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Microstructural and mechanical characteristics of SiC/SiC composites with modified-RS process

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Abstract

This paper deals with the efficiency of modified-reaction sintering techniques including a impregnation pressure and a cold pressure as well as the applicability of new high performance fiber, in order to develop high performance SiC/SiC composites. SiC/BN coated Hi-Nicalon fiber, SiC coated Tyranno ZMI fiber and Tyranno SA fiber were used in this composite system. Microstructural characteristics of reaction sintered SiC/SiC composites were investigated by means of SEM, EDS and TEM. Mechanical properties and fracture mechanisms of SiC/SiC composites were also evaluated through the three-point bending test. Improved SiC/SiC composites with high density and high strength were successfully fabricated by the sequential application of low pressure impregnation and cold pressing processes. An excellent chemical stability of Tyranno SA fiber during the reaction sintering process was also revealed. Tyranno SA fiber reinforced SiC/SiC composites with no interfacial coating exhibited good flexural strength and elastic modulus, compared to those reinforced by BN/SiC coated Hi-Nicalon and SiC coated Tyranno ZMI fibers. However, this composite system needed an appropriate interfacial coating for proper CMC composite behavior.

1. Introduction

Silicon carbide (SiC) based ceramic matrix composites (CMCs) have been extensively studied in recent years for use in fusion energy systems such as the first wall of the fusion reactor, and advanced gas turbine engines in aerospace vehicles. Among CMCs, SiC fiber reinforced SiC matrix composites (SiC/SiC) have provided considerable potential for numerous advanced structural applications, since these exhibit excellent high temperature strength, good fracture toughness compared with monolithic ceramic materials and low induced radioactivity under severe radiation environments [1–3]. Recent development of high performance SiC fibers, such as Hi-Nicalon, Hi-Nicalon type S and Tyranno SA, which possess low oxygen content and high temperature stability, has also prompted the investigation on a wide variety of fabrication processes for SiC/SiC composites.

The majority of recent works for SiC/SiC composites are concentrated on the improvement of fabrication processes including chemical vapor infiltration (CVI), polymer impregnation and pyrolysis (PIP) and melt infiltration, namely, reaction sintering (RS) as well as the evaluation of mechanical and irradiation properties [4–15]. The reaction sintering process can be recognized as an attractive technique because it offers high density, good leak-tightness, good thermal conductivity and reasonable production cost. Several studies have shown that reaction sintered SiC/SiC composites have a thermal conductivity higher than 50 W/m K at room temperature, in comparison to those fabricated by PIP and CVI processes, and possess first matrix cracking strength of about 200 MPa [16,17]. However, several drawbacks such as the residual silicon phases in the matrix portion and the damage of reinforcing fibers still impose a severe limitation on the practical application of reaction

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sintering process. The presence of residual silicon phases, which results from the infiltration of molten silicon into green SiC/SiC preform, may cause microstructural instability, reduced creep resistance, and undesirable irradiation behavior of SiC/SiC composites. Therefore, in order to improve the reaction sintering process for developing high performance SiC/SiC composites, it is important to conduct the appropriate reaction of carbon and silicon, based on the detailed analysis of their microstructures. It is also necessary to examine new type of SiC fibers capable of avoiding the damage from the molten silicon.

The primary purpose of the present study is to investigate the efficiency of modified reaction sintering process by the combination of slurry impregnation pressure and cold pressing, accompanied with the evaluation of microstructural and mechanical characteristics of reaction sintered SiC/SiC composites. The applicability of new type of SiC fiber to reaction sintering process is also examined.

2. Experimental

2.1. Materials and fabricating process

The processing routes and the raw materials used for the fabrication of SiC/SiC composites were shown in Table 1. The reinforcing materials were a flat braided Hi-Nicalon fiber (Nippon Carbon), a three-dimensional Tyranno ZMI fiber and a two-dimensional-woven Tyranno SA fiber (Ube). The configuration ratio of Tyranno ZMI fabric was $X:Y:Z = 1.0:1.0:0.2$, in which X and Z mean the longitudinal direction and the thickness direction, respectively. The BN/SiC and SiC coating layers were applied on the surface of Hi-Nicalon fiber and Tyranno ZMI fiber, respectively, using the chemical vapor deposition process. The matrix slurry was SiC powder, carbon powder and water with some dispersant. Two kinds of commercial SiC particles, whose average sizes are 0.3 and 4 μm, were utilized. The average size of commercial carbon particle was 85 nm.

