

A GRADIENT SELF-SEALING OXIDATION PROTECTIVE COATING FOR CARBON/CARBON COMPOSITES

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Introduction

Oxidation protective coating is an effective method to improve the oxidation resistance of carbon/carbon(C/C) composites [1]. Si-Mo-B alloy seems to be one of the best candidates for a coating material for C/C composites due to its excellent oxidation resistance within broad temperature range. The formation of B_2O_3 can seal the cracks effectively below 1273 K and SiO_2 can provide excellent oxidation protection at 1273 K [2]. The present work is to propose a simple and low-cost slurry method to produce an effective and gradient self-sealing multilayer coating for C/C composites. The C/SiC gradient layer prepared by slurry and pack cementation was employed as bonding layer between C/C composites and the outer coating. The gradient Si-Mo-B coating acting as middle layer was produced by slurry method, and the glass exterior layer was also prepared by slurry method in order to retain the integrity of the coating during its exposure to an oxygen containing atmosphere at high temperature and improve the oxidation protective ability of the coating further.

Experimental

Small substrates were cut from bulk two dimensional C/C composites with a density of 1.70 g/cm^3 . They were hand-polished with 100 and 400 grit SiC papers, successively, cleaned ultrasonically with ethanol and dried at about 373 K for several hours. The C/SiC gradient inner layer was prepared by slurry and packs cementation, the preparation details were reported in [3]. The Si-Mo-B middle coatings were prepared on the surface of C/SiC coated C/C composites by slurry method. The commercially available powders of Si (300 mesh), Mo (500 mesh) and B (450 mesh) were weighed to the desired composition and then mixed by tumbling in a ball mill up to 10 h. There were three kinds slurry with the increasing of the content of Mo and the decreasing of the content of B. Slurry made by mixing the above mixture powders and ethanol was brushed directly to the surface of the C/SiC coated C/C specimens orderly. The coated specimens were then heat-treated at 1673 K in an argon protective atmosphere for 30-80 min to form the gradient Si-Mo-B coatings. The glass layer was similarly produced by slurry method. Details of the methods used to form the glass coating have been given previously [4].

The coating thickness was controlled artificially by brush times. Thermogravimetry (TG) oxidation tests in simulated air were conducted in METTLER TOLEDO STARe Thermal Analysis System (thermobalance with a sensitivity of ± 0.0001

mg) from room temperature to 1823 K. The simulated air used in the test was a mixture of argon and oxygen with the Ar/O₂ volume ratio of 22:78. The rate of increasing temperature was 5 K/min. The isothermal oxidation tests were carried out at 1173 K and 1873 K in air in an electrical furnace. The cumulative weight change of the coated samples after every thermal cycle from 1873 K or 1173 K to room temperature was measured by a precision balance (sensitivity = $\pm 0.1 \text{ mg}$) and reported as a function of oxidation time and the thermal cycling times.

The crystalline structure and morphologies of the unoxidized and oxidized specimens were measured by X-ray diffraction (XRD, X'Pert PRO) and scanning electron microscopy (SEM, JSM-6460) with energy dispersive spectroscopy (EDS).

Results and Discussion

Fig.1 (a) exhibits the surface micrograph of the gradient coating. It could be found that the coating surface was very smooth, shapely and integrated. The grey phase that kept particulate was dispersedly in the amorphous glass phase. By XRD analysis, the grey phase could be discriminated as $MoSi_2$, which was added in the glass to increase the thermal stability of the glass coating. Cross-section SEM image of the as-prepared multilayer coating is displayed in Fig.1 (b). It revealed that an obvious three-layer coating structure was achieved. The thicknesses of the C/SiC inner layer, the gradient Si-Mo-B coating and the glass outer layer were about 120, 100 and 80 μm , respectively. No gaps appeared at the interfaces between them, indicating a good bond with each other of the three layers. In addition, no obvious cracks can be found from the cross-section of the as-prepared multilayer coating, which inferring the good compatibleness of them.

Fig.2 shows the TG oxidation curve of the coated C/C composites from room temperature to 1823 K in air flow. With the increasing of oxidation temperature, the oxidation behavior of the coated C/C composites could be divided into three regions. Clearly, no oxidation took place below about 700 K because carbon would not be oxidized at low temperature [5]. With increasing temperature of 700-1200 K, the coated specimens began to react with oxygen and the weight loss vs oxidation temperature follows a quasi-linear manner. The temperature at which the coated sample lost biggest weight was at about 1200 K and the weight loss reach the peak value of 0.77 %. During the oxidation test, the content of B_2O_3 in the coating was little due to the limited oxidation time and the melt temperature range of the glass and SiO_2 is 1373-1923 K [5], the cracks in the coating could not entirely self-cure when the oxidation temperature is lower than 1200 K. So the coated specimens exhibited weight loss. Between 1200 K and 1823 K, the coated specimens exhibited durative weight gain due to the passive oxidation of the Si-based coating materials. When the oxidation temperature reached 1823 K, the weight loss was only 0.4 %. According to the above analyses, it could be concluded that the coating had poor oxidation resistance at about 1200 K, so it is necessary to

investigate the long-term oxidation behavior of the coating at about 1200 K.

