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Ultra-high temperature ceramic TaB_2–TaC–SiC coating for oxidation protection of SiC-coated carbon/carbon composites

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Abstract

In order to improve the oxidation resistance of the TaB_2–SiC based coating applied on carbon/carbon (C/C) composites, TaC phase was in-situ introduced and a TaB_2–TaC–SiC ultra-high temperature ceramics (UHTCs) coating was prepared on the surface of SiC coated C/C composites by in-situ synthesis method. The results showed that the outer coating consists of smooth non-angular TaB_2 phase, regular hexagonal prism shape TaC phase and SiC phase, which are synchronously obtained during the preparation of the coating. The multilayer coating could protect the C/C composites against oxidation for 400 h at 1773 K in air with only 1.43% weight loss. A double self-healing oxidation layers (inner SiO_2 glass layer and outer compound Ta–Si–O silicate glass layer) formed on the surface of the coating provides a dual oxidation protection for the coating, which was responsible for the excellent oxidation resistance.

Keywords: B. Composites; B. Surfaces; D. Borides; D. Carbon

1. Introduction

Carbon/carbon (C/C) composites are considered as a leading candidate material for high temperature thermal structural applications due to the outstanding characteristics, including low density, good thermal shock resistance, high strength-to-weight ratio and low coefficient of thermal expansion [1–3]. However, owing to the oxidation of carbon above 723 K, their wide applications in oxidizing atmosphere are limited. In order to solve this problem, multilayer coating technique [4–6] has been considered an effective way. Due to the mismatch of coefficient of thermal expansion between ceramics and C/C composites, most of the ceramic coating cannot be applied directly on the surface of C/C. While SiC coating has good compatibility with C/C composites, and therefore it is widely used as an internal buffer layer.

Recently, due to the high melting temperatures ($>3000\,^{\circ}C$), high hardness, high thermal and electrical conductivity, excellent chemical stability, good thermal shock and oxidation resistance [7–12], ultra-high temperature ceramics (UHTCs) materials have attracted many attentions, which are considered as potential candidates for applications such as thermal protection structures for space vehicles, refractory crucibles, plasma-arc electrodes, rocket engines and so on. Tantalum carbide (TaC) and tantalum diboride (TaB_2) are such a typical UHTCs, which have attracted many attentions these years [13–18].

In our previous work, we have successfully prepared the TaB_2–SiC–Si [19] coating on the SiC coated C/C composites by the in-situ synthesis method, which can protect the C/C from oxidation for 300 h at 1773 K. However, its oxidation resistance is not too high. Moreover, we have found that the addition of TaC is helpful to improve the oxidation resistance of coating for C/C [20]. Therefore, the introduction of TaC phase is promising to improve the oxidation resistance of the TaB_2–SiC based coating.

The in-situ synthesis method is a good method for producing multi-component UHTCs coatings [21,22]. All the phases in the

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coatings can be synchronously obtained during the preparation of the coating from cheaper and more abundant precursors at relatively lower temperature. In addition, structural controllability is one advantage of the in-situ synthesis method, which can be used to achieve the coating with desired component by adjusting the ratio of raw materials. TaB_2 phase can be obtained through the in-situ reaction by co-reducing Ta_2O_5 and B_2O_3 using C, while TaC phase can be obtained through the in-situ reaction by reducing Ta_2O_5 using C. So if suitable amount of C is used, TaB_2 and TaC phase can be synchronous obtained in the coating. Therefore, in this work, in order to improve the oxidation resistance of TaB_2–SiC based coating, Ta_2O_5, B_2O_3, graphite and Si were used as raw materials to prepare the UHTCs TaB_2–TaC–SiC multiphase oxidation protective coating by the in-situ synthesis method on SiC coated C/C composites. All the phases are synchronously obtained during the heat-treatment process. The preparation, microstructures, oxidation resistance and mechanism at 1773 K of the TaB_2–TaC–SiC/SiC multiphase oxidation protective coating were investigated.

