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C/SiC/$MoSi_2$−SiC−Si multilayer coating for oxidation protection of carbon/carbon composites

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Abstract: C/SiC/$MoSi_2$−SiC−Si oxidation protective multilayer coating for carbon/carbon (C/C) composites was prepared by pack cementation and slurry method. The microstructure, element distribution and phase composition of the as-received coating were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The results show that the multilayer coating was composed of $MoSi_2$, SiC and Si. It could effectively protect C/C composites against oxidation for 200 h with the mass loss of 3.25% at 1873 K in static air. The mass loss of the coated C/C composites results from the volatilization of SiO_2 and the formation of cracks and bubble holes in the coating.

Key words: C/C composites; C/SiC; $MoSi_2$; SiC; multilayer; coating; oxidation

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1 Introduction

Carbon/carbon (C/C) composites are promising materials for rocket nozzles, noses, leading edges of reentry vehicles and gas turbine engine components due to their high specific strength, high vaporization temperature, low coefficient of thermal expansion (CTE) and high retention of mechanical properties at high temperatures [1,2]. However, the fact that C/C composite oxidizes above 600 K requires the development of protective anti-oxidation coating for high temperature applications [3,4]. To prevent oxidation and consequential gasification of C/C, the multilayer coating with different function of each layer is the most effective solution [5−8]. A wide investigation about oxidation protection system for C/C is a silicon carbide (SiC) conversion coating due to its good physical and chemical adaptability with C/C matrix and excellent oxidation resistance under an oxidation environment below 1923 K. However, the mismatch of CTE between SiC and C/C leads to cracks in the protective SiC coating during processing that allow for the inward diffusion of oxygen [9,10]. In our previous work, C/SiC gradient layer has been proposed. The gradient distribution of Si and C in the coating could minimize the mismatch of CTE between C/C matrix and outer coating to some extent and improve the oxidation resistance of the multilayer coating [11].

Regarding the outer layer, $MoSi_2$-based coating seems to be one of the best candidate coating materials for C/C composites because of its excellent oxidation resistance at high temperature [12,13]. The vitreous SiO_2 glass formed during the oxidation of the coating has very low oxygen permeability (10^{-13}g/(cm·s) at 1473 K, 10^{-11}g/(cm·s) at 2473 K) [14], it can effectively protect C/C composites from oxidation at high temperature. $MoSi_2$-based coating has been prepared on C/C composites by pack cementation. However, the coating could only provide the oxidation protection for C/C composites for 103 h at 1773 K because of the cross-coating cracks formed in the coating [7].

In the present work, a $MoSi_2$−SiC−Si multiphase coating with the C/SiC gradient layer acting as bonding layer was proposed for oxidation protection of C/C composites. Distribution of free silicon in the coating could efficiently fill the cracks and holes in the coating and relax the mismatch of thermal expansion coefficient

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between the coating and C/C composites [15]. In addition, the $MoSi_2$, SiC and Si phase could form a multiphase coating structure, which is advantageous to relax the thermal stress in the coating due to the formation of a great deal of phase interfaces [16].

The C/SiC/$MoSi_2$−SiC−Si multilayer coating is prepared on C/C composite by pack cementation and slurry method. The phase compositions and microstructure of the coating are characterized. The oxidation resistance and failure mechanism at 1873 K in static air are also investigated.

2 Experimental

Cubic specimens (10 mm×10 mm×10 mm) used as substrates were cut from two-dimensional bulk C/C composites with a density of 1.70 g/cm^3. They were hand-abraded with 100 and 400 grit SiC papers, successively, then cleaned ultrasonically with ethanol and dried at about 373 K for 2 h. The C/SiC gradient inner layer was prepared by slurry and packs cementation [11]. The $MoSi_2$−SiC−Si coating was prepared on C/SiC coated C/C specimens by slurry method. The commercially available powders of Mo (48 μm) and Si (25 μm) were weighted to the desired composition of 60%−80% Si, 20%−40% Mo (mass fraction) and then mixed by tumbling in a ball mill for 5 h. Slurries made by the mixture of powders and ethanol were brushed directly onto the surface of C/SiC layer. The thickness of the coating was controlled artificially by brush times. The coated specimens were then heat-treated at 1773 K in argon for 30−80 min to form the $MoSi_2$−SiC−Si outer layer.

