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Letter

Influence of Cr content on the microstructure and anti-oxidation property of $MoSi_2$–$CrSi_2$–Si multi-composition coating for SiC coated carbon/carbon composites

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ABSTRACT

A $MoSi_2$–$CrSi_2$–Si multi-composition coating was prepared on the surface of SiC coated carbon/carbon (C/C) composites by pack cementation in argon. The crystalline structure of the multi-composition coating was measured by X-ray diffraction. The morphology and the element distribution were analyzed by scanning electron microscopy and energy dispersive spectroscopy, respectively. The influence of Cr content in pack powder on the microstructure and oxidation resistance of the multi-layer coating were investigated. The results indicated that with the increase of Cr content in pack powder, the compound including $MoSi_2$ and $CrSi_2$ content increased. While frequency of crack in the coating obviously increased with the increase of compound content. The multi-layer coating prepared with Cr content of 10 wt.% exhibited excellent oxidation protection for C/C composites at 1600 °C in air for 400 h.

1. Introduction

Carbon/carbon (C/C) composites have been considered as the most promising candidate materials for high temperature applications in aeronautical and aerospace fields because of their excellent properties at high temperatures [1,2]. However, rapid oxidation at high temperatures limits their application in oxygen-containing environment [3]. Applying coating is considered an effective method to prevent them from oxidation under such conditions.

Recently, multi-composition and multi-layer coatings have been synthesized and applied widely to enhance the oxidation resistance of C/C composites [4–6]. SiC is usually used as a bonding and buffer layer because of its good compatibility with C/C composites [7]. Multi-compositions such as alloys [8], ceramics [9] and glasses [10] are candidates for the outer layer materials. Of them, refractory $MoSi_2$-containing cermet coating system is one of the most promising candidates for protection of C/C composites at high temperatures [11,12]. However, this oxidation protection system encounters problems at high temperature and long time. The failure of these coatings is caused by holes and bubbles forming in the SiO_2 glass layer at higher temperatures, providing channels for oxygen to diffuse. Moreover, the oxidized film from the $MoSi_2$-based coating oxidation volatilizes gradually, resulting in the excessive consumption of the coating material [13,14]. Therefore, the formation of a stable vitreous film without holes and bubbles throughout oxidation process is essential. A $MoSi_2$–$CrSi_2$–Si multi-composition is the promising coating material for the outer layer 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 [15–17].

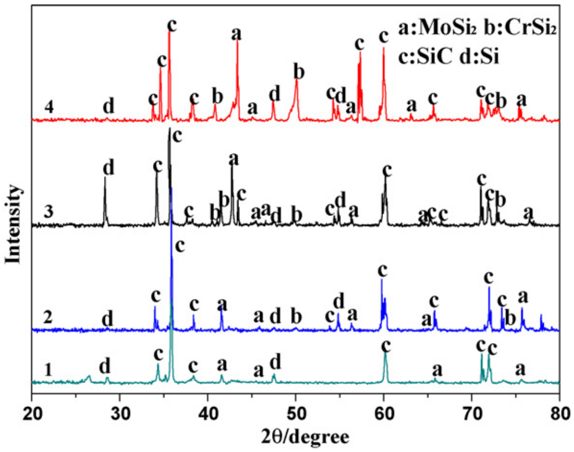

Fig. 1. X-ray pattern of the $MoSi_2$–$CrSi_2$–Si coating surfaces prepared with different pack chemistries: (1) Cr 0 wt.%; (2) Cr 5 wt.%; (3) Cr 10 wt.%; (4) Cr 15 wt.%.

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Up to now, many methods have been explored for preparation of coatings such as chemical vapor deposition (CVD) [18], plasma spray [19], slurry method [20] and pack cementation [21]. Of them, pack cementation is an effective way to deposit coatings with composition gradient on all the substrate surfaces, and can provide a dense coating in a simple and rapid way. In the present work, a $MoSi_2$–$CrSi_2$–Si/SiC multi-layer coating was prepared on C/C composites by this way. Moreover, Cr content in pack chemistries was crucial of the microstructure and oxidation resistance of the multi-composition coating. Therefore, the influence of Cr content in pack powder on microstructure and anti-oxidation property of the coating were specially investigated.

