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Fabrication of short-fiber-reinforced SiC composites by polycarbosilane infiltration

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Abstract

Green sheets of the composites using polycarbosilane (PCS)-infiltrated (coated) Tyranno SA short fibers, submicron SiC powder and Al_2O_3–Y_2O_3–CaO mixtures as sintering additives were prepared by tape-casting. These green sheets were stacked and hot-pressed at 1750 °C. Most of all SiC short fibers were oriented along the tape casting direction. The bulk density of the composites was about 2.66 g/cm^3. The bending strength was measured at room and high temperatures and the highest value was about 260 MPa at room temperature and 1000 °C. The fracture behavior of the composites showed a completely brittle fracture at room and high temperatures up to 1400 °C. Results of scanning electron microscope investigation showed that there were little pulled-out fibers in the tensile stress zone of the fracture surface independent of test temperature. A mechanically weak and chemically tight interface layer was not successfully formed by the present coat method.

Keywords: Mechanical properties; Polycarbosilane; Polymer infiltration; SiC short fibres; SiC/SiC

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1. Introduction

Silicon carbide (SiC) is one of the leading candidate ceramic materials for engineering applications because of its excellent high temperature mechanical properties, potentiality of high thermal conductivity and good corrosion and wear resistance. Furthermore, SiC expected to be used as structural materials for future fusion reactors since SiC ceramics show low activation due to its low atomic number and good resistance to high-energy neutron irradiation up to very high neutron fluences.[1] Therefore, a number of investigations have been carried out to develop the manufacturing process and to improve reliability of this ceramic.[2–4] Over the past years, various kinds of SiC based composites, including particulate-, whisker- and fiber-reinforced SiC composites, have been extensively investigated. Fiber reinforced composites exhibit significant improvement of mechanical (ductile) properties in comparison with the monolithic SiC ceramic.[4–7]

SiC continuous-fiber-reinforced SiC composites were generally fabricated by chemical vapor infiltration (CVI), polymer infiltration and pyrolysis (PIP), melt infiltration (MI) and hot-pressing (HP) methods.[8–11] The reports on mechanical and thermal properties of SiC/SiC composites reinforced with short fibers were very limited.

Short-fiber-reinforced composites will increasingly be used in a wide range of application because of their easy adaptability to conventional manufacturing techniques and then low cost of fabrication.[12] The increasing number of applications of short fiber-reinforced composites makes it more important to understand their mechanical and thermal properties, which depend strongly on fiber orientation and volume fraction.[13,14]

Technique of fabricating ceramics by pyrolysis of organometallic polymers has many possibilities in producing new materials. Polycarbosilane (PCS) has been widely used as a precursor polymer for SiC fibers and fiber-reinforced composites or nano-structured ceramics. In the processing for fiber-reinforced composites, a polymeric precursor solution, prepared with an organic solvent such as toluene or hexane, is mixed with fiber and SiC powder. The decomposition of precursor

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polymer could affect interface between fiber and matrix in the fiber-reinforced composites.[15]

The present authors have reported that short-fiber-reinforced SiC composites with BN-coated Hi-Nicalon fibers could be fabricated from green sheets of SiC containing Al_2O_3–Y_2O_3–CaO sintering additives by hot-pressing at 1750 °C. Although these composites achieved nearly full density, they fractured in a brittle manner and showed insufficient fiber pullout besides of slight increase in fracture toughness.[16] The prime reason of insufficient fiber pullout was supposed to the thermal degradation of fibers during sintering. Then, in order to improve the mechanical properties of short-fiber-reinforced SiC composites, we tried to fabricate composites using Tyranno SA fiber, which shows higher strength and thermal conductivity at high temperature than that of Hi-Nicalon fiber.[17] As a result, whereas maximum strength and thermal conductivity were improved, this attempt was also failed to obtain non-brittle material since higher reactivity of Tyranno SA fibers with the sintering additives.[18] It has been well recognized that the mechanical behavior of fiber-reinforced composites is closely related to the fiber-matrix interfacial properties. Employing a reaction barrier as well as a weak layer between fiber and matrix has been expected to improve the mechanical performance.

