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Double SiC coating on carbon/carbon composites against oxidation by a two-step method

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Abstract: To improve the oxidation resistance of C/C composites, a double SiC protective coating was prepared by a two-step technique. Firstly, the inner SiC layer was prepared by a pack cementation technique, and then an outer uniform and compact SiC coating was obtained by low pressure chemical vapor deposition. The microstructures and phase compositions of the coatings were characterized by SEM, EDS and XRD analyses. Oxidation behaviour of the SiC coated C/C composites was also investigated. It was found that the double SiC coating could protect C/C composites against oxidation at 1773 K in air for 178 h with a mass loss of 1.25%. The coated samples also underwent thermal shocks between 1773 K and room temperature 16 times. The mass loss of the coated C/C composites was only 2.74%. Double SiC layer structures were uniform and dense, and can suppress the generation of thermal stresses, facilitating an excellent anti-oxidation coating.

Key words: carbon/carbon composites; SiC; oxidation; coating

1 Introduction

Carbon/carbon (C/C) composites possess unique characteristics such as high specific strength, high retention of mechanical properties and high specific strength and modulus at high temperatures [1-3]. However, C/C composites are prone to oxidization above 723 K in an environment containing oxygen and the oxidation rate increases quickly with temperature increasing [4–6]. So, the oxidation problem is an urgent barrier to the application of C/C composites as high-temperature structure materials.

SiC ceramic coating is considered an effective method for protecting C/C composites and extending the service life of them at high temperature. It is attributed to its excellent anti-oxidation property and good compatibility with C/C composites [7,8]. When the SiC coated C/C composites are placed in air at high temperature, the glassy SiO₂ film will form on the surface of the coating, which provides efficient barrier to limit oxygen diffusing into the C/C substrate. However, due to the thermal expansion mismatch between SiC and C/C composites, SiC coatings are apt to crack. The cracks in the coating offer the path through which oxygen can diffuse into the C/C matrix [9,10]. Thus, to solve this problem, an outer-layer coating system is usually prepared, such as SiC/SiC–ZrB₂ [11], SiC/SiO₂ [12], SiC/ZrB₂–MoSi₂ [13], SiC/mullite [14], MoSi₂/SiC coating [15], C/SiC/MoSi₂–Si and MoSi₂–Mo₅Si₃/SiC [16,17]. These outer-layer coating systems could effectively protect samples against oxidation for some time. However, due to the thermal expansion coefficient of outer-layer coating is different from that of the inner SiC coating, when the sample suffers multiple thermal cycles, the coating would be cracked and even flaked off. Hence, it is considered that SiC as a good candidate for outer-coating which had no thermal expansion mismatch and could fill the cracks effectively.

SiC prepared by atmosphere pressure chemical vapor deposition (APCVD) was indicated to be promising candidates for outer-layer coating. In the previous work, APCVD SiC outer-layer coating could fill the cracks of the inner SiC layer by pack cementation and improve its oxidation resistance [18,19]. However, SiC prepared by low pressure chemical vapor deposition (LPCVD) possesses more uniform composition and more compact structure than the APCVD SiC [20], which is

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expected to have better protective ability.

In the present work, a double SiC coating is prepared by a two-step method. The first step is to prepare a SiC inner layer by pack cementation, and the second step is to prepare a SiC outer layer by LPCVD. The microstructure and the anti-oxidation performance of the coating at 1773 K are investigated. The thermal shock tests between 1773 K and room temperature (RT) are investigated.

2 Experimental

Specimens with size of d5 mm×15 mm, were cut from bulk C/C composites with a final density of 1.70 g/cm³. These specimens were hand-polished using 80, 200 and 500 grit SiC papers in turn, then cleaned with ethanol and dried at 373 K for 10 h. The double SiC coating was prepared by a two-step technique of pack cementation and low pressure chemical vapor deposition (LPCVD). In the first step, using Si and C as the raw materials, the SiC inner coating was prepared by pack cementation. The powder compositions were as follows: 70%-80% Si, 10%-20% graphite and 5%-15% Al₂O₃. Al₂O₃ was used as penetration enhancer to promote the diffusion reaction between Si and C. The pack mixtures and C/C specimens were put in a graphite crucible and then were heated to 2173-2373 K for 2-4 h in argon atmosphere to form a SiC inner coating. In the second step, SiC outer coating was deposited on the SiC inner coating by low pressure chemical vapor infiltration (LPCVD). CH₃SiCl₃ was used as precursor during this process. The parameters for LPCVD were as follows: temperature 1423–1523 K, pressure 4–10 kPa, time 20 h, dilute hydrogen flow 800-1200 mL/min, Ar flow 300-500 mL/min, bubbling hydrogen 80-120 mL/min.

