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Microstructure and anti-oxidation properties of multi-composition ceramic coatings for carbon/carbon composites

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Abstract

To protect carbon/carbon (C/C) composites from oxidation at elevated temperature, an effective WSi_2–$CrSi_2$–Si ceramic coating was deposited on the surface of SiC coated C/C composites by a simple and low-cost slurry method. The microstructures of the double-layer coatings were characterized by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy analyses. The coating exhibited excellent oxidation resistance and thermal shock resistance. It could protect C/C composites from oxidation in air at 1773 K for 300 h with only 0.1 wt.% mass gain and endure the thermal shock for 30 cycles between 1773 K and room temperature. The excellent anti-oxidation ability of the double-layer WSi_2–$CrSi_2$–Si/SiC coating is mainly attributed to the dense structure of the coating and the formation of stable vitreous composition including SiO_2 and Cr_2O_3 produced during oxidation.

Keywords: Carbon/carbon composites; Ceramic; Coating; Oxidation

1. Introduction

Carbon/carbon (C/C) composites have many unique properties at high temperature, such as high strength-to-weight ratio, high thermal shock resistance and low coefficient of thermal expansion. Therefore, they are suitable for aeronautical and aerospace applications [1,2]. However, a severe limitation of C/C composites is their extreme oxidation sensitivity when exposed to an oxidizing environment even below 773 K, which frequently becomes an urgent barrier to the use of C/C composites as structural materials in high-temperature oxidizing systems [3]. Applying coatings on C/C composites is considered an effective way to prevent oxidation under such conditions.

Refractory Si-containing ceramic coating is one of the most promising candidates for protecting C/C composites at high temperature. However, owing to the mismatch of thermal expansion coefficient between ceramics and C/C composites, the ceramic coating cannot be directly applied on the surface of C/C composites. A multi-layer coating with gradient compositions is a better choice to solve this problem. SiC ceramic is widely used as an internal buffer layer because of its excellent anti-oxidation property and good compatibility with C/C composites [4,5]. In our previous research [6–8], multi-layer coatings exhibited excellent anti-oxidation ability. However, these multi-layer systems encounter problems at high temperature and long time. The failure of these coatings is due to holes and bubbles formed in the SiO_2 glass layer at higher temperatures, providing channels for the oxygen to diffuse. Moreover, the unitary SiO_2 glass might be volatilized gradually and the coating composition is also consumed heavily [9,10].

For the extension of the service life of the oxidation protective coating, a stable vitreous film with low oxygen permeability in oxidation process becomes important. Tungsten disilicide (WSi_2) and chromium disilicide ($CrSi_2$) have excellent properties such as high melting points, high temperature oxidation resistance, and corrosion resistance etc. [11–13]. The W–Si ceramic reported by Cheng et al. [14] was used as sealant layer to prevent C/C composites from oxidation at 1973 K. Furthermore, $CrSi_2$ could form more perdurable glass when Cr ion melts in SiO_2 to form more

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complicated molecular network during oxidation [10,15]. This vitreous composition has lower volatility and oxygen permeability at high temperatures. However, up to now, scant research has been reported about using WSi_2–$CrSi_2$–Si ceramic as the oxidation protective coating for C/C composites.

Many techniques such as pack cementation [16], chemical vapor deposition (CVD) [17], laser-induced chemical decomposition (LICD) [18], and slurry method have been developed to prepare the oxidation protective coating. Among these techniques, the slurry method is applied conveniently at low temperatures, involves low cost, and can avoid microcracks and interfacial cracks in the coating [19]. In this technique, the formation of dense structure in the coating is crucial for the anti-oxidation performance. In the present work, a WSi_2–$CrSi_2$–Si coating was prepared by slurry method and applied to the surface of SiC coated C/C composites. The microstructures and the anti-oxidation properties of the coating were investigated.

