

Oxidation Behaviour and Mechanism of MoSi₂-CrSi₂-SiC-Si Coating for Carbon/Carbon Composites from Room Temperature to 1873 K

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Abstract. A MoSi₂-CrSi₂-SiC-Si coating was prepared on the surface of carbon/carbon (C/C) composites by a two-step pack cementation method. The microstructure and oxidation behaviour of the coating were studied. These results illustrated that the coating could effectively protect C/C composites from oxidation in air above 1600 K, due to the protection of the compound glass. The weight loss of the coated C/C specimens was only 0.4% after oxidation at 1873 K for more than 150 h. The coating lacked effective oxidation resistance for C/C composites from 800 to 1600 K, as no obvious glass layer covered the coating surface and the cracks cannot be sealed because of the high viscosity of the compound glass.

1 Introduction

Carbon/carbon (C/C) composites have many unique properties at high temperature, such as high strength-to-weight ratio, low coefficient of thermal expansion (CTE) and high thermal shock resistance. Therefore, they are attractive materials for applications in aeronautical and aerospace fields [1, 2]. However, the oxidation of C/C composites above 723 K in an oxidizing atmosphere limits their applications as thermal structure materials [3]. Applying coatings is considered an effective method to prevent oxidation under such conditions.

To prevent C/C composites against oxidation, many coating systems, especially the silicide coatings have been explored to enhance the isothermal oxidation resistance of C/C composites [4-6]. In previous work, the MoSi₂-CrSi₂-SiC-Si ceramic is proposed base-on the optimization as the coating materials because a kind of stable compound glass film including SiO₂ and Cr₂O₃ without holes and bubbles can be formed, thus effectively improve the oxidation resistance of the C/C composites. This coating system exhibits good oxidation protective ability at high temperatures [7-9]. However, the oxidation resistance and oxidation failure mechanism is usually tested and analyzed at single temperature. Compared with the application of C/C composites in practical environment, it is not enough to entirely reflect the oxidation protection ability and failure of the coating. Moreover, many of researchers focus on the oxidation protection ability and failure of the coated C/C composites at high temperatures. Therefore, study on the oxidation resistance and oxidation failure mechanism of the coated C/C composites at various temperatures is essential.

In this work, the MoSi₂-CrSi₂-SiC-Si coating was

prepared on the surface of C/C composites by two-step pack cementation in argon. The oxidation resistance of the MoSi₂-CrSi₂-SiC-Si coating from room temperature to 1873 K has been investigated and the results have been analyzed.

2 Experimental

2.1 Preparation of coated C/C composites

Small specimens (15 mm×15 mm×15 mm for isothermal oxidation test and 8 mm ×8 mm×8 mm for thermalgravimetric test) used as substrates were cut from C/C composite bulk with a density of 1.72 g/cm³. The specimens were hand-polished using 320 grit SiC paper, then cleaned with distilled ethanol and dried at 373 K for 3 h. The precursor powder of the porous SiC coating for the first step pack cementation was mixed as follows: Si 60-80 wt.%, graphite 15-25 wt.% and Al₂O₃ 5-15 wt.%. Then the C/C specimens and mixtures were put into a graphite crucible and heat-treated at 1973-2073 K for 2-3 h in argon to produce the porous SiC layer. The precursor powder of the MoSi₂-CrSi₂-SiC-Si coating for the second step pack cementation were mixed as follows: MoSi₂ 10-15 wt.%, Si 55-75 wt.%, Cr 5-15 wt.%, graphite 5-10 wt.% 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 2073-2173 K for 2-3 h.

2.2 Oxidation test

The isothermal oxidation test was performed in air in an electric furnace. The coated specimens were put directly

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into the electric furnace; thereafter they were taken out and cooled to room temperature. Mass of the specimens was measured and recorded by an electronic precision balance with sensitivity of ± 0.1 mg (Sartorius CP224S), and then they were put into the furnace again for the next oxidation period.

