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Letter

Microstructure and anti-oxidation property of Si–W–Cr coating for SiC coated carbon–carbon composites

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ABSTRACT

To protect carbon/carbon (C/C) composites from oxidation at high temperature, a Si–W–Cr coating was prepared on the surface of SiC coated C/C composites by a simple pack cementation technique. The microstructure and phase composition of the as-received multi-coating were examined by SEM, XRD and EDS. The coating obtained by first step pack cementation was porous α-SiC structure. New phases of WSi_2 and $CrSi_2$ together with α-SiC deposited on the porous SiC inner layer. Oxidation test shows that the weight loss of single SiC coated C/C is up to 8.21% after 9 h in air at 1773 K, while the weight loss of Si–W–Cr/SiC coated C/C composites is only 2.26% after 51 h. After thermal cycling between 1773 K and room temperature for 40 times, the weight loss is only 3.36%. The weight loss of coated C/C composites was primarily due to the reaction of C/C matrix and oxygen diffusing through the penetrable cracks in the coating.

1. Introduction

Carbon/carbon (C/C) composites are considered as one of the most promising thermal structural materials for engine, aircraft and aerospace applications due to their excellent mechanical properties at high temperatures [1,2]. However, they undergo fast oxidation when exposed to an oxidizing environment above 723 K, which often limits the use of C/C composites as structural materials in high-temperature oxidizing systems [3]. To solve this problem, applying coatings on C/C composites is a logical method.

So far, refractory Si-based ceramic coatings have been proved as one of the most promising candidates for protecting C/C composites from oxidation, because the SiO_2 film will be formed on the surface of the coatings while the coated C/C composites are exposed in air at high temperature. SiO_2 film has very low oxygen permeability (10^{-13} g/cm s at 1200 °C, 10^{-11} g/cm s at 2200 °C) and can efficiently prevent oxygen from diffusing into C/C substrate [4–6]. However, the ceramic coating cannot be applied directly on the C/C surface, owing to the mismatch of coefficient of thermal expansion (CTE) between ceramics and C/C composites. A multi-layer coating is the best choice to tackle this problem which makes SiC as the bonding and buffer layer because of its good compatibility with C/C composites [7,8].

For effective protection of C/C composites from oxidation, a stable vitreous film with low oxygen permeability formed during oxidation process is necessary. Tungsten disilicide (WSi_2) and chromium disilicide ($CrSi_2$) are intermetallic compounds with both ceramic and metal properties such as high melting points, high temperature oxidation resistance, and corrosion resistance etc. [9–12]. A Si–W–Cr multi-composition is suggested as the outer layer material because the stability of pure SiO_2 glass can be improved by the formation of vitreous composition including SiO_2 and Cr_2O_3 during oxidation [13,14].

There are several methods to prepare oxidation protective coating on C/C surface such as pack cementation [15], chemical vapor deposition (CVD) [16], laser-induced chemical deposition (LICD) [17]. Among these methods, pack cementation is easy and can provide strong interface boding [18]. Therefore, in the present work a Si–W–Cr/SiC multilayer coating was prepared by pack cementation. The microstructure and anti-oxidation properties of the coating were investigated.

2. Experimental

The specimens (10 mm × 10 mm × 10 mm) used as substrates were cut from bulk two dimensional C/C composites with a density of 1.70 g/cm^3. The specimens were abraded with 400 grit SiC paper, then cleaned with ethanol and dried at 373 K for 2 h. Powder compositions of inner SiC coating for the first step pack cementation process were as follows: 60–75 wt.% Si, 9–20 wt.% graphite, and 5–10 wt.% Al_2O_3. All the powders, with the granularity of 300 mesh, were analytical grade and mixed by a blender for 2 h. The pack mixtures and C/C specimens were put in a graphite crucible, and then heat-treated at 2073–2373 K for 2 h in an argon protective atmosphere to form porous inner SiC coating. During this process, most of the silicon reacts with graphite in the pack compositions and some silicon would diffuse into C/C and react with carbon matrix. Both of them follow the chemical reaction as Eq. (1)

