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Journal of the European Ceramic Society 29 (2009) 2129–2134
www.elsevier.com/locate/jeurceramsoc

Technical note

Carbothermal synthesis of boron nitride coating on PAN carbon fiber

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Received 16 July 2008; received in revised form 25 November 2008; accepted 2 December 2008
Available online 22 January 2009

Abstract

Boron nitride (BN) thin coating has been formed on the surface of chemically activated polyacrylonitrile (PAN) carbon fiber by dip coating method. Dip coating was carried out in saturated boric acid solution followed by nitridation at a temperature of 1200 °C in nitrogen at atmospheric pressure to produce BN coating. Chemical activation improved surface area of PAN fiber which favours in situ carbothermal reduction of boric acid. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) have shown the formation of boron nitride. The X-ray photoelectron spectroscopy reveals that the coating forms a composite layer of carbon, BN/BO_xN_y and some graphite like BCN with local structure of B–N–C and $B(N–C)_3$. The oxidation resistance of the coated fiber was significantly higher than uncoated carbon fiber. Tensile strength measurement reveals that the BN coated fiber maintained 90% of its original strength. As compared to chemical vapor deposition (CVD), this process is simple, non-hazardous and is expected to be cost effective.

Keywords: Carbon; Fiber; Boron nitride; Coating; Strength

1. Introduction

Boron nitride has unique chemical and physical properties, such as low density, high melting point, high thermal conductivity, superior chemical inertness and high electrical resistivity.[1,2] Accordingly the material is widely used both as bulk materials and as in other forms such as thin films, fibers and coatings in electronic and ceramic composite applications.[3,4]

Carbon fiber carbon matrix (C/C) composite has widespread application in military and commercial air craft brakes[5] due to their unique combination of thermal, mechanical and wear properties. However, their inherent susceptibility to oxidation around 450 °C limits their potential applications. Efforts have been made to improve the oxidation resistance of carbon–carbon composites by incorporating BN as coating on C–C composite, infiltration of BN into porous C–C, or BN matrix in a carbon fiber lay up (C–BN).[6] BN has been proposed because of its graphite like structure and its better oxidation resistance. Several researchers found that carbon fiber/boron nitride matrix (C/BN) or BN interfacial coating in fiber reinforced ceramic-matrix-composite (CMC) have better oxidation resistance and superior mechanical properties.[7–9] Higher oxidation resistance is due to the fact that at higher temperature, BN forms a protective B_2O_3 layer.[6,10] Another important application of thin BN coating is an interfacial layer for controlling the bonding in fiber-reinforced CMCs.[4,11] 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.[12–14] Up till now, boron nitride thin coatings for fibers in reinforced CMC materials have been prepared primarily by chemical vapor deposition method.[15–17] However, CVD techniques have some disadvantages too. For instance, CVD process may require high vapor pressure of some hazardous and expensive chemical precursors, such as BCl_3 and NH_3, for boron nitride CVD coating.

Several researchers[18,19] 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 apply coating through conventional dip coating technique. The activation treatment of the carbon fiber significantly varied the surface

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doi:10.1016/j.jeurceramsoc.2008.12.004

properties e.g. surface area, surface microstructure, of the carbon fibers.[9] This increase in surface area reduces nitridation temperature. BN coating on carbon fiber were characterized and mechanical properties of the coated fibers were evaluated. The advantage of this method is that it is simple, using much cheaper and less toxic chemical precursor i.e., H_3BO_3 and N_2.

2. Experimental

2.1. Sizing removal of PAN fiber

The fibers used in this study were all high strength polyacrylonitrile (PAN) based fibers (Nikunj, 8H-satin). These fibers were obtained with sizing hence surface treatment required for sizing removal. The as-received PAN fiber woven was treated at 700 °C for 18 h, in a tube furnace with flowing N_2.

2.2. Preparation of activated carbon fiber

After sizing removal 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 surfaces. The specific surface area of the activated samples, were determined by nitrogen adsorption at −195.75 °C performed on a Micromeritics ASAP 2010C automatic analyzer.

