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Optimizing the fabrication process for superior mechanical properties in the FCVI SiC matrix/stoichiometric SiC fiber composite system

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Abstract

The optimization of the fabrication of SiC composites with stoichiometric SiC fibers (Hi-Nicalon Type S and Tyranno SA) was carried out by the forced thermal-gradient chemical vapor infiltration (FCVI) process. These SiC/SiC composites had a low porosity (11%) with uniform pore distribution and uniform thickness of carbon interphase between advanced SiC fibers and SiC matrix. The tensile strength was slightly increased with the thickness of the carbon interphase in the range of 75–300 nm. The effectiveness of the carbon interphase for the excellent mechanical properties was confirmed by scanning electron microscopy observation.

1. Introduction

The continuous-fiber ceramic-matrix composites have the potential for excellent high-temperature mechanical properties with non-catastrophic failure. The continuous SiC-fiber reinforced SiC-matrix (SiC/SiC) composites are one of the candidate materials for fusion structural applications due to their excellent high-temperature mechanical properties and their low induced radioactivity after neutron irradiation [1–4]. Among the various fabrication processes, the forced flow thermal-gradient chemical vapor infiltration (FCVI) is one of the best techniques for the fabrication of SiC/SiC because of the high purity and the minimized damage of fiber during the composite fabrication [5]. Recently, stoichiometric SiC fibers have been produced including Hi-Nicalon Type S [6] and Tyranno SA [7], which possess superior mechanical and thermal properties as well as superior performance under neutron irradiation compared with their SiC-based predecessors. Because the properties of these advanced fibers, e.g. thermal conductivity, waviness, tensile modulus and fiber diameter, are very different from their predecessors, the optimization of the fabrication process of matrix and interphase is now being focused on. This study has also included general process optimization of properties through the uniformity, the densification and the thickness stability of interphase.

We adopted two kinds of advanced SiC fabrics as a preform in this study: 2D-plain weave of Tyranno SA and Hi-Nicalon Type S. The boron nitride interphase has been applied for high temperature application, while it is undesirable for fusion applications because nitrogen transmutes into ^{14}C that has a very long half-life of the beta emitter by fusion neutrons, and also boron simultaneously produces helium and enhances radiation damage through recoil interaction. Therefore carbon, porous-SiC and multilayer-carbon/SiC interphase are being studied for fusion applications [8]. We selected the

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carbon interphase in this study with the thickness ranging from 75 to 300 nm. The room temperature tensile properties of composites were evaluated. The observation of optical and scanning electron microscopy (SEM) were also carried out.

2. Experimental procedure

We adopted two kinds of advanced SiC fabric as a preform: 2D-plain weave of Tyranno SA (Ube Industries, Ube, Japan) and Hi-Nicalon Type S (Nippon Carbon Co., Ltd., Tokyo, Japan). The precursor for carbon deposition was 99% purity propylene (C_3H_6, Matheson, Morrow, GA, USA). The technical grade methyltrichlorosilane (MTS, CH_3SiCl_3, Gelest Inc., Tullytown, PA, USA) was also used for SiC infiltration.

The SiC fabric layers with a fabric layer orientation of (−30°/0°/30°) were restrained in a graphite fixture. The fiber volume fraction was about 35 vol.%. The fiber preform was 75 mm in diameter and 12.5 mm thick. The carbon interphase coating on the fibers was deposited at 1100 °C and at 5 Pa with flow rates of 50 cm^3/min C_3H_6 and 1000 cm^3/min Ar. After the interphase layer was deposited, the preforms were infiltrated at 1100–1200 °C under atmospheric pressure with a typical MTS flow rate of 0.5 g/min carried by 750 cm^3/min of H_2. The back pressure was monitored and the FCVI process was automatically finished after the back pressure reached 6.9×10^4 Pa. The infiltration conditions are shown in Table 1.

To investigate the distribution of the porosity and the carbon interphase thickness, the plate was cut into nine sections as shown in Fig. 1. The density of each section was calculated from the dimensions and the mass of the plate to evaluate the porosity distribution in the composite. The microstructure of the composites was observed by optical microscopy and SEM.

