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Short communication

Oxidation resistant yttrium silicates coating for carbon/carbon composites prepared by a novel in-situ formation method

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Abstract

Yttrium silicates interlayer coatings of the SiC/yttrium silicates/borosilicate glass multi-layer coating system were prepared by a novel in-situ formation method using Si and Y_2O_3 as starting materials in an oxidation atmosphere. The surface and cross-section microstructures of the coatings were characterized by XRD and SEM analyses. Oxidation resistance of the coated samples was tested. Results showed that dense yttrium silicate interlayer coatings with good bond to SiC and borosilicate glass were prepared and the as-prepared multi-layer coating could protect C/C composites from oxidation at 1873 K in air for 202 h with a weight loss of 2.87×10^{-3}g/cm^2.

Keywords: B. Composites; D. Carbon; Coatings; Oxidation

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1. Introduction

It is widely recognized that carbon/carbon (C/C) composites are unique as high-temperature structural materials. They have the highest specific strength among all structural materials at temperatures above 1173 K. Hence, they have become preferred materials for different aerospace and re-entry vehicles applications. However, most of these applications have to consider oxidizing atmosphere, and carbon starting to oxidize at about 673 K [1,2]. The prevention of C/C extensive oxidation represents a real challenge. Oxidation-resistant coating is considered to be one of the most reasonable choices for high-temperature protection of C/C composites, and it should meet several requirements such as the mechanical and chemical stability at extremely thermal and oxidative environments, good thermal shock resistance and low oxygen permeability. Three-layer-structure coatings such as SiC/high-temperature ceramics/sealant glass are considered as suitable coatings for protecting C/C composites in oxidation atmosphere at high temperature according to the requirements [3,4]. High-temperature ceramics such as $MoSi_2$, mullite, Al_2O_3, zircon as good corrosion resistant materials were explored to form the interlayer [5–9]. Yttrium silicates seem to be one of the best candidates as the interlayer material at high temperature because of its equivalent thermal expansion coefficients as the one for SiC, low evaporation rate and oxygen permeation constant [10]. Therefore, it was applied to protect carbon-contained composites with the bonding layer of SiC [11,12].

However, the oxidation resistance of yttrium silicates coatings for carbon-containing composites depends on the preparation technology to a great extent. A Y_2O_3 and SiO_2 mixture slurry dipping with a later sintering process could be used to prepare Y_2SiO_5 and $Y_2Si_2O_7$ coatings, but it showed a spallation of the yttrium silicates coating after they were exposed in air at 1873 K for approximately 50 h due to the oxidation of SiC internal layer [12]. In our former research, the plasma spray technique was used to produce a gradient yttrium silicates coating under argon atmosphere, which exhibited excellent oxidation resistance at 1773 K [13]. However, plasma spray technique in a protective atmosphere is too complex to control easily. In order to simplify the preparation technology, we developed a novel in-situ formation method to produce the yttrium silicates coating under oxidation atmosphere.

The scope of the investigation reported here was to produce a SiC/yttrium silicates/glass multi-layer coating. SiC and outer glass sealant coatings were produced by pack cementation and

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slurry dipping, respectively. The interlayer yttrium silicate layer was prepared by a novel in-situ formation method. The prepared multi-coating exhibited good oxidation protection.

2. Experimental

Small specimens (10 mm × 10 mm × 10 mm) as substrates were cut from bulk 2D-C/C composites (prepared in Xi'an, China) with a density of 1.72 g/cm^3. Before the coating process, the specimens were hand-polished using 340 grit SiC paper, then cleaned with distilled water and dried at 373 K for sufficient time. SiC coating was prepared by a pack cementation process with Si, C and Al_2O_3 powders in an argon atmosphere at 2073 K for 2 h. The preparation details were reported elsewhere [6].

After the preparation of SiC bonding layer, an in-situ formation process was conducted. First, a slurry mixture of Si and Y_2O_3 was applied to the SiC coatings surface. Commercially available analytical grade Si and Y_2O_3 powders with particle size from 5 to 20 μm were used. The slurry was made by mixing the Si (40–80 wt.%), Y_2O_3 (20–60 wt.%), distilled water and a little PVA (0.1–0.5 wt.%) as binder. After applying the slurry to the surface of SiC bonding layer, the samples were dried in a dryer at 353 K for sufficient time. Then, the samples were sintered at 1773–1873 K for 1 h in an argon atmosphere. Next, the samples were put in an electrical furnace to pre-oxide in air flow by natural convection at 1773–1873 K for 2–10 h to transform the Si and Y_2O_3 into yttrium silicates.

After the preparation of yttrium silicate coatings, a borosilicate glass was applied directly on their surface. Then the samples were heated at 1773 K in Ar for 2 h. The preparation details are reported elsewhere [12].