2. Experimental

Two kinds of specimens used as substrates were cut from C/C composite bulk with density of 1.72 g/cm^3. The specimens for oxidation test are cubic, with the size of 10 mm × 10 mm × 10 mm, while the rectangular specimens for mechanical test have the size of 55 mm × 10 mm × 4 mm. The specimens were hand-polished using 320 grit SiC paper, then cleaned with distilled ethanol and dried at 393 K for 2 h. The powder precursor of the SiC internal coating by pack cementation was mixed as follows: Si 60–80 wt.% (300 mesh), graphite 10–25 wt.% (300 mesh), and Al_2O_3 5–15 wt.% (300 mesh). C/C specimens and pack mixtures were put into a graphite crucible and heat-treated at 2173–2373 K for 2 h in argon to produce the SiC layer. The WSi_2–$CrSi_2$–Si ceramic coating was obtained on the surface of SiC coated C/C composites by slurry method. The commercially available powders of Cr, W and Si were of analytical grade and were mixed according to the following proportion: W 10–25 wt.% (300 mesh), Cr 5–10 wt.% (300 mesh), and Si 50–85 wt.% (300 mesh) in a blender with ethanol for 1 h. The solid and liquid ratio of the slurry was adapted to 2:1 (bulk ratio) to insure that the brushing of the slurry onto the specimens was easy and uniform. After applying the slurry onto the surface of the SiC coated samples, the samples were dried in a drier at 373 K for 2 h. Then the as-prepared specimens were heated in a low argon flow to 1673–1773 K and held at that temperature for 20–60 min. The coating thickness was controlled by the brushing time.

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 rectangular specimens were put into electrical furnace at 1773 K for 10 min, after which they were taken from electrical furnace and cooled at room temperature for 10 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 30 cycles. Owing to the cooling at room temperature (about 298 K) for 10 min, the cooling rate is at least 100 K/min. Because of the isothermal environment at 1773 K in electrical furnace, the temperature of the specimens reaches 1773 K in an instant. The weight change of the specimens was measured by an electronic balance with sensitivity of ±0.1 mg. Cumulative weight change percentages ($\Delta W\%$) of the specimens were calculated by the following equation

$$\Delta W\% = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where m_0 and m_1 are the weight of the specimens before oxidation and after oxidation respectively.

Flexural strengths of the coated specimens before and after oxidation were measured in accordance with Q/Gb95-92 [20] using three-point bending method with a servohydraulic machine (CMT5304-30KN). The span dimension was 40 mm to give span-to-depth ratio of 10 and the loading rate was 0.2 mm/min. Additionally, flexural tests of the coated specimens before and after oxidation are repeated five times respectively to ensure the accuracy of the data. The crystalline structure of the multi-coatings was measured with X-ray diffraction (XRD, X'Pert Pro MPD). The morphology and the elemental distribution of the multi-composition ceramic coating were analyzed by scanning electron microscope (SEM, JSM6460), equipped with energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure of the coating

Fig. 1 shows the SEM image and XRD pattern of the SiC coating on C/C composites. It reveals that a dense and homogenous SiC coating obtained by pack cementation method mainly consists of α-SiC, β-SiC and Si. Some microcracks are also found on the coating surface because of the quick cooling from high temperature to room temperature. Oxygen can easily diffuse to C/C matrix through these microcracks, so the monolayer SiC coating cannot provide effective oxidation protection for the C/C composites for a long time.

The SEM surface morphology of the multi-composition coating shows a dense and crack-free surface structure (Fig. 2), from which it can be inferred that double-layer WSi_2–$CrSi_2$–Si/SiC coating can provide better oxidation protection for C/C composites than the monolayer SiC coating. X-ray diffraction analysis shows that the WSi_2–$CrSi_2$–Si ceramic coating is composed of WSi_2, $CrSi_2$, SiC and Si (Fig. 2).