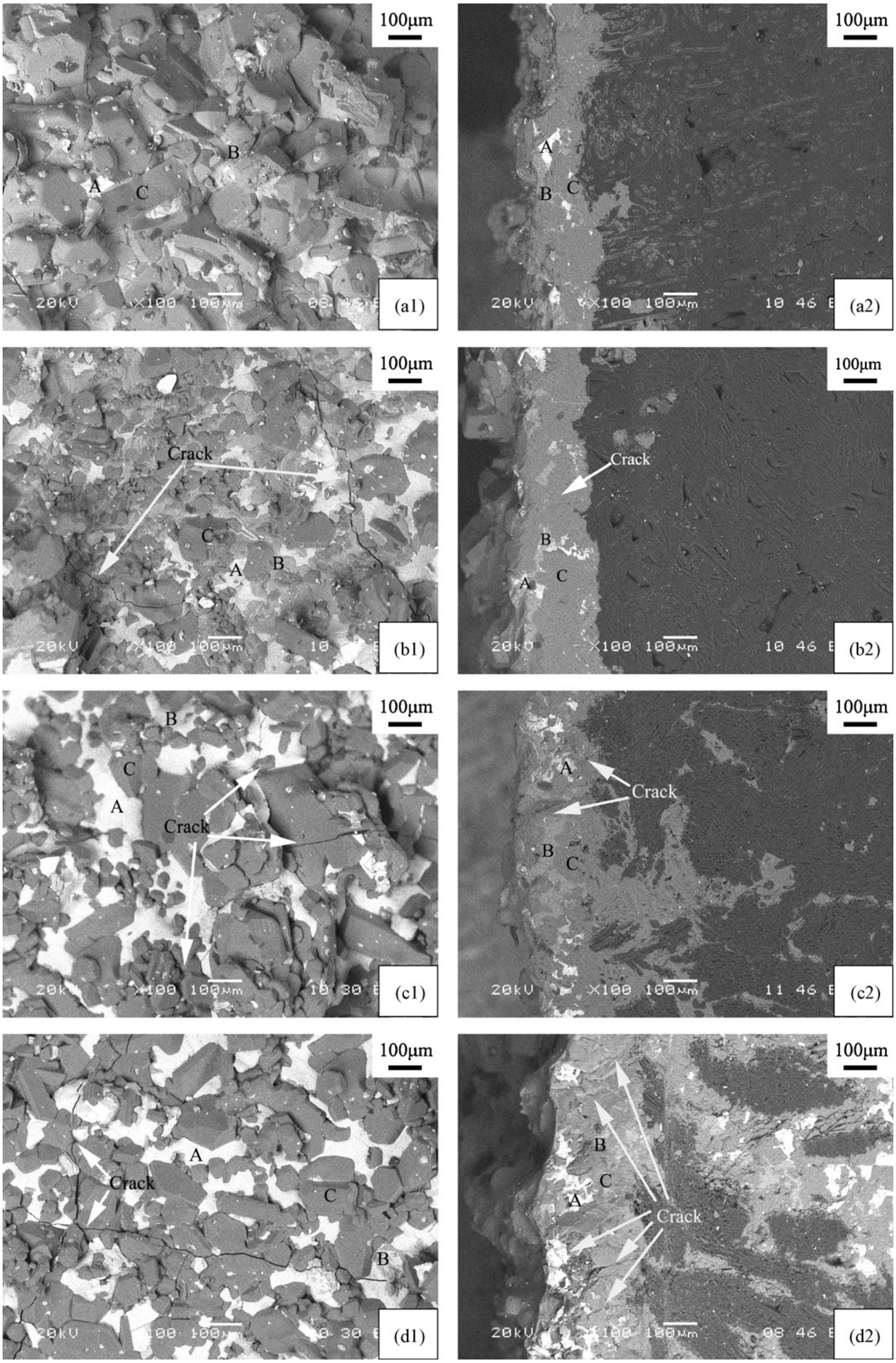

Fig. 2. Backscattering electron images of the $MoSi_2$–$CrSi_2$–Si coating prepared with different pack chemistries: (a1 and a2) Cr 0 wt.%; (b1 and b2) Cr 5 wt.%; (c1 and c2) Cr 10 wt.%; (d1 and d2) Cr 15 wt.%.

