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Effect of heat treatment on the mechanical properties of PIP–SiC/SiC composites fabricated with a consolidation process

Shuang Zhao*, Xingui Zhou, Jinshan Yu

Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, PR China

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Abstract

Continuous SiC fiber reinforced SiC matrix composites (SiC/SiC) have been considered as candidates for heat resistant and nuclear materials. Three-dimensional (3D) SiC/SiC composites were fabricated by the polymer impregnation and pyrolysis (PIP) method with a consolidation process, mechanical properties of the composites were found to be significantly improved by the consolidation process. The SiC/SiC composites were then heat treated at 1400 °C, 1600 °C and 1800 °C in an inert atmosphere for 1 h, respectively. The effect of heat treatment temperature on the mechanical properties of the composites was investigated, the mechanical properties of the SiC/SiC composites were improved after heat treatment at 1400 °C, and conversely decreased with increased heat treatment temperature. Furthermore, the effect of heat treatment duration on the properties of the SiC/SiC composites was studied, the composites exhibited excellent thermal stability after heat treatment at 1400 °C within 3 h.

Keywords: B. Composites; C. Mechanical properties; D. SiC; Heat treatment; Polymer impregnation and pyrolysis

1. Introduction

Continuous SiC fiber reinforced SiC matrix composites (SiC/SiC) have been studied and developed for high temperature applications such as gas turbines and aerospace propulsion systems, as well as nuclear applications such as fusion and advanced fission reactors. Reasons for employing SiC/SiC composites are their excellent characteristics such as high operating temperature, chemical stability and low radio-activation [1–11].

Polymer impregnation and pyrolysis (PIP) is a conventional technique for fabricating SiC matrix composites with complex shapes, microstructural control and low cost. The disadvantages of PIP are in the low density, low purity and amorphous structure of the resultant matrix. It has been suggested that enhanced matrix crystallization and improved stoichiometry could be attained by elevating the pyrolysis temperature [12–15]. PIP–SiC/SiC composites pyrolyzed at 1750–1800 °C were fabricated by Katoh et al. [16], and their outstanding radiation stability was demonstrated. Nannetti et al. [17] prepared PIP–SiC/SiC composites with a final high-temperature pyrolysis treatment at 1700 °C, after which the thermal diffusivity of the composites increased noticeably. The author [18] has previously shown that the mechanical properties of PIP–SiC/SiC composites, pyrolyzed at 1100 °C, were significantly improved after heat treatment at 1400 °C.

In this study, 3D SiC/SiC composites were fabricated by the PIP method with a consolidation process, the density and the mechanical properties of the composites were characterized. Heat treatments at temperatures of 1400 °C, 1600 °C and 1800 °C were carried out and the effect of heat treatment on the mechanical properties of the SiC/SiC composites was investigated.

2. Experimental procedure

2.1. Fabrication of the composites

KD-I SiC fiber bundles (provided by National University of Defense Technology, NUDT, China) were used as the reinforcement. General characteristics of the fiber are listed in Table 1 [19]. PCS with the molecular weight of ~1300 and the soften point of ~180 °C (NUDT, China) was used as the precursor of SiC

*Corresponding author. Tel.: +86 15274943949; fax: +86 73184573165.
E-mail address: zhsh6007@126.com (S. Zhao).

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matrix. Xylene (Analytical Reagent) was used as a solvent for PCS.

Four steps were taken to fabricate SiC/SiC composites by PIP method

1) SiC fiber bundles were braided into 3D (3-dimensional, 4-directional) fabrics with a fiber volume fraction of about 40%. The fabrics were then coated with a 0.5 μm thick pyrocarbon (PyC) layer to provide an interface to control bonding between the matrix and fibers.
2) The coated fabrics were impregnated with PCS solution by a vacuum infiltration method. Then the fabrics were taken out and dried.
3) The fabrics were stacked into an especial mold and heated up to 180 °C. A pressure-assisted consolidation process was applied with a unidirectional pressure of 9 MPa for 1 h.
4) The consolidated bodies were pyrolyzed at 1100 °C in an inert Argon atmosphere. The impregnation and pyrolysis processes were repeated more than 10 cycles without pressurization until weight increase of the composites was less than 1%.