In the present work, therefore, SiC short-fiber-reinforced SiC composites were prepared using PCS-coated Tyranno SA fibers. The effects of processing parameters on mechanical properties of the SiC short-fiber-reinforced SiC composites using PCS-coated Tyranno SA fibers were investigated.

Table 1
Properties of the Tyranno SA silicon carbide fiber

Type (SiC fiber)	Tyranno SA
Density (g/cm^3)	3.02
Diameter (μm)	10
Tensile strength (GPa)	2.8
Young's modulus (GPa)	420
Elongation (%)	0.7
Specific heat at R.T. (J/w K)	1.4
Thermal conductivity at R.T. (W/m K)	64.6
C/Si ratio (atomic)	1.08
Chemical composition (wt.%)	Si:C:0 = 67.8:31.3:0.3
Structure	Crystalline

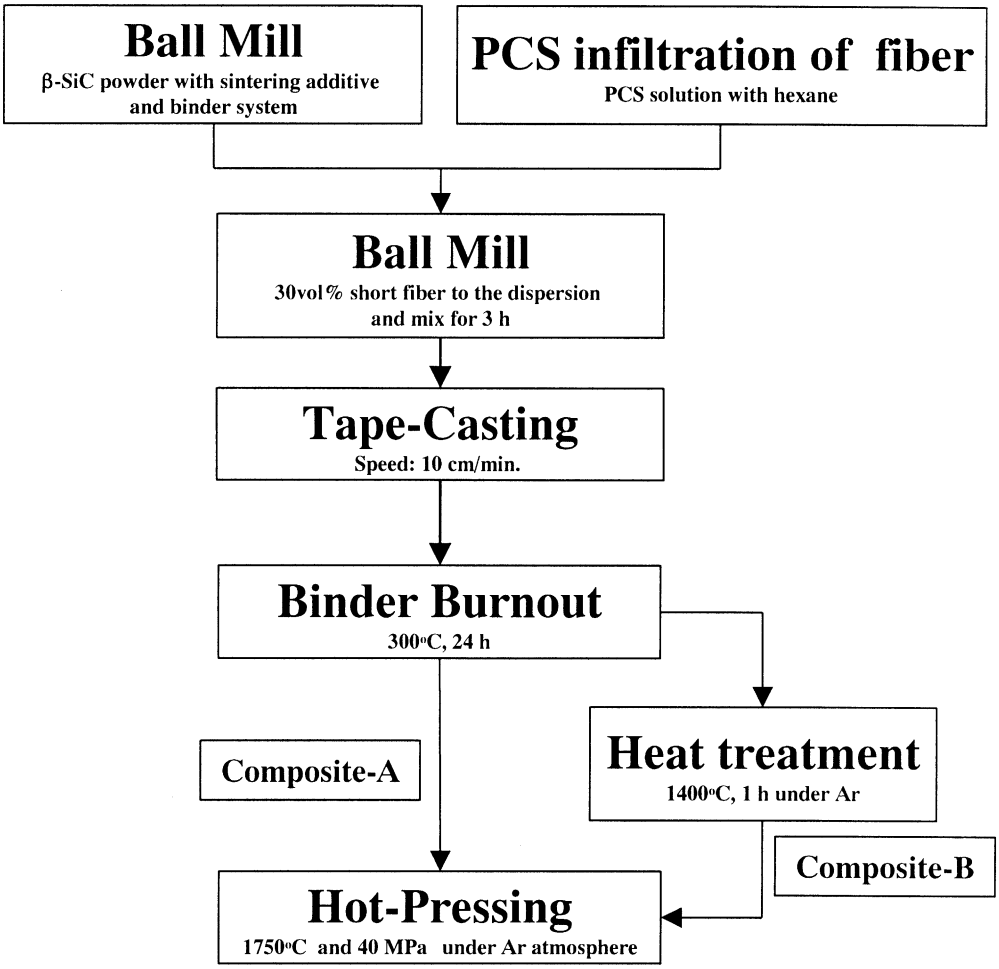

Fig. 1. Fabrication process of short-fiber-reinforced SiC composites by polycarbosilane infiltration and hot-pressing.

