Carbothermal Synthesis of Boron Nitride Coatings on Silicon Carbide

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Pure BN coatings have been synthesized on the surface of SiC powders and fibers by a novel carbothermal nitridation method. Three stages are involved in the process: first, formation of a carbon layer on the SiC by the extraction of Si with chlorine; second, nitridation of the resulting nanoporous carbide-derived carbon (CDC) coating by a saturated boric acid solution; and finally, nitridation in ammonia at atmospheric pressure to produce the pure BN coating. X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and electron energy loss spectroscopy (EELS) were used to characterize the phase, elemental composition, and surface morphology of the coatings. The intermediate carbon layer acts as a template for BN growth, facilitates the formation of BN, and prevents the degradation of SiC fibers during nitridation. The whole process is simple, cost-effective, and less toxic due to the use of H₂BO₃ and NH₃ as precursors at atmospheric pressure compared with most commonly used chemical vapor deposition (CVD) methods. Uniform BN coatings obtained by this method prevent the bridging of fibers in the tow. The coating of powders is possible, which cannot be achieved by conventional CVD methods.

I. Introduction

BORON NITRIDE (BN) has received considerable attention within the last few years due to its favorable mechanical, electrical, optical, and chemical properties over a wide range of temperatures.1,2 Such excellent properties promote the broad applications of BN, which include high-temperature insulators, self-lubricating and heat-dissipating coatings, passivation layers, diffusion masks, and wear-resistant coatings. Structurally and chemically well-defined films are required3 in many of these applications.

BN, like carbon, has four crystalline structural modifications: cubic (c-BN), wurtzite (w-BN), hexagonal (h-BN), and rhombohedral (r-BN), which correspond to diamond (zinc blende form), hexagonal diamond (wurtzite form), hexagonal, and rhombohedral graphite, respectively.4–6

An important application of thin BN coatings is as an interfacial layer for controlling the bonding in fiber-reinforced ceramic-matrix composites (CMCs).7,8 The CMCs reinforced by SiC fibers or whiskers have attracted great attention due to their highly improved fracture toughness. However, carbon-rich interface layers in such SiC/SiC-based composites show low oxidation resistance at elevated temperatures in air or water vapor,9–14 which leads to oxidation embrittlement of the CMC and degradation of their mechanical properties. BN has a better oxidation resistance than carbon. At high temperatures, when BN reacts with the oxygen ingressed through the interfaces between fibers and the matrix, it forms B₂O₃, which could react with SiO₂ to form a glassy protective layer to prevent the further reaction at the interface of the CMCs. Thus, synthesis of BN coatings on SiC fibers is one of the most promising techniques to improve performance of the fiber-reinforced CMCs at high temperatures.15–18

Up to now, most of the BN coatings were prepared by chemical vapor deposition (CVD).19–21 Also, plasma-assisted chemical vapor deposition (PACVD),22 magnetron sputtering, and pulsed laser deposition (PLD)3 were used for the synthesis of different BN coatings.

Recently, the introduction of an intermediate carbon layer was found to be helpful to reduce the BN synthesis temperature at ambient pressure. Carbothermal reduction–nitridation is widely used to produce nitride powders.23,24 Direct nitridation of carbon nanotubes to obtain BN-coated nanotubes has also been demonstrated by Bando.25 However, for the dense graphitic carbon, such nitridation is a slow process and thick coating requires a temperature higher than 1500°C, which will damage the SiC fibers made from polymeric precursors. Relatively low temperature (~1200°C) in situ BN coating preparation has been conducted on Nextel 312™ in ammonia by reacting with the 14 wt% boria in the fiber, but it is only limited to boria-containing fibers and the thickness of the BN coating is less than 40 nm. Synthesis of BN coatings by transformation from carbon coatings produced by dipping was also proposed27,28 but the coatings obtained by such methods were not uniform enough for composite applications. Furthermore, fiber bridging during those processes decreased the efficiency of the coatings for the fiber tows or fabrics.

