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Microstructure observation and analysis of 3D carbon fiber reinforced SiC-based composites fabricated through filler enhanced polymer infiltration and pyrolysis

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Abstract

3D C/SiC-BN composites were fabricated by filler enhanced polymer infiltration and pyrolysis (FE-PIP) through in situ conversion of active filler boron into h-BN in the high temperature treatment process. The bending strengths and microstructures of composites were studied here. Interphase layers deposited on the fiber surfaces can prevent the strong bonding between fiber reinforcements and composite matrix and repair the defects on the fiber surface, which can improve the bending strength and toughness of composites. The bending stress of C/SiC-BN composites without interphase layer is about 170 MPa while those of composites with PyC or PyC/SiC interphase layers are higher than 300 MPa. Some large pores were left in the interwoven zones while intra-bundle zones were relatively dense, only a small amount of micro-pores could be observed. It could also be concluded that the length of pulled-out fibers was much longer and the pulled-out fiber surface was smoother when interphase layers were deposited. Because the matrix derived from the pyrolysis of slurries adheres to the fiber bundles, some phases with layered structures could be observed in the matrix near the reinforcements. The microstructure evolution of 3D fiber reinforced ceramic matrix composites were also analyzed in this work based on the observation of both 3D C/SiC-BN composites and 3D C/SiC composites fabricated by FE-PIP, where boron and SiC particles were applied as active fillers and inert fillers respectively.

Keywords: C/SiC-BN composites; Active filler; Microstructure analysis

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1. Introduction

Due to their excellent high temperature performance, much attention was focused on the development of ceramic matrix composites consisting of SiC matrix in the past decades, such as C/SiC and SiC/SiC composites [1–3]. These CMCs have been designed for the production of structural parts that could be used at high temperatures, under load and in corrosive atmospheres, including advanced engines, gas turbine for power/steam co-generation, heat exchangers, as well as nuclear reactors of the future [1]. Chemical vapor infiltration (CVI), liquid silicon infiltration (LSI) and precursor impregnation and pyrolysis (PIP) are most frequently used for the fabrication of CMCs. PIP process is considered to be an effective manufacturing technique for preparing fiber reinforced ceramics as a result of its advantages such as low processing temperature, controllable ceramic compositions, availability of complex reinforcements and near-net shape technologies. In the PIP process, a fiber preform is impregnated with a ceramic precursor in the molten state or in solution. The precursors are then converted into ceramic phase upon pyrolysis at elevated temperatures. However, as a result of the extraordinary high

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volume shrinkage and a pronounced density increase in the polymer-ceramic conversion, there is significant volume shrinkage. The ceramic yields of most precursors are lower than 70% and the volume shrinkages accompanied in pyrolysis process are larger than 60%. Therefore, in order to achieve a high enough densification level, several impregnation/pyrolysis repetitions have to be performed, which makes the process both expensive and time-consuming. A new approach to overcome this problem is the impregnation of the fiber preforms with mixtures of organo-metallic polymers and inorganic fillers to limit excessive shrinkage in ceramic conversion process [2]. There are two kinds of fillers, namely inert fillers and active fillers. Inert filler remains inactive during the pyrolysis and its composition and volume will keep unchanged. However, active filler reacts with the pyrolysis by-products and/or protective gases to form carbides or nitrides at elevated temperatures [3–5].

There are some reports concerned with the fabrication of fiber reinforced ceramic matrix composites via active-filler-controlled polymer pyrolysis (AFCOP) process [4,6–8]. In the AFCOP process, the volume shrinkage that occurs in the polymer pyrolysis process is commonly compensated by the volume expansion caused by active filler reaction, and no polymer infiltration and pyrolysis (PIP) process are performed. In this work, not only active fillers were applied, PIP process was also performed to get composites with high densities. Furthermore, the active filler conversion process was optimized for benefits to the densification of composites. The microstructures and mechanical properties of 3D C/SiC-BN composites were investigated. Meanwhile, the microstructure evolution of 3D fiber reinforced ceramic matrix composites fabricated by FE-PIP process was analyzed based on the microstructure observation of C/SiC-BN composites and C/SiC composites.

