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Effect of Ar dilution flow rate on LPCVD a boron-doped carbon coating from BCl₃-C₃H₆-H₂-Ar mixtures

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A boron-doped carbon coating was deposited from a $BCl_3-C_3H_6-H_2-Ar$ system by LPCVD. The effects of the Ar dilution flow rate on deposition rates, morphologies, compositions and bonding states were investigated. Deposition rates were almost the same, about 250 nm/h with different Ar dilution flow rate. Surface morphologies were also almost the same. The flat conchoidal aspect of the fracture surface transformed to a laminated structure with an increase in the Ar dilution flow rate. The carbon concentration was above 76.3 at.%, and the boron concentration was less than 17.9 at.%. The boron concentration increased with an increase in the Ar dilution flow rate, corresponding to a decreasing carbon concentration. The main bonding state of boron was B-sub-C and BC₂O. The whole deposition process was dominated by a PyC formation reaction, which led to almost the same deposition rate with different Ar dilution flow rates.

Key words: boron-doped carbon, Low pressure chemical vapor deposition, Dilution gas, Deposition rate, Morphologies and compositions

Introduction

Carbon-containing composites such as C/C, C/SiC and SiC/SiC exhibit outstanding mechanical properties, particularly at high temperatures [1]. However, their applications are severely limited in oxidizing environments due to the poor oxidation resistance of carbon fibers and carbon interfaces in these composites [2]. Boron-doped carbon has been studied as a means of preparing oxidation-resistant carbon [3-11]. It was also discovered that these carbon-bearing materials are new host materials for intercalation compounds of fluoro-acids or akali metals and anodes for lithium ion rechargeable batteries. [6, 12-16]

There are several methods for preparing boron-doped carbon. Lowell [3] synthesized a boron-substituted graphite structure by heating graphite flakes and B_4C . He found that the lattice constants varied according to the boron concentration and the maximum boron solubility was 2.35 at.% at 2350 °C. Yogo *et al.* [17] also synthesized BC_x samples with 0.5-5.7 wt.% boron by high pressure pyrolysis of an organoborane copolymer. Chemical vapor deposition (CVD) is a more suitable technique to prepare carbon materials with a high content of homogeneously distributed boron, as reported by Way *et al.* [15] and Cermignani *et al.* [4]. These authors have prepared $B_xC_{l,x}$ materials from BCl₃-C₆H₆ gaseous mixtures and

obtained maximum boron contents of 15-17 at.%. Derre et al. [18] have reached a boron content in carbon of 22 at.% from BCl₃-C₂H₂ gaseous mixtures and Kouvetakis et al. [13] synthesized BC₃ by CVD of C_6H_6 and BCl₃ at 800 °C. Electron diffraction of BC₃ showed 00l and hk0 reflections which correspond to the graphite-like structure, but no single crystal has been obtained so far. A more detailed study by Shen [6] revealed that the concentration of boron decreased with increasing deposition temperature. The BC₆ was acquired at 1000 °C. Jacques et al. have deposited BC_x from BCl_3 - C_3H_8 [5] gaseous mixtures and achieved a boron content of 33 at.%. Fecko et al. [7] prepared BC₃ by atmospheric pressure chemical vapor deposition (APCVD). A recent study by Hu and Chung [19] revealed the synthesis of BC_x by heat treatment of boron-containing pitch using 9chloroborafluorence as a precursor.

Pyrocarbon (PyC) was an important component in C/C [20-25], C/SiC [26-28] and SiC/SiC composites [29-32]. In C/C composites, PyC was usually used as a matrix. In C/SiC and SiC/SiC composites, PyC was used as an interphase. C_3H_6 was the usual carbon precursor of PyC if it is prepared by CVD or CVI [23-32], however, no report on boron-doped carbon deposited from BCl₃- C_3H_6 gaseous mixtures was found. It is apparent that the oxidation resistance of C/C, C/SiC and SiC/SiC composites would be improved if boron was introduced in PyC during deposition procedure. Therefore, we choose C_3H_6 as a carbon resource to prepare boron-doped carbon materials.

In the present studies, we have attempted to evaluate the effects of the Ar dilution flow rate on the deposition

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Fig. 1. Schematic of the vertical hot-wall reactor used to deposit coatings using a BCl_3 - C_3H_6 - H_2 -Ar system.

Table 1. Process parameters of LPCVD boron-doped carbon



Fig. 2. The relationship between deposition rate and Ar flow.

Substrate	BCl ₃ (m <i>l</i> .minute ⁻¹)	C ₃ H ₆ (ml.minute ⁻¹)	H_2 (ml.minute ⁻¹)	Ar(ml.minute ⁻¹)	T (K)	t (h)	Pressure (Pa)
Carbon fiber	10	10	200	200~500	1223	20	1000

rate, morphology, elemental contents and bonding states in boron-doped carbon deposited from $BCl_3-C_3H_6-H_2$ gaseous mixtures. The effect of the Ar dilution flow rate on the infiltration behavior of boron-doped carbon is also demonstrated. Finally, a deposition mechanism is discussed.

