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Short communication

Effect of activation on boron nitride coating on carbon fiber

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Abstract

Boron nitride (BN) thin coating has been formed on the surface of chemically activated polyacrylonitrile (PAN) carbon fibers by dip coating method. The chemical activation of PAN fibers was carried out by two different chemicals, i.e. nitric acid (HNO_3) and silver nitrate ($AgNO_3$) solution. The chemical activation changes the surface properties, e.g. surface area and surface microstructure of the carbon fibers. These surface modifications ultimately influence properties of boron nitride coating on carbon fibers. The boron nitride coating on carbon fibers showed better crystallinity, strength and oxidation resistance when carbon fibers were activated by HNO_3. This improvement in strength and oxidation resistance is attributed to better crystallinity of boron nitride coating on HNO_3 activated PAN fibers.

Keywords: B. Fibers; C. Strength; D. Carbon; Chemical activation; Boron nitride

1. Introduction

Carbon fiber carbon matrix (C/C) composite has widespread application in military and commercial air craft brakes [1] due to their unique combination of thermal, mechanical and wear properties. However, their inherent susceptibility to oxidation around 450 °C limits on their potential applications. Efforts have been made to improve the oxidation resistance of Carbon fiber carbon matrix (C/C) composite with applying an interfacial coating of BN [2,3]. BN has four polymorphic modifications: hexagonal (h-BN), rhombohedral (r-BN), zinc blend type cubic (c-BN) and wurtzite type (w-BN) [4]. The c-BN and w-BN are hard and dense high pressure stable phases [4]. Beside the above-mentioned crystalline structures, there are another form of BN called amorphous (a-BN) and turbostratic BN (t-BN). In case where boron nitride is synthesized at relatively low temperature for example at 900 °C or below, a-BN is generated whereas synthesis or heat treatment at higher temperature (>900 °C) forms t-BN, t-BN forms which on further heat treatment forms h-BN. The t-BN structure can be described based on the structure of h-BN as follows: the individual B–N hexagonal layers are stacked roughly parallel to each other and exhibit random rotation and translation about the normal of layers [4]. BN interfacial coating on carbon fiber has been proposed because of its graphite like structure and its better oxidation resistance than carbon. Several researchers found that carbon fiber/boron nitride matrix (C/BN) or BN interfacial coating in fiber-reinforced ceramic–matrix-composite (CMCs) has better oxidation and mechanical properties [5,6]. To this effect, crystallinity of boron nitride coating can play an important role. The a-BN or t-BN are not resistant against oxidation with respect to h-BN because there will be more entrapment of oxygen because of the loose structure. On the other hand crystallization reduces the extent of oxygen intake [2]. Another important application of thin BN coating is an interfacial layer for controlling the bonding in fiber-reinforced ceramic matrix composites (CMCs) [7]. The mechanical properties of CMCs are largely dependent on the fiber–matrix bonding, which must be weak enough to allow crack deflection along the interface, yet strong enough to retain load transfer from the matrix to the fibers [7].

Several researchers [8,9] have investigated boron nitride coating on fibers by dip coat technique where boric acid was used as precursor material and N_2/NH_3 was used for nitridation. In this paper, we have activated the carbon fiber before develop BN coating from boric acid by dip coating technique. Carbothermal synthesis of BN on chemically activated carbon fiber was reported elsewhere [10]. Due to interaction of activating chemical agents during the activation treatment, the

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surface properties, e.g. surface area, surface microstructure of the carbon fibers were significantly varied [11]. So in the present paper, the effect of different activation agent on crystallinity of the BN coating and its effect on oxidation resistance and tensile strength of fibers were studied and described.

2. Experimental procedure

Polyacrylonitrile (PAN) based high strength carbon fibers (Nikunj, 8H-satin) were used for the present study. The as-received woven PAN fiber was heat treated at 700 °C for 18 h in a tube furnace under flowing N_2. This high temperature carbonization developed consolidated graphite like carbon structure. After the heat treatment, these carbon fibers were chemically activated by following two different methods:

(1) *Nitric acid treatment*: The PAN fibers were placed in a beaker containing concentrated HNO_3 and were heated on water bath maintaining temperature of reactant at 80–85 °C for 120 min. After reaction, the fibers were removed from the acid and rinsed in distilled water several times to remove all the remaining nitrates on its surface.
(2) *Silver nitrate treatment*: The fibers were impregnated in 0.1 M sliver nitrate solution for 1 h followed by drying at 80 °C in an oven. After drying, these fibers were heated in a graphite resistance heating furnace at 750 °C for 5 min in N_2 atmosphere.

