

SiC–MoSi₂/ZrO₂–MoSi₂ coating to protect C/C composites against oxidation

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Abstract: To improve the oxidation resistance of carbon/carbon (C/C) composites in air at high temperatures, a SiC–MoSi₂/ZrO₂–MoSi₂ coating was prepared on the surface of C/C composites by pack cementation and slurry method. The microstructures and phase compositions of the coated C/C composites were analyzed by scanning electron microscopy and X-ray diffraction, respectively. The result shows that the SiC–MoSi₂/ZrO₂–MoSi₂ coating is dense and crack-free with a thickness of 250–300 μm. The preparation and the high temperature oxidation property of the coated composites were investigated. The as-received coating has excellent oxidation protection ability and can protect C/C composites from oxidation for 260 h at 1773 K in air. The excellent anti-oxidation performance of the coating is considered to come from the formation of ZrSiO₄, which improves the stability of the coating at high temperatures.

Key words: carbon/carbon composites; SiC–MoSi₂/ZrO₂–MoSi₂; coating; oxidation resistance

1 Introduction

Carbon/carbon (C/C) composites possess extraordinary and unique characteristics over traditional materials, such as low density, high specific strength, resistance to thermal shock and retention of mechanical properties at high temperatures, which makes them have great advantages used as thermal structural components in the aircraft and aerospace fields [1–3]. However, the oxidation of C/C composites begins to be significant above about 773 K, which limits their application [4]. As a result, oxidation is a major problem for C/C composites for the applications as high-temperature structural materials. Coating is an efficient method for protecting C/C composites used in high-temperature environment [5,6].

MoSi₂ is an excellent material for oxidation resistant coating because of the self-sealing performance at high temperatures [7]. SiC also has outstanding anti-oxidation properties due to the self-sealing performance of SiO₂ formed from the oxidation of SiC. Previous studies [8–10] indicated that the multi-phase coatings containing MoSi₂ and SiC were proved to have good oxidation

protective ability for C/C composites. However, the following two factors may cause serious failure of the coatings, one is that long time service at high temperatures reduces the thickness of the coating by the volatilization of SiO₂; the other is that SiO₂ possesses low viscosity at high temperatures, meaning that gaseous products can escape from the SiO₂ film easily and produce holes in the coating [11].

ZrO₂ possesses high melting point, and can react with SiO₂ to produce ZrSiO₄ [12–14]. Zircon (ZrSiO₄) is an excellent refractory material. It exhibits several attractive properties for high temperature structural applications such as high melting point, excellent chemical stability and low thermal expansion coefficient [15]. Therefore, if the MoSi₂ coating is doped with ZrO₂, the stability of the glassy SiO₂ at high temperatures would be improved, which is advantageous to the oxidation resistance of MoSi₂ coating. Moreover, few literatures have concerned about introducing ZrO₂ in MoSi₂ coating. In this work, a SiC–MoSi₂/ZrO₂–MoSi₂ coating was designed and prepared by a two-step method of pack cementation and slurry coating. The phase compositions and microstructures of the as-prepared SiC–MoSi₂/ZrO₂–MoSi₂ multilayer coating were characterized.

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Meanwhile, the anti-oxidation properties of the multi-layer coating were also investigated.

2 Experimental

Small specimens (10 mm×10 mm×10 mm) used as substrates were cut from bulk 2D C/C composites with a density of 1.70 g/cm³. These specimens were hand-polished using 100 and 400 grit SiC paper in turn, then cleaned ultrasonically with ethanol to remove any loose particles and dried at 373 K for 2 h.

The SiC–MoSi₂/ZrO₂–MoSi₂ coating was prepared by a two-step technique of pack cementation and slurry coating. In the first step, Si, C and Mo were used as raw materials, the SiC–MoSi₂ inner layer was prepared by pack cementation. The powder compositions were as follows: 50%–60% Si, 10%–25% graphite, 15%–25% Mo and 5%–15% Al₂O₃ (mass fraction). The first pack mixtures and C/C specimens were put in a graphite crucible, and then were heated to 2073–2273 K and held for 2–4 h in argon atmosphere to form a SiC–MoSi₂ inner coating. In the second step, the ZrO₂–MoSi₂ outer layer was prepared by slurry coating. The powders for preparing the outer layer were composed of Si, Mo and ZrO₂. Using PVA (polyvinyl alcohol) as dispersant, the above powders were mixed ultrasonically in a beaker. The as-obtained slurry was brushed directly on the surface of SiC–MoSi₂ coated samples. The samples were heat treated at 2173–2473 K for 2 h in an argon protective atmosphere to form the ZrO₂–MoSi₂ outer coating. For comparison, SiC–MoSi₂/MoSi₂ coating was prepared by the same pack cementation and slurry coating.

