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Mechanical and thermal properties of silicon-carbide composites fabricated with short Tyranno® Si-Zr-C-O fibre

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Silicon carbide (SiC) composites reinforced with 10–50 mass% (10.5–51.2 vol%) of short Tyranno® Si-Zr-C-O fibre (average length ~0.5 mm) and 0–10 mol% of Al_4C_3 as a sintering aid were fabricated using the hot-pressing technique. Firstly, the effect of Si-Zr-C-O fibre addition on the relative density (bulk density/true density) of the SiC composite hot-pressed at 1800 °C for 30 min was examined by fixing the amount of Al_4C_3 to be 5 mol%. Although the relative density was reduced to 87.4% for 10 mass% of Si-Zr-C-O addition, further increases in the amount of Si-Zr-C-O fibre increased density to a maximum of 92.8% at 40 mass% of fibre addition. Secondly, the effect of varying the amount of Al_4C_3 addition on the relative density was examined by fixing the amount of Si-Zr-C-O fibre to be 40 mass%. The optimum amount of Al_4C_3 addition for the fabrication of dense SiC composite was found to be 5 mol%. The fracture toughness of the hot-pressed SiC composites with 20–40 mass% of Si-Zr-C-O fibre addition (amount of Al_4C_3: 5 mol%) was 3.2–3.4 $\text{MPa} \cdot \text{m}^{1/2}$ and approximately 1.5 times higher than that (2.39 $\text{MPa} \cdot \text{m}^{1/2}$) of the hot-pressed SiC composite with no Si-Zr-C-O fibre addition. SEM observation showed evidence of Si-Zr-C-O fibre debonding and pull-out at the fracture surfaces. The hot-pressed SiC composite with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions showed excellent heat-resistance at 1300 °C in air due to the formation of a SiO_2 layer at and near exposed surfaces.

1. Introduction

Silicon carbide (SiC) ceramics are promising candidates in the field of high-temperature structural materials due to their excellent oxidation, corrosion, and creep resistance. However, SiC ceramics exhibit poor fracture toughness and, as such, much attention has been paid to the fabrication of SiC ceramics reinforced with continuous fibres. For example, the fracture toughness of SiC composites containing continuous carbon fibres has reached 20 $\text{MPa} \cdot \text{m}^{1/2}$ at 1400–1600 °C in an Ar atmosphere [1] although the heat resistance of such composites is known to be poor in air due to oxidation of the carbon above 500 °C [2].

In order to improve the oxidation resistance, in addition to fracture toughness, SiC-based fibres in the Si-C-O and Si-Ti-C-O systems have also been used to reinforce SiC ceramics. For example, unidirectional (1D) and two-dimensional (2D) Si-Ti-C-O fibre composites almost retain their initial bending and tensile strength, even after being heated to 1500 °C in air [3]. Recently, three-dimensional (3D) Si-Ti-C-O fibre-reinforced SiC composites have been fabricated by repeated polymer impregnation and pyrolysis (PIP) of polycarbosilane or polytitanocarbosilane into a 3D textile perform [4]. The fracture toughness of such ceramic matrix composites (CMCs) has reached 40 $\text{MPa} \cdot \text{m}^{1/2}$ at room temperature. However, matrix densification using PIP or chemical vapour infiltration (CVI) has several disadvantages including extended processing time, high cost, and relatively high residual porosity (typically >10% [5]). As a low cost alternative to these methods, SiC composites reinforced with short

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or chopped fibres are also known to possess enhanced fracture toughness, high temperature creep behaviour, and abrasion resistance [6].

In addition to this, thermal damage of the Si-Ti-C-O fibres within the SiC matrix still occurs upon heating to 1000–1200 °C in vacuum or air [7, 8]. In order to increase the thermal damage resistance, fibres in the Si-Zr-C-O system have been developed by substituting Zr for Ti in Si-Ti-C-O fibres [9]. As a comparison, the tensile strength of Si-Ti-C-O fibres heat-treated at 1600 °C for 1 h in an Ar atmosphere is almost zero whereas that of Si-Zr-C-O fibres is still 1.11 GPa [9]. However, almost no information exists regarding the fabrication of SiC composites with short Si-Zr-C-O fibres. Thus, the present work deals with (i) determination of the optimum conditions for the fabrication of dense SiC composites reinforced with short Si-Zr-C-O fibres, and (ii) evaluation of the mechanical properties for the resulting composite.

2. Experimental procedure

2.1. Starting materials

Ultrafine SiC powder was prepared by the pyrolysis of triethylsilane ($(C_2H_5)_3SiH$) at 1100 °C in an argon atmosphere. In order to eliminate any residual carbon, the SiC powder was further treated at 500 °C for 2 h in air. On the other hand, ultrafine Al_4C_3 powder was prepared by the pyrolysis of trimethylaluminum ($(CH_3)_3Al$) at 1100 °C in an argon atmosphere. The specific surface areas of the resulting SiC and Al_4C_3 powders were $39.2\ m^2 \cdot g^{-1}$ and $66.8\ m^2 \cdot g^{-1}$, respectively, whilst the average primary particle sizes calculated from values of specific surface areas and true densities were 66.3 nm and 35.2 nm, respectively.

