

## Effects of dip-coated BN interphase on mechanical properties of SiC<sub>f</sub>/SiC composites prepared by CVI process

Yang ZHOU, Wan-cheng ZHOU, Fa LUO, Dong-mei ZHU

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

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**Abstract:** BN interphase was successfully synthesized on SiC fiber fabrics by dip-coating process using boric acid and urea as precursors under N<sub>2</sub> atmosphere. The morphology of BN interphase was observed by SEM, and the structure was characterized by XRD and FT-IR spectra. The SiC<sub>f</sub>/SiC composites with dip-coated BN interphase were fabricated by chemical vapor infiltration (CVI) process, and the effects of BN interphase on the mechanical properties of composites were investigated. The results show that the SiC fibers are fully covered by BN interphase with smooth surface and turbostratic structure (*t*-BN), and the thickness is about 0.4 μm. The flexural strengths of SiC<sub>f</sub>/SiC composites with and without BN interphase are about 180 and 95 MPa, respectively. Compared with the as-received SiC<sub>f</sub>/SiC composites, the composites with BN interphase exhibit an obvious toughened fracture behavior. From the microstructural analysis, it can be confirmed that the BN interphase plays a key part in protecting the fibers from chemical attack during matrix infiltration and weakening interfacial bonding, which can improve the mechanical properties of SiC<sub>f</sub>/SiC composites remarkably.

**Key words:** SiC<sub>f</sub>/SiC composites; BN interphase; dip-coating; CVI; mechanical properties

### 1 Introduction

SiC<sub>f</sub>/SiC composites exhibit a combination of attractive physical-chemical properties such as high strength, stability at elevated temperature, high corrosion resistance, low thermal expansion and low activation characteristics. Because of these superior properties, SiC<sub>f</sub>/SiC composites have been widely studied and used for in nuclear fusion reactors and high temperature aerospace [1–5]. However, owing to the inherent brittle failure behavior of SiC matrix, the fracture toughness of the composites is not high.

For fiber-reinforced ceramic composites, the concept of weak interphase was promoted to increase the fracture toughness [6–9]. The weak fiber/matrix interphase has significant influence on the fracture behavior and mechanical properties of ceramic matrix composites (CMCs). This can attribute to the occurrence of various well identified energy-dissipating mechanisms, i.e., crack deflection, fiber-matrix debonding, fiber sliding and fiber pullout [10,11].

Pyrocarbon (PyC) was once the most commonly used weak interphase in the past. However, these composites often experienced severe embrittlement when they were tested at high temperature in oxidizing atmospheres [4,12]. So far, materials with a layered crystal structure such as hexagonal boron nitride (*h*-BN) have received much attention for use in SiC-based composites systems, since they have improved oxidation resistance compared to PyC. Hexagonal boron nitride (*h*-BN) is a promising interphase material for SiC<sub>f</sub>/SiC composites, which is attributed to its unique properties such as high thermal conductivity, high temperature stability, high thermal shock resistance, and self-lubricating [12–14]. A barrier against oxidation by formation of B<sub>2</sub>O<sub>3</sub> provides a better protection for fibers with the consequence to maintain the integrity of the composites for a longer duration under loading [12].

Up to now, the BN interphase is elaborated most by chemical vapor deposition (CVD) from BCl<sub>3</sub>/BF<sub>3</sub>–NH<sub>3</sub>–H<sub>2</sub>/N<sub>2</sub>/Ar mixtures at a moderate temperature. However, it is associated with several disadvantages, including hazardous precursors and byproduct,

degradation of fiber caused by reaction with HF or HCl, high cost and scale-up problems [15,16]. Dip-coating method has received considerable attention in recent years, which is attributed to its advantages compared to the chemical vapor deposition (CVD). The dip coating process, which is simple and practical, is used to synthesize coatings on nanowires, carbon nanotubes and powders [17].

