JOURNAL OF MATERIALS SCIENCE 28 (1993) 5770–5774

Toughness enhancement by polycarbosilane coating on SiC whiskers incorporated in Si_3N_4 matrix composite

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Si_3N_4 matrix composite was fabricated by hot pressing with 20% SiC whiskers coated with polycarbosilane (PCS). The preceramic polymer on the whiskers was pyrolysed during sintering to form a carbon-rich layer at the whisker/matrix interface. Mechanical properties were measured, and compared to those of the composites with whiskers purified with HCl and HF. Elastic modulus and bending strength of the composite with PCS-coated whiskers were lower than those of the composites with other whiskers. Fracture toughness was measured by single-edge notched beam (SENB) and single-edge precracked beam (SEPB) methods. The toughness, including crack-growth resistance measured by the SEPB method, increased from 7.2 MPa $m^{1/2}$ to 7.9 MPa $m^{1/2}$ by PCS-coating on the whisker, while the toughness measured by the SENB method decreased from 6.5 MPa $m^{1/2}$ to 5.7 MPa $m^{1/2}$. The layer derived from PCS facilitated debonding at the whisker/matrix interface and activated the wake-toughening. Optical microscopic observation of the crack propagation near the interface confirmed enhancement of interfacial debonding by the PCS-coating.

1. Introduction

Toughening of ceramic material by whisker incorporation is based on several mechanisms, including crack deflection, whisker-bridging and pull-out. If the matrix/whisker interfacial bonding is strong, a matrix crack propagates through the whisker and makes the whisker fail, resulting in no substantial toughening. Therefore, debonding at the whisker/matrix interface is a prerequisite for the activation of these toughening mechanisms [1]. It is reported that the interfacial debonding occurs when the ratio of energy release rate at the interface to that of the fibre is less than 1/4 [2]. Becker *et al.* revealed that the whisker pull-out length is dramatically reduced when the whisker has a high surface oxygen content in SiC whisker/Al_2O_3 composite [3]. The toughness of the composite with low oxygen content whisker was about 2 MPa $m^{1/2}$ higher than that of the composite with high oxygen content whisker. Homeny *et al.* have evaluated the effect of whisker surface treatment on the toughness of SiC whisker/Al_2O_3 composite [4]. Two kinds of the whisker were heated in air, H_2–N_2, and H_2–Ar atmospheres at 500–1600 °C to modify the whisker surface. They found that the presence of silicon oxycarbide and free carbon and/or hydrocarbon species on the whisker surface evidently weakened the degree of the whisker/matrix bonding, while the presence of silicon dioxide promoted good bonding. These results suggest that a coating of carbon or carbon-rich material on the whisker surface promotes debonding at the whisker/matrix interface and enhances the composite toughness.

In this study, SiC whiskers with an average diameter of 2.8 μm were coated with polycarbosilane (PCS) by dipping in the polymer solution. Polycarbosilane is known as a preceramic polymer that yields silicon carbide on its thermal decomposition. Final composition of the pyrolysis product from the polymer is SiC_{1+x} ($x = 0.4$–0.6) [5, 6], the product thus contains a large amount of excess carbon. The microstructure of the polymer-derived ceramic is a mixture of fine-grained SiC and graphite with amorphous grain-boundary phase when decomposed at below 1200 °C. At higher temperatures, grain growth of the carbide and free carbon takes place. Chemical analysis shows that the pyrolysis product has a composition of 38 at % Si, 59 at % C, 2 at % O, and 1 at % H when pyrolysed at 1600 °C in argon [6], indicating that it is composed of 64 mol % SiC and 36 mol % carbon. Such carbon-rich product can be expected to produce weaker bonding at the whisker/matrix interface when it was deposited on the whisker surface. Brennan reported the formation of a carbon-rich interfacial zone on Nicalon fibre in LAS-glass composite [7]. The layer was very thin (~10–40 nm) but extremely carbon-rich, allowing crack deflection to occur along the fibre/matrix interface. In our study, matrix Si_3N_4 was sintered with magnesium oxide to accelerate the liquid sintering, so that the SiC layer from PCS on the whisker directly contacts the oxide. It is quite possible that a carbon-rich layer is formed at the whisker/matrix interfacial zone, as in the Nicalon/LAS-glass composite.