2. Experimental procedure

2.1. Raw materials and fabrication of composite

The high strength and high modulus SiC fiber used in this study was the Tyranno SA fibers (Ube Indus., Co., Japan), whose properties are summarized in Table 1. The non-coaled SiC fibers, an average diameter of 10 μm and an average length of 1 mm, used for the fabrication of the composites were chopped from the continuous fiber. PCS coating solution of 30 wt.% concentration was prepared using hexane as a solvent. Polycarbosilane (PCS, NIPUSI-Type S, Nippon Carbon, Japan) was used for the coating of SiC short fibers. Density, melting point and average molecular weight of PCS powder used in this study were 1.10 g/cm^3, 234 °C and 1580 g/mol, respectively.

The SiC short fibers were dipped with the PCS–hexane solution for 30 min under reduced pressure and then dried at 130 °C. The starting powder for the matrix components was prepared by ball-milling of a sub-micron β-SiC powder and various kind of sintering additives (14 wt.% Al_2O_3, 4 wt.% Y_2O_3, 2 wt.% CaO) with a dispersing agent for 24 h in ethanol using Al_2O_3 balls. An Al_2O_3–Y_2O_3–CaO system was chosen for fabrication of the composites as sintering additives, because of their low liquid forming temperature.[19] The fabrication procedure for the short-fiber-reinforced SiC composites is described in Fig. 1.

A well-stirred solution of binder and coated short fibers were added to the SiC-additives solution. This solution was further mixed by ball-milling for 3 h, followed de-air process using a rotary pump for 30 min to obtain the final slurry for tape-casting. The green sheets were prepared by means of laboratory scale doctor-blade equipment, and stacked along the same direction of the sheet forming. Thus the short fibers were mostly aligned unidirectionally. Thickness of the green sheets was about 300–350 μm. Volume fraction of short fibers was about 30 vol.%. After drying the green body, pyrolysis of the added precursor was induced during sintering (composite-A) or separate heat treatment before sintering (composite-B) to form interface between fiber and matrix. The stacked green body was hot-pressed at 1750 °C in Ar under a pressure of 40 MPa for 1 h.

2.2. Characterization of composites

Bulk density of the specimens was measured by the Archimedes method. Three-point bending test (test bars 3.5×2.5×34 mm) was carried out with a crosshead speed of 0.1 mm/min and a lower span of 30 mm at room in air and high temperatures up to 1400 °C in vacuum. Bending bars were cut parallel to the fiber axis. Before load was applied at the high temperature test, the specimens were soaked at the test temperature for 30 min to obtain temperature uniformity. All data were averages of two or three tests for each condition.

