DOUBLE-LAYER OXIDATION PROTECTIVE SiC/W-Mo-Si COATING FOR CARBON/CARBON COMPOSITES

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Abstract

A SiC/W-Mo-Si double-layer oxidation protective coating for carbon/carbon composites was prepared by a two-step pack cementation technique. XRD and SEM show that the coating obtained by the first step pack cementation was a thin inner buffer layer of SiC with some cracks and pores, and a new phase of $(W_xMo_{1-x})Si_2$ appeared after the second step pack cementation. Oxidation test shows, after 175h oxidation in air at 1773K and thermal cycle between 1773K and room temperature for 18 times, the weight loss of the SiC/W-Mo-Si coated C/C composites was only 2.06%. During the initial oxidation period, the disilicides in the coating mainly reacted with oxygen to form WO_3, MoO_3 and SiO_2 for high partial pressure of oxygen on their surface, and the weight of the sample decreased quickly due to volatilization of WO_3 and MoO_3. As the oxidation test prolonging, more SiO_2 glass was generated and more defects were sealed, which reduced the partial pressure of oxygen on the surface of the disilicides and made more disilicides react with oxygen to form $(W_xMo_{1-x})_5Si_3$ and SiO_2. The weight loss rate of the sample gradually decreased before 175h. The oxidation protective failure of the SiC/W-Mo-Si coating after oxidation for 200h was attributed to the formation of some penetration cracks in the coating.

Key words: Carbon composites; Coatings; Heat treatment

Introduction

Carbon/carbon (C/C) composites have been widely used as high temperature structural materials for their excellent high-temperature mechanical properties. Unfortunately, C/C composites oxidize in an oxidation atmosphere above 723K. Tungsten disilicide (WSi_2) and molybdenum disilicide ($MoSi_2$) are intermetallic compounds with high melting points and excellent resistance to high-temperature oxidation. And the mechanical properties of $WSi_2/MoSi_2$ composite are better than those of single WSi_2 or $MoSi_2$. However, up to now, no literature has been reported about $WSi_2/MoSi_2$ coating for oxidation protection of C/C composites.

In the present work, a SiC/W-Mo-Si coating was prepared on the surface of C/C composites by pack cementation. The oxidation protective ability and anti-oxidation mechanism of the as-received coating in air at 1773K were studied.

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Experimental

The double-layer coating SiC/W-Mo-Si was prepared on C/C substrates ($10 \times 10 \times 10$ mm^3) by a two-step pack cementation process. The powder composition of producing SiC internal coating by the first step pack cementation at was as follows: 60-85 wt.% Si, 10-20 wt.% graphite and 2-8 wt.% Al_2O_3. The powder composition for preparing W-Mo-Si outer coating by the second step pack cementation was as follows:10-25 wt.% W, 5-15 wt.% Mo, 60-75 wt.% Si, 2-5 wt.% graphite and 1-3 wt.% Al_2O_3. The two step pack cementations were performed at 2073K-2373K and 2373K-2573K, respectively, with the same time of 2h. The as-coated specimens were heated at 1773K in air in an electrical furnace to investigate the isothermal and thermal cycling oxidation behavior. The morphology and crystal structure of the coating were analyzed with scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Results and discussion

Fig.1 (a) shows the surface micrograph of the SiC coating prepared by the first step pack cementation, on which some cracks and pores can be seen. The cross-section micrograph (Fig.1 (b)) reveals the SiC coating is uneven and only around 25 μm in thickness. Fig.2 shows the surface and cross-section SEM images of the SiC/W-Mo-Si coated C/C composites. A few microcracks can be seen on the surface of the multi-coating. The average thickness of the multi-coating is around 110 μm, and it is compact and penetration crack or holes are not found in the coating.

