MICROSTRUCTURE AND ANTI-OXIDATION PROPERTY OF A $MoSi_2$-SiC-Si COATING FOR CARBON/CARBON COMPOSITES

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Abstract

To protect carbon/carbon (C/C) composites from oxidation, a dense coating has been produced by a two-step pack cementation technique. XRD and SEM analysis show that, the as-obtained coating was composed of $MoSi_2$, SiC and Si with a thickness of 80-100μm. The $MoSi_2$-SiC-Si coating has excellent anti-oxidation property, which can protect C/C composites from oxidation at 1773K in air for 200h and the corresponding weight loss is only 1.04%. The weight loss of the coated C/C composites is primarily due to the reaction of C/C substrate and oxygen diffusing through the penetration cracks in the coating.
Key words: carbon/carbon composites, coating, oxidation

Introduction

Carbon/carbon (C/C) composites are considered as the promising candidate materials for high temperature structural applications. However, the oxidation above 723K limited their use to inert atmosphere. Therefore, the investigation of oxidation protective system for these composites is very important for their successful utilization.

SiC ceramic coating has been applied widely for the anti-oxidation of C/C composites at high temperature. While the SiC coating obtained by pack cementation usually possesses a porous structure, which is disadvantageous to its oxidation protection for C/C composites. Molybdenum disilicide ($MoSi_2$) has a high melting point, excellent high temperature oxidation and corrosion resistance, which is expected to provide efficient protection for SiC coated C/C composites. So, a multi-phase coating by filling the holes in SiC coating with $MoSi_2$, might be an efficient method for improving the oxidation resistance of C/C composites. However, the mismatch of the coefficient of the thermal expansion between $MoSi_2$-SiC and C/C may result in the cracking of the coating, which will lead to the protection failure of the coating. To solve this problem, free Si is designed to be added into the $MoSi_2$-SiC coating, which will considerably increase the content of the phase interface and improve the toughness of the $MoSi_2$-SiC coating.

In the present work, a $MoSi_2$-SiC-Si coating was prepared by a two-step pack cementation technique. The microstructure and oxidation protective ability of the as-received coating were investigated.

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Experimental

Small specimens, with the dimension of 10mm×10mm×10mm, were cut from bulk 2-D C/C composites with a density of 1.75g/cm^3. Firstly, the specimens were hand-polished using 100 and 400 grit SiC papers in turn. Then they were cleaned with distilled water and dried at 373K for 2 h in an oven. Using Si and C as the original materials, the inner porous SiC layer was prepared on the surface of C/C composites by pack cementation at 1873K for 2h in an argon protective atmosphere. $MoSi_2$ and Si were introduced in the SiC inner layer by another pack cementation technique at 2373K for 2h with the following composition: 50-70 wt.% Si (300 mesh), 0-20 wt.% C (300 mesh) and 10-30 wt.% $MoSi_2$ (300 mesh). All the above pack powders were analytical grade.

The oxidation test of the coated samples was carried out at 1773K in air in an electrical furnace. Samples were weighed for several times at room temperature by electronic balance with a sensitivity of ±0.1mg during oxidation test. Cumulative weight changes (weight loss percentage, %) of the samples were calculated and were reported as a function of the oxidation time.

The morphologies and crystalline structures of the coating were analyzed by JSM-6460 scanning electron microscopy (SEM) with an energy dispersive spectroscopy (EDS), and Rigaku D/max-3C X-ray diffraction (XRD).

Results and Discussion

Fig.1 shows the XRD patterns of the coating surface obtained from the two-step pack cementation technique. It can be seen that the coating is composed of α-SiC, Si and $MoSi_2$.

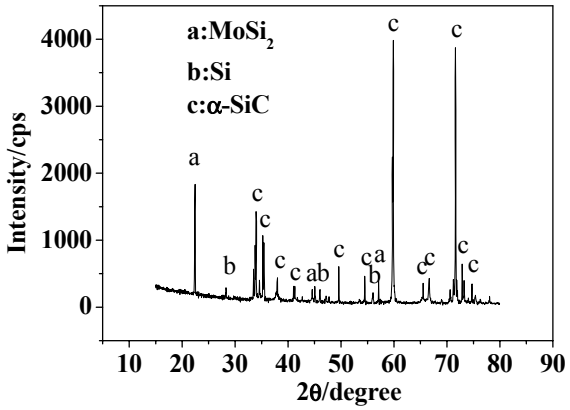

Figure1. X-ray patterns of the coating obtained by two-step pack cementation technique.

Form the surface backscattering electron image of the coated samples (Fig.2), there are three kinds of crystalline particles characterized as brown, grey and white in the coating. Form the results of the EDS analysis, it can be distinguished as SiC, Si and $MoSi_2$, respectively. The white phase ($MoSi_2$) and grey phase (Si) are filled in the holes among the SiC grains on the coating surface.

