A Si-Mo-Cr OXIDATION PROTECTIVE COATING FOR C/SiC COATED CARBON/CARBON COMPOSITES

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Abstract

To protect carbon/carbon(C/C) composites from oxidation, a novel Si-Mo-Cr alloy oxidation protective coating has been produced by pack cementation. The phase composition and microstructure of the as-prepared coatings were characterized by XRD, SEM and EDS analyses. XRD result indicates the Si-Mo-Cr external layer was primarily composed of SiC, $MoSi_2$, $CrSi_2$ and residual Si. Oxidation test shows that, the as-prepared coating characterized by excellent oxidation resistance and thermal shock resistance could effectively protect C/C composites from oxidation at 1773K in air for 186h and endure the thermal cycle between 1773K and room temperature for 9 times, and the corresponding weight loss is only 0.33%. The slight weight loss is mainly attributed to the formation of microcracks on the coating surface.

Keywords: Carbon/carbon composites; Coating; Oxidation;

Introduction

Carbon/carbon (C/C) composites is one of the most promising thermal structure composites for a number of aerospace applications including engineering materials for advanced vehicles, leading edges, rocket nozzles, disk brake and propulsion systems. Unfortunately, these composites undergo severe oxidation under an oxidizing atmosphere above 723K. Oxidation protective coating is considered as an efficient method to tackle the oxidation problem and extend the service life of C/C composites.

Molybdenum disilicide ($MoSi_2$) is well recognized for its outstanding oxidation resistance at high temperature due to the formation of vitreous SiO_2 layer, which could effectively protect C/C composites from oxidation. Unfortunately, SiO_2 layers were consumed heavily when heated in the open air for a long time. The reason of which may be SiO_2 glass was volatilized gradually at high temperature. Therefore, the chromium was introducing into the Si-Mo coatings by pack cementation. It was expected that the Cr_2O_3 will be formed during the oxidation test, which will improve the stability of the SiO_2 glass and the new stable glass layer could protect the C/C composites at higher temperature.

In the present work, a novel Cr-modified Si-Mo alloy coating was prepared on the surface of C/SiC coated C/C composites. The C/SiC gradient inner layer were firstly prepared by slurry and pack cementation, and then the Cr-modified Si-Mo alloy coating was produced on the surface of the C/SiC coated specimens by pack cementation. The microstructure and anti-oxidation property in air at 1773K of the as-received coating were investigated.

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Experimental

The bulk two dimensional C/C composites used as substrates with a density of 1.70g/cm^3 were cut into small specimens with a size of 10×10×10mm. Before coating process, the specimens were polished with 400 grit SiC paper, and then were ultrasonically cleaned with ethanol and dried at 373K. The C/SiC gradient inner layer was prepared by two-step technique. The details of preparing the coating had been reported. The pack cementation technique was employed to prepare the Si-Mo-Cr alloy coating on the surface of C/SiC coated C/C composites. High purity Si (300 mesh) , Mo (500 mesh), Cr (500mesh) and graphite (350mesh) powers were weighed to the desired composition of 50-80wt. % Si, 10-30 wt. % Mo, 5-15% wt. Cr and 5-15% wt. graphite and then mixed by tumbling in a ball mill up to 20 h. The as-prepared C/SiC coated C/C specimens and pack mixtures were put in a graphite crucible, and then were heat-treated at 2073-2273K for 2 h in an argon atmosphere to form Cr-modified Si-Mo alloy coating.

The oxidation resistance test was performed at 1773K in air in an electrical furnace. The crystalline structure of the coated specimens was measured with X' Pert PRO X-ray diffraction (XRD). The morphologies and element distribution of the as-prepared coating was analyzed by JSM-6460 scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Results and discussion

Fig.1 displays the backscattering electron image of the Cr modified Si-Mo coating surface. It indicated that three kinds of crystalline particles characterized as brown, grey and white are found in the coating. By XRD (Fig.2) and EDS analysis, the brown, white and grey phases can be distinguished as the SiC matrix, the mixture of $MoSi_2$ and $CrSi_2$ and residual Si respectively. The $MoSi_2$, $CrSi_2$ phase is the product of the reaction between Si, Mo and Cr during the heat treatment of pack cementation.