2. Experimental procedure

C/SiC-BN and C/SiC composites were fabricated by filler enhanced polymer infiltration and pyrolysis (FE-PIP) process, boron and SiC particles were applied as active fillers and inert fillers respectively. Boron (Tangshan WeiHao Magnesium Powder Co., Ltd., Tangshan, China) and Nano-SiC (Kai'er Nanometer Technology Development Co., Ltd, Hefei, China) were mixed with PCS (National University of Defense Technology, Changsha, China) by ball-milling for 48 h to form homogeneously dispersed slurries for fabrication of C/SiC-BN composites and C/SiC composites, using xylene as solvent to form homogenous slurry. Carbon fibers (M35, Toray, Tokyo, Japan) were used to braid 3D fiber preforms by Nanjing Fiberglass Research and Design Institute (Nanjing, China) with fiber volume fraction of ~40%. Carbon fiber preforms were first deposited with PyC (~100 nm) or PyC/SiC (~100 nm/100 nm) interphases by CVI, meanwhile, some fiber preforms were used as received for comparison. 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 3KPa and 1050 °C. Fiber preforms were impregnated by the aforementioned slurry and pyrolyzed. Then the samples were densified with 5 cycles of PIP using PCS as the polymer before nitridation. In order to avoid the reaction of boron with other species on the first stage of densification, the pyrolysis temperature were set to be 800 °C before nitridation process and Ar was applied as protective gas. Then the samples were heat-treated at 1800 °C in N_2 atmosphere for 1 h to convert boron into h-BN (nitridation). After nitridation, the samples were further densified by PIP and the pyrolysis temperature was set to be 1100 °C. For comparison, 3D C_f/SiC composites were fabricated at the same time.

The samples were cut and ground into 5 mm × 3 mm × 40 mm for three-point-bending tests in an Instron-5566 machine, operated at a crosshead speed of 0.5 mm/min and a span of 36 mm. Both the polished cross-sections and the fracture surfaces were observed by electron probe microanalyzer (EPMA, JXA-8100, JEOL, Tokyo, Japan) to characterize the microstructures of the composites.

3. Results and discussions

It can be observed from the SEM microstructures of boron powders (Fig. 1) that most of the particles are composed of sub-micron particles but there are some large aggregates with size of several micrometers.

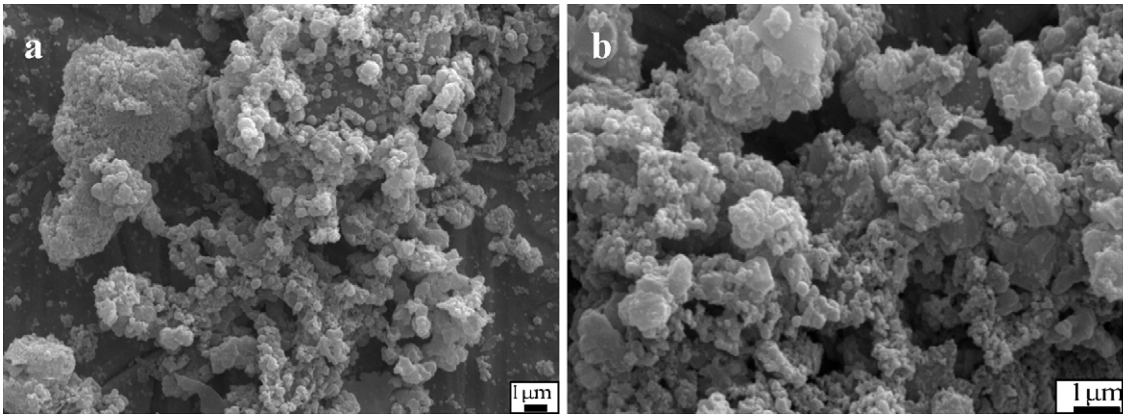

Fig. 1. SEM micrographs of boron powders.