Si_3N_4 matrix composites with three kinds of SiC whiskers were prepared. One type of whisker was washed with HCl to remove residual impurities containing transition metals, the second was washed with

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HF after HCl treatment to remove the surface SiO_2 layer, and the third was coated with PCS subsequent to these acid treatments. They were sintered by hot pressing and their mechanical properties, including bending strength, fracture toughness, elastic modulus and hardness, were evaluated with respect to the surface modifications of the whiskers.

2. Experimental procedure

Si_3N_4 (Ube Industry Co. Ltd, SN-E-10, average grain size 0.2 μm, α phase > 95 %, oxygen 1.24 wt %) was doped with 5 wt % MgO (Iwatani Chem. Ind. Co., MTK-30, average grain size 0.25 μm, purity > 99.9%) by ball-milling with Si_3N_4 balls and ethanol in a polyethylene bottle for 24 h. Silicon carbide whisker (Tokai Carbon Co. Ltd, TWS-1000) has an average diameter of 2.8 μm and an average length of 70 μm. Impurities are 0.1 wt % SiO_2, 3570 p.p.m. Fe, 40 p.p.m. Co and 180 p.p.m. Ca. These impurities, including metal atoms, are regarded as being residue of catalysts for whisker production. Polycarbosilane (Nippon Carbon Co. Ltd), has a number average molecular weight of 1590 and a weight-average molecular weight of 3600. Its density is 1.12 $g\,cm^{-3}$ and the melting point is 232 °C.

The procedure for whisker-surface treatment is as follows. As-purchased whisker was first washed with concentrated hydrochloric acid (36%) to remove metallic impurities. Then, after repeatedly washing with distilled water, the whisker was dipped into 46.5% hydrofluoric acid for 5 h to remove SiO_2, and washed again with water. After drying, the whisker was mixed with 2% hexane solution of PCS. Then the solvent was extracted by a rotary evaporator. The amount of PCS sufficient to coat the whisker with the 1 μm thick polymer layer was determined on the basis of average thickness and length of the whisker. Three kinds of whisker, that is, one treated with HCl (whisker A), one with HF (whisker B) and one coated with PCS (whisker C), were dispersed in pH-controlled water (pH > 11, adjusted by aqueous ammonia) and mixed with Si_3N_4 by throwing it into each whisker dispersion. The whisker content was 20 wt %. The powder–whisker mixture slip thus prepared, after neutralizing with HCl, was cast into a Buchner funnel to form a green compact which was then cut into shape to fit the hot-pressing mould.

Sintering was carried out by hot-pressing at 1850 °C for 30 min under a pressure of 30 MPa. The sintering atmosphere was 0.98 MPa nitrogen for composites with whiskers A and B. For the composite with whisker C, PCS on the whisker was decomposed by gradual heating of the green compact from room temperature to 500 °C in vacuum, and to 1200 °C under a nitrogen flow. At temperatures over 1200 °C, uniaxial pressure was charged under nitrogen of 0.98 MPa.

Bulk density was measured by the Archimedean method after the sample surface was ground on a 200 diamond wheel. Elastic modulus was obtained by measuring bending strain in a test piece about 1 mm thick, 4 mm wide and 40 mm long, according to JIS R-1602. Three-point bending strength was measured with a span of 20 mm and a crosshead speed of 0.5 $mm\,min^{-1}$ at room temperature (JIS R1601). The test bar was 3 mm thick, 4 mm wide and 40 mm long. Its tensile surface was polished with 1 μm diamond paste. An average value was obtained from four test pieces. For both measurements, the tensile plane was perpendicular to the hot-pressing direction, that is, parallel to the whisker orientation plane.