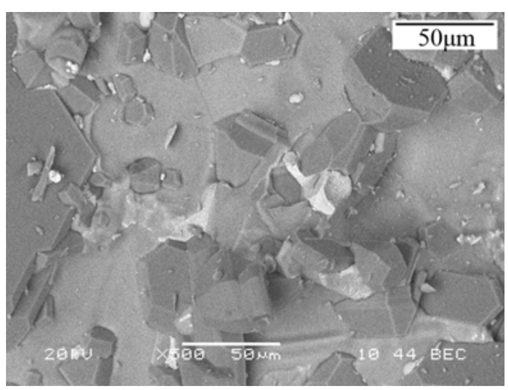

Figure 1. Backscattering electron image of the Si-Mo-Cr alloy coating surface

The cross-section SEM image of the as-prepared coating is exhibited by Fig.3. It is revealed that the multilayer coating is uneven in thickness, from 120 to 200μm, and there are no penetration cracks or big holes in the coating. In addition, the as-obtained multilayer coating is very dense due to the effective filling of Si, $MoSi_2$ and $CrSi_2$ in the pinholes of the C/SiC gradient inner layer. During the heat treatment of pack cementation, it is easy for molten silicon to infiltrate into pinholes as a result of the increasing wettability and the decreasing viscosity of molten silicon with increasing temperature. Therefore, the dense Cr-modified Si-Mo exterior coating can be prepared by the pack cementation technique, which is expected to have good oxidation protective ability

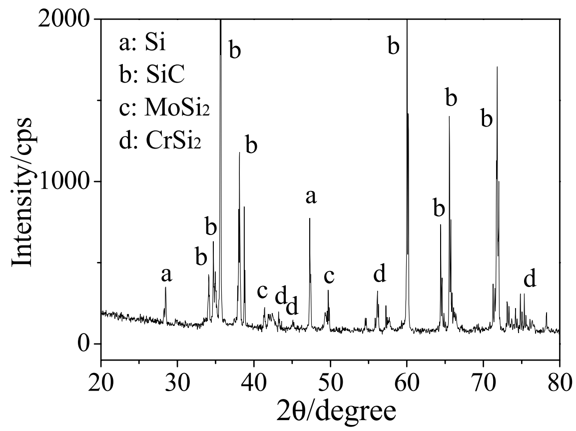

Figure 2. XRD pattern of the as-prepared coating surface

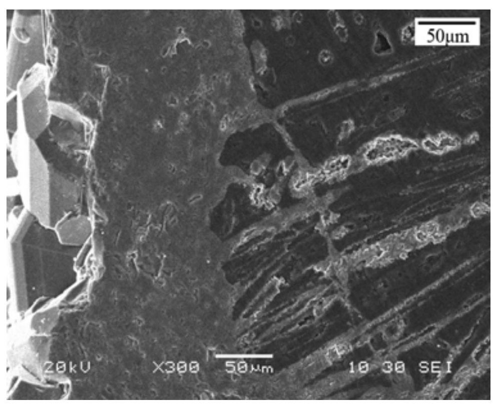

Figure 3. Cross-section SEM image of the coated specimens with Si-Mo-Cr alloy coating