The matrix slurry of SiC (4 μm) and carbon were injected into the braided preform of Hi-Nicalon fiber under a high pressure impregnation of 6 MPa. The preforms of Tyranno SA fiber and Tyranno ZMI fiber were also prepared by the matrix slurry of SiC (0.3 μm) and C under a low impregnation pressure of 0.9 MPa. The preform of Tyranno SA SiC fiber was compacted by a cold pressure of 3.5 MPa, after the injection of matrix slurry. SiC/SiC composites were fabricated by infiltrating the molten silicon into each fiber preforms under a vacuum atmosphere. The fabricating temperature and its holding time of all composites were 1450°C and 7.2 ks.

2.2. Microstructure analysis and three-point bending test

The microstructure analysis of SiC/SiC composites was carried out using the scanning electron microscope (SEM) and the energy dispersive spectrometer (EDS). The transmission electron microscopic (TEM) study was also conducted to examine unreacted carbon phase and isolated silicon phase in the matrix portion of SiC/SiC composites. Thin foils for the TEM analysis were processed by focused ion beam (FIB) device, which provided a single thin foil that contains matrix, fiber and interfacial coating layers.

In order to investigate the mechanical properties of SiC/SiC composites, three point bending tests were carried out at room temperature. Five pieces of samples were used in this test. The dimension of the test sample was $1 \times 4 \times 25$ mm^3. The span length and the crosshead speed used in the bending test were 18 mm and 0.5 mm/min, respectively. Fiber pullout and interfacial delamination behaviors were also observed to explain the fracture mechanism of SiC/SiC composites.

3. Results and discussion

3.1. Microstructural analysis of SiC/SiC composites

3.1.1. Effect of high pressure impregnation

Microstructure of Hi-Nicalon fiber reinforced SiC/SiC composites prepared by the high pressure impreg-

Table 1
Processing routes and resultant densities of SiC/SiC composites

CMC system	Reinforcement	Matrix slurry		Interphase	Slurry impregnation step	Sintered density (mg/m^3)
		SiC (μm)	C (nm)			
A	Hi-Nicalon	4.0	85	BN/SiC	High pressure (6 MPa)	2.8
B	Tyranno ZMI	0.3	85	SiC	Low pressure (0.9 MPa)	2.3
C	Tyranno SA	0.3	85	–	Low pressure (0.9 MPa) and Cold pressure (3.5 MPa)	2.9

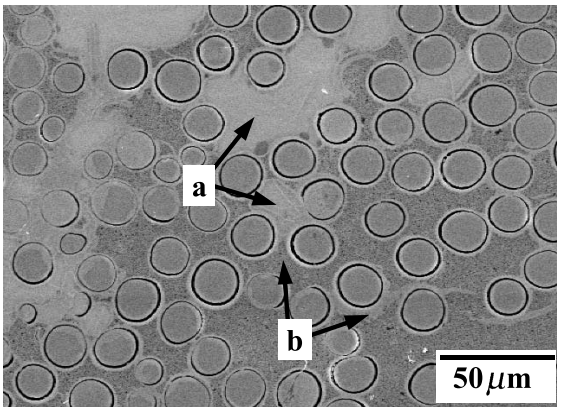


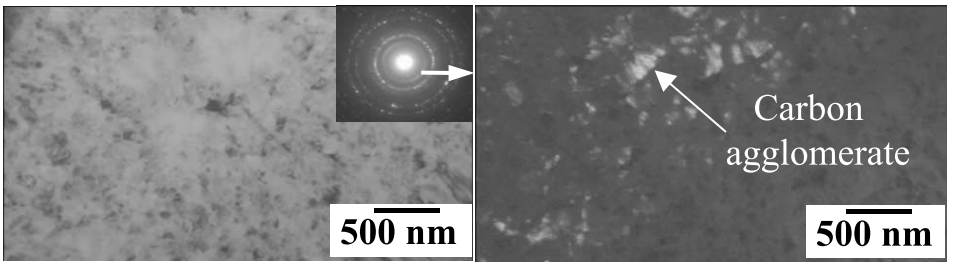
Fig. 1. Microstructure of Hi-Nicalon fiber reinforced SiC/SiC composites prepared by the high pressure impregnation of 6 MPa.