In this work, BN interphase of SiC<sub>f</sub>/SiC composites was fabricated by dip-coating process in boric acid and urea solutions followed by nitridation at nitrogen atmosphere. The morphology and structure of BN interphase were characterized. The effects of BN interphase on the mechanical properties of SiC<sub>f</sub>/SiC composites were investigated.

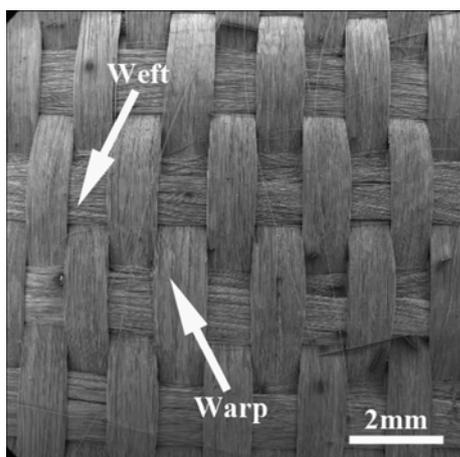
## 2 Experimental

### 2.1 Materials

The SiC fiber fabrics were provided by Su Zhou SaiLiFei (SLF) Ceramic Fiber Co., LTD, China. The parameters of SiC fiber are listed in Table 1. The fabric structure is 2.5D shallow bending joint, as shown in Fig. 1. The fiber volume fraction of the fabrics is 45%.

**Table 1** Parameters of SiC fiber

Parameter	Value
Diameter/ $\mu\text{m}$	11–14
Density/( $\text{g}\cdot\text{cm}^{-3}$ )	~2.5
Mole ratio of C/Si	~1.16
Number of filaments/(fil·yarn <sup>-1</sup> )	~600
Tensile strength/MPa	1500–1800
Chemical compositions of surface layer	Si–C–O

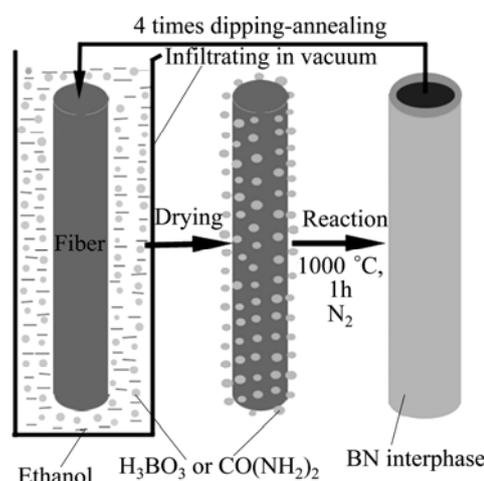


**Fig. 1** SEM image of SiC fiber fabrics

### 2.2 Preparation of BN interphase

Before dip-coating, the SiC fiber fabrics were degreased in vacuum at 600 °C for 30 min, then washed with acetone and ethanol, respectively. In order to prepare the precursor solution, boric acid and urea (mass

ratio of 1:9) were dissolved in 300 mL distilled water under stirring until it became transparent. Prior to CVI, the BN interphase was deposited on SiC fiber by dip-coating process. The degreased SiC fiber fabrics were dipped in the precursor solution and ultrasonically vibrated for 15 min, then infiltrated in vacuum for 10 min. After infiltration, the fabrics were dried in air for 12 h. Finally, the coated fiber fabrics were placed in a furnace for nitridation at 1000 °C at a rate of 10 °C/min under nitrogen atmosphere, and four times of dipping-annealing treatment were applied. The schematic diagram for the preparation of BN interphase is shown in Fig. 2.



**Fig. 2** Schematic diagram for preparation of BN interphase on SiC fiber by dip-coating process

### 2.3 Characterization

The surface morphology of BN interphase was examined by scanning electron microscopy (SEM, TESCAN, VEGA 3). The phase structure and the chemical bonds of the nitridation production from BN precursor were characterized by X-ray diffraction (X<sup>''</sup> Pert PRO MPD, PANalytical, Almelo, the Netherlands) and Fourier transform infrared spectroscopy (Nicolet Nexus 670), respectively. The chemical compositions of BN interphase were also characterized by SEM equipped with EDS.

