

Structure and properties of Si–Ti–C–O fibre-bonded ceramic material

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Si–Ti–C–O fibre-bonded ceramic material was synthesized from pre-oxidized Si–Ti–C–O fibre with an oxide layer 400–600 nm thick, by hot-pressing at 2023 K under 50–70 MPa. The interstices in the Si–Ti–C–O fibre-bonded ceramic material were packed with an oxide material which existed on the surface of the pre-oxidized Si–Ti–C–O fibre, and the oxide material formed a small amount of the matrix phase (≤ 10 vol %). At the fibre–matrix interface, aligned turbostratic carbon, which was oriented around the fibre, was formed during hot-pressing. The existence of the interfacial carbon layer indicated the Si–Ti–C–O fibre-bonded ceramic material to have a fibrous fracture pattern with high fracture energy. The Si–Ti–C–O fibre-bonded ceramic material showed excellent durability even at 1773 K in air, because a protective oxide layer is formed on the surface at a high temperature (above 1273 K) in air. Moreover, the Si–Ti–C–O fibre-bonded ceramic material almost maintained its initial strength in the bending and tensile tests, even at 1773 K in air.

1. Introduction

The formation of ceramic matrix composite (CMC) reinforced with continuous inorganic fibres such as Si–C–O fibre, Si–Ti–C–O fibre or carbon fibre, has been actively studied in recent years [1–11]. The main purpose of these studies was to improve fracture toughness of ceramics. A common concept of these CMCs is that the interface between the reinforcement and the matrix makes it more difficult for a crack to penetrate through the fibre and matrix. In general, a weakly bonded fibre–matrix interface leads to toughened, composite-like behaviour, whereas a strongly bonded interface results in a brittle composite [12–15]. So, moderately weak bonding between the reinforcement and the matrix is indispensable to obtain toughened composite material. In the CMCs mentioned above, it has been determined that the interfacial shear stress is moderately weakened by achieving high fracture toughness. On the other hand, the heat-resistance and oxidation-resistance of this type of CMC are strongly influenced by thermostability of the reinforcement, and so the mechanical property of this type of CMCs decreases at temperatures above 1573 K in air, because of decomposition or oxidation of the reinforcement.

In order to obtain a ceramic material with high fracture toughness and higher heat-resistance in air than that found in conventional ceramic matrix composites, the Si–Ti–C–O fibre-bonded ceramic material, synthesized by hot-pressing pre-oxidized Si–Ti–C–O fibre at high temperature, has been developed [16]. The oxide layer on the surface of the pre-oxidized Si–Ti–C–O fibre adhered to the fibres and formed a kind of matrix, to yield a densified oxide matrix composite material with slight deformation of the

fibre. The Si–Ti–C–O fibre-bonded ceramic material has very high heat-resistance up to 1873 K in air, and shows a fibrous fracture pattern with high fracture energy. The structure and properties of the Si–Ti–C–O fibre-bonded ceramic material are reported.

2. Experimental procedure

2.1. Synthesis of Si–Ti–C–O fibre-bonded ceramic material

Continuous Si–Ti–C–O fibre (Tyranno fibre®, UBE Industries Ltd), which is synthesized from poly-titanocarbo-silane, was used as a raw material of the Si–Ti–C–O fibre-bonded ceramic material [17]. The Si–Ti–C–O fibre was heat treated in air at 1373 K for 40 h, and then pre-oxidized Si–Ti–C–O fibre, with oxide layer 400–600 nm thick, was obtained. Prepreg sheet obtained from the pre-oxidized Si–Ti–C–O fibre was laminated. The Si–Ti–C–O fibre-bonded ceramic material (Tyrannohex®) was prepared by hot-pressing the laminated material at a temperature of 2023 K under 50–70 MPa using a hot-pressing machine (Fujidempa Co. Ltd, type EVHP-R-50).

2.2. Measurements

The three-point bending strengths were measured using a Shimadzu Auto-Graph (DSS-500 testing machine) at temperatures up to 1773 K in air. Testing was done at a crosshead speed of 0.5 mm min^{-1} , using a span of 30 mm. The specimen size was $4 \text{ mm} \times 3 \text{ mm} \times 40 \text{ mm}$.

The tensile strength was measured using a MTS tensile-testing-machine (808-type) at temperatures up to 1773 K in air. The shape and dimensions of the specimens are shown in Fig. 1.

