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Oxidation behavior of SiBC matrix modified C/SiC composites with different PyC interphase thicknesses

Xiaoyu Cao, Xiaowei Yin*, Xiaokang Ma, Xiaomeng Fan, Laifei Cheng, Litong Zhang

Science and Technology on Thermostructural Composite Materials Laboratory, Northwestern Polytechnical University, P.O. Box 547, You-Yi Xi-Lu Road No. 127, Xi'an, Shaanxi 710072, PRChina

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Abstract

A series of SiBC matrix modified C/SiC composites (C/SiC–SiBC) with different pyrolytic carbon (PyC) interphase thicknesses (50–300 nm) were fabricated by a joint process of chemical vapor infiltration, slurry infiltration and liquid silicon infiltration. Oxidation behavior of C/SiC–SiBC composites with different PyC interphase thicknesses in the temperature range of 800–1200 °C was studied. When the C/SiC–SiBC composites were exposed at 800 °C for 10 h the oxidation kinetics was controlled by diffusion rate of oxygen through matrix micro-cracks and coating defects, and the effect of PyC interphase thickness on weight loss was apparent. At higher oxidation temperatures (> 1000 °C) the in-depth diffusion of oxygen was slowed down due to healing of matrix micro-cracks by borosilicate glass, and the oxidation kinetics was controlled by diffusion rate of oxygen through coating defects. Weight loss of all the C/SiC–SiBC composites was greatly reduced and was less affected by PyC interphase thickness. The flexural strength of C/SiC–SiBC composites rapidly decreased after oxidization at 800 °C although thicker PyC interphase brought a little improvement and it rose up as temperatures increased above 1000 °C due to the non-uniform degradation of carbon fibers.

Keywords: Oxidation behavior; C/SiC composites; Self-healing; Melt infiltration; Chemical vapor infiltration

1. Introduction

Carbon fiber reinforced SiC matrix composites (C/SiC) fabricated by chemical vapor infiltration (CVI) have been developed as thermo-structural materials for the applications such as air-breathing engines, hot-gas valves and aerospace thermal structures [1–5]. C/SiC composites have the advantages of low density, high modulus and high strength. However matrix pores exist in C/SiC composites due to the "bottom-neck effect" during CVI process, which will act as diffusion paths of oxidizing species, restricting the application of C/SiC composites in oxidation environment. Liquid silicon infiltration (LSI), slurry infiltration and their combination have been used to produce dense C/SiC composites to fill the matrix pores by Si [6,7] or self-healing components such as B_4C, SiB_4, and SiBC [8–12]. The porosity of dense C/SiC composites is effectively reduced to less than 5% but higher processing temperature (> 1420 °C) aggravates the mismatch between coefficient of thermal expansion (CTE) of the fiber and matrix and brings larger thermal residual stress (TRS) on the composites, resulting in the formation of intrinsic matrix micro-cracks while cooling down from the fabrication temperature to room temperature [13–14]. How these matrix micro-cracks affect the oxidation behavior of C/SiC–SiBC composites at high temperature environment has rarely been investigated.

In our previous work, different PyC interphase thicknesses had been applied to release TRS and the C/SiC–SiBC composites with different matrix micro-crack densities were obtained [15]. In this paper, the evolution of matrix micro-cracks in temperature range of 800–1200 °C was studied and its effect on the weight loss and the retained flexural strength

*Corresponding author. Tel.: +86 29 88494947; fax: +86 29 88494620.
E-mail address: yinxw@nwpu.edu.cn (X. Yin).

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of the C/SiC–SiBC composites was investigated. Oxidation mechanism of C/SiC–SiBC composites at different temperatures was discussed.

2. Experimental

2.1. Material preparation

T-300 carbon fiber (Toray Co., Japan) consisting of bundles of 1000 filaments was used as reinforcement. Carbon fiber preforms were prepared by stacking plain weave carbon cloths in a perforated graphite holder. The volume fraction of fiber was 40%. A series of C/SiC–SiBC composites with different PyC interphase thicknesses were fabricated. The fabrication process was described in detail in our previous work [15]. Finally a SiC layer with a thickness of ~100 μm was deposited by CVI on the surface of the composites. The C/SiC–SiBC composites with PyC interphase thickness of ~50 nm, 180 nm and 300 nm were denoted as specimen C-50, C-180 and C-300, respectively. The matrix micro-crack densities of the as-received composites were 4.76, 4.29 and 3.61 mm^{-1} for specimen C-50, C-180 and C-300, respectively, which was calculated in the previous work [15].