In this paper, we present a novel method to synthesize BN coatings by the nitridation of carbon layers on β-SiC powders and Tyranno SiC fibers at relatively low temperatures (<1200°C) and atmospheric pressure.

II. Thermodynamic Modeling

Synthesis of BN coatings on the SiC materials involves three stages. The first is the chlorination of SiC to produce a carbon layer with a desired thickness by the extraction of Si from SiC according to the following chemical reaction:

\[ \text{SiC(s)} + 2\text{Cl}_2(g) \rightarrow \text{SiCl}_4(g) \uparrow + \text{C(s)} \]

The second step is to infiltrate the resulting nanoporous carbide-derived carbon (CDC) coated SiC with saturated boric acid solution using a low vacuum (<1 atm) at 100°C. The final step is nitridation in an ammonia atmosphere at ambient pressure to produce the BN coating.
During the nitridation process, the ammonia is decomposed to nitrogen and hydrogen when the temperature is higher than 227°C. The boric acid dehydrates to form boria, which reacts with nitrogen to form BN. The presence of carbon facilitates this process by reaction with hydrogen. The reactions associated with this procedure are the following:

$$2\text{NH}_3(g) = \text{N}_2(g) + 3\text{H}_2(g)$$

$$2\text{H}_3\text{BO}_3 = \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}(g) \uparrow$$

$$2\text{B}_2\text{O}_3 + 9\text{C} + 4\text{NH}_3(g) = 4\text{BN} + 3\text{CH}_4(g) + 6\text{CO}(g) \uparrow$$

Thermodynamic simulation was conducted in a closed system by using ChemSage 4.1 Gibbs energy minimization software. It helps to optimize the BN synthesis temperature and gives a clear description of how the reactions proceed during processing. Figure 1(a) shows the thermodynamic calculation results for the synthesis of BN at temperatures from 800°C to 1200°C in a closed system at 1 atm. The initial reactants for this reaction include 1 mol of H$_3$BO$_3$, 3 mol of carbon, which is sufficient for the reaction, and 0 to 5 mol of NH$_3$ with a 0.5 mol increase for each step. The temperature range selected was to prevent the possible degradation of polymer-derived SiC fibers by holding the process temperature below 1200°C as well as to reduce the production cost using a quartz tube furnace. As seen from the calculations, the H$_3$BO$_3$ can be completely converted to BN at temperatures above 1000°C with proper control of the amount of incoming ammonia. However, it is necessary to mention that this cannot truly represent the case of reaction due to kinetic limitations. The practical synthesis temperature may be higher to achieve full transformation from carbon to BN and produce coatings with the required thickness of 100–300 nm. In Fig. 1(b), 1 mol of H$_3$BO$_3$, 3 mol of carbon, and 3 mol of NH$_3$ are used for calculating the equilibrium composition over the same temperature range. This analysis shows that the synthesized BN coating is thermodynamically stable and coexists with the gas mixture of the products at high temperatures.

### III. Materials and Experiments

(1) Materials

β-SiC powders, supplied by Superior Graphite Co., USA, with purity of 99.8% and 1 µm particle size, and Tyranno ZMI SiC fibers (56% silicon, 34% carbon, 9% oxygen, and 1% zirconium), produced by UBE Industries of Japan, were used as the raw materials for the synthesis of BN coatings by the proposed method. β-SiC powder was used as a model system to understand the process mechanism due to its easier sample preparation for XRD and TEM studies. Tyranno ZMI SiC fibers were used in our work to show the feasibility of BN synthesis because of their higher tensile strength compared with other types of SiC fibers (Tyranno SA, Hi-Nicalon, Sylramic, etc) and well-studied formation of intermediate carbon coatings on this fiber. However, the method is applicable to virtually any SiC material that can be coated with a uniform CDC film.

(2) Experimental Procedure

The whole synthesis process includes three main steps: chlorination, infiltration, and nitridation. The detailed process for each step is presented below with respect to the different types of SiC.