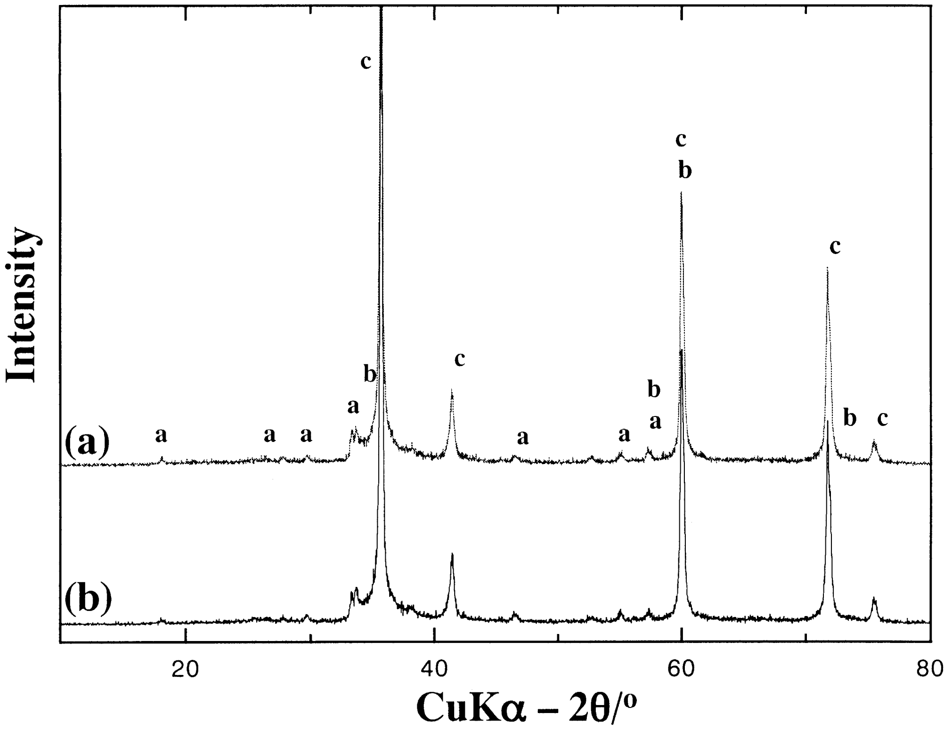

Fig. 2. XRD patterns of the SiC/SiC composites sintered at 1750 °C for 1 h: (a) composite A, (b) composite B (a: $Y_3Al_5O_{12}$, b: α-SiC, c: β-SiC).

Microstructure and fracture surface after bending test was observed by scanning electron microscopy (SEM: Hitachi S-3500H) after CF_4-O_2 plasma etching. The samples for transmission electron microscopy were prepared as follows. Thin foils were cut from the composite perpendicular to the fiber axis and mechanically ground to a thickness of 60–70 μm, then they were further thinned to about 20 μm by dimpling, followed by ion-thinning until perforation. The microstructure observation and composition analysis were carried out in a transmission electron microscope (TEM: Hitachi H-9000) equipped with an energy-dispersive X-ray spectrometer (EDS: Kevex Delta III). The constitution phases of the composites were determined by X-ray diffractometry (XRD: Philips PW-1700).

3. Results and discussion

The bulk densities of the samples as a function of fabrication condition were little changed. The bulk densities of composite-A and composite-B were about 2.665 g/cm^3, 2.662 g/cm^3, respectively. This value was lower than that of the composites fabricated without PCS coating (about 3.1 g/cm^3).[18] The open porosities of composite-A and composite-B were about 1.0% and 0.85%, respectively. The reason for the low bulk density was due to the pore resulting in shrinkage of PCS during processing and the presence of free carbon, which is one of the pyrolysis products of PCS. It was reported that the pyrolysis products of PCS at 1000 °C in Ar included SiO_2 (4.7 wt.%) and free C (12.3 wt.%) besides SiC (80.6 wt.%).[20]

XRD patterns of the composite-A and-B hot-pressed at 1750 °C containing 30 vol.% short fiber are shown in Fig. 2. As shown in the figure, β-SiC, α-SiC and $Y_3Al_5O_{12}$ (YAG) were observed in both composites. The presence of YAG in the composite should improve sinterbility and then interfacial strength between fiber and matrix, as a result it promotes tendency of brittle fracture.[21,22]

Fig. 3 shows the microstructure of the composites using the coated fiber hot-pressed at 1750 °C. From the SEM photographs, the SiC matrix was found to have a relatively uniform microstructure composed of fine SiC grains with smaller size than 1 μm. It is supposed that grain growth of SiC in the matrix did not occur during hot-pressing at relatively low temperatures for the densification of SiC. Usually, the liquid phase sintering of silicon carbide was done at higher temperatures than 1900 °C. In this case, exaggerated grain growth is attributed to high sintering temperature and resulting phase transformation from β to α.[23] As shown in the figure, trace of PCS could be observed in marked region. The average grain size of PCS-derived SiC was as small as about 100 nm. It was reported that pyrolysis of PCS at 1000 °C yields an amorphous powder, and crystallization begins above 1200 °C. Very fine crystals of β-SiC, about 2–100 nm in diameter, are obtained.[24] Formation of PCS-derived layer around fiber was not uniform both in the composite-A or -B. Trace of high-porosity layer was observed around the fiber in the composite-B. The interface between fiber and matrix was not distinct in the composite-A.

