Mechanical Properties of SiC Whisker-Reinforced Mullite Composites (Part 2)

—The Effects of Diametrical Change and Carbon-Coating of Whiskers—

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炭化ケイ素ウイスキー強化ムライト複合材料の機械的性質 (第2報) —ウイスキー径及びウイスキーへのカーボン被覆の影響—

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The effects of whisker diameter and carbon-coating of whiskers on the flexural strength and the fracture toughness of SiC-whisker-reinforced mullite composites were studied, and quantification of a crack deflection was attempted. The flexural strength and the fracture toughness gradually increased with increasing the amount of SiC whiskers. The strength slightly decreased with increasing whisker diameter and after coating the SiC whiskers with carbon. In contrast, the fracture toughness slightly increased. The toughening of SiC-whisker-reinforced mullite composites is contributed to mainly by the increase of the elastic modulus by the addition of SiC whiskers with high elastic modulus and the occurrence of debond-bridging in the SiC whisker-mullite matrix interface, but is accompanied by slight crack deflection and whisker-pullout.

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1. Introduction

High-purity mullite ceramics have received considerable attention for their structural applications at high temperatures because the creep rate of mullite is very low, even at 1400°C.¹⁻⁷ The fracture toughness (about 2.1 MPa·m^{1/2}) however, is lower than those of other structural ceramics. Thus, we tried to improve the fracture toughness of mullite by reinforcing it with SiC whiskers.

The strength and fracture toughness of SiC-whisker-reinforced mullite composites have already been reported by many researchers.⁸⁻¹⁰ Becher et al.¹¹ reported debond-bridging in the whisker-matrix interface as a toughening mechanism of the SiC-whisker-reinforced alumina and mullite composites. Furthermore, Yamade et al.¹² measured the interface shear strength between the SiC fiber and mullite matrix using an indentation fiber push-through technique. Many researchers have reported crack deflection as a toughening mechanism of SiC-whisker-reinforced oxide¹³ and silicate-glass¹⁴ matrix ceramics. On the other hand, one of the authors has already studied the strengthening and toughening mechanism of SiC-whisker-reinforced silicate-glass ceramics, and reported that toughening of the composites was contributed to mainly by load transfer from the glass matrix to SiC whiskers, and the whiskers were broken before crack face was bridged.¹⁵⁻¹⁷

Well-dispersed whiskers are required in the ceramic matrix to reveal the strengthening and toughening mechanisms of whisker-reinforced ceramic composites. If the dispersal is poor, the addition of whiskers results in the occurrence of defects. That is, it becomes difficult to elucidate the strengthening and toughening mechanisms of the composites because the properties are considerably

affected by an unsuitable composite processing.

In previous papers,^{18,19} we reported that the dispersal was improved by the addition of a dispersant. In this paper, the effects of diametrical change and carbon-coating of whiskers on the mechanical properties of SiC-whisker-reinforced mullite composites fabricated under the optimum dispersal condition reported previously¹⁹ were studied. By comparing the strength, fracture toughness and the extent of crack deflection, the strengthening and toughening mechanisms for SiC-whisker-reinforced mullite composites were investigated.

2. Experimental procedure

The average diameter of the mullite powder (Chichibu Cement Co.) used in this study was 1.3 μm. The symbols, average diameters and lengths of SiC whiskers (Tokai Carbon Co.) are shown in Table 1. The organic material characterized in the previous paper¹⁸ was used as a dispersant. The mullite powder and SiC whiskers was stirred for 10 h in an alumina ball-mill with ethanol containing the

Table 1. Diameter and Length of SiC Whiskers

Symbol of whisker	Diameter μm	Length μm
W(A)	0.4	30
W(AC)	0.5	35
W(B)	1.1	45
W(BC)	1.2	45

The whiskers W(AC) and W(BC) are coated with carbon.

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dispersant and the mixture was then dried in a rotary evaporator. The mixed powder was hot-pressed at a pressure of 29.4 MPa at 1650°C for 2 h with a graphite die of 20 mm in diameter. The cylindrical specimen was cut into rectangular bars of 4 mm in width, 2 mm in thickness and 20 mm in length. The rectangular bars were mirror-polished with 1 μm diamond paste in order to measure their strength.

Flexural strength was measured at a crosshead speed of 0.5 mm/min by a three-point bending fixture with a span of 16 mm, and fracture toughness was determined by an indentation fracture technique (Vickers indentation load of 98 N).