(A) Chlorination: The process for synthesis of intermediate carbon films on SiC uses a chlorine extraction method. The carbon coatings obtained are conformal and do not change the shape or surface quality of the samples. They have nanoscale porosity, low friction coefficient, and excellent adherence to SiC.

(i) Powders: β-SiC powder was treated in pure chlorine at a flow rate of 10 standard cubic centimeters per minute (sccm) at 1000°C for 3 h in a quartz tube furnace with diameter of 2.5 cm. XRD and Raman spectroscopy analysis confirmed that the SiC was totally converted into carbon.

(ii) Fibers: Tyranno ZMI SiC fibers (~10 µm in diameter) were treated in pure Cl$_2$ with gas flow of 10 sccm for 3 h at 550°C and 650°C in atmospheric pressure to form carbon coatings on fibers with thicknesses of ~0.15 and ~1.5 µm, respectively.

(B) Infiltration: Boric acid was used as the most economical precursor for the synthesis of BN. Unlike other precursors, it does not contaminate the samples by metal impurities. A vacuum chamber was used to infiltrate saturated H$_3$BO$_3$ (99.99% purity) solution into the carbon layer formed on the SiC. The reduced pressure in the chamber induced the release of the gases absorbed on the surface of the nanoporous CDC layer, so that better infiltration could be achieved.

(i) Powders: The CDC powders obtained in the first step of the process were mixed together with H$_3$BO$_3$ powders with a stoichiometric ratio of 9:4. Then the mixture was ground in a mortar to achieve a grain size of ~1 µm. Infiltration of the powders by H$_3$BO$_3$ occurred during the heating for nitridation because B$_2$O$_3$ melts at 450°C.

(ii) Fibers: The CDC-coated fibers were placed in the vacuum infiltration chamber and pumped down for about 30 min. Then they were infiltrated with a saturated H$_3$BO$_3$ solution at 100°C. Cold distilled water was used to wash out the excess of H$_3$BO$_3$ from the fiber surface at room temperature. To achieve good infiltration effect for the nanoporous carbon coating, this step was repeated two or three times.

![Fig. 1.](image-url)
(C) Nitridation: Infiltrated CDC-coated SiC samples (powders and fibers) were loaded in a horizontal quartz tube furnace with inner diameter of 2.5 cm. Before each experimental run, the furnace was purged with argon for at least 30 min. Then the furnace was heated to the desired operating temperature at a rate of 10°C/min with ammonia (grade 4: purity 99.99%, BOC gases) flowing into the reaction tube at a flow rate of 10 sccm. The sample was held at the set temperature for a certain period of time to secure the completion of the reaction, and then cooled down in the furnace under the ammonia flow for protection. The specific treatment temperatures and times for different SiC samples are shown in Table I.

(3) Characterization

The composition and structures of the samples nitrided under various conditions were examined by X-ray diffraction (XRD; Siemens Model D500, CuKa radiation), Raman spectroscopy (Renishaw 100, Ar ion laser at an excitation wavelength of 514.5 nm), scanning electron microscopy (SEM; AMRAY 1830), high-resolution transmission electron microscopy (HRTEM; JEOL 2010F), and electron energy loss spectroscopy (EELS).

Tensile strength and Young's modulus of the SiC fibers before and after nitridation were measured according to ASTM 3379-75 using a SATEC Model T-5000 universal testing machine equipped with a S/N U.K. 327 load cell with permitted maximum load of 2.5 N. Single fibers extracted from a tow were fixed on paper frames using a hard acrylic resin (Super Glue, DURO). The 25 mm standard gauge length was used and the crosshead speed was set to 0.5 mm/min. The diameter of the final SiC fiber core has been used for the calculation of mechanical properties. For each treatment condition, at least 10 fibers were mechanically tested.