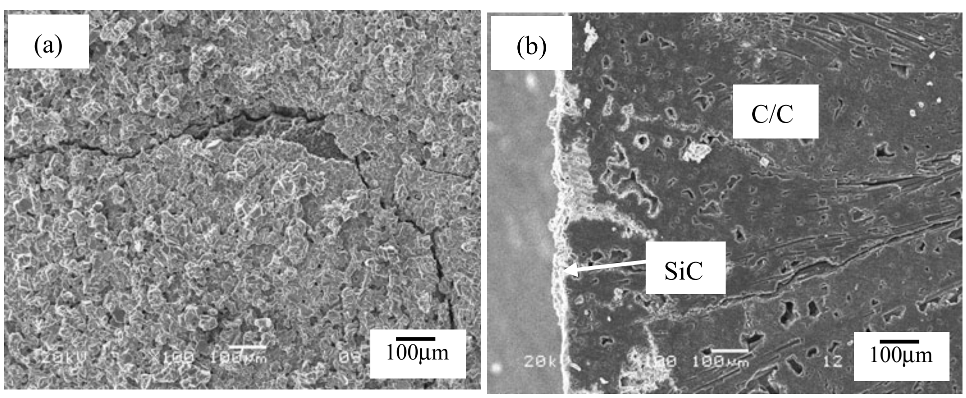

Fig 1. SEM micrographs of the SiC coating prepared by the first-step pack cementation
(a) surface; (b) cross-section

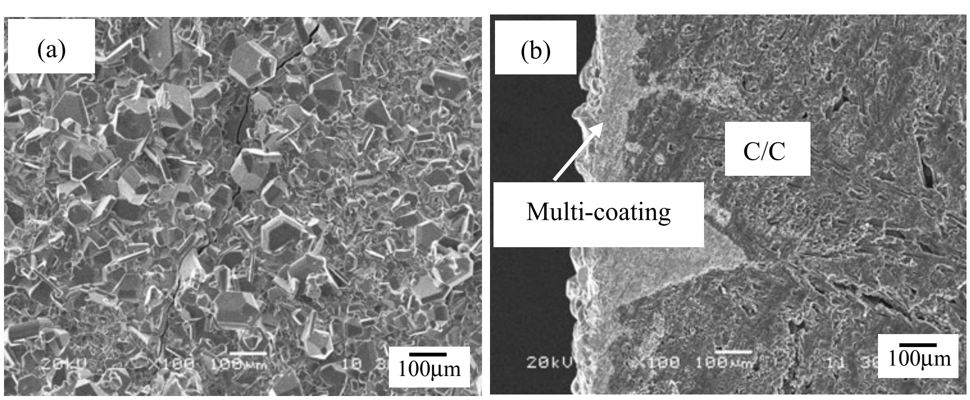

Fig 2. SEM micrographs of the SiC/W-Mo-Si coated C/C composites obtained by the two-step pack cementation (a) surface; (b) cross-section

Fig.3 shows the XRD patterns of the multi-coating surface before oxidation and after oxidation at 1773K for 200h. From Fig.3, It is concluded that during oxidation test the coated C/C reacted with oxygen as follows:

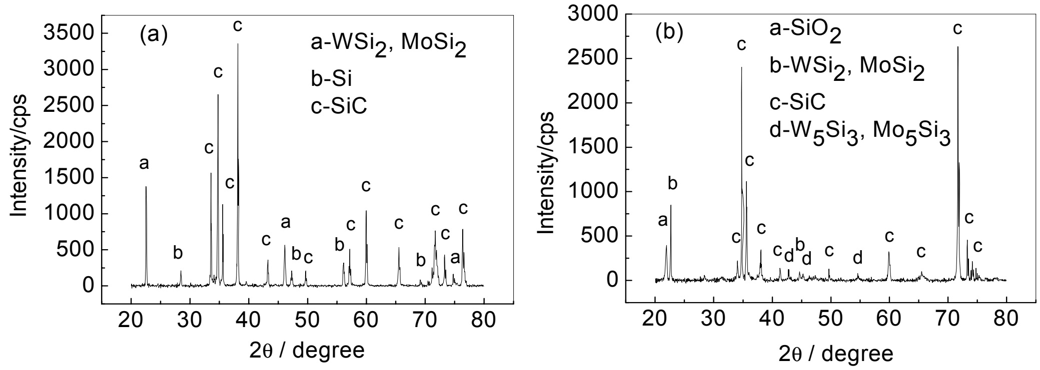

Fig 3. X-ray patterns of the surface of the SiC/W-Mo-Si coating prepared by the two-step pack cementation (a) before oxidation; (b) after oxidation in air at 1773 K for 200 h.

$$SiC(s) + 2O_2(g) \rightarrow CO_2(g) + SiO_2(s) \quad (1)$$
$$Si(s) + O_2(g) \rightarrow SiO_2(s) \quad (2)$$
$$2WSi_2(s) + 7O_2(g) \rightarrow 2WO_3(g) + 4SiO_2(s) \quad (3)$$
$$2MoSi_2(s) + 7O_2(g) \rightarrow 2MoO_3(g) + 4SiO_2(s) \quad (4)$$
$$5WSi_2(s) + 7O_2(g) \rightarrow W_5Si_3(s) + 7SiO_2(s) \quad (5)$$
$$5MoSi_2(s) + 7O_2(g) \rightarrow Mo_5Si_3(s) + 7SiO_2(s) \quad (6)$$
$$2C(s) + O_2(g) \rightarrow 2CO(g) \quad (7)$$
$$C(s) + O_2(g) \rightarrow CO_2(g) \quad (8)$$

When the coating reacts with oxygen as Eqs.(1), (2), (5) and (6), the weight of the sample would increase, but decrease from the reactions (3), (4), (7) and (8).

