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Oxidation and ablation protection of multiphase $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating for graphite prepared by dipping-pyrolysis and reactive infiltration of gaseous silicon

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ABSTRACT

A novel monolayer $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating with defect-free structure for protecting graphite materials was prepared by dipping-pyrolysis combined with reactive infiltration of gaseous silicon. The phase synthesis, microstructure, oxidation and ablation resistance properties of the prepared $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating were studied. Results demonstrated that the as-prepared coating exhibited excellent low and high temperature oxidation resistance, after isothermal oxidation at 900 °C and 1500 °C for 1320 h and 2080 h, respectively, the mass gains were 0.14% and 1.74%, respectively. The excellent anti-oxidation performance at 900 °C was ascribed to the defect-free structure of coating, while the formed compound Hf-Ta-Si-O glassy oxide layer on the coating surface was responsible for the excellent oxidation resistance at 1500 °C. Moreover, the $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating had good ablation resistance, after ablation for 60 s, the mass and linear ablation rates of the coated sample were 1.05 mg/s and -10.2 μm/s, respectively. The ablation behaviors of the coated sample mainly included thermal-physical and thermal-chemical erosion along with thermos-mechanical denudation.

1. Introduction

Carbon materials, such as carbon fiber reinforced carbon composites (C/C) and graphite, possess light weight, outstanding high temperature stability and mechanical properties, and low coefficient of thermal expansion, making them the most promising thermal-structural materials for aeronautical and aerospace fields [1–3]. Unfortunately, carbon materials are prone to be oxidized and convert into CO and CO_2 gases above 450 °C in the oxygen-containing atmosphere, which will lead to the degradation of mechanical properties and the limitation of their applications [4,5]. An effective solution to elevate the oxidation and ablation resistance of carbon materials is employing ceramic coatings on carbon materials surfaces [6].

Multiphase and multilayer SiC-based coatings have been attracting significant attentions due to their favorable oxidation and ablation resistance abilities [7,8]. SiC in the coating can be oxidized to form SiO_2 film with low diffusivity of oxygen on the coating surface, which acts as a protective barrier and prevents oxygen from infiltrating into the coated sample [9]. Up to now, many kinds of SiC-based coatings have been developed for protecting carbon materials from oxidation and ablation, like ZrB_2-SiC [10,11], $MoSi_2$-SiC [12], SiC-glass [13], TaB_2-SiC [14,15], HfB_2-SiC [16], Y_2SiO_5/SiC [17], $CrSi_2$–SiC [18], mullite/SiC [19], SiC-tungsten [20], ZrB_2-SiO_2/SiC [21], HfC-ZrC-SiC [22], etc. Among the above-mentioned coatings, SiC-based coatings containing ultra-high temperature ceramics (UHTCs) borides (such as TaB_2, ZrB_2 and HfB_2), possess better anti-oxidation properties with a wide temperature domain because of their two main advantages: (1) B_2O_3 generated form the oxidation of TaB_2, ZrB_2 and HfB_2 has good liquidity, which can heal some defects in the coating and improve the low temperature oxidation resistance ability (below 1000 °C); (2) the oxidation products, Ta_2O_5, ZrO_2 and HfO_2 can increase the viscosity of the formed silica glass layer on the coating surface and reduce the generation of cracks, thereby improving the high temperature oxidation resistance property (1500 °C). In addition, UHTCs borides have high melting point ($>$ 3200 °C), high chemical stability, high hardness and good thermal conductivity, making them suitable anti-ablation materials [23].

To date, various techniques of coating preparation have been used for SiC-based UHTCs borides coatings, for instance, pack cementation

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[24,25], plasma spray [26], brushing process [27], painting [28], chemical vapor deposition (CVD) [29] and so on. Although these techniques present certain superiority, the prepared coatings cannot provide effective protection of low temperature (below 1000 °C) or long-time oxidation at high temperature (1500 °C) due to the defect-contained structure of the coatings. Furthermore, the current SiC-based UHTCs borides coatings usually need two or more layers to obtain favourable oxidation resistance, which is time-consuming and complicated. Hence, it is necessary to prepare monolayer SiC-based UHTCs borides coatings with defect-free structure for the protection of carbon materials. In our previous work, a dense monolayer $MoSi_2$-SiC-Si coating was prepared on graphite surface by dipping-pyrolysis combined with reactive infiltration of gaseous silicon [30], such coating possessed good anti-oxidation ability with a wide temperature domain from 800 °C to 1600 °C in air. Additionally, a C/SiC transition layer was formed at the interface of coating and graphite, obtaining good bonding strength and thermal shock resistance [31].

It is reported that the coexistence of HfB_2 and TaB_2 in the coating can greatly improve the anti-oxidation ability of HfB_2-SiC or TaB_2-SiC coating, which is ascribed to their synergistic effect of oxidation products [32]. In the present work, a novel monolayer $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating with defect-free structure on graphite surface was prepared by dipping-pyrolysis combined with reactive infiltration of gaseous silicon. $Hf_{0.5}Ta_{0.5}B_2$ phase was synthesized through in-situ reaction among HfC, TaC, B_4C and gaseous silicon. The phase synthesis and microstructure were studied. The oxidation and ablation resistance properties of the fabricated $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating were investigated. The anti-oxidation and anti-ablation mechanisms of the prepared coatings were also investigated.

