BN/SiC Coating on SiC Tows Prepared by Chemical Vapor Infiltration

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Abstract. Boron nitride (BN) and silicon carbide (SiC) coatings were prepared in sequence on desized SiC tows by chemical vapor infiltration (CVI) at the temperature of 950°C. BN was synthesized by the reaction between boron trichloride (BCl3) and ammonia (NH3) while SiC was from the thermal decomposition of methyl trichlorosilane (MTS). The thickness of the coatings was uniform on a certain cross section of a monofilament, and the thickest/thinnest ratio is less than ~2 across the whole SiC tows for both SiC and BN coatings, as observed by scanning electron microscopy (SEM). Distinct β-SiC powder X-ray diffraction (XRD) pattern was obtained for as-prepared CVI SiC while as-prepared BN coating only showed a bump and a tiny peak corresponding to hexagonal BN (h-BN). This result was verified by transmission electron microscopy (TEM) images, in which CVI BN only had curved diffraction fringes within small pockets, known as turbostratic structures (t-BN). However, t-BN possesses similar short-range structure to h-BN as demonstrated by 11B solid-state NMR spectrum. SiCf/SiC minicomposites using the interphase coating mentioned above is currently under investigation.

1. Introduction
Continuous silicon carbide fiber reinforced silicon carbide composites (SiCf/SiC) adopt a bunch of beneficial properties of SiC, such as high temperature strength, oxidation resistance, creep resistance, and low density, while overcome the brittleness of monolithic SiC by introducing continuous SiC tows as reinforcement. The presence of the reinforcement results in a phenomenon called “pseudo ductility” during the deformation of the material, by crack deflection and crack bridging to avoid catastrophic failure usually happened to monolithic ceramics.[1] A thin layer of interphase, ~1 μm or even less, is normally a critical component for SiCf/SiC composites to adjust the interactions between the reinforcement and matrix. Candidate interphase materials include pyrolytic carbon (PyC), [2, 3] boron nitride (BN), [4-6] SiC, [7] silicon nitride (Si3N4), [8] and modified ones such as boron-containing carbon. [9] The application of SiCf/SiC includes the hot-section components of aero-engines as well as fuel cladding materials in nuclear technology. High-pressure turbine shrouds made of SiCf/SiC with
environmental barrier coating (EBC) have already entered service in LEAP engines for Airbus A320neo (2016) and Boeing 737 MAX (2017). [10]

In this work, BN/SiC composite coatings on 2\textsuperscript{nd} generation SiC tows were prepared by isothermal/isobaric chemical vapor infiltration (CVI). BN was synthesized through boron trichloride-ammonia-nitrogen (BCl\textsubscript{3}-NH\textsubscript{3}-N\textsubscript{2}) route, while SiC was synthesized through methyl trichlorosilane-hydrogen (MTS-H\textsubscript{2}) route. Scanning electron microscopy (SEM), X-ray powder diffraction (powder XRD), transmission electron microscopy (TEM) and \textsuperscript{11}B solid-state nuclear magnetic resonance (solid-state NMR) spectroscopy were utilized to characterize the morphology, degree of crystallinity, crystal constant, and local structure of the CVI BN/SiC coating.

2. Experiment

2.1. Chemical vapor infiltration (CVI)

BN and SiC coatings had been prepared in sequence on desized SiC tows by CVI process. The reaction was carried out in a resistance-heating reactor while the process is isothermal and isobaric. All the gas precursor inlets were on top of the reactor and the waste was fast evacuated from the bottom by a set of two roots and one liquid ring pumps to maintain the total pressure. Second generation SiC tows as well as T300 carbon tows were placed vertically in the reactor to be deposited, with the two ends being hung to the graphite dispensing plates. After the reaction temperature was reached, stabilization time (~30 min) was added in order for the substrate (the fibers) to reach the temperature and for the sizing to decompose.

BN was synthesized at the temperature of 950\textdegree C, by the reaction between BCl\textsubscript{3} and NH\textsubscript{3}. The molar ratio of BCl\textsubscript{3}/NH\textsubscript{3} is 1~3 and the total pressure is 1~5 mbar. N\textsubscript{2} was used to purge the jacket of the CVI reactor.

