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Short communication

Properties of C_f/SiC composites modified by a boron- containing phase

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Abstract

C_f/SiC composites added with a self-healing boron-containing phase (C_f/SiC-B) was fabricated by slurry infiltration. The slurry was mixed with a boron-containing precursor and boron powders. By vacuum impregnation process, it can be well permeated into the fiber preforms and filled within the fiber intra-bundle zones. After heat treatment, the slurry was converted into B_4C and SiC phases. It was found that the addition of the boron-containing phase led to a significant increase in the SiC matrix crystallinity. Compared with pyrolytic carbon (PyC) interphase, non-catastrophic failure was observed for the C_f/SiC-B composites with SiC interphase. Experimental results show that the oxidation resistance of C_f/SiC-B composites was improved, and that boron oxides formed during C_f/SiC-B composites' exposure in air at 700 °C.

Keywords: C_f/SiC composites; Boron-containing phase; C. Mechanical properties; Oxidation resistance

1. Introduction

Because of their attractive properties, such as low density, high strength and toughness, carbon fiber reinforced silicon carbide matrix (C_f/SiC) composites are considered to be one kind of potential materials for structural applications at high temperature [1–3]. However, attributed to both the drawback of fabrication processes and the coefficient of thermal expansion (CTE) mismatch, there inevitably exist large amounts of pores and cracks in the composites, either of which provide easy accesses for the oxidizing substance to the carbon phase when placed in oxidizing environments. As a consequence, the oxidation of the carbon phase in C_f/SiC composites may happen at as low as 500 °C, leading to the severe degradation of mechanical properties. According to previous researches on the oxidation behavior of C_f/SiC composites, huge weight loss of the specimens happened in the temperature range between 700 and 1200 °C [4]. Introducing boron-containing phases, such as B [5], B_4C [6] and SiB_4 [7] can be an efficient way to protect carbon phases in C_f/SiC composites from oxidation, because they can form boric oxide sealants that will fill matrix cracks above 500 °C, leading to the elimination or decrease of pathways for oxygen diffusion. This mechanism is called "seal-healing" oxidation resistance. Chemical vapor infiltration (CVI) [7,8] and liquid polymer infiltration (LPI) [9] are the major two ways utilized to introduce boron-containing phases into C_f/SiC composites. Compared to CVI process, LPI method has shorter processing period and lower cost [10].

In this paper, 3D needled C_f/SiC composites with a boron-containing phase (C_f/SiC-B) were fabricated by slurry infiltration using boron containing precursor and boron powders as boron sources. The microstructure of the boron containing phase in the composites were investigated,

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and the mechanical properties and oxidation resistance of C_f/SiC-B were also studied.

2. Experimental

3D needled carbon fiber (T700) fabric with fiber volume fraction of about 30% was used in the preparation of the fiber preforms. PyC and SiC interphases were deposited on fiber surface by chemical vapor infiltration (CVI). The source gas for PyC was ethene and those for SiC were methylchlorosilane (MTS) and H_2, the molar ratio of H_2 to MTS was 10. The deposition conditions for both PyC interphase and SiC interphase were 3 KPa and 1000 °C. A commercially available boron powder with an average particles size of 1 μm was employed for slurry infiltration. The slurry was prepared by dispersing a boron containing precursor, polycarbosilane (PCS) and boron powders in divinylbenzene (DVB) solvent. A homogeneously dispersed slurry was obtained after ball milling for about 24 h. Then the slurry was utilized to impregnate aforementioned fiber preforms, then cross-linked in an oven at 120 °C for 6 h, and finally pyrolyzed at 900 °C in Ar atmosphere. Subsequently, the pyrolyzed composites underwent 10 PIP cycles using PCS solution (without filler) to reach a relatively high density. The specimens were heat-treated at 1500 °C for 1 h in Ar atmosphere during the PIP cycles.