In order to investigate the influence of BN interphase on the mechanical properties of SiC<sub>f</sub>/SiC composites, the composites without and with BN interphase were prepared by CVI. SiC matrix was obtained by thermally cracking MTS (methyl tri-chlorosilane, CH<sub>3</sub>SiCl<sub>3</sub>) in the presence of argon as carrier and diluents gas with mass flow rate of 1:15 at 2–3 kPa and 1000 °C. The infiltration time is 16 h.

Flexural test specimens measuring 40 mm in length, 4 mm in breadth, and 3 mm in thickness were prepared from composites without and with BN interphase through water jet cutting. The cut surfaces and edges of

the samples were polished to get smooth edges. Room temperature flexural strength was determined by three-point bending tests with span length of 30 mm and crosshead rate of 0.5 mm/min using the universal testing machine according to ASTM C1341 standard. Finally, the as received cross sections of composites after three-point bending tests were characterized by SEM.

### 3 Results and discussion

#### 3.1 Characterization of BN interphase

The morphologies of the as-received, degreased and coated fibers were investigated by SEM, as shown in Fig. 3. It can be seen that the surface of the as-received SiC is rough, some pimples and impurities can be found on the surface (Fig. 3(a)). In contrary, the surface of the degreased SiC fiber is very smooth (Fig. 3(b)). The surface morphology of dip-coated BN interphase is smooth and uniform, and the thickness is about 0.4  $\mu\text{m}$  and (Fig. 3(c)), the spalling of BN interphase can be found too (Fig. 3(d)). During the synthesis process, the interphase will suffer a tensile stress due to the volume contraction from the evaporation transformation of organic materials and the mismatch of thermal expansion coefficients between the interphase and the SiC fiber. Once the stress reaches a critical value, the interfacial

debonding between the interphase and fiber occurs, which is responsible to the spalling of BN interphase [18].

In order to investigate the crystallization state of the interphase, the product from boric acid and urea at nitridation temperature of 1000  $^{\circ}\text{C}$  was analyzed by XRD, as shown in Fig. 4. The XRD pattern of the product reveals three broad bands around 26 $^{\circ}$ , 42 $^{\circ}$  and 76 $^{\circ}$ , corresponding to (002), (10) bands and (110), respectively, characteristic of turbostratic BN [13,15]. The turbostratic boron nitride was applied to a three-dimensionally disordered modification of hexagonal boron nitride (*h*-BN) with only two-dimensional ordering, due to random rotation and translation of the BN hexagons in the single atom planes [13,19]. The broad bands show that the crystallization of BN is not complete.

The element contents of BN interphase coated on SiC fiber were analyzed by SEM and EDS (Fig. 5), and B and N were detected. COFER and ECONOMY [20] studied the relations between crystallization degree of BN and its sensitivity towards O<sub>2</sub> and H<sub>2</sub>O. It showed that its sensitivity towards O<sub>2</sub> and H<sub>2</sub>O decreased with increasing crystallization degree. The BN interphase, which was not well-crystallized, could absorb H<sub>2</sub>O or O<sub>2</sub> from the air, leading to the occurrence of oxygen in the coating [19].