Silicon carbide was synthesized at the temperature of 950\textdegree C, following the purging steps by a generous amount of N\textsubscript{2} after the synthesis of BN, by the thermal decomposition of MTS in H\textsubscript{2}. MTS was mixed with H\textsubscript{2} before being carried into the reactor. The molar ratio of H\textsubscript{2}/MTS is 15~20, and the total pressure is 5~20 mbar.

CVI SiC coating on T300 carbon tows was prepared by the same method, for the purpose to remove the contribution from SiC fibers when carrying out powder XRD for CVI SiC. Thin (200~300 nm) BN coated SiC tows were prepared to make TEM sample.

2.2. Characterization

SEM was performed on a FEI Nova NanoSEM 450 microscope to observe the morphology of coatings. Sample-to-lens distance was ~5 mm, accelerating voltage was 18 kV and the secondary electron mode was selected. SiC tows with coatings was cut by surgical blade to expose the cross-section area. The cut fibers were pasted to aluminum-based conductive adhesive tape on the edge of an aluminum bar, and another piece of nonwoven fabric-based conductive adhesive tape was pasted to the other side of the fibers, to fix the fibers and to enhance conductivity.

Powder XRD was performed on a Shimadzu LabX XRD-6000 powder X-ray diffractometer equipped with a copper target. The range of 2\theta was 10~80\textdegree, while the scan speed is 5\textdegree/min and the sampling pitch is 0.04\textdegree. The tows could be pasted by scotch tape on two ends and transferred to the sample stage of X-ray diffractometer upon needed. However, if possible, grinding the SiC tows by agate motor immediately before test is highly recommended since a smoother XRD line could be obtained.

TEM was performed on a FEI Tecnai F20 microscope and the beam energy was 200 kV. Bright field images were collected. The BN coated SiC fibers were first cut into short pieces and placed into a 5 mL Eppendorf tube filled with ethanol. The tube was capped and fixed in a beaker of deionized water before being ultrasonicated for ~30 min. Copper mesh with porous carbon support was used to collect coating fragments. The copper meshes were dried and observed under SEM first, and the positions of thin coatings was carefully recorded.
Magic angle spinning (MAS) NMR spectroscopy is a powerful technique that has been widely used in studying the atomic arrangements of solids. $^{11}$B MAS NMR spectra can provide detailed structural and dynamic information of important functional boron-containing materials. SiC fibers with BN coatings were ground and packed into zirconia rotors. The spectra were collected on a 9.4 T Bruker Advance III spectrometer equipped with a 4.0 mm MAS probe tuned to 128.4 MHz. $^{11}$B chemical shift was referenced to the $^{11}$B resonance of boric acid at 19.6 ppm. Magic angle spinning rate was 14 kHz and 2048 scans were recorded.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)
Cross-section SEM images were collected and the thickness of the coatings were measured by the NIH Java image processing program image J. As shown in Figure 1b, the BN layer was 1045 ± 40 nm and the SiC layer was 1330 ± 40 nm. During sample preparation, SiC fibers were pasted to aluminium bar as vertically as possible, and for the thickness measurement, mis-aligned SiC fiber should be avoided. The variation of coating thickness was noticed to depend on the vertical and radial location of the tows in the reactor as well as on the position of the monofilament within a tow. The thickest/thinnest ratio in each batch could be as large as ~2.

Figure 1. (a) The cross-section SEM images of BN/SiC coated SiC fibers. (b) Enlargement of the region circled by dashed red lines in (a).