Heat treatments in an inert Argon atmosphere were carried out in a Hi-Multi 5000 sinter stove.

2.2. Characterization Evaluation

The bulk density and open porosity of the composite were determined by Archimedes′ principle, using kerosene oil as an immersion medium. Flexural strength and modulus of the composites were characterized by the three-point bend test according to the general guidelines of the Chinese Standard GBT 6569–2006. The dimensions of a test sample were 4 × 4 × 65 mm^3, the span length and the cross head speed were 50 mm and 0.5 mm/min, respectively. Fracture toughness was measured by single edge notch beam (SENB) method according to GBT 23806–2009, with the specimen size of 4 × 8 × 65 mm^3, the notch length of 4 mm, the crosshead speed of 0.05 mm/min and the support span of 40 mm. Five specimens were tested to estimate the scatter in the mechanical tests. Morphology of the specimens was analyzed by scanning electron microscopy (SEM, Hitachi S-4800).

Table 1
Typical characteristics of the KD-I SiC fiber.

Trademark	KD-I
Diameter (μm)	13.3
Density (g/cm^3)	2.45
Tensile strength (GPa)	1.8–2.2
Elastic modulus (GPa)	150–200

3. Results and discussion

3.1. Effect of the consolidation process on the properties of the SiC/SiC composites

The density, porosity and mechanical properties of the SiC/SiC composites with and without a consolidation process application are reported in Table 2. The properties of the SiC/SiC composites fabricated without the consolidation process are cited from author's previous work [18]. The two types of composites were fabricated with the same fiber, interface and precursor, so their only difference was a consolidation process, which was applied during the preparation procedures. The results indicated that the consolidation process was very beneficial. The density of the composites was increased from 2.01 g/cm^3 to 2.18 g/cm^3. The mechanical properties were also improved, the flexural strength in particular increased significantly from 230.2 MPa to 521.2 MPa.

The mechanical properties the SiC/SiC composites were improved through the consolidation process for two reasons: First, the pores in the composites were eliminated to a high degree, which was beneficial for reducing crack initiation probability. Second, the thickness of the composites was reduced (from 6 mm to 4 mm) so the fiber volume fraction increased. The cross sections of the specimens are shown in Fig. 1. A number of pores can be seen between the fiber bundles of the SiC/SiC composites fabricated without the consolidation process (Fig. 1a). These interlaminar pores formed defects and acted as crack initiation sites. Conversely, the SiC/SiC composites fabricated with the consolidation process had much fewer pores (Fig. 1b). As a result, the mechanical properties of the composites were improved because of the reduced porosity and the higher fiber volume fraction.

3.2. Effect of heat treatment temperature on the properties of the SiC/SiC composites

The SiC/SiC composites fabricated with the consolidation process were heat treated at 1400 °C, 1600 °C and 1800 °C in an inert atmosphere for 1 h. The weight loss, density and open

Table 2
Effect of consolidation process on the properties of the SiC/SiC composites.

Property	Without consolidation process	With consolidation process
Density (g/cm^3)	2.01	2.18
Open porosity (%)	10.1	7.4
Flexural strength (MPa)	230.2	521.2
Flexural modulus (GPa)	74.2	89.5
Fracture toughness (MPa $m^{1/2}$)	15.6	22.9

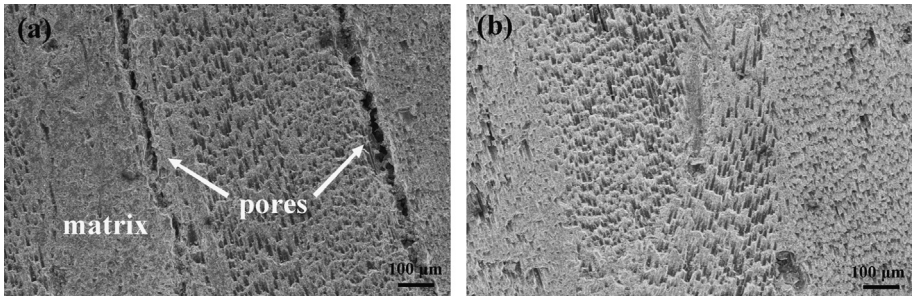

Fig. 1. Cross sections of the SiC/SiC composites fabricated (a) without and (b) with the consolidation process.