nation of matrix slurry (6 MPa) is shown in Fig. 1, including composition of each portion, which is identified by EDS quantitative analysis, as shown in Table 2. The Hi-Nicalon fiber reinforced SiC/SiC composite showed a dense matrix morphology, accompanying severe deformation of fibers. Overall composite density determined by Archimedes' method was about 2.8 mg/m^3 (See Table 1). However, the EDS analysis indicated that the matrix morphology was composed of two types of SiC phases with different ratios of silicon and carbon. Especially, a large amount of silicon-rich phases were formed dominantly in the vicinity of Hi-Nicalon fibers. This is considered to be due to molten silicon, that reacts with carbon, flows easily between Hi-Nicalon fibers during the melt silicon infiltration process, and then appears to fill large matrix pores and openings.

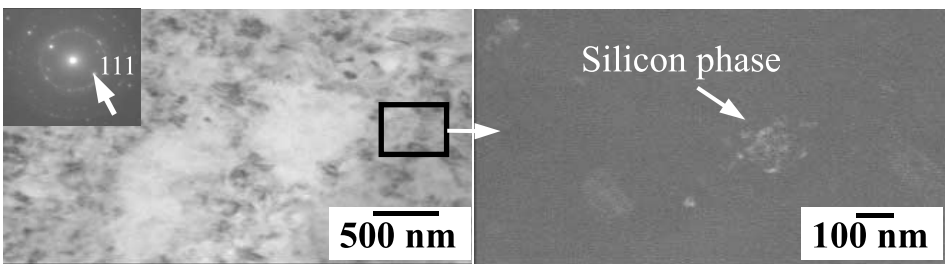
Table 2
Composition of a and b portions displayed in Fig. 1, as identified by the EDS quantitative analysis.

	Si (at.%)	C (at.%)
a	44.8	55.2
b	29.4	70.6

Fig. 2 shows the TEM micrographs on the isolate silicon and the unreacted carbon in the matrix region of SiC/SiC composites. The corresponding electron diffraction patterns were also included. The weak beam dark field images were determined by picking up the amorphous ring of the carbon and the ⟨1 1 1⟩ diffraction part of the silicon so that the grains in limited orientation are brightly imaged. It was found that the unreacted carbon and the isolated silicon were finely distributed in the matrix region. The carbon agglomerates were larger than the carbon particle (85 nm) that was used for the preparation of C/SiC matrix slurry.



(a) Carbon phase in matrix region



(b) Silicon phase in matrix region

Fig. 2. TEM micrographs on the isolated silicon and the unreacted carbon existed in the matrix region of SiC/SiC composites.

Such a presence of unreacted carbon and isolated silicon is considered to result in the difference of matrix composition in SiC/SiC composites. Therefore, it can be concluded that the matrix morphology of reaction sintered SiC/SiC composites is composed of at least three different phases, crystallized β-SiC phase, unreacted carbon phase and isolated silicon phase. In particular, since strength characteristics of the reaction sintered SiC material strongly depend on the content of isolated silicon phases [18], this phase must be suppressed to optimize the reaction sintering process for the fabrication of high performance SiC/SiC composites.