Fig. 3 exhibits the cross-section micrograph of the multi-layer coating. It can be seen that the multi-layer coating was about 200 μm in thickness without visible cracks and pores. No obvious gap is found between the inner SiC coating and the outer WSi_2–$CrSi_2$–Si ceramic coating, which indicated good interaction between them. In addition, no penetrating cross-crack is found in the coating. There are two kinds of crystalline particles (characterized as white and grey) observed in the coating. By EDS analysis, the white region in the outer coating

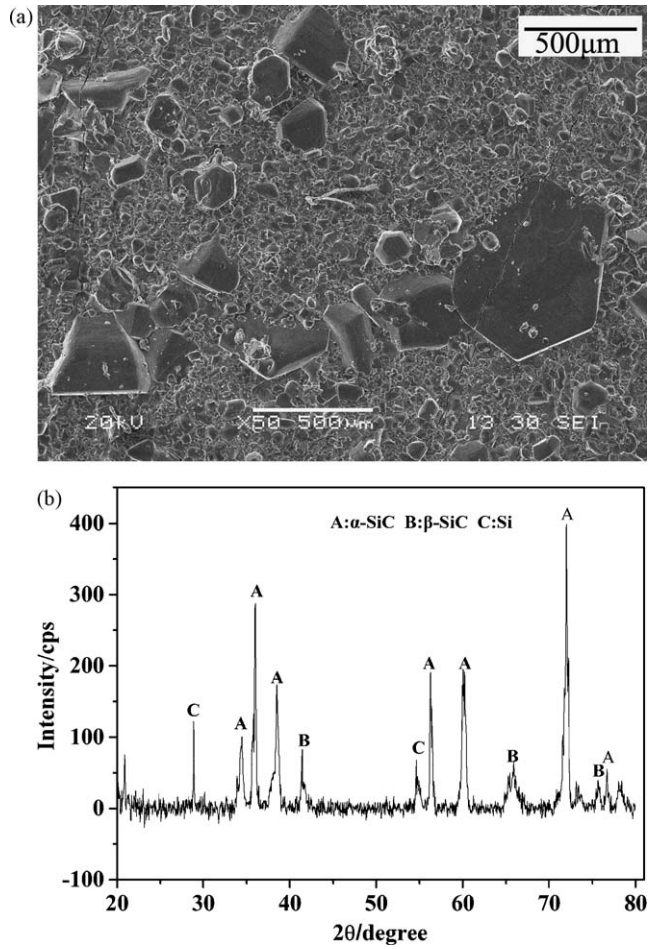

Fig. 1. SEM image and X-ray pattern of the SiC coated C/C composites.

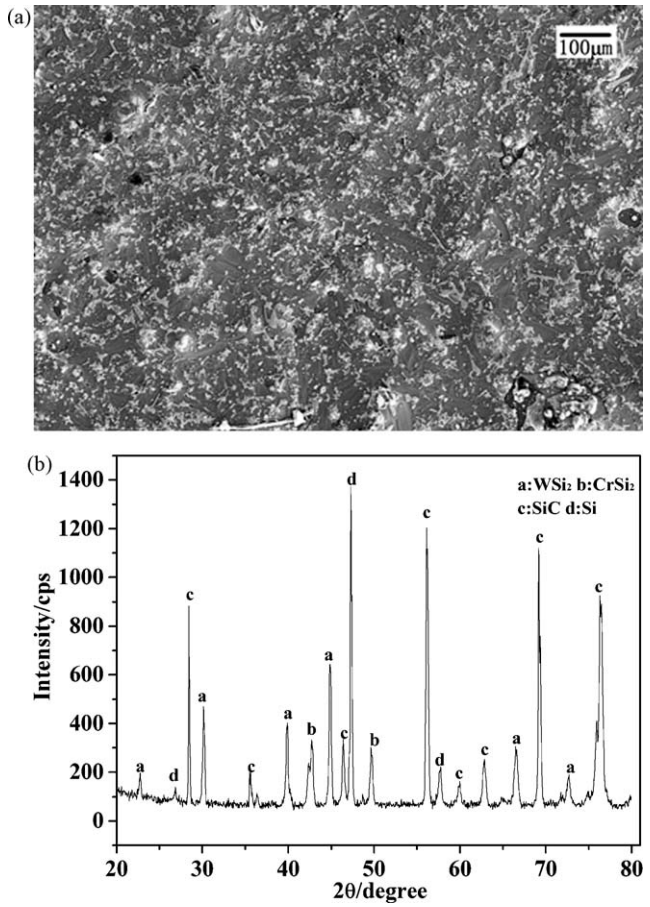

Fig. 2. SEM micrograph and X-ray pattern of the WSi_2–$CrSi_2$–Si coating obtained by slurry method.

is a kind of ceramic mixture including WSi_2 and $CrSi_2$. The grey particles are Si. During heat-treatment in the slurry process, as the melting point of Si is 1683 K, Si would melt and infiltrate into the SiC coating via the cracks in the coating efficiently. In addition, the free Si in the multi-coating can release the stress caused by the mismatch of thermal expansion coefficient between ceramic and SiC, which would be beneficial for the improvement of the thermal shock resistance of the coating.