According to the manufacturer's analysis, the Si-Zr-C-O fibre (ZE grade; Ube Industries, Ltd., Ube, Japan) had a composition of Si, 58.9 mass%; Zr, 1.0 mass%; C, 38.4 mass%; and O, 1.7 mass%. The average diameter and length of the Si-Zr-C-O fibre were 13 μm and ~0.5 mm, respectively.

2.2. Fabrication of the composites

The starting SiC powder was initially mixed with the desired amount of Al_4C_3 powder (ranging from 1 to 10 mol%) in the presence of n-hexane using a zirconia mortar and pestle. The resulting powder was then mixed with 10–50 mass% (10.5–51.2 vol%) of Si-Zr-C-O fibre in the presence of n-hexane. Following drying, approximately 1.5 g of the mixture was uniaxially pressed at 50 MPa and then isostatically pressed at 100 MPa to form a cylindrical compact with a diameter and thickness of 20 mm and ~2 mm, respectively. In addition to this, approximately 2.0 g of the mixture was pressed under similar conditions in order to form a rectangular solid specimen with sizes $40 \times 4 \times 3\ mm^3$. The cylindrical compact and rectangular specimen were then hot-pressed at 1800 °C for 30 min under 31 MPa in an argon atmosphere and furnace cooled.

The cylindrical compact was used for the relative density measurement, examination of crystalline phases, microstructural observation, and Vickers hardness measurement, whereas the rectangular specimen was used for the fracture toughness measurement.

2.3. Evaluation

The relative density of the hot-pressed compact was calculated by dividing the bulk density by the true density. The bulk density was measured on the basis of mass and dimensions whilst true density was measured picnometrically at 25.0 °C using n-hexane as a replacement liquid after the hot-pressed compact was pulverized using a zirconia mortar and pestle. Crystalline phases of the hot-pressed compact were examined using an X-ray diffractometer (XRD; Model RINT-2000PC, Rigaku, Tokyo, Japan; 40 kV, 40 mA) with monochromated CuKα radiation whilst crystalline phases on and near the surfaces were examined using a thin-film XRD (TF-XRD). Vickers hardness was measured on surfaces of hot-pressed and polished compact in the direction of hot-pressing using a microhardness tester (Model M-400 MUK-E, Akashi, Tokyo, Japan) with results being averaged from typically ten measurements. The fracture toughness of the hot-pressed specimen was measured using the single edge notched beam (SENB) technique and three point bend configuration after a notch of width 0.15 mm and depth 1.5 mm was introduced into the specimen center using a diamond saw. Fracture surfaces of the hot-pressed compact were observed using a scanning electron microscope (SEM; Model S-4500, Hitachi, Hitachinaka, Japan) whilst the heat-resistance was examined using thermogravimetry (TG; Model Thermo Plus TG8120, Rigaku, Tokyo, Japan) between 1000 °C and 1300 °C for 20 h in air. The heating rate from room temperature up to the desired temperature was $10\ ^\circ C \cdot min^{-1}$ and approximately 20 mg of the sample, cut from the main specimen, was used for this experiment.

3. Results and discussion

3.1. Effect of Al_4C_3 addition on the hot-pressing of SiC composite

Densification of SiC cannot proceed without the use of sintering aids such as Al_2O_3 [10], Al_2O_3-Y_2O_3 [11], AlN-Y_2O_3 [12], AlN [13], Al [13], and Al-B-C [14]. The present work utilised Al_4C_3 as a sintering aid for the following reasons: (i) Al_4C_3 is effective in promoting the sintering of SiC [15], (ii) the authors could prepare ultrafine Al_4C_3 powder by the chemical vapour deposition method [16], and (iii) the Al_4C_3 powder under consideration could be dispersed homogeneously within the SiC powder when considering that its average particle size (35.2 nm) was somewhat smaller than that (66.3 nm) of the SiC.

In order to avoid thermal damage to the Si-Zr-C-O fibres, hot-pressing of the SiC composite should be conducted at the lowest possible temperature. The effect of hot-pressing temperature on the relative density of SiC composite with no Si-Zr-C-O fibre addition was first examined by fixing the amount of Al_4C_3 addition to be 5 mol%. Results are shown in Fig. 1, together with a

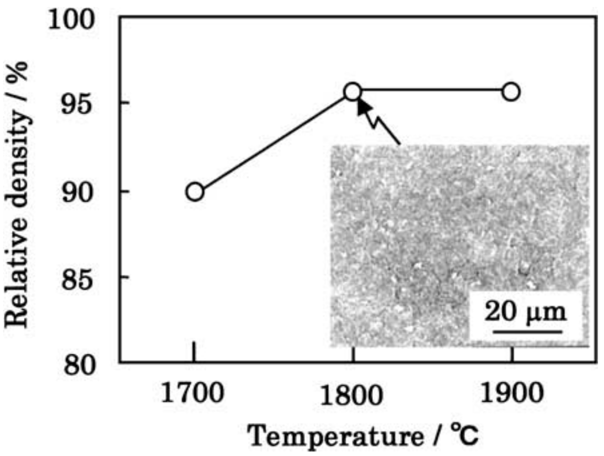

Figure 1 Effect of hot-pressing temperature (hot-pressing time: 30 min) on the relative density of SiC composite with 5 mol% of Al_4C_3 addition but with no Si-Zr-C-O fibre addition, together with a typical SEM micrograph of the fracture surfaces.