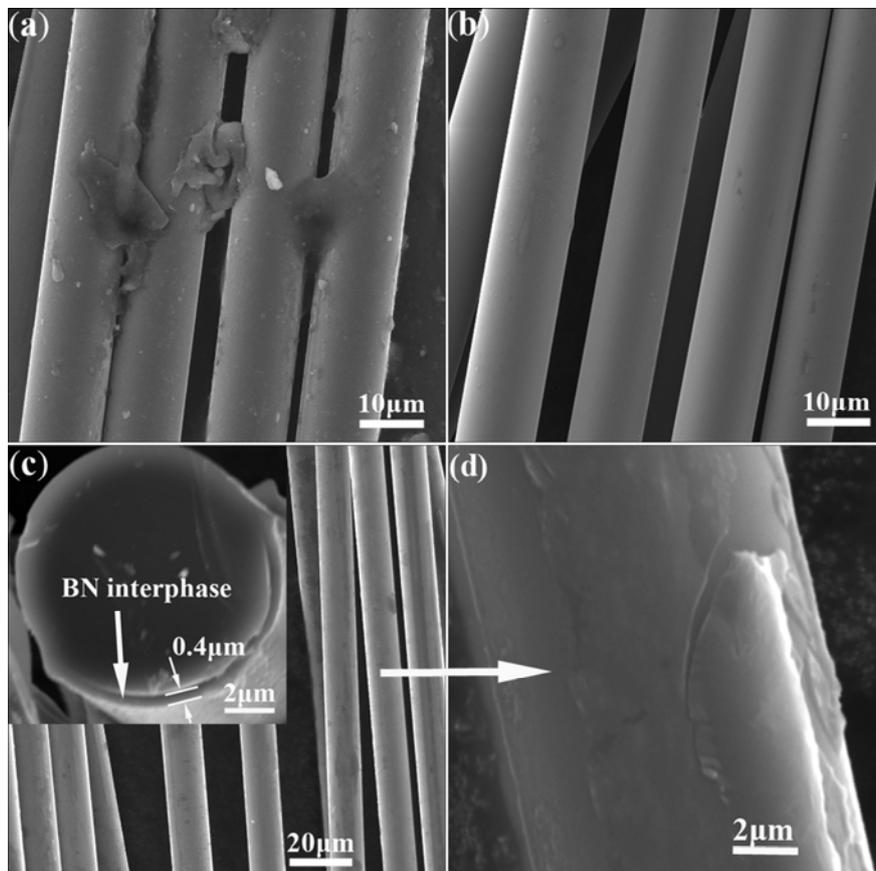


Fig. 3 SEM images of as-received SiC fiber (a), degreased SiC fiber (b) and SiC fiber with BN interphase (c), (d)

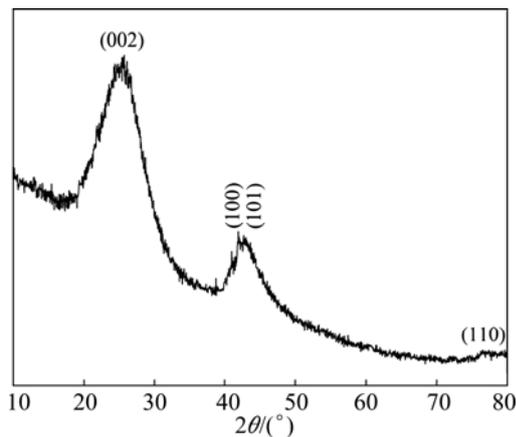


Fig. 4 XRD pattern of product from boric acid and urea at nitridation temperature of 1000 °C

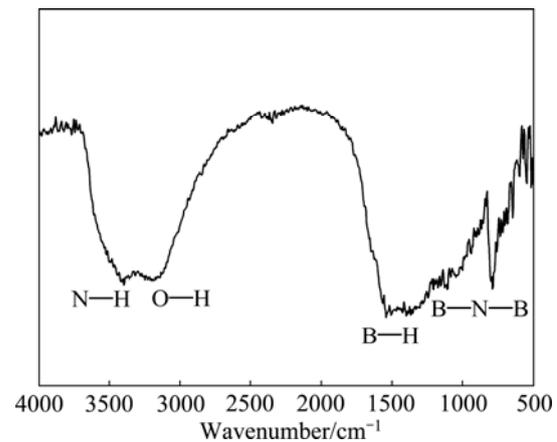


Fig. 6 FT-IR spectrum of product from boric acid and urea at nitridation temperature of 1000 °C