3.1.2. Effect of low pressure impregnation and cold press processes

Fig. 3 shows the SEM micrographs on intra-fiber bundles of SiC/SiC composites reinforced with Tyranno SA fiber and Tyranno ZMI fiber. The SiC/SiC green preforms used for the reaction sintering process were prepared by the low pressure impregnation of matrix slurry (0.9 MPa). The resultant densities of SiC/SiC composites reinforced with Tyranno SA fiber and Tyranno ZMI fiber were measured to be 2.2 and 2.3 mg/m^3, respectively, which were inferior to that of Hi-Nicalon fiber reinforced SiC/SiC composites by the high pressure impregnation. A large amount of pores were created in intra-fiber bundles of all composites, since the low pressure impregnation of 0.9 MPa was not enough to infiltrate the matrix slurry into fiber bundle. The debonding cracking between fiber bundles as well as large amount of matrix crackings were also observed in the cross-section of SiC/SiC composites. Moreover, it was found in Fig. 3(b) that the Tyranno ZMI fibers were severely damaged by molten silicon, even if CVD–SiC coating layer was deposited on the surface of Tyranno ZMI fiber. On the contrary, Tyranno SA fibers were not damaged. Such a damage of Tyranno ZMI fiber is maybe considered to result from the defect of CVD–SiC coating layer and the low crystallization of Tyranno ZMI fiber.

The microstructure of Tyranno SA fiber reinforced SiC/SiC composites prepared by the combination process of low pressure impregnation of matrix slurry (0.9 MPa) and cold pressure (3.5 MPa) is shown in Fig. 4. These SiC/SiC composites showed a dense morphology with less pores and cracks in intra-fiber bundles, when the low pressure impregnation and the cold pressing were successively induced for the preparation of fiber preform. The density of composites was 2.9 mg/m^3, which was at a similar level to that by the introduction of high pressure impregnation for the Hi-Nicalon fiber reinforced SiC/SiC composite (See Table 1)). As shown in Fig. 4(b), the matrix slurry was sufficiently impregnated into intra-fiber bundles and then transformed to dense SiC matrix with some pores. It can

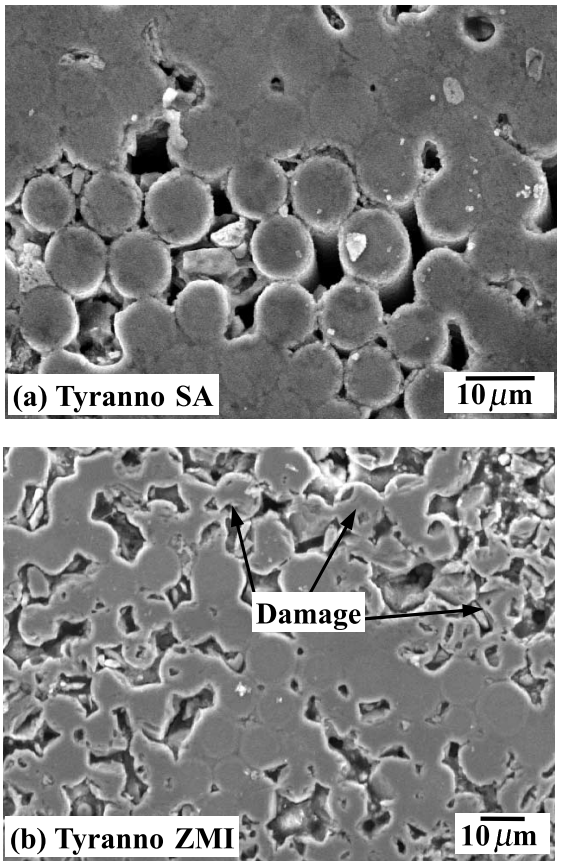


Fig. 3. SEM micrographs on fiber bundles of SiC/SiC composites prepared by the low pressure impregnation of 0.9 MPa.

also be seen from Fig. 4(c) that the cold pressure of 3.5 MPa has no effect on the damage of Tyranno SA fiber under the fabrication process of fiber preform. Especially, it must be noted that Tyranno SA fibers without interfacial coating layer represent no detectable damage under the infiltration of molten silicon, due to its excellent crystallization. However, the SiC matrix with the compositional fluctuation of the silicon and the carbon still remained in intra-fiber bundles of SiC/SiC composites, as displayed in the EDS analysis results (a and b) of Table 3. That is to say, a large amount of silicon rich phases was created in intra-fiber bundles.

