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Mechanical Properties and Fracture Behaviour of SiTiCO Fibre/SiAlON Composite

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Abstract: Unidirectional SiTiCO fibre (Tyranno fibre®) reinforced SiAlON ($Si_2Al_4O_4N_4$) was fabricated by the filament winding method. The fibre/matrix green sheets were stacked and hot-pressed at 1773 K for 1.8 ks under a nitrogen atmosphere. The composite with a fibre content of 42 vol% showed significantly higher flexural strength (800 MPa) than that of monolithic SiAlON ceramics (570 MPa). A strength decrease due to the matrix degradation was observed at high temperature (1273 K and 1473 K). The fracture toughness of the composite measured by SENB (single edge notched beam) method was 8.0 MPa·$m^{0.5}$, being two times higher than that of monolithic ceramics (4.0 MPa·$m^{0.5}$). The work-of-fracture of the composite measured by static and dynamic methods was 9.62 kJ/m^2 and 8.29 kJ/m^2, respectively. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The major intention of fibre reinforcement for ceramics is to enhance the reliability of the material by toughening through changing its fracture behaviour from brittle to non-brittle. The fracture resistance is expected to be extensively increased by the fibre reinforcement. Ceramic matrix composites (CMCs) with various inorganic fibres, such as precursor-derived SiC fibre,[1–12] CVD-SiC fibre[13–21] or carbon fibre,[22–24] have been reported. One of the key points for a high-performance CMC is to produce it without fibre degradation. The polymer-derived SiC fibre, being widely used reinforcement for CMC, decomposes with the crystallization of SiC grains when heated above 1500 K, and its strength degrades significantly.[25,26] The temperature required for sintering engineering ceramics such as silicon nitride or silicon carbide is too high for the fibre. Recently, highly heat-resistive SiTiCO fibre has become commercially available (Tyranno fibre®, Lox-M type supplied from Ube Industries, Ltd). The fibre contains 12 wt% oxygen, and retains its tensile strength of over 1 GPa even after exposure in Ar at 1773 K for 3.6 ks.[27] If the processing temperature is lower than 1773 K, one can fabricate the CMC with this high strength fibre. For low-temperature processing of CMCs, the CVI method and polymer precursor method are well-known. These methods, however, often suffer from time-consuming processes and/or poor mechanical performance of the matrix on account of residual pores. On the contrary, normal sintering based on powder metallurgy, if it is carried out at a temperature sufficiently low for the fibre, has the advantage over these noble methods from the viewpoint of cost-performance and superior matrix properties.

In this study, unidirectionally oriented Lox-M type Tyranno fibre® is incorporated into β-SiAlON ceramics. β-SiAlON, one of the non-oxide engineering ceramics, has a thermal expansion coefficient comparable to that of the fibre and its sinterability is relatively high. The ceramic is known to have moderate strength with excellent resistance against high-temperature oxidation and molten metal. The compound is a solid solution in which Si and N are substituted by Al and O in the β-Si_3N_4 lattice. The general formula is $Si_{6-z}Al_zO_zN_{8-z}$ ($z \leq 4.2$). Its properties strongly depend on the composition, that is, the substitution ratio z. The strength decreases and oxidation

resistance and sinterability increase with increasing z value.[28–30] β-SiAlON with $z=4$ ($Si_2Al_4O_4N_4$) is selected in this paper as the sinterability is relatively high at this composition. A sintering temperature of 1973–2073 K is required for the material, but it is too high for the fibre. Therefore, a sintering additive, 3 wt% Y_2O_3, is doped to lower the processing temperature. Thus the SiTiCO fibre/SiAlON composite is fabricated by hot-pressing at 1773 K for 1.8 ks. Its mechanical properties and fracture resistance in static and dynamic conditions are investigated.

2 EXPERIMENTAL PROCEDURES

Lox-M grade Tyranno fibre® is supplied from Ube Industries Ltd. The average diameter, measured directly in the composite cross-sectional photo, is 8.0 μm, and the density is 2.37 Mg/m^3.[27] Its tensile strength and elastic modulus are 3.5 GPa and 188 GPa, respectively. The filament number per yarn is 1600.

The starting powder for the matrix β-SiAlON with $z=4$ is composed of Si_3N_4 (LC-12, Hermann C. Stark Co. Ltd), Al_2O_3 (TM-D, Taimei Chemical Ind. Co.), and AlN (Type G, Tokuyama Soda Co. Ltd). 3 wt% Y_2O_3 (Fine-grain grade, Nippon Yttrium Co. Ltd) is added to the mixture as a sintering additive.