Fig.3 shows the cross-section SEM image of the coated samples. It can be seen that, the as-received coating is a dense structure with the thickness of 80-100μm. There are no penetrable cracks or large holes in the coating.

Fig.4(a) shows the micrograph of the phase interface between $MoSi_2$ and SiC. It can be seen that

the interface bonding of these two phases is weak on the coating surface. This weak interface bonding is advantageous to baffle the extending of the cracks in the coating due to the debonding of the SiC-$MoSi_2$ interface and the turning of the cracks (Fig.4(b).

Fig.5 shows the cross-section backscattering electron image of the coating. It can be seen that the

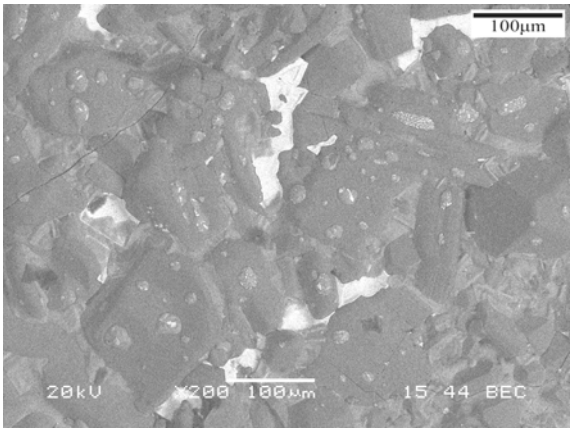

Figure 2. Surface backscattering image of the coated sample.

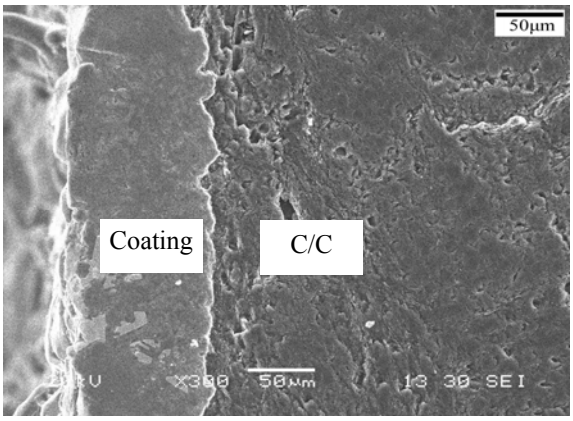

Figure 3. Cross-section SEM image of the coated samples.

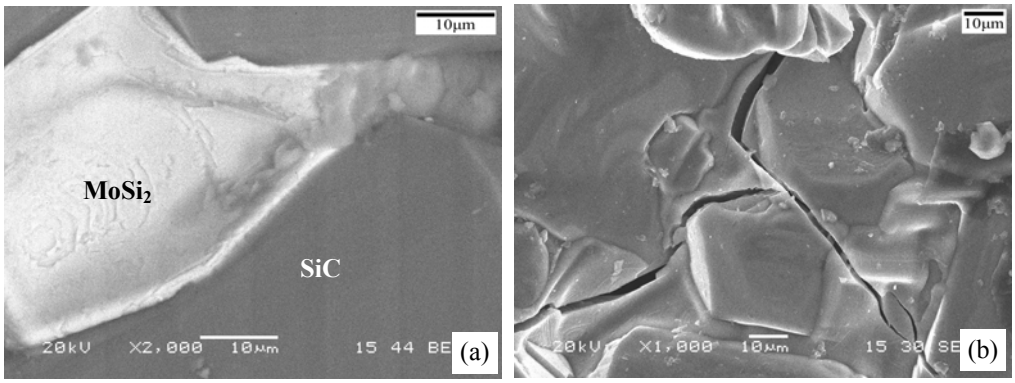

Figure 4. SEM images of the phase interface between $MoSi_2$ and SiC.

white $MoSi_2$ and grey Si are existent not only on the coating surface but also inside the coating. From

Fig.5(b), which is the magnified SEM image of the rectangle area marked by the black dashed, the SiC grain with a regular figure is surrounded by $MoSi_2$ phase. During the heat treatment of pack cementation, Si and $MoSi_2$ in the original pack powders will melt and penetrate easily into the holes in the porous SiC coating. Therefore, though having a high coefficient of thermal expansion, $MoSi_2$ can be