Fracture toughness was measured by single-edge notched beam (SENB) and single-edge precracked beam (SEPB) methods. For SENB measurement, a straight notch was introduced by a diamond blade with a thickness of 100 μm at the centre part of the sample bar 3 mm thick, 4 mm wide and 18 mm long. Notch depth was about 0.9 mm. In SEPB measurement, pop-in precrack was introduced into the test bar 4 mm thick, 3 mm wide and 18 mm long. Details are described elsewhere [8]. The depth of the precrack was about 1 mm including the straight saw notch, having a depth of 0.5 mm for the initiation of the pop-in cracking. In both SENB and SEPB measurements, test pieces were subjected to three-point bending with a crosshead speed of 0.5 $mm\,min^{-1}$ and $S/W = 4$, where W is the thickness of the test piece and S is the span. The pop-in precrack and straight-through notch were parallel to the hot-pressing direction, so that cracks would extend perpendicular to the whisker orientation direction. Toughness value was calculated on the basis of an equation described in JIS-R1607. Four and eight pieces were tested to obtain an average value for SENB and SEPB methods, respectively.

In SENB measurement, fracture initiates from the notch root. The stress distribution around a notch with finite root radius, ρ, is different from that around a crack. Fracture toughness for notched specimen, $K_{c,n}$, should be corrected to determine the exact fracture toughness, K_{IC}, for a cracked specimen. Usami *et al.* reported the relation of the fracture toughness between a crack and a notch to be [9]

$$K_{c,n}/K_{IC} = 1/2(\rho/2r)^{1/2} \quad (1)$$

when $\rho \gg r$, where ρ is a notch root radius, that was measured directly by optical microscopy. The term r is the size of a coarse grain adjacent to the notch root. In their grain fracture model, Usami *et al.* [9] assume that unstable fracture initiates when a crack from the root propagates through the grain or along the grain boundary and the stress intensity factor exceeds a critical value at the crack tip. In the composite studied here, such a coarse grain is nothing but an incorporated whisker, because even its thickness is about three times greater than matrix Si_3N_4 grains. As the whiskers align two-dimensionally owing to unidirectional shrinkage during hot pressing, and their orientation direction is perpendicular to the notch direction, we assumed that $r = 2.8$ μm, the average diameter of the whisker.

Vickers hardness was measured by indentation with a diamond pyramid at a load of 490 N for 30 s.

3. Results and discussion

3.1. Density and elastic modulus

Table I shows bulk and relative densities of the composites with whiskers A, B and C. The composites with

TABLE I Bulk and relative density, open porosity and elastic modulus of 20 wt % SiC whisker/Si_3N_4 composites with whiskers treated by various surface modifications

Whisker	Surface modification	Bulk density ($g cm^{-3}$)	Relative density (%)	Open porosity (%)	Elastic modulus (GPa)
A	HCl treatment	3.16	98.8	1.1	317
B	HF treatment	3.16	98.8	1.3	300
C	PCS coating[a]	3.12	97.5	0.9	286

[a] PCS = polycarbosilane.

whiskers A and B were almost fully densified. The relative density of the composite with whisker C was slightly lower than those of other composites, but its open porosity was comparable to those of other composites. On the calculation of relative density, bulk density was divided by the theoretical one ($3.2 g cm^{-3}$), which was derived by assuming that PCS has produced SiC and graphite. Although we have no detailed information about the structure of the product from PCS on the whisker, if amorphous phase remains after pyrolysis and it has a density the same as that of Nicalon fibre, the theoretical density is $3.17 g cm^{-3}$. In this case, the relative density of the composite with whisker C is 98.4%, being comparable to those of other composites and leaving no discrepancy with the results on open porosity.

Elastic moduli of the composites are also shown in Table I. The composite with whisker A had the highest elastic modulus, while the modulus tended to decrease as the whisker surface was modified in such a way as to weaken the interfacial bonding. When considering the elastic modulus of a multi-component solid, porosity and other structural imperfections should be taken into account. Mackenzie [10] proposed an equation for the effect of porosity on elastic modulus that enabled us to estimate Young's modulus of a material containing porosity, p, as

