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Structure and oxidation behaviors of C/C-SiC coated with Al_2O_3–$CrAl_{0.42}Si_{1.58}$–SiC–Al_4SiC_4 oxidation protection system

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A multicomposition resistant coating for SiC coated carbon/carbon (C/C) composites was produced by pack cementation technique in an argon atmosphere. This multicomposition coating was characterized by X-ray diffraction and scanning electron microscopy technique, and the oxidation behaviors of C/C with this multicomposition coating were also investigated in air using thermogravimetry. The results indicate that a dense coating with an average thickness of 200 μm can be got using pack cementation technique. The coating is composed of Al_2O_3, $CrAl_{0.42}Si_{1.58}$, SiC, and Al_4SiC_4. This multicomposition coating could effectively protect the composites from exposure to atmosphere at 1873 K for 49 h with the weight loss of the coated C/C composites being only 1.84%.

Keywords: carbon/carbon composites; coating; oxidation

1. Introduction

Carbon/carbon composites (C/C) exhibit excellent high-temperature mechanical properties and are considered as the unique thermostructural materials in many potential applications, such as the engine, aerospace, and the thermonuclear fusion where most of the ceramic and metallic materials cannot be used. However, their applications are limited in oxidative environments by the fact that the carbon materials could be oxidized above 400 °C [1,2]. It is therefore important for their applications to increase the resistance of the materials towards air oxidation at high temperature.

Under such a circumstance, oxidation-resistant coatings are the logical choice for protecting C/C composites. SiC is a widely used coating material owing to its excellent antioxidation properties and good compatibility with the C/C [3–6]. Al_2O_3 and Cr_2O_3 ceramic coatings are promising candidate materials for high-temperature applications. Al_2O_3 coating produced by plasma spraying shows a good high-temperature wear and corrosion resistance [7,8]. In recent works, coatings with Al_2O_3 and Cr_2O_3 had been developed to protect nickel materials, steel, and alloys from high-temperature oxidation and corrosion by employing pulsed laser deposition (PLD), chemical vapor deposition (CVD), plasma spraying technique, and plasma detonation technique [9–13]. As for C/C composites, ion assisted electron beam physical vapor deposition (EB PVD) and pack cementation technique had been used to deposit (Cr–Al) bilayer and Al_2O_3–mullite–SiC–Al_4SiC_4 multicomposition coating [14,15]. Pack

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cementation is a good method to deposit coatings on all the sample surfaces, and it is widely used in producing oxidation protective coating on metal and C/C composites surface [16,17]. However, the reports about using this technique to produce Al_2O_3–$CrAl_{0.42}Si_{1.58}$–SiC–Al_4SiC_4 coating on the C/C surface have not been seen so far.

In the present work, a multicomposition coating containing Al_2O_3, $CrAl_{0.42}Si_{1.58}$, SiC, and Al_4SiC_4 on SiC coated C/C composites was firstly produced by pack cementation method. The structure of the as-received coating and its antioxidation property in air at 1873 K were investigated.

2. Experimental

The C/C composites used were two-dimensional materials with a density of 1.80 g/cm^3 prepared by chemical vapor infiltration (CVI) in our laboratory. The small specimens ($10 \times 10 \times 10\,mm^3$) used as substrates were cut from the as-prepared bulk C/C. Prior to pack cementation procedure, the specimens were hand polished using 400-grit SiC paper, then cleaned with ethanol, and dried at 373 K for sufficient time. The C/C surface was modified in order to obtain a SiC thin layer. The surface modification of the C/C composites had been described elsewhere [17].

The pack powder composition for the pack cementation process is listed in Table. 1. The pack mixtures were weighed and were ball milled for 4 h or so. The SiC coated C/C specimens and the pack mixtures were put in a graphite crucible with a graphite lid, and then the crucible was placed into an electric furnace. After that, the furnace was heated to 2173 K and this temperature was held for 2 h in an argon protective atmosphere to form a multicomposition coating. On completion of the coating deposition, the pack was allowed to furnace cool, and the samples were removed from the pack and ultrasonically cleaned to remove any loosely embedded pack materials.