Boric acid (H_3BO_3, Merck India Ltd.) and treated polyacrylonitrile (PAN) carbon fibers were used as the raw materials for the synthesis of BN coating on carbon fiber by carbothermal reduction. Carbon fibers were dip coated into a saturated boric acid solution followed by nitridation into a horizontal graphite heated resistance furnace at 1200 °C in N_2 atmosphere for 2 h. Crystallinity of the coated material was investigated by X-ray diffraction (XRD). The XRD patterns of the samples were recorded in X'Pert Pro MPD diffractometer (PANalytical) using X'Celerator operating at 45 kV and 40 mA using Ni filtered CuKα radiation with step size 0.05° (2θ) from 10° to 70°. The percent crystallinity of a sample is defined by the intensity ratio of the diffraction peaks and of the sum of all measured intensities. But, even a completely crystalline sample has some background intensity which arises from imperfections of sample, the X-ray optics of the instrument, sample fluorescence and scatter. This constant background ($Bgr._{const}$) intensity is subtracted from the total intensity ($I_{tot.}$).

$$\text{Crystallinity}(\%) = 100 \times \frac{\sum I_{net.}}{\sum I_{tot.} - Bgr._{const}} \quad (1)$$

The background intensity was determined (separating crystalline peaks or $I_{net.}$ from an amorphous hump) and a constant background value was estimated with respect to original sample (boron nitride powder, 99.5% crystallinity). The percentage of crystallinity was calculated by X'PertHighScore Plus software (PANalytical) [12] using Eq. (1).

Transmission electron microscopy (TEM) was carried out for cross-section of coated carbon fibers. Oxidation resistance of coated fibers were measured in air up to 1200 °C in a DTA/TGA instrument (STA 409C, NETZSCH Gerätebau GmbHs). Single fiber tensile strength was measured following ASTM 3379-75 using Instron universal testing machine.

3. Results and discussion

XRD patterns of the original BN powder, HNO_3 activated boron nitride coated fiber and $AgNO_3$ activated boron nitride coated fiber are shown in Figs. 1 and 2. The percentage of crystallinity with respect to original sample (99.5% crystallinity) has been calculated by using Eq. (1) from XRD analysis. Fig. 3 shows the variation of crystallinity of the boron nitride coated carbon fibers. The crystallinity of HNO_3 activated boron nitride coated fiber is 1.5 times more than that of silver nitrate activated fibers. As all the processing parameters were same for both the cases, except chemical activation step, HNO_3 activation may be the primary reason for increase in crystallinity of BN coating on carbon fiber surface. TEM analysis of cross-section of the coated fiber was carried out for measuring BN coating thickness. For TEM sample preparation, a branch of BN coated carbon fibers were put inside the resin. Very thin cross-section slices of the fibers were cut from the resin-coated fibers in an ultra-microtome. Fig. 4 shows that the coating was non-uniform and the coating thickness varies from 20 nm to 40 nm, irrespective of activation. During the activation process the chemical activating agent impregnated into the bulk. On pyrolysis, impregnated fiber develops a much richer carbon containing material with much more ordered structure. Once the agent was removed during heat treatment, porosity is generated in carbon fibers [13]. Chemical activation is proven to be a very efficient method to obtain carbon fibers with high surface area, ordered structure with narrow micropore

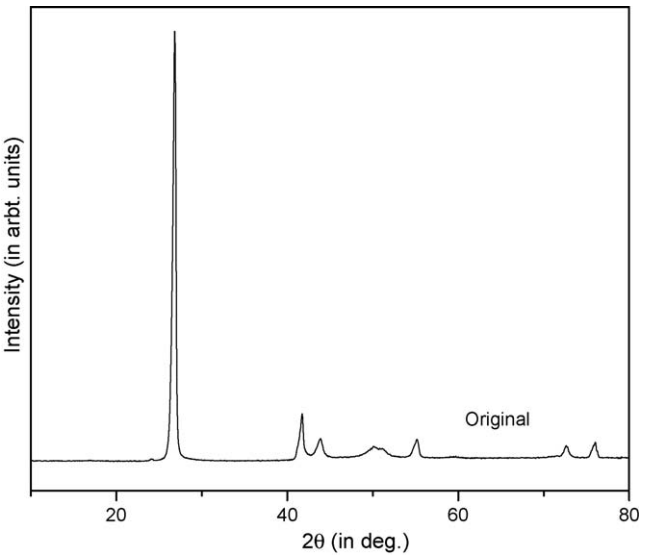

Fig. 1. XRD pattern of original (99.5% crystallinity) sample.

