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Short communication

A Si–SiC oxidation protective coating for carbon/carbon composites prepared by a two-step pack cementation

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Abstract

To prevent carbon/carbon (C/C) composites from oxidation, a Si–SiC coating has been prepared by a two-step pack cementation technique. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis show that the coating obtained by the first step pack cementation is a porous β-SiC structure, and a dense structure consisting α-SiC, β-SiC and Si is obtained after heat-treatment by the second step pack cementation. By energy dispersive spectroscopy (EDS) analysis, a gradient C–SiC transition layer can be formed at the C/C-coating interface. The as-received coating has excellent oxidation protection ability and can protect C/C composites from oxidation for 166 h at 1773 K in air. The weigh loss of the coated C/C is due to the formation of bubble holes on the coating surface and through-coating cracks in the coating.

Keywords: D. Carbon; D. SiC; Oxidation

1. Introduction

Carbon/carbon (C/C) composites have been attracting extensive attention due to their excellent mechanical properties at high temperature, such as high strength-to-weight ratio and high retention of mechanical properties at high temperatures, which makes them promising materials used in aircraft and aerospace fields [1]. However, these composites will be oxidized during their exposure to an oxidizing atmosphere above 723 K [2]. Their oxidation will result in an obvious decrease of their mechanical properties and limit their applications as high temperature structural materials [3]. SiC ceramic coating is an efficient method for protecting C/C composites at high temperature due to its excellent anti-oxidation property and good compatibility with C/C composites [4,5]. In addition, the glassy SiO_2 film will be formed on the surface of the coating while the SiC coated C/C composites are placed in air at high temperature, which can efficiently prevent oxygen from diffusing into the C/C matrix.

However, the mismatch of thermal expansion coefficient between SiC coating and C/C composites usually leads to cracking of SiC coating [6,7]. The through-coating cracks will offer entrance channels for oxygen and result in the failure of the coating. The free silicon distributed in the SiC coating can relax the stress at the end of the cracks and heal up the cracks [8]. It is also expected to decrease the frequency of cracks and improve the oxidation protection ability of SiC coating to some extent. Pack cementation has been used to prepare porous or dense SiC coating by adjusting its preparation conditions [5].

To obtain a dense Si–SiC coating, a two-step pack cementation was designed in the present work. The first step was to prepare a porous SiC inner layer, and the second step was to fill Si and SiC in the holes and cracks in the SiC inner layer. The microstructure and anti-oxidation property of the coating were investigated.

2. Experimental

Small specimens (10 mm × 10 mm × 10 mm) used as the substrates were cut from bulk 2D C/C composites with a density of 1.75 g/cm^3. These specimens were hand-polished using 300 grit SiC paper, then cleaned with distilled water and dried at 393 K for 2 h. Powder compositions for the two-step pack

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cementation process were as follows: 65–80% Si, 10–25% graphite and 5–15% Al_2O_3 for the first step, and 70–85% Si, 5–15% SiC, 7–15% graphite and 2–15% Al_2O_3 for the second step. The role of Al_2O_3 added in the pack powders was to increase the rate of diffusing reaction. All the above powders, with the granularities of 300 meshes, were analytical grade and were mixed by a blender for 2 h. The first pack mixtures and C/C specimens were put in a graphite crucible, and then were heated to 1873–2073 K and held at that temperature for 2 h under slight argon flow to form a porous SiC coating. Subsequently, the as-received SiC coated C/C were immersed in the second pack mixtures. The second pack cementation process was performed at 2173–2373 K for 2 h to obtain a dense Si–SiC coating.

The oxidation test was carried out at 1773 K in air in a furnace. The sample was weighed at room temperature by electronic balance with a sensitivity of ±0.1 mg during oxidation at 1773 K. The morphology and crystalline structure of the coating were analyzed by JSM-6460 scanning electron microscopy (SEM), Rigaku D/max-3C X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure of the coating

Fig. 1 shows X-ray patterns of the surfaces of the as-received coatings. It can be seen that the inner layer obtained by the first step pack cementation is β-SiC. After the second step pack cementation, the coating is composed of Si, α-SiC and β-SiC. α-SiC was primarily resulted from the transition of β-SiC as the pack temperature was up to 2273–2373 K.

Fig. 2(a) displays the SEM micrograph of the surface of the coating produced by the first step pack cementation. Obviously, the β-SiC inner layer is of a porous structure, which might be incapable for protection of C/C composites against oxidation at high temperature. After the second pack cementation process, the coating becomes dense and crack-free, shown from Fig. 2(b), which is expected to have good oxidation protection ability.

Fig. 3 displays the backscattering electron image of the coated sample. The thickness of the coating is about 100 μm; little penetration cracks or holes can be found in the coating. Moreover, there is no obvious interface between the coatings obtained by the two different pack cementation processes. There are two kinds of crystalline particles characterized as white (spot 1) and grey (spot 2) in the coating. By EDS analysis (Fig. 3), the white and grey phases can be distinguished as free Si and SiC, respectively.