The oxidation test was conducted at 1873 K in air in an electrical furnace to investigate the isothermal oxidation behaviors of the as-coated specimens. During the test, the samples were taken out of the furnace at given time and weighed by a photoelectric analytical balance with a sensitivity of ± 0.1 mg. The ML (% mass loss) could be calculated with the following equation

$$\mathrm{ML}\ (\%\ \text{mass loss}) = \frac{m_0 - m_1}{m_0} \times 100\% \tag{1}$$

where m_0 is the original mass of the coated C/C composites; m_1 is the mass of the coated C/C composites after oxidation at high temperature for given time.

To identify the morphology and phase composition of the multicomposition coatings, scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements were performed. The elements existing in the coating were analyzed by energy-dispersive spectroscopy (EDS).

Table 1. The composition for the pack cementation process.

Chemicals	Purity	Mesh	Content (wt.%)
Al_2O_3	Analytical grade	325	40–50
Cr_2O_3	Analytical grade	300	10–20
Si	Analytical grade	300	8–25
C (graphite)	Analytical grade	325	10–15

3. Results and discussion

3.1. Structure of the multicomposition coating

Figure 1(a) shows the XRD pattern of the inner layer. A SiC layer as a bond coating was formed. Figure 1(b) provides the XRD patterns of the multicomposition surfaces achieved by the pack cementation. It can be seen that some new phases, such as SiC, $CrAl_{0.42}Si_{1.58}$, and Al_4SiC_4, exist in the coating besides Al_2O_3 while Cr_2O_3 disappeared in the layer.

During the preparation of the multicomposition coating, the following reactions among the pack powder compositions would have happened.

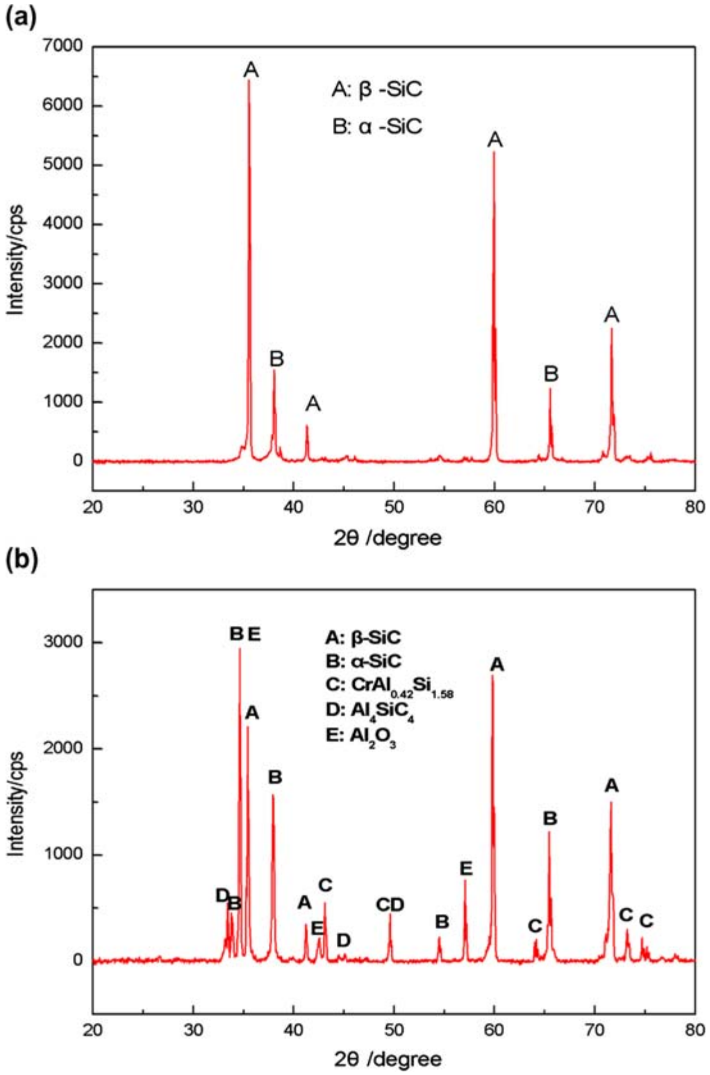

Figure 1. Surface XRD patterns of the SiC coated C/C composites and the multicomponent coated C/C-SiC composites prepared by pack cementation: (a) surface XRD pattern of the C/C-SiC composites; (b) surface XRD pattern of the multicomponent coated C/C-SiC composites.