2. Experimental

Small specimens (10 mm × 10 mm × 10 mm) used as substrates were cut from C/C composite bulk with a density of 1.72 g/cm^3. The specimens were hand-polished using 320 grit SiC paper, then cleaned with distilled ethanol and dried at 120 °C for 2 h. The $MoSi_2$–$CrSi_2$–Si/SiC multi-layer coating was prepared on C/C composites by two-step pack cementation. The powder composition of the porous SiC buffer coating for the first step pack cementation was mixed as follows: Si 60–80 wt.%; graphite 15–25 wt.%; Al_2O_3 5–15 wt.%. Then the C/C specimens and the first pack mixtures were put into a graphite crucible and heat-treated at 1600–1700 °C for 2 h in argon to produce a porous SiC layer [7]. $MoSi_2$ and Si powders were mixed according to the mass proportion as 1:3. Then Cr powder and some additive were mixed in this certain proportion of $MoSi_2$ and Si powders for the second step pack cementation. The mass percentages of Cr in the second pack mixtures were 5, 10 and 15 wt.%, respectively. The as-prepared SiC coated C/C specimens and the second pack mixtures were put in a graphite crucible, and then were heat-treated in argon at 1800–1900 °C for 2 h. For comparison, another kind of silicide coating was prepared without Cr in pack powder by the same pack cementation process.

The isothermal oxidation test was carried out at 1600 °C in air in an electrical furnace. The crystalline structure of the multi-layer coating was measured with X-ray diffraction (XRD, X'Pert Pro MPD). The morphology and the element distribution of the multi-layer coating were analyzed by scanning electron microscopy (SEM, JSM6460), equipped with energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure of the coating

Fig. 1 shows XRD patterns of the surface of the coatings prepared with different pack powder. After adding Cr in pack powder, $CrSi_2$ phase is detected. The $MoSi_2$–$CrSi_2$–Si/SiC multi-layer coating is composed of $MoSi_2$, $CrSi_2$, SiC and Si.

From Fig. 2(a1 and a2), the multi-layer coating prepared without Cr is dense, and no pore or cracks can be found. It is clear that there are three kinds of crystalline particles characterized as white, brown and grey. By EDS and XRD analysis, in the $MoSi_2$-SiC-Si coating, the white, grey and brown can be distinguished as $MoSi_2$ (**A**), Si (**B**) and SiC (**C**). Fig. 2(b1, b2, c1, c2, d1 and d2) shows backscattering electron images of the multi-layer coating prepared with Cr content of 5, 10 and 15 wt.% in pack powder, from which it can be seen clearly that the coatings have also similar three phases, characterized as white, brown and grey. By EDS and XRD analysis, the white is distinguished as a compound (**A**) of $MoSi_2$ and $CrSi_2$, and the grey and brown are Si (**B**) and SiC (**C**), respectively. During the second step pack cementation, Si melts and penetrates easily into the porous SiC coating. The $MoSi_2$ and Cr grains also penetrate into the porous SiC with the flow of liquid Si. Cr can react with Si to form $CrSi_2$, according to XRD shown in Fig. 1. Therefore, the multi-composition layer consisting of $MoSi_2$, $CrSi_2$ and Si are embedded into the porous SiC layer as shown in Fig. 2(b1,c1,d1). With the increase of Cr content in pack powder, the compound content increases. However, the number of cracks in the coating obviously increases with the increasing of compound content, implying the thermal expansion coefficient of the multi-layer coating may become larger with the increase of compound content. Therefore, these cracks may be formed due to the thermal stress caused by the mismatch of thermal expansion coefficient between the coating and C/C composites.