Table 3
Effect of heat treatment temperature on the weight loss, density and porosity of the SiC/SiC composites.

Heat treatment temperature (°C)	Weight loss (%)	Density (g/cm^3)	Open porosity (%)
14007.42.18	0.8	2.16	8.4
1600	14.0	1.86	29.1
1800	35.3	1.55	46.8

Table 4
Effect of heat treatment temperature on the mechanical properties of the SiC/SiC composites.

Heat treatment temperature (°C)	Flexural strength (MPa)	Flexural modulus (GPa)	Fracture toughness (MPa m$^{1/2}$)
–	521.2	89.5	22.9
1400	576.7	98.3	25.7
1600	123.5	46.1	9.7
1800	43.1	33.7	1.7

porosity of the SiC/SiC composites with different heat treatment temperatures are reported in Table 3. There was no notable weight loss after heat treatment at 1400 °C, and the changes of density and open porosity were also minimal. However, the weight loss of the SiC/SiC composites after heat treatment at 1600 °C was up to 14.0%, and the density also greatly decreased to 1.86 g/cm^3 while the porosity increased to 29.1%. After heat treatment at 1800 °C, the weight loss was 35.3% and the density was only 1.55 g/cm^3.

The notable changes of the SiC/SiC composites resulted from the decomposition reactions and carbothermic reductions when the temperature exceeded 1500 °C. The KD-I SiC fibers and the SiC matrix of the composites were made from PCS polymer at intermediate temperatures (1300 °C for the fibers and 1100 °C for the matrix), and both consist of crystalline β-SiC, amorphous Si–C–O and free carbon phases. The following reactions took place when the temperature exceeded 1500 °C and caused the weight loss and the density changes [20,21]:

$$SiC_{1+x} \rightarrow SiC + xC \quad (1)$$

$$SiC_{1+x} + \text{trace}O \rightarrow SiC + CO \quad (2)$$

$$SiC_xO_y \rightarrow SiC + SiO(g) \quad (3)$$

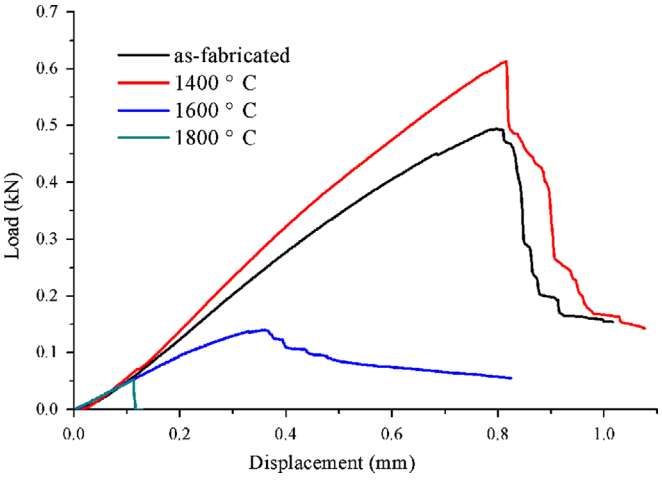

Fig. 2. Load-displacement curves of the SiC/SiC composites with different heat treatment temperatures.

$$SiC_xO_y \rightarrow SiC + CO \quad (4)$$

The mechanical properties of the SiC/SiC composites at different heat treatment temperatures are reported in Table 4. The SiC/SiC composites fabricated with the consolidation process exhibited excellent flexural strength and fracture toughness. After heat treatment at 1400 °C, the mechanical properties of the

composites were improved, the flexural strength was 576.7 MPa and the fracture toughness was 25.7 MPa $m^{1/2}$. However, the mechanical properties of the composites were degraded drastically after heat treatment at 1600 °C and 1800 °C.