Fig. 5 shows the matrix microstructure of inter-fiber bundles for Tyranno SA fiber reinforced SiC/SiC composites prepared by the combination process of low pressure impregnation of matrix slurry (0.9 MPa) and cold pressure (3.5 MPa). The composition of c and d portions in Fig. 5 was also shown in Table 3. It was found from the results of Table 3 that near stoichiometric SiC matrix with no significant compo-

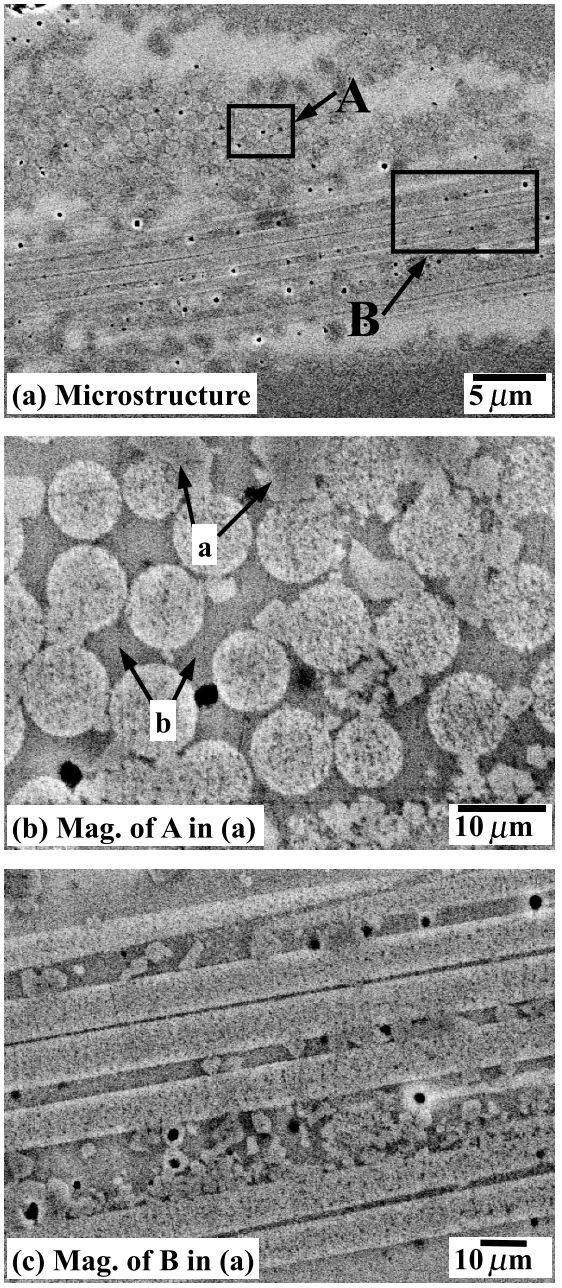


Fig. 4. Microstructure of Tyranno SA fiber reinforced SiC/SiC composites prepared by the combination process of low impregnating pressure (0.9 MPa) and cold pressure (3.5 MPa).

sitional fluctuation was created in inter-fiber bundles, in comparison to that in intra-fiber bundles (Fig. 4(b)). Therefore, in order to improve the microstructural characteristics of reaction sintered SiC/SiC composites, it is necessary to form the uniform microstructure of near stoichiometric SiC phases in inter-fiber bundles, through the control of fabricating routes including slurry impregnation pressure, cold pressure, starting particle size and matrix slurry preparation.

Table 3
Composition of each portion displayed in Figs. 4 and 5, as identified by the EDS quantitative analysis

	Si (at.%)	C (at.%)
a	63.2	36.3
b	47.2	52.8
c	45.6	54.4
d	45.0	55.0

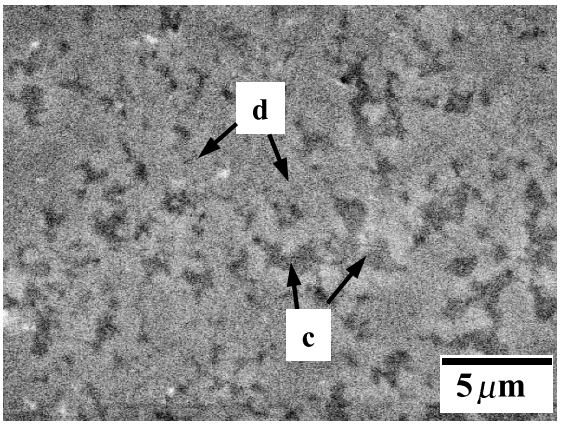


Fig. 5. Matrix microstructure in inter-fiber bundle in Tyranno SA fiber reinforced SiC/SiC composites.

