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Effect of Deposition Temperature on Dynamics and Mechanism of Deposition for Si–B–C Ceramic from $BCl_3/SiCH_3Cl_3/H_2$ Precursor

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The deposition rate, phase, chemical composition and microstructure of deposits were determined from 950 to 1100 °C. With increasing temperature, the deposition rate increases, and the morphology changes from smooth to coarse, meanwhile, the concentration of silicon increases while that of boron decreases. The deposition process is controlled by chemical reactions, and the activation energy is 271 kJ/mol. At relatively lower temperature (below 1000 °C), the deposition process is dominated by formation of B_4C. While at higher temperature (above 1000 °C), it is governed by formation of SiC. B_4C and SiC disperse uniformly in the Si–B–C co-deposition system and form a dense network structure.

KEY WORDS: Si–B–C ceramic; Chemical vapor deposition (CVD); Deposition mechanism; Morphology

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1. Introduction

Continuous carbon or silicon carbide fiber reinforced silicon carbide ceramic matrix composites (CMC-SiC) have been developed and tested in the high-temperature and long-time structural applications such as components of turbine engines due to their excellent physical and mechanical properties, especially low density, high specific strength, high specific modulus and reliability[1–4]. However, a large amount of residual pores and micro-cracks are inevitably induced in the matrix and coatings of CMC-SiC during fabrication and annealing[5]. These residual pores and micro-cracks can improve toughness of CMC-SiC by crack deflection with energy dispersion; however, they also provide routes for oxidative medium, and therefore lead to oxidation of carbon fibers and interphase pyrolytic carbon (PyC), which limits the long-term application of CMC-SiC under severe oxidizing conditions at high temperature[6–8].

Consequently, it is necessary to develop a kind of self-healing matrix or coating to protect the carbon fiber and PyC. CMC-SiC modified with B_xC[9–11] and Si–B–C[12–14] ceramics, which have been developed, show excellent oxidation resistance during a large temperature range, *i.e.* from 450 to 1500 °C. Boron oxide and borosilicate glass from oxidized B_xC and Si–B–C ceramics, can seal micro-cracks and pores existing in the matrix and coating, which can protect carbon fiber and interphase PyC from oxidizing.

Chemical vapor deposition (CVD) has been widely used to prepare B_xC and Si–B–C ceramics. In previous work, the B_xC ceramic was well investigated using different precursors, such as $BCl_3/CH_4/H_2$[15,16], $BCl_3/C_3H_6/H_2$[17], $B_2H_6/CH_4/H_2$[18]. For Si–B–C ceramic, BCl_3/CH_3SiCl_3(MTS)/H_2 system was investigated at 40 kPa (0.395 atm) from 927 to 1127 °C by Goujard *et al*[19]. The investigation of the Si–B–C ceramic deposition process from BCl_3/MTS/H_2 precursor was carried out through Fourier transform

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Table 1 Process parameters of CVD Si–B–C system

Substrate	T/°C	MTS/ml·min^{-1}	BCl$_3$/ml·min^{-1}	H$_2$/ml·min^{-1}	Ar/ml·min^{-1}	t/h	Pressure/Pa
Carbon cloth	950–1100	14	7	280	40	30	1000±10

infrared (FT-IR) spectroscopy by Berjonneau *et al*[20,21]. The CVD deposits of $BCl_3/MTS/CH_4/H_2$ system were studied at 33 MPa by Golda and Gallois[22]. However, for different deposition devices and parameters, such as temperature, the deposition process and mechanism are not exactly the same.

To better control the deposition process of Si–B–C ceramic, it is necessary to understand the deposition dynamics and mechanism at different temperatures. In our previous work, the effect of temperature on yield of products in $BCl_3/MTS/H_2$ system has been studied by thermodynamics calculation using FactSage thermodynamics software[23]. In this work, the Si–B–C ceramic was fabricated *via* CVD from $BCl_3/MTS/H_2$ precursor. The deposition rate, microstructure, chemical composition and phase of deposits were investigated to understand the deposition mechanism.

2. Experimental

2.1 Experiment

Methyltrichlorosilane (CH_3SiCl_3, MTS of 98.0% purity) and boron trichloride (BCl_3 of 99.99% purity) were used as silicon, carbon and boron source, respectively. Hydrogen (H_2 of 99.999% purity) was carrier gas and reactant. Argon (Ar of 99.999% purity) was used as a dilution gas for the reactants.

A schematic diagram of the experimental apparatus used for the deposition of Si–B–C ceramic is shown in Fig. 1. The deposition reactor was a vertical, hot-well deposition furnace (90 mm in diameter, 600 mm in length, and temperature error about 10 °C). Carbon cloth woven with T-300 carbon fiber bundles (Toray Co., Japan) was used as deposition substrates. The process parameters of CVD Si–B–C system are summarized in Table 1.

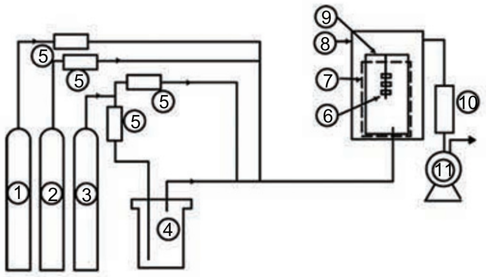

Fig. 1 Schematic diagram of CVD Si–B–C apparatus. 1—BCl_3 gas, 2—Ar gas, 3—H_2 gas, 4—MTS, 5—Mass flow meter, 6—Substrate, 7—Graphite heating element, 8—Stainless-steel jacket, 9—CVD chamber, 10—Trap, 11—Vacuum pump

2.2 Microstructure analysis

The morphology and thickness of Si–B–C coating were characterized using scanning electron microscopy (SEM, JEOL6700F, Tokyo, Japan). Transmission electron microscopy (TEM) observations and high resolution image of coating nearby carbon fiber were preformed using JEM 2100 (JEOL, Japan) and equipped with a thin-window energy-dispersive spectroscope (EDS, Oxford). TEM sample was prepared by using the precision ion polishing system (PIPS). Tested coating was embedded with epoxy-resin, and then mechanical pre-thinning and dimple grinding were performed. After that, the sample was cut and glued onto copper ring of 3 mm in diameter before ion thinning. The chemical composition of deposits was determined by electron probe microanalysis (EPMA, JXA-8100, JEOL, Japan). The deposits were ground to powder for chemical bonding analysis by using Raman spectrometry (Lab Ram II, Dilor, France). The phases of deposits were investigated by X-ray diffraction (XRD, X′Pert Pro, Philips, Netherlands).

3. Results and Discussion

Average deposition rate (μm/h) for Si–B–C ceramic is expressed as the thickness growth per unit of time. For each specimen, at least ten different positions around cross-section edge were observed *via* SEM to get an average value of deposition thickness. The average deposition rate at each temperature is shown in Table 2. Meanwhile, relationship between deposition rate and temperature is shown in Fig. 2. With increasing temperature, the deposition rate increases, and the result is well fitted the Arrhenius formula,

Table 2 Average deposition rate of Si–B–C ceramic at each temperature

Deposition temperature/°C	Deposition rate/(μm/h)
950	0.2
1000	0.56
1050	1.6
1100	3.57

$$v = A\mathrm{e}^{-E_a/RT} \quad (1)$$

where v refers to deposition rate, A means frequency factor, R is gas constant, T remarks absolute temperature, and E_a refers to activation energy. As shown in Fig. 2, the activation energy E_a for this deposition reaction is 271 kJ/mol.

Raman spectra of Si–B–C ceramic deposited at different temperatures are shown in Fig. 3. Peaks at