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Microstructure, ablation behavior and thermal retardant ability of C/C-HfB_2 composites prepared by precursor infiltration pyrolysis combined with chemical vapor infiltration

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ABSTRACT

C/C-HfB_2 composites were fabricated by precursor infiltration pyrolysis combined with chemical vapor infiltration. Ablation behavior, oxidation performance and thermal retardant ability of the prepared composites were investigated. The results showed that the oxidation products of HfB_2 could enhance the oxidation performance and ablation property of C/C-HfB_2 composites. During ablation in the heat flux of 2.38 MW/m^2 under oxyacetylene torch, a protective HfO_2 layer was covered on ablated surface, acting as an efficient barrier to heat transfer and denudation of the oxyacetylene torch. As the heat flux increased to 4.18 MW/m^2, thermal energy concentration and denudation enhancement of the oxyacetylene torch resulted in the spalling of the HfO_2 layer. Based on microstructure evolution, thermal retardant ability test, thermogravimetric analysis and measurement of residual flexural strength, oxidation as well as ablation mechanism of the C/C-HfB_2 composites was discussed.

1. Introduction

Current studies on hypersonic vehicles are focused on the thermal protection systems, which are operated in the extreme environments above 2000 °C [1–3]. Therefore, materials with outstanding thermomechanical and thermochemical properties are required. In such harsh conditions, traditional alloys and monolithic ceramics are difficult to meet the requirements [4]. Carbon/carbon (C/C) composites, regarded as carbon fibers reinforced carbon composites, possess low density, good thermal shock resistance and high strength-to-weight ratio, having been considered as the potential candidates for use in this field [5–8]. Unfortunately, the applications of C/C composites are limited due to their poor oxidation resistance [2,6,8–11].

The addition of ultra-high temperature ceramics (UHTCs) is a good approach to solve the aforementioned problems. UHTCs (Carbides, nitrides and borides of refractory metals) are aroused wide concern attributed to their high-melting points, good mechanical properties, oxidation performances and ablation resistances [12–16]. Despite such an attractive combination of properties, their intrinsic features including low fracture toughness and poor thermal shock resistance are the two major concerns for operating in rigorous environments [17]. With the incorporation of UHTCs into C/C, the materials are expected to possess good chemical stability in oxidizing environment and sufficient thermal shock resistance in high-low cyclic temperatures condition [14,18–20]. So, appropriate processing methods have been carried out on the fabrication of C/C-UHTCs, such as chemical liquid-vapor deposition [2], chemical vapor infiltration (CVI) [3], precursor infiltrations and pyrolysis [21], carbothermal reduction reaction [14], slurry infiltration [18–20], hot pressing [22], microwave hydrothermal [23] and reactive melt infiltration [24]. Due to its high melting point (3250 °C), high hardness and excellent chemical stability [25,26], HfB_2 is proved to be a promising candidate to improve the ablation properties of C/C composites. A. Paul et al. fabricated C/C-HfB_2 by slurry infiltration [18–20]. However, the agglomeration of the HfB_2 particles could block the pores in the outer layer of the C/C preforms and then made it more difficult for the successive densification. To ensure the service reliability of C/C-HfB_2 composites, it is of great significance to resolve the problem of agglomeration and find out the valid dispersion method of HfB_2. Precursor infiltrations and pyrolysis (PIP) is a common method to introduce UHTCs into C/C preforms. It usually consists of two

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processes including infiltration of a low viscosity precursor and pyrolysis at high temperatures. Compared with slurry infiltration, this method possesses a larger infiltration depth, which can be expected to improve the uniformity of HfB_2 and realize the net shape manufacturing. However, the shrink of UHTCs during pyrolysis usually contributes to the formation of cracks and pores. As a result, it is necessary to fill the pores of C/C-HfB_2 composites after PIP. In our previous work [27], reactive melt infiltration (RMI) was used to improve the density and uniformity of C/C-HfB_2 composites. But the inevitable reactions between the molten mixtures and carbon fibers resulted in the degradation of mechanical property. So, it makes sense to finding an alternative method of RMI. Furthermore, as an important parameter of thermo-structural components, it is also essential to investigate the corresponding thermal retardant ability of C/C-HfB_2 composites in combustion environment while previous works about C/C-UHTCs mainly concentrated on their ablation properties [2,6–14,18–20].

In this paper, C/C-HfB_2 composites were firstly prepared by PIP, and then densified by pyrolysis carbon through CVI (as an alternative method of RMI). Ablation behavior and thermal retardant ability (TRA) of the prepared C/C-HfB_2 (C/C-HB) composites were investigated using an oxyacetylene torch with different heat fluxes. Thermogravimetric (TG) analysis was carried out to illustrate the effect of HfB_2 addition on the oxidation resistant property of C/C composites. Based on TRA test, TG analysis and evolution of flexural strength, the oxidation and ablation mechanisms of the C/C-HB composites are discussed.