3.2. Oxidation resistance of the multi-layer coatings

The long-term isothermal oxidation curves of the coated C/C composites at 1600 °C in air are shown in Fig. 3. The weight loss of the coated samples prepared without Cr is 3.3% after oxidation at 1600 °C for 50 h. The $MoSi_2$–$CrSi_2$–Si coating prepared with 5 wt.% Cr has better oxidation protection ability for C/C composites than that prepared without Cr. The weight loss of the coated samples prepared with 5 wt.% Cr is 1.5% after oxidation at 1600 °C for 100 h. During oxidation, the SiO_2–Cr_2O_3 glass film cannot cover the whole coating surface because of the low content of compound content. Therefore, the oxidation protection ability of the $MoSi_2$–$CrSi_2$–Si coating prepared with 5 wt.% Cr is reduced heavily with extending oxidation time. When Cr contents are 10 and 15 wt.% in pack powder, respectively, the oxidation protection ability of the coating is improved obviously. After oxidation for 400 h, the weight losses of the coated samples prepared with 10 and 15 wt.% Cr are 0.7% and 1.1%, respectively. The protective temperature and time is higher and longer than that of other coating systems reported in Refs. [13–15,22]. With increase of Cr content in pack powder, the SiO_2–Cr_2O_3 glass can cover the whole coating surface. The SiO_2 exhibits very low oxygen permeability and the Cr_2O_3 can improve its stability [15–17]. Therefore, the SiO_2–Cr_2O_3 glass film can provide effective protection at high temperatures. The weight loss of the coating prepared with Cr content of 15 wt.% increases gradually, which may be caused by larger amount of cracks in the coating prepared with excessive Cr content as shown in Fig. 2(d1 and d2). In conclusion, prepared with Cr content of 10 wt.%, the $MoSi_2$–$CrSi_2$–Si coating exhibits the best oxidation protection ability for C/C composites.

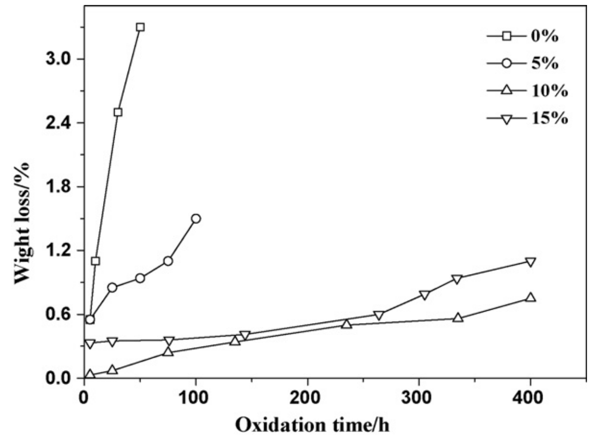

Fig. 3. Isothermal oxidation curves of the coated C/C composites prepared with different Cr contents in air at 1600 °C.

Fig. 4 shows SEM images of the multi-layer coating prepared with different pack chemistries. A glass film with holes and bubbles is detected on the surface of the coating prepared without Cr shown in Fig. 4(a1). Moreover, from XRD analysis as shown in Fig. 5(1), the intensities of SiO_2 of the coating prepared without Cr is very low, implying that the pure SiO_2 cannot form a dense glass film to cover the coating surface at 1600 °C. The holes and bubbles provide channels for the oxygen to diffuse. Therefore, the obvious oxidation mark of C/C composites is found shown in Fig. 4(a2). The multi-layer coating prepared without Cr cannot provide oxidation protection for C/C composites at 1600 °C. After adding Cr, the glass film without holes or bubbles is found clearly as shown in Fig. 4(b1, c1, and d1). Some cracks are also found on the coating surface. These cracks are generated in the stage of quick cooling when the samples are taken out of electrical furnace for weighting, and can be sealed by glass when the coating is heated to 1600 °C again. The crystalline particles can be detected and only become smaller in comparison with the one before oxidation shown in Fig. 2(b1, c1 and d1). From XRD analysis as shown in Fig. 5(2), characteristics of SiO_2 and Cr_2O_3 can be observed. It indicates that this glass film is composed SiO_2 and Cr_2O_3 [15–17]. Owing to very little compound content in the coating prepared with Cr content of 5 wt.%, the coating compositions are not enough to form the SiO_2–Cr_2O_3 glass throughout the oxidation process. The glass layer volatilizes gradually and cannot effectively prevent oxygen diffusing in the coating, resulting in excessive depletion of the coating. Therefore, the thickness of the