The slurry for filament winding is prepared by ball-milling of the powder mixture mentioned above with polyvinylbutyral and polyethyleneglycol as binder, dibutylphthalate as plasticizer, linseed oil as deflocculation aid and ethanol as dispersion medium. The fibre is continuously dipped into this prepared slurry and wound on a winding drum. The impregnated fibre/matrix-powder sheet is cut into a rectangular shape with a size of 40×40 mm after drying. The obtained green sheets (3–5 sheets) are stacked and formed as a green compact with the unidirectionally oriented fibre by die-pressing at 523 K under a pressure of 30 MPa. The organic additives are burned in a vacuum furnace by heating up to 973 K. Hot-pressing is carried out at 1773 K for 1.8 ks under a pressure of 20 MPa in a nitrogen atmosphere. Unidirectional pressing is applied to the green compact along the direction perpendicular to the fibre orientation axis. The SiAlON matrix is synthesized during the sintering. Monolithic SiAlON ceramics with the same z value are also fabricated under the same conditions.

The sintered composite body is ground on its surface by a diamond wheel. The bulk density is measured by the water immersion method. Three-point bending strength at room temperature, 1273 K and 1473 K was measured in air for three test specimens of 1 mm (for the composite) or 3 mm thick (for monolithic SiAlON), 4 mm wide and 40 mm long, with a span of 30 mm and a crosshead speed of 0.0083 mm/s.

Fracture toughness was measured by SENB (single edge notched beam) 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 specimens were tested with a span of 16 mm and a crosshead speed of 0.0083 mm/s. Work-of-fracture, a measure of the fracture resistance of the material, is estimated based on the area surrounded by the load–deflection curve and the ligament area. Impact fracture resistance is evaluated by a Charpy impact test. The test piece is a rectangular bar with the same size and artificial notch as the SENB test piece except the length (40 mm). The stress applied on the hammer-head of the Charpy impact instrument is monitored by a stress-sensor during the fracture. The WOF is calculated based on the load vs displacement curve. Four specimens are tested.

The composite microstructure was observed by an optical microscope. Fibre volume percentage was determined based on the number of filaments embedded in a certain cross-sectional area in the photo and the average fibre diameter. The fibre volume percentage is 42%.

3 RESULTS AND DISCUSSION

3.1 Density and microstructure

The bulk density and open porosity of monolithic SiAlON and SiTiCO fibre/SiAlON composite measured by the water immersion method are shown in Table 1. The monolithic ceramic has a very small amount of open porosity, suggesting that it has been sintered almost fully. The open porosity of the composite is 9.34%, being significantly higher as compared to that of the monolith. The fibre incorporation apparently hinders the matrix sintering. The relative density of the composite, defined as the ratio of its bulk density to the pore-free density, is 91.0%. The pore-free, ideal bulk density of the composite is calculated by assuming that the matrix has the same density as that of monolithic SiAlON. The calculated relative density is consistent with the measured open porosity.

The microstructure of the composite cross-section shows that pores exist in the places where the fibres

Table 1. Bulk density, open porosity and relative density of monolithic SiAlON and SiTiCO fibre/SiAlON composite

	Bulk density (Mg/m^3)	Open porosity (%)	Relative density* (%)
Monolithic SiAlON	3.28	0.15	—
SiTiCO fibre/SiAlON	2.64	9.34	91.0

*Relative density of the composite is the ratio of its bulk density to theoretical density, which is calculated by assuming that the matrix full density is 3.28 Mg/m^3, the bulk density of monolithic SiAlON.

gather closely, as indicated by the arrows [Fig. 1(a)], but the matrix seems to be well densified. Most of the filament is sufficiently surrounded by the matrix. In the microstructure observed by lower magnification [Fig. 1(b)], we find that there exist fibre-less layer structures as indicated by the arrows in the photo. This non-uniform fibre incorporation is derived by excess slurry on the impregnated green sheet, exuded under the tensile stress on the winding drum during the filament winding.

X-ray diffractometry reveals that the composite matrix consists of β-SiAlON, confirming that the synthesis of the compound was completed during the sintering process.

