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# The oxidation resistance of two-temperature synthetic $HfB_2$-SiC coating for the SiC coated C/C composites

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ABSTRACT

To explore oxidation resistance of $HfB_2$-SiC coatings, the $HfB_2$-SiC coating was prepared at 2173 K (sample A) and 2373 K (sample B) by in-situ synthesis for SiC coated Carbon/carbon (C/C) composites. Compared with sample A, $HfB_2$ phases of sample B are more and the coating is thicker. At 1773 K in air, the C/C substrate of sample A can be protected for 319 h with 1.63% weight loss percentage, while the C/C substrate of sample B can be protected for 753 h with only 0.487% weight loss percentage, which indicates that 2373 K is easier to generate $HfB_2$ phases and beneficial to protect samples from oxidation. After 40-time thermal cycle, the weight loss percentages of sample A and B are 1.85% and 0.78%, respectively, which reveals that the latter has a better thermal shock resistance.



## 1. Introduction

As the thrust-weight ratio of the engine increasing and the applied temperature of the turbine inlet rising, the C/C composites with high strength become the preferred material. C/C composites are a new type of inorganic non-metallic based composites with excellent resistance to high temperature, corrosion, heat shock, and so on [1–4]. While C/C composites are easy to be oxidized under high temperature surrounded by oxidizing atmosphere, and the higher the temperature is, the quicker the oxidation rate increases [5]. Researches showed that the carbon matrix began to be oxidized at 643 K in the air, 923 K in the water vapor and 1023 K in the $CO_2$, which makes its mechanical performance drop significantly [6,7]. When C/C composites oxidize losing weight 1%, whose strength decrease 10%; while the weight loss of oxidation reaches 10%, the elastic modulus and bending strength reduce 30% and 50%, respectively [8]. Anti-oxidative coating is an effective way to strengthen the oxidation resistance of C/C, which can isolate C/C substrates from oxygen at high temperature [9]. Therefore, for the sake of working stably at high temperature in air environment for a long time, and withstanding the heat cycle from high temperature to room temperature, C/C composites must rely on coating technology to resist oxidation [10,11]. Silica-based ceramic coating has good compatibility with C/C substrates, and SiC can generate continuous, uniform and dense $SiO_2$ glass layer after high temperature oxidation as well; therefore, the silica-based ceramic coating is considered to be one of the most ideal material as the inner coating [12–15]. However, silicate glassy layer is volatile at the ultra-high temperature above 1500 °C, and a number of bubbles and holes would be formed in silicate glass layer after a long time of utilization.

Ultra high temperature ceramics (UHTCs) [16,17] a kind of thermal-protection structure materials, have many merits; for instance, high melting point (>3000 °C), high oxidation protection ability, high specific strength, high heat conductivity, corrosion resistance, good chemical stability and so on [18–20], which can make sure the chemical and physical stability in ultra high temperature above 2000 °C of air environment. UHTCs mainly include carbide and boride of transition metal Zr, Ta and Hf, and their composite materials. Among them, hafnium diboride ($HfB_2$) [21–23] has a series of outstanding comprehensive performance, such as high melting point (3380 °C) and heat conductivity (104 $Wm^{-1}K^{-1}$), excellent resistance of thermal shock and oxidation, so that it can be applied to the severe environment. Therefore, introducing $HfB_2$ phase into the silica-based ceramic coating is

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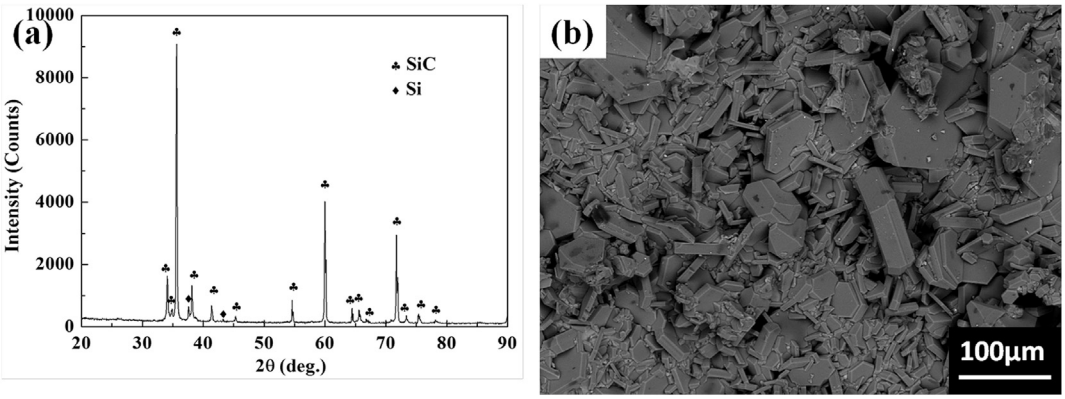


