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Preparation and mechanical properties of high-purity Al_2O_3 fibre/Al_2O_3 matrix composite

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Al_2O_3 matrix composites with unidirectionally oriented high-purity Al_2O_3 fibre with and without carbon coating, were fabricated by the filament-winding method, followed by hot-pressing at 1573–1773 K. The composite with non-coated Al_2O_3 fibre exhibited a bending strength (594 MPa) comparable to that of monolithic Al_2O_3 (589 MPa). While the composite with a carbon-coated fibre had lower strength (477 MPa), it showed improved fracture toughness (6.5 MPa $m^{1/2}$) compared to the composite with an uncoated fibre (4.5 MPa $m^{1/2}$) and monolithic Al_2O_3 (5.5 MPa $m^{1/2}$). This toughness enhancement was explained based on the increased crack extension resistance caused by the fibre pull-out observed by SEM at the notch tip.

1. Introduction

Ceramic-matrix composites (CMC) have recently attracted much attention because they have higher fracture resistance and reliability compared to monolithic ceramics. An oxide fibre/oxide matrix composite is suitable for stable use in an atmospheric environment at high temperatures. A matching combination of the matrix and fibre, such as Al_2O_3/Al_2O_3, is attractive, because of being free from the problems of thermal expansion mismatch and chemical compatibility [1]. The purpose of this study was to fabricate an Al_2O_3 matrix composite reinforced with unidirectionally oriented high-purity Al_2O_3 fibre and to evaluate its mechanical properties.

The fibre/matrix interface is known to dominate the strength and toughness of a composite. If the interfacial bonding is too strong, the incorporated fibre fails with a propagating matrix crack. In such a case, any effective toughening mechanism, such as fibre pull-out or fibre bridging, will not work. A fibre coating which promotes the interfacial debonding and activates the toughening mechanism is desirable. In this study, carbon was coated on the fibre by pyrolysis of imide copolymer and its effect on the composite mechanical properties was elucidated.

2. Experimental procedure

The matrix starting powder was a fine-grained α-type Al_2O_3 powder (TM-D, Taimei Chem. Ind. Co.). It had an average particle size of 0.25 μm. Al_2O_3 fibre "ALMAX®" was supplied by the Mitsui Mining Material Co. Its Al_2O_3 content was over 99.5 mass %. The filament diameter was 10 μm, and the filament number per yarn was 1000. The density was 3.6 $Mg\,m^{-3}$, and it had an elastic modulus of 330 GPa and a tensile strength of 1800 MPa. Carbon coating on the fibre was conducted as follows. The Al_2O_3 fibre, without a sizing agent, was dipped into a 2% solution of bismaleimide-triazine copolymer resin (Mitsubishi Gas Chemical Inc.) in *N*-methyl-2-pyrrolidone and wound on a drum. After drying, the fibre was heat treated at 873 K for 7.2 ks under a nitrogen atmosphere. The resin on the fibre was converted to a carbon layer by this heat treatment [2].

Unidirectional Al_2O_3 fibre/Al_2O_3 composite was fabricated based on the filament-winding method. The matrix slurry contains 28 mass % Al_2O_3 powder, 9 mass % binder (polyvinylbutyral, polyethyleneglycol), 9 mass % plasticizer (dibutylphthalate), 1 mass % deflocculation aid (linseed oil), and 53 mass % solvent (ethyl alcohol). Al_2O_3 fibre was wound on to a drum after dipping into the slurry. The dried green sheet was then cut into the rectangular form having the size of 40 mm by 40 mm. Six sheets were die-pressed to obtain the green compact at 523 K under a pressure of 30 MPa. The fabricated green compact was then hot-pressed at 1573, 1673, and 1773 K for 1.8 ks under a pressure of 19.6 MPa in vacuum. The organic additives were burned out by gradual heating (0.083 $K\,s^{-1}$) up to about 773 K.

The sintered composite body was surface ground with a diamond wheel. Bulk density was measured by the water-immersion method. Three-point bending strength was measured for three test pieces 1 mm thick (for the composite) or 3 mm thick (for monolithic Al_2O_3), 4 mm wide and 40 mm long with a span of 30 mm and a crosshead speed of 0.0083 $mm\,s^{-1}$.

Fracture toughness was measured by the single-edge notched beam (SENB) method. A straight-through notch with a depth of about 1.5 mm, was machined by a 0.1 mm thick diamond blade perpendicular to the fibre orientation direction on the centre part of the test bar 4 mm thick, 3 mm wide and 20 mm long. Four pieces were tested with a span of 16 mm and the crosshead speed of 0.0083 mm s^{-1}.