SEM micrograph of the fracture surfaces. The relative density was observed to increase from 90.1% (1700 °C) to 96.0% (1800 °C) but remained unchanged for a further increase in hot-pressing temperature to 1900 °C. A SEM micrograph of the SiC composite hot-pressed at 1800 °C showed the existence of closely packed polyhedral grains with sizes on the order of 0.5 μm.

The above results indicate the optimum hot-pressing temperature of the SiC composite for the conditions employed to be 1800 °C. On the basis of this information, the effect of Al_4C_3 addition on the relative density of SiC composite with no Si-Zr-C-O fibre addition was examined by fixing the hot-pressing temperature to be 1800 °C. Results are shown in Fig. 2, together with the corresponding Vickers hardness data. The relative density was seen to be in the range 96–98% and independent of the amount of Al_4C_3 addition. In contrast to this, the average Vickers hardness was reduced from 25.8 GPa to 16.7 GPa as the amount of Al_4C_3 addition increased from 0.05 to 5 mol%.

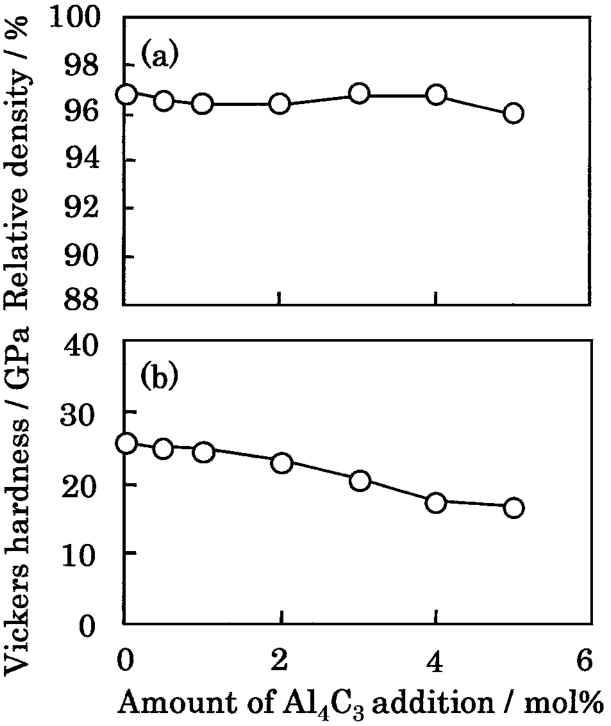

Figure 2 Effect of Al_4C_3 addition (amount: 0.05 to 5 mol%) on the (a) relative density and (b) Vickers hardness of SiC composite with no Si-Zr-C-O fibre addition hot-pressed at 1800 °C for 30 min.

In order to clarify the densification behaviour, crystalline phases of these hot-pressed SiC composites were examined using an XRD and found to be compromised of α-SiC, β-SiC, Al_4SiC_4, and Al_4O_4C. As shown above, the relative density of the hot-pressed SiC composite with no Si-Zr-C-O fibre addition appears to be independent of the amount of Al_4C_3 addition. Such a densification process may be related to the reaction between SiC and Al_4C_3 in that, according to the XRD data, Al_4SiC_4 was detected from the hot-pressed composites together with α-SiC and β-SiC. The reaction of SiC with Al_4C_3 to form Al_4SiC_4 during hot-pressing may be expressed as follows: [17]

$$Al_4C_3 + SiC \rightarrow Al_4SiC_4 \tag{1}$$

In contrast to this, the formation of Al_4O_4C may be associated with oxygen physically adsorbed onto the starting powder.

$$Al_4C_3 + 3O_2 \rightarrow Al_4O_4C + 2CO \tag{2}$$

$$Al_4C_3 + 2O_2 \rightarrow Al_4O_4C + 2C \tag{3}$$

The Al_4SiC_4 and Al_4O_4C phases would not be expected to participate in the formation of a liquid phase at the hot-pressing temperature utilised (1800 °C) as this is significantly below their melting temperatures of 2080 °C and 1890 °C, respectively [18, 19]. According to the phase diagram in the Al-C system [18, 20], a liquid phase may form when a portion of the Al_4SiC_4 is pyrolysed at a temperature of 1800 °C: [21]

$$Al_4SiC_4 \rightarrow 4Al + Si + 4C \tag{4}$$

The liquid phase formed during hot-pressing would appear to assist rearrangement of the SiC grains and thereby promote densification. Although mass transfer may be promoted by the solid solution of Al into SiC, Mitomo *et al.* [22] have reported the degree of solid solution of Al compounds into SiC to be below 0.5 mass%, even in the temperature range of 2200–2400 °C. Thus, it is suggested that the extent of the solid solution of Al into SiC would appear to be negligible at a hot-pressing temperature of 1800 °C. The absence of free Al and Si in the hot-pressed SiC composites suggests that they presumably evaporated whilst the liquid phase formed with carbon.