$$\text{Si (1)} + \text{C (s)} \rightarrow \text{SiC (s)} \tag{2}$$

$$\text{SiC (s)} + \text{Al}_2\text{O}_3\text{ (s)} + \text{C (s)} \rightarrow \text{Al}_4\text{SiC}_4\text{ (s)} + \text{CO(g)} \tag{3}$$

$$\text{Cr}_2\text{O}_3\text{ (s)} + \text{Al}_2\text{O}_3\text{ (s)} + \text{SiC (s)} + \text{C (s)} \rightarrow \text{CrAl}_{0.42}\text{Si}_{1.58}\text{ (s)} + \text{CO (g)} \tag{4}$$

These reactions resulted in the disappearance of Cr_2O_3 and the formation of SiC, $CrAl_{0.42}Si_{1.58}$, and Al_4SiC_4.

Figure 2 shows SEM micrograph and the spot EDS analyses of the surface of the as-made coating on C/C-SiC composites prepared by the pack cementation process. Obviously, there are three kinds of crystalline particles (shown as white 1, gray-white 2, and gray 3) on the coating. By spot EDS analysis, the composed elements of the gray 3 and gray-white 2 phase are mainly Si, C, and Al, while those of the white phase 1 are mainly Si, C, Al, Cr, and O. Based on this fact together with the XRD analysis in Figure 1(b), it is believed that the gray phase 3 and gray-white phase 2 are composed of SiC and Al_4SiC_4, whereas the white phase 1 is composed of Al_2O_3 and $CrAl_{0.42}Si_{1.58}$. It also can be seen that there are hardly any cracks on the coating surface, which indicates that the as-received multicomposition coating has a better physical compatibility with the C/C.

The cross-section image of the multicomposition coating (Figure 3) shows that the as-received coating with a thickness of around 200 μm is perfectly dense, and no obvious interface is found between the SiC bonding layer and the multicomposition outer layer.

3.2. *Oxidation test*

The results of the isothermal oxidation test in air at 1873 K are shown in Figure 4. It can be found that the coated composite shows a weight gain within 18 h, and the weight gain rate decreases with the oxidation time. After that, the weight loss is found, and the weight loss and the weight loss rate increase with the time. The sample still possesses a weight gain of 0.62% when it is exposed to air at 1873 K for 32 h. After oxidation in air for 49 h, the weight loss of the coated C/C composites is only 1.84%, which indicate that the Al_2O_3–$CrAl_{0.42}Si_{1.58}$–SiC–Al_4SiC_4 multicomposition coating possess an excellent barrier property.

3.3. *Analysis of oxidation mechanism and failure of the coating*

The isothermal oxidation behaviors and the high oxidation resistance of the coated C/C all relate to the Al_2O_3–$CrAl_{0.42}Si_{1.58}$–SiC–Al_4SiC_4 multicomposition coating.

Owing to its good physical compatibility with the C/C, there are almost no cracks on the coating, which together with the dense structure of the coating can effectively prevent the diffusion of O_2 into the composite. Therefore, oxidation reactions occur mainly on the surface of the multicomposition coating at the early stage of oxidation test. Figure 5 shows the XRD pattern of the coating after oxidation. SiC, $CrAl_{0.42}Si_{1.58}$, and Al_4SiC_4 disappeared and the mullite ($3Al_2O_3 \cdot 2SiO_2$), Al_2O_3 and Cr_2O_3 were formed after oxidation at 1873 K for 49 h, which indicates that the SiC, Al_4SiC_4, and $CrAl_{0.42}Si_{1.58}$ were oxidized into mullite, Al_2O_3, and Cr_2O_3 these reactions can be described as follows:

$$\text{SiC (s)} + \text{O}_2\text{ (g)} \rightarrow \text{SiO}_2\text{ (s)} + \text{CO}_2\text{ (g)} \tag{5}$$