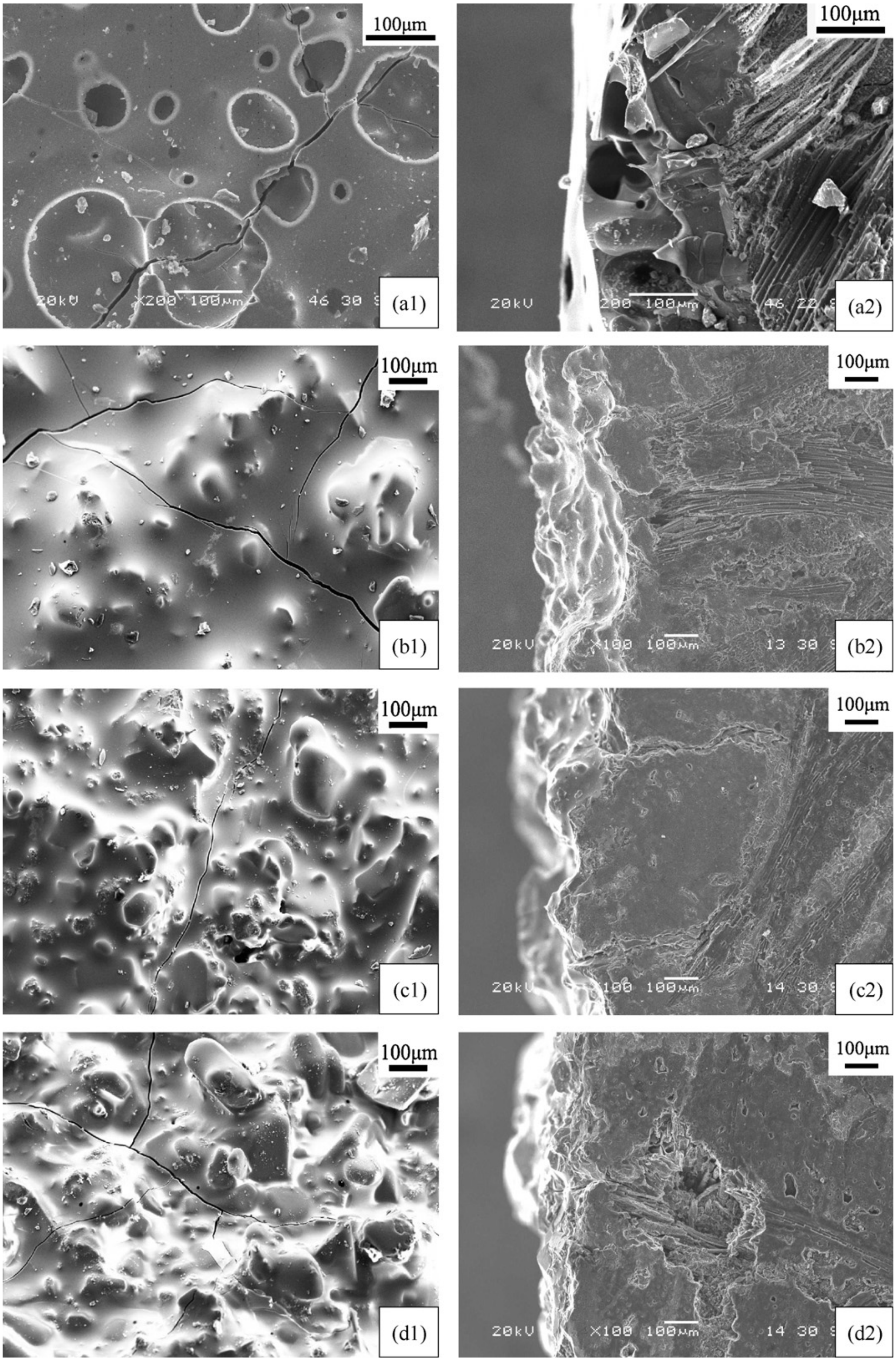

Fig. 4. SEM images of the $MoSi_2$–$CrSi_2$–Si coating prepared with different pack chemistries after oxidation at 1600 °C: (a1 and a2) Cr 0 wt.% for 50 h; (b1 and b2) Cr 5 wt.% for 100 h; (c1 and c2) Cr 10 wt.% for 400 h; (d1 and d2) Cr 15 wt.% for 400 h.