The results of the isothermal oxidation test of the coated specimens in air at 1173 and 1873K are illustrated in Fig.3. The weight loss of the gradient multilayer coating is only 1.25% after oxidation for 100 h. The excellent long-term oxidation protective ability could be attributed to the formation of B_2O_3 glass sealant, which could fill the cracks and prevent the oxygen from diffusing into C/C matrix. In addition, the oxidation protective ability of the coating at 1873 K was also excellent. After oxidation at 1873 K for 150 h, the weight loss of the coated specimen was 3.36%.

Fig.4 (a) presents the surface micrograph of the coated specimens after oxidation for 150 h at 1873 K. The surface became smoother than that before oxidation and several holes and cracks were also found in the coating surface. These cracks might self-seal at the oxidation temperature and had little effect on the oxidation resistance of the coating. From the cross-section image of the coated sample after oxidation, the multilayer coating was as dense as that before oxidation and the C/C matrix was not obviously oxidized, as shown in Fig. 7(b). While there were no obvious interface among three layers due to the effective diffusion of coating materials during the oxidation test. At 1873K, borosilicate glass prepared in this work possesses more poor stability than the glass reported by Fu et al. [4]. Therefore, the volatility of the glass at 1873 K was more serious, resulting in the bigger weight loss of the coated sample. Therefore, the weight loss of the coated sample was primarily due to the volatilization of the glass coating at 1873 K. That is to say, the C/C matrix had not been attacked.

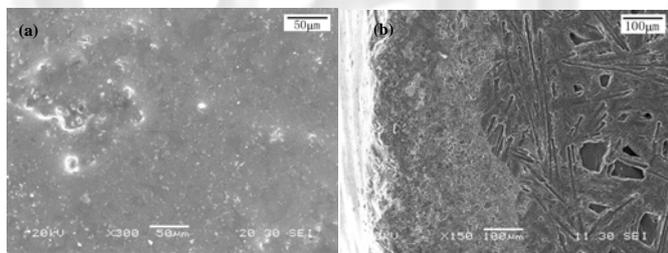


Fig. 1 SEM images of the coating: (a) surface, (b) cross-section.

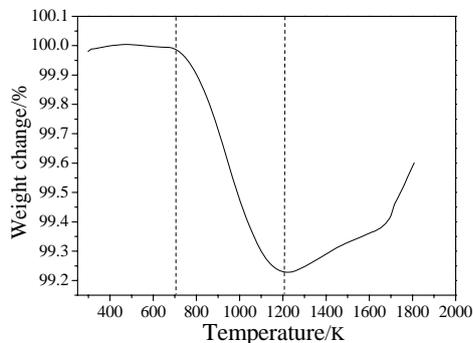


Fig. 2 The TG oxidation curve of the coated specimens

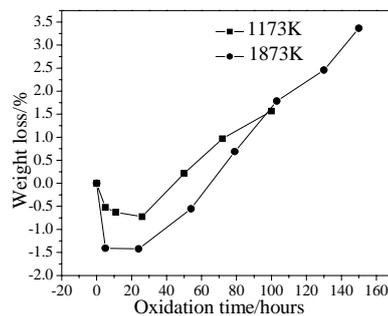


Fig. 3 Isothermal oxidation curves of the coated specimens

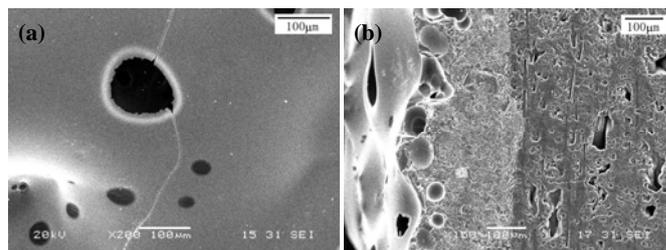


Fig. 4 SEM images of the coated specimen after oxidation at 1873K in air: (a) surface, (b) cross-section.

Conclusions

Three-layer coating including C/SiC inner layer, Si-Mo-B middle layer and glass sealant layer was prepared by pack cementation and slurry method. The as-prepared coating is characterized by excellent oxidation protective ability and thermal shock resistance. It can effectively protect C/C composites for more than 100 h at 1173 K and 150 h at 1873 K in air. It can also undergo at least 40 thermal cycles between 1873 K and room temperature with high retained strength. The excellent oxidation protective ability of the coating is attributed to seal-sealing property and the gradient structure. The weight loss of the coated C/C composites at 1873 K is likely to be caused by the volatility of the glass layer.

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