Tensile tests were carried out at room temperature with a cross-head speed of 0.5 mm/min and a gauge-size ($l \times w \times t$) $15 \times 3 \times 2.3$ mm^3. The strain of the specimen was measured with bonded strain gauges. Three-point bending test were also carried out at room temperature with a cross-head speed of 0.5 mm/min and a span-length of 18 mm, using the test specimen bar of ($l \times w \times t$) $25 \times 4 \times 2.3$ mm^3.

3. Results and discussion

Fig. 1 shows the distribution of the thickness of the carbon interphase between SiC fiber and SiC matrix in specimens 2 and 5 measured from cross-section SEM images. In specimen 5, we found that the lower position

Table 1
Fabrication parameters of FCVI process

Specimen	Fiber	H_2 gas rate (dm^3/min)	MTS rate (g/min)	Temperature (°C)	Run time (h)
1	Hi-Nicalon Type S	0.75	0.5 (21.5 h) 0.33 (3.5 h)	1200	25
2	Hi-Nicalon Type S	0.75	0.5	1200	31
3	Hi-Nicalon Type S	0.75	0.5 (26 h) 0.33 (4.5 h)	1100	30.5
4	Tyranno SA	0.35	0.17	1200	66
5	Tyranno SA	0.75	0.5	1200	50
6	Tyranno SA	0.75 (16) 0.35 (6)	0.5 (16 h) 0.17 (6 h)	1200	22

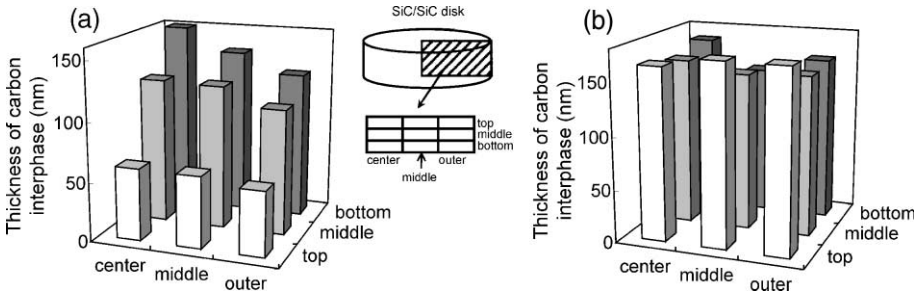

Fig. 1. Distribution of thickness of carbon interface. (a) Specimen 5 and (b) specimen 2.

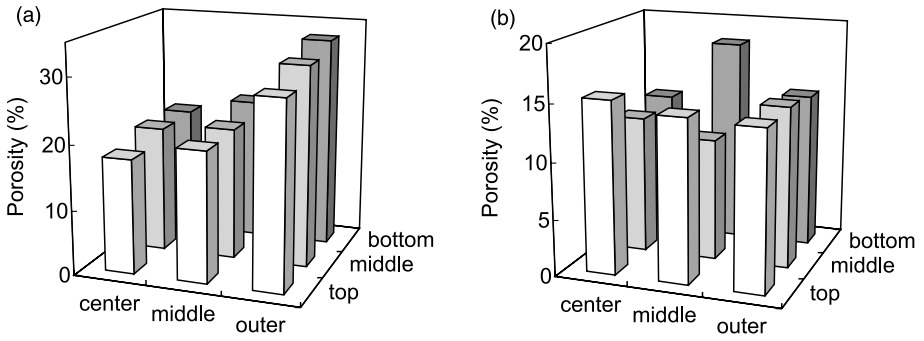

Fig. 2. Distribution of porosity. (a) Specimen 2 and (b) specimen 3.

in the composite had the thicker carbon interphase: the average thickness of carbon interphase at the bottom is about 145 nm whereas about 60 nm on top. This tendency was attributed to a concentration gradient in the C_3H_6 gas. Since the material gas traveled from the bottom to the top surface of the specimen, the thickness of the specimen was so large that the concentration of C_3H_6 was decreased due to its consumption at the lower part of the specimen. To mitigate this problem the preform was flipped midway through the interphase infiltration. The distribution of the carbon interphase thickness was remarkably improved and we obtained the specimens with near uniform through-thickness carbon interphase thickness (see specimen 2 in Fig. 1(b)).