2.3. Preparation of BN coating

Boric acid (H_3BO_3) from (Merck India Ltd.) and treated PAN base carbon fiber were used as the raw materials for the synthesis of in situ BN coating on carbon fiber by carbothermal reduction. Boric acid was used as the precursor for the synthesis of BN. A vacuum chamber was used to infiltrate saturated H_3BO_3 (99.99% purity) solution into the carbon surface and followed by the fibers were dried at 100 °C. The infiltration step was repeated two to three times to improve the coating thickness. These coated fibers were loaded in a carbon crucible and put into a horizontal graphite heated resistance furnace. The nitridation reaction was carried out at 1200 °C in N_2 atmosphere for 2 h. The nitrogen used in this study had a purity of 99.99%.

2.4. Characterization

Scanning electron microscopy (SEM, Leo S430) was employed to investigate the carbon fiber morphologies. X-ray photoelectron spectroscopy (XPS) measurements were carried out for the BN coated carbon fibers, using a PerkinElmer spectrometer employing Mg K_α radiation of 1253.6 eV at a base pressure of 6.67×10^{-8} Pa at 26.85 °C. The overall instrumental resolution was about 0.3 eV. Sputtering performed with Ar ions with a emission current of 20 mA and 4 kV with base pressure maintained at 1.33×10^{-4} Pa. Pass energy for general scan and core level spectra kept at 100 eV and 60 eV, respectively. During photoemission studies, small specimen charging was observed which was later calibrated by assigning the C 1s signal at 284.6 eV. Oxidation resistance of coated and uncoated carbon fibers were measured in air up to 1200 °C in a DTA/TGA instrument (STA 409C, NETZSCH Gerätebau GmbH). Tensile strength of the carbon fibers before and after BN coating was measured at room temperature following ASTM 3379-75 using Instron universal testing machine. 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 0.5 mm/min, was set. At least 25 fibers were mechanically tested for each treatment condition for a single data point.

3. Results and discussion

Shining nature of PAN fiber was reduced after sizing removal step due to the removal of polymer coating. Chemical activation made it more black and fibers were separable. The specific surface area of the simple heat treated PAN carbon fiber improves from 0.61 m^2/g to 10.12 m^2/g and 20.62 m^2/g after activate the carbon fiber in HNO_3 for 2 h and 4 h, respectively. Chemical activation is proven to be a very efficient method to obtain carbons with high surface area, ordered structure and narrow micropores distribution.[20] This higher surface area in activated fiber favours in situ carbothermal reduction of B_2O_3.

The surfaces of the carbon fiber before and after chemical activation were examined through SEM. Fig. 1a shows the surface of the carbon fiber heat treatment at 700 °C in N_2 for 18 h. The heat treated carbon fiber shows smoother surface than the carbon fiber surface after chemical activation by HNO_3, shown in Fig. 1b. The elongated pores on the carbon fiber surface after chemical activation are distinct. During the activation process,

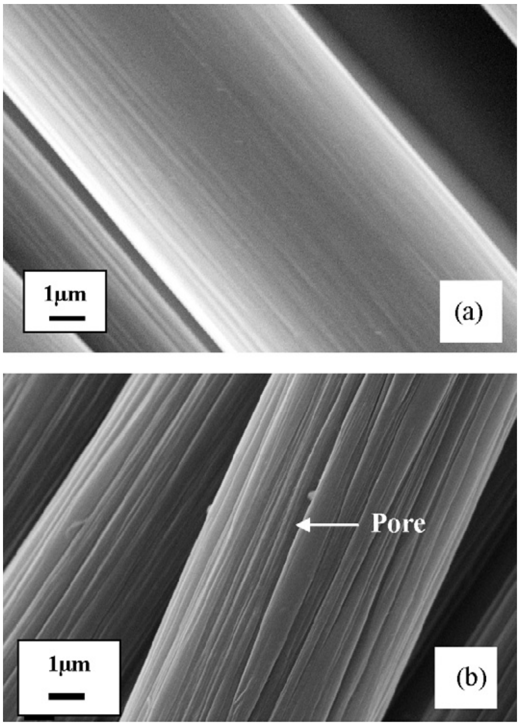

Fig. 1. SEM images of the carbon surface (a) surface of PAN fiber heat treated at 700 °C for 18 h, in N_2 and (b) surface of PAN fiber after chemically activated by HNO_3 for 2 h.