The as-coated specimens were placed upon a corundum support and heated at 1873 K in air flow by natural convection in a corundum tube furnace to investigate the isothermal oxidation behavior. After the set time of oxidation at 1873 K, the samples were directly extracted from the furnace and quickly cooled to room temperature. Samples weight was measured by precision scales and then the samples were put directly into the furnace again for the next oxidation period. Cumulative weight changes (g/cm^2) of the samples were calculated and were reported as a function of time. The crystalline structure of the yttrium silicate coatings were measured with the Rigaku D/max-3C X-ray diffractometer (XRD). The surface and cross-section morphologies of the as-prepared multi-layer coatings were analyzed using JSM-5800 scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the XRD spectra of the coated C/C at 1773 K for different pre-oxidation time. After 2 h oxidation at 1773 K, some Y_2SiO_5 and a little $Y_2Si_2O_7$ are formed though some original materials (Si and Y_2O_3) did not react. The formation of the Y_2SiO_5 and $Y_2Si_2O_7$ should be attributed to the reaction shown in Eqs. (1)–(3) for some SiO_2 scales are also determined in the XRD analysis.

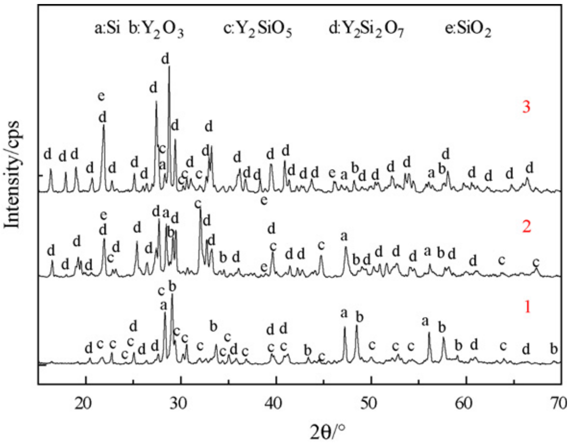

Fig. 1. XRD spectra of the coated C/C at 1773 K for different pre-oxidation time: (1) 2 h; (2) 4 h; and (3) 6 h.

$$Si + O_2 \rightarrow SiO_2 \quad (1)$$

$$SiO_2 + Y_2O_3 \rightarrow Y_2SiO_2 \quad (2)$$

$$SiO_2 + Y_2SiO_5 \rightarrow Y_2Si_2O_7 \quad (3)$$

With the increase of the pre-oxidation time, the contents of Si, Y_2O_3 and Y_2SiO_5 decrease. After 8 h oxidation at 1773 K, nearly mono-phase $Y_2Si_2O_7$ is obtained, which infers that the yttrium silicates coating could be simply prepared by this method.

SEM surface morphology of the yttrium silicates coating after pre-oxidation at 1773 K for 6 h (Fig. 2) shows a smooth surface of yttrium silicates with some circle-like micro-cracks. The formation of this kind of cracks infers that compression stress may be generated in the yttrium silicates coating, which is due to the lower thermal expansion coefficient of $Y_2Si_2O_7$ (3.2–4.0 × 10^{-6}/°C) when compared with SiC (4.3–5.4 × 10^{-6}/°C) [14]. The existence of a small compressive stress in the coating is helpful for the bonding of the SiC and yttrium silicate

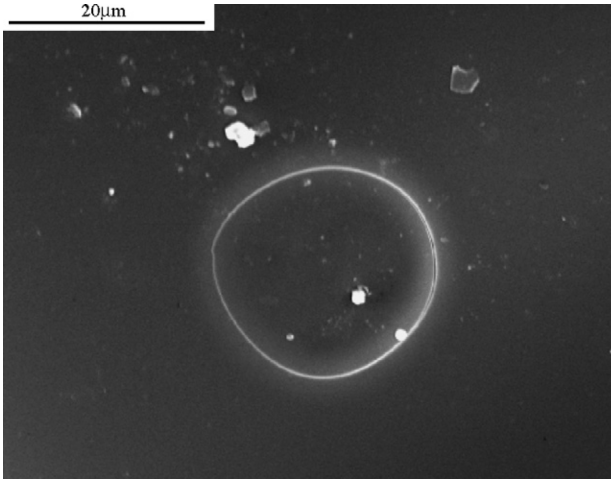

Fig. 2. SEM surface morphology of the yttrium silicates coating after pre-oxidation at 1773 K for 6 h.

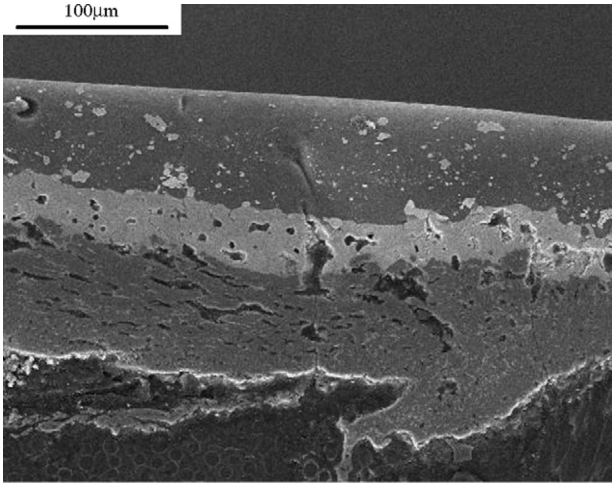

Fig. 3. Cross-section microstructure of the as-prepared SiC/yttrium silicates/ glass multi-layer coating.

coating, and maybe helpful for the multi-layer coating to endure the eroding gas force in severe environments.

