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Microstructure and oxidation behaviors of dense mullite-silicon carbide-silicon coating for graphite fabricated by dipping-pyrolysis and reactive infiltration

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ABSTRACT

A new-designed mullite-SiC-Si coating with dense structure for protecting graphite materials was prepared by dipping-pyrolysis combined with reactive infiltration. The phase synthesis, microstructure and anti-oxidation property of the fabricated mullite-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 1600 °C for 752 h and 550 h, respectively, the mass gains were 0.1% and 0.99%, respectively. The excellent anti-oxidation performance was ascribed to the dense structure of coating and the formed glassy oxide layer on the coating surface. The oxidation process of mullite-SiC-Si coating was controlled by the diffusion of oxygen, and the as-prepared coating after oxidation was composed of oxide layer and dense mullite-SiC-Si layer. In contrast to SiC-Si coating, the high temperature stability of mullite-SiC-Si coating was greatly improved.

1. Introduction

Carbon materials including C/C composites and graphite are considered as the most promising thermal-structural materials in aeronautical and aerospace fields due to their outstanding high temperature stability and mechanical properties [1–3]. However, easy oxidation of carbon materials above 450 °C in oxidizing atmosphere limits their extensive applications [4–6]. Applying ceramic coatings on the surfaces of carbon materials is an effective solution to prevent oxygen from oxidizing carbon substrates [7,8].

SiC is preferably selected as external coating owing to its excellent thermal stability and compatibility with carbon materials [9,10]. In addition, glassy SiO_2 formed on the surface of SiC coating owns low oxygen diffusivity and good self-sealing property, which can act as a barrier layer and restrain the oxygen attacking the carbon substrate [11]. However, single SiC layer possesses a limited anti-oxidation property at high temperature (1600 °C), because some bubbles and holes will be formed in the coating during long-time oxidation. These defects will weaken the high temperature stability of SiC coating, thereby leading to the degradation of the protective ability [12,13]. Introducing high temperature components in SiC coatings is an effective way to improve the high temperature stability of SiC coatings.

To date, various SiC-based ceramic coatings have been developed to protect carbon substrates from oxidation, such as ZrB_2-SiC [14,15], ZrB_2-$MoSi_2$-SiC [16], $MoSi_2$-SiC [17], TaB_2-SiC [18], HfB_2-SiC [19], $Y_2Si_2O_7$-SiC [20], $CrSi_2$-SiC [21], mullite-SiC [22] and SiC-glass [23], etc. Among these coatings, mullite modified SiC coating is considered as a more promising multi-phase coating because of the matched coefficients of thermal expansion (CET) between mullite ($4.4–5.6 \times 10^{-6}$/°C) and SiC ($4.3–5.4 \times 10^{-6}$/°C) [24]. Additionally, mullite has high melting point (1840 °C), good high temperature stability, good erosion resistance and low permeability of oxygen at high temperature, which is suitable for improving the high temperature anti-oxidation ability of SiC coating [25]. However, the existing coating technologies, like pack cementation [26], pulsed-laser deposition (PLD) [27], hydrothermal electrophoretic deposition [28], hot dipping [29], plasma spraying [30], melt infiltrated [31], chemical vapor deposition [32] and sol-gel [33], cannot fabricate dense mullite and mullite-contained coatings. Some structural defects (cracks and holes) are usually formed in the coating during the preparation process or cooling stage, which will affect the oxidation resistance of coatings. Dipping-pyrolysis combined with reactive infiltration process is an effective approach for fabricating dense ceramic coatings without structural defects [34]. Besides, reactive infiltration is also a good technology for sintering net-shape

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forming ceramic matrix composites with specific advantages of low cost and easy operation [35].

The aim of this work was preparation of dense mullite-SiC-Si coating on graphite surface by dipping-pyrolysis with the combination of gaseous silicon infiltration. The phase components and microstructures of coating were studied. The oxidation resistance performances of the as-obtained coatings at 900 °C and 1600 °C in air were investigated. The anti-oxidation mechanism of mullite-SiC-Si coating was also discussed.

2. Experimental

2.1. Preparation of mullite-SiC-Si coating

Graphite specimens (10 mm × 10 mm × 5 mm) used as substrates were machined from a graphite bulk, the density of which is 1.77 g/cm^3. Phenolic resin solution (carbon yield = 40 wt%, thermosetting) (Shandong Jining Huakai Resin Co. Ltd., Shandong, China), SiC powders (D_{50} = 0.5 μm–10 μm, > 95 wt% pure, Shandong, Weifang, Changle, Xinyuan silicon carbide powder Co. Ltd., Shandong, China), mullite powders (D_{50} = 1–3 μm, 99 wt% pure, Lingshou, Fengju, Minerals Processing Factory, Shijiazhuang, Hebei, China) and silicon particles (5–8 mm, Si ≧ 99.4 wt%, Shenyang, Boyu Metal Co., Ltd., Shenyang, China) were used as raw materials. The graphite specimens were hand-abraded using 400 and 800 # sandpapers, then cleaned by ultrasonic using ethanol and dried at 130 °C for 2 h.