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

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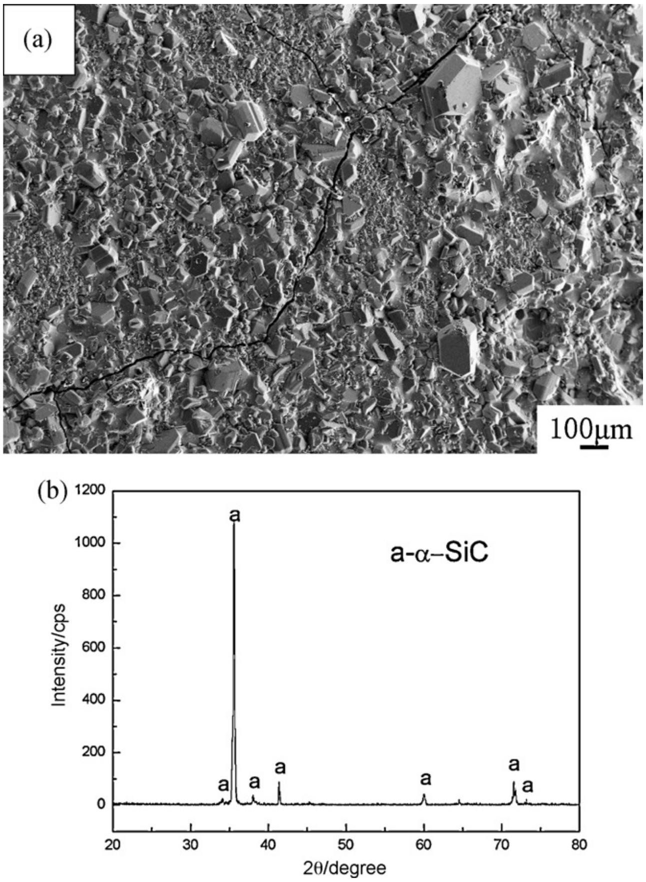

Fig. 1. SEM micrograph and X-ray pattern of the surface of the SiC coated C/C composites obtained in the first step pack cementation process.

The precursor powder of the Si–W–Cr outer coating for the second step pack cementation were mixed as follows: 30–40 wt.% W, 35–40 wt.% Si, 10–15 wt.% Cr, 5–10 wt.% graphite and some additives. The as-prepared SiC coated specimens and the second step mixtures were put in a graphite crucible, and then were heat-treated in argon at 2273–2573 K for 2 h. During this process, some chemical reactions besides Eq. (1) would occur as follows:

$$Cr(s) + 2Si(s) \rightarrow CrSi_2(s) \quad (2)$$

$$W(s) + 2Si(s) \rightarrow WSi_2(s) \quad (3)$$

The isothermal oxidation test was carried out in air in an electrical furnace at 1773 K. Thermal shock test was also investigated between 1773 K and room temperature. The specimens were put into electrical furnace at 1773 K for 3 min, after which they were taken out of the furnace and cooled at room temperature for 3 min and weighted, and then the specimens were put directly into the furnace again for the next oxidation period. The thermal shock test was then repeated for 40 cycles. Cumulative weight changes of the samples after every thermal cycle from high temperature to room temperature was measured by a precision balance and was recorded as a function of time. The % mass loss was calculated using Eq. (4)

$$\%\,\text{mass loss} = \left[\frac{(m_0 - m_1)}{m_0}\right] \times 100\% \quad (4)$$

where m_0 is the original mass of coated C/C composites; m_1 is the mass of the coated C/C composites after oxidation at high temperature. The morphology and crystalline structure of the SiC coating were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure of the coating

Fig. 1 shows SEM image and X-ray pattern of the surface of SiC coated C/C composites. It reveals that the inner buffer coating mainly consists of α-SiC. Some cracks are also found on the SiC coating surface due to the mismatch of CTE between SiC coating and C/C composites. Through these cracks, oxygen can easily diffuse into C/C matrix and react with matrix. So the single SiC coating may not protect C/C composites from oxidation for a long time.

