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A modified dip-coating method to prepare BN coating on SiC fiber by introducing the sol–gel process

Jianggao Liu [a], Shubin Wang [a,b,*], Pengyang Li [a], Mengjie Feng [a], Xinwang Yang [a]

[a] School of Materials Science and Engineering, Beihang University, Beijing 100191, China
[b] Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing 100191, China

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ABSTRACT

Boron nitride (BN) coatings were synthesized on silicon carbide (SiC) fibers by a modified dip-coating method using boric acid and urea as BN precursors and acrylamide as gel-casting monomer heated at 850 °C for 3 h under N_2 atmosphere. For comparison, a conventional dip-coating method was also adopted to prepare BN coatings under the same conditions. The structure of BN coatings was characterized by X-ray diffraction, Fourier transform infrared spectroscopy and transmission electron microscopy. The morphology of the fibers after impregnation and heat treatment was observed by the electron micrographs. Fiber tensile strength was evaluated by single fiber tensile test. The effects of polyacrylamide on the formation of BN coatings were also investigated. The results show that the BN coatings, prepared by two cycles of impregnation in the modified dip-coating process, covered the SiC fibers well, and exhibited a compact turbostratic–amorphous hybrid structure with a thickness of 550 nm. The tensile strength of the coated SiC fibers increased by ~22% after the conventional dip-coating method was modified. The introduction of the sol–gel process enabled the BN precursors to form a film on the surface of SiC fibers with an even distribution in the impregnation process and to retain the evenness in the heat treatment process. Based on the two effects, the conventional dip-coating method was improved.

1. Introduction

Silicon carbide (SiC) fibers are widely used as reinforcement in ceramics matrix composites (CMCs) because of their excellent properties, such as high strength, high modulus, high temperature resistance, high oxidation resistance, and high chemical corrosion resistance [1]. However, under high temperature preparation, these fibers easily form a strong adhesion with ceramic matrix, leading to a brittle composite with poor mechanical properties [2]. Thus, an interphase is necessary to make the fiber–matrix bonding weak enough to allow crack deflection along the interface, yet strong enough to transfer load from the matrix to the fibers [3]. Numerous studies have shown that pyrolytic carbon (PyC) [4–8] and hexagonal boron nitride (h-BN) [9–13] can be used to solve the interface problem in CMCs reinforced with SiC fibers. However, h-BN is reported to be a more suitable SiC fiber coating than PyC for the reason that h-BN has higher antioxidative property [14].

Currently, two methods are mainly adopted to prepare h-BN coatings on fibers, namely, chemical vapor deposition (CVD) method [15–17] and dip-coating method [18–20]. Compared with the CVD method, the dip-coating method is simple in operation, inexpensive and able to obtain coatings on both surface and interior fibers of fabrics, which are widely used in CMCs [21]. However, to get further applications, the dip-coating method still needs to be improved in the aspects of controllability, uniformity and integrity. In our previous work, two key deficiencies were found in the conventional dip-coating method limiting the uniformity and integrity of BN coatings. One deficiency is that the precipitation of BN precursors from the residual solution on the surface of impregnated fibers is such a random process that BN precursors can hardly be evenly distributed. The other one is that the existence of gravity and capillary force greatly weakens the ability of the liquid intermediate products, formed in the heat treatment process, to cover the fibers completely and evenly. As a result, poor-quality BN coatings are formed with many elongated defects, which were also reported by other researchers [18,19]. To overcome the two deficiencies, the sol–gel process was considerably adopted in this study. Ease of controlling the homogeneity and physical characteristics during synthesis steps and the ability to form coating materials are the most suitable advantages to overcome the two deficiencies. Besides, the sol–gel method can be easily introduced into the dipping process. As for the gel-casting monomer used in a sol–gel method, acrylamide is inexpensive and its gel-casting process is fast reproducible and easily scaled up [22]. Furthermore, acrylamide has been used in preparing h-BN particles [23]. Therefore, acrylamide is chosen as the gel-casting monomer for the modified dip-coating method.

In this study, BN was coated onto SiC fibers via a modified dip-coating method by introducing the sol–gel method into the dipping process with

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* Corresponding author at: School of Materials Science and Engineering, Beihang University, Beijing 100191, China.
E-mail address: shubinwang@buaa.edu.cn (S. Wang).

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acrylamide as the gel-casting monomer. The effects of the sol–gel process on the morphology and chemical composition of the fiber coatings and the tensile strength of the SiC fibers were investigated.

2. Experiment

2.1. Sizing removal of SiC fiber

The KD-I SiC fiber bundles (provided by National University of Defense Technology, China) were used as samples for dip coating in this study. These fibers were obtained with sizing; hence, surface treatment was required for sizing removal. The as-received fibers were cleaned in acetone solution for 24 h. Through this process, the cleaned fibers were achieved.