The composite microstructure was observed by SEM and an optical microscope. Fibre volume percentage was determined based on its area fraction in the cross-sectional photo of the composite.

3. Results and discussion

The composite with original and carbon-coated Al_2O_3 fibre and monolithic Al_2O_3 is referred to as AA, CA, and MA, respectively.

3.1. Observation of composite structure

Optical micrographs of AA and CA samples fabricated at 1573, 1673 and 1773 K are shown in Fig. 1a–f, taken perpendicular to the fibre orientation direction in Fig. 1a–d, but parallel to the fibre direction in Fig. 1e and f. The dark line at the fibre/matrix interface in the CA sample, as indicated by an arrow in Fig. 1b, is considered to be the carbon layer coated on the fibre. There is no such line in the AA sample (Fig. 1a).

Fig. 1a and b indicate that the matrix Al_2O_3 surrounds the fibre sufficiently, suggesting that the matrix slurry has successfully impregnated into the fibre tow during the filament-winding process. The fibre content seems higher in the AA sample than in the CA sample. In fact, the measured fibre contents were 58 and 33 vol % for AA and CA samples, respectively. The difference is probably due to the wettability of the fibre. The heats of wetting of α-Al_2O_3 and graphone (graphitized carbon black) with 1-butanol are 239 and 114 mJ m^{-2} at ambient temperature, respectively [3]. Although the slurry was prepared with ethanol rather than 1-butanol, the tendency of the thermodynamic relation concerning the wetting phenomenon should not differ very much. The fibre with a carbon coating is considered to be less wettable to the slurry than the original Al_2O_3 fibre, so that the slurry could less impregnate into the former fibre yarn.

Fig. 1c and d are cross-sectional photos of AA and CA samples fabricated at 1673 K. The structure of AA sample changed from that fabricated at 1573K. Al_2O_3 fibres seem to join each other, as shown in Fig. 1c. The fibres make bridges between them, suggesting that they have started to sinter. No such interconnection between the fibres was observed in the CA sample (Fig. 1d). The carbon layer probably hinders such a fusion between the fibres.

When fabricated at 1773 K, it is difficult to distinguish the matrix and the Al_2O_3 fibre in the composites (Fig. 1e and f). Brighter regions are Al_2O_3 fibres in the AA sample, as indicated by arrows in the picture, but the fibre/matrix interface is not clear. It is not surprising that the fibre and the matrix, both Al_2O_3, have sintered to make a sintered structure, because the processing temperature was high enough for extensive sintering to occur. On the contrary, the interface looks clear in the CA sample (Fig. 1f). The carbon coating on the fibre has remained even after sintering at 1773 K.

3.2. Density

Fig. 2 shows the bulk density of the samples sintered at various temperatures. Monolithic Al_2O_3 (sample MA) has almost full density when sintered at a temperature higher than 1673K. The density of both AA and CA increases with increasing sintering temperature. The open porosity of sample AA and CA is less than 3% when sintered at 1773 K. The carbon coating did not affect the sintering behaviour.

3.3. Bending strength

The bending strengths of MA, AA, and CA samples sintered at various temperatures are shown in Fig. 3. Monolithic Al_2O_3 ceramic has the highest strength when sintered at 1673 K. Its density becomes nearly full at this temperature. The strength degradation by the sintering at 1773 K is probably due to grain coarsening. The strengths of the composites AA and CA both increase with increasing sintering temperature. Strength improvement may be attributed to the matrix porosity which decreases with increasing sintering temperature. The strength of the AA sample sintered at 1773 K, 594 MPa, is comparable to the maximum strength of the monolithic MA sample (589 MPa). The incorporation of Al_2O_3 fibre does not reduce the strength of Al_2O_3 ceramics, as long as it is nearly fully sintered. On the other hand, the strength of CA is lower than that of AA. The carbon coating on the fibre may make a weak bonding in the composite.

3.4. Fracture toughness

Fig. 4 shows the fracture toughness of MA, AA, and CA samples. The CA sample exhibits remarkable toughness enhancement. Its toughness of 6.5 MPa $m^{1/2}$ is higher than that of the monolithic MA sample by 1.0 MPa $m^{1/2}$. On the other hand, the composite AA with as-purchased Al_2O_3 fibre, has lower toughness (4.4 MPa $m^{1/2}$).

To elucidate this toughness enhancement in the CA sample, the fracture behaviour of the composites was examined. Sub-critical crack extension is reported for polycrystalline Al_2O_3 and sapphire [4–6]. This phenomenon is readily observed in the controlled fracture. A distinctive deviation from the elastic behaviour in the load–deflection curve observed in the SENB test indicates crack extension from the machined notch tip [7]. For both AA and CA composite, such a deviation from the elastic behaviour before the maximum load point is observed, as shown in Fig. 5. Sub-critical crack extension has surely occurred in these composites. If any toughening mechanism works during this crack extension, the fracture resistance (*R*-curve effect) will increase.