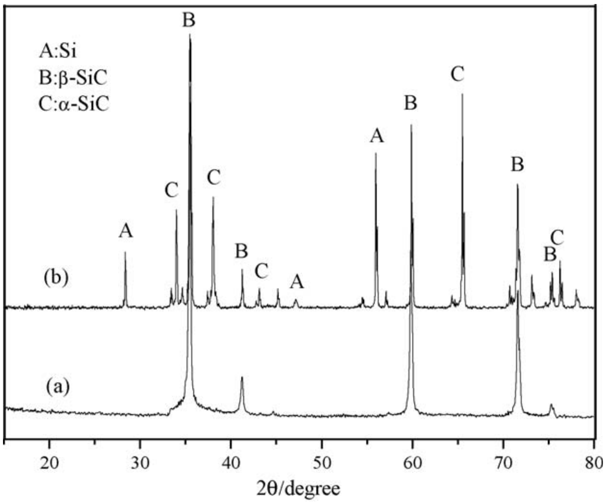

Fig. 1. X-ray patterns on the surfaces of the coatings obtained by (a) first step pack cementation and (b) two-step pack cementation process.

Fig. 4 shows of the SEM image of the C/C-coating interface and its element line scanning results. From the C/C substrate to the coating at their interface, the concentration of the Si element increased gradually in the range of almost 10 μm, implying that a gradient C–SiC bonding layer was obtained during the pack cementation process, which is advantageous to improve the thermal shock resistance of the coating.

3.2. Oxidation protection ability of the coating

The isothermal oxidation curve of the coated C/C composites at 1773 K in air is shown in Fig. 5. It can be seen that the weight loss of the SiC inner layer coated sample was up to 21% after 10 h oxidation at 1773 K in air. The poor

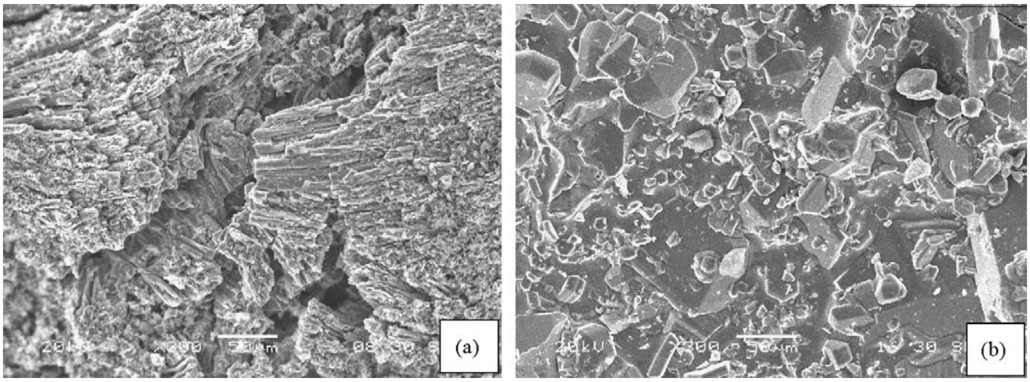

Fig. 2. SEM micrographs of the surfaces of the coatings obtained by (a) first step pack cementation and (b) two-step pack cementation process.

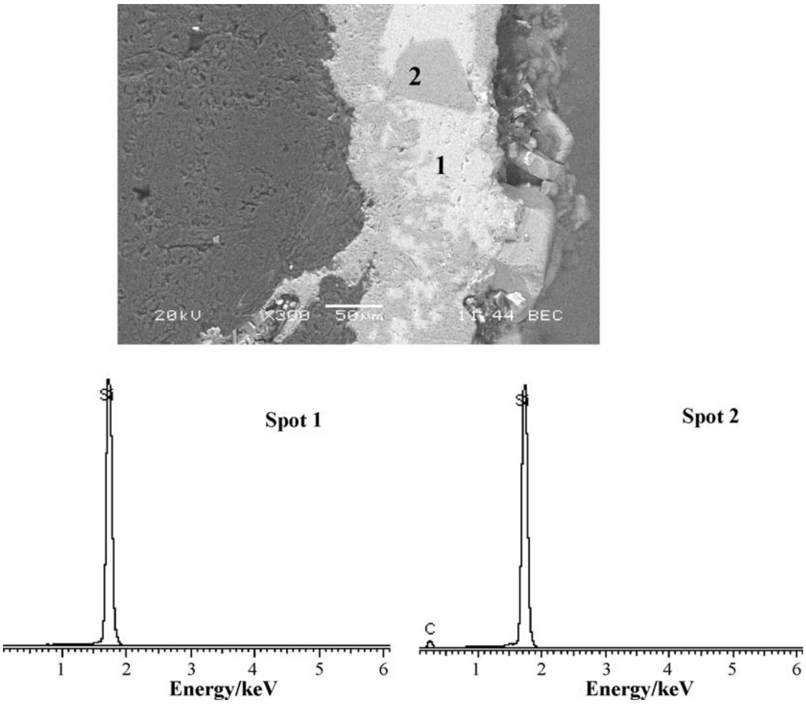

Fig. 3. SEM micrograph and spot EDS analyses of the cross-section of the coating.