Experimental

Boron trichloride (BCl₃ \geq 99.99 vol.% and iron < 10 ppm) was used as a boron source for CVD boron-doped carbon. The carbon source was provided by propylene (C₃H₆ \geq 99.95 vol.%) gas. Hydrogen (H₂ \geq 99.999 vol.%) was another reactant. Argon (Ar \geq 99.999 vol.%) were used as a dilution gas for the reactants.

A schematic of the experimental system used for the deposition of boron-doped carbon is shown in Fig.1. For this system, the reagents (BCl₃, C_3H_6 and H_2) were delivered by gases flowing through mass-flow meters. Reagents were carried to the reactor in stainless-steel lines and then introduced into the furnace. The deposition reactor was a vertical, hot-wall deposition furnace; the temperature within the reactor was controlled with a thermocouple. The pressure within the reaction vessel was measured using a pressure transducer. A buffer and a vacuum pump, which were used to operate at reduced pressure, were located downstream from the reactor. T-300 carbon fiber bundles from Japan Toray were employed as substrates. The process parameters of LPCVD borondoped carbon are summarized in Table 1.

The cross-section morphologies of the deposit were observed with a Hitachi S-2700 scanning electron micro -scope(SEM, S-2700). X-ray photoelectron spectroscopy (XPS)(AXIS ULTRA, KRATOS ANALYTICAL Ltd.) was used to analyze the various bonds in which boron is involved. XPS analyses were performed using 1486.71 eV monochromatic A1 Ka radiation (15 kV, 10 mA). To compensate for surface charges effects, binding energies were calibrated using the C 1 s hydrocarbon peak at 284.8 eV.

Results and discussion

Deposition rate

The deposition rate was calculated through following formulae:

$$H_{av} = \frac{H_1 + H_2 + \dots + H_{10}}{10} \tag{1}$$

$$v = \frac{H_{av}}{t} \tag{2}$$

In formulae (1) and (2), H_{av} refers to the average thickness of deposits, in nm; Hi (i = 1, 2, 3 ··· 10) refers to the thickness of deposits in different areas, in nm; v refers to the average deposition rate, in nm/h;*t* refers to the deposition time, in h. In order to acquire an average thickness, ten different positions were observed.

Fig. 2 shows the function of the average deposition rate with the Ar dilution flow rate. The average deposition rates are almost 250 nm/h. The discrepancy of the maximum and minimum values is only 20 nm/h as shown in Fig. 2. It is apparent that the influence of the Ar dilution flow rate on the deposition rate is low. These results show the deposition rate depends on the deposition temperature. The deposition process is controlled by kinetic or surface reactions.

Morphologies

Fig. 3 shows the surface morphologies of boron-doped carbon deposited with different Ar dilution flow rate. There are uniform, smooth and compact deposits on



Fig. 3. Surface morphologies of boron-doped carbon deposited with different Ar dilution flow rate (a) 200 ml \cdot minute⁻¹ (b) 300 ml \cdot minute⁻¹ (c) 400 ml \cdot minute⁻¹ (d) 500ml \cdot minute⁻¹.



Fig. 4. Cross-sectional morphologies of CVD boron-doped carbon with different Ar dilution flow rate (a) 200 ml·minute⁻¹ (b) 300 ml·minute⁻¹ (c) 400 ml·minute⁻¹ (d) 500 ml·minute⁻¹.

carbon fiber. The diameters of the coated fiber are almost same after deposited with different Ar dilution flow rate. It is apparent that the effects of Ar dilution flow rate on surface morphologies and deposit thicknesses are almost the same. The mechanisms are discussed in the following part.

Fig. 4 shows the cross-section morphologies of borondoped carbon on single fibers with different Ar dilution



Fig. 5. Cross-section morphologies of CVD boron-doped carbon in fiber bundle with different Ar dilution flow rate (a) 200 ml minute⁻¹ (b) 300 ml minute⁻¹ (c) 400 ml minute⁻¹ (d) 500 ml minute⁻¹.

Table 2. Element content of boron-doped carbon deposited with different Ar dilution flow rate

Ar flow rate	Content (at.%)			
(ml.minute ⁻¹)	В	С	0	
200	17.9	76.3	5.8	
300	14.4	81.7	3.9	
400	13.0	83.8	3.2	
500	11.8	86.2	2.0	

flow rate. The thicknesses of deposits are almost $5.0 \mu m$, which show the Ar flow rate has no influence on the thicknesses of deposits. However, the cross-sectional morphologies are influenced by the Ar flow rate. The morphologies are compact and non-layered when the Ar flow rate is 200 ml.minute⁻¹. Then nano-delamination occurs when the Ar flow rate is 300 ml.minute⁻¹. There is obvious delamination when the Ar flow rate is above 400 ml.minute⁻¹.

Fig. 5 shows the infiltration behavior of boron-doped carbon in carbon fiber bundles. The deposits of about 1-2 μ m thicknesses are uniformly infiltrated in fiber bundles.