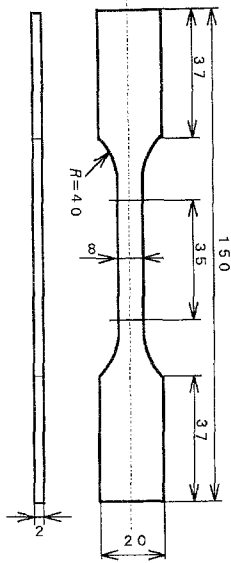


Figure 1 Shape and dimensions (in mm) of the tensile specimen.

The cross-section and fracture surface of the Si-Ti-C-O fibre-bonded ceramic material were observed by scanning electron microscopy (Hitachi FE-SEM, S-5000). The microstructure of the fibre-bonded ceramic material was examined by high-resolution transmission electron microscopy (Jeol, JEM-2010).

Interlaminar shear strengths (ILSS) were measured through JIS-K7057, short-beam shear method by three-point bending. Fracture toughness was measured by the SEVNB method using a Shimadzu Autograph (DSS-500 testing machine).

Chemical analysis of Si-Ti-C-O fibre and the fibre-bonded ceramic material was performed for four elements: silicon (by a gravimetric method), titanium (by a calorimetric method), carbon (by a combustion volumetric method), and oxygen (by gas analysis).

3. Results and discussion

The amorphous Si-Ti-C-O fibre, although showing high heat-resistance and excellent mechanical properties up to 1527 K, crystallizes to β -SiC and TiC above 1673 K in inert gas atmosphere with the evolution of both SiO and CO. However, the crystalline grain growth can be inhibited in an oxygen atmosphere even at a temperature of 1673 K or over, because the dense oxide film, which is formed on the surface of the fibre, suppresses the evolution of SiO and CO [18]. Accordingly, it was expected that the mechanical properties of the Si-Ti-C-O fibre could be maintained up to higher temperatures by pre-forming the oxide layer on the surface of the Si-Ti-C-O fibre. Moreover, the oxide layer plays a role in bonding the Si-Ti-C-O fibres. For these reasons, the pre-oxidized Si-Ti-C-O fibre was used as a raw material for the fibre-bonded ceramic material.

The cross-section of the Si-Ti-C-O fibre-bonded ceramic material is shown in Fig. 2. The spaces between the fibres were uniformly packed with the oxide material which existed on the surface of the pre-oxi-

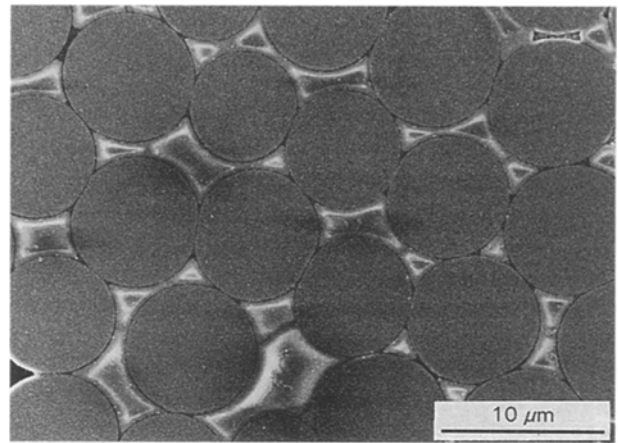


Figure 2 Cross-section of Si-Ti-C-O fibre-bonded ceramic material.

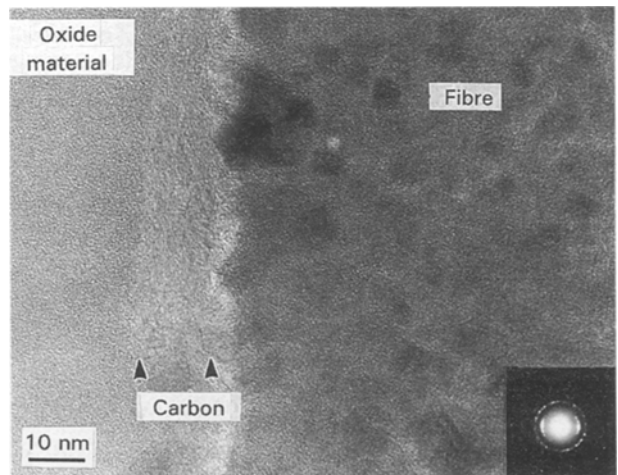


Figure 3 TEM image of the fibre-matrix interface.

dized Si-Ti-C-O fibre. So, the Si-Ti-C-O fibre-bonded ceramic material is a kind of oxide-matrix composite material reinforced by the Si-Ti-C-O fibre. However, the quantity of the oxide matrix (~ 10 vol%) is much less than that of common ceramic-matrix composite material (30–70 vol%).