Bending strength of the composites sintered at 1750°C and measured at room and high temperatures are shown in Fig. 4. Bending strength was mostly maintained up to 1000 °C but decreased at 1200 °C in the both specimens. In the case of composite-A, maximum strength was about 230 MPa at 1000 °C and about 130 MPa at 1400 °C, whereas in the case of composite-B, maximum strength was about 230 MPa at 1000 °C and about 110 MPa at 1400 °C. Bending strength of the composite-A was relatively higher than that of the composite-B at 1400 °C. Kim et al.[19] reported that bending strength of polycarbosilane added SiC fabricated by hot-pressing was higher than that of SiC ceramic without poly-

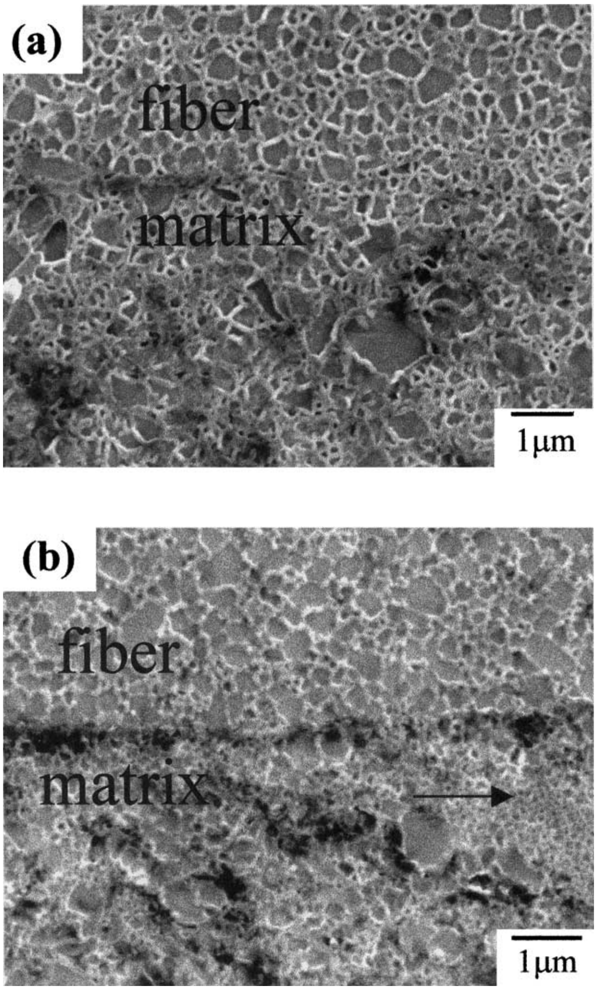

Fig. 3. Microstructures of SiC short-fiber-reinforced SiC composites sintered at 1750 °C (a) composite A, (b) composite B.

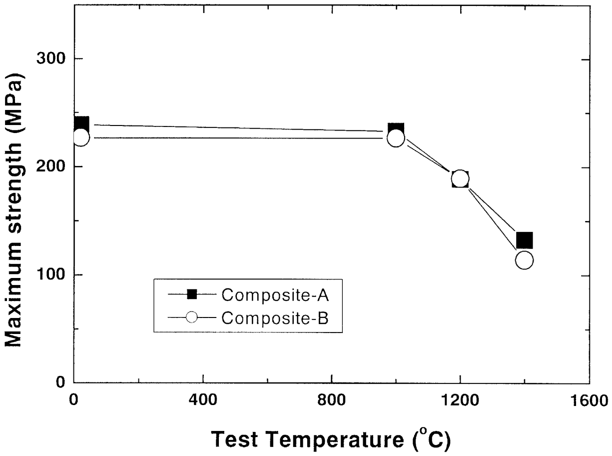

Fig. 4. Maximum strength of SiC short-fiber-reinforced SiC composites sintered at 1750 °C as a function of test temperature.

carbosilane, where the former was much finer grain size than the latter. The reason for the lower strength of the composite obtained in this study may be attributed to degradation of the fiber during sintering. Grain growth of SiC in the fibers was accelerated due to reaction with oxide compounds, produced from PCS after pyrolysis, and sintering additives. Also, these composites have much higher content of carbon and SiO_2, which is also derived from the pyrolysis of PCS, as compared to conventionally sintered SiC. At 1400 °C, weakening of matrix grain boundary phase dominates the strength of the composites.