3.2. Oxidation resistance of the multi-layer coatings

The isothermal oxidation curves of the coated C/C composites at 1773 K in air are shown in Fig. 4. The double-layer coating has excellent oxidation protective ability. After oxidation for 300 h, the weight gain of the SiC/WSi_2–$CrSi_2$–Si coated C/C composites is only 0.1%, and the corresponding weight gain rate is only 1×10^{-5} g/cm^2 h. This oxidation protective performance is better than that of Mo–Si–Cr coating reported by Zhang et al. [10] and other multi-layer coating systems [6–9,11]. According to the oxidation curves shown in Fig. 4(a), the oxidation behavior of the double-layer coated sample could be divided into three stages. In the initial stage of oxidation, the multi-composition ceramic coating is exposed to the atmosphere and reacts with oxygen directly. Therefore, the oxide products are generated on the surface of the coating quickly. Within 12 h, the mass gain rate reaches a maximum value of 9.3×10^{-5} g/cm^2 h. From 12 to 100 h, the outer WSi_2–$CrSi_2$–Si coating is partially oxidized and forms a

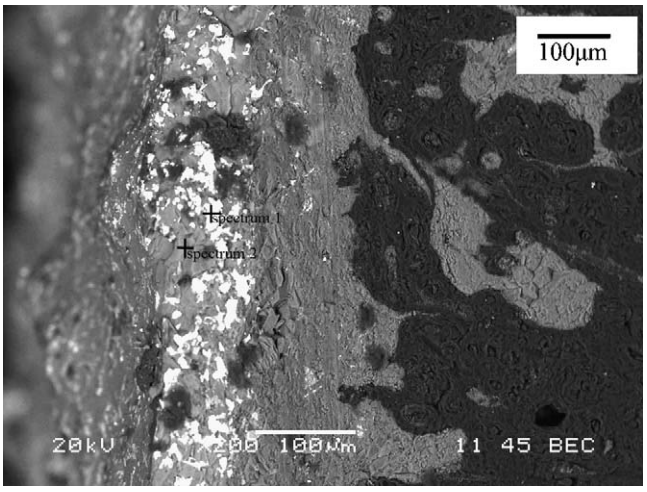

Fig. 3. Backscatter micrograph of the cross-section of the multi-layer coating on the C/C composites.