The Si–W–Cr coating was prepared on the porous SiC coated C/C composites by second step pack cementation. SEM image of the as-received coating surface shows there are two kinds of crystalline particles (characterized as white and grey) and some microcracks can be found in the white phase. By XRD and EDS analysis (Fig. 2), the grey phase is SiC and the white one consists of WSi_2, $CrSi_2$ and SiC.

Fig. 3 exhibits the cross-section of the as-received multilayer coating. It can be seen that the coating obtained by two-step pack cementation is about 250 μm in thickness and no visible penetrable cracks and large holes are found. The cracks in the inner layer SiC coating were filled with the white WSi_2–$CrSi_2$–SiC phase. There is also no obvious gap between inner SiC coating and outer Si–W–Cr ceramic coating. Therefore, the dense multilayer Si–W–Cr/SiC coating for C/C composites was obtained by two-step pack cementation, which is expected to have better oxidation resistance than single SiC layer in air at 1773 K.

3.2. Anti-oxidation property of the multilayer coating

To investigate the oxidation resistance of the as-prepared multilayer coating, the isothermal oxidation test 1773 K and thermal shock test between 1773 K and room temperature in air were carried out. Fig. 4(a) shows the isothermal oxidation curves of the single SiC coating and the multilayer coating. It can be found that the weight loss of the single SiC coated C/C composites reaches 8.21% after oxidation for 9 h. After depositing the Si–W–Cr outer coating on SiC-coated C/C composites, the oxidation resistance of the single SiC coating has been improved largely. After oxidation for 51 h of the Si–W–Cr/SiC multilayer coated C/C composites, the weight loss is only 2.26%. Fig. 4(b) shows the thermal shock oxidation result of the coated C/C specimens. It could be found that there are no increasing trend of weight loss rate after 40 times thermal cycling, which indicates that the multilayer coating exhibited excellent thermal shock resistance between 1773 K and room temperature. As shown in Fig. 4(a), the oxidation behavior of the multilayer coated C/C composites could be divided into two processes: mass gain and mass loss process. During the process of oxidation tests, the coating and C/C matrix would react with oxygen as follows:

$$SiC(s) + 2O_2(g) \rightarrow CO_2(g) + SiO_2(s) \quad (5)$$

$$WSi_2(s) + 7O_2(g) \rightarrow 2WO_3(g) + 4SiO_2(s) \quad (6)$$

$$4CrSi_2(s) + 11O_2(g) \rightarrow 2Cr_2O_3(s) + 8SiO_2(s) \quad (7)$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad (8)$$

$$2C(s) + O_2(g) \rightarrow 2CO(g) \quad (9)$$

In the first process (1–6 h), the sample presented weight gain because the weight gain coming from formation of SiO_2 and Cr_2O_3 glass was more than the volatilization of CO_2 and WO_3. Reactions (5)–(7) lead to a net weight gain through calculating. Moreover, the SiO_2 and Cr_2O_3 glass enwrapping the sample could effectively prevent the oxygen penetrating into the matrix and reacting with carbon matrix. Therefore, the weight gain was more than weight loss of the sample and it mainly depended on reactions (5)–(7). During the last process (6–51 h), the sample exhibited mass loss which indicated the carbon matrix was oxidized by oxygen penetrated from SiO_2 and Cr_2O_3 glass. Chemical reactions were listed as (8) and (9), which lead to a net weight loss through calculating. On the one side, the SiO_2 and Cr_2O_3 glass volatilized seriously with the oxidation time increasing. On the other side, many holes