Fig. 2 shows the distribution of the porosity in specimens 2 and 3. The porosity in specimen 2 was relatively large (24%) and we found that the lower and outer positions in the composite had the higher porosity. This tendency was improved by decreasing the MTS and H_2 gases flow rates at the latter part of the FCVI process. The porosity decreased from 24% to 17% and a much better uniform porosity in the composites was obtained. Because the termination of the FCVI process was controlled by the back-pressure that was decreased with decreasing the gas flow rate, the FCVI process was extended by the decrease in the flow rate. The characterization of the specimen is shown in Table 2. Fig. 3 shows the average porosity as a function of the fiber

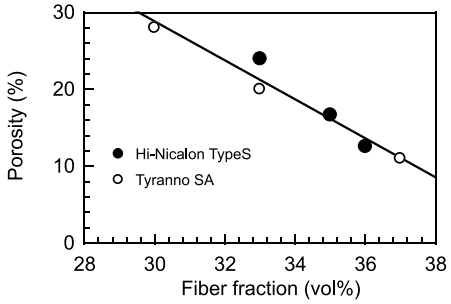

Fig. 3. Porosity of SiC/SiC fabricated by FCVI process as a function of fiber volume fraction.

volume fraction which is very effective in decreasing the porosity. The average porosity decreased to 11% by increasing the fiber volume fraction to 37 vol.%, but seemed to be independent of fiber type and infiltration time. Since the mean space between bundles with higher fiber volume fractions is smaller than those with lower fiber volume fractions, the closed porosity at higher fiber volume fraction is smaller than that of lower fiber volume fraction. Even in the specimen that had a smallest porosity (11%), a high amount of large inter-bundle pores and small pores around the fibers were observed by optical microscopy and SEM.

Typical stress–strain curves during the tensile test are shown in Fig. 4 and the average tensile and bending

Table 2
Characterization of SiC/SiC composites fabricated by FCVI process

Specimen	Fiber volume fraction (vol.%)	Carbon interphase thickness (nm)	Density (g/cm^3)	Porosity (%)	Average tensile strength (MPa)	Average bending strength (MPa)
1	36	75	2.70	12.6	143	–
2	33	150	2.39	24	145	303
3	35	300	2.58	16.7	152	–
4	33	75	2.54	20	93	–
5	37	150	2.76	11	107	453
6	30	300	2.28	28	110	–

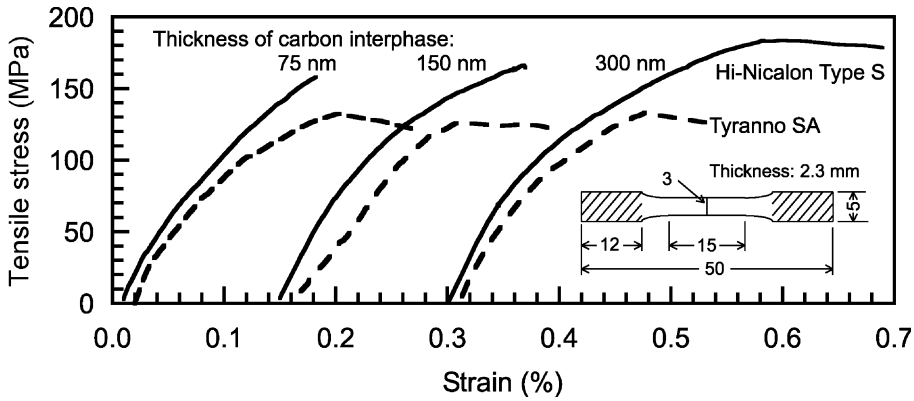

Fig. 4. Stress–strain relationship during the tensile test on SiC/SiC composites. Solid lines indicate the composites with Hi-Nicalon Type S and broken lines indicated those with Tyranno SA.