multi-layer coating prepared with Cr content of 5 wt.% decreases excessively (Fig. 4(b2)). From Fig. 4(c2), after 400 h oxidation, the penetrating cracks are found in the coating. Some cracks have been formed during preparation as shown in Fig. 2(c1). When the samples suffer thermal shock, these cracks are apt to form penetrating cracks due to the mismatch of thermal expansion between the coating and C/C composites. These cracks and penetrating cracks can be sealed by the SiO_2–Cr_2O_3 glass as the coated samples are put into the 1600 °C electric furnace. However, during the changed temperature process from 1600 °C to room temperature, some penetration cracks are open, through which oxygen can diffuse and react with C/C composites. Therefore, the weight loss of the sample is pri-

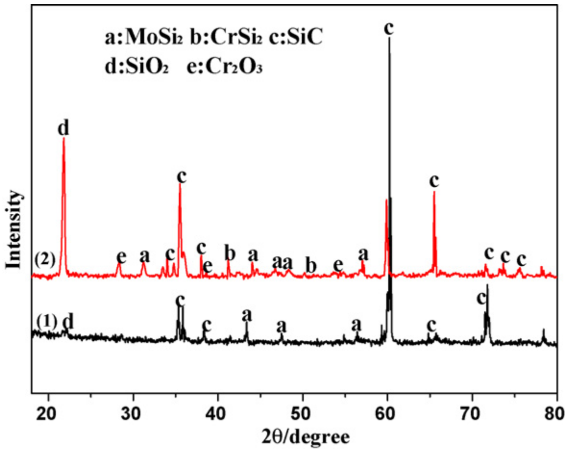

Fig. 5. X-ray patterns of the multi-layer coating prepared with different pack chemistries after oxidation at 1600 °C: (1) Cr 0 wt.% for 50 h; (2) Cr 10 wt.% for 400 h.

marily caused by the existence of some penetration cracks in the coating during the changed temperature process. Prepared with Cr content of 15 wt.%, the compound including $MoSi_2$ and $CrSi_2$ content in the coating is the largest among these coatings as shown in Fig. 2(d2), implying the thermal expansion coefficient of the multi-layer coating may be largest. Therefore, the number and dimension of penetrating cracks in the coating may increase. The penetrating cracks in multi-layer coating provide channels for oxygen that lead to the oxidation of C/C composites. From Fig. 4(d2), the obvious oxidation mark of C/C composites is found. Additionally, the thickness of the multi-layer coating prepared with 10 and 15 wt.% does not change obviously compared with the samples before oxidation shown in Fig. 2(c2 and d2). It reveals that the compound glass film can protect the coating composition below glass layer to prevent the consumption of the coating.

Additionally, the multi-layer $MoSi_2$–$CrSi_2$–Si/SiC coatings prepared with different pack chemistries have also endured thermal shock cycles between 1600 °C and room temperature when the samples are taken out of electrical furnace for weighing. However, no obvious debonding is found, implying good thermal compatibility between $MoSi_2$–$CrSi_2$–Si and SiC coating.

4. Conclusions

A $MoSi_2$–$CrSi_2$–Si multi-composition coating is prepared on the surface of SiC coated C/C composites by pack cementation. The results indicate that with the increase of Cr content in pack powder, the compound including $MoSi_2$ and $CrSi_2$ content increases. While frequency of crack in the coating increases with the increase of compound content. The multi-layer coating prepared with Cr content of 10 wt.% exhibits excellent oxidation protection at 1600 °C in air for 400 h.

Acknowledgements

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