It is also noted that the Vickers hardness is reduced with increasing amount of Al_4C_3 addition. As described above, Al_4SiC_4, Al_4O_4C, and other reaction products shown in Equations (3) and (4) may have been present, presumably at the grain boundary regions. The Vickers hardness of pure Al_4SiC_4 is ~12 GPa [21] whereas that of SiC is typically 25 GPa [23] and thus thickening of the grain boundary region with increasing Al_4C_3 addition would reasonably be expected to reduce the Vickers hardness of these materials.

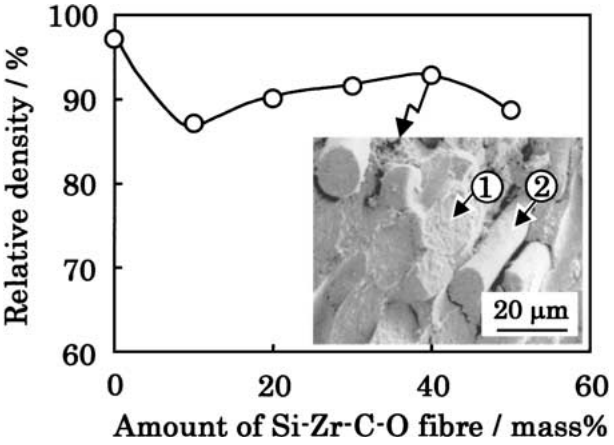

Figure 3 Effect of Si-Zr-C-O fibre addition on the relative density of SiC composite with 5 mol% of Al_4C_3 addition hot-pressed at 1800 °C for 30 min, together with a SEM micrograph of the fracture surfaces. ①: Si-Zr-C-O fibre cut by the main crack; ②: Si-Zr-C-O fibre that debonded and pulled out.

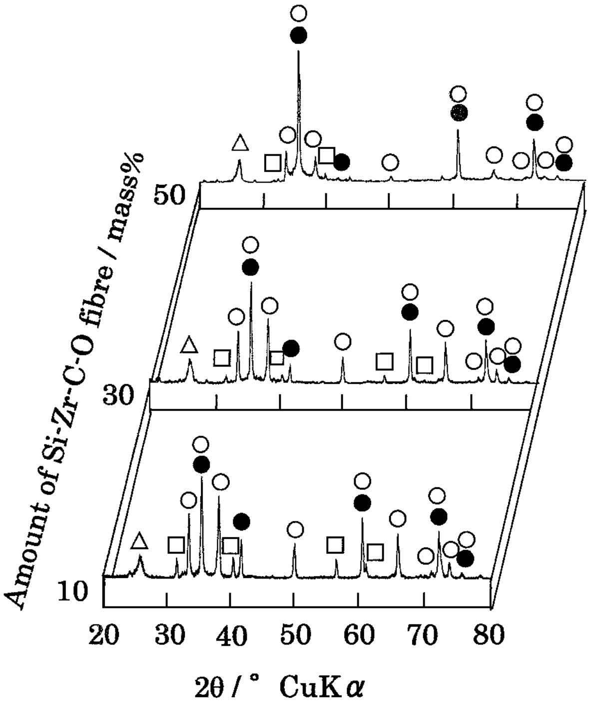

Figure 4 XRD patterns for the SiC composites with 5 mol% of Al_4C_3 and various amounts of Si-Zr-C-O additions hot-pressed at 1800 °C for 30 min. ○: α-SiC ●: β-SiC □: Al_4SiC_4 △: C.

3.2. Densification of SiC composite with Al_4C_3 and Si-Zr-C-O fibre additions

Firstly, the effect of Si-Zr-C-O fibre addition on the relative density of hot-pressed composite was examined by fixing the amount of Al_4C_3 addition to be 5 mol%. Results are presented in Fig. 3, together with a typical SEM micrograph of the fracture surfaces. Although the relative density of the hot-pressed SiC composite with no Si-Zr-C-O fibre addition was 96.0%, this value was reduced to 87.4% for 10 mass% of Si-Zr-C-O fibre addition. However, the relative density increased with a further addition of Si-Zr-C-O fibre and attained 92.8% for the case of 40 mass% fibre addition. A further increase in the amount of Si-Zr-C-O fibre addition to 50 mass%, however, reduced the relative density to 88.6%. A SEM micrograph of the fracture surfaces of the hot-pressed composite with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions showed that, whilst some fibres were cut by the crack propagation (arrow mark ①), others were debonded and pulled out at the fracture surfaces (arrow mark ②). Such fracture behaviour is typical of that observed in short fibre-reinforced CMCs whilst the presence of fibre debonding and pull-out suggests the presence of Si-Zr-C-O fibres to enhance fracture toughness with details being described later. In addition, it is noted from SEM observations that the Si-Zr-C-O fibres do not appear to suffer thermal damage even at the hot-pressing temperature of 1800 °C.