2.3 Characterization

The thermogravimetric test was carried out on Mettler Toledo Star TGA/SDTA 851 thermal analyser in simulated air from room temperature to 1773 K with the heating rate of 10 K/min. The crystalline structure of the coating was measured with X-ray diffraction (XRD, X'Pert Pro MPD). The morphology and the element distribution of the multi-component coating were analysed 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 images of the $\text{MoSi}_2\text{-CrSi}_2\text{-SiC-Si}$ coating prepared by two-step pack cementation. It is clear that a dense structure and no visible cracks (Fig. 1(a)) can be found from the coating surface. After preparation by two-step pack cementation, the coating (Fig. 2) is composed of MoSi_2 , CrSi_2 , SiC and Si, respectively. Fig. 1(b) displays cross-section backscattered electron microscopy of the coating, from which it can be seen that the coating has three phases, characterized as white, brown and grey. By EDS and XRD analysis, the white, grey and brown can be distinguished as a mixture (A) of MoSi_2 and CrSi_2 , Si (B) and SiC (C), respectively [7-9]. 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 liquid Si. Cr can react with Si to form CrSi_2 , according to XRD shown in Fig. 2(2). Therefore, the white (MoSi_2 and CrSi_2) and grey (Si) phases is embedded into the porous SiC coating. The white and grey phases in the coating can form plentiful interfaces. These interfaces can relax the thermal stress and decrease the frequency of the cracks in the coating [10]. In addition, the thickness of the coating is about 250 μm and no visible cracks can be found in the coating.

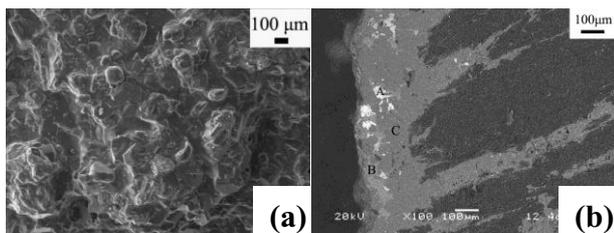


Fig. 1 SEM images of the $\text{MoSi}_2\text{-CrSi}_2\text{-Si}$ coating by two-step pack cementation: (a) surface; (b) cross-section backscattered electron microscopy.

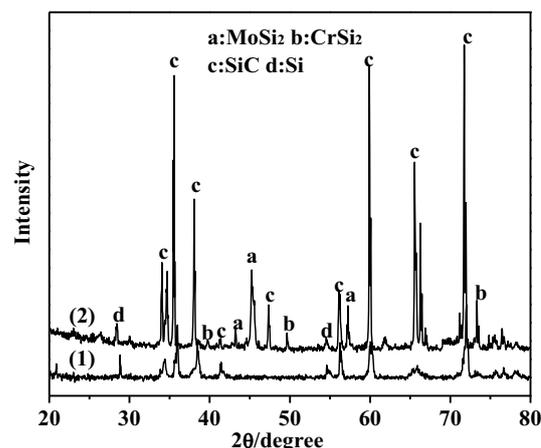


Fig. 2 X-ray patterns of the coating surfaces: (1) the first step pack cementation, (2) the second step pack cementation.

3.2 Oxidation resistance of the coatings

In order to verify oxidation resistance of the $\text{MoSi}_2\text{-CrSi}_2\text{-SiC-Si}$ coating in a variable temperature environment, the TGA of the coated C/C composites is measured in simulated air from room temperature to 1773 K as shown in Fig. 3. According to this curve, the oxidation behavior of the coated C/C composites can be divided into three regions, marked as 1, 2 and 3. It is clear that the $\text{MoSi}_2\text{-CrSi}_2\text{-SiC-Si}$ coated specimens lose mass significantly from 900 to 1600 K (process 2), and the mass loss of the coated specimens is up to 6% after heating at 1600 K. Above 1600 K (process 3), the coated specimens gain mass. It seems that the $\text{MoSi}_2\text{-CrSi}_2\text{-SiC-Si}$ coating can effectively protect C/C composites from oxidation above 1600 K, but lacks the protection ability for C/C composites from 900 to 1600 K.

