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Oxidation behaviors and mechanisms of CVD Si-B-C ceramic in wet oxygen from 700 °C to 1400 °C

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ABSTRACT

Si-B-C ceramic is an effective self-healing component to improve the oxidation resistance of C/SiC composites for long-life applications in aircraft and aerospace fields. To clarify protection mechanisms, oxidation behaviors and mechanisms of CVD Si-B-C ceramic in wet oxygen from 700 °C to 1400 °C were investigated in this work. Microstructure, bonds transformation and phase evolution of Si-B-C ceramic after oxidation were analyzed. The weight loss of Si-B-C ceramic increased linearly with time between 700 °C and 1000 °C, while it changed in a non-linear way above 1200 °C. The oxidation production of Si-B-C ceramic in wet oxygen is mainly composed of $Si(OH)_4$, SiO_2, H_3BO_3, B_2O_3 and B_2O. The oxidation resistance of Si-B-C in wet oxygen is better than that of single-phase B_4C ceramic because borosilicate glass is rapidly formed, which can effectively resist the wet oxygen. No fiber oxidation is found up to 1400 °C.

1. Introduction

Carbon fiber reinforced silicon carbide matrix composites (C/SiC) have been widely used to fabricate thermostructural components in aircraft and aerospace fields because of their attractive properties such as high specific strength, low density and high mechanical properties at elevated temperature [1–4]. However, pores and cracks inevitably exist in coatings and matrix due to thermal mismatch between carbon fibers and silicon carbide matrix [5]. They provide routes for oxidative medium and lead to the oxidation of composites, limiting the long-life applications for C/SiC composites in severe oxidizing environment at high temperatures.

In recent years, boron-containing additives, such as BC and SiB_4, have been introduced into C/SiC composites to develop self-healing ceramic matrix composites for long-life applications [6–12]. Previous results showed that composites modified with Si-B-C ceramics exhibited good oxidation resistance in severe high-temperature environment [13–15], because borosilicate glass mixed by silica and borate glass was formed at low temperature, and then sealed the cracks and pores existing in composites originally.

As we all known, borosilicate glass is sensitive to water vapor which always coexists with oxygen in application atmospheres. So, the oxidation behaviors and protection mechanisms of Si-B-C ceramics for C/SiC composites should be investigated in wet oxygen. However, few studies have been published until now.

The purpose of this investigation is to understand the oxidation behaviors of Si-B-C ceramic, reveal the protection mechanisms of Si-B-C ceramics for C/SiC in wet oxygen in the temperature ranging from 700 °C to 1400 °C, and then establish oxidation models.

2. Experimental procedures

SiC-coated C/SiC composite was prepared by chemical vapor infiltration (CVI) and chemical vapor deposition (CVD) [16]. Si-B-C ceramic was deposited on its surface by CVD method using boron trichloride and methyltrichlorosilane (MTS) as precursors. The deposition conditions were as following: temperature was 1050 °C, pressure was 2 kPa, time was 60 h, the molar ratio of MTS and BCl_3 was 2, and the molar ratio of H_2 and MTS was 10.

Oxidation tests in wet oxygen were conducted in an alumina tube furnace for 6 h at 700, 1000, 1200, 1300 and 1400 °C, respectively, as sketched in Fig. 1. Four samples were tested for each specific temperature. The samples were placed in the furnace and heated up to a given temperature in argon atmosphere with a rate of 5 °C/min, and then the mixed gas of $14\%H_2O:8\%O_2:78\%Ar$ were inlet with a flow rate of 7.0 cm/s.

Weight of the samples were measured with an analytical balance (Mettler Toledo, AG 204, Switzerland) (sensitivity = 0.1 mg)

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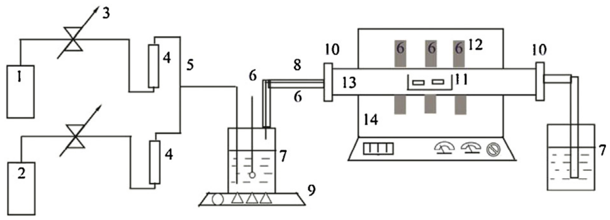

Fig. 1. Sketch of water vapor coupling with oxygen experiment device.
(1) Oxygen (2) argon (3) control valve (4) flowmeter (5) tee valve (6) thermometer (7) wild-mouth bottle (8) heater band (9) water bath furnace (10) seal ring (11) Al_2O_3 crucible and sample (12) heating element (13) furnace tube (14) furnace body.

before and after oxidation. Weight change of the samples was calculated by the following equation:

$$\Delta m = \frac{m_t - m_0}{m_0} \times 100\% \tag{1}$$

where m_0 and m_t are the weight of the sample before and after oxidation respectively.

Surface and cross-section morphologies of the oxidized samples were observed using scanning electron microscope (SEM, JEOL6700F, Tokyo, Japan). Energy dispersive spectrum (EDS) was employed to identify element species. The phase compositions were determined by X-ray diffraction (XRD) with a Cu Kα radiation. Data were digitally recorded in a continuous scan mode in the angle (2θ) range from 20° to 80° with a scanning rate of 0.02°/s. The evolution of bonds were identified by X-ray photoelectron spectroscopy (XPS, K-Alpha; Thermo Scientific) using a monochromatic Al Kα X-ray source.