2. Experimental procedures

Small specimens (10 mm × 10 mm × 10 mm) were cut from two dimensional C/C composites with a density of 1.70 g/cm^3. All specimens were hand-polished with 400 grit SiC paper first, then ultrasonically cleaned with ethanol and dried at 373 K for 3 h; finally, the specimens were used to prepare coating. The inner SiC coating was obtained by the first-step pack cementation, and the Si (60–80 wt%) (Jiuling Smelting Co., Ltd, Shanghai, China), graphite (10–25 wt%) (Carbon Plant, Xi'an, China), Al_2O_3 (5–15 wt%) (Guoyao Chemical Reagent Co., Ltd, Shanghai, China) powders were used as raw materials. The Al_2O_3 in the pack powders was used to increase the rate of diffusing reaction. While the outer TaB_2–TaC–SiC coating was obtained by the in-situ reaction method on SiC-coated C/C composite, and the Ta_2O_5 (25–40 wt%) (Guoyao Chemical Reagent Co., Ltd, Shanghai, China), B_2O_3 (15–30 wt %) (Tianli Chemical Reagent Co., Ltd, Tianjin, China), graphite (15–25 wt%) (Carbon Plant, Xi'an, China), Si (35–50 wt%) (Jiuling Smelting Co., Ltd, Shanghai, China) powders were used as raw materials. The weight composition of the as-formed TaB_2–TaC–SiC coating is TaB_2 (28.1 wt%)–TaC (7.3 wt%)–SiC (64.6 wt%). TaB_2 and TaC phases were synthesized through the in-situ reaction by co-reducing Ta_2O_5 and B_2O_3 using graphite. In the process of the preparation of the inner and outer coating, all the raw powders and specimens were put in a graphite crucible, and then heat-treated at 2373 K for 2 h in normal argon atmosphere to form the coating. The heating rate was 5–10 K/min.

The isothermal oxidation tests of the coated samples were carried out in static air in an electrical furnace at 1773 K. The samples were put inside or taken out of the electrical furnace directly at certain period. The specimens were weighed at room temperature by electronic balance with a sensitivity of ±0.1 mg before and after the oxidation. Cumulative weight change percentages (ΔW%, weight loss percentage) of the specimens were calculated and reported as a function of oxidation time. The crystalline structure of the multiphase coatings was analyzed by X-ray diffraction (XRD, X'Pert Pro, PANalytical, Almelo, the Netherlands). The morphology and the elemental distribution of the multiphase coating were measured with scanning electron microscope (SEM, JSM6460, JEOL Ltd., Mitaka, Japan) which were equipped with energy dispersive spectroscopy (EDS).

3. Experimental results and discussions

3.1. Microstructure of the coating

Fig. 1 exhibits the XRD pattern of the SiC coating surface. It can be seen that the inner buffer coating prepared by pack cementation mainly consists of pure SiC phase that has peaks with strong intensity, no other impurity peaks can be seen. SiC was prepared by reaction (1). The surface SEM image of the SiC coated C/C composites was shown in Fig. 2. It reveals that no microcrack can be found on the surface of the coating, which indicates the good compatibility of SiC coating with C/C composites. In addition, it can be seen that the SiC coating is not very dense and some voids can be seen, which is helpful for the combination between the inner and outer coating. And therefore, the SiC coating is suitable to be used as an inner buffer layer between the outer layer and the C/C substrate.

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

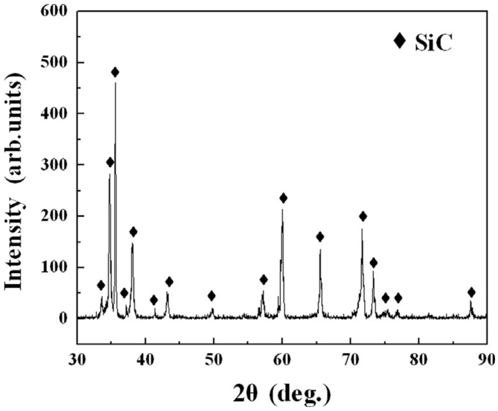

Fig. 1. XRD pattern of the SiC coated C/C composite.

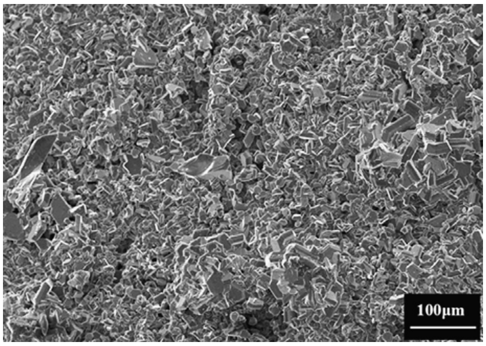

Fig. 2. Surface SEM image of the SiC coated C/C composites.

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