The isothermal oxidation curve of SiC/W-Mo-Si coated C/C composites (Fig.4) shows that the weight loss of the sample was only 2.06% after oxidation at 1773K for 175h in air. During the oxidation test, the as-coated specimen had endured thermal cycling between 1773K and room temperature for 18 times without visible cracking or debonding, and no elevating trend of the weight loss rate, implying that the coating has good thermal shock resistance.

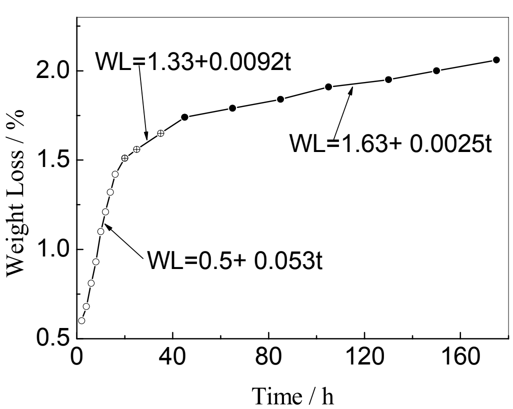

Fig 4. Isothermal oxidation curve of the SiC/W-Mo-Si coated C/C composites in air at 1773K

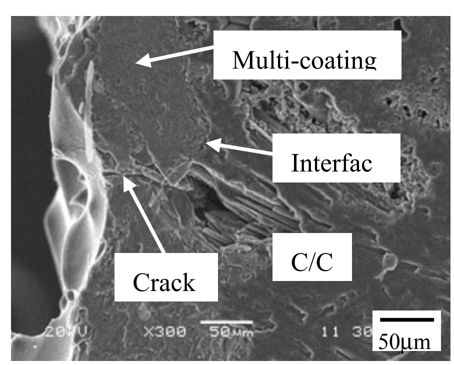

Fig 5. Cross-section SEM micrograph of the multi-coating coated C/C composites after oxidation in air at 1773K for 200h.

From Fig.4, the isothermal oxidation curve of the sample consists of three line-like sections. In the initial stage of oxidation (0h-20h), the sample was exposed to the atmosphere. W, Mo and Si elements in the disilicides were oxidized to form WO_3, MoO_3 and SiO_2 as Eqs. (3) and (4) due to high oxygen pressure. The volatilization of WO_3 and MoO_3 covered weight gain coming from the formation of SiO_2 glass, which resulted in the quick weight loss rate of the sample. In the second period (20h-45h), more SiO_2 glass was generated and more microcracks were sealed, which reduced the partial pressure of oxygen on the disilicides and made some disilicides below SiO_2 layer react with oxygen incompletely as Eqs.(5) and (6). In the third period (45h-175h), the partial pressure of oxygen on the surface of the disilicides fell continuingly due to the formation of more vitreous SiO_2 and more disilicides reacted according to Eqs.(5) and (6), which made the weight loss rate of the sample decrease further. The SiC/W-Mo-Si coating was of no effect suddenly and the weight loss of the sample was up to 20.88% after oxidation in air at 1773K for 200h. A penetrable crack could be seen in the cross-section SEM image of the multi-coating on C/C composites after oxidation in air at 1773K for 200h (Fig.5), through which oxygen would diffuse quickly to C/C matrix and react with C/C as Eqs. (7) and (8), causing the coating invalid suddenly.

Conclusions

A novel W-Mo-Si/SiC coating could be prepared on C/C composites by a two-step pack cementation technique and protect C/C composites from oxidation in air at 1773K over 175h. With the oxidation prolonging, more SiO_2 glass is generated and more microcracks are sealed, which reduces the partial pressure of oxygen on the surface of the disilicides and makes more disilicides below SiO2 layer react with oxygen incompletely, causing the weight loss rate of the sample gradually decrease before 175h. The invalidation of the coating is attributed to the formation of penetrable cracks in the coating.

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