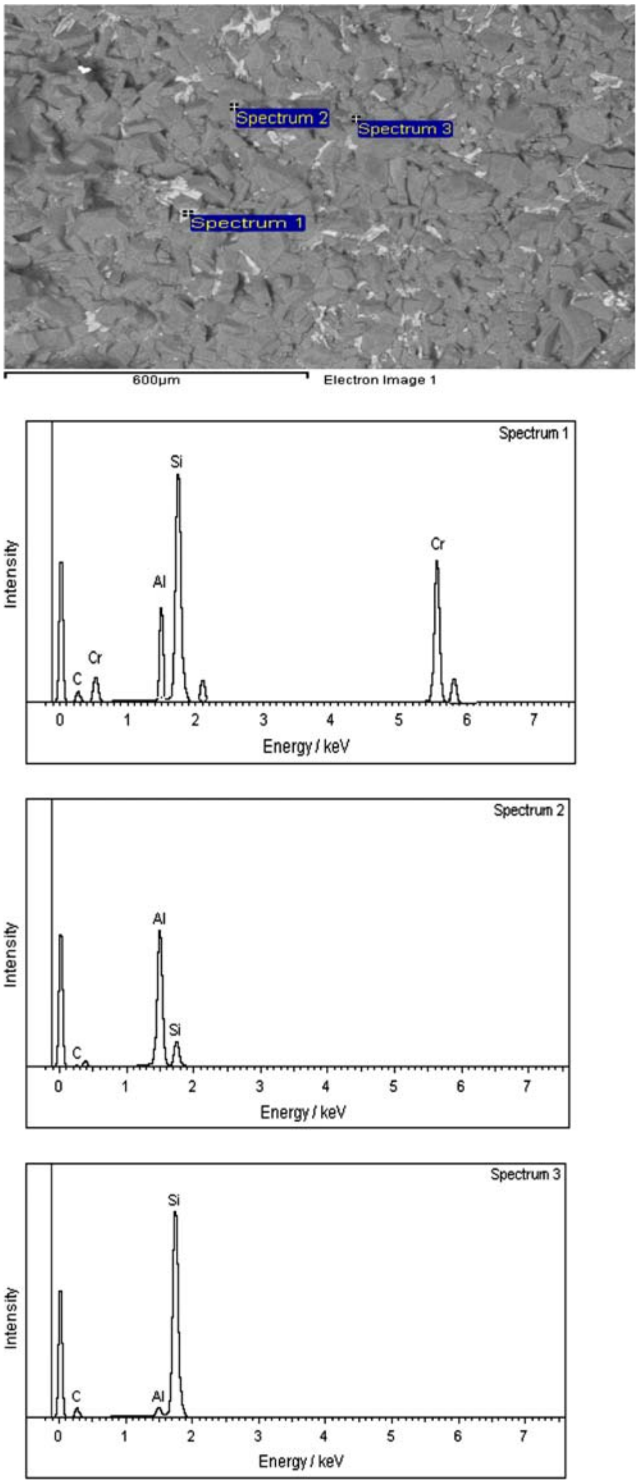

Figure 2. SEM micrograph and the spot EDS analyses of the surface of coating as made on C/C-SiC composites prepared by the pack cementation process: SEM micrograph (spectrum 1–3: the spot EDS analyses).

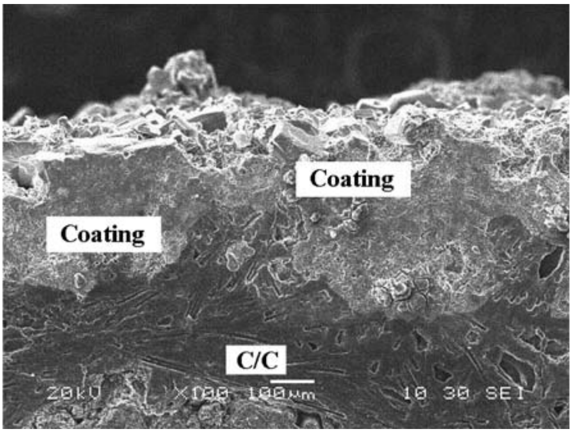

Figure 3. The SEM cross-section image of the as-prepared coating.