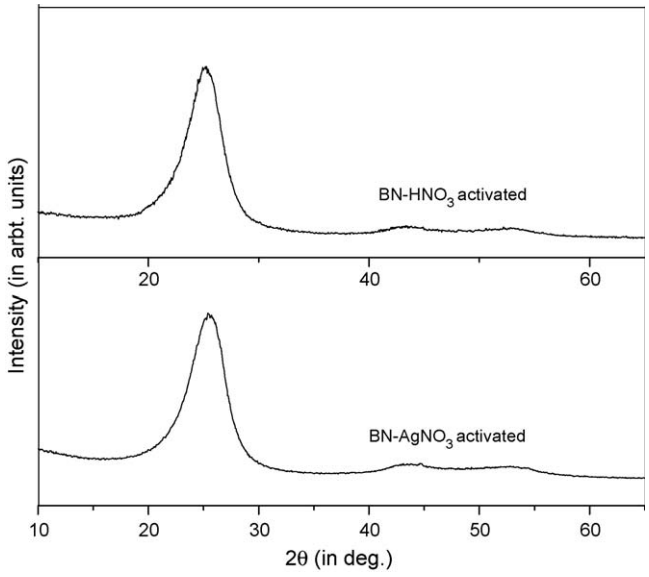

Fig. 2. XRD patterns of HNO_3 and $AgNO_3$ activated BN coated carbon fiber.

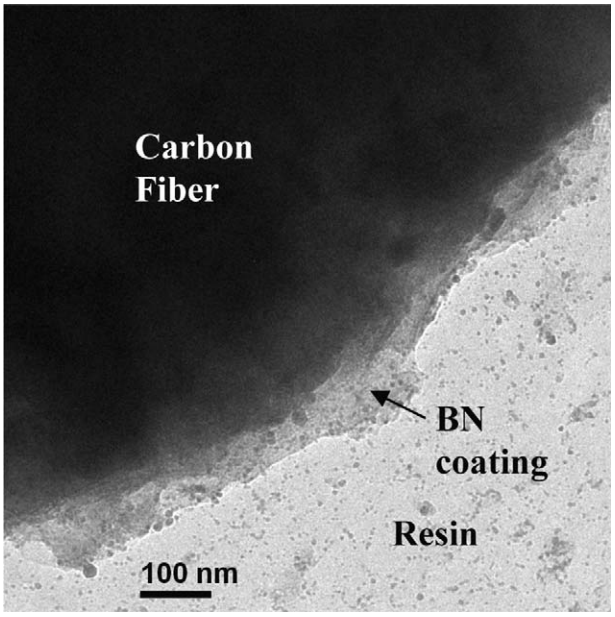

Fig. 4. TEM image of cross-sectional of the boron nitride coated carbon fiber activated by HNO_3, coating thickness varies from 20 nm to 40 nm.

distribution [13]. This higher surface area in activated fiber favours in situ carbothermal reduction of B_2O_3. Activation process generated pores subsequently reduce the strength of the fiber. Therefore, single fiber tensile strength measurement is a very important investigation in such systems. Fig. 5 shows the single fiber tensile strength of coated and uncoated fibers. The strength of as-received fiber increased, after 18 h heating at 700 °C in N_2 atmosphere. This heat treatment reduces surface area by eliminating the surface pores which was also observed by Wang et al. [11]. In both the HNO_3 and $AgNO_3$ activated boron nitride coated fibers showed less tensile strength than as-received PAN fibers. This trend is intuitive because activation process generates pores which reduce the PAN fibers strength. From Fig. 5 it is also observed that HNO_3 activated fibers showed better tensile strength than $AgNO_3$ activated fibers. Improvement in strength may be due to more crystallinity of BN on PAN surface (Fig. 3) and narrow micropore distribution in PAN fibers due to activation by HNO_3. The TGA curve, in Fig. 6 compares the oxidation resistance of boron nitride coated PAN fiber activated by HNO_3 and $AgNO_3$, respectively. In case of HNO_3 activated fibers, the significant weight loss was observed around 750 °C whereas around 550 °C sharp weight loss was observed in $AgNO_3$ activated boron nitride coated fibers. The sharp weight loss in both the fibers is due to oxidation of carbon fibers. Therefore, the significant thermal stability in HNO_3 activated boron nitride coated fibers over $AgNO_3$ fibers is because of better crystalline BN coating on carbon fibers. This crystalline BN coating acts as a diffusion barrier which protects carbon fiber from oxygen at elevated temperature.