strengths are summarized in Table 2. In the tensile test, each specimen exhibited a non-linear stress–strain behavior with non-catastrophic failure behavior. The average tensile strength of specimen 2 and 5 were about 143 and 95 MPa, respectively, in contrast with the bending strength of these specimens (303 and 453 MPa, respectively). Although the tensile strength was rather small, the bending strength was reasonable compared to that of typical composites with conventional SiC fiber [8,9]. One of the reasons of this low tensile strength is due to the fiber fabrics orientation because the tensile strength is caused by the interaction between tensile stress and shear stress at the interphase and the fracture strength by those stresses have a strong dependence on fiber orientation: the fiber fabrics orientation in the present work was (−30°/0°/30°) while that in typical commercial SiC/SiC composites is (0°/90°). In the bending test, each specimen exhibited a non-brittle fracture behavior associated with fiber-bridging and fiber pull-out after debonding, demonstrating the effectiveness of the carbon interphase. The optimization of the interphase is one of the important factors to improve the mechanical properties of SiC/SiC composites. For the bending strength, the optimum carbon interphase thickness is in the range of 170–1000 nm [10,11]. Because the load is mainly maintained by unfractured fibers and friction

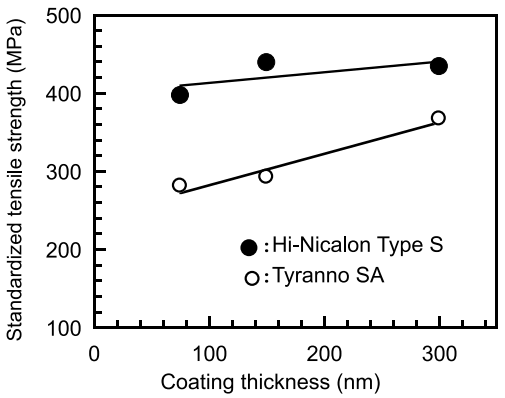

Fig. 5. Standardized tensile strength as a function of thickness of carbon interphase.

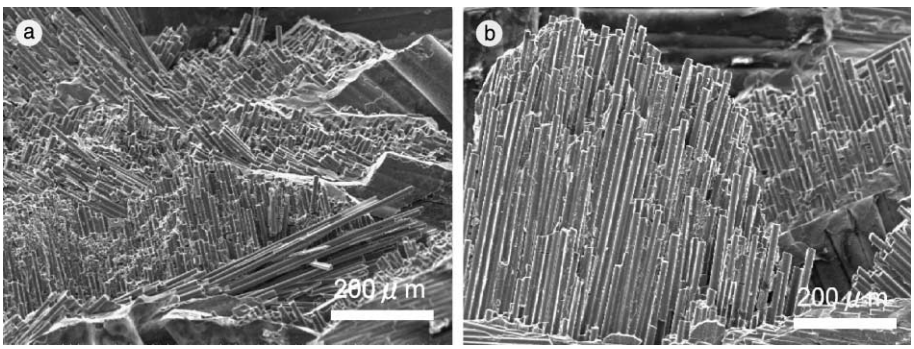

Fig. 6. Fracture surfaces of tensile tested SiC/SiC composites. (a) Specimen 5 and (b) specimen 2.

between fractured fiber and interphase above the matrix cracking stress, we evaluated the relationship between carbon interphase thickness and standardized tensile strength (tensile strength divided by the fiber volume fraction of the composite (Fig. 5)). It seems that the standardized tensile strength was slightly increased with the thickness of the carbon interphase in the range of 75–300 nm. Fig. 6 shows the tensile fracture surface of specimens 2 and 5. A large number of fibers retained at the maximum load and a high fiber strength are required for the excellent tensile strength [12]. The fiber pull-out was observed in the tensile fracture surface. In addition, the length of fiber pull-outs in the tensile specimens was almost similar. This indicated that many fibers broke at the same time at a maximum load and exhibited good mechanical properties. This behavior therefore confirmed the effectiveness of the carbon interphase and the strength retention of SiC fibers during the FCVI process.

4. Conclusion

The process optimization of FCVI-SiC based composites with advanced SiC fibers such as Hi-Nicalon Type S and Tyranno SA was carried out. The new SiC/SiC composites exhibited a significant improvement in the porosity reduction (11%) and uniform distribution of pores by decreasing the flow rate of MTS and H_2 gases at the latter part of the FCVI process. The uniform carbon interphases between the advanced SiC fibers and the FCVI-SiC matrix could be obtained by reversing the gas-flow direction mid-way through the coating process. The tensile strength was slightly increased with the thickness of the carbon interphase in the range of 75–300 nm. We confirmed the effectiveness of the carbon interphase and the strength retention of SiC fibers during the FCVI process.

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