Mechanical Properties of Si_3N_4 Matrix Composites Reinforced with SiC Whiskers with Various Coatings

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表面被覆 SiC ウィスカー強化 Si_3N_4 複合体の機械的特性

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SiC whiskers were coated with Ti, Al, Y or C by RF-sputtering or plasma CVD in order to modify the interfacial strength between whisker and matrix. These whiskers with various coatings were used to fabricate Si_3N_4 matrix composites. The mechanical properties of the composites were correlated to the interfacial strength (τ) between whisker and matrix, which was measured for the composites reinforced with SiC continuous fibers with the same coatings as the whiskers. The samples with low τ (5–10 MPa) showed higher fracture energy than those with high τ (90–100 MPa), while the high τ samples exhibited better fracture toughness and strength. These results suggest that whiskers with low τ affect the crack wake by pull-out or crack bridging, while those with high τ affect the crack tip before crack propagation starts.

Key-words: Si_3N_4 , SiC, Whisker, Interfacial strength, Pull-out, Bridging, Fracture energy, Fracture toughness

1. Introduction

Ceramics are promising materials for high-temperature structural applications. However, their use is limited to only a few fields because of their low fracture toughness. The use of composites to raise the fracture toughness has been proposed. Whisker composite is one of the hopeful materials, and it was found to be effective for increasing the fracture toughness of Al_2O_3 .^{1)–3)} Furthermore, a Si_3N_4 matrix composite reinforced with SiC whiskers has also been investigated extensively, and the effects of whiskers on high temperature properties^{4),5)} and fracture energy^{6),7)} have been recognized.

Whisker alignment^{8)–11)} and interfacial properties between whiskers and matrix^{8),12)–14)} have been considered the most important factors to improve the fracture toughness of the composites. Attempts to control the interfacial properties were made mainly for long-fiber composites by modifying the fiber surfaces, such as heat treatment in air¹⁵⁾ or in N_2 ¹⁶⁾ and coatings.^{17)–21)} The results of these studies revealed that weak interfacial bonding was effective for increasing the fracture toughness of long-fiber-reinforced composites.²²⁾ However, the relationship

between the interfacial properties and the mechanical properties of composites with small fillers such as whiskers, flakes or particles, is still not clear because the evaluation of the interfacial properties is difficult.

In this study, Si_3N_4 matrix composites reinforced with SiC whiskers with various coatings were fabricated to investigate the relationship between the interfacial properties and the mechanical properties, such as fracture strength, fracture toughness and fracture energy. The interfacial strength between SiC continuous fibers with the same coatings as SiC whiskers and Si_3N_4 matrix was measured to estimate the interfacial properties. Although this interfacial strength is not the real value between whiskers and matrix because it was measured using continuous fibers, it is thought to be one of the parameters which defines the interfacial properties between whiskers and matrix.

2. Experimental procedures

2.1 Sample fabrication

2.1.1 Surface coating

Ti, Al or Y was coated onto the SiC whiskers (TWS-400, Tokai Carbon Co., Ltd., Japan) surface by RF-sputtering, and the C coating was applied using plasma CVD. Sputtering was performed at the following conditions: RF power of 100 W and the Ar gas pressure of 0.4 Pa. In order to coat them uniformly, whiskers were vibrated by means of an ultrasonic generator. The frequency was 17.7 kHz. CVD was carried out in the rotating sample container as shown in Fig. 1. CH_4 gas or $\text{CH}_4 + \text{H}_2$ gas mixture was introduced into the chamber until the pressure reached 1.3 Pa. The sample container was heated up to 800°C, and the rotation speed was 10 rpm for uniform coating. The thickness of the coating layers was 20–40 nm.

SiC long fibers (SCS-6, Textron Speciality Materials Inc., USA) were used to fabricate the specimens for the push-out test.^{23)–25)} These fibers had a 2- μm thick C-rich layer on the surface. Coatings were applied to the fiber surfaces using the same method as for the whiskers. The thickness of the coating layers

Fig. 1. Schematic drawing of CVD apparatus.

was 100–200 nm.

2.1.2 Whisker-reinforced composite

Commercial grade Si_3N_4 powder (SN-E10, Ube Industries Ltd., Japan) with 5 mass% Y_2O_3 (99.9%, Shin-Etsu Chemical Co., Ltd., Japan) and 5 mass% MgAl_2O_4 (99.9%, Kojundo Chemical Labo. Co., Ltd., Japan), as sintering additives, and 20 mass% SiC whiskers with various coatings were mixed by ball-milling for 16 h using *n*-butanol as the liquid medium. These powder mixtures were hot-pressed in a carbon die at a temperature of 1700°C and at a pressure of 30 MPa for 1h, under 0.1 MPa N_2 gas.

2.1.3 Specimens for push-out test

The fibers with the coatings were composed to the same Si_3N_4 matrix as the whisker composites by hot-pressing. Fibers were aligned at intervals of 2 mm in order to avoid the influence of other fibers. The specimens for push-out test were prepared by slicing the unidirectional composites perpendicular to the fibers.

2.2 Evaluation

The push-out test was conducted by measuring load and displacement continuously by means of a testing machine (type 1361, Instron Ltd., England) with an X-Y stage and Vickers microindenter.²⁶⁾

Rectangular bars, $3 \times 4 \times 40$ mm, were machined for measuring mechanical properties. Fracture strength of the whisker composites was evaluated by the 3-point bending test with a 30 mm span. Fracture toughness was measured by the 4-point bending test, with a 30-mm outer span and a 10-mm inner span, using the single edge-notched beam (SENB) test pieces. The notch width and depth were 0.1 and 0.75 mm, respectively. The fracture toughness measured by SENB method is overestimated when the notch width is over the critical value. However, it is reported that the fracture toughness obtained using 0.1-mm notch width is regarded as the real value.⁶⁾ These tests were performed at a displacement rate of 0.5 mm/min. Fracture energy was obtained from the accurate measurement of the load point displacements by LVDT (linear variable differential transducer)⁶⁾ for chevron-notched (CN) test pieces in 3-point bending test. The size of the CN test piece is shown in Fig. 2. This test was conducted at a displacement rate of 0.05 mm/min.