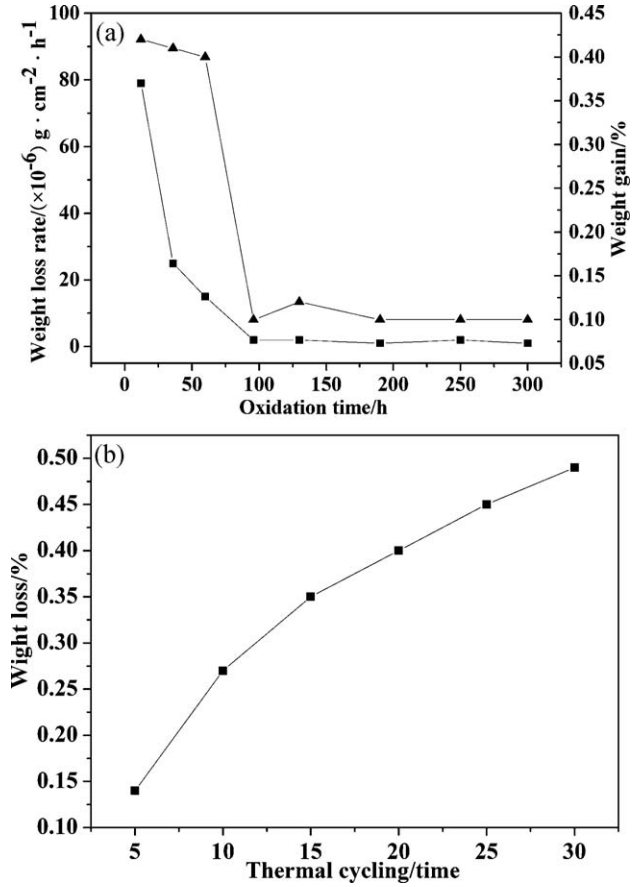

Fig. 4. The oxidation curves of the C/C composites with WSi_2–$CrSi_2$–Si/SiC double-layer coating in air: (a) isothermal oxidation test at 1773 K; (b) thermal cycling oxidation between 1773 K and room temperature.

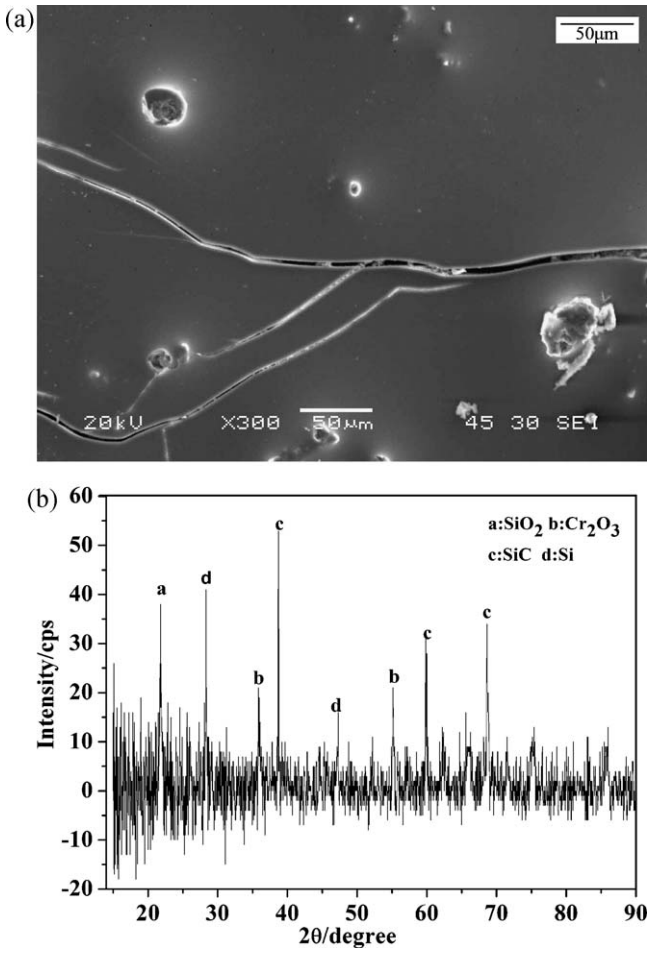

Fig. 5. SEM micrograph of the surface of the multi-composition coating coated C/C composites after oxidation in air at 1773 K for 300 h.

limited amount of SiO_2–Cr_2O_3 glass, so the oxidation protective ability of the coating is determined by the pure SiO_2 glass. The glass layer cannot effectively prevent oxygen diffusing in the coating. With the volatilization of the gaseous WO_3 and glass, the composition of the outer coating is consumed. Therefore, the mass gain rate reduces quickly. Over 100 h, the SiO_2–Cr_2O_3 glass (Fig. 5) can cover the whole coating surface and effectively prevent the underneath dislicides glass layer from further reacting with oxygen. The mass gain changes slowly as the oxidation continues.

The surface micrograph of the multi-composition coating after oxidation at 1773 K for 300 h is shown in Fig. 5. A smooth and stable glass layer with some microcracks can be found on the coating surface. These microcracks are generated in the stage of quick cooling from 1773 K to room temperature, and can be self-sealed by glass when the coating is heated to 1773 K again. Therefore, the glass layer can efficiently prevent oxygen from diffusing into the C/C substrate during oxidation. Cr_2O_3 can improve the stability of the SiO_2 glass [9,10,15]. From the XRD pattern of the coating after oxidation (Fig. 5), amorphous characteristics of glass including SiO_2 and Cr_2O_3 can be observed. Cr_2O_3 could improve the stability of SiO_2 glass. The excellent oxidation resistance may be contributed to the formation of the SiO_2–Cr_2O_3 glass layer with low volatility and oxygen permeability on the surface of the multi-composition coating.

