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In-situ synthesis of SiC-ZrB_2 coating by a novel pack cementation technique to protect graphite against oxidation

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ABSTRACT

A multiphase coating was prepared on a graphite substrate by a two-step technique to enhance the oxidation protection ability of graphite. The first step was to obtain a functionally graded SiC layer and the second one was to develop a SiC-ZrB_2 coating by an in-situ reaction method through a novel pack cementation technique with Zr, Si and B_4C powders. The phase compositions, microstructure and element distribution of the coating were characterized by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy, respectively. The isothermal oxidation and thermal shock tests of the coated samples were performed at 1773 K in air for 10 h. A 650 μm thick graded C–SiC layer was observed at the graphite-coating interface and a SiC-ZrB_2 coating was formed on the first coating. The v coating could efficiently improve oxidation resistance of graphite with a mass gain of +1.7%, as compared with a −63.2% mass loss of the first step coating. The excellent protection ability SiC-ZrB_2 coating could be attributed to the formation of the thermally stable phase $ZrSiO_4$.

1. Introduction

Carbon and graphite materials are extensively used for high temperature applications due to the maintenance of their mechanical and thermal properties. However, the oxidation of graphite above 773 K in air cannot meet the demand of practical application requirement, specifically for high-temperature causing a fall in their mechanical properties. Furthermore, with the increase in oxidation temperature, the rate of graphite chemical reaction with oxygen, as well as the extent of oxidation, is intensely increased. Therefore, more efforts need to be made to improve the ablation resistance of graphite in the oxidizing atmosphere [1–3]. It is well known that the SiC coating is an effective approach for protecting graphite at high temperature, since it can significantly prevent the oxygen diffusion into the graphite by producing a protective layer. In addition, the glassy SiO_2 film will be formed on the surface of the coating while the SiC coated graphite is placed in air at high temperature, which can efficiently inhibit oxygen from diffusing into the graphite. On the other hand, the mismatch of the thermal expansion coefficient between graphite and the SiC coating commonly lead to cracking of SiC coating, facilitating the oxygen diffusion to graphite substrate and the failure of the coating. Therefore, the protective temperature range of SiC coating is narrow, which limits the coating application for protection of graphite against oxidation [4–6].

Studies have reported ultra-high temperature ceramics (UHTCs) can be used as coating materials on carbon materials to provide effective ablation resistance. Among UHTCs and borides, ZrB_2–SiC ceramic coating is a promising solution to improve ablation property of the graphite. The ZrO_2 produced by oxidation of ZrB_2 can react with SiO_2 to form $ZrSiO_4$, which is beneficial to oxidation resistance ability due to its low permeability for oxygen and high thermal stability at high temperature. The high-thermally stable $ZrSiO_4$ can be expected to reduce the consumption of SiO_2 and improve the oxidation resistance of SiC coating at high temperature [6,7]. Yao [8] et al. prepared a ZrB_2–SiC coating on carbon/carbon composites by a pack cementation process with Si, ZrB_2 and B_2O_3 powders at 2173–2473 K. The excellent oxidation protective performance was attributed to the integrity and stability of SiO_2 glass improved by the formation of $ZrSiO_4$ phase during oxidation. Ren [9] et al. synthesized a ZrB_2–SiC gradient coating by a pack cementation process with Si, ZrO_2, B_2O_3 and graphite powders at 2373 K. The effective self-sealing property of the protective silicate glass layer as well as the pinning effect of $ZrSiO_4$ was responsible for the excellent oxidation protective ability of the coating. Moreover, Wang [10] et al. used a two-step pack cementation method with

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ZrB_2, Si and graphite powders at 2273 K to prepare ZrB_2–SiC coating on graphite, which showed ZrB_2–SiC coating endured 15 thermal shock cycles between 1773 K and room temperature with 20.2% weight loss.

The above researches used ZrB_2 in the pack powder at temperatures over 2173 K. Nevertheless, in the present study, a novel pack cementation method with Zr, B_4C and Si powders was developed to prepare an in-situ SiC-ZrB_2 protective coating on graphite at 1873 K. The phase compositions and microstructures of the prepared coating were studied and their oxidation resistance was also investigated at 1773 K in air.

2. Experimental procedures

2.1. Preparation of the coatings

The specimens, with a dimension of 10 mm × 10 mm × 10 mm were cut from graphite with an apparent density of 2.07 g/cm^3, a bulk density of 1.77 g/cm^3, an apparent porosity of 14.56% and a flexural strength of 49.51 MPa. After being hand-abraded using 400 and 800 grit SiC paper, these specimens were cleaned with distilled ethanol and dried at 383 K for 2 h. The preparation process of SiC/SiC-ZrB_2 coating on the graphite was shown in Fig. 1.