3. Results and discussion

3.1 Strength and fracture toughness

Figure 1 shows the relation between average flexural strengths and SiC whisker content for the whisker-reinforced mullite composites. Data points and error bars correspond to the average strengths and standard deviation of 8–10 specimens, respectively. Flexural strength increased from 365 MPa for monolithic mullite to 704 MPa for 30 vol% W(A) and to 684 MPa for 30 vol% W(B) with increasing amount of whiskers. However, the strength decreased abruptly on the addition of 40 vol% SiC whiskers. On the other hand, the relative density of these composites maintained a constant value of about 99% up to 30 vol% SiC whiskers. However, the relative density decreased to about 89% for W(A) and about 92% for W(B) on the addition of 40 vol% SiC whiskers. That is, the decrease in strength upon the addition of 40 vol% SiC whiskers corresponds to the drop in relative density. The effects of diametrical change and carbon-coating of whiskers are also shown in Fig. 1. The strength of SiC-whisker-reinforced mullite composites slightly decreased with increasing whisker diameter and upon coating SiC whiskers with carbon.

Figure 2 shows the fracture toughness as a function of the size of the crack that appeared in the circumference of a Vickers indentation. The apparent fracture toughness for all four types of SiC-whisker-reinforced mullite composites increased with increasing indentation load, that is, with lengthening crack size. It is assumed that the dependence of fracture toughness on the crack size corresponds to the *R*-curve behavior already reported for ceramics which contain elongated grains. In this study, because the apparent fracture toughness was close to the maximum value at an in-

Fig. 1. Flexural strength and relative density of sintering body as a function of SiC whisker content.

Fig. 2. Apparent fracture toughness as a function of indentation load or crack length.

Fig. 3. Fracture toughness as a function of SiC whisker content.

dentation load of 98 N, the value was adopted as the fracture toughness of the specimen.

Figure 3 shows the relation between the fracture toughness of SiC-whisker-reinforced mullite composites and the whisker content. The fracture toughness of SiC-whisker-reinforced mullite gradually increased with increasing whisker content from 2.1 $\text{MPa}\cdot\text{m}^{1/2}$ for monolithic mullite to 5.7 $\text{MPa}\cdot\text{m}^{1/2}$ for W(A) and 6.2 $\text{MPa}\cdot\text{m}^{1/2}$ for W(B) at 30 vol% SiC whiskers. The effects of diametrical change and carbon-coating of whiskers on the fracture toughness of the composite are also shown in Fig. 3. The fracture toughness of these composites slightly increased with increasing whisker diameter and upon coating the SiC whiskers with carbon.

3.2 Fracture surface

Figure 4 shows the fracture surfaces after measuring the flexural strength of SiC-whisker-reinforced mullite composites. Whisker pulled out of matrix and their sockets are observed in these photographs. The evidences of whisker-pullout became sparse in the composites using the small-diameter whisker W(A), while there was more on using the large-diameter whisker W(B) or carbon-coating the small-diameter whiskers W(AC), and the most on carbon-coating the large-diameter whiskers W(BC). However, the whiskers were nearly all broken close to the fracture surface of the matrix. That is, the length of whiskers pulled out was short and the whisker sockets were shallow.

3.3 Crack configuration

Figure 5 shows the propagation of a crack induced by

Vickers indentation on the mirror-polished surfaces of the monolithic mullite and whisker-reinforced mullite composites. Crack paths in the whisker-reinforced mullite become more irregular than those in the monolithic mullite. There are two mechanisms to described how a crack, progressing in a zigzag manner, contributes to toughening of the composites.

(A) When a progressing crack reacts with grain boundaries, or with particles or whiskers, the crack is tilted or twist at an angle. As a result, toughening is induced because the K_{II} and K_{III} modes add to the stress intensity factor of K_I . Faber and Evans²⁰⁾ derived a theory to analyze the crack deflection with this model.

(B) Fracture surface energy increased with an increase in the fracture surface area which becomes rough due to the zigzag progression of the crack. As a result, the toughening is induced.

The way of crack development observed in this study does not show a form illustrated in the geometrical figures to which the Faber and Evans' theory can be applied. Thus, the authors tried to determine the extent to which the increase in the surface area by irregular crack progression contributes to the increase of fracture toughness.