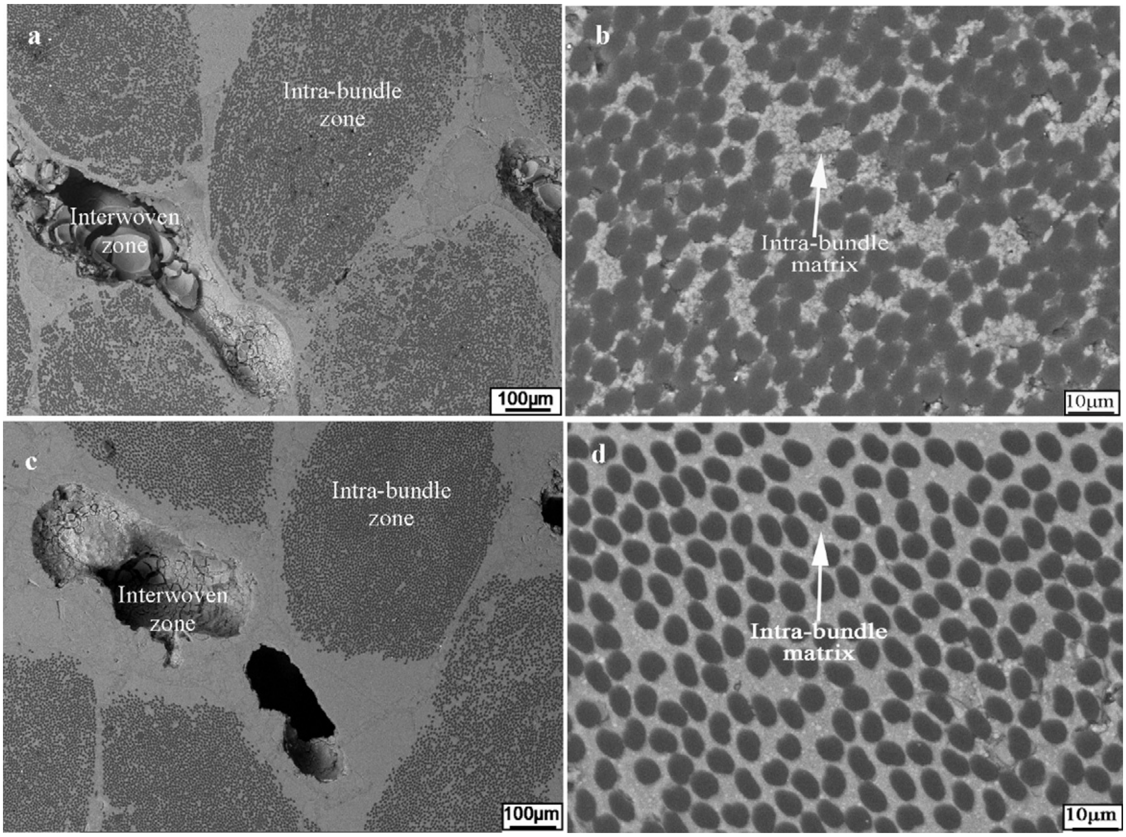

Fig. 2. SEM micrographs of composites on polished cross-sections. (a, b) C/SiC-BN composite; (c, d) C/SiC composite.

The Microstructures of composites fabricated using boron as active filler and nano-SiC as inert fillers are shown in Fig. 2. It can be concluded from the micrographs with low magnification (Fig. 2a and c) that some large pores can be found in the interwoven zones while only very small amount of micro-pores existed in the intra-bundle zones of both C/SiC-BN and C/SiC composites.

It can be also found that there are many cracks left in the inner-wall of interwoven pores. This phenomenon may be caused by the high volume shrinkage up to 60% in the polymer-to-ceramic conversion process due to weight loss and density increase [2,9,10]. Meanwhile, it can also be observed that there are two phases with different contrasts in the matrix of both C/SiC and C/SiC-BN composites. The main phases in the matrix of both composites shows a gray contrast, however, some phases with dark contrast dispersed in the matrix of C/SiC-BN composite while some particles with white contrast dispersed in that of C/SiC composite. In the slurry impregnation process, both boron particles and nano-SiC particles will infiltrate into the fiber bundle zones as well as PCS. PCS will convert into amorphous SiC when pyrolyzed and crystallized in the nitridation process. Boron particles will react with nitrogen to form h-BN in the nitridation process while nano-SiC particles keep unchanged. According to the mechanism of back-scattered electron image, h-BN possesses a dark contrast and nano-SiC particles possess a white contrast. The excessive carbon in PCS-derived SiC matrix [11] may account for its gray contrast.