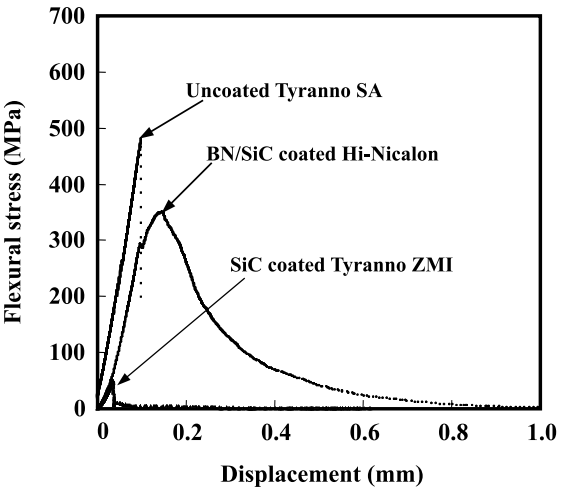


Fig. 6. Fracture behaviors of SiC/SiC composites reinforced with BN/SiC coated Hi-Nicalon fiber, SiC coated Tyarnno ZMI fiber and uncoated Tyarnno SA fiber.

3.2. Fracture properties of SiC/SiC composites

Fig. 6 represents the fracture behaviors of SiC/SiC composites reinforced with BN/SiC coated Hi-Nicalon fiber, SiC coated Tyarnno ZMI fiber and uncoated Tyarnno SA fiber. SiC/SiC composites reinforced with BN/SiC coated Hi-Nicalon fiber and SiC coated Tyarnno ZMI fiber represented noncatastrophical behavior, a stable crack propagation beyond the maximum load, whereas the uncoated Tyranno SA fiber reinfored SiC/SiC composite exhibited a typical brittle fracture behavior. This is probably related to the variation of the crack propagation path associated with interfacial delamination, fiber pull-out and fiber fracture. The mechanical properties of SiC/SiC composites fabricated with different reinforcing fibers are shown in Table 4. The uncoated Tyranno SA fiber reinforced SiC/SiC composite seems to maintain its strength after the infiltration of molten silicon. The average flexural strength and the average elastic modulus of uncoated Tyranno SA fiber reinfored SiC/SiC composites represented about 497.7 MPa and about 318.4 GPa, respectively, which were superior to those reinforced by BN/SiC coated Hi-Nicalon fiber and SiC coated Tyarnno ZMI fiber. The dramatic deterioration in strength properties of Tyarnno ZMI fiber reinforced SiC/SiC composites appears to be attributed to the damage of fibers by the molten silicon, since the SiC coating is not enough to protect the fiber.

Fig. 7 shows the fracture profiles of SiC/SiC composites fabricated with different reinforcing fibers. The BN/SiC coated Hi-Nicalon fiber reinforced SiC/SiC composites dominantly represented pull-out of fibers and extensive interfacial delamination, which promoted noncatastrophical fracture behavior. On the other hand, the uncoated Tyranno SA fiber reinforced SiC/SiC composites exhibited typical fracture profiles without the evidence of fiber pull-out and interfacial delamination. The damage of Tyranno SA fibers by the molten silicon was also not observed in the fracture profile. However, the surface of Tyranno ZMI fibers was fairly damaged by the molten silicon. Such a fiber damage is considered as a main factor to reduce the mechanical properties of Tyranno ZMI fiber reinforced SiC/SiC

Table 4
Mechanical properties of SiC/SiC composites fabricated with different reinforcing fibers