Phase compositions of the composites were determined via X-ray diffraction (XRD). The topography of polished cross-sections and fracture surfaces of the composites were analyzed by scanning electron microscopy (SEM). Microstructures of the composites were examined by transmission electron microscopy (TEM). Selected area electron diffraction (SAED) diagrams were recorded for the matrix of the same samples.

In order to carry out strength measurement, the specimens were cut and ground into 5 mm × 4 mm × 60 mm rectangular bars. Three-point bending strength was tested at room temperature on an Instron 5566 test machine at a crosshead speed of 0.5 mm/min and at a span of 50 mm. The specimens for oxidation tests were cut into a size of 4 × 5 × 20 mm, and their weight changes were calculated by analytic balance.

3. Results and discussion

3.1. *Composition and microstructure of C_f/SiC-B composites*

In the XRD spectra (Fig. 1), the observed major peaks at 35.8°, 60.0° and 72.2° associate with (1 1 1), (2 2 0), (3 1 1) planes of β-SiC crystals. Meanwhile, the broaden peak at 26.6° can be attributed to the (0 0 2) reflection of graphitic carbon, which results from carbon fibers; and, B_4C exists in the sample of C_f/SiC-B, determined by the peak at 37.89°, corresponding to the (0 2 1) plane of B_4C. Compared with C_f/SiC samples, β-SiC crystalline grains grow bigger after adding the boron-containing phase (Fig. 1). The average crystal sizes of the composites can be calculated from the XRD data using Scherrer's equation:

$$L = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where L is the averaged crystal size, K the Scherrer constant, which is chosen as 0.89 by assuming the particle to be spherical, λ the wavelength of X-ray (0.15406 nm), β the full width at half maximum (FWHM) of the reflection in radians, and θ the diffraction angle. The results show that the size of β-SiC (1 1 1) nanocrystal in C_f/SiC is 2.6 nm, in C_f/SiC-B is 28.8 nm. These indicate that the presence of boron in the matrix promotes the crystallization of β-SiC to form much larger nanocrystals in the corresponding ceramic phase. The result is consistent with those of previous study [11,12].

It is generally accepted that, for ceramics without addition of low melting sintering additives, the solid-state diffusion may greatly contribute to the densification and the grain growth. However, the self-diffusion coefficients of substance having strong covalent bonds like Si–C, C–C is rather small. In addition, the atomic diffusion of Si may be further hindered by the uniform distribution of turbostratic C in the pyrolyzed SiC [13]. The SiC matrix derived from pyrolyzed PCS is usually carbon rich [14], i.e., with the carbon in excess intimately mixed with small nanocrystalline SiC on atomic scale. However, the boron precursor and boron powders are susceptible to oxygen and H_2O [15], leading to the formation of B_2O_3 or HBO_3 that existed in composites before heat-treatment, which can be evidently observed from FIRT results. Those boron oxides appear around the SiC grain boundary and lead to the growth of SiC grains after heat-treatment at 1500 °C, which mean that they may act as low melting sintering additives.

Fig. 2 shows the TEM microstructure of the C_f/SiC-B composites. It can be seen that, SiC grains with a mean size of more than 20 nm has a relatively uniform distribution in

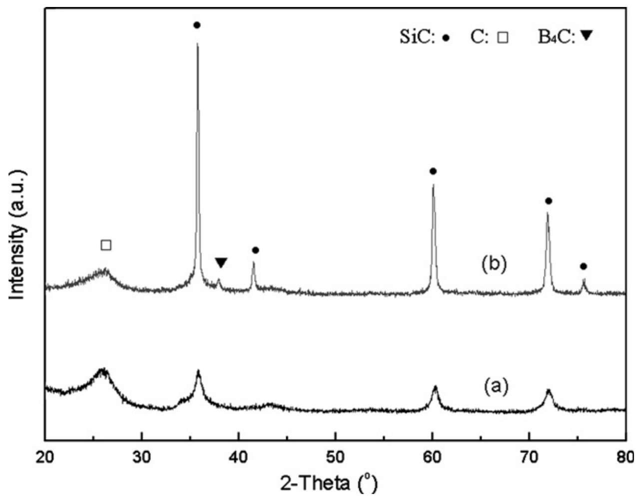

Fig. 1. X-ray diffraction patterns of samples heat-treated at different temperatures 1500 °C, (a) C_f/SiC and (b) C_f/SiC-B.

the matrix of fiber intra-bundle areas. In the SAED pattern, there are β-SiC and B_4C evidently agreed with the result of XRD.