The development of the crack was traced with a digitizer in order to evaluate the extent of crack deflection. We defined a value divided by the distance of actual crack progression (L_R) by the straight distance between two points, A and B, in the crack (L_0), as the extent of crack deflection (L_R/L_0), as shown in Fig. 6. Table 2 shows the extent of crack deflection obtained for 20 and 30 vol% SiC-whisker-reinforced mullite composites. The crack deflection became more remarkable in the composites with the large-diameter

Table 2. Degrees of Crack Deflection

SiCw content (vol%)	M	W(A)	W(AC)	W(B)	W(BC)
20	1.10 ±0.03	1.19 ±0.06	1.25 ±0.07	1.27 ±0.09	1.34 ±0.12
30	1.10 ±0.03	1.23 ±0.10	1.35 ±0.09	1.39 ±0.10	1.46 ±0.13

The symbol M shows mullite matrix.

Fig. 4. SEM micrographs of fracture surface. "W" and "H" indicate the pulled-out whiskers and their sockets, respectively.

Fig. 5. Propagation of a crack induced by a Vickers indentation for mullite and 20 vol% SiC-whisker-reinforced mullite composites.

Fig. 6. Schematic crack deflection profile to define the extent of crack deflection.

Fig. 7. The ratio of strength, fracture toughness and the extent of crack deflection in 20 and 30 vol% SiC-whisker-reinforced mullite composites to those in mullite.

whiskers and most when the large-diameter whiskers were coated with carbon.

Figure 7 shows the ratios of strength, fracture toughness and the extent of crack deflection (L_R/L_M) in 20 and 30 vol% SiC-whisker-reinforced mullite composites to the values (L_M) in the monolithic one. Upon adding 20 and 30 vol% SiC whiskers W(A), the fracture toughness increased 2.3 and 2.7 times, and the strengths increased 1.8 and 1.9 times, respectively. On the other hand, the extent of crack deflection increased only 1.1 times. That is, the increase in the fracture toughness upon adding SiC whiskers corresponds to the increase in the strength but not to the increase of crack deflection.

When the whisker diameter increased from 0.5 to 1.2 μm , the fracture toughness increased only 1.1 times in the composites reinforced with 20 and 30 vol% SiC whiskers, while the strength of the composite slightly decreased to 0.94 and 0.97 times, respectively. On the other hand, the extent of crack deflection increased only 1.1 times.

When the whiskers were coated with carbon, the fracture toughness increased negligibly in 20 vol% SiC whisker W(A) and W(B) composites, while the strength of the composites slightly decreased to 0.96 and 0.99 times, respectively. On the other hand, the extent of crack deflection in composites increased only 1.1 times owing to the carbon coating. The composites containing 30 vol% SiC whiskers showed a similar tendency in fracture toughness, strength and the extent of crack deflection to those of 20 vol%.

In summary, it is estimated that crack deflection contributes little to the enhancement of the fracture toughness.

Figure 8 shows some examples of interaction between a crack and whiskers. Whisker-pullout (P), crack-bridging by whiskers (B) and debonding of the whisker-matrix interface (D) are observed in the SEM micrographs. It was already described that many SiC whiskers were broken near the fracture surface of the matrix and that the length of whiskers pulled out was also short, that is, the whisker sockets were shallow. It is unlikely that whisker-pullout

significantly contributes to the toughening mechanism of a SiC-whisker-reinforced mullite composite. On the other hand, debonding of the whisker-matrix interface was observed in the composite with large-diameter whiskers and more observed in that with the carbon-coated large-diameter whiskers, but was rarely observed in the specimen with small-diameter whiskers.

4. Discussion

Figure 9 is the schematic illustration for the stress intensity factors of a composite and a monolithic mullite and the extent of crack development.²¹⁾ The toughening stages for the composite are divided into two steps. The stress intensity factor (K) in stage I is smaller ($K < K_{IC}^c$) than the critical stress intensity factor (K_{IC}^c) of the composite, while that in stage II is larger ($K > K_{IC}^c$). In stage II, the fracture resistance increases with increasing crack length, that is, the apparent fracture toughness shows behavior that follows the R -curve.

The critical stress intensity factors of the composite, K_{IC}^c , in stage I is expressed by the following equation.

$$K_{IC}^c = K_{IC}^m + \Delta K_0^c \quad (1)$$

K_{IC}^m is the critical stress intensity factors of the monolithic mullite and ΔK_0^c originates from the increase in the elastic modulus of the composite upon adding SiC whiskers with high elastic modulus.

On the other hand, if the increment of the stress intensity factor K in stage II is described by ΔK^c , the measured stress intensity factor K^T is expressed by

$$K^T = K_{IC}^c + \Delta K^c = K_{IC}^m + \Delta K_0^c + \Delta K^c \quad (2)$$

$$\Delta K^T = \Delta K_0^c + \Delta K^c \quad (3)$$

ΔK^T corresponds to the overall increment of fracture toughness upon adding SiC whiskers to monolithic mullite ($K_{IC} = 2.1 \text{ MPa} \cdot \text{m}^{1/2}$).