oxidation protection ability of the SiC inner layer is resulted from its porous structure. The Si–SiC coating obtained by the two-step pack cementation lost only 0.61% mass after exposure to air at 1773 K in air for 166 h. That is to say, the oxidation resistant property of SiC coating prepared by the first step pack cementation can be improved largely by densification during the second pack cementation process. The oxidation behavior of the Si–SiC coated C/C composites could be divided into two processes seen from the oxidation curve (Fig. 5). Less than 100 h, the sample exhibits increasing weight due to the oxidation of the coating. Between 100 and 166 h, the sample loses weight slowly, which might be resulted from the formation of some microcracks or small holes in the coating.

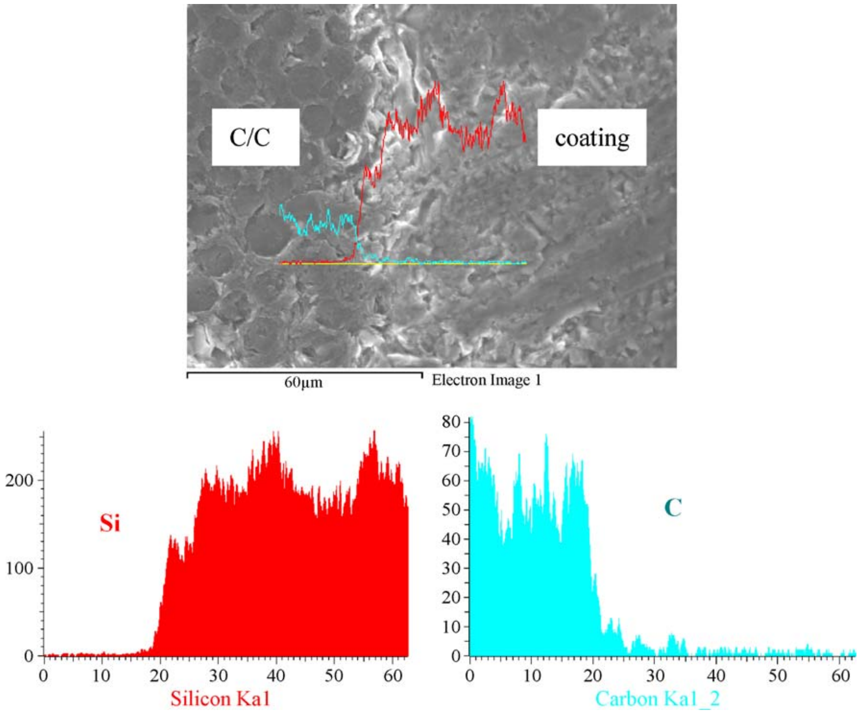

Fig. 4. The element line scanning results of the interface between coating and C/C composite.

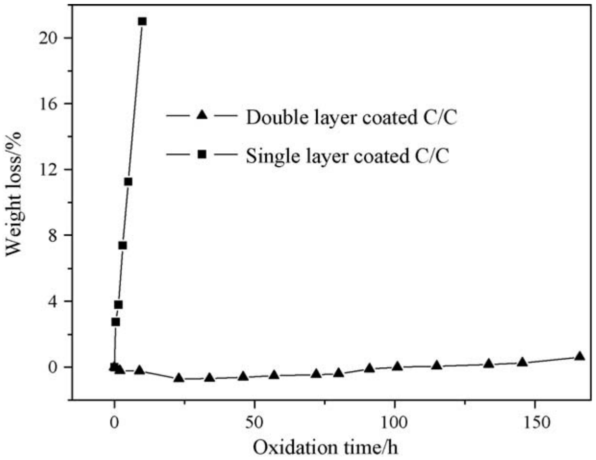

Fig. 5. Oxidation curve of the coated C/C composites at 1773 K in air.