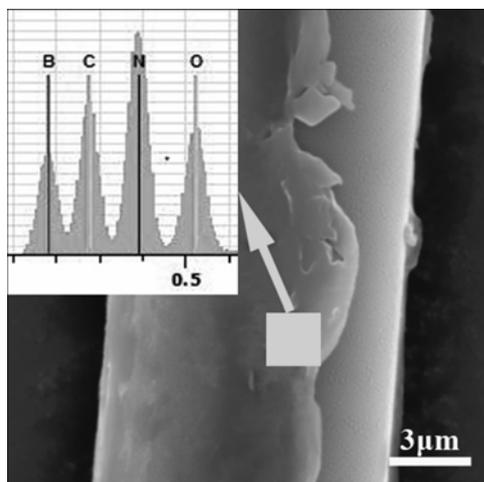


Fig. 5 EDS analysis of BN interphase

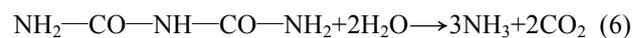
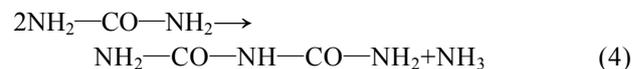
The FT-IR spectrum of the product from boric acid and urea is shown in Fig. 6. It can be found that the absorption peaks around 780 and 1380  $\text{cm}^{-1}$  are detected, which are attributed to B—N—B bending vibration and B—N stretching vibration of  $\text{sp}^2$  hybridization, respectively [15,16]. The absorption bands at 780 and 1380  $\text{cm}^{-1}$  indicate the formation of hexagonal BN (*h*-BN) and turbostratic BN with amorphous structure [16]. Since the reaction temperature is low in the present work, most of BN is amorphous [21]. Besides the absorption bands of BN, the FT-IR spectrum shows the O—H and N—H bands in the range of 2800–3600  $\text{cm}^{-1}$ , which indicates that the decomposition and reaction of the precursor are not complete [13].

According to the results above, it is confirmed that the BN interphase with turbostratic and amorphous hybrid structure deposits successfully on the SiC fiber.

### 3.2 Formation mechanism of BN

Three possible mechanisms have been reported for the synthesis of BN using boric acid and urea. The first

is a direct chemical reaction between boric acid and urea [22]. The second is that boric acid reacts initially with urea to form a polyurea-boron complex, and then heated to form the BN phase [23]. The third is that the boric acid is converted to boric anhydride ( $\text{B}_2\text{O}_3$ ) and reacts with ammonia produced by the decomposition of urea. The formation of boron nitride could be described by the main equations as follows [14,17]:



In this study, it is confirmed that the mass loss process of mixture at elevated temperature can be divided into many stages according to TGA test. So the BN formation mechanism can not be simply attributed to the direct reaction between boric acid and urea. However, the other two mechanisms, such as the formation of the polyurea-boron complex and the pyrolysis of urea to ammonia, then subsequently nitriding in a nitrogen atmosphere, would be assumed to be both involved in the BN dip-coating process [16]. Because of this melt-solidification process, the precursors mix each other well and coat uniformly on the fiber surface [14].

### 3.3 Mechanical properties of SiC<sub>f</sub>/SiC composites

Typical flexural stress/displacement curves of the two composites are shown in Fig. 7. As shown in Fig. 7(a), the composites without BN interphase show very low flexural strength (95 MPa) and fail in

catastrophic and brittle manner. For the composites with BN interphase, the curve indicates a standard toughened fracture behavior (Fig. 7(b)). When the load reaches the maximum, it will not decrease sharply, but persevere from 0.20 to 0.25 mm, then drop off gradually. The matrix is highly cracked, and relatively long pull-out lengths are observed.