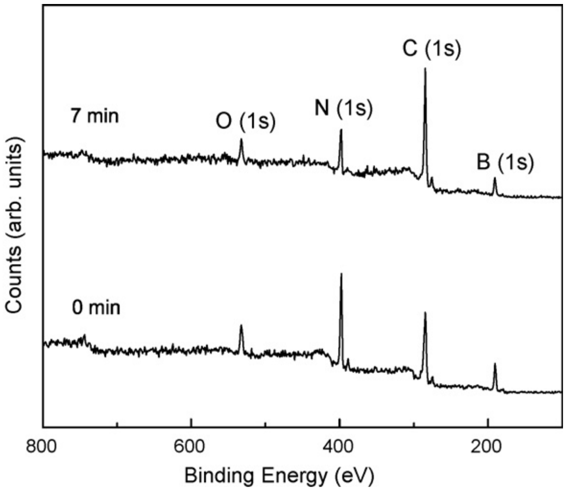

Fig. 2. XPS survey spectra of BN coated carbon fibers for top surface of BN coating composition (0 min) and underneath composition (7 min, sputtering).

the HNO_3 impregnate into the bulk and on heat treatment at 80–85 °C of the impregnated fiber develops pores in the carbon fiber.[20]

In order to identify chemical bondings of the coating, XPS were conducted on coated carbon fibers. Fig. 2 shows the survey scan XPS spectrum for pre-sputtering (0 min, top surface composition) and post-sputtering conditions (7 min, inner surface composition), indicate the presence of B 1s (190.6 eV), C 1s (284.6 eV), N 1 s (398.0 eV) and O 1s (532.6 eV). Fig. 3 shows the 1s core level spectra of B, N, C and O for coated carbon fiber sample after 7 min, sputtering. The full width half maximum (FWHM) of B 1s, N 1s, C 1s and O 1s peaks are 2.53 eV, 2.24 eV, 2.24 eV and 2.31 eV, respectively. The broad FWHM suggests that there are more than one type of bonding scheme for B, N, C and O atoms. The XPS spectra were therefore resolved to investigate possible chemical bonding existing in the coating. As shown in Fig. 3a, the deconvolution of B 1s spectra gives two peaks centered at 190.8 eV and 192.1 eV. It was reported that B 1s spectra have peaks at 188.4 eV and 189.4 eV for B_4C and $BC_{3.4}$, respectively and 190.8 eV for h-BN.[21] According to NIST data base, B 1s spectra of B_2O_3 should be observed at around 193 eV.[22] Thus the resolved peak at 190.8 eV can be attributed to B–N bonding and the other peak at 192.1 eV[18] suggests that there might be some oxynitrides (BO_xN_y) contained along with some B_2O_3 species in the BN coating. This shift of B 1s peak towards higher energy is owing to the higher electronegativity of oxygen to that of nitrogen. The binding energy of B 1s spectra clearly indicates that carbidic bonding fractions are absent in the coating. In Fig. 3b, the deconvolution of the N 1s spectrum gives two peaks centered at 398.4 eV and 399.6 eV. The former can be assign to the N–B bonding and the later to the N–C bonding.[23] The deconvolution of the C 1s spectrum gives two peaks centered at 284.9 eV and 285.6 eV as shown in Fig. 3c. The resolved peak at 190.8 eV can be attributed to C–C bonding[24] and C 1s energies >285 eV are assigned to C atoms which are bonded to the more electronegative N.[24] The binding energy of C 1s involved in ethylamine is 285.6 eV, this allows us to assign the peaks at 285.6 eV to C–N bonding.[24] The deconvolution of the O 1s spectrum gives two peaks centered at 532.5 eV