$$E = E_0(1 - f_1 p + f_2 p^2) \quad (2)$$

where E and E_0 are the elastic moduli of a solid with and without pores, and f_1 and f_2 are constants. The modulus without porosity, E_0, was calculated to be 325 GPa by applying the equation for the composite with whisker A. Putting these data into Equation 2, the elastic modulus of the composite with whisker C was estimated to be 309 GPa, being rather higher than the measured value (286 GPa). In addition to porosity, there should be certain reason(s) which have lowered the modulus beyond that expected from the Mackenzie's equation. One reason for the elasticity loss is the presence of polymer-derived SiC, as pointed out in the discussion of the density of the composite. Differing from sintered SiC ceramics, PCS-derived SiC has a low elastic modulus. The reported value for Nicalon fibre is 180–200 GPa [11]. Provided that PCS on the whisker has produced such SiC, its amount is 4 vol %, which will account for the decrease in elasticity of the composite. Another reason is structural imperfection caused by the whisker surface modification. Weak bonding will occasionally form microcracking at the interface on loading. Such microcracking is known to cause remarkable reduction in elasticity [12].

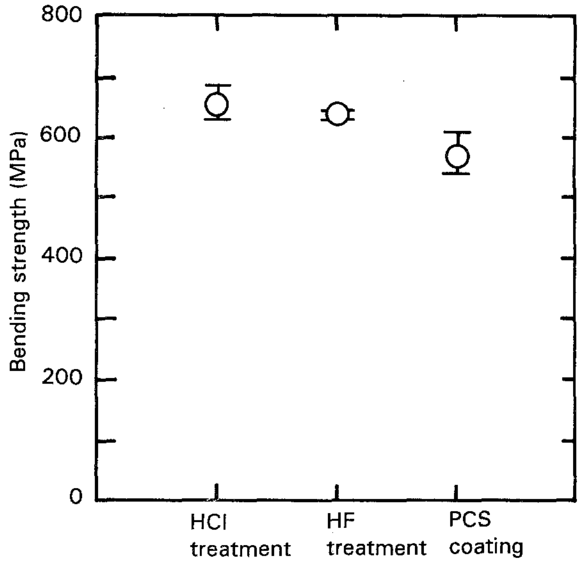

Figure 1 Bending strength of the composites with various surface-treated whiskers.

3.2. Bending strength and hardness

Fig. 1 shows the variation of room-temperature bending strength of the composites with various kinds of whisker. The difference in the strength between the composites with whiskers A and B was small, but the composite with whisker C showed about 80 MPa lower value than them. Porosity, which is known to degrade strength drastically, in the latter composite is, in fact, greater than those in the other composites, but its difference is less than 1.5%. Another reason for the strength loss is perhaps the weak interface between grains and the whiskers. The weak grain boundary along the whiskers may act as a fracture origin far larger than matrix grains, causing the strength degradation.

Fig. 2 shows the variation of Vickers hardness. A clear decrease in the hardness was observed for the composite with PCS-coated whisker. This is probably due to the increased number of potential sites which will allow grains to move along the grain boundary, suggesting the existence of weak grain boundaries in the composite.

3.3. Fracture toughness

Fig. 3 shows fracture toughness of the composites with whiskers A, B and C, measured by SENB and SEPB methods. The toughness measured by SENB method decreased, while the toughness by SEPB method increased with decreasing interaction between the matrix and the whisker.

In the SENB sample, fracture initiates from the notch root so that there is no toughening in the wake region behind the crack front. Therefore, the toughness determined by the SENB method includes no substantial R-curve effect nor long-range fracture resistance arising as often observed in coarse-grained

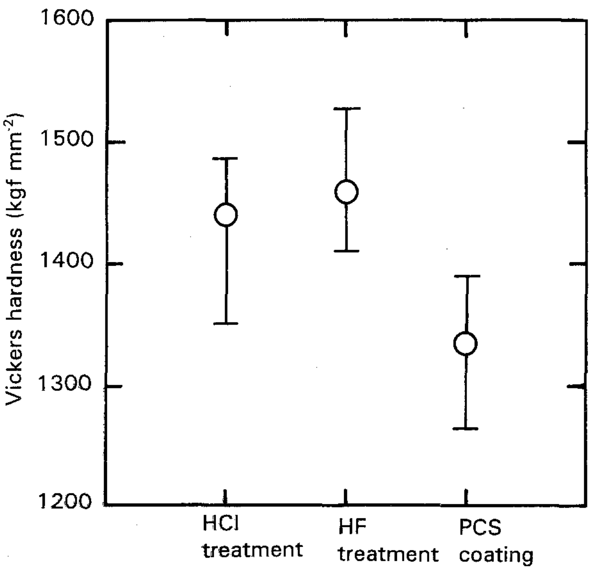

Figure 2 Vickers hardness of the composites with various surface-treated whiskers.