The fracture surface morphologies of the SiC<sub>f</sub>/SiC composites without and with BN interphase are shown in Fig. 8. For the as-received SiC<sub>f</sub>/SiC composites, the

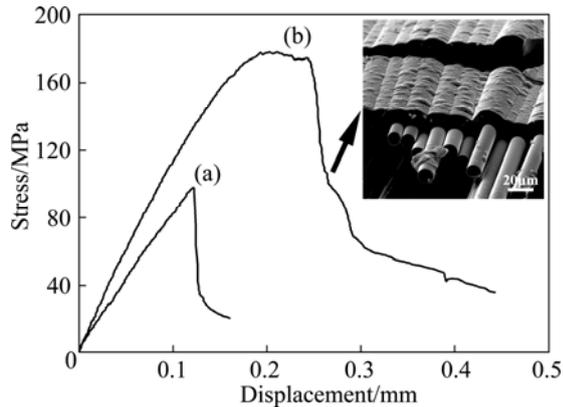


Fig. 7 Stress–displacement curves of SiC<sub>f</sub>/SiC composites without BN interphase (a) and with BN interphase (b)

fracture surface is very even, and nearly no pullout fiber can be found (Fig. 8(a)). In contrast, it is very clear from the fracture surface micrograph that the BN interphase has improved the bonding strength between the interphase and the matrix to a bond weak enough to facilitate good fiber pullout (Fig. 8(b)). The BN interphase around pullout SiC fiber is shown in Fig. 8(c), and fiber debonding and crack deflection between interphase and matrix can be found too (Fig. 8(d)).

In general, the mechanical properties of the continuous fiber reinforced ceramic matrix composites (CFRCMCs) are determined by the in situ fiber strength and interfacial characteristics [24]. For SiC fibers without BN interphase, in the process of matrix infiltration, the fibers may be damaged by corrosive gas [25]. At the same time, the interfacial bond strength between the fiber and matrix is strong due to the lack of appropriate interphase and the rough surface characteristics of as-received SiC fiber [10,15]. The strong interfacial bonding and low in situ fiber strength make the fiber reinforcing mechanisms be out of service, so a brittle fracture behavior occurs.

For the composites with BN interphase, on one hand, the coated BN interphase before matrix infiltration can reduce the damage of SiC fiber. On the other hand, the