The fracture surface near the notch tip of AA and CA samples was then examined by SEM after the SENB test. The result is shown in Fig. 6a and b for AA and CA samples, respectively. The AA sample has a

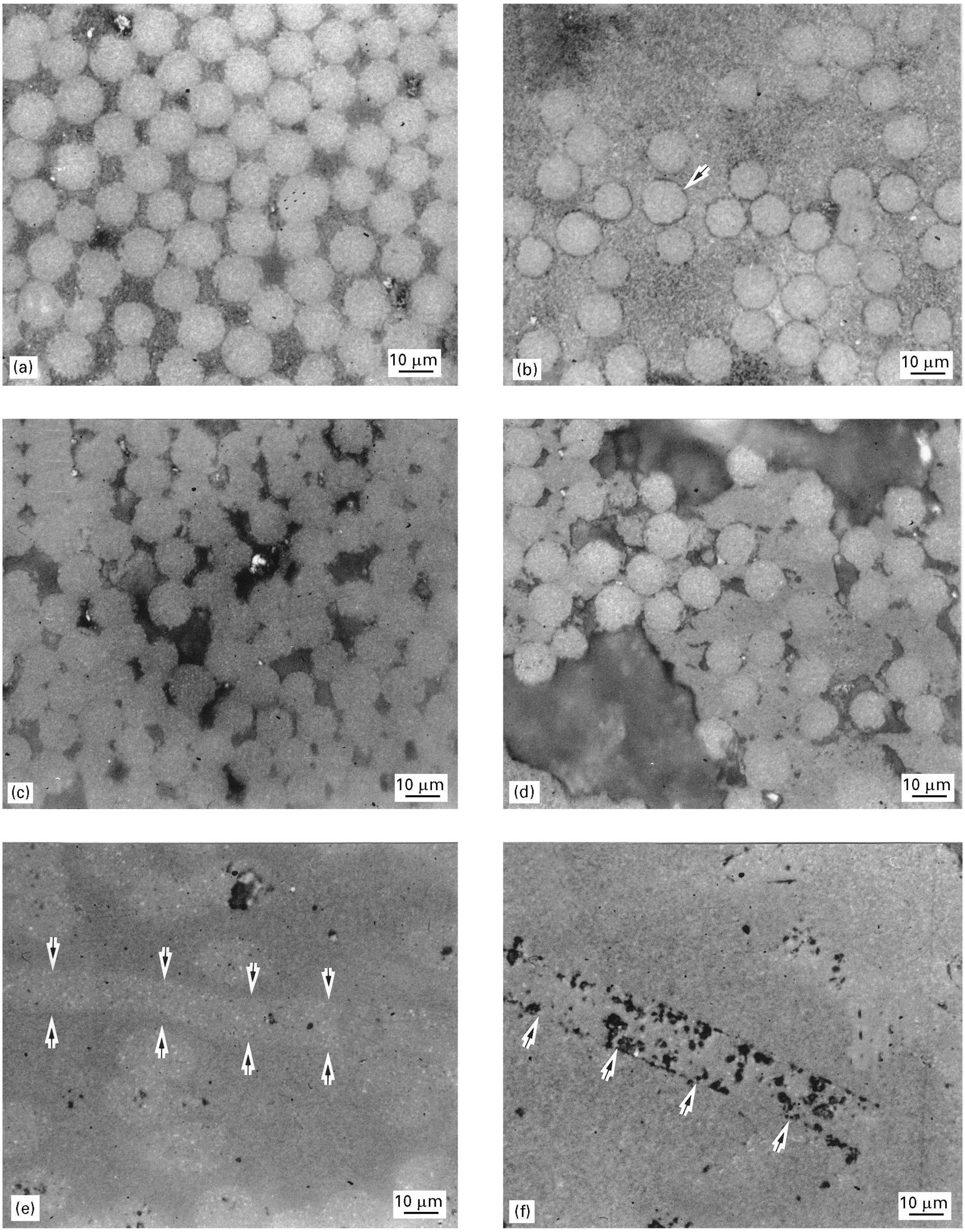

Figure 1 Optical micrographs of Al_2O_3/Al_2O_3 composite. The composite with the original Al_2O_3 fibre (sample AA, a, c, e) and the carbon-coated fibre (sample CA, b, d and f) were fabricated at 1573, 1673 and 1773 K, respectively.

flat fracture surface. The incorporated fibres have failed with the matrix as the crack extends from the notch tip, as indicated by the arrows in the Fig. 6a. This should be due to strong bonding at the fibre/matrix interface. No interfacial debonding, the prerequisite for fibre bridging or fibre pull-out, has occurred. On the other hand, in the CA sample, fibre pull-out can be observed such as indicated by the arrows in Fig. 6b. Such fibre pull-out is regarded to increase the crack extension resistance, *R*. Toughness enhancement in the CA composite, therefore, is possibly attributed to this *R*-curve effect.