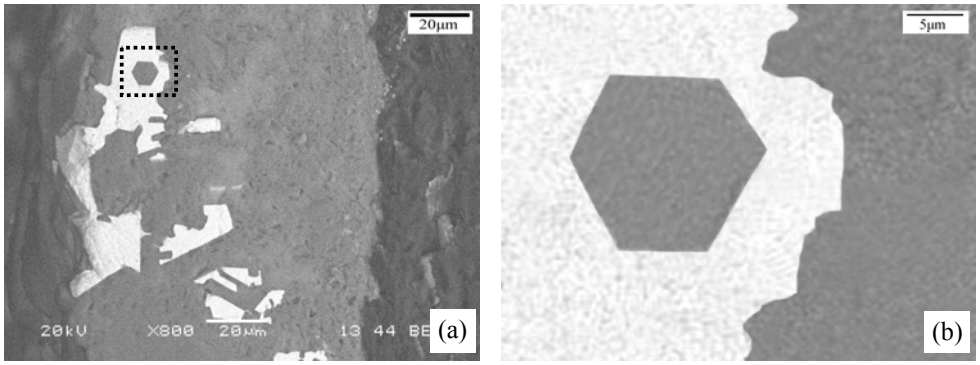

Figure 5. The cross-section backscattering electron image of the coating.

applied as the coating material due to its distribution in SiC coating. Plentiful interfaces could relax the thermal stress and decrease the frequency of the cracks in the coating. Moreover, free Si existed in the coating can increase the density of the coating and increase the content of the phase interface further, which is helpful to improve the oxidation protective ability of the coating.

The isothermal oxidation curve of the coated C/C composites at 1773K in air is shown in Fig.6. The as-prepared $MoSi_2$-SiC-Si coating has excellent anti-oxidation property, which can protect C/C composites from oxidation at 1773K in air for 200h and the corresponding weight loss is only 1.04%. Because the oxidation of the coating materials is an increasing process, the C/C composites substrate might loss weight during oxidation test, and the oxidation mark of C/C could be found from the SEM images of the coated sample after oxidation.

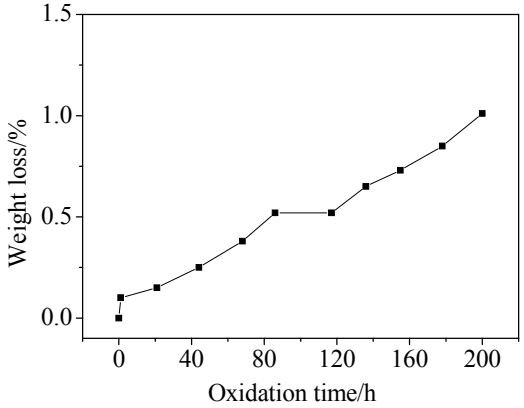

Figure 6. The 1773K isothermal oxidation curves of the coated C/C in air.

Fig.7 shows the surface and cross-section images of the coated samples after oxidation at 1773K in air for 200h. Smooth glass thin film was formed on the coating surface (Fig.7(a)), which could play a role of sealing microcracks in the coating at the oxidation temperature. Some microcracks can also be found on the coating surface after oxidation from Fig.7(a). During oxidation test, the samples were taken out of the furnace directly to air within several seconds for weighting, the cooling rate of the

samples from 1773K to room temperature was almost 10K/s. Owing to this quick cooling, the coating would suffer pull stress because of its bigger thermal expansion coefficient than that of C/C composites, which resulted in the formation of some microcracks on the coating. From the cross-section image of the coated sample after oxidation at1773K in air for 200h (Fig.7 (b)), a penetration crack can be found in the coating and a big hole is formed beneath the coating near this penetration crack. Therefore, the penetration cracks provide a channel for the diffusion of oxygen and are the main reason for the oxidation of C/C substrates.

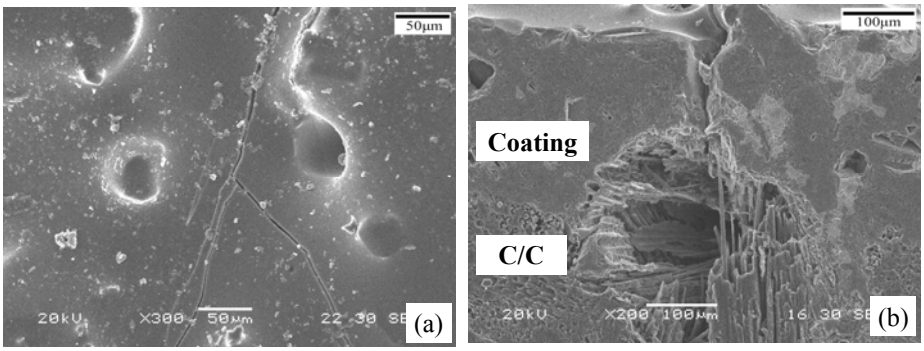

Fig.7 Surface (a) and cross-section (b) SEM images of the $MoSi_2$-SiC-Si coated sample after oxidation at 1773K in air for 200h.

Conclusions

A dense $MoSi_2$-SiC-Si oxidation protective coating was prepared on the surface of C/C composites by a two-step pack cementation technique. The as-received coating possesses excellent oxidation resistance, which can effectively protect C/C composites from oxidation at 1773K in air for more than 200h. The oxidation of C/C substrate is considered to be caused by the formation of penetration cracks in the coating.

Acknowledgements

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