To investigate the oxidation process of the as-coated samples, the oxidation test was carried out in air in an electric furnace at 1773 K. The C/C composites coated with a single SiC layer by pack cementation were used as reference under the same condition during the whole process of oxidation test. The cumulative mass change of the sample after every thermal cycle was reported as a function of oxidation time. For thermal shock tests, the coated samples were kept for 10 min in a furnace at 1773 K and for 10 min at room temperature alternatively 16 times. Mass change of the sample was measured by an electronic balance with a sensitivity of ± 0.1 mg. Anti-oxidation ability was evaluated by mass loss percentage.

The morphology and element distribution of the coating were analyzed by X-ray diffraction (XRD, Rigaku D/max-3C) with a Co K_a radiation (λ =0.1542 nm) produced at 40 kV and 35 mA. The analyzed range of the diffraction angle 2 θ was between 10° and 90° with a step

width of 0.033°. The microstructure and morphology of the composites were analyzed by scanning electron microscopy (SEM, EDS, Supra 55).

3 Results and discussion

3.1 Phase composition and microstructure of coating

Figure 1 shows the SEM image and the XRD pattern of the SiC inner coating prepared by the first pack cementation. It can be seen that some cracks exist in the coating (Fig. 1(a)). These cracks could be self-seal partially at high temperature, but C/C substrate would still be oxidized due to 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 found that the inner coating is composed of α -SiC, β -SiC and Si. The existence of Si could not only relieve the mismatch of the thermal expansion coefficient between SiC coating and C/C, but also improve the oxidation resistance of its oxidation product SiO₂[21].



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

Figure 2 shows the cross-section image of SiC inner coating and its element line scanning results. From Fig. 2(a), it can be seen that an interlock structure between the C/C substrate and the interface of SiC inner

layer is formed, which is helpful to the bonding strength. Figure 2(b) displays EDS element line analysis of the inner coating. It can be seen that the concentration of the Si element increases gradually from the C/C substrate to the coating at their interface, implying that a gradient C-SiC bonding layer was obtained during the pack cementation process, which is advantageous to improving the thermal shock resistance of the coating.

Fig. 2 Cross-section SEM image (a) and EDS element line scan analysis (b) of SiC coating

Figure 3 shows the SEM image and XRD patterns of the double SiC coating prepared by the two-step technique of pack cementation and LPCVD. From Fig. 3(a), it can be seen that no crack exists on the surface of coating. The grains of SiC formed by LPCVD are fine and uniform, and can fill the holes or cracks efficiently. Figure 3(b) exhibits the cross-section of the as-received SiC coating. The coating is about 110 µm in thickness without any penetrable cracks or holes. Meanwhile, there is also no obvious crack or gap between the inner SiC and the outer SiC coating, which indicates the two kinds of SiC layer are embedded into each other and display a good bonding. In addition, LPCVD SiC deposited on SiC inner layer by pack cementation belongs to homogeneity epitaxy. Thus, they possess the same lattice structure and thermal expansivity. So the double SiC coating is expected to have good oxidation resistance and thermal shock resistance. XRD

analysis (Fig. 3(c)) shows that no Si and α -SiC peaks exist, and only β -SiC is detected, which means that the phase structure of SiC is controlled well during the LPCVD process. It also indicates that the SiC outer coating covers up the whole surface of the inner SiC coating effectively.

Fig. 3 SEM images (a, b) and XRD pattern (c) of double SiC coating by pack cementation and LPCVD: (a) SEM image showing surface morphology; (b) SEM image showing cross-section; (c) XRD pattern

3.2 Oxidation protective ability of coating

Figure 4 shows the isothermal oxidation curves of the double SiC coating and the single SiC coating in air at 1773 K. During the oxidation test, the coating might mainly undergo the following three reactions [22–25]:

$$2\operatorname{SiC}(s) + 3\operatorname{O}_2(g) \longrightarrow 2\operatorname{SiO}_2(s) + 2\operatorname{CO}(g) \tag{1}$$

$$\operatorname{SiC}(s) + 2O_2(g) \longrightarrow \operatorname{SiO}_2(s) + \operatorname{CO}_2(g)$$
(2)

$$2C(s) + O_2(g) \longrightarrow 2CO(g) \tag{3}$$

From Fig. 4, it can be seen that after oxidation at 1773 K in air for 15 h, the mass loss of the single layer SiC coated sample is up to 11.2%. The double SiC coated sample loses only 1.25% mass after exposure to air at 1773 K for 178 h. Its oxidation protective ability is better than SiC coating prepared by APCVD reported by WANG et al [19].

Fig. 4 Isothermal oxidation curves of samples in air at 1773 K

In the early 28 h of oxidation, the double SiC coated sample gains mass firstly. Beyond 28 h, the mass starts decreasing. Because the oxidation of the coating is an increasingly severe process, the slight mass decrease beyond 28 h oxidation might be attributed to the consumption of glass or the oxidation of C/C composites during oxidation test. That is to say, the introduction of SiC outer coating prepared by LPCVD could efficiently improve the oxidation resistance of SiC inner coating prepared by pack cementation.