To investigate the oxidation process of the as-coated samples, the oxidation test was carried out at 1773 K in air in an electrical furnace. The samples were weighed at room temperature by electronic balance with a sensitivity of ±0.1 mg. The anti-oxidation ability was evaluated by mass loss.

The phase composition, morphology and element distribution of the coating were analyzed by Rigaku D/max-3C X-ray diffraction (XRD) and JSM-6460 scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS).

3 Results and discussion

3.1 Structure and morphology of SiC–MoSi₂/ZrO₂–MoSi₂ coating

Figure 1 shows the SEM image and XRD pattern of the SiC–MoSi₂ inner coating prepared by pack cementation. It can be seen that the inner layer obtained by the first step pack cementation is dense except the existence of several microcracks (see Fig. 1(a)).

Although these cracks could be self-sealed partially during the high temperature oxidation test, C/C matrix would be oxidized by oxygen diffusing through the cracks at the temperature between the crack sealing temperature and the original oxidizing temperature of C/C composites. From Fig. 1(b), it can be seen that the inner coating is composed of MoSi₂, SiC and a small quantity of Si.

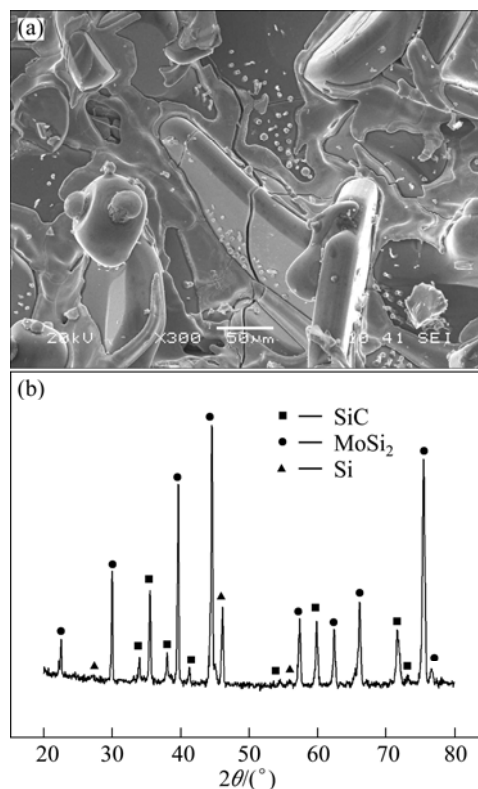


Fig. 1 SEM image (a) and XRD pattern (b) of SiC–MoSi₂ inner coating prepared by pack cementation

Figure 2 shows the SEM image and XRD pattern of the ZrO₂–MoSi₂ outer coating prepared by slurry coating. As shown in Fig. 2(a), the coating has no big-size crack, while it is a little loose, owing to the volatilization of the dispersants that left holes during the process of sintering reaction at high temperatures. From Fig. 2(b), it can be seen that the coating is composed of ZrO₂, MoSi₂, SiC and Si. MoSi₂ is formed by the reaction between Si and Mo. In addition, no Mo but a small quantity of Si is detected, meaning that Mo has been consumed completely during the process of heat treatment.

Figure 3 shows the cross-section of the SiC–MoSi₂/ZrO₂–MoSi₂ coating prepared by the two-step technique of pack cementation and slurry coating. It can be observed that the thickness of the coating is about 250–300 μm, and the coating is dense and crack-free. The EDS analysis shows that the white phase can be distinguished as the mixture of ZrO₂ and MoSi₂.

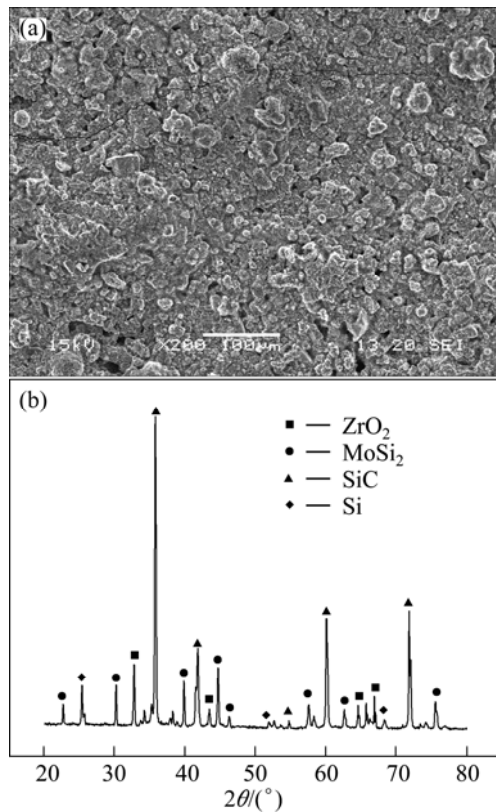


Fig. 2 SEM image (a) and XRD pattern (b) of $\text{ZrO}_2\text{-MoSi}_2$ outer coating prepared by slurry coating