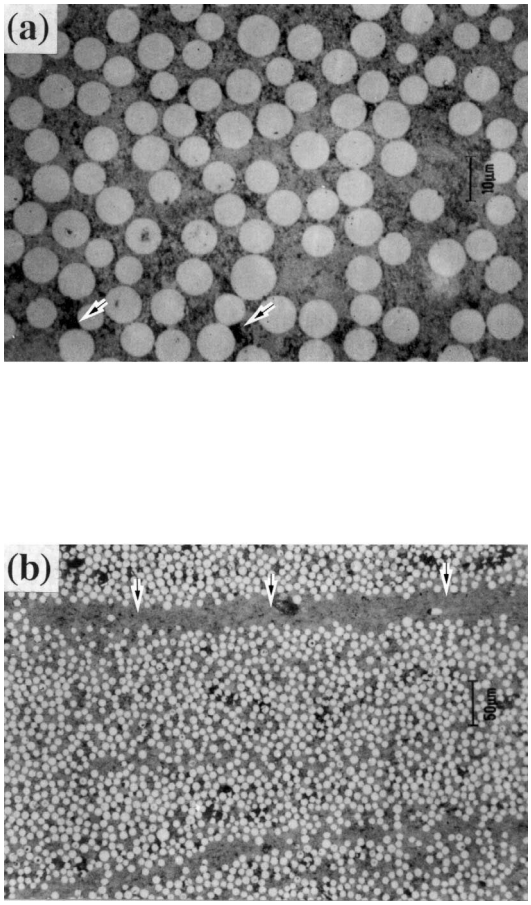

Fig. 1. Microstructure of SiTiCO(f)/SiAlON composite. The composite cross-section perpendicular to the fibre orientation direction is observed by an optical micrometer with (a) higher and (b) lower magnifications.

3.2 Flexural strength at ambient and high temperatures

Figure 2 shows the temperature dependence of the bending strength of monolithic SiAlON and the composite. For the test specimen with a thickness of 3 mm, shear fracture due to interlamellar delamination takes place. The shear strength is also shown in Fig. 2.

The room temperature strength of the composite is 794 MPa, which is significantly higher than that of the monolithic ceramics (568 MPa). Its fracture behaviour is a typical non-brittle type. Even after fracture takes place from the tensile surface at the maximum load, the composite does not show unstable rapid fracture but can bear the load up to greater deformation of the specimen.

When the test is carried out at high temperature, the strength of the monolithic ceramics and of the composite both degrade. The strength of the composite at 1273 K and 1473 K is 499 MPa and 403 MPa, respectively, both being higher than those of monolithic ceramics by 150–200 MPa. On the contrary, the shear strength of the composite shows no such thermal degradation, as shown in Fig. 2. The shear stress is applied so as to delaminate along the fibre/matrix interface, so that the shear fracture takes place from the inner part of the test specimen, while the bending strength initiates from the tensile surface of the specimen. This

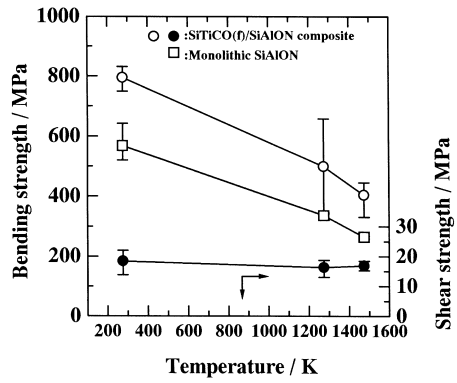

Fig. 2. Temperature-dependence of the bending of monolithic SiAlON (□) and SiTiCO(f)/SiAlON composite (○), and the interlamellar shear strength of the composite (●).

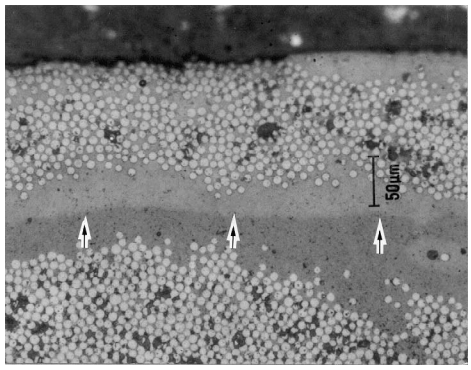

Fig. 3. Cross-sectional view of SiTiCO(f)/SiAlON composite after the bending test at 1273 K.

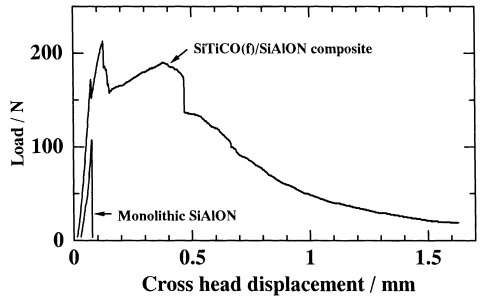

Fig. 4. Load–deflection curves of SiTiCO(f)/SiAlON and monolithic SiAlON recorded during the SENB test.