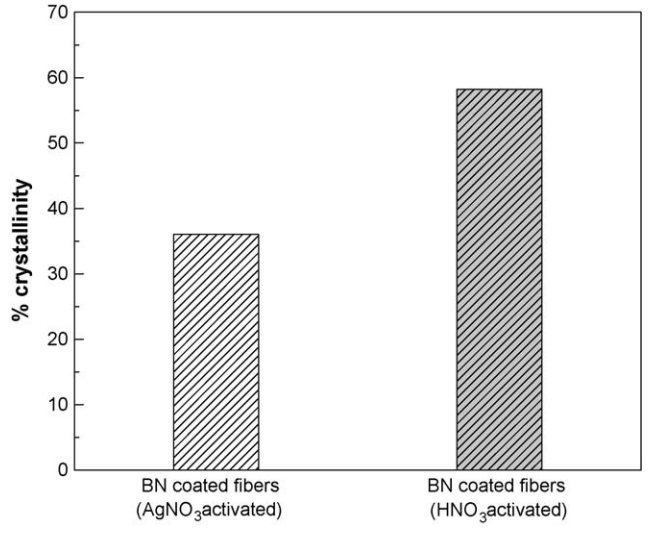

Fig. 3. Crystallinity of $AgNO_3$ and HNO_3 activated BN coated carbon fiber.

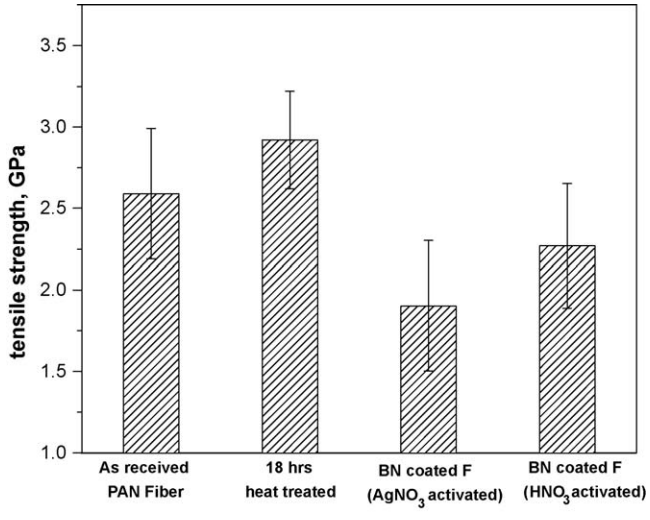

Fig. 5. Comparison of single fiber tensile strength of PAN carbon fibers processed at different processing conditions.

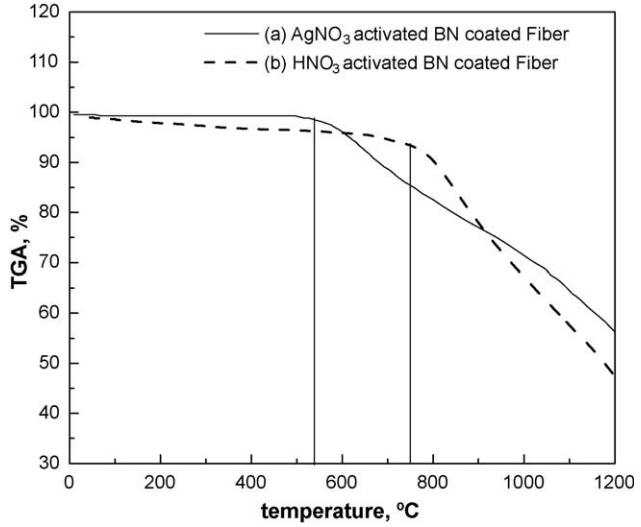

Fig. 6. Oxidation behavior of boron nitride coated carbon fibers: (a) $AgNO_3$ activated; (b) HNO_3 activated.

4. Conclusions

From the above investigation and analysis, it can be concluded that the activation of carbon fiber has definite effect on boron nitride coating. Activation of carbon fiber by HNO_3 is found to be better than that of $AgNO_3$ activated fibers. It also improves the oxidation resistance of boron nitride coated carbon fiber.

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