The surface micrographs of SiC coating after oxidation at 1773 K for 166 h are shown in Fig. 6. It can be seen that the Si–SiC coating surface has changed into glass (Fig. 6(a)) due to the formation of SiO_2 by the oxidation of Si and SiC in the coating at 1773 K in air, which can efficiently prevent oxygen from diffusing to the C/C substrate. At 1773 K, gases generated from the oxidation of SiC or C/C would get out through the SiO_2 film because of the low viscosity of glass layer, resulting in the formation of holes (shown in Fig. 6(a)). These holes provide the entrance channels for oxygen to diffuse into the C/C matrix. Moreover, some cracks can be found on the coating surface in Fig. 6(b). These cracks might be formed during the quick cooling from 1773 K to room temperature for weighing up during the isothermal oxidation test and they would self-seal when the coated C/C sample was heated to 1773 K again. However, C/C matrix would be oxidized by oxygen diffusing through the penetration cracks in the coating at the temperatures between the crack sealing temperature and the beginning oxidizing temperature of C/C composites.

Fig. 7 shows the cross-section images of the coated samples after oxidation at 1773 K in air. From Fig. 7(a), C/C substrate was oxidized badly after oxidation for only 10 h because of the porous structure of SiC inner layer obtained by the first step pack cementation. For the Si–SiC coated sample, after oxidation for 166 h, a slight oxidation mark of the C/C substrate can be found near a penetration crack in the coating. Therefore, the weight loss of the Si–SiC coated C/C composites was primarily for reasons of the oxidation of the

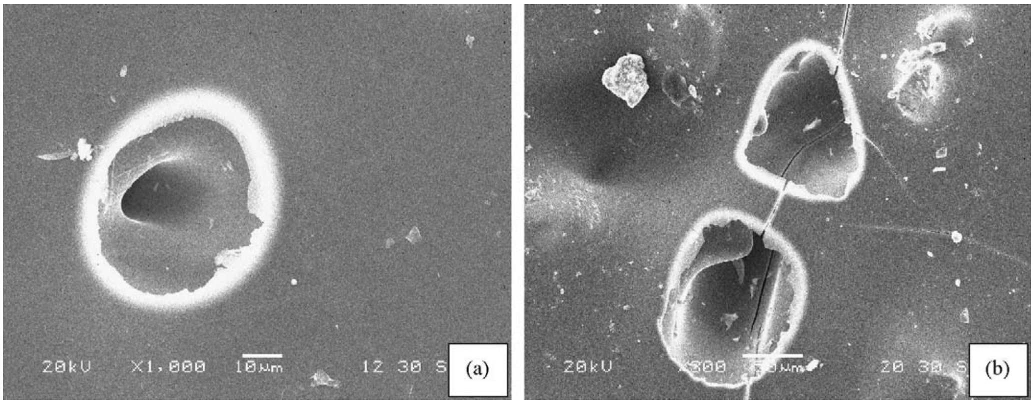

Fig. 6. Surface micrographs of the Si–SiC coating after oxidation at 1773 K for 166 h: (a) holes and (b) microcracks.

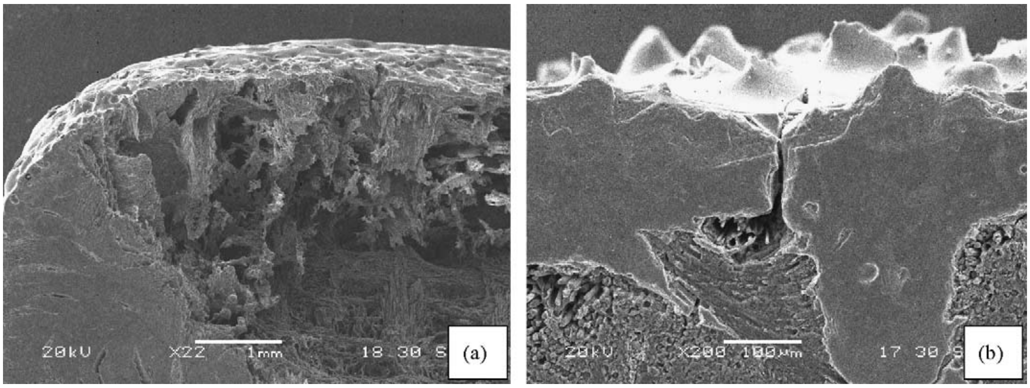

Fig. 7. SEM cross-section of the as-prepared coating on C/C composites after oxidation at 1773 K: (a) C/C with a SiC inner layer obtained by first step pack cementation after oxidation for 10 h and (b) C/C with a Si–SiC coating obtained by two-step pack cementation after oxidation for166 h.

C/C by the oxygen diffusing through the penetration cracks in the coating.

4. Conclusions

A dense Si–SiC coating can be obtained by a two-step pack cementation technique. The as-received coating is composed of α-SiC, Si and β-SiC. The Si–SiC coating has better oxidation protection ability than β-SiC coating obtained by one-step pack cementation, and could efficiently protect C/C from oxidation at 1773 K for 166 h. The weight loss of the coated sample is thought to occur owing to the formation of holes on the coating surface and the penetration cracks in the coating.

Acknowledgements

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