Although the microstructure of SiC–B_4C matrix and their interfacial region require further clarification, it is clear that the boron-containing phase can improve the crystallinity of pyrolyzed SiC; and, the improved crystallinity of SiC will benefit oxidation resistance and mechanical properties.

Fig. 3 shows the polished cross-section morphology of 3D needled C_f/SiC-B composites. It can be found that intra-bundle fibers were embedded by the boron containing matrix (Fig. 3(a)). Attributed to its good wetting ability to carbon fiber, the boron-containing slurry can be permeated into the fiber intra-bundle zones, then converted into a boron-containing phase to wrap carbon fibers by pyrolysis. Based on Hagen–Poiseuille equation [16], the capillary pressure relates to the mean diameter of effective pores. Due to smaller pore diameter of fiber intra-bundle, the capillary pressure of fiber intra-bundle areas is higher than that of inter-bundle areas, which results in the reserve of slurry just in the fiber intra-bundle areas. According to EDS elements analysis in Fig. 3(b), the main elements of the boron containing matrix within intra-bundle zones were B, C and Si. Therefore, boron-containing phase can be simply introduced by slurry infiltration into carbon fiber intra-bundle zones.

3.2. Mechanical properties of C_f/SiC-B composites

The fracture surfaces of C_f/SiC-B composites with SiC or PyC interphase after three-point bending test were shown in Fig. 4, respectively. It is found that the sample with PyC interphase presented almost no fiber pull-out (Fig. 4(a)). In contrast, long fiber pull-out was observed in the sample with SiC interphase (Fig. 4(c)), indicating that a large amount of energy had been consumed during the failure process [17]. Furthermore, SiC interphase can prevent the chemical reaction between carbon fibers and the boron containing matrix, thus ensuring the happening of crack deflection and fiber debond. In the inter-bundle zones, the matrix close to larger pores was broken because of stress concentration as shown both in Fig. 4(b, c), which was probably rooted in the residual thermal stress induced by the escape of gaseous products during heat-treatment or the coefficient of thermal expansion mismatch between two matrices. These will affect the mechanical properties of C_f/SiC-B composites.

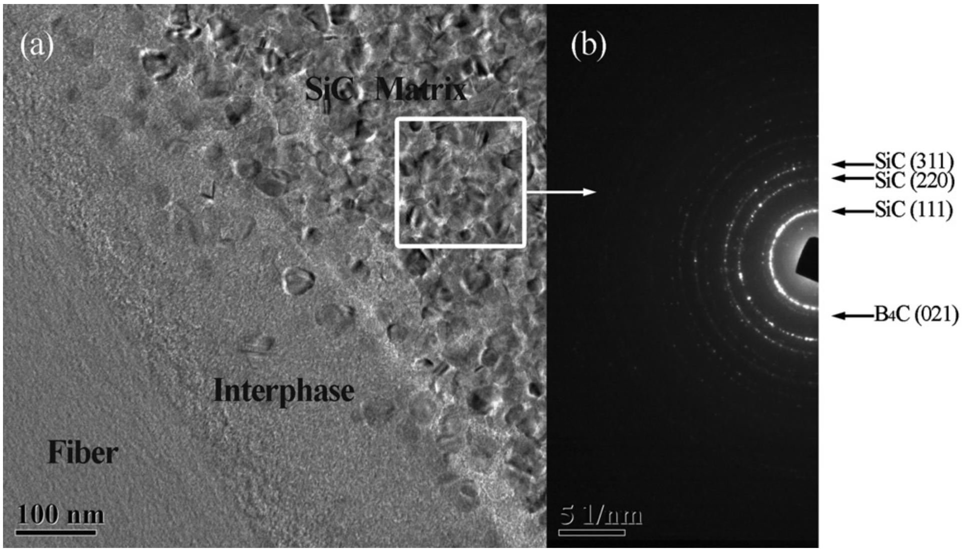

Fig. 2. TEM images of the different regions in C_f/SiC-B.