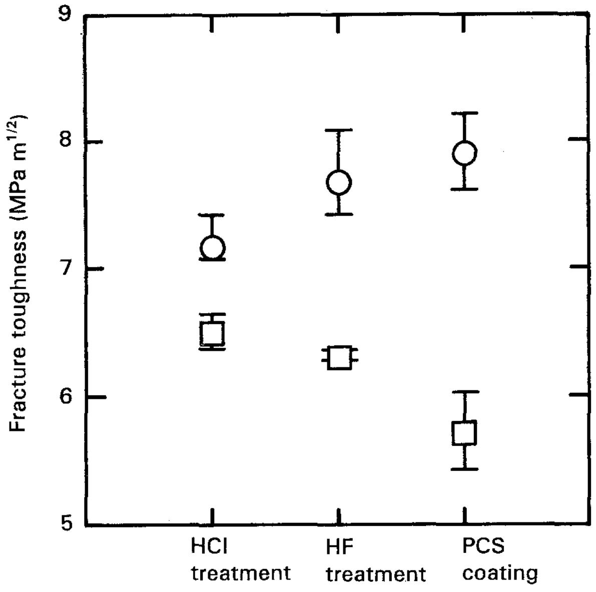

Figure 3 Fracture toughness of the composites with various surface-treated whiskers. (○) SEPB, (□) SENB.

ceramics, so it is regarded as fracture initiation resistance. The SENB toughness decreased from 6.5 MPa m$^{1/2}$ for the composite with whisker A to 5.7 MPa m$^{1/2}$ by PCS-coating on the whisker. The tendency of the toughness variation in Fig. 3 indicates that the crack initiation resistance decreases with decreasing bonding strength at the interface. It is not surprising that cracks start to propagate in the ceramics composed of weak grain boundaries.

On the other hand, a very sharp pop-in precrack is introduced in the SEPB test piece. Nishida *et al.* [13] pointed out that there is significant fracture-surface traction in the wake of the pop-in precrack formed in ceramics composed of coarse grains. The composite studied here contains a certain amount of whisker with large grain size compared with the matrix grain size. Therefore, such fracture-surface traction may exist with high probability, especially when the whisker/matrix interface separates easily. The SEPB toughness showed remarkable increase from 7.2 MPa m$^{1/2}$ for the composite with whisker A to 7.9 MPa m$^{1/2}$ for that with whisker C, indicating that the contribution of wake-toughening increased as the interfacial bonding became weak by surface modifications.