On the basis of the relative density data and SEM observation, the densification process is classified into three stages according to the amount of Si-Zr-C-O fibre addition: (i) 10 mass% addition, (ii) 10–40 mass% addition, and (iii) 50 mass% addition. For the case of 10 mass% Si-Zr-C-O fibre addition, local concentration of the Si-Zr-C-O fibre within the SiC matrix disturbs the homogeneous densification of the matrix and results in porosity at the interface between the SiC and Si-Zr-C-O fibres. In the case of 10–40 mass% of Si-Zr-C-O fibre addition, however, the Si-Zr-C-O fibres are dispersed homogeneously within the SiC matrix and thus do not significantly inhibit densification. Finally, for the case of 50 mass% Si-Zr-C-O fibre addition, it may be difficult to eliminate porosity located within the Si-Zr-C-O fibre agglomerates.

In order to make clear the above densification behaviour, crystalline phases of the hot-pressed SiC composite with Si-Zr-C-O fibre addition were examined using XRD. Typical results for the SiC composites with 5 mol% of Al_4C_3, as a function of Si-Zr-C-O fibre addition, are shown in Fig. 4. The presence of α-SiC, β-SiC, Al_4SiC_4, and C was noted for the SiC composites with 10–50 mass% of Si-Zr-C-O fibre addition. No appreciable changes in XRD patterns were observed for the different Si-Zr-C-O fibre addition. This suggests changes in the relative density of hot-pressed SiC composites to be chiefly related to the state of Si-Zr-C-O fibre dispersion within the SiC matrix, as already mentioned, rather than due to any chemical reaction.

Since the relative density of the hot-pressed SiC composite with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions attained 92.8%, the effect of Al_4C_3 addition on the relative density of the SiC composite was examined by fixing the amount of Si-Zr-C-O fibre addition to be 40 mass%. Results are shown in Fig. 5, together with a typical SEM micrograph of the fracture surfaces. Although the relative density of the hot-pressed SiC composite with no Al_4C_3 addition was only 66.8%, this increased with Al_4C_3 addition and reached 92.8% for 5 mol% of Al_4C_3 addition. However, the relative density decreased with further increases in the amount of Al_4C_3 addition and was 76.3% for the case of 10 mol% of Al_4C_3 addition. SEM observation showed some interstices to exist between the SiC matrix and Si-Zr-C-O fibres (see arrow marks).

Typical XRD results for the hot-pressed SiC composites with 0 mol% and 10 mol% of Al_4C_3 addition (the amount of Si-Zr-C-O fibre addition: 40%) are shown in

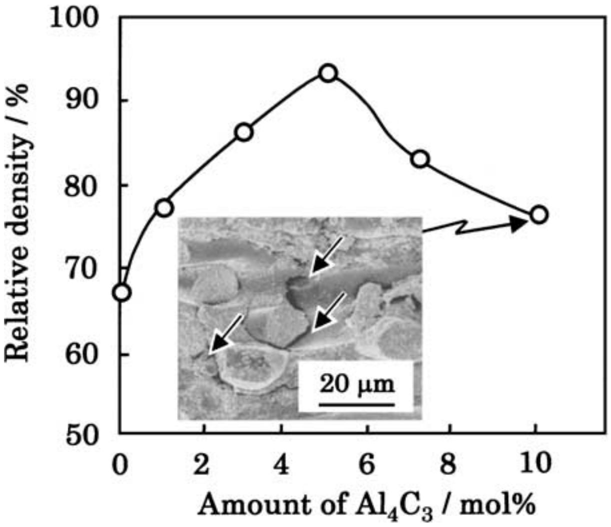

Figure 5 Effect of Al_4C_3 addition on the relative density of SiC composite with 40 mass% of Si-Zr-C-O fibre addition hot-pressed at 1800 °C for 30 min, together with a SEM micrograph of the fracture surfaces. The arrow marks indicate the interstices between SiC matrix and Si-Zr-C-O fibre.

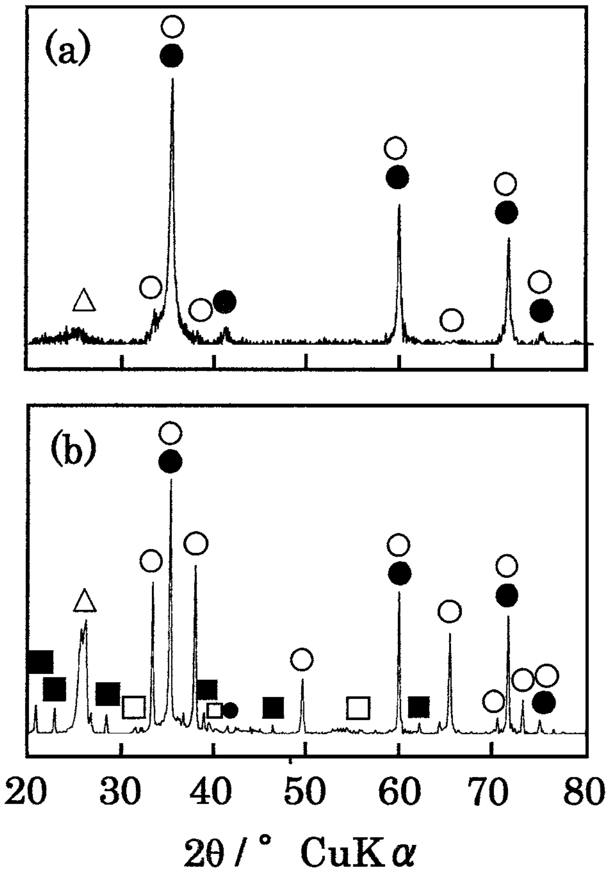

Figure 6 XRD patterns for the (a) SiC composite with no Al_4C_3 addition and (b) SiC composite with 10 mol% of Al_4C_3 addition hot-pressed at 1800 °C for 30 min. Note that the amount of Si-Zr-C-O fibre addition was 40 mass% in both composites. ○: α-SiC ●: β-SiC □: Al_4SiC_4 ■: Al_4O_4C △: C.