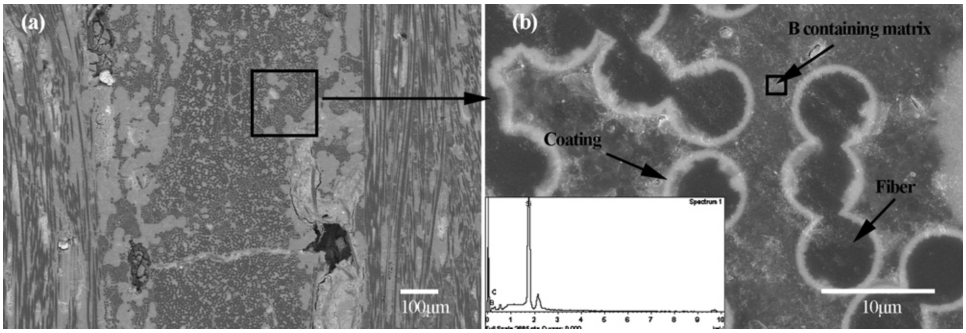

Fig. 3. SEM images of the polished cross sections of C_f/SiC-B (a) low resolution, (b) high resolution and with EDS.

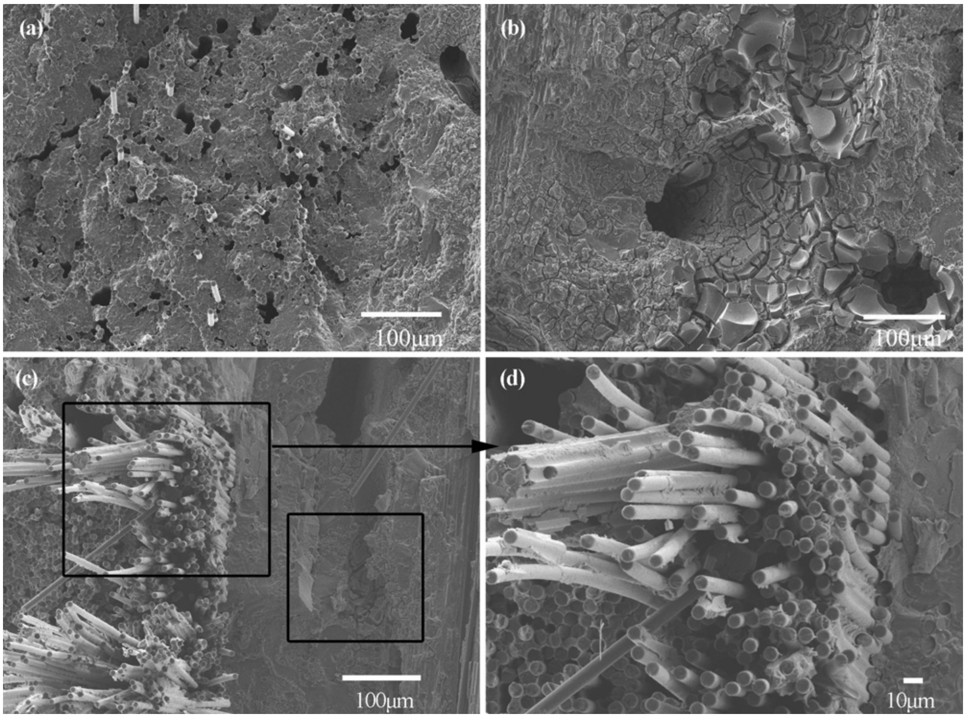

Fig. 4. SEM images of the fracture surfaces of C_f/SiC-B with PyC (a, b) and SiC interphase (c, d).