Fracture behavior (load–displacement curves) of the SiC/SiC composites are shown in Fig. 2. SEM micrographs of the fracture surfaces can be seen in Fig. 3. The SiC/SiC composites in the as-fabricated and 1400 °C and 1600 °C heat treatment conditions exhibited non-brittle fracture behavior, where extended regions could be seen after the initial failure in Fig. 2, and a large amount of long pulled-out fibers were seen on the fracture surfaces of the composites (Fig. 3a–c), the pull-out lengths exceeding 200 μm. After heat treatment at 1800 °C, the composites became brittle, resulting in the sudden loss of load bearing capacity and a flat fracture surface with no crack deflection or arrest at the fibers (Fig. 3d).

The fibers and the interfaces of the SiC/SiC composites were analyzed by SEM micrographs of higher magnification. As shown in Fig. 4a and b, debonding and pullout of the fibers were seen on the fracture surfaces of the composites in the as-fabricated and 1400 °C heat treatment condition, rupture and peeling of the PyC interface layer were also observable. These were typical of crack arrest, deflecting and branching behavior, which led to pseudo-ductile fracture mode of the composites. The improvement

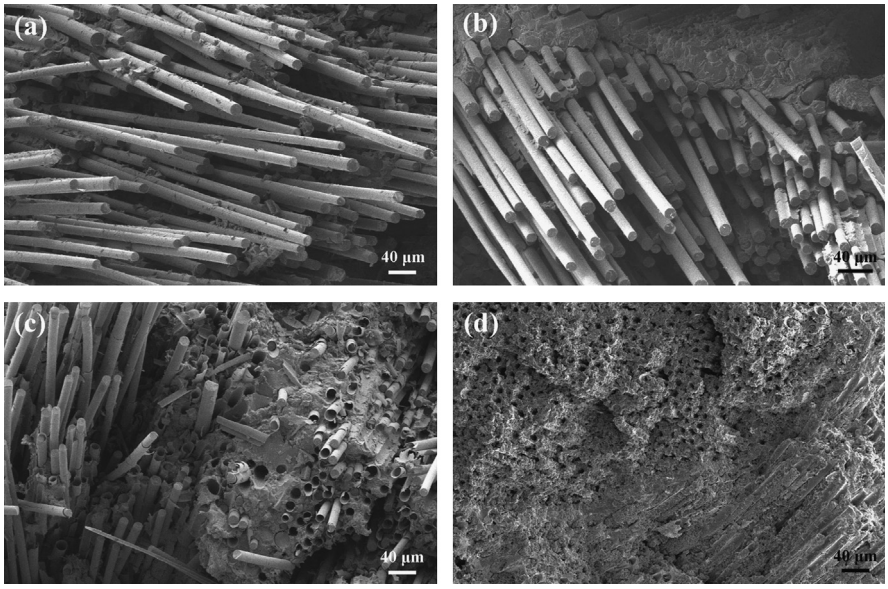

Fig. 3. Fracture surfaces of the SiC/SiC composites with different heat treatment temperatures, (a) as-fabricated, (b) 1400 °C, (c) 1600 °C and (d) 1800 °C.