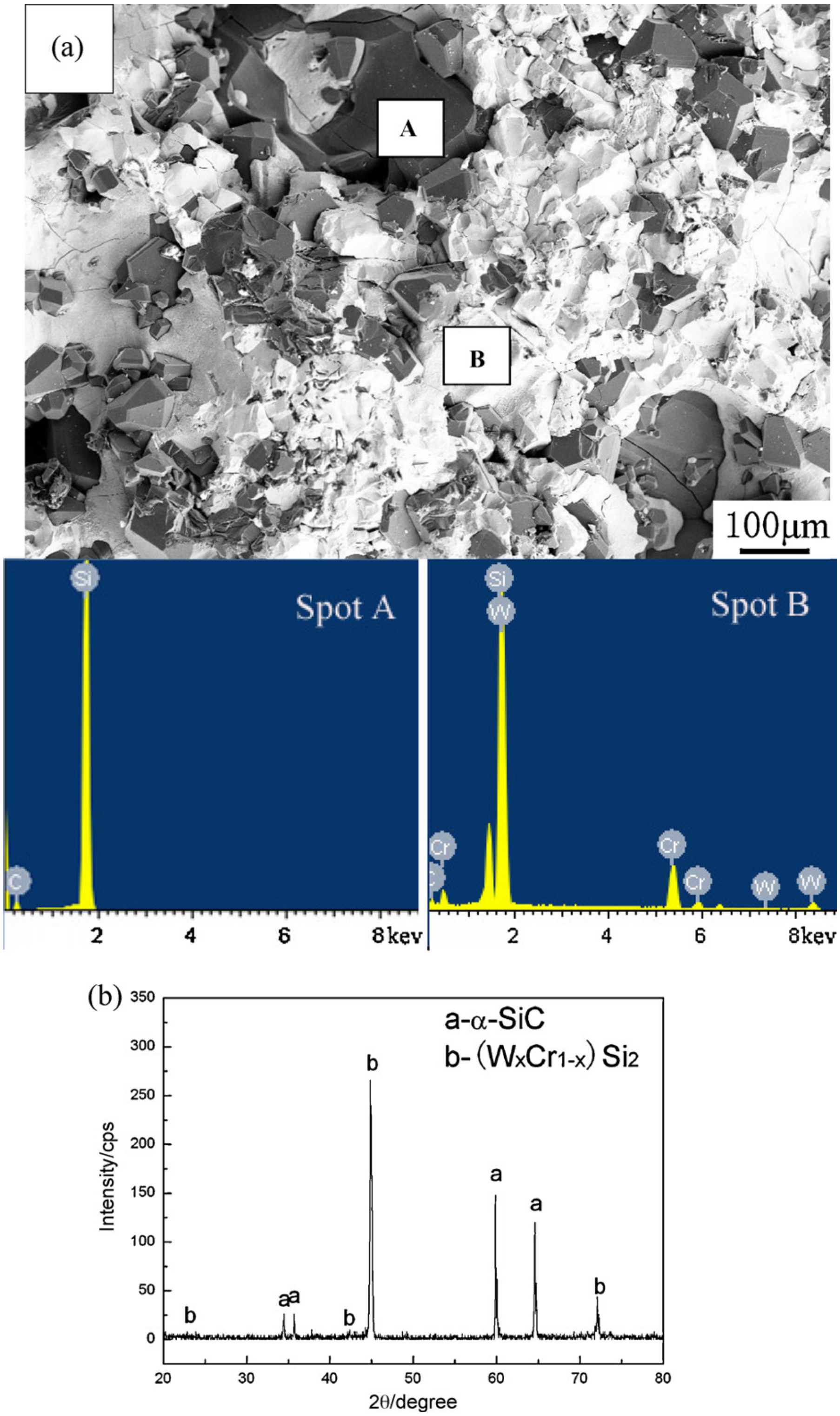

Fig. 2. SEM image and X-ray pattern of the WSi_2–$CrSi_2$–SiC coating prepared by pack cementation.

and cracks were formed in the glass because of the escape of the CO_2, CO and WO_3 during reaction and thermal cycle during testing the weight of the sample, respectively. The holes and cracks supplied channels for oxygen which led to serious oxidation of C/C matrix. Therefore, the weight loss was more than weight gain of the sample and it mainly depended on reactions (8) and (9). To sum up, only reactions (8) and (9) could lead to weight loss. So the real loss of weight was the oxidation of carbon matrix which manly took place in second process according to reactions (8) and (9).