IV. Results and Discussion

Uniform BN coatings were obtained by the nitridation of the H₃BO₃-infiltrated CDC under the conditions listed in Table I. The nitridation process was conducted in the quartz tube furnace at 1 atm at temperatures below 1200°C, which are low compared with the generally required temperatures for the production of BN (1400°C–1700°C) at atmospheric pressure.¹⁹–²²,35–3⁷

(1) BN Coatings of SiC Powders

(A) X-ray Diffraction Analysis: X-ray diffraction analysis was conducted for the SiC powders after each step of treatment, as shown in Fig. 2. β-SiC powders (Fig. 2(a)) were completely converted into carbon by chlorination in pure Cl₂ at 1000°C for 3 h (Fig. 2(b)). The broad peak in the XRD pattern shows that the carbon powders obtained are mainly amorphous, while small peaks of graphite are also visible. BN coatings were obtained after the nitridation of CDC powders at 1165°C for 60 min in ammonia (Fig. 2(c)). The BN obtained was mainly composed of amorphous phase, which was induced by the amorphous carbon. Some hexagonal BN (JCPDS: 34-0421) was also present in the coatings formed by this method. Under nitridation, boric acid powder first dehydrated to form boria when the temperature was above 100°C, then part of the boria sublimated at temperatures over 170°C,³ and the remainder completely reacted with ammonia at the synthesis temperature.

Detailed discussion of the structures of such BN coatings is an important advantage compared with other oxygen-containing BN coatings synthesized from H₃BO₃.⁴¹,⁴²

There is no crystalline boria remaining among the reaction products according to the XRD pattern.

(B) TEM and EELS Analysis: Three distinct layers with different compositions were detected by the EELS analysis from the nitrided CDC SiC powders as shown in Fig. 3. The outermost layer of the powder is pure BN coating with an average thickness of 50–70 nm, in which the carbon was totally consumed during the reaction. The intermediate layer is a mixture of BN and carbon with a thickness of 75–110 nm and the inner layer (core) of the particle is unreacted pure carbon. The total thickness of the BN coating is around 120–180 nm. Formation of BN and mixed BN/C layers is most probably attributed to the maximization of energetically favorable C–C and B–N bonds, rather than the B–C and N–C bonds.³⁵–⁴⁰ The introduction of CDC layer not only helps to facilitate the formation of BN by decreasing the Gibbs energy of the reactions, but also helps to consume the excess B₂O₃ on the fiber. Therefore, no oxygen was detected in the BN layers, which is an important advantage compared with other oxygen-containing BN coatings synthesized from H₃BO₃.

Figure 4 shows the HRTEM images of BN-coated CDC powders. Hexagonal and amorphous BN were found in the coatings. By the combination of HRTEM and EELS analysis, the mechanism of formation of BN in this method could be understood. The inner layer of the coating at the BN/C interface is mainly composed of amorphous BN. A certain amount of hexagonal BN crystals, with spacing dₐ₀₂ = 0.336 nm as shown in Fig. 4(b), appeared in the middle of the BN coatings and nanocrystalline h-BN became dominant in the surface layer of the coatings. A small amount of cubic BN with spacing d₁₁₁ = 0.209 nm was also observed at the interface with the CDC layer. The mechanism of its formation is probably similar to that of nanocrystalline diamond growth on chlorination of SiC.³¹,⁴³

Table I. Nitridation Conditions for CDC-Coated SiC Samples

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thickness of CDC coating (µm)</th>
<th>Nitridation temperature (°C)</th>
<th>Nitridation time (min)</th>
<th>Color description after nitridation</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-SiC Powder</td>
<td>Complete transformation</td>
<td>1165</td>
<td>65</td>
<td>White</td>
</tr>
<tr>
<td>Tyranno ZMI SiC Fibers</td>
<td>1.5</td>
<td>1150</td>
<td>60</td>
<td>Gray</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>1150</td>
<td>60</td>
<td>Brown</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>1150</td>
<td>80</td>
<td>Violet</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>1165</td>
<td>65</td>
<td>Blue</td>
</tr>
</tbody>
</table>
It can be assumed that the amorphous and diamond-structured BN formed by the reaction with ammonia at the C/BN interface transformed to the more stable hexagonal modification as the reaction front propagated toward the particle core during the nitridation. The presence of hexagonal BN in the intermediate layer of BN coatings suggests this mechanism. The increased temperature during nitridation makes the conversion from $a$-BN to $h$-BN more kinetically favorable. The small amount of boron oxides generated from the reactants at the beginning of the nitridation also helps to form the hexagonal-structured boron nitride. The same phenomenon has been reported during the synthesis of BN by CVD.