Fig. 5 shows the load–displacement curves of samples with PyC or SiC interphase. The sample with SiC interphase exhibits typical non-catastrophic failure behavior with multiple fracture steps on the stress–displacement curves, and possesses a much higher flexural strength (144 ± 8 MPa) than the sample with PyC interphase (34 ± 9 MPa). Due to the sensitivity of boron-containing precursor to oxygen and water, boron oxides may be formed during fabrication. The existing boron oxides did some damage to PyC interphase without the protection of SiC interphase and led to a stronger bonding strength between fiber reinforcements and matrix. A rather strong fiber and matrix interaction restricted the propagation of matrix cracks at the fiber/matrix interface. Therefore, it may account for the lower bending stress and no pulled-out fibers in composite without SiC interphase. As a result, the flexural behavior of C_f/SiC-B composites in this study was improved by the tailored fiber-matrix interface.

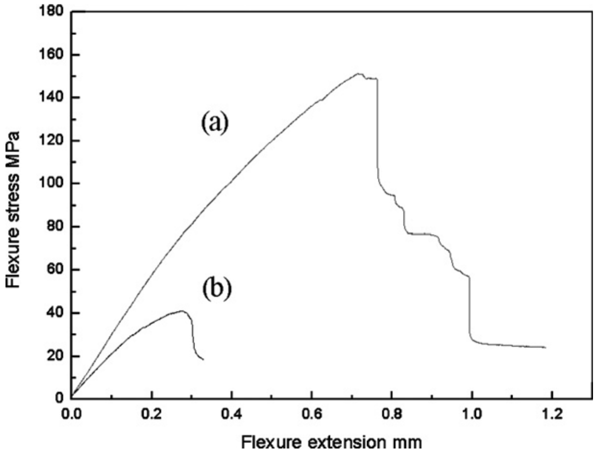

Fig. 5. Typical load–displacement curves of C_f/SiC-B with PyC (a) and SiC interphase (b).

3.3. Oxidation resistance of C_f/SiC-B composites

The cross-section morphologies of both C_f/SiC and C_f/SiC-B composites that were oxidized at 700 °C for 20 h in air were shown in Fig. 6. The oxidation of carbon fibers takes place simultaneously and quickly in the whole C_f/SiC composites; and, because of diffusion of oxygen into fiber intra-bundle areas via matrix microcracks, there are almost no carbon fiber presented in Fig. 6(a, c). The weight loss of the C_f/SiC composite sample was 30%, which indicates that the C_f/SiC composites were almost invalidated. However, only a few of fibers close to the edge of the C_f/SiC-B sample were burnt out after being oxidized at 700 °C for 20 h, as shown in Fig. 6(b), with 4.5% weight loss. A glassy material can be found around the holes in the fiber intra-bundle zones (Fig. 6(d)). Therefore, it indicates that oxygen still can diffuses through matrix microcracks in C_f/SiC-B composites, and few parts of fibers were burnt out. Due to low oxidation rate of B_4C at 700 °C [18], there were only thin and patchy sealant layers coated on the surface of pores and matrix cracks. This layer cannot completely fill matrix cracks, resulting in a few weight loss in the early time. However, after the formation of self-healing phase, the diffusion of oxygen was hindered.