Fig. 3 shows the TEM image of the fibre-matrix interface. A 0.34 nm interlayer spacing of carbon (002) planes can be observed around the fibre, beneath the pre-existing oxide material. Its thickness is 10–20 nm, and the carbon layer was found to be oriented around the fibre. From the results of selected-area electron diffraction of the carbon layer, the carbon is presumed to be turbostratic in structure. The interfacial carbon layer plays an important role in producing the fibrous fracture pattern with high fracture energy. Near the interfacial carbon layer, pull-out of the fibres occurred, as can be seen in Fig. 4.

The physical properties of the Si-Ti-C-O fibre-bonded ceramic material are shown in Table I. The porosity of the Si-Ti-C-O fibre-bonded ceramic material is less than 1%, which is a very small value compared with other composite materials reinforced by long fibres. So, the Si-Ti-C-O fibre-bonded ceramic material was found to be a relatively dense material. In addition, the Si-Ti-C-O fibre-bonded

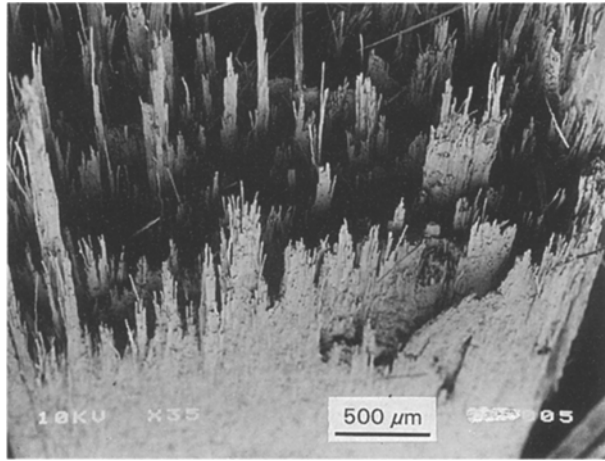


Figure 4 Fracture surface of the Si-Ti-C-O fibre-bonded ceramic material.

TABLE I. Physical properties of Si-Ti-C-O fibre-bonded ceramic material

Fibre content	(%)	> 90
Specific Gravity	(g cm ⁻³)	2.45
Porosity	(%)	< 1
Composition	(wt %)	Si, 4 8-5 7; C, 3 0-3 2; O, 1 3-1 5; Ti, 2 . 0

ceramic material exhibits a low density (2.45 g cm⁻³), whose value is lower than that of crystalline SiC/SiC composite (CERACEP) (2.6 g cm⁻³) with a large porosity of 10%. The value is very similar to that of the Si-Ti-C-O fibre used as a raw material. The chemical compositions of the Si-Ti-C-O fibre-bonded ceramic material is very similar to that of the Si-Ti-C-O fibre used as a raw material. Moreover, the crystalline grain size of β-SiC of the Si-Ti-C-O fibre-bonded ceramic material was about 8 nm, which is smaller than that of a former type of fibre-sintered ceramics, using unoxidized Si-Ti-C-O fibre [19]. In the case of the former type, the crystalline grain size was about 15 nm. From these results, during hot-pressing, the release of CO and SiO gas from the fibre with crystalline grain growth of β-SiC is found to be inhibited by the oxide material pre-existing on the surface of the fibre used as a raw material.

Fig. 5 shows the load-displacement curves of the Si-Ti-C-O fibre-bonded ceramic material (unidirectional composite), which was produced by hot-pressing at 2023 K, in the bending test in air up to 1773 K. At a temperature of 1773 K, though a slight reduction in bending strength was observed, almost the initial strength could be maintained. Moreover, non-linear fracture patterns with high fracture energy were observed up to 1773 K.