4. Conclusion

Al_2O_3 fibre/Al_2O_3 composite was fabricated by the filament-winding method. The strength of the composite was comparable to that of monolithic Al_2O_3.

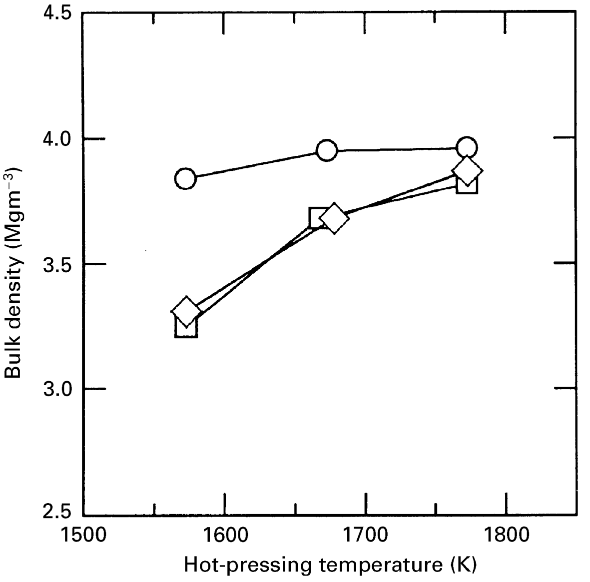

Figure 2 Bulk density of (○) monolithic Al_2O_3 (sample MA), and Al_2O_3 composite with (□) the original Al_2O_3 fibre (sample AA) and (◇) with the carbon-coated fibre (sample CA), sintered at various temperatures.

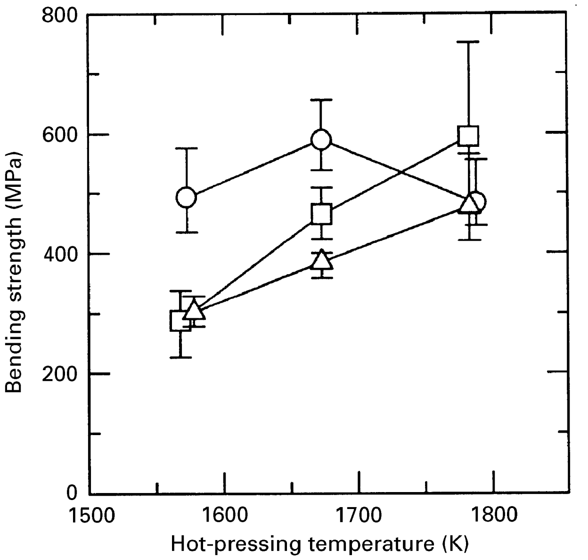

Figure 3 Bending strength of (○) monolithic Al_2O_3 (sample MA), and Al_2O_3 composite (□) with the original Al_2O_3 fibre (sample AA) and (△) with the carbon-coated fibre (sample CA), sintered at various temperatures.

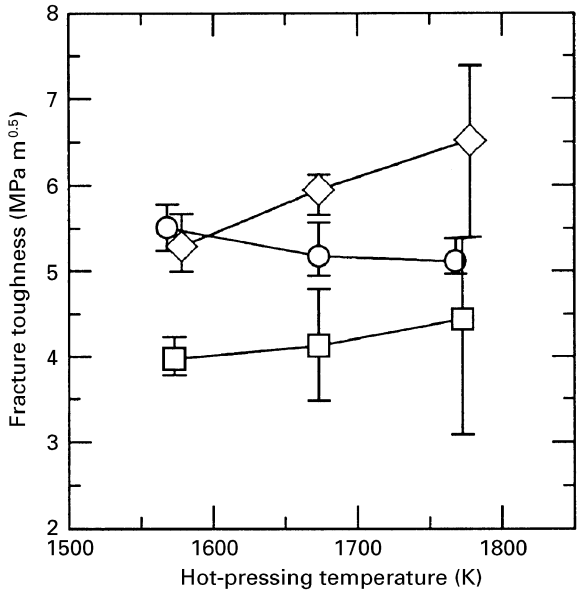

Figure 4 Fracture toughness of (○) monolithic Al_2O_3 (sample MA), and Al_2O_3 composite (□) with the original Al_2O_3 fibre (sample AA) and (◇) with the carbon-coated fibre (sample CA), sintered at various temperatures.