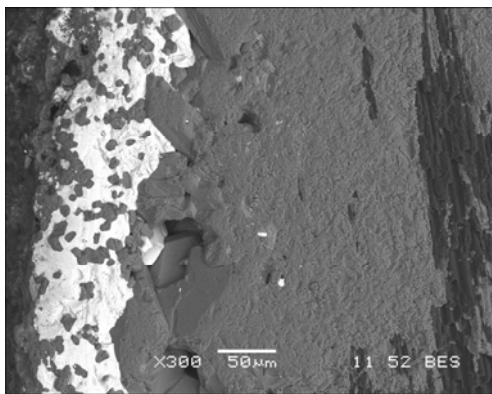


Fig. 3 SEM image showing cross-section of $\text{SiC-MoSi}_2/\text{ZrO}_2\text{-MoSi}_2$ coating prepared by two-step technique of pack cementation and slurry coating

3.2. Oxidation process analyses of $\text{SiC-MoSi}_2/\text{ZrO}_2\text{-MoSi}_2$ coating

Figure 4 shows the isothermal oxidation curves of the coated C/C samples at 1773 K in air. During the oxidation test, the coating mainly undergoes the following four chemical equations:

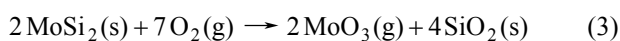
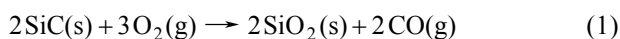


Figure 4 represents the isothermal oxidation curves of the C/C samples with $\text{SiC-MoSi}_2/\text{MoSi}_2$ coating and $\text{SiC-MoSi}_2/\text{ZrO}_2\text{-MoSi}_2$ coating. As shown in Fig. 4(a), it can be seen that the oxidation process of the $\text{SiC-MoSi}_2/\text{MoSi}_2$ coated C/C composites could be divided into three stages. At the initial stage of oxidation (less than 15 h), the coated sample gains mass rapidly. After a short period of platform (between 15 and 20 h), the coated sample starts to exhibit the trend of mass loss. After oxidation at 1773 K in air for 160 h, the mass loss of the coated sample is up to 2.42%. As shown in Fig. 4(b), it can be seen that the $\text{SiC-MoSi}_2/\text{ZrO}_2\text{-MoSi}_2$ coated sample loses only 1.31% mass after exposure to air at 1773 K for 260 h. That is to say, the introduction of ZrO_2 could improve the oxidation resistance of $\text{SiC-MoSi}_2/\text{MoSi}_2$ coating. Compared with Fig. 4(a), it can also be found that the oxidation process of $\text{SiC-MoSi}_2/\text{ZrO}_2\text{-MoSi}_2$ coated sample is similar to that of $\text{SiC-MoSi}_2/\text{MoSi}_2$ coated sample. The main difference is focused on the following two aspects, one is that the period of platform that the mass basically remains unchanged is much longer (between 20 and 116 h); the

