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A SiC/ZrB_2–SiC/SiC oxidation resistance multilayer coating for carbon/carbon composites

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ABSTRACT

To extend the oxidation protective temperature range of coating for carbon/carbon (C/C) composites, a SiC/ZrB_2–SiC/SiC multilayer coating was prepared by a three-step method of pack cementation, slurry and chemical vapor deposition. The prepared coating is composed of three layers with about 150 μm in thickness. It can protect C/C composites from oxidation for more than 300 h at 1173 K which is attributed to the oxidation ability of ZrB_2. The coating can also effectively protect C/C composites from oxidation at 1773 K for 217 h which is due to the SiO_2–$ZrSiO_4$ compound glass during oxidation test.

1. Introduction

Carbon/carbon (C/C) composites are considered as the most promising candidate thermal structure components in aerospace and astronautics application due to their excellent mechanical properties at high temperature [1–3], where these composites are required to undergo a service of thermal cycling between high temperature and room temperature [4–6]. However, the oxidation above 723 K is an urgent barrier to the use of C/C composites as structural materials in high temperature oxidizing systems [2,7].

The ceramic coating is an effective way for protection of C/C composites from oxidation at high temperature. The reported ceramic coatings, such as $C/SiC/MoSi_2$–Si [8], $MoSi_2/SiC$ coating [9], $SiC/MoSi_2$–$CrSi_2$–Si multilayer coating [10], SiC/SiC/Si-W multilayer coating [11] and so on, have been proved to have good oxidation protective ability for C/C composites at 1773–1873 K. However, the silicon-base ceramic coating exhibits poor oxidation resistance below 1473 K or during thermal cycling between high temperature and room temperature, because that the oxidation rate is slow and the viscosity of SiO_2 glass is too high to seal the cracks effectively in the coatings [12–14]. Therefore, the protective temperature range of silicon-based coating is too narrow, which limits its ultimate application for protection of C/C thermal structure components against oxidation.

ZrB_2 based ceramics have important application in the field of thermal protection systems and other components for hypersonic aerospace vehicles [15–18]. For ZrB_2 oxidized in air at elevated temperature, ZrO_2 and liquid B_2O_3 are formed [17,19]. Below 1473 K, molten B_2O_3 glass has high wettability and considerable surface tension to heal up the cracks in the coating that improves the oxidation resistance at medium temperature (1073–1473 K) [12,13,20]. The addition of SiC with volume fraction of 10–30% increases the oxidation resistance of ZrB_2 by promoting the formation of silicate-based glasses that inhibit oxidation at high temperatures (1473–1873 K) [16,17,19,21,22]. So in this work, ZrB_2–SiC coating applied conveniently at low temperature was designed as middle layer to provide oxidation protection for C/C composites at middle-high temperature (1073–1873 K).

In addition, SiC coating is considered as one of the best bonding layer between C/C composites and many kinds of outer layer because of its good physical and chemical adaptability of coating to matrix and bonding layer to outer layer [10,14,23,24].

The focus of this paper is to develop a multilayer coating composed of SiC inner layer, ZrB_2–SiC middle layer and SiC outer layer by a three-step method of pack cementation, slurry and chemical vapor deposition (CVD), respectively, which can be expected to protect C/C composites among board temperature range in air for long-term application. The microstructure and oxidation ability of the coating at 1173 and 1773 K in air were investigated. The thermal cycling property between 1773 K and room temperature was also studied.

2. Experimental

Small samples (10 × 10 × 10 mm) as substrates were cut from bulk 2D C/C composites (prepared by thermal chemical vapor infiltration) with a density of 1.7 g/cm^3. Before coating, the samples

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were hand-abraded with 400 and 800 grit SiC paper, The samples were then ultrasonically cleaned and dried at 373 K. The SiC bonding layer was formed on the surface of C/C composites by the process of pack cementation with Si (300 mesh), C (325 mesh) and Al_2O_3 (300 mesh) powders at 1973–2273 K for 2 h in argon protective atmosphere. The preparation details have been reported elsewhere [25].

The ZrB_2–SiC layer was prepared from commercially available powders of ZrB_2 (800 mesh) and polycarbosilane (PCS), with molecular weight of 1300 and softening point of 473 K which is expected to improve the sintering behavior of ZrB_2 [26]. Firstly the PCS as the precursor of SiC was solved in xylene (mass ratio 1:4). Then ZrB_2 was added into the dissolved PCS to make the slurry. The weight ratio of ZrB_2 and PCS was 3–5:1. The slurry was brushed directly on the surface of SiC coated C/C composites. The samples were dried at 373 K and then carried out a heat-treatment at 1473–1873 K for 2 h in an argon atmosphere with the heating programme of 2 K/min, and then cooled inside furnace with temperature decreasing rate of 4 K/min. The thickness of ZrB_2–SiC layer is about 40–80 μm controlled artificially by brush times.

The SiC outer layer was prepared by CVD at 1173–1373 K with Methyltrichlorosilane (MTS, CH_3SiCl_3) as the precursor for 2–5 h. H_2 was used as both the carrier gas and diluents gas.