The isothermal oxidation tests were carried out at 1873 K in static air in an electrical furnace. The coated C/C specimens were put out of the furnace directly after given time oxidation at 1873 K and then cooled to room temperature quickly in air. The mass of the specimens were measured at room temperature by an electronic balance with a sensitivity of ±0.1 mg. Then they were put directly into the furnace again for the next oxidation period. The cumulative mass change of the specimens after every thermal cycle was reported as a function of oxidation time. The crystalline structure and morphology of the specimens were characterized using X-ray diffraction (XRD, X'Pert Pro) and scanning electron microscopy (SEM, JSM-6460) with energy dispersive spectroscopy (EDS).

3 Results and discussion

3.1 Microstructure of coating

Figure 1 shows the surface SEM micrograph and XRD pattern of the $MoSi_2$−SiC−Si coating. It reveals the formation of a dense and unsmooth coating structure without crack. The corresponding XRD pattern shows that the as-prepared coating is composed of $MoSi_2$, SiC and Si. The multiphase and dense structure is beneficial to improving the oxidation resistance of the coating [7,15].

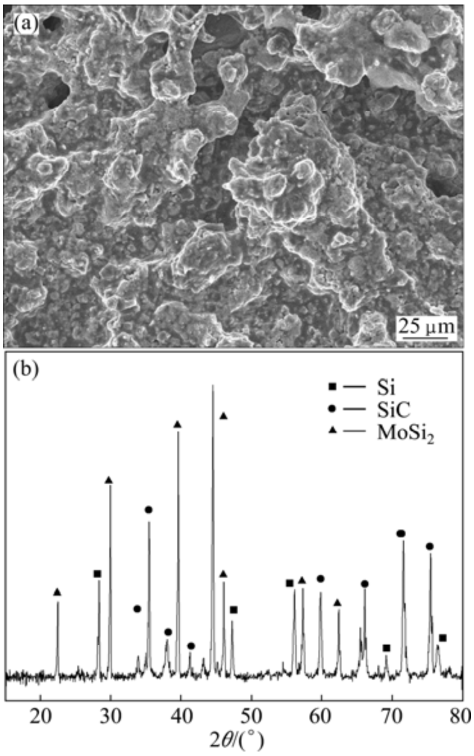

Fig. 1 Surface SEM micrograph (a) and XRD pattern (b) of $MoSi_2$−SiC−Si coating

Figure 2 shows the cross-section SEM micrograph and element line scanning result of the C/SiC/$MoSi_2$−SiC−Si multilayer coating. It can be found that the multilayer coating is about 130 μm in thickness and there is no penetration crack or big hole in the coating. In addition, there is no obvious interface between the $MoSi_2$−SiC−Si layer and C/SiC inner layer, which verified the effective infiltration and reaction of the melted Si originally present in the slurry mixtures during the heat treatment. By element line scanning analyses, the concentration distribution of Mo, Si and C as a function of depth are also exhibited in Fig. 2. The $MoSi_2$ phase mainly distributes in the outside of the multilayer coating and the $MoSi_2$−SiC−Si outer coating is about 40 μm in thickness. Near the interface between the C/SiC inner layer and C/C composites, there is a transition layer with the concentration of Si element decreasing and C element increasing gradually across almost 30 μm, implying that a concentration gradient C/SiC coating is obtained in the pack cementation process, which will provide a good oxidation resistance for the multilayer coating [11].

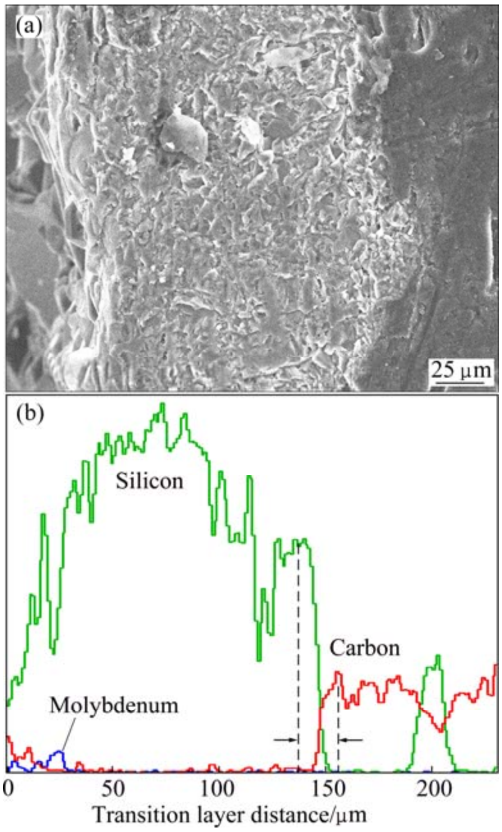

Fig. 2 Cross-section SEM image (a) and element line scanning (b) of multilayer coating

