W(A) and carbon-coated SiC whiskers W(AC) in eight organic solvents were evaluated by measuring the zeta potential and sedimentation velocity. Ethanol and 2-propanol were selected from these organic solvents and the dispersibility was studied in detail. The following results were obtained:

(1) The electric charge of the SiC whisker W(A) is positive in ethanol, and negative in 1-propanol, 1-butanol and 2-propanol. On the other hand, the charge of the carbon-coated SiC whisker W(AC) is negative in both ethanol and 2-propanol.

(2) The charges of W(A) and W(AC) whiskers in ethanol and 2-propanol decreased with the addition of a dispersant. Their charges showed minima of -42 mV at the addition of 0.001 g/l dispersion in ethanol and -43 mV at 0.002 g/l in 2-propanol.

(3) The dispersibility of the W(AC) whisker was worse than that of the W(A) whisker. The dispersibility of W(A) and W(AC) whiskers was improved by the addition of a dispersant.

(4) It was estimated that the dispersibility of W(A) and W(AC) whiskers was considerably affected by the steric hindrance of the polymer used as a dispersant and slightly affected by electrostatic repulsion.

References