The isothermal oxidation tests of coated samples were carried out in air in an electrical furnace at 1173 and 1773 K, respectively. For thermal cycling test, the coated samples were kept for 10 min in furnace in air at 1773 K and for 10 min in room temperature alternatively for 50 times. There were three effective samples used for oxidation and thermal cycling tests. The samples were weighted at room temperature by electronic balance with a sensitivity of ±0.1 mg. The cross-section of samples for microscopy was prepared by diamond saw blade and hand-abraded with 1500 and 2000 grit SiC paper. The crystalline structure and morphology of the as-obtained coating and oxidized coating were examined by X-ray diffraction (XRD, X' Pert PRO), scanning electron microscopy (SEM, JSM-6460) with energy dispersion spectroscopy (EDS) and Renishaw Invia Raman spectrometer.

3. Results and discussion

3.1. Microstructure of SiC/ZrB_2–SiC/ SiC coating

Fig. 1(a–c) exhibits microstructure of ZrB_2–SiC middle layer and CVD SiC layer. Fig. 1(a) reveals the surface morphology of ZrB_2–SiC layer is composed of small uniform particles with size of about 15 μm and there is no obvious crack in the coating. The cross-section image (Fig. 1(b)) shows there are some micro-holes in the coating, which due to the slurry method and low heat treatment at 1473–1873 K. The porosity of ZrB_2–SiC layer is 5–8% calculated by using Image J. The porous structure may influence the oxidation protective ability of the coating. The oxygen can diffuse into the coating through the micro-holes and oxidize C/C matrix. So the dense CVD SiC was deposited on the surface of ZrB_2–SiC layer in order to improve the oxidation resistance ability of the coating. Fig. 1(c) shows the surface morphology of the CVD SiC coating. It can be seen that the SiC grains equably deposited on the matrix that ensure the densification of the coating. The SiC outer layer can improve the compactness of the whole multilayer coating and provide good oxidation protection for C/C composites at 1773 K.

Cross-section image and EDS analyses of the as-prepared SiC/ZrB_2–SiC/SiC multilayer coating are shown in Fig. 2(a and b). The whole coating is composed of three layers with about 150 μm in thickness as shown in Fig. 2(a). The inner SiC layer acting as bonding layer is dense and can minimize the thermal stress caused by the mismatch of thermal expansion coefficient (TEC) between C/C composites and coating ($\alpha_{ZrB2} = 5.9 \times 10^{-6}\,K^{-1}$ [27], $\alpha_{SiC} = 4.5 \times 10^{-6}\,K^{-1}$ [28], $\alpha_{Si} = 2.6 \times 10^{-6}\,K^{-1}$ [29], and $\alpha_{C/C} = 1.0 \times 10^{-6}\,K^{-1}$ [14]). The middle layer is loose and about 60 μm in thickness. No penetrating crack was found in this layer. The dense CVD SiC layer improved the compactness of the whole multilayer coating. By EDS analysis, the element distribution of the SiC/ZrB_2–SiC/SiC coating is show in Fig. 2(b). It can be found the multilayer coating processes the three-layer structure which high amount of Si is distributed in both inner and outer layer, the Zr element mainly fo-

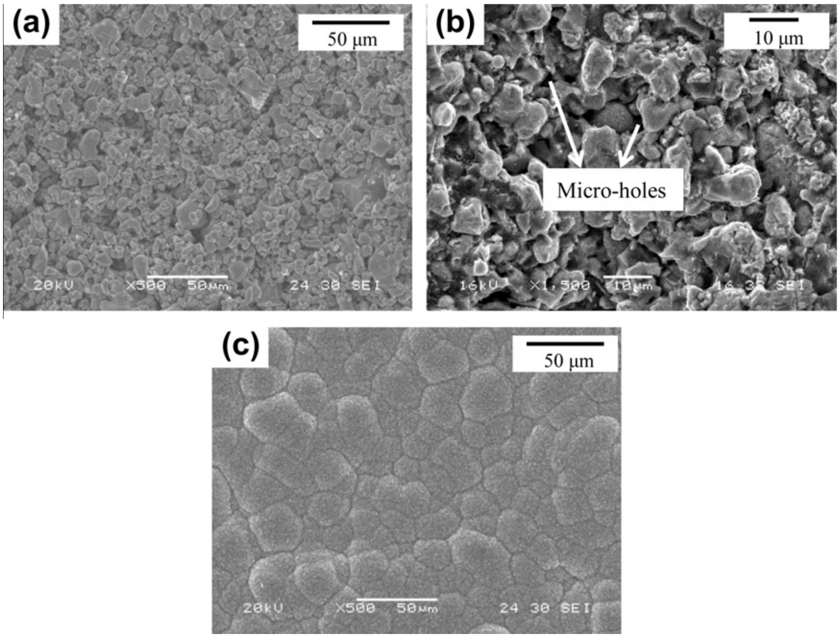

Fig. 1. SEM micrographs of ZrB_2–SiC middle layer by slurry and CVD SiC outer layer. (a) Surface image of ZrB_2–SiC layer, (b) Cross-section image of ZrB_2–SiC layer; and (c) Surface image of CVD SiC layer.