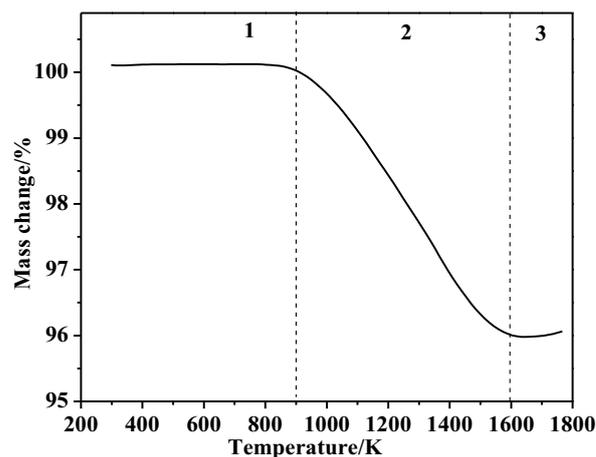


Fig. 3 Mass change of the coated specimens in simulated air from room temperature to 1773 K with the rate of 10 K/min.

Oxidation curves of the $\text{MoSi}_2\text{-CrSi}_2\text{-SiC-Si}$ coated C/C composites at different temperatures are shown in Fig. 4. From Fig. 4(a), the mass loss of the coated specimens is 11%, 16% and 18.5% after oxidation for 10 h at 1073, 1173 and 1273 K, respectively. The oxidation curve of the coating at 1073, 1173 and 1273 K is straight line with the increase of the oxidation time. In Fig. 4(b),

the mass loss of the coated specimens is 0.1%, 0.18% and 0.4% after oxidation for 150 h at 1673, 1773 and 1873 K, respectively. Moreover, it is clear that the oxidation curve of the coating at 1673 and 1773 K is about parabola with the increase of the oxidation time. However, the oxidation curve of the coating at 1873 K is similar straight line with the increase of the oxidation time. The results show that the oxidation resistance of the coating from 1673 to 1873 K is better than that from 1073 to 1273 K.

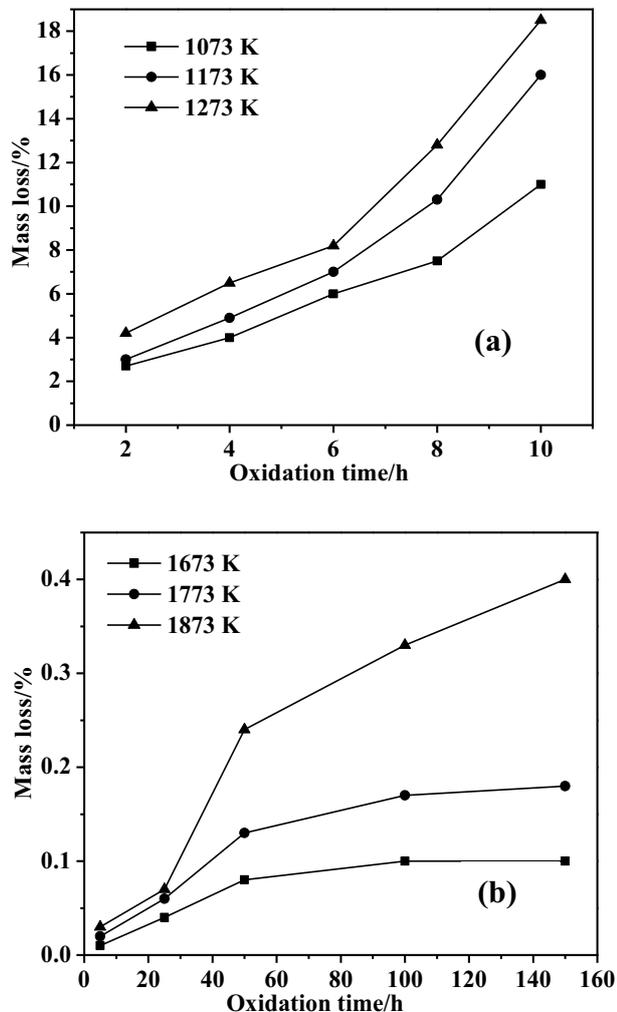


Fig. 4 Oxidation curves of the coated C/C samples at different temperatures: (a) from 1073 to 1273 K; (B) from 1673 to 1873 K