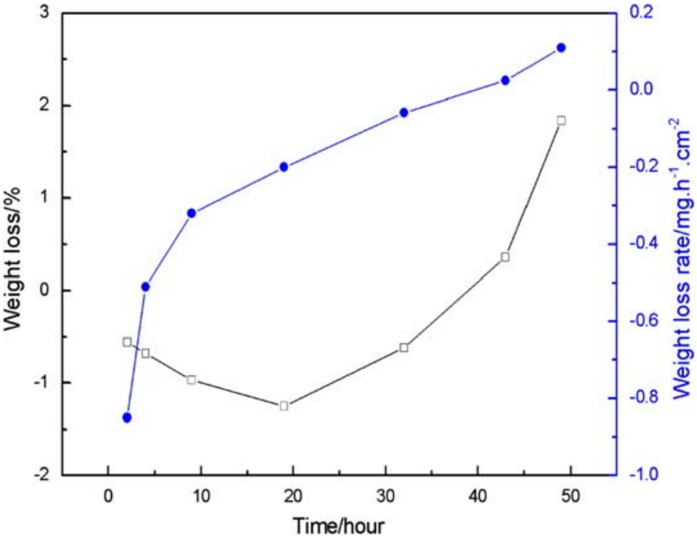

Figure 4. The isothermal oxidation curves of the samples in air at 1873 K (minus weight loss means weight gain).

$$CrAl_{0.42}Si_{1.58}\,(s) + O_2\,(g) \rightarrow 3Al_2O_3 \cdot 2SiO_2\,(s) + Cr_2O_3\,(s) + SiO_2\,(s) \tag{6}$$

$$Al_4SiC_4\,(s) + O_2\,(g) \rightarrow SiO_2\,(s) + Al_2O_3\,(s) + CO_2\,(g) \tag{7}$$

$$SiO_2\,(s) + Al_2O_3\,(s) \rightarrow 3Al_2O_3 \cdot SiO_2\,(s) \tag{8}$$

It can be seen from the reactions (5) and (7) that the oxidation of SiC and Al_4SiC_4 will lead to the weight gain of coated C/C. At 1873 K, SiO_2 and mullite resulted from the oxidation of SiC, Al_4SiC_4, and $CrAl_{0.42}Si_{1.58}$ will be the flexible glass. As the above mentioned reactions went on, a full glass coating was produced on the coating. Cr_2O_3 and Al_2O_3 possess the same

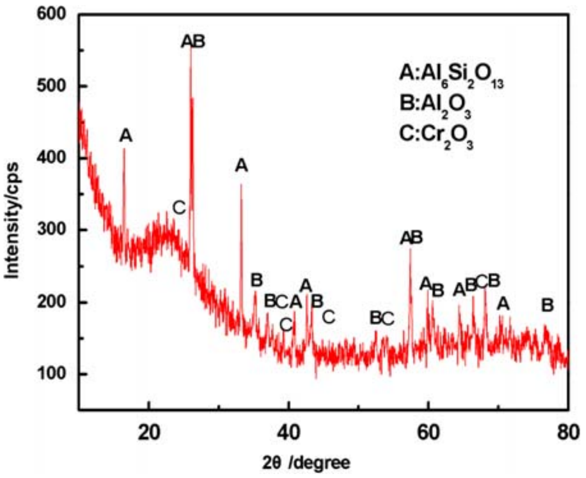

Figure 5. XRD pattern of the coating after oxidation at 1873 K for 49 h.

crystal shapes and could melt each other at high temperature. Mullite ceramic coatings are promising candidate materials for high-temperature applications [15]. So they were the main composites of some antioxidation glass coating to protect C/C composites [18,19], metal, and other materials [8–14]. Although a few of defects such as cracks or pores may exist in the coating, the coating still can act as the protector of C/C because of the sealing of glass to the defects. So, it is the main reason that the coated C/C possesses the high oxidation resistance.