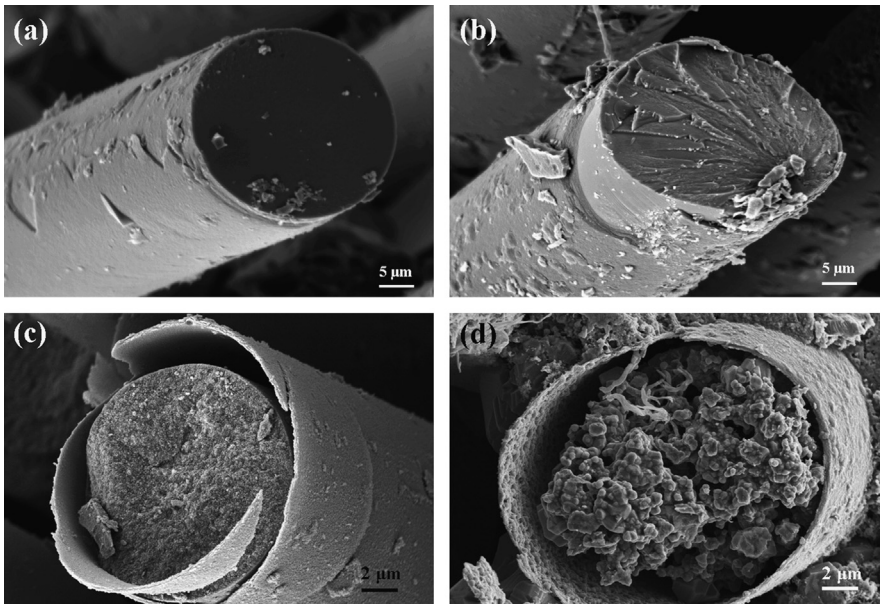

Fig. 4. Morphology of the fibers and interfaces of the SiC/SiC composites with different heat treatment temperatures, (a) as-fabricated, (b) 1400 °C, (c) 1600 °C and (d) 1800 °C.

of mechanical properties of the composite after heat treatment at 1400 °C could be attributed to the undegraded fibers, the crystalline matrix, and the well functioned interface. After heat treatment at 1600 °C, pulled-out fibers still could be observed (Fig. 4c). However, the fibers were severely damaged, and the interface was weaker so load transfer capacity of the matrix was reduced, resulting in the degradation of the mechanical properties. After heat treatment at 1800 °C, the fibers became porous and failed catastrophically and the composites showed brittle behavior.

3.3. Effect of heat treatment duration on the properties of the SiC/SiC composites

In order to further study the effect of heat treatment on the properties of the SiC/SiC composites with the consolidation process, the composite specimens were heat treated at 1400 °C in an inert atmosphere for different durations ranging from 0.5 h to 3 h.

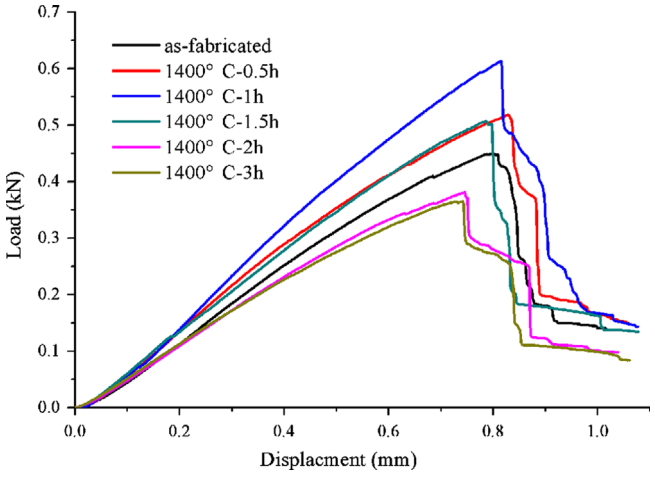

Fig. 5. Load–displacement curves of the SiC/SiC composites with different heat treatment durations.

The weight loss, density and open porosity of the SiC/SiC composites after heat treatments with different durations are listed in Table 5. The weight loss remained less than 1% within 2 h, meanwhile the density and porosity changed slightly. After 3 h, the weight loss was only 1.2%, and the density was 2.07 g/cm^3, indicating that the SiC/SiC composites were relatively stable at 1400 °C.

The mechanical properties of the SiC/SiC composites after heat treatment with different durations are shown in Table 6. The flexural strength and fracture toughness of the composites increased in heat treatment procedures with duration up to one hour. Higher heat treatment durations had a detrimental effect on the mechanical properties of the composites. However, the flexural strength and fracture toughness of the composites after heat treatment at 1400 °C for 3 h were up to 462.7 MPa and 15.1 MPa m$^{1/2}$, indicating excellent thermal stability of the SiC/SiC composites.

The load–displacement curves recorded during the three-point bending tests are shown in Fig. 5. Specimens exhibited a similar pseudo-ductile fracture behavior. SEM micrographs of the fracture surfaces of the composites are shown in Fig. 6, a large quantity of long pulled-out fibers could be seen, indicative of arrest, deflection and branching of the cracks, which led to the pseudo-ductile fracture mode of the composites.