2.2. Preparation of BN precursor sol

The preparation of BN precursor sol is shown in Fig. 1. A solution of 6 g of urea and 4 g of boric acid in the mixture of 20 mL of ethanol (AR) and 10 mL of deionized water (AR) was prepared and then 1 g of acrylamide (AM), and 0.04 g of N,N′-methylenebisacrylamide (MBAM) monomers were added into the premixed solution. When the mixing was completed, ammonium persulfate (APS) was added to the system which caused the copolymerization of monomers to form a transparent sol. For comparison, another solution of 6 g of urea and 4 g of boric acid in the mixture of 20 mL of ethanol (AR) and 10 mL of deionized water (AR) was prepared as a conventional impregnation solution.

2.3. Preparation of BN coatings

The cleaned fibers were dipped into the solution and the sol respectively for 10 min and then dried at 60 °C for 15 min. Three dip-dried cycles were carried out for the fibers dipped in the solution, which has been proved to be the most suitable dip-dry cycles for the conventional dip-coating method [18–21]. While three dip-dried cycles: 1, 2, 3 were carried out for the fibers dipped in the sol. After the impregnating process, the sol without any fibers was stirred at 60 °C to form a gel. Finally, all impregnated fibers were heated to 850 °C at a rate of 5 °C/min for 3 h in a furnace with N_2 atmosphere, while the gel was heat-treated at different temperatures for 3 h under N_2 atmosphere.

2.4. Characterization

Scanning electron microscopy (SEM, JSM-7500F) was employed to investigate the SiC fiber morphologies. The phases of the nitridation products from the gel were characterized by X-ray diffraction (XRD, D/Max 2200 PC). The chemical compositions of the coatings on SiC fibers and the nitridation products from the gel were characterized via Fourier transform infrared (FT-IR) spectroscopy (Nicolet, Avatar-360). The texture and structure of the coatings were examined by High-resolution transmission electron microscopy (HR-TEM, JEOL, JEM-2100F). Single fibers extracted from a tow were fixed on paper frames using a hard acrylic resin. The 25 mm standard gauge length was used and the cross-head speed of 3 mm/min was set. At least 20 fibers were mechanically tested for each treatment condition for a single data point.

3. Results and discussion

3.1. Characteristic of the products from the gel at different nitridation temperature

The XRD patterns of the products from the gel at different nitridation temperatures are shown in Fig. 2. There is a strong peak around a 2θ value of 26.4° shown in the XRD pattern of the product nitrided at 1050 °C, which corresponds to the (002) crystal plane of h-BN [24]. Other diffractions at 42° (100), 44° (101), 55° (004), and 76° (110) are also discernible in this pattern, indicating that the h-BN has a good crystalline degree. When the nitridation temperature reaches 950 °C and 850 °C, the strongest peak of BN becomes broad. As its strength decreases, a pattern of amorphous components are noticeable, resulting in a broad peak ranging from 20° to 30°. As many studies [18,25,26] have reported, when the diffractions are discernible only at about 26° and 42°, turbostratic BN (t-BN) is formed. However, when the nitridation temperature reaches 750 °C, the characteristic peaks of B_2O_3 are detected, indicating that the nitridation reaction cannot get finished under this condition.

The FT-IR spectra of the products from the gel at different nitridation temperatures are shown in Fig. 3. For the products at nitridation temperatures of 850 °C, 950 °C and 1050 °C, absorption peaks around 780 and 1380 cm^{-1} are detected, which are due to the in-plane bending vibration of B–N–B bond and the stretching vibration of sp^2 hybridized B–N bond, respectively [24]. Fig. 3 also shows that the peaks around 780 and 1380 cm^{-1} become increasingly broad and blunt as the nitridation temperature decreases, suggesting that the quantity of B–N–B and B–N bonds weakened with the decrease of the nitridation temperature. Three peaks around 2920 cm^{-1} are also detected. These peaks can be attributed to the vibrations of methyl, methylene and methylidyne groups [27]. The existence of C–H bonds indicates that some carbon residues of the pyrolysis of polyacrylamide were formed, which resulted from the

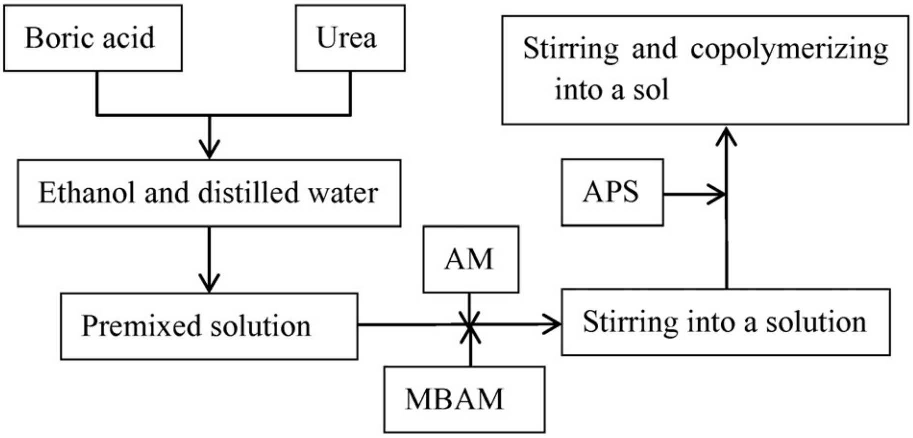

Fig. 1. The preparation of BN precursor sol.