Applied Surface Science 382 (2016) 27–33

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Formation of boron nitride coatings on silicon carbide fibers using trimethylborate vapor

Mengjiao Yuan, Tong Zhou, Jing He, Lifu Chen*

Key Laboratory of High Performance Ceramic Fibers (Ministry of Education), College of Materials, Xiamen University, Xiamen 361005, PR China

ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form 19 March 2016
Accepted 12 April 2016
Available online 16 April 2016

Keywords:
Boron nitride
Fiber coatings
Composites

ABSTRACT

High quality boron nitride (BN) coatings have been grown on silicon carbide (SiC) fibers by carbothermal nitridation and at atmospheric pressure. SiC fibers were first treated in chlorine gas to form CDC (carbide-derived carbon) film on the fiber surface. The CDC-coated SiC fibers were then reacted with trimethylborate vapor and ammonia vapor at high temperature, forming BN coatings by carbothermal reduction. The FT-IR, XPS, XRD, SEM, TEM and AES were used to investigate the formation of the obtained coatings. It has been found that the obtained coatings are composed of phase mixture of *h*-BN and amorphous carbon, very uniform in thickness, have smooth surface and adhere well with the SiC fiber substrates. The BN-coated SiC fibers retain ~80% strength of the as-received SiC fibers and show an obvious interfacial debonding and fiber pullout in the SiC_f/SiOC composites. This method may be useful for the large scale production of high quality BN coating on silicon carbide fiber.

1. Introduction

Boron nitride (BN) is widely used as the surface coating on silicon carbide (SiC) fibers to control the interface bonding between the fibers and the matrix in SiC fiber-reinforced ceramic-matrix composites [1–5]. In comparison with pyrolytic carbon coating, BN coating has better oxidation resistance [6,7]. In addition, it forms B_2O_3 when oxidized at high temperatures, which acts as a barrier against oxidation and increases the service duration under oxidizing environments [8].

BN coating is normally prepared by chemical vapor deposition (CVD) [9–13]. BCl_3 or BF_3 is usually used as the source of boron, and NH_3 is used as the source of nitrogen. The chemical reactions involved are described by Eqs. (1) and (2) [10].

$$BCl_3(g) + NH_3(g) = BN(s) + 3HCl(g) \quad (1)$$

$$BF_3(g) + NH_3(g) = BN(s) + 3HF(g) \quad (2)$$

Both the reactants (BCl_3 or BF_3) and the exhaust gas species (HCl or HF) are highly corrosive. Therefore the un-reacted reactants and the exhaust must be recycled or digested to reduce the cost and prevent environment pollution. Another problem remains in the CVD processing is the heterogeneity of deposition thickness when the fibers are collected into tows [14]. Some individual fibers in a fiber tow may touch with the adjacent fibers, resulting in the contact of bare fibers without BN coating between them. When this occurs, the efficiency of the reinforcements is reduced. As the consequence, the toughness and strength of the composites are adversely affected.

Recently, a novel method was reported to prepare BN coating *in-situ* on carbon fibers or SiC fibers. A thin layer of porous carbon was first formed *in-situ* on the fiber surface. The fibers were then impregnated with boric acid. During the subsequent pyrolysis in ammonia gas (NH_3), carbothermal reductions took place, converting the carbon layer into BN coating. The reactions are shown in Eqs. (3) and (4) [15–17].

$$2B_2O_3(g) + 9C(s) + 4NH_3(g) = 4BN(s) + 6CO(g) + 3CH_4(g) \quad (3)$$

$$B_2O_3(g) + 3C(s) + 2NH_3(g) = 2BN(s) + 3CO(g) + 3H_2(g) \quad (4)$$

Das [18] soaked activated polyacrylonitrile (PAN) carbon fiber in aqueous boric acid solution, and then initiated the carbothermal reduction at 1200 °C and under atmospheric pressure to form BN coating. Chen [15] prepared a carbide-derived carbon (CDC) coating on SiC fibers by chlorination method as shown in Eqs. (5) and (6) [19–27].

$$SiC(s) + 2Cl_2(g) = C(s) + SiCl_4(g) \quad (5)$$

$$SiC_xO_y(s) + 2Cl_2(g) = (x\text{-}y)C(s) + SiCl_4(g) + yCO(g) \quad (6)$$

The CDC coating had well-defined boundary with the SiC fiber core, but it adhered very well with the interior SiC fiber substrates.

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* Corresponding author.
E-mail address: lfchen@xmu.edu.cn (L. Chen).

http://dx.doi.org/10.1016/j.apsusc.2016.04.080

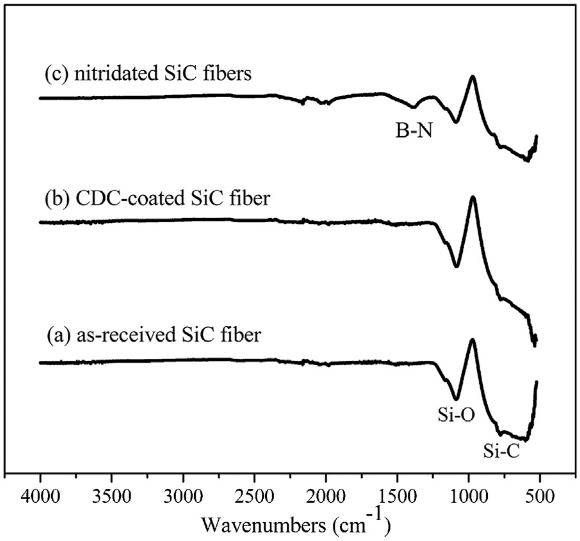

Fig. 1. FT-IR spectrums of: (a) as-received SiC fiber, (b) CDC-coated SiC fiber, and (c) nitridated SiC fiber.