Fig. 5(a) shows the SEM image of the coating after oxidation at 1773 K in air for 51 h. It can be seen that a smooth glass layer with some microcracks and holes formed on the coating surface. The glass consisted of SiO_2 and Cr_2O_3 as shown in Fig. 6. WO_3 was not tested because of the volatilization and low content after oxidation at 1773 K for 51 h. The melt point of WO_3 is 1746 K and

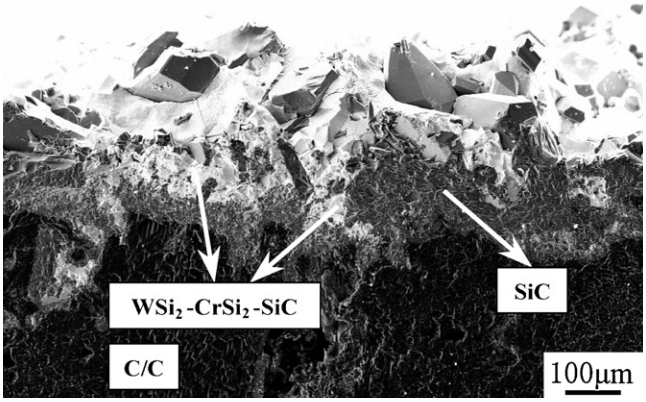

Fig. 3. Cross-section SEM micrograph of the multilayer coating coated C/C composites.

the volatilization of WO_3 is serious at high temperature. During the oxidation experiment at 1773 K, WO_3 and SiO_2 formed according to chemical reactions (6). Some liquid WO_3 could penetrate through cracks in the coating and prevent oxygen infiltration into C/C matrix. However, a majority of WO_3 volatilized from the SiO_2 and Cr_2O_3 glass layer during oxidation process, which induced many holes existing in the glass layer. The holes provided entrances for oxygen infiltrating into C/C matrix and that would result in the invalidation of coating. Therefore, the negative effect of WO_3 was more than active effect of it. From the cross-section image of the coating after oxidation, a penetrable crack was formed in the coating due to the big mismatch of CTE between coating and C/C composites. At the end of the penetrable crack, the C/C matrix was oxidized by oxygen infiltrating through the crack. Therefore, the weight loss of the multi-coating coated C/C composites was primarily caused by the penetrable cracks in the coating. How to eliminate the penetrating cracks formed during the oxidation tests need further research.