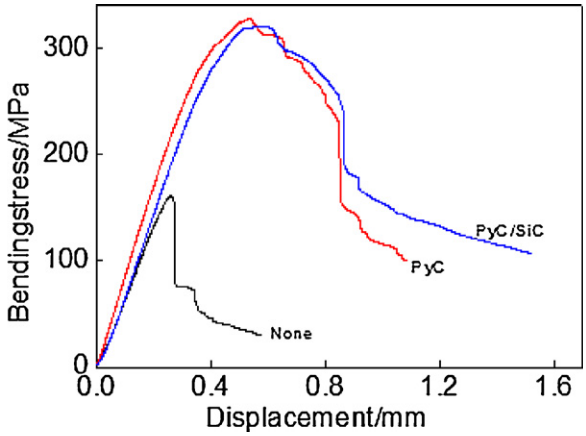

Fig. 3. Bending stress-displacement curves of C/SiC-BN composites with different interphases.

Fig. 3 shows the bending stress-displacement curves of C/SiC-BN composites with different interphase layers. It can be concluded that all samples show typical non-brittle fracture behaviors in three-point-bending testing. There are very small differences among the elastic modulus of three composites concerning the slopes of linear stage with different bending curves. However, great differences in bending stresses can be observed after interphase layers were deposited. When no interphase was deposited on the surface of carbon fibers, the bending stress was about 170 MPa, while with the PyC or PyC/SiC interphase layer was deposited, the bending stresses increased to higher than 300 MPa and the non-brittle fracture

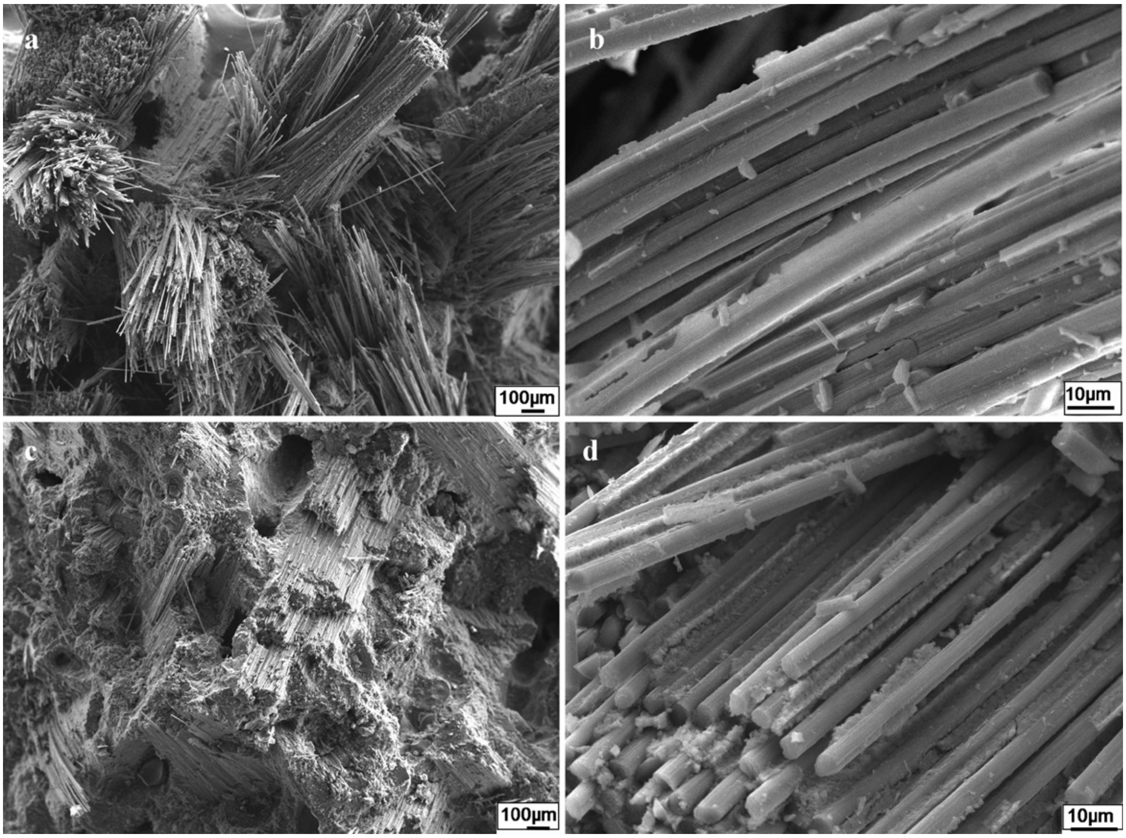

Fig. 4. Influence of interphase on the fracture surface morphologies of Cf/SiC-BN composites. (a, b) with PyC interphase; (c, d) with no interphase.