Because the CDC coating was porous with uniform nano-size pores, it could be easily impregnated with boric acid. Multiple impregnations were needed to achieve better infiltration of boric acid for the adequate conversion of the CDC coating into BN coating in accordance with Eqs. (3) and (4). The nitridation was carried out in ammonia gas at 1150 °C. The resultant BN coating was very uniform in thickness and partially crystallized into h-BN. It is very important to note that the strength of the BN-coated SiC fibers is essentially not affected, making this method potentially useful to prepare BN coating on SiC fiber surface for industrial applications.

However, the multiple impregnations make the coating process lengthy. Moreover, a good infiltration of the boric acid is largely limited by the nature of the CDC coating (porosity, pore size and pore size distribution). Therefore, it is difficult to control the degree of nitridation of the CDC coating.

To overcome the above problems, we have developed an improved method to prepare BN coating on SiC fiber surface. An intermediate CDC carbon coating is first prepared by the established chlorination methods [24–27]. BN coating is then formed by carbothermal reduction using trimethylborate ($B(OCH_3)_3$) vapor as the source of boron instead of boric acid. In this paper, the preparation technique is presented and the properties of the obtained coating are characterized.

2. Experiments

2.1. Materials

Silicon carbide fibers (Amosic-202, China) were used as the substrates. The chemical composition of the as-received SiC fibers is as follows (by weight): Si 69.0%, C 30.2% and O 0.8%. Trimethylborate ($B(OCH_3)_3$, Tianjin Jinke Fine Chemicals Technology Lab., China) was employed as the source of boron. NH_3 gas of high purity was used as the nitridation gas. $B(OCH_3)_3$ is a colorless liquid at room temperature. Its boiling point is 68 °C. It is highly volatile, with a vapor pressure of 14.799 kPa at 25 °C. It is moisture-sensitive, and hence should be handled under the protection of inert gas. In comparison with boric acid impregnation, the trimethylborate is constantly introduced as a vapor phase together with ammonia vapor. Therefore, the degree of nitridation can be controlled by the nitridation temperature and duration.

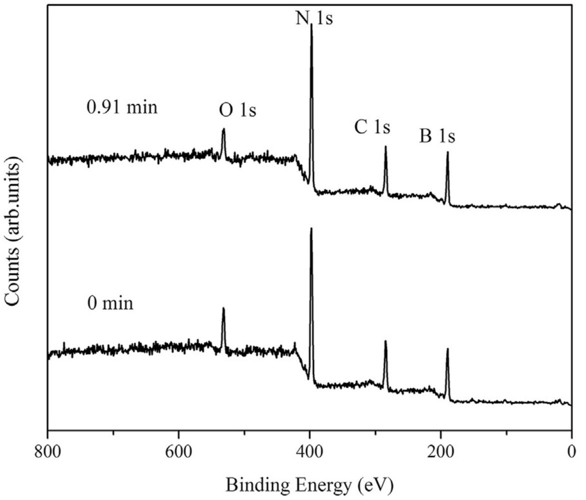

Fig. 2. XPS spectra for the surface (0 min sputtering) and the interior (0.91 min sputtering) compositions.

2.2. Experimental procedure

SiC fibers were treated in high purity chlorine gas Cl_2 at 800 °C for 60 min. The flow rate of chlorine gas was 80 ml/min. The CDC-coated SiC fibers were placed in a graphite boat and put into a horizontal Al_2O_3 tube furnace with an inner diameter of 30 mm. N_2 (99.99%) bubbled through a bottle containing liquid trimethylborate at 25 °C, and then passed through the furnace tube. The flow rate of nitrogen was 80 ml/min. Ammonia gas (99.99%) was also passed through the furnace tube at the flow rate of 80 ml/min. The furnace was then heated to 1300 °C at a ramp rate of 5 °C/min. After residence for 180 min, the ammonia and trimethylborate vapor supply was cut off, leaving only pure N_2 gas to flow in the furnace tube to protect the fibers from oxidation. After holding for additional 60 min to ensure complete carbothermal reduction, the furnace was cooled down to the room temperature under the protection of flowing N_2.

2.3. Characterization

X-ray diffraction (XRD; Bruker-Axs, USA) was used for phase identification. Scanning electron microscopy (SEM; Hitachi SU70, Japan) and high-resolution transmission electron microscopy (TEM; JEM-2100, Japan) were used for microstructure examination. The TEM specimen was prepared by special embedding and ion milling methods according to literature [28]. The chemical structure was analysed by Fourier transform infrared spectroscopy (FT-IR; Thermo IS10, USA).

X-ray photoelectron spectroscopy (XPS; PHI Quantum 2000, USA) analysis was carried out by employing Al $K\alpha_{1,2}$ radiation of 1486.60 eV. Sputtering was performed with Ar ions at an emission current of 20 mA and 4 kV. Pass energy for general scan and core level spectra were kept at 187.85 eV and 58.70 eV, respectively. Specimen charging was observed, which was calibrated by assigning the C 1s signal at 284.8 eV.

Auger electron spectroscopy (AES; PHI660, USA) was used for analyzing the chemical compositions across the fiber diameter. The primary electron beam (5 kV, 100 nA) was at 45° with respect to the surface normal. The sputtering rate (for SiO_2) was estimated to be 16 nm/min.

The resistance of the fibers was measured by two-point probe method and using Sourcemeter 2400 (Keithley, USA). Two aluminum plates were attached on the two ends of the fibers and silver paste was used as the electrodes.