Fig. 6. The SiC composite with 0 mol% of Al_4C_3 addition contained α-SiC, β-SiC, and C (Fig. 6a) whilst that with 10 mol% of Al_4C_3 addition contained α-SiC, β-SiC, C, Al_4SiC_4, and Al_4O_4C (Fig. 6b).

It is shown above that the relative density of the hot-pressed SiC composite is reduced when the amount of Al_4C_3 addition exceeds 5 mol%. As already described, a liquid phase in the Al-C system may be expected to occur during hot-pressing and help the rearrangement of SiC grains, thereby increasing the relative density of hot-pressed SiC composite with Si-Zr-C-O fibre addition. However, for the case of more than 5 mol% Al_4C_3 addition, a reaction between Al_4C_3 and the Si-Zr-C-O fibre to form SiO gas appears to be dominant compared to that between Al_4C_3 and SiC to form Al_4SiC_4. After releasing SiO gas, pores may be created at the interface between the SiC matrix and Si-Zr-C-O fibres, as was indeed the case with interstices being noted in these regions (see Fig. 5).

The results so far suggest the optimum amounts of Al_4C_3 and Si-Zr-C-O fibre for the fabrication of dense SiC composites to be 5 mol% and 40 mass%, respectively. Since the relative density of this composite was 92.8%, further densification may be expected with increasing hot-pressing time. On the basis of this expectation, the hot-pressing time of SiC composites with 5 mol% of Al_4C_3 addition was increased from 30 min to 2 h. Results are shown in Fig. 7, as a function of the amount of Si-Zr-C-O fibre addition, together with a typical SEM micrograph of the fracture surfaces. The relative density of the SiC composites hot-pressed for 2 h was noted to increase from 91.9% to 95.9% upon increasing the amount of Si-Zr-C-O fibre addition from 20 mass% to 40 mass%. However, the SEM micrograph indicated all Si-Zr-C-O fibres in this case to be cut by propagation of the main crack with no evidence of fibre debonding or pull-out. For such a case the contribution of the fibres to enhancing the fracture toughness would be significantly less compared to when a significant degree of fibre pull-out exists (see Fig. 3).

Therefore, although an increase in hot-pressing time increased the relative density of the hot-pressed SiC composite with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions from 91.9% to 95.9%, it most likely would result in decreased fracture toughness. The authors have plans to investigate the effect of Si-Zr-C-O

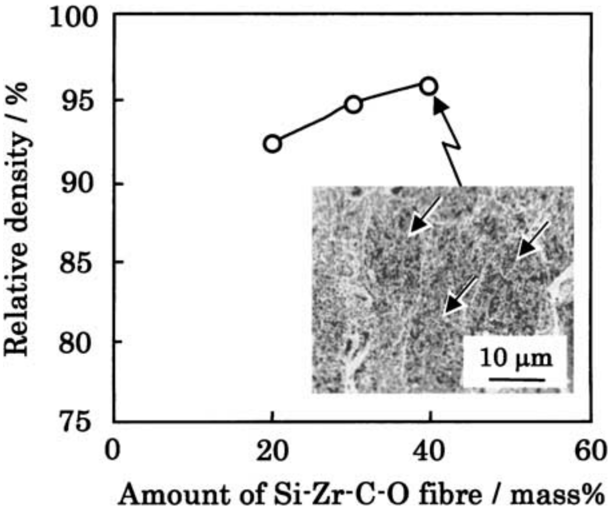

Figure 7 Changes in relative density of SiC composite (amount of Al_4C_3 addition: 5 mol%) with increasing Si-Zr-C-O fibre addition, together with a typical SEM micrograph of the fracture surfaces. Hot-pressing conditions: 1800 °C, 2 h. Arrow marks indicate the location of Si-Zr-C-O fibres.

fibre oxidation on the relative density of SiC composite in order to promote the degree of fibre pull-out at the fracture surfaces and details will be reported elsewhere.

3.3. Mechanical and thermal properties of hot-pressed SiC composites with Si-Zr-C-O addition

The previous sections demonstrated that relatively dense SiC composites with Si-Zr-C-O fibre addition could be fabricated using the hot-pressing technique. In the present section, mechanical and thermal properties of these hot-pressed SiC composities will be examined.