(2) BN Coatings of SiC Fibers

SiC fibers coated with 150–250 nm (thin coating) and 1.5 $\mu$m (thick coating) CDC layers were nitrided at 1150°C for various periods of time, respectively.

(A) X-ray Diffraction Analysis: The XRD analysis of the nitrided fibers is shown in Fig. 5. Like the powders, BN coatings synthesized on the SiC fibers with thin CDC layers are mainly composed of amorphous BN (Figs. 5(b) and (c)), while hexagonal BN was the dominant structure on the SiC fibers with thick CDC layers (Fig. 5(d)). The probable reason is that the thick carbon coating allows production of a relatively thick BN layer, from which the amorphous BN formed at the beginning of the reaction tends to convert to the hexagonal modification. Also longer nitridation time helps to increase the content of $h$-BN crystals in the coatings. This is consistent with the results obtained on powders. In addition, the increase of the diffraction peaks from SiC in the pattern can be attributed to the crystallization of SiC in the fiber from its original amorphous phase during the high-temperature treatment. The longer the chlorination and nitridation times used, the more obvious SiC peaks appear. This is not desirable for SiC fibers, so optimization of...
the nitridation condition is required to suppress the fiber crystallization.

(B) Raman Spectra Analysis: Figure 6 shows the Raman spectra of the SiC fibers after nitridation under various conditions. All of the fibers had the same CDC layers of about 0.15 μm thickness. The D and G bands originate from the free carbon in the raw fibers, while the amorphous SiC does not show any peaks in Raman spectra. With increasing nitridation time and temperatures, the peak in the D band position increases in intensity, shifts gradually to higher wavenumbers, and eventually reaches the position of 1367 cm\(^{-1}\), which is the characteristic peak of h-BN.\(^{46}\) It gives additional confirmation that BN can be successfully produced on SiC fibers by this method. Moreover, for the same thickness of carbon coating on the SiC fibers, longer reaction time or higher temperatures help to form the relatively thick BN coatings.

(C) EELS and HRTEM Analysis: The fibers used for preparation of the TEM samples were nitrided in ammonia at 1150°C for 80 min. Judging from EELS and TEM analysis, the layer formed on the surface of the CDC-coated SiC fibers is similar to the coating on the CDC SiC powder. It is composed of pure BN (~80–100 nm) at the surface and a mixture of BN with some carbon, which have not been totally consumed during the reaction, adjacent to the interface of the SiC/CDC coating. A uniform and smooth BN coating with good adherence to the fiber core is clearly seen in the HRTEM image in Fig. 7. However, the thickness of the BN coating observed in Fig. 7 must be calculated accounting for the geometric factors in TEM analysis. The diameter of such BN-coated fiber is 10.8 μm as known by SEM, so the real thickness of the BN coating on the SiC fiber is around 200 nm by the geometric calculation.

Moreover, the crystal structures of the BN formed in the coating layer were also detected by the HRTEM analysis as shown in Fig. 8. Coatings are primarily composed of amorphous and hexagonal BN. Also longer nitridation time and higher treatment temperature help to increase the relative amount of hexagonal BN crystals. The results obtained from fibers are consistent with those from the powders.

(D) Mechanical Properties of the Coated Fibers: Tensile tests were performed on the SiC fibers before and after nitridation

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**Fig. 4.** Typical HRTEM images of BN structures formed after the nitridation of CDC SiC powders at 1165°C for 60 min: (a) amorphous BN and (b) hexagonal BN.

**Fig. 5.** X-ray diffraction patterns for the synthesis of BN coating on Tyranno ZMI SiC fabrics under various nitridation conditions: (a) as-received Tyranno ZMI SiC fibers, (b) CDC (0.15 μm) coated fibers nitrided at 1150°C for 60 min, (c) CDC (0.15 μm) coated fibers nitrided at 1150°C for 80 min, (d) CDC (1.5 μm) coated fibers nitrided at 1150°C for 60 min.