Fig. 5 shows electron images of the coating after oxidation for 10 h at 1173 K. there is no continuous glass layer on the surface of the $\text{MoSi}_2\text{-CrSi}_2\text{-SiC-Si}$ coating and some visible cracks can be detected as shown in Fig. 5(a), which cannot effectively prevent oxygen diffusion in the $\text{MoSi}_2\text{-CrSi}_2\text{-SiC-Si}$ coating. The CTE values of these coating materials, such as $\alpha_{\text{MoSi}_2}=8.1\times 10^{-6}/\text{K}$ [11], $\alpha_{\text{CrSi}_2}=10.5\times 10^{-6}/\text{K}$ [12], $\alpha_{\text{SiC}}=5\times 10^{-6}/\text{K}$ [13] and $\alpha_{\text{Si}}=2.5\times 10^{-6}/\text{K}$ [14] are larger than that of C/C composites ($\alpha_{\text{C/C}}=1\times 10^{-6}/\text{K}$ [11]). During coating preparation or oxidation period, the coating will suffer the thermal stress because of the mismatch of CTE between the coating and C/C substrate, resulting in the formation of cracks in the coating. Moreover, the greater temperature difference is, the larger the frequency of the

cracks is. The number and dimension of cracks will increase in the coating, which can provide more and more channels for oxygen diffusion. However, the viscosity of the compound glass is too high to flow and seal these cracks at this temperature range [15, 16]. Oxygen can diffuse along these cracks and react with C/C composites, resulting in the failure of the coating and the rapid mass loss of the coated specimens. Therefore, it can be seen that the obvious oxidation mark of C/C substrates can be detected as shown in Fig. 5(b). It can be inferred that the coating lacks effective oxidation resistance for C/C composites at intermediate temperatures, due to the high viscosity of the compound glass.

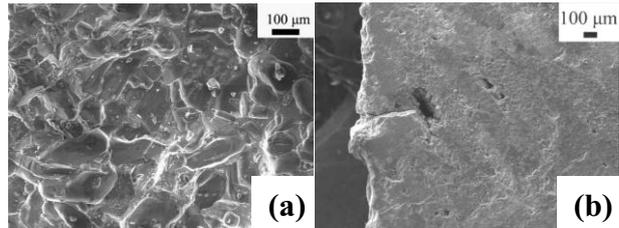


Fig. 5 SEM images along the cross-section of the coating after oxidation for 10 h at 1173 K.

Fig. 6 shows electron images of the coating after oxidation for 150 h at 1773 and 1873 K, respectively. From Fig. 6(a) and (c), a continuous and smooth glass layer with some microcracks can be found on the coating surface after oxidation at 1773 or 1873 K for 150 h. These microcracks are generated in the stage of quick cooling from high temperature to room temperature, and can be sealed by glass when the coating is heated again for the next oxidation period. Therefore, the glass layer can efficiently prevent oxygen from diffusing into the C/C substrate during oxidation. With the increase of the oxidation temperature, some cracks especially penetrating-cross cracks can be found in the coating as shown in Fig. 6(b) and (d), due to the mismatch of CTE between the coating and C/C substrate. These cracks especially penetrating-cross cracks can be sealed by the flowing compound glass, resulting in that the coating exhibits good oxidation protective ability above 1600 K. Although these cracks can be self-sealed when the coating is heated again, C/C matrix is oxidised by oxygen diffusing through these cracks in the coating at the temperature between the crack sealing temperature and the starting oxidising temperature of C/C composites. So, a slight oxidation mark can be found as shown in Fig. 6(b) and (d). Moreover, some defects including pores and pits (Fig. 6(d)) can be generated in the coating after oxidation at 1873 K for 150 h due to the excessive depletion of the coating materials, which can be inferred that the depletion of the coating at 1873 K is heavier than that at 1773 K. Meanwhile, some microcracks are found near the defects because the defects are apt to cracking when the coated C/C specimens suffer thermal shock. Moreover, these defects can be connected through these microcracks, which can provide more and more channels for oxygen diffusion. Therefore, the mass loss of the coating at 1873 K for 150 h is larger than that at 1773 K for 150 h. It can be inferred that the coating can effectively provide

protection oxidation ability for C/C composites at high temperatures, due to generating a compound glass layer [7] and sealing the cracks in the coating. The oxidation mechanism of the coating has two modes. The coating can provide effective protection for C/C composites from oxidation at high temperatures, but lacks effective oxidation resistance for C/C composites at intermediate temperatures. Therefore, the further research about how to improve oxidation resistance of the silicide coating for C/C composites at intermediate temperatures is needed.