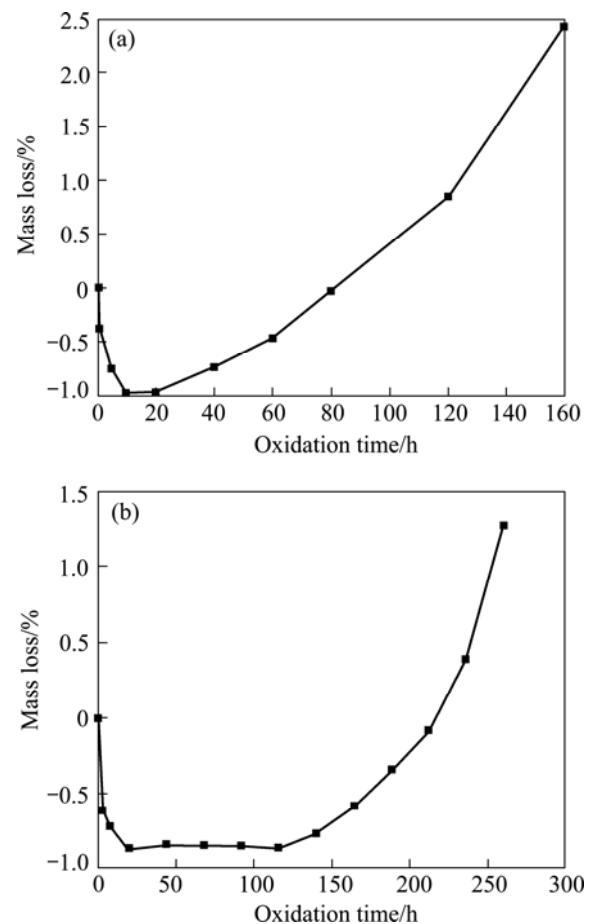


Fig. 4 Isothermal oxidation curves of coated C/C samples at 1773 K in air: (a) $\text{SiC-MoSi}_2/\text{MoSi}_2$ coating; (b) $\text{SiC-MoSi}_2/\text{ZrO}_2\text{-MoSi}_2$ coating

other is that the coated sample loses mass relatively slowly in the whole process, which suggests that the coating can protect the C/C substrate from oxidation at that temperature.

Figure 5 shows the XRD pattern of SiC–MoSi₂/ZrO₂–MoSi₂ coating after oxidation at 1773 K. From Fig. 5, it can be seen that the coating is composed of SiO₂, ZrSiO₄, ZrO₂ and SiC. ZrSiO₄ phase forms due to the reaction between ZrO₂ and SiO₂. SiO₂ might come from the oxidation of SiC, MoSi₂ and Si (Eqs. (1)–(3)). The reason that only a small quantity of SiO₂ is detected could be explained as follows. At about 1773 K, SiO₂ transforms into amorphous glass state. During the oxidation test, the sample is taken out of the furnace directly into air within several seconds for weighing. The cooling rate from 1773 K to room temperature is very quick. Owing to this quick cooling, the majority of the glassy SiO₂ is not able to crystallize before solidification. From Fig. 5, it can also be observed that a large quantity of ZrO₂ is detected while the amount of ZrSiO₄ is little. This phenomenon could be explained by Gibbs free energy in Eq. (4). ΔG of the reaction is calculated by thermodynamic equations [16,17] described as follows:

$$\Delta_r H_m^\ominus(T_2) = \Delta_r H_m^\ominus(T_1) + \int_{T_1}^{T_2} \Delta C_p^\ominus dT \quad (5)$$

$$\Delta_r S_m^\ominus(T) = \Delta_r S_m^\ominus(298.15\text{ K}) + \int_{298.15\text{ K}}^T \frac{\Delta_r C_{p,m}^\ominus}{T} dT \quad (6)$$

$$\Delta G = \Delta H - T \Delta S \quad (7)$$

where $\Delta_r H_m^\ominus$ and $\Delta_r S_m^\ominus$ are the enthalpy of formation and standard molar entropy change, respectively; T_1 is the room temperature and T_2 is the processing temperature; ΔC_p^\ominus is the molar heat capacity at constant pressure which stands for the difference between the processing temperature and the room temperature. The value of ΔG is about -502.6 J/mol at 1773 K, which indicates that the reaction possesses weak spontaneity from the point of thermodynamics, so the amount of ZrSiO₄ is little.

Figure 6 represents the SEM micrographs of the C/C samples with SiC–MoSi₂/MoSi₂ coating and SiC–MoSi₂/ZrO₂–MoSi₂ coating. It can be observed that the surfaces of the above two coatings have changed into glass due to the formation of SiO₂. From Fig. 5, the peak of MoSi₂ in SiC–MoSi₂/ZrO₂–MoSi₂ coating disappears, indicating that MoSi₂ is oxidized completely and produces SiO₂ and MoO₃ (Eq. (3)). However, the MoO₃ phase is not detected due to the MoO₃ (melting point of 1068 K) evaporation at this temperature, resulting in some holes on the coating, as shown in Fig. 6 [18]. At 1773 K, CO₂ and CO generated from the oxidation of SiC and the C/C matrix would get out through the SiO₂ film because of the low viscosity of the glass layer,