Fracture surfaces of the composites-A and -B sintered at 1750 °C and tested at room temperature are shown in Fig. 5. It is observed that fibers were mostly aligned along sheet forming direction and long axis of bend bars, i.e., perpendicular to the hot-press direction. It is reported that the strength and toughness could be improved simultaneously through short-fiber oriented alignment.[25,26] As indicated in the figure, pull-out of short fibers was little observed regardless of fabrication condition, therefore fracture behavior was catastrophic. The fracture morphology was not influenced by the test temperatures. Yang et al.[27] reported that fracture behavior of the non-coated Tyranno SA continuous-fiber-reinforced SiC composite exhibited low bending strength (about 252 MPa) and displayed brittle failure, comparing to high strength (about 300 up to 550 MPa) and non-brittle failure of multi-layer-coating composites with carbon and SiC layer. Their results indicate that fracture behavior of fiber-reinforced composites without interface between fiber and matrix was very difficult to induce non-brittle fracture.

Fig. 6 shows the TEM micrograph of the fiber/matrix interface of the composite-B sintered at 1750 °C. As shown in the figure, the interface is very narrow. It is

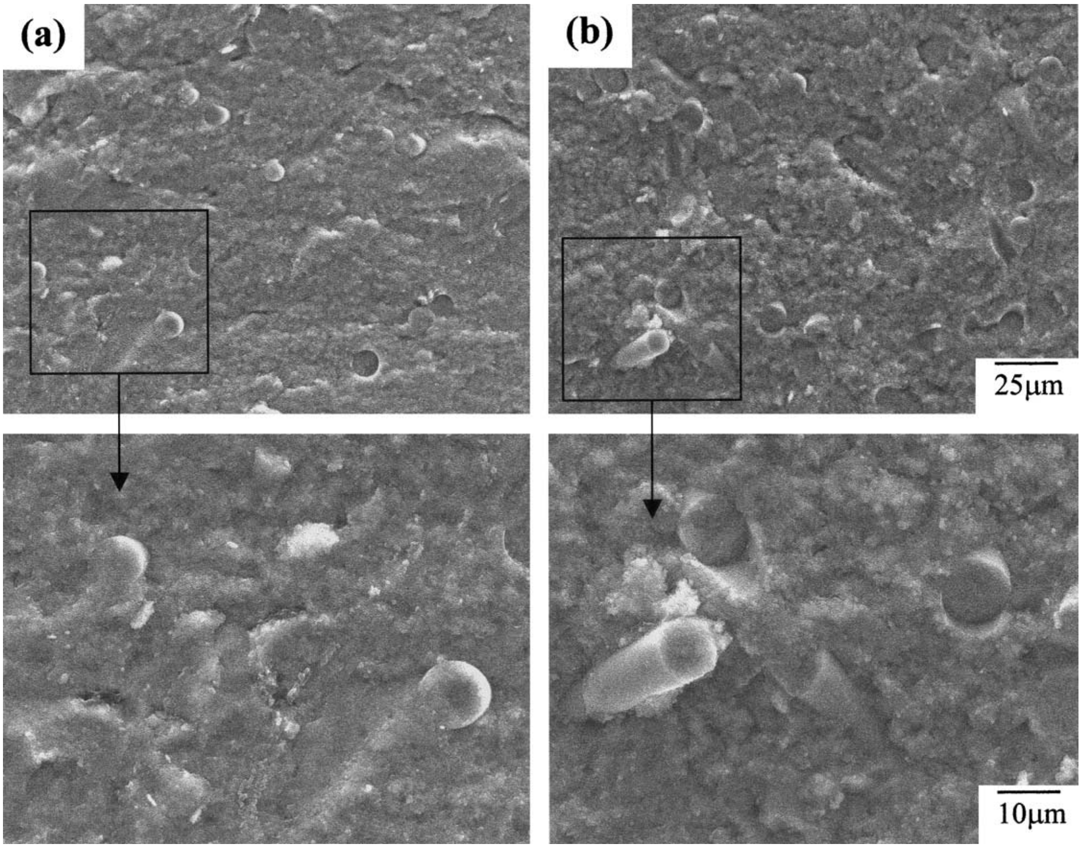

Fig. 5. Fracture surfaces of SiC/SiC composites sintered at 1750 °C and tested at room temperatures, (a) composite-A, (b) composite-B.