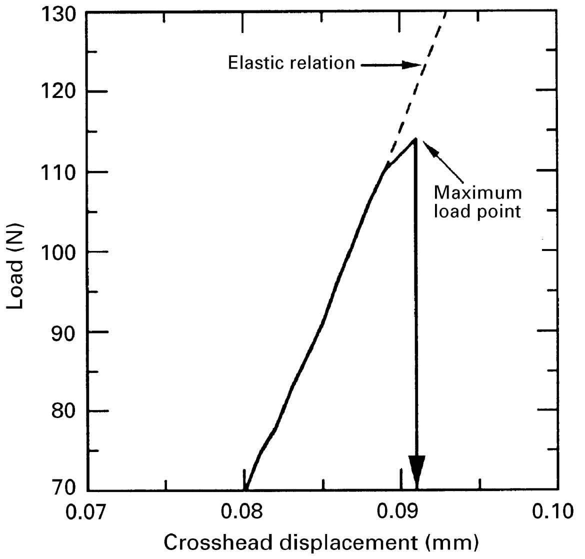

Figure 5 Load–deflection curve recorded during the SENB test of the carbon-coated Al_2O_3 fibre/Al_2O_3 composite. Deviation from the elastic behaviour can be seen before the maximum load point.

Toughness enhancement by fibre pull-out has been observed in the composite with carbon-coated Al_2O_3 fibre. However, there is no extensive toughness improvement observed in the CMC reinforced with SiC fibre [8] or carbon fibre [9]. The possible reason for the lack of such effective toughening is that the Al_2O_3 fibre has no residual original strength after the processing. A weak fibre cannot bear the load applied through the frictional sliding at the fibre/matrix interface during fibre pull-out. The development of low-temperature processing is required for making an Al_2O_3 fibre Al_2O_3 composite with a higher fracture resistance.

With a carbon coating on the Al_2O_3 fibre, debonding at the fibre/matrix interface was enhanced, the composite toughness being improved by fibre pull-out. When as-purchased Al_2O_3 fibre was incorporated, the interfacial joining was too strong to allow debonding. The carbon coating was also effective in hindering the interfibre fusion during the processing. No effective toughening mechanism worked with such combined fibres. However, the weak interface became a structural defect, causing the strength degradation. The carbon layer was sensitive to the oxidative environment. Carbon is not an optimal material for a composite which is expected to be used at high temperatures in air. Therefore, a fibre coating is required which activates the toughening mechanism and has a high oxidation resistivity.

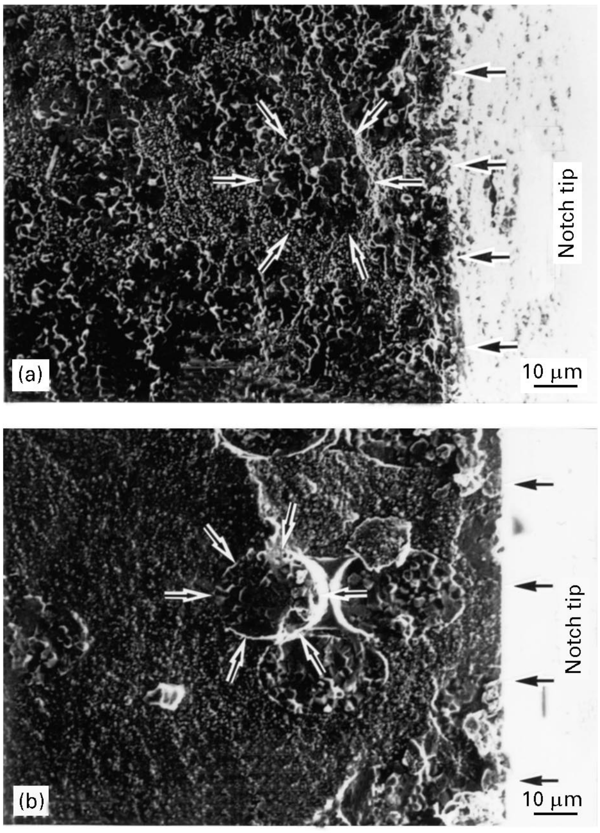

Figure 6 The fracture surface near the notch tip of the SENB test specimen of Al_2O_3 composite with (a) the original Al_2O_3 fibre and (b) the carbon-coated fibre.

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