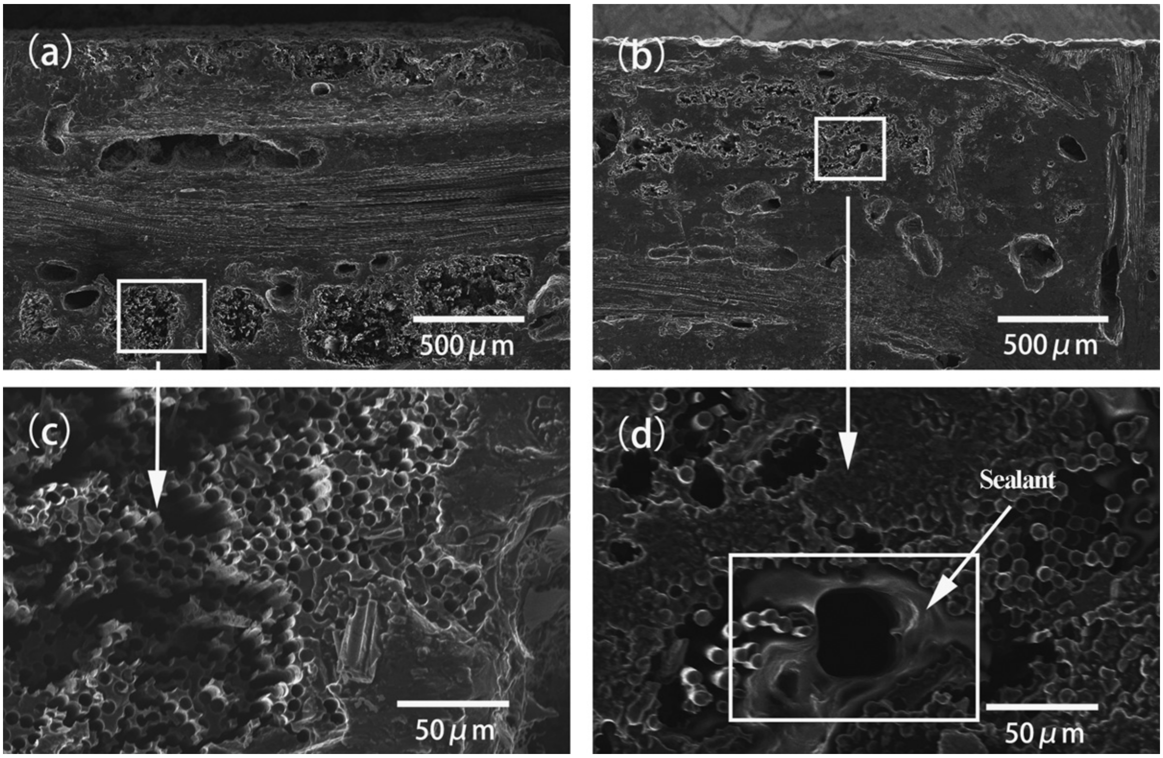

Fig. 6. The cross-section morphologies of the C_f/SiC (a, c) and C_f/SiC-B (b, d) composites after oxidation at 700 °C for 20 h.

4. Conclusion

A novel C_f/SiC with boron-containing phase was modified by the infiltration of slurry, which was obtained by mixing a boron precursor, polycarbosilane (PCS) and boron powders in DVB solvent. The phase composition of boron containing phase contained nanocrystalline SiC and B_4C formed after heat treatment at 1500 °C in argon. The boron element in C_f/SiC composites facilitates the growth of β-SiC nanocrystals. In the C_f/SiC-B composites, carbon fibers are embedded by the boron-containing matrix, due to the good penetrability of the slurry. Chemical reactions happened between the boron-containing matrix and PyC interphase, resulting in the degradation of mechanical properties. Protected by SiC interphase, carbon fibers could be pulled out, and the composites exhibited typical non-catastrophic failure behavior. Acting as an anti-oxidation protective layer, the boron-containing matrix could hinder the inward diffusion of oxygen, and the oxidation of carbon fiber took place only for the direct exposure of fibers at initial time. After being exposed in air at 700 °C for 20 h, the weight loss of C_f/SiC-B composites was 4.5%. Although this boron containing matrix can be easily obtained by slurry infiltration, the microstructure control of it remains to be studied, and the oxidation resistance of C_f/SiC-B composites is looking forward to be further improved.

Acknowledgements

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