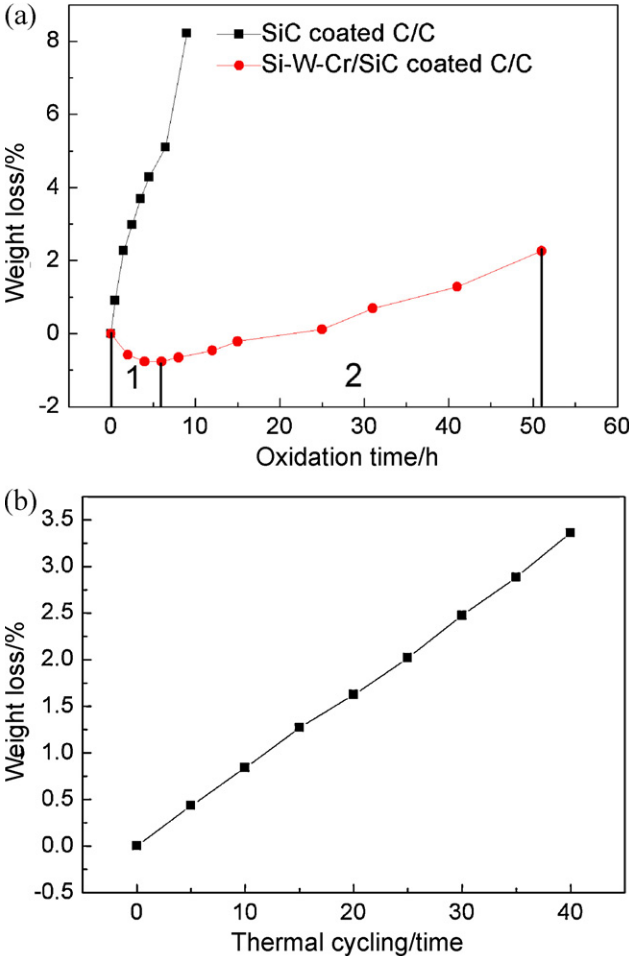

Fig. 4. The oxidation curves of the WSi_2–$CrSi_2$–SiC/SiC coated C/C composites in air: (a) isothermal oxidation test at 1773 K; (b) thermal cycling between 1773 K and room temperature.

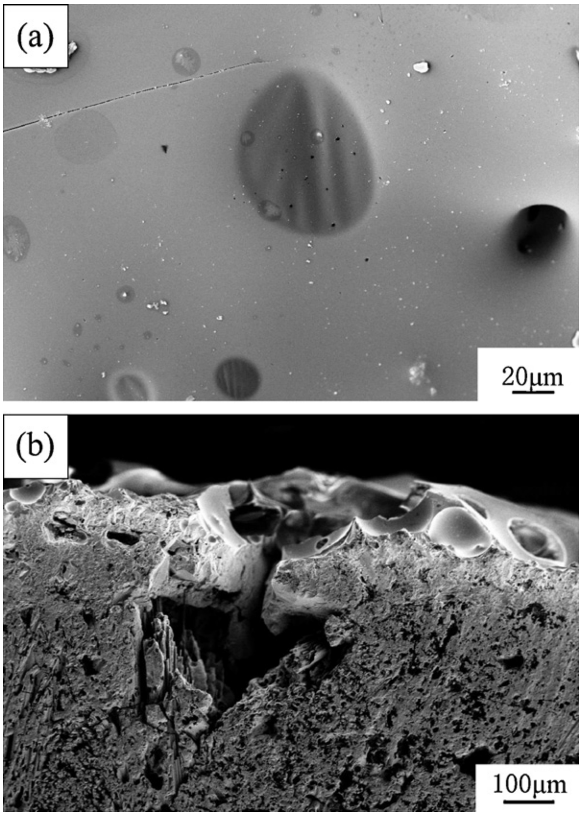

Fig. 5. SEM images of the multi-coating coated C/C composites after oxidation: (a) surface; (b) cross-section.

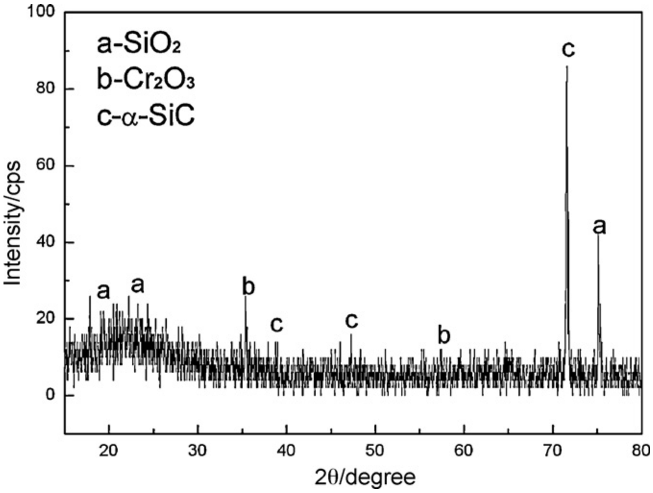

Fig. 6. X-ray pattern of the surface of the multi-coating coated C/C composites after oxidation at 1773 K in air for 51 h.

4. Conclusions

A Si–W–Cr/SiC coating was prepared on the C/C composites by two-step pack cementation. The Si–W–Cr coating could improve largely the oxidation resistance of the single property of single SiC coated C/C composites. The microcracks and holes were found on the surface of the sample after oxidation at 1773 K, and the penetrable cross cracks were considered as the reason of the weight loss of the coated C/C composites.

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