Reinforcing material	Flexural strength (MPa)	Elastic modulus (GPa)
SiC/BN-coated Hi-Nicalon	330.5	247.0
SiC-coated Tyranno ZMI	68.9	71.9
Uncoated Tyranno SA	497.7	318.4

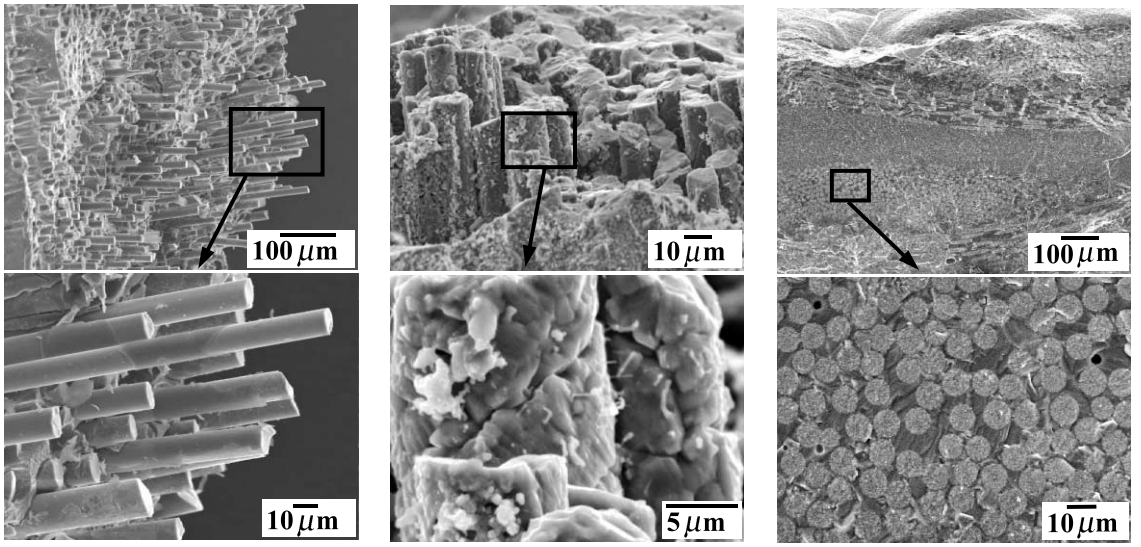


Fig. 7. Fracture profiles of SiC/SiC composites reinforced with BN/SiC coated Hi-Nicalon fiber, SiC coated Tyarnno ZMI fiber and uncoated Tyarnno SA fiber.

composites. In addition, it can be recognized that the Tyranno SA fiber is a new reinforcing material capable of applying to the reaction sintering process, without any kind of interfacial barriers such as SiC, BN and SiC/BN. However, a weak interphase between Tyranno SA fiber and SiC matrix, which promotes fiber pull-out and interfacial delamination, will be necessary to improve the fracture toughness of Tyranno SA fiber reinforced SiC/SiC composites.

4. Conclusions

1. The reaction sintered SiC/SiC composite with a density of 2.9 mg/m^3 was fabricated by the combination of low pressure impregnation and cold pressure.
2. The matrix of inter-fiber bundles represented near stoichiometric SiC phase free from unreacted carbon and silicon domains, whereas the matrix of intra-fiber bundles still exhibited significant compositional fluctuation.
3. The BN/SiC coated Hi-Nicalon fiber reinforced SiC/SiC composite represented a noncatastrophical failure behavior, which resulted from a large amount of fiber pull-outs and the extensive interfacial delamination. The average flexural strength and the average elastic modulus were about 330 MPa and about 250 GPa, respectively.
4. The average flexural strength and the average elastic modulus of uncoated Tyranno SA fiber reinforced SiC/SiC composites measured to be about 500 MPa and 320 GPa, respectively, which were superior to those of reinforced by BN/SiC coated Hi-Nicalon fiber.
5. The Tyranno SA fiber can be selected as the new reinforcing material for the reaction sintering process, since it exhibited no apparent microstructural change or no severe strength degradation after the infiltration of molten silicon. However, an appropriate interfacial coating is essential for the improvement of fracture toughness.

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