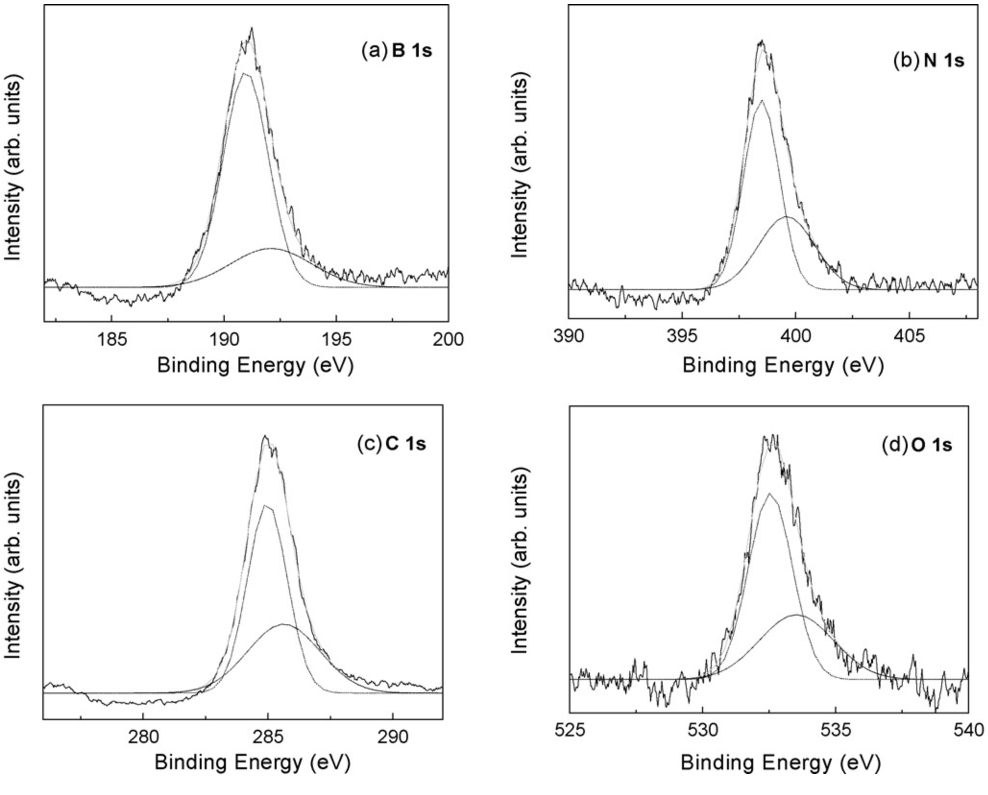

Fig. 3. XPS spectra of (a) B 1s, (b) N 1s, (c) C 1s and (d) O 1s for BN coated carbon fiber sample after 7 min, sputtering.

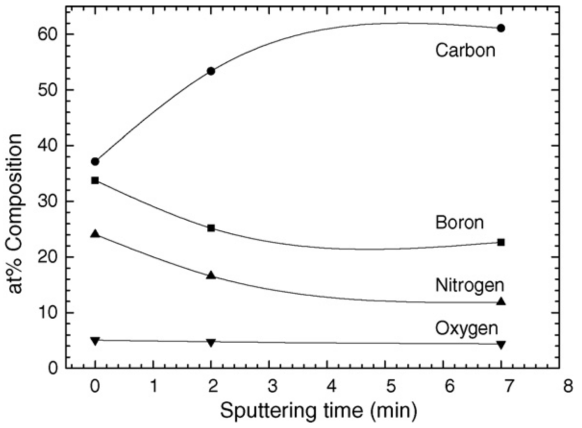

Fig. 4. Elemental at% of C, B, N and O varies from the surface (layer after 0 min, sputtering) of BN coating on carbon fiber to underneath (the layer after 7-min, sputtering).

and 533.5 eV as shown in Fig. 3d. It was reported that the O 1s spectra have peaks at 532.6 eV and 533.2 eV for BO_xN_y and B_2O_3.[25,26] It indicates the coating contains BO_xN_y along with some B_2O_3.