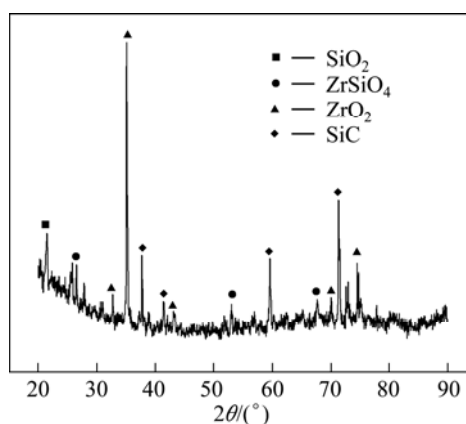


Fig. 5 XRD pattern of surface of SiC–MoSi₂/ZrO₂–MoSi₂ coated C/C sample after oxidation at 1773 K in air for 260 h

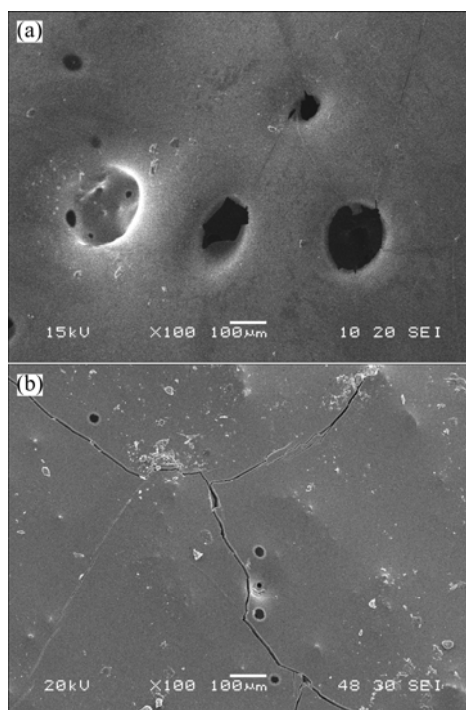


Fig. 6 SEM images of coatings after oxidation at 1773 K in air for different time: (a) SiC–MoSi₂/MoSi₂ coating after oxidation for 160 h; (b) SiC–MoSi₂/ZrO₂–MoSi₂ coating after oxidation for 260 h

which might also result in the formation of holes (see Fig. 6). These holes provide the entrance channels for oxygen to diffuse into the C/C matrix. Compared with the SiC–MoSi₂/MoSi₂ coated sample (see Fig. 6(a)), the size of the holes in SiC–MoSi₂/ZrO₂–MoSi₂ coating obviously decreases (see Fig. 6(b)). From the above analysis, it can be concluded that by adding ZrO₂ in MoSi₂ coating, the stability of the glassy SiO₂ film at high temperature can be reinforced, and the size of holes in the film is also reduced. The existence of ZrSiO₄ phase can enhance the anti-oxidation performance, which might be attributed to the following aspects: 1) the thermal expansion coefficient of ZrSiO₄ is close to that of

SiC, which can eliminate the thermal expansion mismatch between glassy SiO₂ and ZrSiO₄; 2) the ZrSiO₄ phase might have pinning effect on the melting-point (2550 °C) in the case of the fact that the SiO₂ glaze vaporizes fast [18]. This may be the reason that the oxidation protection for MoSi₂-SiC/ZrO₂-MoSi₂ coating is superior to that for MoSi₂-SiC/MoSi₂ coating.

4 Conclusions

1) A dense and crack-free MoSi₂-SiC/ZrO₂-MoSi₂ coating for C/C composites is prepared by a two-step technique of pack cementation and slurry coating. The as-prepared coating has good oxidation protective ability and can efficiently protect C/C composites against oxidation at 1773 K for 260 h.

2) Owing to the generation of ZrSiO₄ through the reaction between ZrO₂ and SiO₂, the stability of the glassy SiO₂ film at high temperatures can be efficiently reinforced, which increases the oxidation resistance of the coating.

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C/C 复合材料表面 SiC-MoSi₂/ZrO₂-MoSi₂ 抗氧化涂层

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摘 要: 为了提高 C/C 复合材料在高温空气中的抗氧化性能, 采用包埋法和涂刷法在 C/C 复合材料表面制备 MoSi₂-SiC/ZrO₂-MoSi₂ 涂层。借助扫描电镜和 X 射线衍射等测试手段对涂层的微观形貌和相组成进行分析, 同时研究涂层的制备过程和高温静态空气中的抗氧化性能。结果表明: SiC-MoSi₂/ZrO₂-MoSi₂ 涂层致密且无穿透性裂纹, 厚度为 250~300 μm, 具有优异的抗氧化性能, 在 1773 K 静态空气中的有效抗氧化时间为 260 h, 这主要是由于涂层中生成了 ZrSiO₄, 有效提高了涂层的高温稳定性。

关键词: 炭/炭复合材料; SiC-MoSi₂/ZrO₂-MoSi₂; 涂层; 抗氧化性能

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