The coatings on the whiskers were observed with

Fig. 2. Schematic drawing of CN test piece.

a transmission electron microscope (TEM: JEM-200CX, JEOL Ltd., Japan). The fractured surfaces of the CN test pieces were investigated with a scanning electron microscope (SEM: JSM-T330A, JEOL Ltd., Japan). The distribution of coating elements, Ti, Al, Y and C, in the long-fiber composites was analyzed using an electron probe microanalyzer (EPMA: type V6, Shimadzu Ltd., Japan).

3. Results and discussion

3.1 Distribution of coating elements

The distribution of Ti for the surface of the test piece with Ti-coated fibers before push-out is shown in Fig. 3. The results of line analysis through the center of the fiber are also shown in Fig. 3. It was confirmed that Ti was present only along the interface between the fibers and the matrix. The same results were obtained for other coatings (Al, Y and C).

3.2 Interfacial strength

The interfacial strength for the specimens with coated fibers are shown in Table 1. They could be classified into two groups: Ti- and Al-coated group, which showed high interfacial strength, and the Y-

Fig. 3. Ti distribution of surface for push-out test piece (Ti coating).

Table 1. Mechanical Properties

Coating element	Bending strength /MPa	Fracture toughness / $\text{MPa}\cdot\text{m}^{1/2}$	Fracture energy /J/m ²	Number of whiskers /mm ²	Interfacial strength /MPa
Ti	1170±20	9.2±0.2	158	2700	95
Al	1180±50	9.0±0.1	172	3300	100
Y	1010±30	8.4±0.0	177	6800	5
C	980±30	8.3±0.0	185	7500	8
non	1080±20	8.7±0.0	161	3000	

*Measured using SiC long fibers

and C-coated group, in which interfacial strength was low. In order to find the cause of the difference between these two groups, the surfaces of the test pieces after push-out were observed by SEM. Figure 4 shows the typical SEM micrographs of each group; (a) is the Ti coating, and (b) is the Y coating. The coating layers were so thin that they could not be seen in these pictures. It was found that debonding occurred at different locations; in the cases of Ti and Al coatings, which showed high interfacial strength, the debondings were thought to have occurred between the SiC and the surface C-rich layer. This indicates that the interfacial strength between the fibers and the matrix was higher than that between the SiC and the C-rich layer. In the case of the Y and C coatings, which showed low interfacial strength, the debondings were thought to have occurred at the interface between the fibers and the matrix. This means that the Y and C coatings result in weak bonding between the fibers and the matrix.

3.3 Whisker coating

The thickness of the coatings on the whisker surfaces was measured using TEM. Most whiskers were coated uniformly. Figure 5 shows the TEM micrographs of whiskers with the coatings. The thickness of Ti, Al and Y coatings was 30–40 nm, and that of the C coating was 15–30 nm.

The damage to the surface coatings caused by the ball-milling was also checked using TEM. The thickness of the Ti, Al and Y coating layers did not change noticeably, while the thickness of the C coating was decreased to 10–15 nm. This appeared to be due to the difference in the coating methods and

Fig. 5. TEM micrographs of whisker surfaces with various coatings ((a) Ti coating, (b) Al coating, (c) Y coating and (d) C coating).

mechanical properties of the coating layers.

3.4 Mechanical properties

The mechanical properties of the composites are shown in Table 1. It was found that samples could be divided into two groups according to the interfacial strength. In the case of high interfacial strength, the bending strength and fracture toughness were relatively high, and fracture energy was low, while in the group with relatively low interfacial strength, the bending strength and fracture toughness were somewhat low, and fracture energy was high.

Figure 6 shows the SEM micrographs for the frac-

Fig. 4. SEM micrographs of SiC fiber/ Si_3N_4 matrix interfaces after push-out test ((a) Ti coating and (b) Y coating).

Fig. 6. SEM micrographs of fractured surfaces for CN test pieces ((a) Ti coating and (b) Y coating).

Fig. 7. SEM micrographs of fractured surfaces for CN test pieces (Y coating).

tured surfaces of CN test pieces; (a) shows the Ti coating and (b) the C coating. A careful examination of Fig. 6 revealed whiskers pulled out, as shown by the arrows in Fig. 7 and the number of whiskers pulled out was counted. The results are also shown in Table 1. A correlation was found between the number of whiskers and the fracture energy, suggesting that lower interfacial strength is effective in raising the fracture energy by the crack wake mechanism of pull-out or crack bridging, while higher interfacial strength is beneficial to increase the fracture toughness because it affects the crack tip before crack propagation starts.

4. Conclusion

The following conclusions can be reached from the results of this investigation.

(1) Ti and Al coatings on the whiskers appear to increase the interfacial strength between whisker and matrix, while Y and C coatings appear to reduce it.

(2) When the interfacial strength was high, bending strength and fracture toughness were relatively high, and fracture energy was low. On the other hand, in the group with low interfacial strength, bending strength and fracture toughness were somewhat low, and fracture energy was high.

(3) Whiskers with low interfacial strength probably affect the crack wake by pull-out or crack bridg-

ing, while those with high interfacial strength have more effect on the crack tip before crack propagation starts.

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