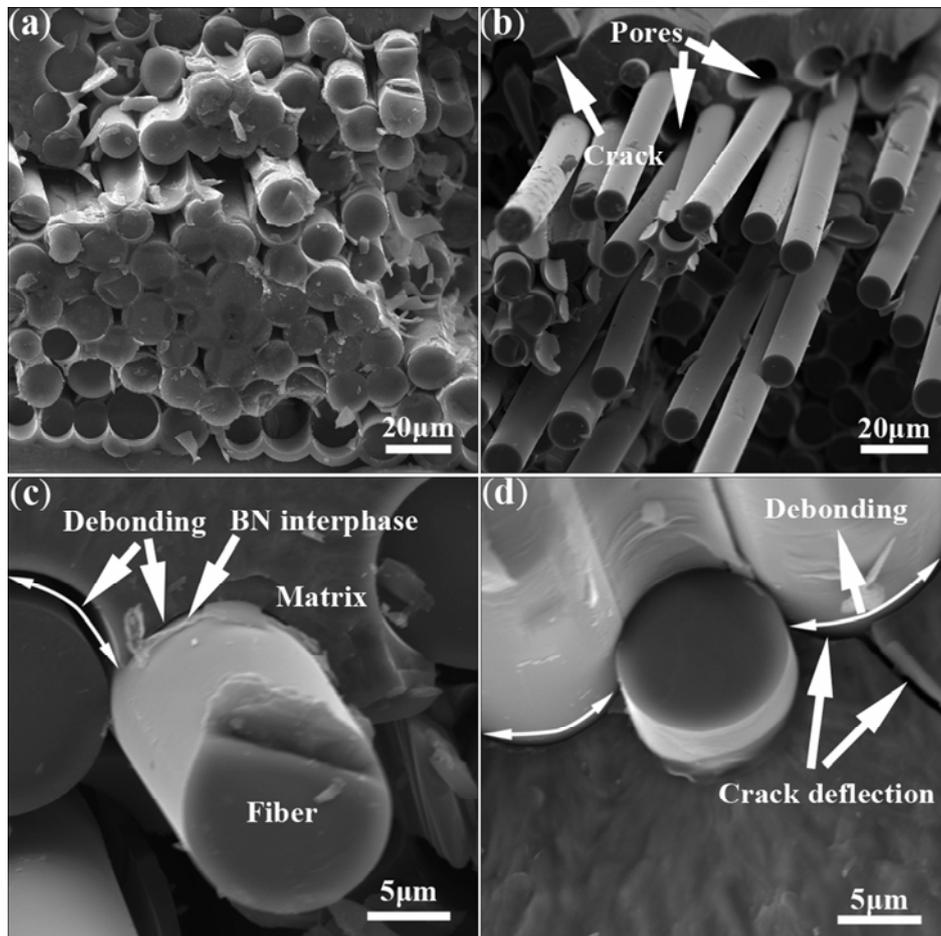


Fig. 8 SEM images of fracture morphologies of SiC<sub>f</sub>/SiC composites without BN interphase (a) and with BN interphase (b)–(d)

pulled out fiber surface looks smooth, indicating the weak interfacial bond strength between the fiber and matrix [4]. Due to the proper combination between the fiber and matrix, most matrix cracks deflect round when they meet the BN interphase during fracture process of the composites [15]. As a result, the roughing effect of fiber enhances, and the flexural strength of the SiC<sub>f</sub>/SiC composites is considerably improved (180 MPa).

## 4 Conclusions

1) The smooth and uniform BN interphase were successfully synthesized on SiC fiber by dip-coating process after four times of dipping-annealing treatment using boric acid and urea as precursors at 1000 °C in nitrogen atmosphere. The thickness of BN interphase was about 0.4 μm and the composition was turbostratic BN (*t*-BN).

2) Compared with the as-received SiC<sub>f</sub>/SiC composites, the composites with dip-coated BN interphase exhibited an obvious toughened fracture behavior, the flexural strength of which was about 2 times that of the as-received SiC<sub>f</sub>/SiC composites.

3) The interfacial bond strength between the fiber and matrix was modified to that of a weak bond by the introduction of BN interphase and facilitated the fiber debonding and other fracture processes such as crack deflection and fiber pullout in the composites, leading to better mechanical properties.

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## 浸渍-涂覆型 BN 界面相对化学气相渗透法制备 SiC<sub>f</sub>/SiC 复合材料力学性能的影响

周 洋, 周万城, 罗 发, 朱冬梅

西北工业大学 凝固技术国家重点实验室, 西安 710072

**摘 要:**以硼酸和尿素为先驱体,采用浸渍-涂覆法在氮气气氛中在 SiC 纤维表面制备 BN 界面相。利用 SEM/EDS、XRD 和 FT-IR 对 BN 界面相的形貌和结构进行表征。采用化学气相渗透法(CVI)制备 SiC<sub>f</sub>/SiC 复合材料,并研究 BN 界面相对复合材料力学性能的影响。结果表明:光滑的 BN 界面相覆盖在 SiC 纤维表面,厚度约为 0.4 μm,为紊乱层状的 *t*-BN 物相。有无 BN 界面相的复合材料弯曲强度分别为 180 和 95 MPa,并且有 BN 界面相的复合材料表现出明显的韧性断裂行为。微观结构分析表明,BN 界面相在基体渗透过程中保护纤维免受化学腐蚀,减弱纤维和基体之间的界面结合强度方面发挥重要作用,这有助于大幅度提高复合材料的力学性能。

**关键词:** SiC<sub>f</sub>/SiC 复合材料; BN 界面相; 浸渍-涂覆法; 化学气相渗透法; 力学性能

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