Composition and bonding states

Table 2 shows elemental contents of boron-doped carbon deposited with different Ar dilution flow rate analyzed by XPS. The boron elemental content decreased and the carbon elemental content increased with an increase in the Ar dilution flow rate. The boron and carbon concentrations are 17.9 at% and 76.3 at.% respectively, when the Ar dilution flow rate is 200 ml.minute⁻¹. However, the boron and carbon concentrations are 11.8 at.% and 86.2 at.% respectively, when the Ar dilution flow rate is 500 ml.minute⁻¹. The oxygen concentration decreases from 5.8 at.% to 2.0 at.% with the Ar dilution flow rate increasing from 200 ml.minute⁻¹ to 500 ml.minute⁻¹.

The deconvoluted B1s XPS spectrums of boron-doped carbon coatings deposited with different Ar dilution flow rates are given in Fig. 6. The corresponding bonding states and bonding contents are included in Table 3. These results show there are the same bonding states of boron with different Ar dilution flow rate. According to the XPS results, the XPS spectra of boron can be deconvoluted into five peaks, which are marked a, b, c, d and e in Fig.6. The components (a) and (b) at 188.0 and 188.9 eV respectively can be associated with a boron-carbon bonding such as the B-C bond (187.8 eV) and B-sub-C (188.8 eV) as shown in Table 3, which is also proposed by Cermignani et al. [4]. As shown in Table 3, the high energy areas such as (c), (d) and (e) at 190.0, 191.8 and 193.2 eV respectively can be associated with BC_2O (190.0eV), BCO_2 (192.0eV) and B_2O_3 (193.0eV), which are correspond to boron atoms being more and more oxidized. In all these bonding states, the binding energy of the B-C bonding is the same as the standard binding energy of B-C in B₄C. The B-sub-C bonding state refers to the state where a carbon atom



Fig. 6. The deconvoluted B Is XPS peak for boron-doped carbon with different Ar dilution flow rate (a) 200 ml \cdot minute⁻¹ (b) 300 ml \cdot minute⁻¹ (c) 400 ml \cdot minute⁻¹ (d) 500 ml \cdot minute⁻¹.

Table 3. Bonding states and their content of boron-doped carbon deposited with different Ar dilution flow rate and analyzed by XPS

Area content (at.%)	а	b	с	d	e
Bonding Energy (ev)	188.0	188.9	190.0	191.8	193.2
Bonding state	B-C (187.8)	B-sub-C ^a (188.8)	BC ₂ O (190.0)	BCO ₂ (192.0)	$B_2O_3(193.0)$
200 ml.minute ⁻¹	16.1	33.0	36.3	10.6	4.0
300 ml.minute ⁻¹	16.9	32.0	33.1	11.8	6.2
400 ml.minute ⁻¹	17.4	32.6	34.3	11.0	4.8
500 ml.minute ⁻¹	14.4	34.8	32.9	12.3	5.7

^aB-sub-C refers to carbon atom in graphite structure is substituted by boron atom.

is substituted by a boron atom in the graphite crystal structure. The binding energy of the B-O bonding state is the same as the standard binding energy of B-O bond in B_2O_3 .

It is obvious that the bonding state contents with different Ar dilution flow rates are almost the same as shown in Fig. 6 and Table 3. It is apparent that the B-sub-C and BC₂O are major bonding states. The total content of B-sub-C and BC₂O is above 65.0 at.% with every Ar dilution flow rate. The maximum content of the B-C bonding state is only 17.4 at.%. The B-C bonding state contents are slightly different with different Ar dilution flow rates.

Deposition process mechanism

It is apparent that the deposition rates, morphologies, compositions and bonding states of deposits are relevant to the deposition reaction. In the $BCl_3-C_3H_6-H_2$ -Ar system, there may be three types of deposits, which are boron carbide, boron and carbon. The deposition reaction equations are as follows:

$$C_3H_6 \to 3C + 3H_2 \tag{3}$$

$$BCl_3 + C_3H_6 + H_2 \rightarrow B - sub - C + HCl \tag{4}$$

$$12BCl_3 + C_3H_6 + 15H_2 \to 3B_4C + 36HCl$$
(5)

$$2BCl_3 + 3H_2 \rightarrow 2B + 6HCl \tag{6}$$

According to the XPS results, reaction (3) is the major reaction during the whole deposition process since the carbon content is above 76.3 at.%, which leads to almost the same deposition rates with different Ar flow rates. Reactions (4) and (5) are subordinate reactions since the boron contents are less than 17.9 at.%. No reaction (6) exists during the deposition process since the B-B bonding state was not found by XPS analysis.

Conclusions

(1) The deposition rate is not influenced by the Ar dilution flow rate. The deposition rates are about 220 nm/minute⁻¹ with all Ar dilution flow rates.

(2) Surface morphologies were also almost the same. The flat conchoidal aspect of the fracture surface would transform to laminated cross-section morphologies with increasing Ar dilution flow rates.

(3) The carbon concentration was above 76.3 at.%, and the boron concentration was less than 17.9 at.%. The boron concentration increased and with an increase

in the Ar dilution flow rate, corresponding with a decrease carbon concentration. The main bonding states of boron were B-sub-C and BC₂O.

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