2.2. Oxidation experiment

The oxidation test was conducted in static air in a tube furnace at 800, 1000 and 1200 °C for 10 h separately. The specimens were directly pushed into the furnace when the furnace was heated up to a given temperature, pulled out from the tube furnace after 1, 3, 5, 7 and 10 h, and then cooled in air for weighting. The weight changes of specimens were measured by an analytical balance (Mettler Toledo, AG 204, Switzerland). Cumulative weight changes of the samples were calculated using the following equation:

$$\Delta m = 100(m - m_0)/m_0$$

where m and m_0 are the weight of the samples after and before oxidation respectively. Three samples were measured in each case for statistical significance.

2.3. Characterization

The morphologies and fracture surfaces of the specimens were observed with a scanning electron microscope (JEOL-6700F, Tokyo, Japan). X-ray diffraction (XRD) investigation was carried out by using a Rigaku D/max-2400 diffractometer (Tokyo, Japan) with Cu Kα radiation. The density and open porosity of the specimen were measured with the Archimedes method.

Mechanical property of the specimens was characterized under bending load before and after oxidation test. The flexural strength was tested in an Instron 1195 machine using the three-point bending method with a span of 30 mm and a loading rate of 0.5 mm/min. The specimen size was $3 \times 5 \times 40$ mm^3.

3. Results and discussion

The density of the as-received specimen is in the range of 2.17–2.30 g/cm^3 and the porosity is in the range of 4.1–4.5%. During LSI, liquid silicon reacted with B_4C particles to form SiC, a ternary phase $B_{12}(C,Si,B)_3$ and SiB_4 denoted as the SiBC matrix. More details of reaction process were described in our previous work [15]. The in-situ formed matrix filled the residual pores and distributed uniformly in the inter-bundle pores (Fig. 1).

3.1. Weight changes of C/SiC–SiBC composites at different temperatures

The weight of the specimens exposed at 800, 1000 and 1200 °C for 10 h is measured and the weight change as a function of oxidation time is presented in Fig. 2. After oxidized at 800 °C the weight losses of all the specimens increased linearly as oxidation time increased, and the final weight loss decreased from 3.1% of specimen C-50 to 1.2% of specimen C-300 as PyC interphase thickness increased. It can be inferred that PyC interphase thickness has a dramatic effect on weight loss of C/SiC–SiBC composites at 800 °C (Fig. 2(a)). The decreased matrix micro-crack density of specimen C-300 means less oxidizing species diffusion paths and thus less oxidation of carbon fiber, which results in the decreased weight loss of specimen C-300. At higher temperatures (1000–1200 °C) there was a sharp weight loss of all the specimens at the first 1 h and then the weight loss increased with oxidation time, especially at 1200 °C. The final weight losses of the different specimens were all below 0.4%, as seen in Fig. 2(b, c). The difference among them gradually turned smaller, as seen in Fig. 2(d). PyC interphase thickness exerted less effect on weight loss of the specimens.

The component of specimen C-300 after oxidation at 800, 1000 and 1200 °C was tested by XRD. As shown in Fig. 3, the oxidation production of $B_2O_3 \cdot xSiO_2$ glass occurs at 800 °C and it remains at 1200 °C. It can be inferred that the formation of borosilicate glass by the oxidation of SiBC matrix starts at 800 °C. The borosilicate glass remained steady at 1200 °C.

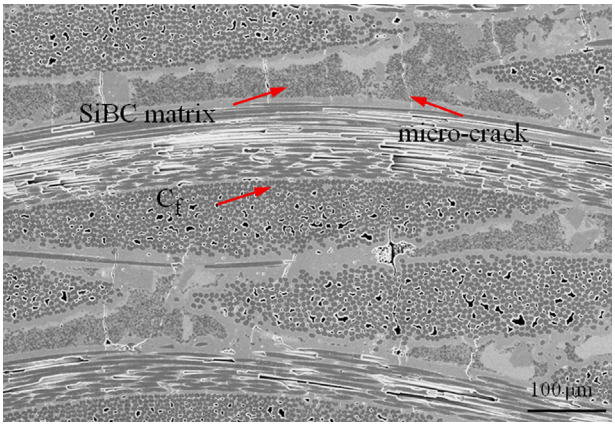

Fig. 1. The microstructure of the as-received C/SiC–SiBC composites.