Two kinds of suspension slurries were prepared for dipping graphite substrates. One of them was resin-SiC slurry, and the other one was resin-mullite-SiC slurry. The mass fractions of SiC, alcohol and phenolic resin in the resin-SiC suspension were 50 wt% (30 wt% 0.5 μm, 70 wt% 10 μm), 40 wt% and 10 wt%, respectively. The mass fractions of SiC, mullite, alcohol and phenolic resin in the resin-mullite-SiC suspension were 30 wt% (30 wt% 0.5 μm, 70 wt% 10 μm), 20 wt%, 40 wt% and 10 wt%, respectively. Phenolic resin was first dissolved into ethanol to form phenolic resin solution. After that, SiC or SiC-mullite powders were added into the aforementioned solution, then stirred by magnetic and dispersed by ultrasonic to obtain two kinds of homogeneous suspensions. The graphite substrates were dipped by the obtained resin-SiC suspension for 2–3 s, then taken out from the suspension slurry. After dried naturally at room temperature, the specimens with resin-SiC precoatings were toughened by curing process at 150–170 °C for 2–3 h. Subsequently, the dipping-curing process of resin-SiC coated specimens was repeated using the resin-mullite-SiC suspension, followed by pyrolysis in nitrogen at 700 °C for 2 h. Then, the mullite-SiC precoatings coated specimens were put into a graphite crucible containing silicon blocks at the bottom. Particularly, the samples were separated with silicon blocks using a porous graphite plate. Finally, the crucible was heated to 1900 °C and held for 20 min in a vacuum furnace to obtain mullite-SiC-Si coating.

2.2. Open porosity and anti-oxidation tests

Archimedes method was applied to measure the open porosities of the samples after pyrolysis (mullite-SiC) and reactive infiltration (mullite-SiC-Si). The oxidation tests of the coated samples were performed in electric furnace at 900 °C and 1600 °C, respectively. The coated samples were put into the furnace in a ceramic crucible, subsequently heated to the given temperature and held at that temperature for several hours of oxidation. Then the samples were taken out from the furnace to measure their weights by an electronic balance with a sensitive of 0.1 mg. The mass 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.

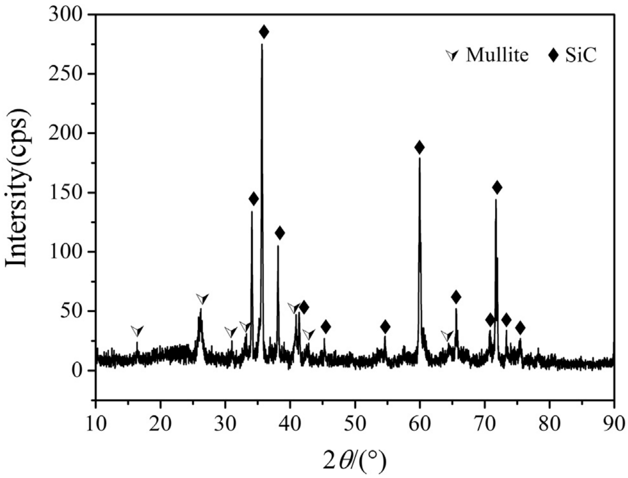

Fig. 1. XRD pattern of the mullite-SiC precoating surface.

2.3. 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 CuKα radiation (λ = 0.154056 nm) operating at 40 kV and 200 mA. The 2θ 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 depicts the XRD pattern of mullite-SiC precoating surface. It can be seen that the primary phases of precoating are mullite and SiC, which are derived from raw materials. Carbon diffraction peaks are not detected in the XRD pattern, this is because that the pyrolytic carbon originated from the pyrolysis of phenolic resin is amorphous. Surface and cross-section micrographs of the precoating and corresponding EDS analyses are presented in Fig. 2. Fig. 2(a) reveals a porous and loose surface, and the porosity of precoating coated graphite is 10.65%. The formation of these pits on the precoating surface is mainly due to the volume shrinkage of phenolic resin during pyrolysis process at 700 °C. As seen in Fig. 2(b), big particles are surrounded by small particles. According to the EDS analyses in Fig. 2(c), these two particles are SiC and mullite, respectively, which is consistent with the XRD result in Fig. 1. From Fig. 2(d), it can be seen that the cross-section of precoating consists of two uniform layers, they are outer mullite-SiC layer and inner SiC layer, respectively. The SiC layer presents good combination with graphite and mullite-SiC layer, no obvious cracks appear among them. Based on the EDS map-scanning element analyses in Fig. 2(e), a portion of aluminum and oxygen elements exist in the SiC layer, indicating that a part of mullite particles infiltrates into the inner SiC layer during the dipping process.

Fig. 3 illustrates the XRD pattern of mullite-SiC-Si coating surface after reactive infiltration of gaseous silicon. Besides dominant phases of mullite and SiC, Si diffraction peaks appear in the XRD pattern, suggesting that residual silicon exist in the as-prepared coating after gaseous silicon infiltration process.

Fig. 4 shows the surface and cross-section morphologies of mullite-SiC-Si coating and EDS map-scanning element analyses. As shown in Fig. 4(a), it appears to have a dense and smooth coating surface, and no pits can be observed. The porosity of mullite-SiC-Si coated graphite is