behavior was more obvious. Consistent with the non-brittle fracture behavior, some pulled-out fibers can be observed on the fracture surface of C/SiC-BN composites shown in Fig. 4. When PyC interphase layer was deposited, the length of pulled-out fibers is much longer than that of pulled-out fibers in composite with no interphase. It can also be observed from the surface morphology of pulled-out fibers, some matrix clung to the fiber when no interphase was deposited while that of composite with PyC interphase is much smoother. When no interphase layer was deposited, fiber bundles in composite preform were relatively loose compared to those with deposited interphases. Therefore, it is much easier for boron particles to infiltrate into the loose fiber bundles, and lead to a higher content of boron in the composite, especially in the intra-bundle zones. Furthermore, in the composite fabrication process, when composites were exposed to air, it was is inevitable for the composites to absorb some water from air. As a result of the sensitivity of boron to water, some B_2O_3 may be formed. The existing B_2O_3 may do some damage to the unprotected carbon fibers and lead to a stronger bonding strength between fiber reinforcements and matrix. The above-mentioned reasons may account for the lower bending stress and shorter pulled-out fibers in composite without interphase.

As it has been shown in Fig. 2, some large pores are easy to be found in the interwoven zones. When the microstructures around the interwoven pores were studied, some interesting phenomena can be found, as shown in Fig. 5. In the present study, fracture surface of C/SiC-BN composites with short pulled-out fibers is applied to study the microstructures around inter-bundle of pores, as it is much easier to get more details. The matrix near the fiber bundles differs greatly from that around the inner wall of pores. Some phases with layered crystal structure can be observed in the matrix near the fiber bundles. According to the fabrication process, the phases with layered structures is h-BN derived from the nitridation of boron [12].

4. Microstructure evolution of CRCMC composites

Fig. 6 illustrates the microstructure evolution of 3D fiber reinforced ceramic matrix composites fabricated through FE-PIP process. In the slurry-impregnation process, slurry will fill the pores of composite performs. After slurry infiltration, when the preforms are dried with in vaporization of solvent, the slurry will prefer clinging to the fiber bundles and some pores will form, especially in the interwoven zones. In the slurry pyrolysis process, some cracks and micro-pores will form as a result of shrinkage that occurs in the polymer-ceramic conversion process. The formed cracks and micro-pores will act as the diffusion paths for precursor solution infiltration. In the following PIP densification and high temperature heat-treatment process (for active filler reaction), the size and content of infiltration paths will decrease, which means the filling of remaining pores and cracks will become more