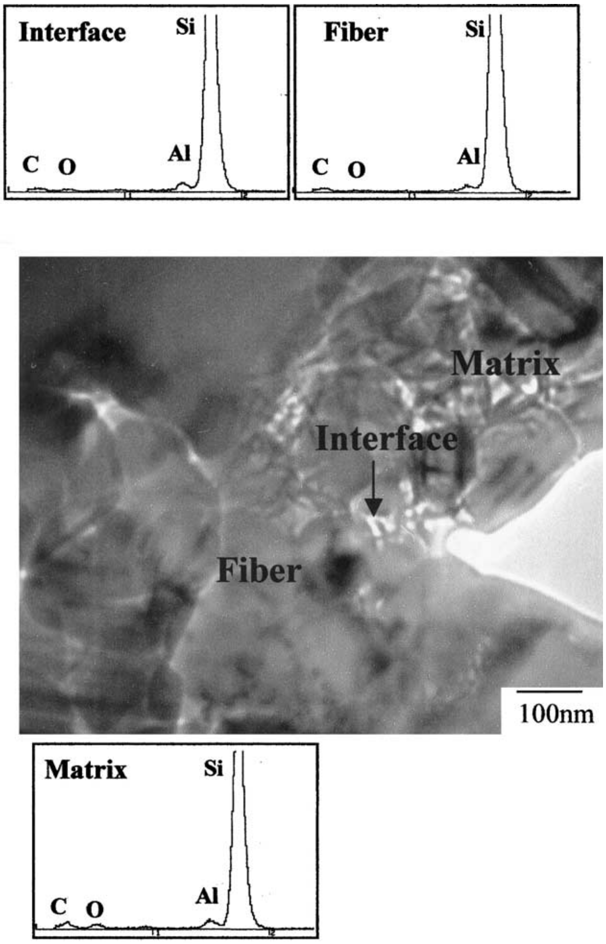

Fig. 6. TEM micrographs of the fiber/matrix interface of the composite-B containing 30 vol.% short fibers sintered at 1750 °C.

well known that the fiber/matrix interfacial characteristics play a critical role in controlling the fracture properties of the composites.[28,29] The presence of C, O, Al and Si elements not only in matrix but also at interface in the fiber was detected by EDS, as shown in the figure. Based on the TEM analysis, it was indicated that there were no effective diffusion barrier between the fiber and the matrix component. It means relatively strong contact between fiber and matrix should be formed, and then some elements were migrated into fibers to reduce its mechanical property.

From these results, in order to better control of fiber/matrix interactions to improve the pseudo-ductility, improvement of interfacial layer between fiber and matrix is necessary. Coating layers should be chemically stable components and without reaction with matrix, or form diffusion barrier between fiber and matrix components during processing and in service at high temperature. Furthermore, the kind of sintering additives should be changed without increasing porosity to obtain high strength, and without increasing densification temperature to restrict degradation of fiber properties. Therefore, formation of more chemically tight but mechanically loose bonded layer is requested. For this purpose, multi-layer coating such as carbon and SiC double layer coating is a candidate.

4. Conclusion

Green sheets of the composites using polycarbosilane (PCS)-coated Tyranno SA short fiber with Al_2O_3–Y_2O_3–CaO as sintering additives were prepared by tape-casting, and then there were stacked and hot-pressed at 1750 °C to fabricate SiC short-fiber-reinforced SiC composite. The short fibers were mostly aligned along sheet forming direction and long axis of bend bars, i.e., perpendicular to the hot-press direction. Diffusion of sintering aids into the fibers was observed. The pullout of short fibers was little observed regardless of fabrication conditions, therefore fracture behavior of the composites was catastrophic. The fracture morphology was not also influenced to the test temperatures. The PCS coating on short fibers by the present process did not form an uniform, weak and reaction barrier layer between the fiber and the matrix to induce fiber pullout.

Acknowledgements

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