Figure 5 shows the SEM image and XRD pattern of the double SiC coating after oxidation at 1773 K for 178 h. From Fig. 5(a), it can be observed that the surface of the double SiC coating has changed into glass due to the formation of SiO₂, which can efficiently prevent oxygen from diffusing into the C/C substrate due to its low oxygen permeability. However, some cracks exist in the coating. These cracks might form during the cooling process from 1773 K to room temperature for weighing. Some holes exist in the coating, which may be attributed to the escape of gases. At 1773 K, CO₂ and CO generated from the oxidation of SiC and the C/C substrate (Eqs. (1)–(3)) would get out through the SiO₂ film because of the low viscosity of the glass layer, which might result in the formation of holes (Fig. 5(a)). These holes also provide the entrance channels for oxygen to diffuse into the C/C substrate, leading to its slight oxidation. The coating is chemically composed of SiO_2 and SiC, as revealed by the XRD pattern of the oxidized surface of the coating shown in Fig. 5(b). SiO_2 might come from the oxidation of SiC (Eqs. (1) and (2)).

Fig. 5 SEM image (a) and XRD pattern (b) of double SiC coating after oxidation at 1773 K for 178 h

Figure 6 shows the cross-sectional micrograph of the double SiC coated C/C composites after oxidation for 178 h. Many holes or small cracks are found in the coating. The SiO₂-glass is seemed to consume gradually by prolonging oxidation time, and oxygen can diffuse through the glass film and react with SiC gradually, resulting in the formation of thermally stable SiO₂. The double coating is about 90 mm in thickness after oxidation, and compared with the original 110 mm, the consumption rate of the coating is slow.

Fig. 6 Cross-sectional BES micrograph of double SiC coated C/C composites after oxidation for 178 h

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3.3 Thermal shock resistance of coating

Thermal shock resistance of the double SiC coating was investigated between 1773 K and RT as shown in Fig. 7. With the increase of thermal treatment cycles, the mass loss of the sample increases linearly, and the total mass loss of coated samples is observed to be 2.74% after 16 cycles.

Fig. 7 Mass losses curve of double SiC coated C/C composites during thermal shock between 1773 K and RT

Figure 8 shows the back electron scattering (BES) micrograph of the cross-section of the coating after 16 cycles of thermal shock. Penetrable cracks are found in the coating. It is attributed to the difference in the thermal expansion coefficient between the coating and the C/C substrate. The micrograph also shows the coating failed and holes exist at the end of the penetrable cracks. The oxygen diffuses through those cracks, resulting in the oxidation of C/C composites.

Fig. 8 Cross-sectional micrograph of double SiC coated C/C composites after 16 thermal shocks between 1773 K and RT

During the whole oxidation test, the samples suffered 13 thermal cycles from 1773 K to RT. It can be found that the mass loss of the coated sample during each thermal cycle of oxidation is comparatively smaller than that during each cycle of thermal shocks in the same temperature range. The results show that the thermal cycles during oxidation tests supply sufficient time to form a SiO_2 film for sealing the cracks. However, the time duration is too short to form enough amount of SiO_2 film to seal the pre-existing cracks formed during the thermal shocks.

4 Conclusions

1) The outer SiC coating prepared by LPCVD method is uniform and compact, greatly enhancing the anti-oxidation performance of the single layer coated C/C composites.

2) Double SiC coating efficiently protects C/C composites against oxidation at 1773 K for 178 h. After 16 cycles of thermal shocks between 1773 K and RT, the mass loss is only 2.74%. The failure of the coating after thermal shock is largely attributed to slow formation of sealing SiO₂ film, which causes the formation of penetrable cracks and holes in the coating, accelerating the oxidization of C/C composites.

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C/C 复合材料表面两步法制备 SiC 涂层的抗氧化性能

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摘 要:为了提高炭/炭(C/C)复合材料的抗氧化性能,采用包埋与低压化学气相沉积相结合的方法在 C/C 复合材料表面制备双层 SiC 涂层。利用 SEM、XRD 和 EDS 观察与分析涂层的微观形貌和相组成;测试涂层试样在 1773 K 高温下的抗氧化性能。结果表明:双层 SiC 涂层可以在 1773 K 的高温下有效地保护 C/C 复合材料 178 h,质量损失仅为 1.25%。试样经受 16 次 1773 K 至室温急冷急热循环后,氧化质量损失仅为 2.74%。C/C 复合材料表面双层 SiC 涂层的结构致密、成分均匀,具有较强的抗氧化性能。

关键词: C/C 复合材料; SiC; 氧化; 涂层

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