3.3.1. Mechanical properties

Firstly, the effect of the amount of Si-Zr-C-O fibre addition on the Vickers hardness and fracture toughness of the hot-pressed SiC composite was examined by fixing the amount of Al_4C_3 addition to be 5 mol%, with results being presented in Fig. 8. Whereas the average Vickers hardness of the hot-pressed SiC specimen with no Si-Zr-C-O fibre addition was 16.7 GPa, it decreased to a minimum (3.4 GPa) at 10 mass% of Si-Zr-C-O fibre addition and then increased to another maximum (12.9 GPa) at 30 mass% of fibre addition, and finally decreased to 6.6 GPa at 50 mass% of fibre addition. Changes in average Vickers hardness values of the SiC composites with Si-Zr-C-O fibre addition were correlated to relative density, showing that higher relative density resulted in higher Vickers hardness values. It was also noted that, overall, individual Vickers hardness values were distributed over a relatively wide range, presumably as a result of the large difference in Vickers hardness between mainly the matrix and fibres, although some effect might also be attributed to the reaction products and porosity.

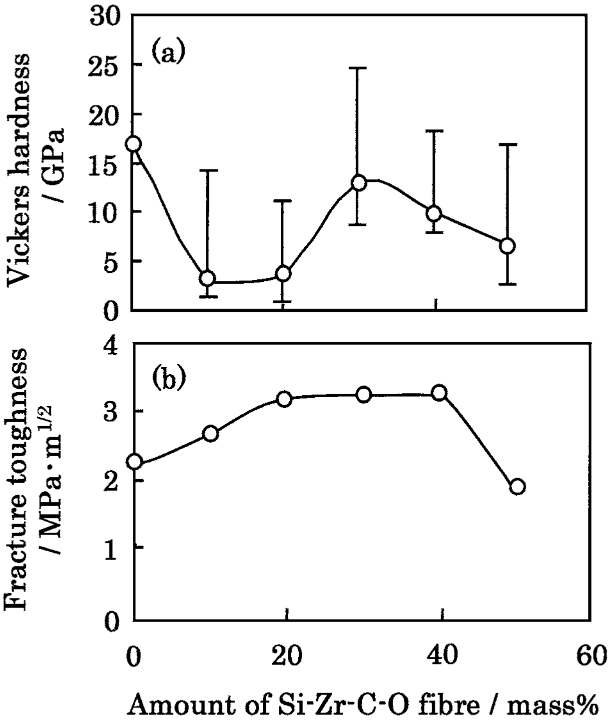

Figure 8 Effect of Si-Zr-C-O fibre addition on the (a) Vickers hardness and (b) fracture toughness of SiC composite with 5 mol% of Al_4C_3 addition hot-pressed at 1800 °C for 30 min.

The fracture toughness of the hot-pressed SiC composite with no Si-Zr-C-O fibre addition was 2.39 MPa · m$^{1/2}$. On the other hand, the fracture toughness of the hot-pressed SiC composite increased to 3.2–3.4 MPa · m$^{1/2}$ for 20–40 mass% of Si-Zr-C-O fibre addition. However, a further increase in amount of Si-Zr-C-O fibre addition to 50 mass% decreased the fracture toughness to 1.83 MPa · m$^{1/2}$. The fracture toughness (2.39 MPa · m$^{1/2}$) of the hot-pressed SiC composite with no Si-Zr-C-O fibre addition was similar to that of the SiC with Al addition hot-pressed at 1800 °C [12]. Fracture toughness (3.2—3.4 MPa · m$^{1/2}$) of the hot-pressed SiC composites with 20—40 mass% of Si-Zr-C-O fibre addition was approximately 1.5 times higher than that of the SiC composite with no Si-Zr-C-O fibre addition. Such increases are attributed to the effect of fibre debonding and pull-out (see Fig. 3).

3.3.2. Thermal properties

In this section, the thermal resistance of hot-pressed SiC composite with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions was investigated. Fig. 9 shows typical mass changes found during heating of the composite up to and holding at 1300 °C for 20 h in air. Following an initial 16% mass decrease as the composite was heated, the mass then increased as the temperature was raised to 1300 °C. However, mass changes whilst being held at 1300 °C for 20 h were generally on the order of 3%.

Crystalline phases present on the surfaces of heat-treated composite in air were examined using TF-XRD with results being given in Fig. 10. The overall trend of the TF-XRD patterns indicated the presence of α-SiC, β-SiC, and SiO_2 in heat-treated specimens. The reflection intensity attributed to SiO_2 was fairly constant, whereas those of α-SiC and β-SiC were enhanced, with increasing incident angle. Such a result is consistent with the SiO_2 mainly being present on and near the surfaces of the heat-treated specimens.

The mass loss upon heating the composite to 1300 °C is ascribed to the oxidation of the free carbon in the SiC

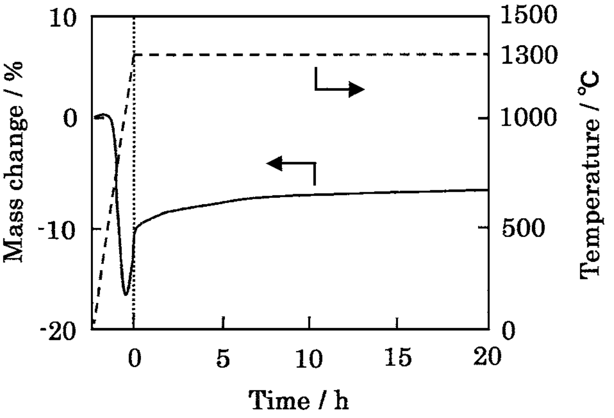

Figure 9 Typical mass changes in air during the heating of SiC composite with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions hot-pressed at 1800 °C for 30 min. Note that the heating rate up to the desired temperature (1300 °C) was 10°C · min^{-1}.