3.2 Oxidation resistance of the coating

Figure 3 shows the isothermal oxidation curve of C/C composites with the C/SiC/$MoSi_2$−SiC−Si multilayer coating at 1873 K in static air. It can be found that the multilayer coating exhibits good oxidation resistance, which can effectively protect C/C composites for 200 h at 1873 K in static air with the mass loss of 3.25%. The service temperature is higher than that of the Si−Mo fused slurry coating (reported to be 1643 K) prepared by FANG et al [12] and the CVD-SiC/Si−Mo multilayer coating (reported to be 1673 K) prepared by YAN et al [17]. The oxidation protection time of this coating is longer than that of the Si−Hf (Zr)−Cr coating (reported to be 1 h at 1873 K) prepared by JOSHI et al [18] and $MoSi_2$−SiC coating (reported to be 115.5 h at 1873 K) prepared by ZENG et al [19].

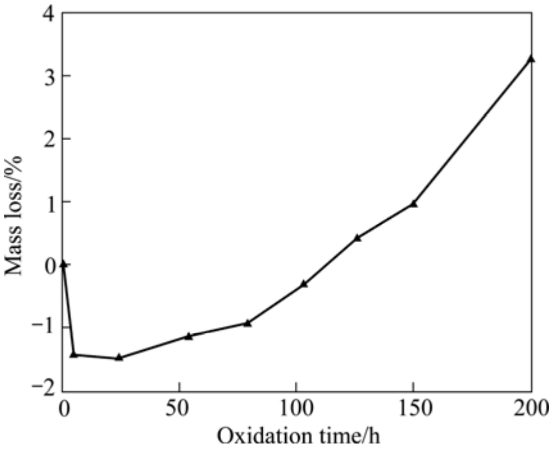

Fig. 3 Isothermal oxidation curves of C/SiC/$MoSi_2$−SiC−Si coated specimens at 1873 K in air

According to the oxidation curve (Fig. 3), the oxidation behaviour of the coated C/C specimens can be divided into three processes. At the initial oxidation stage (less than 5 h), the Si and SiC are exposed to air at high temperature and will act as oxygen getters in reacting with oxygen. Vitreous SiO_2 glass layer is formed on the coating surface, which results in the mass gain of the coated specimens. With the oxidation time extending (5−24 h), the surface of the coating changes entirely into SiO_2 glass, which can efficiently prevent oxygen from diffusing into the C/C matrix due to its very low oxygen permeability. In addition, some mobile glass is also helpful to filling the cracks in the coating. When the oxidation time exceeds 24 h, excessive gas pressure and the quick cooling from 1873 K to room temperature in the course of the oxidation test results in the formation of holes and cracks on the glass layer (Fig. 4(a)). The defects will serve as the path through which oxygen can diffuse to the underlying substrate and result in the mass loss of the coated samples. As a result, the mass loss versus oxidation time follows a quasi-linear manner. The mass loss of the coated specimens increases quickly with the oxidation time extending.

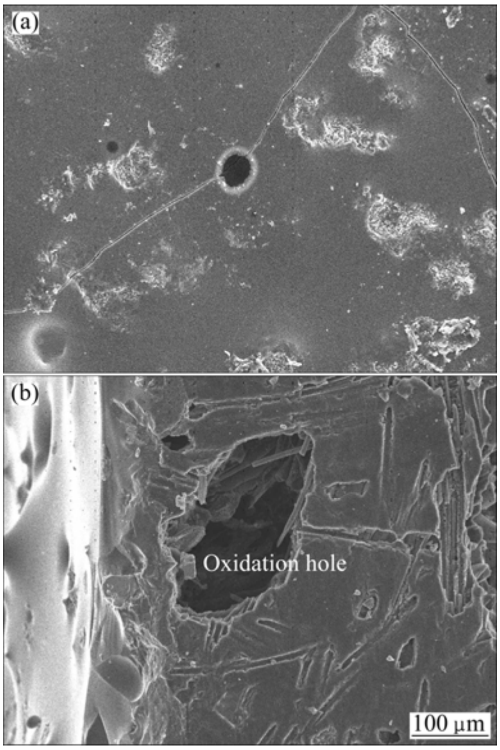

Fig. 4 SEM images of C/SiC/$MoSi_2$−SiC−Si coated C/C composites after oxidation at 1873 K for 200 h: (a) Surface; (b) Cross-section