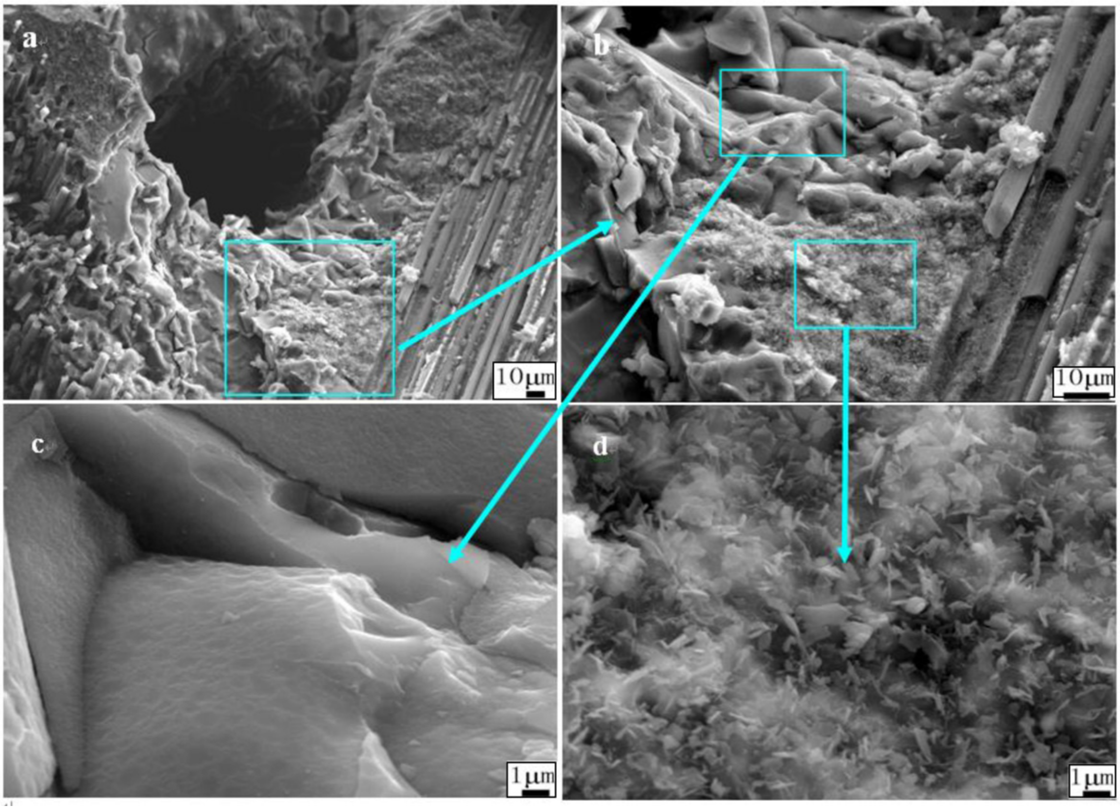

Fig. 5. Microstructures of pores in the fiber bundle zone and that of matrix around the pore in 3D Cf/SiC-BN composite.

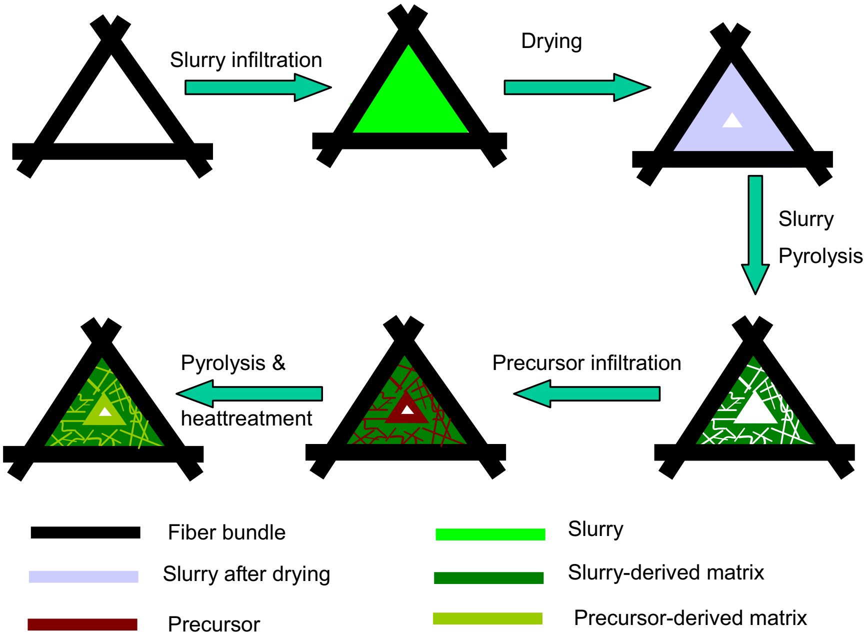

Fig. 6. Schematic illustration of microstructure evolution of 3D composite fabricated by FE-PIP process.

difficult. Due to the large size of inter-woven pores compared to the microcracks and micropores, it is impossible for the inter-woven pores to be fully filled, therefore, some large pores were left in the inter-woven zones and the cracks in the inner wall of interwoven pores cannot be densified.

5. Conclusions

1. Some large pores were left in interwoven zones of 3D C/SiC-BN composites and C/SiC composites while the intra-bundle areas were relatively dense. Fillers in the slurries will

infiltrate into fiber preforms and boron will react with protective filler and/or preceramic pyrolysis product to form h-BN composites.
2. Interphase layers have a great influence on the bending stress and fracture behavior of C/SiC-BN composites. Bending stress of composite without interphase layer is about 170 MPa while that of composite with PyC or PyC/SiC interphase layer is higher than 300 MPa. After interphase layers were deposited on fiber surface, the non-brittle fracture behavior is more obvious and the pulled-out fiber surface is smoother.
3. Due to the preferential clinging of slurry to the fiber bundles, the matrix of composites in different zones possesses different microstructures. Some phases with layered structures can be observed in the matrix near fiber bundles in C/SiC-BN composites, which were derived from slurry containing boron.

Acknowledgements

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