Fig. 6 shows the durability of the Si-Ti-C-O fibre-bonded ceramic material in air at high temperature. As can be seen in this figure, the Si-Ti-C-O fibre-bonded ceramic material exhibited very excellent durability at 1773 K in air. Even when heat treatment was performed at 1873 K in air for 20 h, 70% of the initial strength could be maintained. In this manner, the Si-Ti-C-O fibre-bonded ceramic material is found

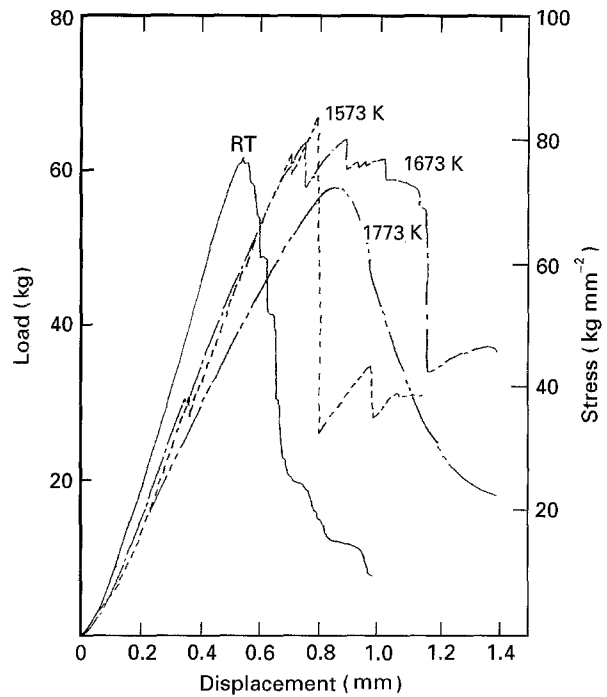


Figure 5 Load-displacement curves of Si-Ti-C-O fibre-bonded ceramic material in three-point bending test at temperatures up to 1773 K in air.

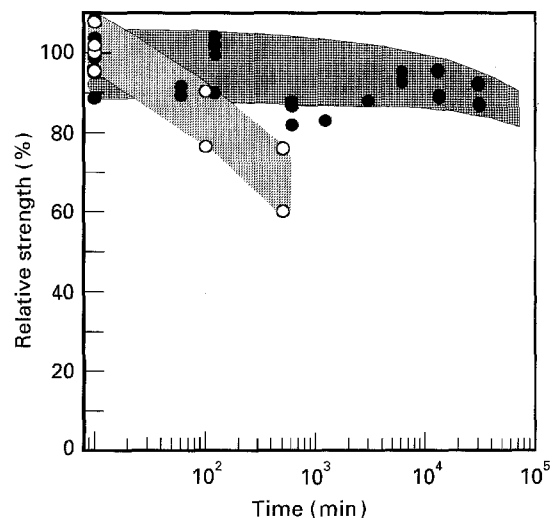


Figure 6 Durability of Si-Ti-C-O fibre-bonded ceramic material in air at high temperature: (●) 1773 K, (○) 1873 K.

to have excellent heat resistance and oxidation resistance in comparison with other composite materials reinforced by long fibres. As the Si-Ti-C-O fibre-bonded ceramic material was produced at a temperature over 1873 K, it is very thermodynamically stable at high temperature. Moreover, the Si-Ti-C-O fibre-bonded ceramic material is coated by a dense oxide film acting as a self-protective layer at high temperature (over 1273 K) in air [20]. It is considered that this excellent durability is caused by the above properties.

The tensile strength of the Si-Ti-C-O fibre-bonded ceramic material (cross-ply composite) up to 1773 K in air, is shown in Fig. 7. The strength did not decrease even at 1773 K. This result shows a very similar tendency to that of the bending test shown in Fig. 5. Other conventional ceramic-matrix composite materials without

protective coating could not maintain their initial strengths at high temperatures (over 1573 K) in air. Accordingly the Si-Ti-C-O fibre-bonded ceramic material is found to have excellent mechanical property at above 1573 K in air.