Figure 4(a) shows the surface micrograph of the C/SiC/$MoSi_2$−SiC−Si coating after oxidation for 200 h at 1873 K. The dense and smooth glass thin film with some microcracks and holes is found on the coating surface. These microcracks caused by the crystallization of amorphous silica may self-seal when the oxidation temperature is increased to above 1373 K again. So these have little influence on the oxidation resistance of the multilayer coating. The SiO_2 glass exhibits very low oxygen permeability, which can provide effective protection for C/C composites at high temperature. In addition, the low viscosity of SiO_2 glass at high temperature also seals the cracks and holes in the coating. However, the stability of SiO_2 glass decreases and evaporates gradually at 1873 K with the extending of oxidation time. The cracks and holes can not be effectively sealed due to the gradual consumption of SiO_2 glass, which will serve as the path through which oxygen can diffuse to the underlying substrate and result in the mass loss of the coated specimens.

As shown from the cross-section SEM image of the coated specimens after oxidation (Fig. 4(b)), the C/C matrix is oxidized and a hole is found at the interface between the coating and C/C matrix. Therefore, the volatilization of glass coating at 1873 K and the formation of cracks and holes are the main reasons for the mass loss of the coated specimens. The thickness of the multilayer coating decreases from 130 to 90 μm after oxidation. The result also proves the volatilization of the glass coating at 1873 K. XRD pattern of the coating after oxidation for 200 h (Fig. 5) shows that the Si phase disappears, while a new SiO_2 phase appears compared with XRD pattern of the coating before oxidation. It verifies that the above-mentioned dense glass layer is SiO_2 glass layer.

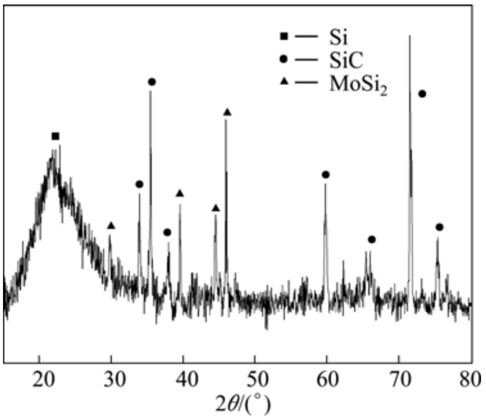

Fig. 5 XRD pattern of multilayer coating after oxidation for 200 h at 1873 K

4 Conclusions

1) A C/SiC/$MoSi_2$−SiC−Si multilayer oxidation protection coating for C/C composites was produced by pack cementation and slurry method. It is composed of $MoSi_2$, SiC and Si.

2) The multilayer coating can protect C/C composites from oxidation for 200 h at 1873 K in static air. Its good oxidation protecitive ability is attributed mainly to the formation of the dense SiO_2 glass layer.

3) The volatilization of SiO_2 and the formation of the cracks and bubble holes on the coating surface are the main reasons for the mass loss of the coated C/C composites.

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炭/炭复合材料 C/SiC/$MoSi_2$−SiC−Si 抗氧化复合涂层

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摘 要：采用包埋法和料浆涂刷法在 C/C 复合材料表面制备 C/SiC/$MoSi_2$−SiC−Si 抗氧化复合涂层。通过扫描电镜(SEM)、电子能谱(EDS)以及 X 射线衍射(XRD)等测试手段对涂层的微观结构、元素分布及晶相组成进行分析，研究涂层试件在 1873 K 静态空气下的抗氧化性能。结果表明：制备的复合涂层主要由 $MoSi_2$、SiC 和 Si 构成；其在 1873 K 静态空气下有效保护 C/C 复合材料达 200 h，带涂层的 C/C 复合材料试样氧化失重率仅为 3.25%。涂层试样的氧化失重主要是由于涂层表面 SiO_2 的挥发及裂纹、孔洞等缺陷的形成引起的。

关键词：炭/炭复合材料；C/SiC；$MoSi_2$；SiC；复合；涂层；氧化

(Edited by Chao WANG)