Fig. 3 shows the cross-section microstructure of the as-prepared SiC/yttrium silicates/glass multi-layer coating. An obvious three-layer coating structure is achieved. The thickness of the three layers is 100, 50 and 100 μm, respectively. No gaps appear at the interface of SiC-to-yttrium silicates and yttrium silicates-to-glass layers, indicating a good bond with each other of the three layers. This confirms the observations in Fig. 2. In addition, no obvious cracks are found in the cross-section of the prepared multi-coatings, which stands for the suitability of thermal expansion coefficients of the three layers.

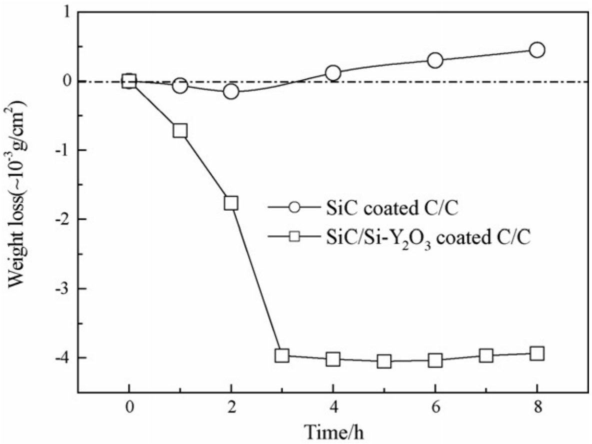

Fig. 4. Isothermal oxidation curves of SiC–C/C and SiC/Si–Y_2O_3 coated C/C at 1773 K.

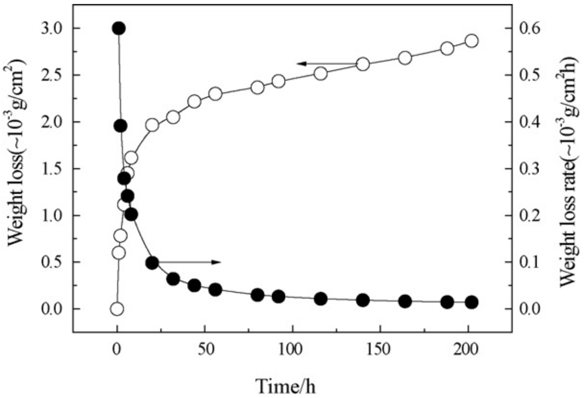

Fig. 5. Isothermal oxidation curves of the SiC/yttrium silicates/glass multi-layer coating coated C/C at 1873 K.

During this novel process to produce yttrium silicates coating, the pre-oxidation process is crucial for the formation of yttrium silicate. It would be harmful if large oxidation of C/C composites occurs during the pre-oxidation process at high temperature. Therefore, the weight changes of the SiC and SiC/Si–Y_2O_3-coated C/C has been investigated at 1773 K. The results are shown in Fig. 4. After 8 h oxidation at 1773 K, the weight loss of SiC-coated C/C is only 0.45 g/cm^2 but SiC/Si–Y_2O_3-coated C/C gains weight after 8 h oxidation at 1773 K, which is due to the reaction of Si and SiC with oxygen and generation of SiO_2. The whole weight change of the samples appeared by two factors. One is the oxidation of the C/C substrate, which is a weight loss process; the other is the oxidation of Si and SiC, which is a weight gain process. Oxidation test results shown in Fig. 4 reveal that the oxidation of Si and SiC give more contribution to the weight change. By observation of the cross-section of the coating–substrate interface (Fig. 3), no obvious oxidation of the substrate appeared, indicating that this new in-situ formation method for preparation of yttrium silicates coatings is reasonable.

Fig. 5 shows the isothermal oxidation curves of the SiC/yttrium silicates/glass multi-layer coating coated C/C at 1873 K. Before 50 h oxidation at 1873 K, the coated C/C loses weight with time according to a parabolic rule whereas the oxidation rate of the as-prepared samples decreases with time quickly. After 50 h oxidation, the weight loss of the coated C/C increases slowly with time and the oxidation rate of the as-prepared sample almost keeps constant. After oxidation at 1873 K for 202 h, the weight loss and the corresponding weight loss rate of the coated C/C are only 2.87×10^{-3} and 1.419×10^{-5} g/cm^2 h, respectively, displaying a perfect protection of C/C composites at high temperature.

4. Conclusions

A yttrium silicates interlayer coating could be simply prepared by a novel in-situ formation method in oxidant atmosphere. The as-prepared SiC/yttrium silicates/glass multi-layer coating exhibits a good oxidation protection for C/C composites as it could protect the C/C composites from oxidation in air at 1873 K for 202 h with a weight loss of the coated C/C of only 2.87×10^{-3} g/cm^2.

Acknowledgements

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