Fig. 6(a) shows backscatter micrograph of the cross-section of the multi-layer coated C/C composites after oxidation in air for 300 h. It can be seen that the double-layer coating is just as dense as before oxidation, and holes or penetrating cracks are not found in the coating. Besides, compared with the samples before oxidation, the regions of the multi-composition ceramic characterized as white shrink obviously. The ceramic particles are consumed gradually with the oxidation time to form the glass film. It is concluded that the W and Cr ion diffuse gradually into the glass film and combine with oxygen, which keep the integrity of the SiO_2–Cr_2O_3 glass. So the mass change of the coated C/C composites is slow.

The thermal shock resistance of the double-layer coating is also investigated between 1773 K and room temperature, as shown in Fig. 4(b). The multi-layer WSi_2–$CrSi_2$–Si/SiC coating exhibits excellent thermal shock resistance. The weight loss of the coated samples is only 0.49% after 30 thermal cycles. Owing to the quick cooling, the coating will suffer from the pull stress as its thermal expansion coefficient ($\alpha_{WSi_2} = 8.5 \times 10^{-6}/K$ [21], $\alpha_{CrSi_2} = 10.5 \times 10^{-6}/K$ [22], $\alpha_{Si} = 2.5 \times 10^{-6}/K$ [23], $\alpha_{SiC} = 5 \times 10^{-6}/K$ [24]) is larger than that of C/C substrates ($\alpha_{C/C} = 1 \times 10^{-6}/K$ [24]), which results in the formation of

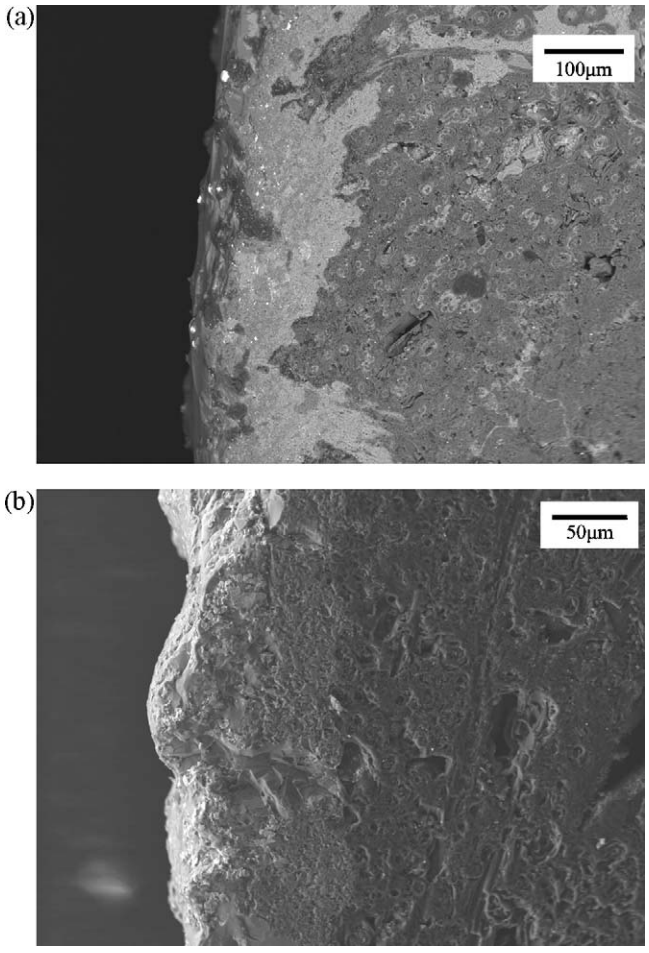

Fig. 6. Backscatter micrographs of the cross-section of the multi-layer coating on the C/C composites: (a) after isothermal oxidation at 1773 K for 300 h; (b) after 30 thermal cycles between 1773 K and room temperature.