3. Results and discussion

3.1. Morphologies of CVD Si-B-C ceramic after oxidized in wet oxygen

Fig. 2 shows the surface morphologies of CVD Si-B-C ceramic after oxidized at different temperatures for 6 h in wet oxygen. For the samples oxidized at 700 °C, the surface morphology is cauliflower-like, and some particles with size of about 20 μm can be found in partial zones. The tiny particles with size of about 2 μm distribute uniformly, which indicates that Si-B-C ceramic has been oxidized into smaller particles. As the temperature increases to 1000 °C, cauliflower-like morphology disappears completely and glass phase with ruptured bubbles emerges in large area. It suggests that Si-B-C ceramic reacts violently with water and oxygen, and then glass phase is formed. Meanwhile, a large amount of low-melting-point phases such as boron oxide and boric acid volatilize quickly. When the temperature is above 1200 °C, the surface becomes smoother because some ruptured bubbles are filled by flowing glass phase.

Fig. 3 displays the fracture morphology of Si-B-C ceramic coated C/SiC composite after oxidation. To prevent Si-B-C ceramic coating from debonding, the samples were coated by resin when polishing. As shown in Fig. 3(a), the uniform and dense Si-B-C ceramic coating with the thickness of about 9 μm is bonded tightly with substrate and there is no obvious difference from surface to the bonded interface after oxidized at 700 °C for 6 h. The oxidation depth is about 3 μm according to the results of linear scanning of EDS. In addition, it can be found that the fibers close to the cracks in SiC matrix are not be oxidized because oxygen is exhausted by the oxidation of Si-B-C ceramic. As displayed in Fig. 3(b), the thickness of Si-B-C ceramic coating is non-uniform after oxidized at 1000 °C for 6 h. Moreover, fibers are also not be oxidized, and the oxidation depth is about 3 μm according to the results of linear scanning of EDS, which is equal to that at 700 °C. While the temperature increases over 1200 °C, Si-B-C coating is oxidized completely and transforms to a single glass coating with the thickness of 1–2 μm, as shown in Fig. 3(c)–(e). The cracks in SiC matrix are filled by glass, and the fibers close to the cracks are protected well from oxidation at 1300 °C and 1400 °C, as shown in Fig. 3(d1) and (e1). Fibers are not oxidized at all at the testing temperatures for 6 h.

Table 1
Bond and atomic content of B 1s peak in Si-B-C ceramic analyzed by XPS after oxidized in wet-oxygen environment for 6 h.

Percentage/at.%	700 °C	1000 °C	1200 °C	1300 °C	1400 °C
B-C (B_4C)	31.08	23.12	–	–	–
B-O (B_2O)	32.07	73.72	83.88	37.75	64.69
B-O (B_2O_3)	12.78	3.16	16.12	62.25	35.31
B-OH (H_3BO_3)	24.07	–	–	–	–

Table 2
Bond and atomic content of Si 2p peak analyzed by XPS in Si-B-C ceramic after oxidized in wet-oxygen environment for 6 h.

Percentage/at.%	700 °C	1000 °C	1200 °C	1300 °C	1400 °C
Si-C (SiC)	–	–	18.41	–	–
Si-OH ($Si(OH)_4$)	24.87	18.03	11.88	13.19	17.35
Si-O (SiO_2)	75.13	81.97	69.71	86.81	82.65

Table 3
Bond and atomic content of O 1s peak in Si-B-C ceramic analyzed by XPS after oxidized in wet-oxygen environment for 6 h.

Percentage/at.%	700 °C	1000 °C	1200 °C	1300 °C	1400 °C
Si-OH ($Si(OH)_4$)	6.23	2.34	10.59	5.72	7.13
B-O (B_2O_3)	36.28	26.54	36.85	39.05	31.59
B-OH (H_3BO_3)	47.02	32.76	–	–	–
Si-O (SiO_2)	10.47	38.36	52.56	55.23	61.28

3.2. Phase analysis

XPS spectra of B1s, Si2p and O1s for Si-B-C ceramic oxidized for 6 h at different temperatures in wet oxygen are shown in Fig. 4. It is known from the peak of B 1s in Fig. 4(a) that after oxidation the bonds include B-C bond in B_4C at 186.3 eV [17,18], B—O bonds in B_2O and B_2O_3 at 188 eV [19] and 193.1 eV [17,20,21], respectively, and B—OH bond in H_3BO_3 at 193.6 eV [22]. Bonds and atomic contents are shown in Table 1. The oxidation products are mainly composed of B_2O and H_3BO_3 as well as a very small amount of B_2O_3 at 700 °C. When the temperature increases to 1000 °C, the oxidation product is mainly composed of B_2O, and the content of B—O bond is 73.72at.%, while the content of B—C bond in B_4C and B—O bond in B_2O_3 are both decreased, and B—OH bond is not found due to the rapid volatilization of H_3BO_3. When the temperature is up to 1200 °C, the oxidation products are only composed of boron oxide in form of B_2O and B_2O_3.

Fig. 4(b) shows the XPS spectra of Si 2p for Si-B-C ceramic. There are only Si—O bond (103.9 eV) [23,24] in SiO_2 and Si—OH bond(103 eV) [25] in $Si(OH)_4$, what more, the bonds have no significant change after oxidation at different temperature. The content of the former is approximate 3–7 times of that of the latter, as listed in Table 2. The result indicates that SiC in Si-B-C ceramic is oxidized into SiO_2 phase mainly, and also form a small amount of $Si(OH)_4$. The peak of SiC at 1200 °C is probably from the SiC matrix due to the rapid volatilization of borosilicate glass coating.

Fig. 4(c) shows the XPS spectra of O 1s for Si-B-C ceramic after oxidation in wet oxygen. B—O bond in B_2O_3 (533 ± 0.2 eV) [20], B—OH bond in H_3BO_3(533.4 eV) [26], Si-OH bond in $Si(OH)_4$ (531.9 eV) [25] and Si—O bond in SiO_2 (533.7 eV) [24,27] are found. Bonds and atomic contents of O 1s peak after oxidation at different temperatures in wet oxygen are shown in Table 3. All four