4. Conclusions

3D SiC/SiC composites were fabricated by PIP method through a consolidation process. The mechanical properties of the composites was significantly improved by the consolidation process due to the elimination of pores and increase of fiber volume fraction by the pressurization.

Table 5
Effect of heat treatment duration on the weight loss, density and porosity of the SiC/SiC composites.

Heat treatment time (h)	Weight loss (%)	Density (g/cm^3)	Open porosity (%)
–	–	2.18	7.4
0.5	0.6	2.16	7.8
1	0.8	2.16	8.4
1.5	0.7	2.13	8.6
2	0.9	2.11	8.7
3	1.2	2.07	9.1

Table 6
Effect of heat treatment duration on the mechanical properties of the SiC/SiC composites.

Heat treatment time (h)	Flexural strength (MPa)	Flexural modulus (GPa)	Fracture toughness (MPa m$^{1/2}$)
–	521.2	89.5	22.9
0.5	561.3	90.3	23.1
1	576.7	98.3	25.7
1.5	540.9	90.3	21.2
2	482.7	80.5	18.7
3	462.7	84.5	15.1

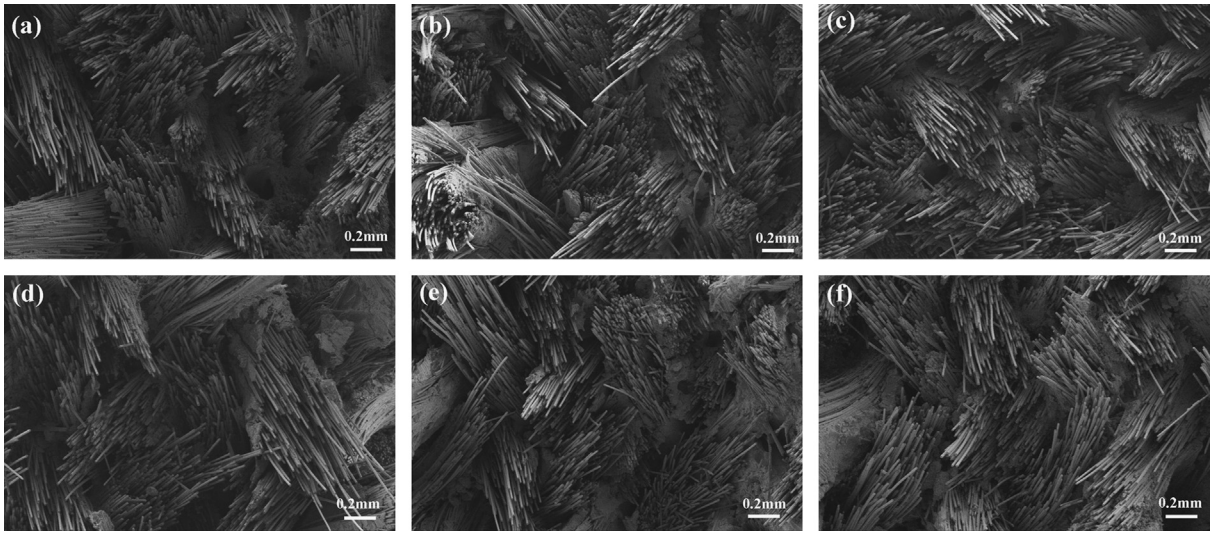

Fig. 6. Fracture surfaces of the SiC/SiC composites with different heat treatment durations, (a) as-fabricated, (b) 0.5 h, (c) 1 h, (d) 1.5 h, (e) 2 h and (f) 3 h.

The SiC/SiC composites were heat treated at 1400 °C, 1600 °C and 1800 °C in an inert Argon atmosphere for one hour. The density of the composites decreased noticeably when the heat treatment temperature exceeded 1600 °C. The mechanical properties of the SiC/SiC composites were improved after heat treatment at 1400 °C mainly because of the crystallization of the matrix, and then decreased at higher heat treatment temperature because of the severe damage to the fibers.

The effect of heat treatment duration on the properties of the SiC/SiC composites at 1400 °C for 0.5–3 h was studied. The composites exhibited excellent thermal stability, as well as pseudo-ductile fracture behavior.

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