The first step coating was formed on the surface of the graphite by the pack cementation technique with a powder mixture composed of 50 wt% Si (400 mesh, Panadyne) 40 wt% α-SiC (α-SiC, 800 mesh, Goodfellow), and 10 wt% α-Al_2O_3 (800 mesh, Panadyne). The graphite samples were embedded in the powder mixture in a graphite crucible, and were then heat-treated at 1873 K for 2 h in an argon protective atmosphere to form the first step SiC coating. The second step coating was also prepared by the pack cementation technique with a powder mixture according to reaction (1) comprising of 16 wt% Si (400 mesh, Panadyne), 52 wt% Zr (800 mesh, Goodfellow), and 32 wt% B_4C (400 mesh, Panadyne) on the surface of the first step coated substrates then heated at 1873 K for 2 h in an argon protective atmosphere.

$$2Zr + Si + B_4C \rightarrow 2ZrB_2 + SiC \qquad (1)$$

2.2. Characterization

The isothermal oxidation test of the coated samples was accomplished at 1773 K in air in an electrical furnace. For thermal shock tests, the coated samples were kept for 30 min in furnace in air at 1773 K and for 10 min in room temperature (RT) alternatively for 20 times. The cumulative weight changes of the coated samples after oxidation were measured by the precision balance and reported as a function of time. The mass loss was calculated using Eq. (2):

$$\%\text{mass loss} = [(m_0 - m_1)/m_0] \times 100 \qquad (2)$$

where m_0 is the original mass of the coated sample and m_1 is the mass of the coated samples after oxidation at 1773 K.

An X-ray diffractometer (XRD, Philips, PW1730) equipped with a copper X-ray source was used for the phase analysis of the coatings. The phases identification was done by the X'Pert Highscore software developed by PANalytical B.V., and a field emission scanning electron microscope (FESEM, Tescan, MIRA3) operating at 15 KV and equipped with energy dispersive X-ray spectroscopy (EDS), secondary electrons detector (SE) and back scattered electrons detector (BSE) were employed for the characterization of the coating morphologies. HSC Chemistry software version 6.0, as developed by Outokumpu Research, was used for such thermodynamic calculations as the variations of Gibbs free energy for the reactions [11].

3. Results and discussion

3.1. Microstructure of the coating

Fig. 2 shows the XRD patterns of the surface of the coatings. It can be seen that the first coating was composed of β-SiC, α-SiC and graphite.

In order to propose the reaction-path mechanism for the formation of the SiC coating, it is worth noting that at the initial stages of the reaction, SiO and CO gaseous phases could be formed as a result of interaction of silicon and carbon with the residual oxygen in the furnace atmosphere. The SiC phase particles can be formed by the reactions of Si with C (Eq. (3)), Si with CO (Eq. (4)) and C with SiO (Eq. (5)), as established by other studies [12–14].

$$Si(l) + C \rightarrow SiC \qquad (3)$$

$$2Si + CO(g) \rightarrow SiC + SiO(g) \qquad (4)$$

$$SiO(g) + 2C \rightarrow SiC + CO(g) \qquad (5)$$

SiC was also formed by a reaction between SiO and CO gaseous

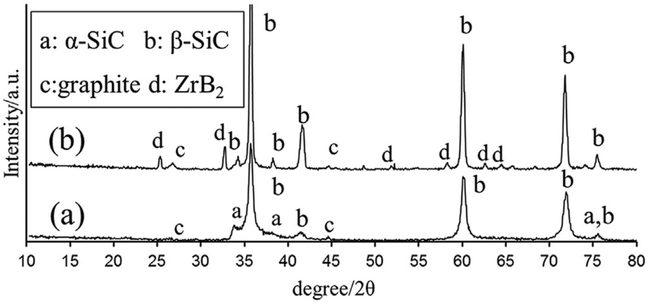

Fig. 2. XRD patterns of: a) the first step coating, b) the second step coating.

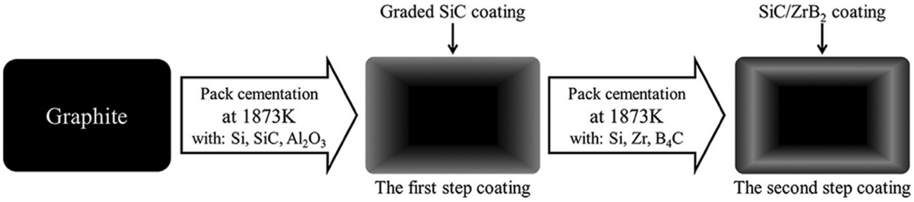

Fig. 1. Schematic illustration image of the preparation of SiC/SiC-ZrB_2 coating on graphite.