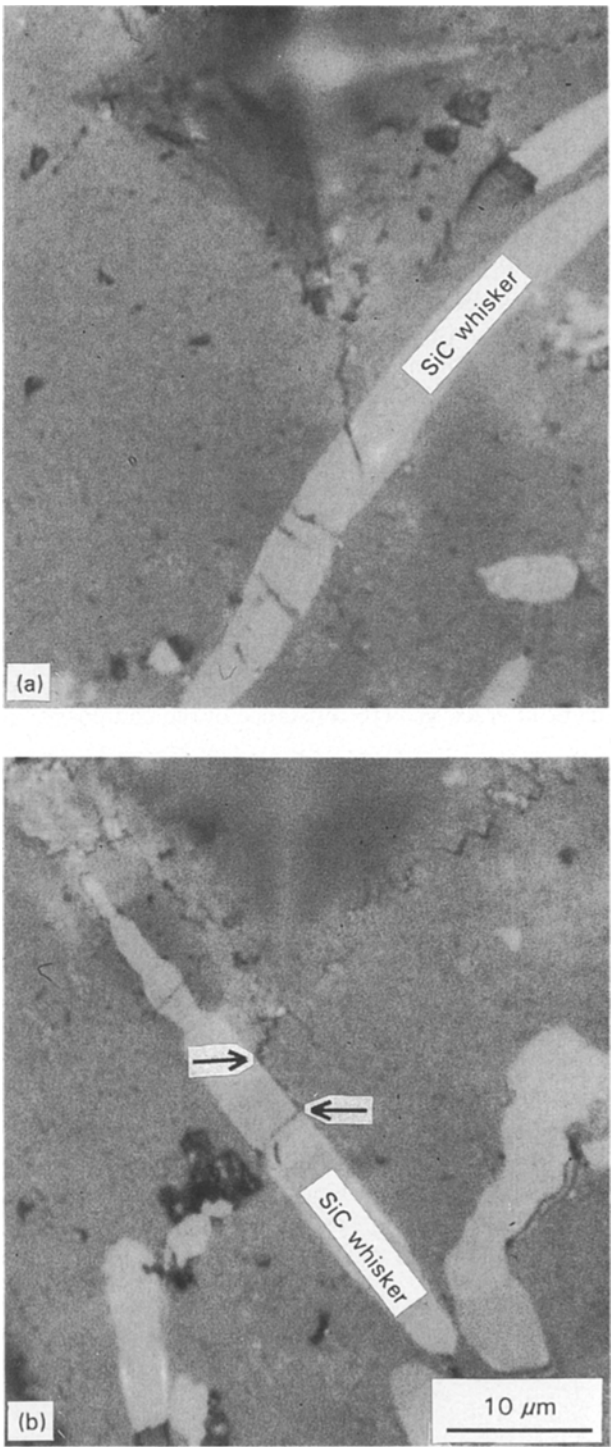

Figure 4 Optical micrographs of composite with (a) HCl-treated whisker, and (b) polycarbosilane-coated whisker.

3.4. Observation of crack propagation behaviour

To ascertain the effect of PCS-coating on the interfacial fracture mechanics, the debonding phenomenon was directly examined by observing the interaction between the whisker/matrix interface and the crack introduced by Vickers indentation with controlled distance and angle to the interface. Fig. 4a and b show optical micrographs of composites with HCl-treated whisker (whisker A) and PCS-coated whisker (whisker C), respectively. In Fig. 4a, the crack from the indentation edge reached the whisker/matrix interface with an angle of about 45° and propagated through the interface to the inside of the whisker. Neither debonding nor crack deflection was observed. On the other hand, in the composite with PCS-coated whisker (Fig. 4b), the crack with the angle of about 60° to the interface deflected at the interface and proceeded along the interface for about 3 μm and then deflected again into the whisker interior by crossing the interface. The debonded interface is indicated by two arrows in the picture.

These results indicate that the coating of the whisker with a polymer-derived layer is definitely effective in facilitating the debonding at the whisker/matrix interface. Such enhanced debonding has promoted wake-toughening and is responsible for the improvement in crack-growth resistance of the composite.

4. Conclusion

For fibre-reinforced ceramic composite, interfacial debonding is a prerequisite to activate the toughening mechanisms. In this study, it was revealed that enhanced debonding by a polymer-derived layer improved the crack-growth resistance by wake-toughening, but the fracture initiation resistance, known as fracture toughness, K_{IC}, was degraded. Strength and elastic modulus were also degraded by the PCS-coating on the whisker. It can be said that the weak whisker/matrix interface enhances crack-growth resistance at the expense of other mechanical properties. Weakened interfacial bonding is, however, profitable for ceramics, in that large-size crack growth is supposed and high crack-growth resistance is required. For example, ceramics can arrest crack extension by thermal shock if it has rising crack-growth resistance. On the other hand, it should be noted that such surface modification will cause easier fracture initiation.

Acknowledgement

This study was carried out in the project for advanced ceramics promoted by the R & D office for Basic Technologies for Future Industry, Agency of Industrial Science and Technology, the Ministry of International Trade and Industry, Japan.

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Received 2 June 1992
and accepted 27 April 1993