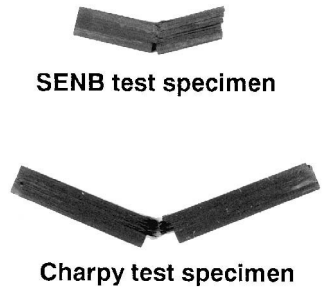

Fig. 5. Test specimens after the SENB test (upper) and Charpy impact test (lower).

fact suggests that the bending strength degradation is attributable to some surface damage.

The tested specimens of the monolithic ceramics and the composite are then examined. Both have a white layer on their surfaces. Figure 3 shows a cross-sectional view of the composite after the bending test at 1273 K. The arrows in the photo indicate the reaction front of the surface layer. Many fibres exist in the surface layer having a thickness of about 100 μm. Hasegawa et al. reported that the oxide layer was built on the surface of SiAlON ceramics when heated in an oxygen stream at high temperatures.[29] When the compound with $z=4$ is oxidized, they reported that only mullite was formed. The surface of monolithic SiAlON before and after the bending test at 1473 K was examined by an X-ray diffractometer. No new line appears except a hump at $2\theta=20$–$30°$, which is thought to reflect amorphous silica probably containing yttrium. This oxide layer may cause the thermal degradation of the strength.

3.3 Fracture resistance

Fracture toughness and WOF of monolithic SiAlON and the composite are shown in Table 2. The toughness of the composite (8.0 MPa·m$^{0.5}$) is just two times greater than that of monolithic ceramics (4.0 MPa·m$^{0.5}$). Typical load–deflection curves are shown in Fig. 4. Before the load reaches the maximum load point, the curve for the composite indicates a deviation from the linear relationship. This departure from the elastic response means that the crack has already propagated from the notch tip. Direct observation of the test specimen reveals that the delamination fracture starts from the notch tip, running parallel to the fibre orientation direction. This delamination at the notch tip greatly reduces stress intensification. At the maximum load point, the tensile fracture takes place but it is arrested immediately by the next fibre layer. In the later stage after this point, quite a lot of delamination and partial tensile fracture occur simultaneously up to the final fracture. The WOF of the composite, therefore, includes all of these microfractures during the test, so that the value is far greater than that of monolithic ceramics that fail in a brittle manner (as shown in Fig. 4).

Impact fracture resistance is elucidated by a Charpy impact test. Dynamic WOF is based on the hammer-head load vs deflection curve. The results are shown in Table 2. Differing from the static fracture test, the composite fails in a tensile manner without delamination. Figure 5 shows the test specimen after SENB and Charpy impact test. The

Table 2. Fracture toughness and WOF (work-of-fracture) of monolithic SiAlON and SiTiCO fibre/SiAlON composite, measured by SENB (single edge notched beam) method

	Fracture toughness (MPa·m$^{0.5}$)	Work-of-fracture (J/m^2)	
		Static	Dynamic
Monolithic SiAlON	4.0 (3.7, 4.2)	148 (129, 164)	430 (421, 439)
SiTiCO(f)/SiAlON	8.0 (7.5, 8.6)	9617 (8831, 10 300)	8289 (7822, 8640)

*The three figures in each column are an average (the minimum, the maximum) data.

SENB test specimen deforms by extensive delamination. The static WOF, therefore, contains quite large amounts of the energy associated with shear deformation. While a Charpy test specimen demonstrates that it fractures with a large amount of fibre pull-out. The dynamic WOF reflects more simple tensile fracture as compared to static data. These results indicate that the composite has very high fracture resistance against both static deformation and mechanical impact.

4 CONCLUSION

Unidirectionally oriented SiTiCO fibre/SiAlON composite is fabricated by the filament winding method, followed by hot-pressing. Remarkable strength improvement from ambient temperature up to 1473 K is achieved by the fibre incorporation. The fracture behaviour of the composite is non-brittle with quite a large amount of energy consumption. Fracture toughness and fracture resistance are both improved by the fibre reinforcement. The composite is a tough and very damage tolerable material. It also shows toughness against impact fracture. All these enhanced mechanical performances are derived from the fibre, that is intact and strong enough to bear high stress. Therefore, the concept to fabricate CMCs at a temperature as low as possible, but high enough to bring about a satisfactory level of matrix properties, is promising. Although SiTiCO fibre/SiAlON composite is found to be a very tough material at ambient temperature, one problem is that the effort for low processing temperature often conflicts with the high temperature performance of the composite. Further improvement in the processing technology for CMCs is desirable.

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