Figure 2. (a) XRD patterns of BN coated SiC fiber (red) and SiC fiber heat-treated at 950°C. (b) XRD pattern of SiC coated T300 carbon fiber (red) and T300 carbon fiber heat-treated at 950°C.
3.2. X-ray powder diffraction (powder XRD)
In the Figure 2aXRD pattern, only a bump at ~25.0° and a hardly discernable peak at ~26.6° could be seen around the position of BN (002) peak which is ~26.7°, indicating that the BN prepared at 950°C was poorly crystallized without any further heat-treatment. CVI SiC showed sharp β-SiC peaks at 35.8°(111), 60.3°(220), 72.1°(311) and a shoulder peak at 33.9°. Considering the peak width at half height of the three major peaks (111), (220) and (311), for CVI SiC, the values are 0.47°, 0.64° and 0.70° respectively; for 2nd generation SiC fibers, the values are 1.34°, 1.17°, and 1.37° respectively. Obviously, the crystal size of the CVI SiC are significantly larger than that of the SiC fiber converted from polycarbosilane (PCS) precursor.

![Figure 3](image)

Figure 3. (a) SEM image of the BN coating fragment on copper mesh with porous carbon support.(b) The TEM image of BN coating at the point marked by a red X in (a).

3.3. Transmission Electron Microscopy (TEM)
To prepare TEM samples, thin BN (200~300 nm) coated SiC fibers were cut into ~10mm long pieces and ultrasonicated in ethanol as described in section 2.2. Copper mesh with porous carbon support was used to collect the BN coating fragments in the supernatant. An example of these fragments is shown in Figure 3a. The area marked by a red X is thin enough (<100 nm) for TEM observation. The interlayer distance was measured to be ~0.338 nm by imageJ, corresponding to the BN (002) face. The highest number of consecutive layers is ~20, corresponding to a grain size of 6~7 nm.

3.4. Solid-state NMR Spectroscopy
Boron has two NMR active isotopes, $^{10}$B and $^{11}$B. $^{10}$B has ground-state spin 3, natural abundance 19.9%, and gyromagnetic ratios $\gamma = 28.747 \times 10^6$ rads$^{-1}$T$^{-1}$; For $^{11}$B, these three values are 3/2, 80.1% and $85.847 \times 10^6$ rads$^{-1}$T$^{-1}$ respectively.[11]Generally, higher natural abundance and gyromagnetic ratio make $^{11}$B a better choice for boron NMR. $^{11}$B 1D Hahn-echo solid-state NMR spectrum was recorded for BN coated SiC fibers. The BN coating was synthesized at 950°C, as described in section 2.1, without further heat-treatment. The NMR spectrum has a typical h-BN shape as that reported, considering the chemical shift range (-10~30 ppm) and line shape.[12] This indicates that although the as-prepared BN coating was proved to be t-BN by XRD and TEM, its local structure was identical to that of h-BN. This fact partially explains why transition from t-BN to h-BN can take place at higher temperatures.
4. Conclusions

BN/SiC composite coatings were prepared on the surface of 2\textsuperscript{nd} generation SiC tows in sequence. The thickness of a single layer can be thinner than 100 nm to thicker than 1 \( \mu \)m by adjusting the deposition time. Field emission SEM is a powerful method to detect the thickness of the deposited coatings, and the SiC/carbon fiber, BN coating and SiC coating are well distinguishable under secondary electron mode. Powder XRD pattern showed a bump at \( \sim 25.0^\circ \) and a hardly discernible peak at \( \sim 26.6^\circ \), corresponding to the BN (002) peak. CVI SiC has significantly sharper XRD peaks than that of 2\textsuperscript{nd} generation SiC fibers, indicating larger grain sizes result from CVI rather than conversion from polymer precursors. TEM image confirmed the turbostratic structure of BN prepared at 950\( ^\circ \)C, while \( ^{11}\)B solid-state NMR of the \( t \)-BN resulted in the same pattern as that of \( h \)-BN, indicating a common local structure for the two forms of BN, which provides a tendency of \( h \)-BN formation at higher temperatures and the possibility that conversion from \( t \)-BN to \( h \)-BN could take place. The ordering process was described to be similar to the carbon graphitization process.\cite{13} The improving of crystalline by heat-treatment and the CVI minicomposites using the coated SiC fibers mentioned in this paper are currently under investigation.

Acknowledgements

The authors would like to thank Dr. GONG Jianghong and all the organizers of CCIC-11 for providing such a wonderful platform, and all ceramics colleagues we met in Kunming for the inspiring ideas you sheared.

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