From XPS analysis the elemental at% composition at different sputtering time was plotted in Fig. 4. The at% of C, B, N and O from the surface (layer after 0 min, sputtering) of BN coating on carbon fiber as well as from underneath (the layer after 7-min, sputtering) are curve fitted and compared in Fig. 4. It is evident from the figure that with increasing sputtering time C increases and B, N and O decreases from BN coating surface to underneath. The oxygen content in the coating is lowest at all sputtering time. Presence of carbon in all the layers indicates carbon diffusion from carbon fiber toward surface which ensures better availability of carbon for carbothermal reduction of B_2O_3. Presence of B 1s, N 1s and O 1s after 7 min, of sputtering indicates formation of a composite layer consist of carbon, BN, BO_xN_y and some graphite like BCN with local structure of B–N–C and B(N–C)$_3$.[23] Fig. 5 shows the variation of N/B, B/C and O/B atomic ratio in the BN coating at different sputtering time. The N/B, B/C and O/B atomic ratios range from 0.71 to 0.52, 0.91 to 0.37 and 0.15 to 0.19, respectively in dip coated BN, which are comparable to those of CVD BN coatings.[18,25] It is evident from Fig. 5 that, the B/N, B/C ratio deceases and O/B ratio increases from surface of the coating to underneath (layer after 7 min, sputtering). This is obvious because the BN coatings were formed by nitriding the B_2O_3 coating on the carbon fiber with N_2 gas. Thus nitridation should start from the surface and proceed to the interior of the coating towards the fiber. As the nitridation process controlled by the N_2 diffusion, it is reasonable that more oxygen was contained in the interior than on the surface of BN coating. The presence of carbon in the coating also enhanced the nitridation process of B_2O_3 to BN.

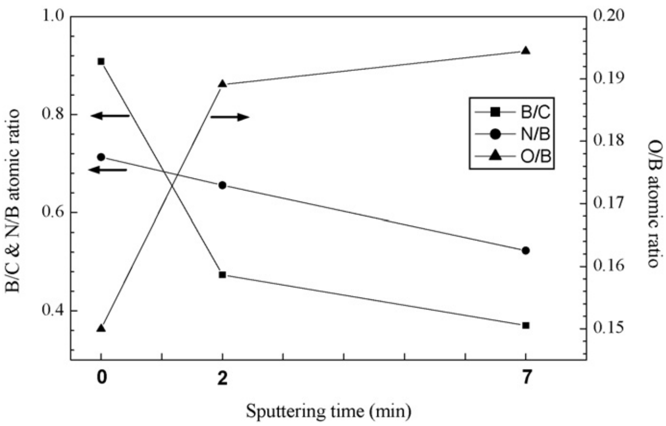

Fig. 5. N/B B/C and O/B atomic ratio variation from the surface of BN coating on carbon fiber to underneath (the layer after 7-min, sputtering).

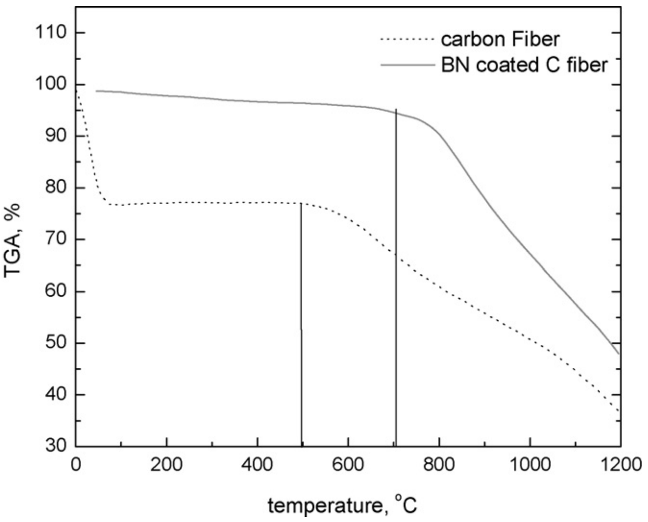

Fig. 6. Oxidation behavior of BN coated and uncoated carbon fiber, in air.