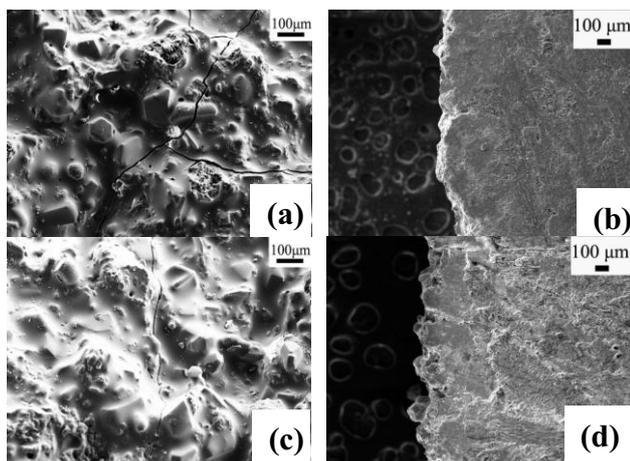


Fig. 6 SEM images of the MoSi₂-CrSi₂-SiC-Si coating after oxidation for 150 h at different temperature: (a) and (b) at 1773 K; (c) and (d) at 1873 K.

4 Conclusions

The MoSi₂-CrSi₂-SiC-Si coating is prepared on the surface of carbon/carbon (C/C) composites by a two-step pack cementation method. The results indicate that the coating can effectively protect C/C composites from oxidation from oxidation in air above 1600 K, due to the protection of the compound glass. The weight loss of the coated C/C specimens is only 0.4% after oxidation at 1873 K for more than 150 h. The coating lacks effective oxidation resistance for C/C composites from 800 to 1600 K, as no obvious glass layer covers the coating surface and the cracks cannot be sealed because of the high viscosity of the compound glass.

Acknowledgements

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References

1. A.V.K. Westwood, B. Rand and S. Lu: Carbon Vol. 42 (2004), p. 3071
2. E. Corral and R. Loehman: J. Am. Ceram. Soc. Vol. 91 (2008), p. 1495
3. N.S. Jacobson and D.M. Curry: Carbon Vol. 44 (2006) p. 1142
4. G.B. Zheng, H. Mizuki, H. Sano and Y. Uchiyama: Carbon Vol. 46 (2008), p. 1808
5. X.R. Ren, H.J. Li, K.Z. Li and Q.G. Fu: J. Eur. Ceram. Soc. Vol. 35 (2015), p. 897
6. K.T. Wang, L.Y. Cao, J.F. Huang and J. Fei: J. Eur. Ceram. Soc. Vol. 33 (2013), p. 191
7. T. Feng, H.J. Li, Q.G. Fu, H. Wu and X.T. Shen: J. Alloy. Compd. Vol. 501 (2010), p. L20
8. H.J. Li, T. Feng, Q.G. Fu, H. Wu and X.T. Shen: Carbon Vol. 48 (2010), p. 1636
9. T. Feng, H.J. Li, Q.G. Fu, X. Yang and H. Wu: Corros. Sci. Vol. 53 (2011), p. 4102
10. H.J. Li, H. Xue, Y.J. Wang, Q.G. Fu and D.J. Yao: Surf. Coat. Technol. Vol. 201 (2007), p. 9444
11. Q.G. Fu, H.J. Li, Y.J. Wang, K.Z. Li and X.H. Shi: Corros. Sci. Vol. 51 (2009), p. 2450
12. B.S. Rabinovich, I.Z. Radovskii and P.V. Gel'd: Powder Metall. Met. Ceram. Vol. 7 (2004), p. 879
13. J.I. Kim, J.W. Kim, D.J. Choi, J.Y. Park and W.S. Ryu: Carbon Vol. 43 (2005), p. 1749
14. X.Y. Wang, H.B. Geng, S.Y. He, Y.O. Pokhyl and K.V. Koval: Int. J. Adhes. Adhes. Vol. 27 (2007), p. 288
15. N.S. Jacobson: J. Am. Ceram. Soc. Vol. 76 (1993), p. 3
16. T. Feng, H.J. Li, Q.G. Fu, X. Yang and H. Wu: Carbon Vol. 50 (2012), p. 2171