2. Experimental

2.1. Preparation of the $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating

Two dimensions of graphite substrates (10 mm × 10 mm × 5 mm and Ø 30 × 10 mm) were machined from a graphite bulk, the density of which was 1.79 g/cm^3. Phenolic resin solution (carbon yield = 40 wt %), SiC powders (D_{50} = 10 μm, > 95 wt% pure), HfC powders (D_{50} = 1–3 μm, 99.9 wt% pure), TaC powders (D_{50} = 1–3 μm, 99.9 wt% pure), B_4C powders (D_{50} = 0.5 μm, 99 wt% pure), and silicon particles (5–8 mm, Si ≥ 99.4 wt%) were chosen as raw materials. Before applying coatings, the graphite substrates were polished to remove the edges and corners using 400 and 800 grit SiC paper, then cleaned ultrasonically with ethanol and dried at 120 °C for 3 h.

The phenolic resin was first mixed with alcohol to form phenolic resin solution. After that, the raw materials containing SiC, HfC, TaC and B_4C were added into the phenolic resin solution, then stirred by magnetic and dispersed by ultrasonic to obtain a homogeneous slurry suspension. The mass fractions of (HfC, TaC and B_4C)(based on the mole ratio in Eq. (2)), SiC, phenolic resin and alcohol were 25 wt%, 25 wt%, 10 wt% and 40 wt%, respectively. The graphite substrates were dipped in the above slurry suspension, subsequently taken out for drying at room temperature to obtain resin-SiC-HfC-TaC-B_4C precoatings coated graphite substrates. Further, the specimens were toughened by curing procedure at 160 °C for 3 h, followed by pyrolysis in nitrogen at 700 °C for 2 h to form C-SiC-HfC-TaC-B_4C precoatings on graphite surfaces. Finally, these precoatings coated specimens were put into a graphite crucible containing silicon blocks at the bottom. In particular, the specimens were separated with silicon using a porous graphite plate. Then, the crucible was heated to 1900 °C and held for 15 min in a vacuum furnace.

2.2. Tests of the apparent porosity and anti-oxidation

Archimedes method was applied to measure the apparent porosities of the precoating and $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating coated samples. The oxidation tests of the coated samples were performed in an electric furnace at 900 °C and 1500 °C, respectively. The coated samples were put into the furnace in a ceramic crucible, subsequently heated to the given temperatures (900 °C or 1500 °C) and held at that temperature for the designed hours of oxidation. Then the coated samples were taken out from the furnace to measure their weights by an electronic balance with a sensitive of 0.1 mg. The weight change was calculated by the following formulate:

$$W\% = \frac{m_2 - m_1}{m_1} \times 100\% \tag{1}$$

where $W\%$ is weight change rate, m_1 and m_2 are the weights of samples before and after oxidation, respectively.

2.3. Anti-ablation test

Anti-ablation test of the $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coated sample (size: Ø 30 × 10 mm) was carried out by oxyacetylene flame for 60 s (according to the GJB323A-96 Standard) [33]. The pressure and flux of oxygen were 0.4 MPa and 0.244 L/s, while those of C_2H_2 were 0.095 MPa and 0.167 L/s, respectively. The erosion direction was perpendicular to the ablated surface of coated sample. The nozzle-sample distance was 10 mm, and the inner diameter of the nozzle tip was 2 mm. The maximal temperature on the surface of ablated sample was above 2130 °C, which was measured by an optical pyrometer. The mass and linear ablation rates of the coated sample were calculated on the basis of the changes of mass and thickness before and after ablation test.

2.4. Morphology and composition analysis of coatings

The phases of coatings were identified using X-ray diffraction (XRD, X'pert pro MRD, Panalytical B.V., Holland) with a Cu Kα radiation (λ = 0.154056 nm) operating at 40 kV and 200 mA. The 2 θ diffraction angle was measured from 10° to 90° with a step width of 0.02°. Scanning electron microscopy (SEM, JSM-7001, JEOL Ltd., Japan) equipped with energy dispersive spectroscopy (EDS) was used to analyze the microstructure and morphologies of coatings.

3. Results and discussion

3.1. Microstructure of coating

Fig. 1 exhibits the surface and cross-section morphologies of precoating coated graphite and the XRD pattern of precoating surface. Fig. 1(a) reveals a loose and coarse surface, from which some pits can be observed. The pyrolysis of phenolic resin causes volume contraction during heat treatment at 700 °C, leading to the formation of porous precoating coated graphite with the apparent porosity of 11.12%. As seen in Fig. 1(b), the precoating with uniform thickness adheres well to the surface of graphite. From Fig. 1(c), there is a good combination between the precoating and graphite, and no cracks or cavities appear. The XRD pattern in Fig. 1(d) indicates that the precoating is composed of HfC, TaC, B_4C and SiC, which are originated from the raw materials. Carbon diffraction peaks are not discovered in the XRD pattern, which is due to the amorphous nature of pyrolytic carbon produced by the pyrolysis of phenol formaldehyde resin at 700 °C in nitrogen atmosphere.

Fig. 2 presents the XRD pattern of $Hf_{0.5}Ta_{0.5}B_2$-SiC-Si coating surface after reactive infiltration of gaseous silicon. It is noted that the characteristic peaks of raw materials (HfC, TaC and B_4C) disappear, and $Hf_{0.5}Ta_{0.5}B_2$ phase (PDF # 98-151-0710) appears in the XRD pattern, indicating the formation of $Hf_{0.5}Ta_{0.5}B_2$ phase. It is known that HfC and TaC can react with B_4C and Si to form HfB_2 and TaB_2 phases, respectively, whereas HfB_2 and TaB_2 are not detected in the XRD pattern. The reason can be explained as follows: the ionic radius of Hf is 72 pm, which is close to the ionic radius of Ta (68 pm) [34]. Based on the solid