As the oxidation test went on, the glass layer become thicker and thicker. The thicker is the glass layer, the harder is the diffusion of CO and CO_2 produced by oxidation reaction out of the composite. Thus, a very high pressure of CO and CO_2 will be formed in the coated C/C. When the pressure is sufficiently high, the gas bubbles appear. After the bubbles break up, a lot of holes with diameter of about 3–70 μm will be left in the coating (Figure 6). Among these holes, some can allow the oxide gases to diffuse into the C/C and react with carbon materials. The oxidation of C/C leaves big holes around the defects under the coating

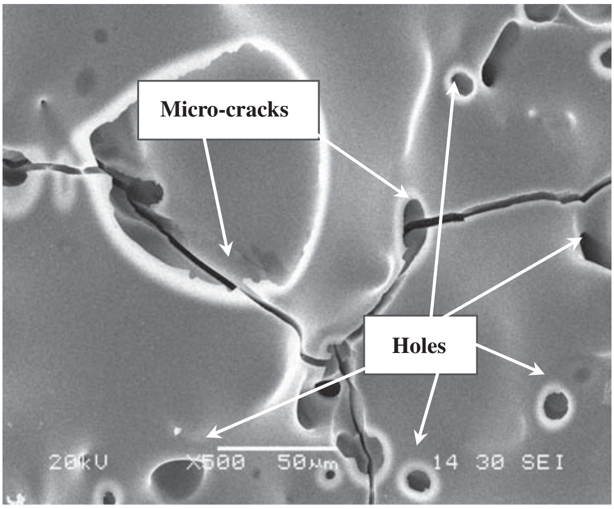

Figure 6. SEM surface of as-made coating after oxidation at 1873 K for 49 h.

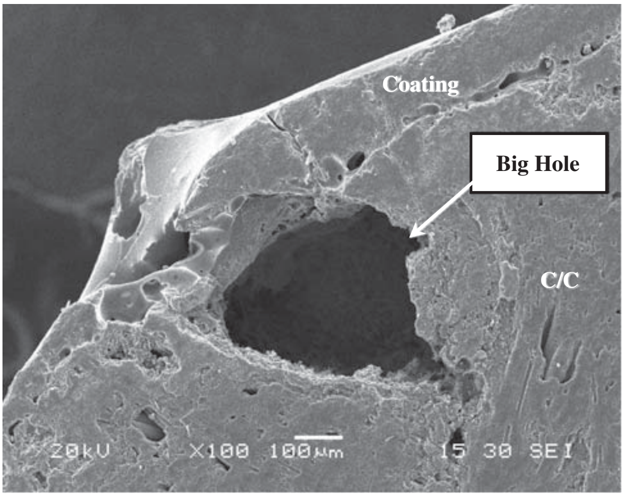

Figure 7. SEM cross-section of as-made coating after oxidation at 1873 K for 49 h.

(Figure 7) and leads to the weight loss of the composite. At the temperature of 1873 K, the oxidation of C/C is controlled by the diffusion of oxygen [20], so with the increase of this kind of holes, the oxidation rate increases, and thus the weight loss rate of coated C/C increase. According to the above discussions, it can be observed that the isothermal oxidation of the Al_2O_3–$CrAl_{0.42}Si_{1.58}$–SiC–Al_4SiC_4 coated C/C composites could be divided into two steps. At the initial stage of oxidation, the oxidation coated C/C is controlled by the reaction between the coating and oxide gases; at the later stage, is controlled by the diffusion of oxide gases through the defects in the coating. The failure of the coating is attributed to the formation of holes and penetrable cracks in it.

4. Conclusions

(1) An Al_2O_3–$CrAl_{0.42}Si_{1.58}$–SiC–Al_4SiC_4 multicomposition coating with a thickness of around 200 µm was produced by a pack cementation process.
(2) This coating could effectively protect the composites from exposure to atmosphere at 1873 K for 49 h with the weight loss of the coated C/C composites being only 1.84%.
(3) The failure of the coating is attributed to the formation of holes and penetrable cracks in it.

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