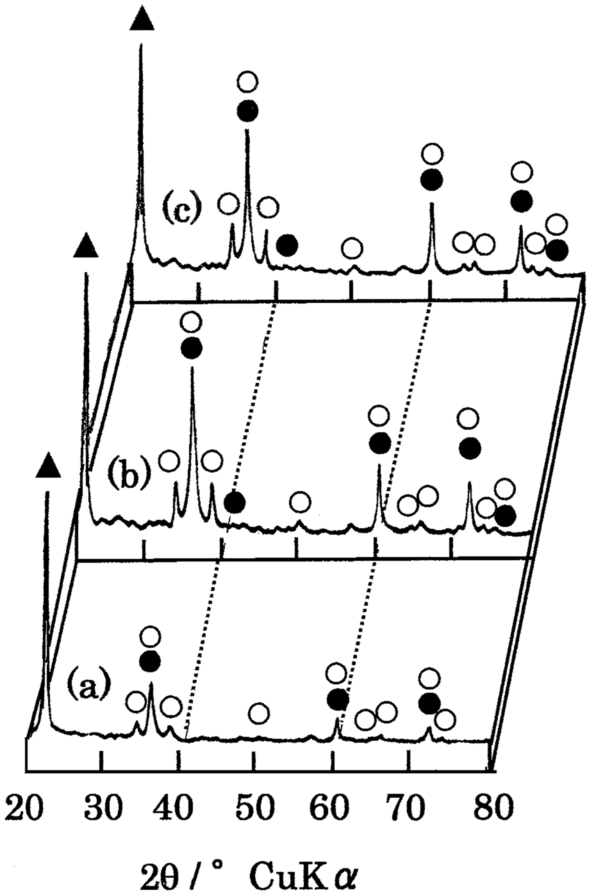

Figure 10 TF-XRD patterns for the hot-pressed SiC composite with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions heat-treated at 1300 °C for 20 h in air. Note that the hot-pressing conditions were 1800 °C for 30 min. Incident angle of TF-XRD: (a) 1°, (b) 2°, (c) 3°. ○: α-SiC ●: β-SiC and ▲: SiO_2.

matrix.

$$C + (1/2)O_2 \rightarrow CO \qquad (5)$$

$$C + O_2 \rightarrow CO_2 \qquad (6)$$

On the other hand, the mass gain of the hot-pressed composite is chiefly attributed to the oxidation of SiC according to the following chemical reactions:

$$SiC + (3/2)O_2 \rightarrow SiO_2 + CO \qquad (7)$$

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2 \qquad (8)$$

Moreover, it is probable that the Si-Zr-C-O fibres exposed to air may be thermally decomposed to form SiO_2 and ZrO_2. Although ZrO_2 could not be detected from the heat-treated specimens, this is attributed to the amount of ZrO_2 produced being below the detection limit of the TF-XRD. It may thus be envisaged that the SiO_2 acts as a protective layer, as a result of which no appreciable mass gain occurs with increasing heat-treatment time.

4. Conclusions

Conditions for the fabrication of dense SiC composites with short Si-Zr-C-O fibre addition were examined using the hot-pressing technique. In addition, Vickers hardness and fracture toughness of the hot-pressed SiC composite were measured together with the heat resistance behaviour. The results were summarized as follows:

1. SiC composites with 10–50 mass% (10.5–51.2 vol%) of Si-Zr-C-O fibre (average length; ∼0.5 mm) addition were fabricated using the hot-pressing technique and 0–10 mol% of Al_4C_3 as a sintering aid. Firstly, the effect of short fibre addition on the relative density of SiC composite hot-pressed at 1800 °C for 30 min was examined by fixing the amount of Al_4C_3 to be 5 mol%. The relative density of the hot-pressed SiC composite with no Si-Zr-C-O fibre addition was 96.0%. On the other hand, the relative density of the SiC composite was reduced to 87.4% at 10 mass% of Si-Zr-C-O fibre addition; however, it was enhanced with further increases in the amount of fibre addition to reach a maximum of 92.8% at 40 mass% of fibre addition. Next, the effect of varying the amount of Al_4C_3 on the relative density was examined by fixing the amount of Si-Zr-C-O fibre addition to be 40 mass%. The optimum amount of Al_4C_3 addition for the fabrication of dense SiC composites was found to be 5 mol%.
2. The fracture toughness of the SiC composite with no Si-Zr-C-O fibre addition (amount of Al_4C_3: 5 mol%) was 2.39 $MPa \cdot m^{1/2}$. On the other hand, the fracture toughness of the SiC composites with 20–40 mass% of Si-Zr-C-O fibre addition was 3.2–3.4 $MPa \cdot m^{1/2}$ with the increase being directly attributed to debonding and pull-out of the fibres.
3. SiC composites with 5 mol% of Al_4C_3 and 40 mass% of Si-Zr-C-O fibre additions possessed excellent heat resistance at 1300 °C in air due to the formation of a protective SiO_2 surface layer.

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