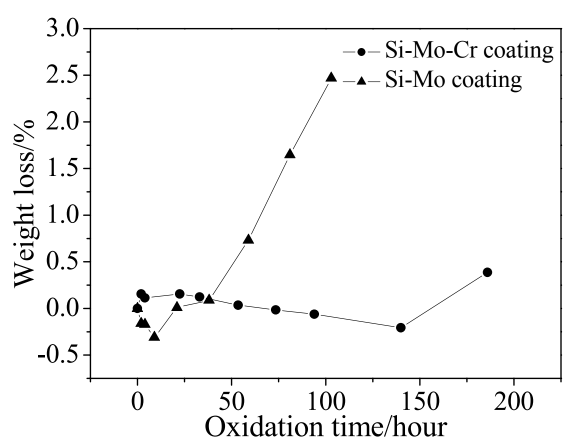

Figure 4. Isothermal oxidation curves of the coated samples in air at 1773K

The isothermal oxidation curves of the coated C/C composites with Si-Mo coating and Cr-modified Si-Mo coating in air at 1773K are illustrated in Fig.4. It can be seen that the as-prepared Cr-modified Si-Mo alloy coating exhibited better oxidation protective ability than the Si-Mo coated specimens. After oxidation in 1773K in air for 103h, the weight loss of the coated specimens of the Si-Mo coating have reached 2.47%, however, the Si-Mo-Cr alloy coated specimens characterized by excellent oxidation protective ability and could efficiently protect C/C composites from oxidation for 186 hours and the corresponding weight loss is only 0.33%. Introducing the Cr into the Si-Mo coating could improve the oxidation resistance of the coating. Fig.5 shows the XRD pattern of the coating after oxidation at 1773K for 186h, compared with X-ray patterns of the coating before oxidation, two new phases of SiO_2 and Cr_2O_3 appeared in the coating. The Cr_2O_3 can improve the stability of the SiO_2 glass at high temperature.

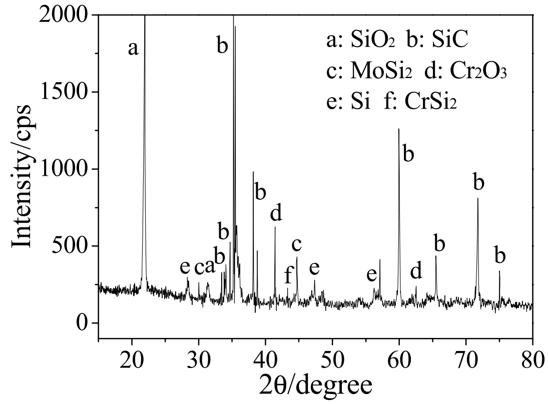

Figure 5. XRD pattern of the coating surface after oxidation at 1773 K for 186 h.

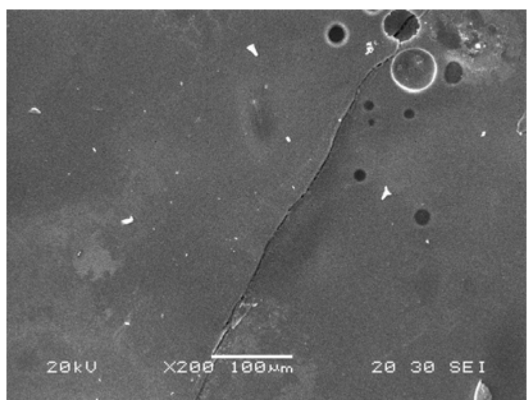

Figure 6. Surface micrograph of the coating after oxidation at 1773 K for 186 h.

Fig.6 shows the surface micrograph of the coated specimen after oxidation at 1773K for 186h. It can be found that a smooth glass layer was formed on the coating surface. In addition, some microcracks are found on the coating surface. The formation of this kind of cracks offers the channels for air and resulting in weight loss of the coated specimens. Therefore, the failure of the coated C/C sample primarily results from the formation of the microcracks in the coating.

Conclusions

A dense Si-Mo-Cr alloy oxidation protective coating was prepared on the surface of C/SiC coated C/C composites by a pack cementation technique. The as-prepared coating is characterized by excellent oxidation protective ability and thermal shock resistance. It can effectively protect C/C composites for 186h in air at 1773K and undergo the thermal cycling between 1773K and room temperature for 9 cycles. The failure of the coating is considered to be caused by the formation of the microcracks in the coating.

Acknowledgements

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