The TGA curve, in Fig. 6 compares the oxidation resistance of boron nitride coated and uncoated carbon fiber, where air was used as the oxidizing gas. In case of uncoated carbon fiber, the sharp weight loss was observed around 100 °C and 500 °C. The weight loss at 100 °C is due to moisture removal whereas the sharp weight loss around 500 °C is due to oxidation of carbon fiber. In boron nitride coated carbon fiber no significant weight loss was observed up to 700 °C which is due to higher oxidation resistance of BN in air. The BN coating on carbon fiber acts as a diffusion barrier which protects carbon fiber from oxygen at elevated temperature. Even on oxidation of BN, as soon as the first layer of B_2O_3 is formed, oxidation is retarded as the B_2O_3 layer forms a protective liquid coating. This phenomenon is responsible for superior oxidation resistance of BN coated carbon fiber.

3.1. Mechanical property of the coated fibers

Chemical activation process greatly increases surface area of carbon fibers by generating pores which subsequently weaken the fiber hence single fiber tensile strength is very important. Fig. 7 shows the single fiber tensile strength of coated and uncoated fibers. The strength of the as-received fiber increases, 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.[27] However after activation by

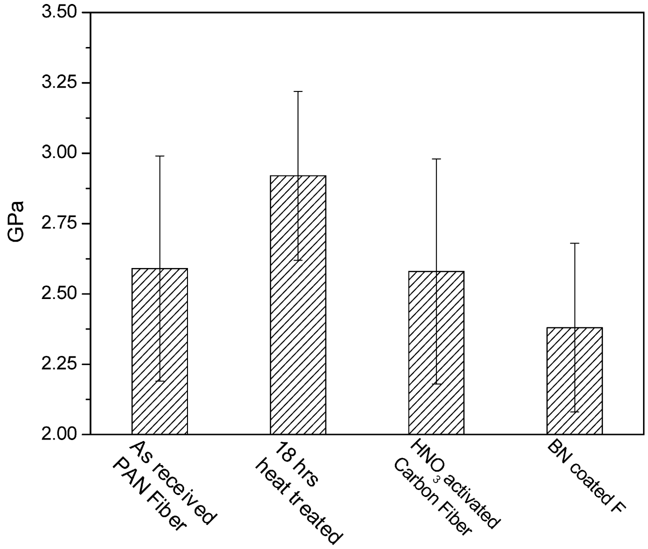

Fig. 7. Comparison of single fiber tensile strengths of BN coated and uncoated carbon fibers.

HNO_3 the strength of the heat treated carbon fiber decreases from 2.92 GPa to 2.46 GPa. During the chemical activation process the activating agent HNO_3, impregnate into the fiber and on heating at 80–85 °C, it etches out carbon and develops a much richer carbon content material with porosity.[20] Due to this pore formation, strength of the carbon fiber decreases. These activated fibers were coated with boric acid and nitrided under N_2 to form BN coating. The tensile strength of BN coated fiber was found to be comparable to activated carbon fibers as described above, inspite of the fact that BN was formed at the expense of carbon from C-fiber. It indicates that the coated fiber forms a composite layer of BN and carbon along with some graphite like BCN with local structure of B–N–C and $B(N–C)_3$ which form at the phase boundaries of C–C bonding region.

4. Conclusions

Boron nitride coating on activated PAN carbon fiber can be obtained by dip coating technique using boric acid and nitrogen. Activation of carbon fiber was found to increase surface area. As a result of this, nitridation temperature was reduced to 1200 °C under N_2 atmosphere. The BN coating thus obtained have a N/B, B/C and O/B ratios range from 0.71 to 0.52, 0.91 to 0.37 and 0.15 to 0.19, respectively, which are comparable to those of CVD BN coatings. The coating layer was found to consist of carbon, BN, BO_xN_y and some graphite like BCN with local structure of B–N–C and $B(N–C)_3$. Oxidation resistance of the coated fiber increased without much sacrifice of mechanical strength.

Acknowledgements

The work described in this paper is supported by the ASL, DRDO Govt. of India. The authors wish to thank the staff-members of Non-Oxide Ceramic and Composite Division, CGCRI for their cooperation and help.

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