**Fig. 1.** XRD pattern (a) and surface backscattered micrograph (b) of the inner SiC coating.

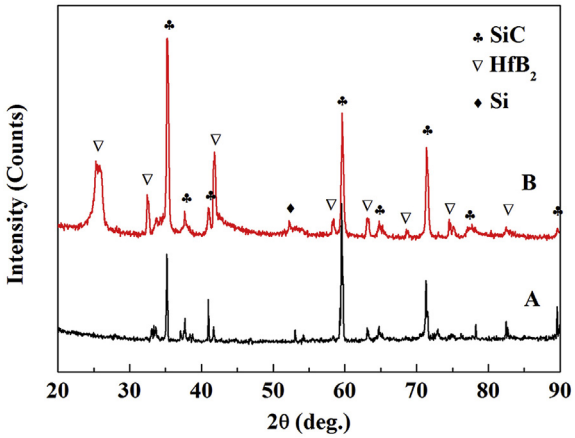


**Fig. 2.** XRD pattern of the outer $HfB_2$-SiC coating.

effective for anti-oxidation and forming stable compound silicate glass. Coatings prepared at low temperatures (such as 1873 K) are porous [24,25] and would weaken the oxidation resistance of the sample, while coatings prepared at high temperatures (2173–2373 K) are compact [26]. In order to ensure the compactness and oxidation resistance of the coating, the outer $HfB_2$-SiC coating was prepared at 2173 K and 2373 K.

In this paper, the oxidation resistance of $HfB_2$-SiC coatings were investigated. The inner SiC coatings were prepared by pack cementation method, and outer $HfB_2$-SiC coatings were fabricated by in-situ synthesis in 2173 K (sample A) and 2373 K (sample B), respectively. The microstructures and oxidation behaviors at 1773 K in air of the two kinds of $HfB_2$-SiC coatings were investigated.

## 2. Experimental procedures

The 2-D C/C composites with the density of 1.7 g/cm$^3$ were selected as the substrate. And the substrates were cut into cubic specimens with 8 × 8 × 8 mm$^3$. In order to avoid stress concentration, the specimens were hand-polished by the abrasive paper until had no obvious edges or corners on the substrate surface and ultrasonically cleaned. Then they were dried for 5 h in a 343 K drying oven before applying coating. The raw materials of graphite (15–35 wt%) and Si (65–85 wt%) powders were chosen to prepare the inner SiC coating by pack cementation method [27]. While $B_4C$ (2–10 wt%), $HfO_2$ (30–40 wt%), graphite (2–10 wt%) and Si (45–65 wt%) powders were combined to prepare the outer $HfB_2$-SiC coating by in-situ synthesis. Firstly, we mixed these powders uniformly and dried, Secondly, the dry mixture powders were putted into a graphite crucible with C/C samples. Finally, they were heat-treated in the normal argon atmosphere for 1–3 h at 2173–2373 K, and the heating rate of the heat treatment furnace was 5–10 K/min. The heat treatment temperature of inner SiC coating was 2373 K, while the heat treatment temperatures of outer $HfB_2$-SiC coating were 2173 K (sample A) and 2373 K (sample B), respectively. The reaction equations were as follows:

$$C\,(s) + Si\,(s) \rightarrow SiC\,(s) \quad (1)$$

$$B_4C\,(s) + 2HfO_2\,(s) + 3C\,(s) \rightarrow 2HfB_2\,(s) + 4CO\,(g) \quad (2)$$

The 1773 K isothermal oxidation test was used for investigating the oxidation resistance of samples under ultra-high temperature air. First of all, using the analytical balance whose accuracy is 0.0001 g weighed the original quality of the samples before testing. Secondly, the oxidation furnace was heated to the test temperature, 1773 K. Subsequently, the samples were put in, which would be taken out to weigh by analytical balance and measure the weight loss percentage at regular intervals. The thermal cycle was used for exploring their thermal shock resistance. In the process of the thermal cycle, the samples were taken out from the furnace after oxidation 3 min at 1773 K, and then kept them at room temperature for 3 min, and repeated. The computation formula of weight loss percentage (W) was as follow:

$$W = \frac{m_0 - m_1}{m_0} \quad (3)$$

The weight of samples before and after oxidation was represented as $m_0$ and $m_1$, respectively. Finally, we could get the weight loss percentage which as a function of time, and draw the weight loss curve of the samples according to the function. The crystalline structure of the coated C/C samples was analyzed by X-ray diffraction (XRD). The microstructure and elemental distribution was researched by the scanning electron microscope (SEM) who equipped with energy dispersive spectroscopy (EDS).

## 3. Experimental results and discussion

### 3.1. Microstructure of the coatings

The XRD pattern and surface backscattered image of the inner SiC coating are shown in Fig. 1. SiC and Si phases were recognized by XRD in Fig. 1 (a), which existed in the SiC coating. So we can draw the conclusion that there was a small amount of silicon left in the raw materials. From Fig. 1 (b), SiC coating is compact without large