The mechanical properties of the Si-Ti-C-O fibre-bonded ceramic material are shown in Table II, which also shows the properties of both cross-plyed composite (two-dimensional) and unidirectional composite. Of these data, the value of fracture toughness is very similar to that of LAS matrix composite investigated by Brennan and Prewo [21]. The value of the unidirectional composite became large at 1573 and 1673 K compared with that at room temperature. It is considered that this phenomenon at those temperatures is attributable to the softening of the oxide matrix. After that, the fracture toughness is slightly reduced at a temperature of 1773 K. It is estimated that the decrease in fracture toughness at that temperature is closely correlated to the above slight decrease in bending strength at that temperature. On the other

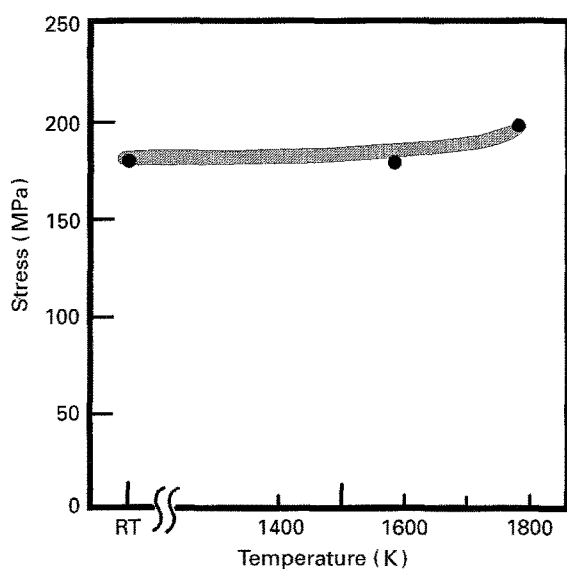


Figure 7 Tensile strengths of Si-Ti-C-O fibre-bonded ceramic material (cross-plyed composite) in air at temperatures up to 1773 K.

hand, the fracture toughness of the two-dimensional composite was smaller than that of the unidirectional composite, and the value was constant at temperatures up to 1773 K. The two-dimensional composite was produced by the use of cross-plyed laminated-material of a unidirectional sheet (thickness 100–200 μm) of the Si-Ti-C-O fibre. The bonding strength of the fibres at the cross-plyed surface is relatively weak in the two-dimensional composite. So, a crack selectively penetrates through the cross-plyed surface. For these reasons, it is considered that the fracture toughness was smaller than that of the unidirectional composite. However, the value was larger than that of monolithic Si_3N_4 ($6.2 \text{ MPa m}^{1/2}$) and the C/C composite ($8.3 \text{ MPa m}^{1/2}$) which was measured using the same method, i.e. the SEVNB method. Accordingly, it was found that the Si-Ti-C-O fibre-bonded ceramic material shows excellent fracture toughness.

4. Conclusion

Si-Ti-C-O fibre-bonded ceramic material is a kind of oxide-matrix composite material whose interstices were packed by oxide material pre-existing on the surface of the pre-oxidized Si-Ti-C-O fibre. The quantity of the matrix is, however, less than 10 vol%, which is a very small value among conventional ceramic composite materials reinforced by long fibres. At the fibre-matrix interface, aligned turbostratic carbon, which was oriented around the fibre, was formed during hot-pressing. The interfacial carbon layer plays an important role in producing the fibrous fracture pattern with high fracture energy. As the Si-Ti-C-O fibre-bonded ceramic material is thermodynamically stable and coated by a dense oxide film, which itself acts as a protective layer at temperatures over 1273 K in air, excellent durability was observed at 1773 K in air. Even when the heat treatment was performed at 1873 K in air for 20 h, 70% of the initial strength could be maintained. Moreover, the Si-Ti-C-O fibre-bonded ceramic material maintained almost its initial strength in the bending and tensile tests, even at 1773 K in air.

TABLE II Mechanical properties of Si-Ti-C-O fibre-bonded ceramic material

Property	Temperature (K)					
			RT	1573	1673	1773
Tensile strength	(MPa)	2D ^a	180	180	–	195
		UD ^b	400	400	–	400
Elongation	(%)	2D	0.2	0.25	–	0.95
Initial Young's modulus	(GPa)	2D	115	90	–	50
		UD	125	100	–	55
Bending strength	(MPa)	2D	350	350	350	350
		UD	700	700	700	650
Fracture toughness	(MPa m ^{-1/2})	2D	13	13	13	13
		UD	17	22	25	21
Interlaminar shear strength	(MPa)	UD	75	–	–	–

^a Two-dimensional.

^b One-dimensional.

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