2. Experimental procedure

2.1. Preparation of the composites

Fig. 1 reveals the preparation procedure of C/C-HB composites, which could be divided into three steps:

(1) 2D C/C composites with the density of 1.0–1.1 g/cm^3 were prepared by a two-step method. Firstly, T300 PAN-based carbon fibers (Yixing Tianniao High Technology Co. Ltd., Jiangsu, China) were used to fabricate the 2D needled carbon fiber felts by alternatively stacking weftless plies and short-cut-fiber webs with a needle punching technique. The fiber volume content of the obtained carbon fiber felt was about 20–25%. Then the prepared carbon fiber felts were densified to 1.0–1.1 g/cm^3 by isothermal chemical vapor infiltration (ICVI) process.

(2) HfB_2 was introduced into C/C composites by PIP. A solution of organic hafnium boride polymer (Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China) and xylene was used as the precursor. The obtained low-density C/C composites in the first step were put in an airtight container, which were evacuated (lower than 0.006 MPa). Because of the pressure difference inside and outside of the container, the liquid precursor was inhaled and immersed the prepared C/C samples for 1–2 h. Then the samples were dried at 90–100 °C in air for 24 h. After that, the samples were put in a graphite crucible and held at 1500–1800 °C for 1–4 h in argon atmosphere. The above process was repeated until the density increased to 1.3–1.4 g/cm^3.

(3) The obtained samples in the second step were densified by pyrolysis carbon through thermal gradient chemical vapor infiltration (TCVI). During this process, CH_4 was used as the carbon source. After that, the prepared composites were graphitized at 2100–2300 °C for 2 h in argon atmosphere. The final density of the prepared C/C-HB composites was about 1.77–1.84 g/cm^3.

2.2. Characterization

2.2.1. Ablation test

C/C-HB composites were machined into cylinder shape (Ø30 × 4 mm) for ablation test. They were hand-abraded with 400 grit SiC papers, and then cleaned ultrasonically in water for 20 min. After that, they were put in a drying oven and dried at about 80 °C for 24 h. Ablation test was carried out using oxyacetylene torch with two different heat fluxes (2.38 and 4.18 MW/m^2), and the corresponding testing parameters were listed in Table 1 [28,29]. According to GJB323A-96 [29], the ablation tests were performed in oxidizing flames. The inner diameter of the oxyacetylene gun tip was 2 mm and the distance between the gun tip and the sample was 10 mm. The angle between the oxyacetylene gun and the tested sample was 90°. Ablation time was 90 s. For the convenience

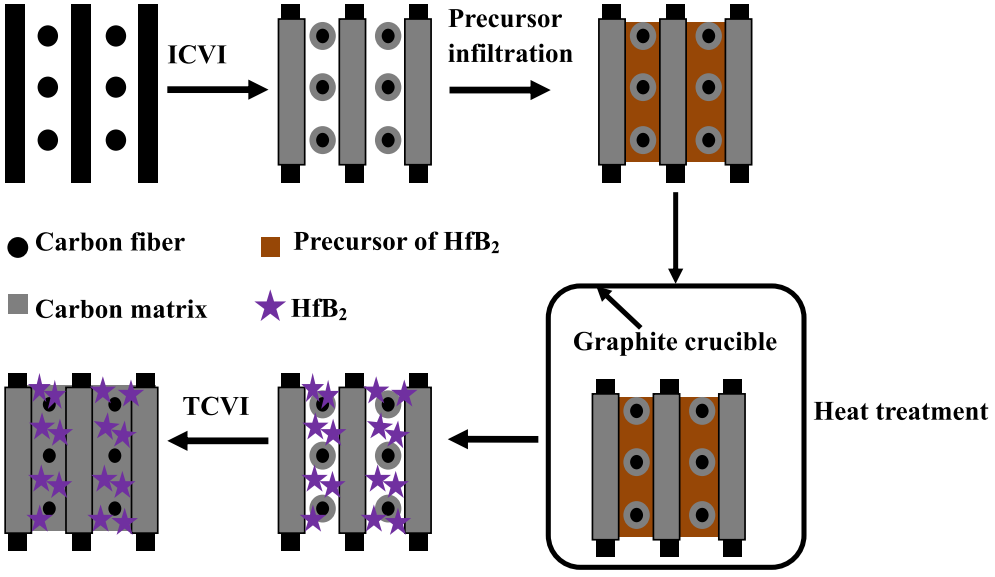

Fig. 1. Schematic illustration of the preparation of C/C-HB composites.