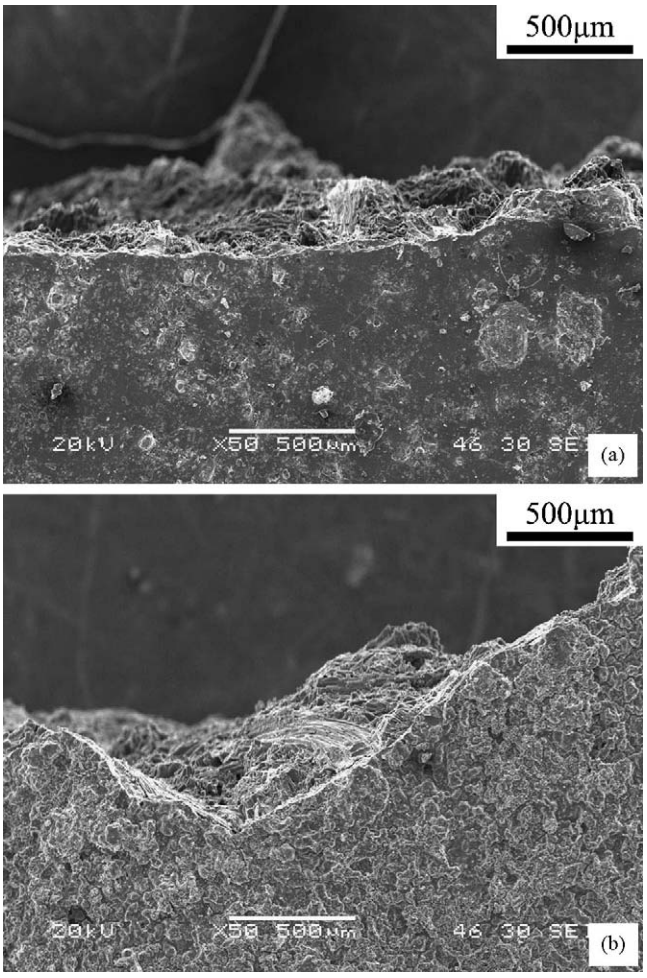

Fig. 7. Micrographs of the fracture surface of the coated C/C composites before and after thermal cycles between 1773 K and room temperature: (a) before; (b) after.

cracks especially penetrating cracks in the coating. Therefore, there are penetrating cross-cracks in the double-layer coating shown in Fig. 6(b). The trend of the weight loss rate is roughly linear, as shown in Fig. 4(b). From Table 1, flexural strengths of the coated specimens before and after thermal shock are 43.06 and 38.46 MPa respectively. Moreover, the average and standard deviation values (Table 1) illuminate that the results of the flexural tests are convincing. The residual strength of the coated samples shows a small strength loss (89.3% retained strength) after 30 thermal cycles. Fig. 7 shows fracture micrographs of the coated samples before and after thermal cycles between 1773 K and room temperature. The fracture of the multi-layer coatings is a typical brittle fracture mode before and after thermal cycles. Though after 30 thermal cycles, the original surface disappears and there are oxidation products and microcracks formed on the new surface as shown in Fig. 7(b), no obvious debonding and large-size cracks are found because of the good thermal compatibility of WSi_2–$CrSi_2$–Si coating and SiC coating.

Table 1
Flexural properties of the as-tested specimens.

	Before thermal shock	After thermal shock
Flexural strength (MPa)	43.06	38.46
Average (MPa)	42.788	37.898
Standard deviation	0.34	0.91

4. Conclusions

A dense WSi_2–$CrSi_2$–Si/SiC coating has been obtained on C/C composites for the oxidation protection at elevated temperature. The buffer layer coating produced by pack cementation consists of α-SiC, β-SiC and Si, and the outer layer coating produced by slurry method is composed of WSi_2, $CrSi_2$, SiC and Si. The double-layer coating can efficiently protect C/C composites from oxidation at 1773 K for more than 300 h, and the corresponding mass gain rate is only 1×10^{-5} g/cm^2 h. The excellent anti-oxidation property of the coating can be attributed to its dense structure and the formation of stable vitreous composition including SiO_2 and Cr_2O_3 produced during oxidation.

Acknowledgements

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