First, the increase of K_{IC}^c in stage I is considered. According to Marshall et al.²²⁾ and McCartney,²³⁾ K_{IC}^c is a function of E^c/E^m and increases with the increase of E^c/E^m . Young's moduli of SiC whisker are 400–700, 670 and 700 GPa, according to the supplier's catalogue (Tokai Carbon Co. catalogue), as reported by Gadkaree and Chyung¹⁴⁾ and Kagawa and Hatsuta,²⁴⁾ respectively. On the other hand, the Young's modulus of mullite was evaluated to be 187 GPa at room temperature. If Young's modulus of SiC whiskers is assumed to be 650, E^c/E^m becomes 1.5 and 1.7 for the composites containing 20 and 30 vol% whisker, respectively. That is, it is estimated that the toughening in stage I is contributed to markedly by the increase of the elastic modulus.

Next, the toughening mechanisms in stage II are considered. Pullout or debonding of whiskers is considered as a toughening mechanism in this stage. It is, however, considered that the contribution of whisker-pullout is considerably smaller than that of debonding, according to the observation of crack development shown in Figs. 5 and 8. On the other hand, Yamada et al.¹²⁾ reported that a SiC fiber was pulled or pushed out from the mullite matrix at 1550°C at which the sintering seems insufficient but not at 1650°C at which the sintering is sufficient.

Becher et al.^{11),25),26)} derived the following equation, if the toughening of SiC-whisker-reinforced mullite composite was contributed to mainly by the debond-bridging of whiskers.

$$\Delta K \propto V_f^{1/2} r^{1/2} \quad (4)$$

This equation indicates that the fracture toughness increases with increasing the whisker diameter. It is apparent from the detailed observation of crack propagation that the debonding of the whisker-matrix interface increases with the use of the large-diameter whiskers and more after coating the whiskers with carbon. The fracture toughness

Fig. 8. Typical examples of whisker-pullout (P), crack-bridging (B) and debonding of whisker-matrix interface (D) occurring due to the interaction between whiskers and progressing crack.

Fig. 9. Toughening stages in a whisker-reinforced composite.²¹⁾ K_C^m , K_C^c : The critical stress intensity factors of monolithic mullite and composite. K^T : Measured critical stress intensity factor.

slightly increases with increasing whisker diameter and on using the carbon-coated whiskers, as shown in Figs. 3 and 7. It is estimated from the comparison of the results obtained in this study with Becher's theory that debond-bridging in the whisker-matrix interface contributes considerably to the toughening mechanism of SiC-whisker-reinforced

mullite composites.^{25),26)} On the other hand, it is assumed that whisker-pullout contributes slightly to the main toughening mechanism. At the present stage, the contribution ratio of debond-bridging in stage II is unknown, because the contribution has not been quantitatively determined.

In summary, it is concluded that the toughening in SiC whisker-reinforced mullite composites is contributed to mainly by both the increase of the elastic modulus and debond-bridging in the whisker-matrix interface, while crack deflection and whisker-pullout contribute only slightly.

5. Conclusions

The effects of diametrical change and carbon-coating of whiskers on the flexural strength and the fracture toughness of SiC-whisker-reinforced mullite composites were studied. Comparing strength, fracture toughness and the extent of crack deflection, the strengthening and toughening mechanisms for SiC-whisker-reinforced mullite composites were considered. The results obtained are as follows.

(1) The flexural strength increased from 365 MPa for monolithic mullite to 704 and 684 MPa for 30 vol% of

W(A) and W(B) reinforced composites, respectively.

(2) The strength of the composites slightly decreased with increasing whisker diameter and on coating SiC whiskers with carbon.

(3) The fracture toughness increased gradually from $2.1 \text{ MPa} \cdot \text{m}^{1/2}$ for monolithic mullite to $5.7 \text{ MPa} \cdot \text{m}^{1/2}$ and $6.2 \text{ MPa} \cdot \text{m}^{1/2}$ for 30 vol% of W(A) and W(B) reinforced composites, respectively.

(4) The fracture toughness slightly increased with increasing whisker diameter and upon coating SiC whiskers with carbon.

(5) The toughening of SiC-whisker-reinforced mullite composites is contributed to mainly by the increase of the elastic modulus upon the addition of SiC whiskers with high elastic modulus and debond-bridging which occurs in the SiC whisker-mullite matrix interface.

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