**Fig. 6.** Raman analysis of Tyranno ZMI SiC fibers (with 0.15-μm-thick CDC layer) before and after nitridation under various treatment conditions: (a) as-received SiC fibers, (b) nitridation at 1150°C for 60 min, (c) nitridation at 1150°C for 80 min, (d) nitridation at 1165°C for 65 min.
to investigate the effect of nitridation on the mechanical properties of these fibers. SEM images of CDC-coated SiC fibers before and after the nitridation are shown in Fig. 9. It can be seen that the fiber retained smooth surface and cylindrical shape after chlorination and nitridation. More important, no fiber-bridging occurred as can be seen in Fig. 9(b). The average breaking stress, ultimate strain, and Young’s modulus were calculated and are compared for these fibers in Table II. Although the high-temperature treatment can cause damage to the mechanical properties of SiC fibers as known from other synthesis attempts, the BN-coated SiC fibers prepared by this method have shown no significant change in mechanical strength as well as a slight increase in Young’s moduli, which indicates the possibility of applications of such BN-coated fibers in CMCs. Since the fibers for testing were taken from the fabric after nitridation, the high strength measured is more good evidence to exclude the possibility of fiber-bridging. Otherwise, the fibers would be inevitably damaged during their separation. The absence of degradation in the SiC fibers during nitridation is mainly attributed to the introduction of the carbon layer between the BN coating and SiC fiber in our method, which is consistent with the reports from Shen. The CDC layer not only participated in the nitridation reactions, but also was sacrificially oxidized by the oxygen from the boria to protect the SiC fibers from degradation as well as to control the thickness of BN coatings. Moreover, the mechanical strength and Young’s modulus of the SiC fibers can also be slightly improved by thin carbon coatings formed during chlorination. However, the mechanical properties of the fibers with thick carbon layers (1.5 μm) are much lower than those of the as-received fibers. A contributing factor is the 15% loss of the fiber cross sections during chlorination at higher temperatures, compared with the thin carbon (0.15 μm) coated fibers with only 1.5% loss. The optimal condition to synthesize BN coatings on thin-carbon-coated SiC fibers is nitridation in ammonia at 1150°C for 60 min. More important, such BN-coated fibers show obvious enhancement in debonding and pullout from the polymer glue in single-fiber stress–strain mechanical tests (Fig. 10), which is an important factor in the toughening of CMCs.

The synthesis of BN coatings by this method is not limited to the SiC powders and fibers, but also can be explored to produce...
thermally and mechanically stable BN coatings on a variety of carbide materials in a simple and cost-effective way.

V. Conclusions

(1) BN coatings of uniform thickness can be synthesized by the nitridation of H3BO3-infiltrated CDC coatings on SiC powders and fibers. Unlike CVD, the proposed method allows homogeneous coatings on SiC particles and whiskers, and does not bridge SiC fibers.

(2) Thermodynamic analysis predicts the possibility of carbothermal synthesis of BN on the surface of SiC at and above 1000°C. However, kinetic limitations do not allow coatings of the required thickness (>100 nm) below 1150°C.

(3) An intermediate CDC layer allows the synthesis of uniform BN coatings with no quality degradation and good bonding to the fiber core.

(4) Amorphous and hexagonal graphitic BN have been formed in the coatings with a gradient of these phases from the BN/C interface to the surface. A small amount of cubic BN nanocrystals was also detected at the very outmost surface layer of the coating.

(5) Thickness and structure of BN coatings can be controlled by the thickness of the CDC layers, nitridation time, and temperatures. However, excessive heat treatment may lead to the crystallization of metastable SiC-based fibers produced from polymeric precursors.

(6) BN coatings can be produced on SiC fibers with no degradation in the mechanical strength. A certain increase in Young's modulus and significant enhancement in debonding and pullout have been achieved for the BN-coated fibers.

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