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ARTICLE

Microstructure and Anti-oxidation Properties of SiC/MoSi$_2$-ZrB$_2$ Coating for Carbon/Carbon Composites Prepared by Magnetron Sputtering Method

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Abstract: A SiC/MoSi$_2$-ZrB$_2$ ceramic coating was prepared by a magnetron sputtering method on carbon/carbon composites to protect it against oxidation. The microstructure of the coating was investigated, and its oxidation behavior at 1273 and 1773 K in air was also studied. The as-received coating exhibits outstanding uniformity in thickness and presents columnar structure. The coated C/C composites perform a superior oxidation resistance, and the weight losses of the samples after oxidation at 1273 and 1773 K for 60 min in oxygen containing environment are 5.6×10^{-2} and 6.3×10^{-2} g/cm^2, respectively.

Key words: C/C composites; SiC/MoSi$_2$-ZrB$_2$ coatings; microstructure; oxidation; magnetron sputtering

Carbon/carbon (C/C) composites are attractive materials for high-temperature applications in aeronautical and aerospace industry such as rocket nozzles, noses, leading edges of reentry vehicles and gas turbine engine components due to their excellent mechanical properties at high temperatures[1,2]. Unfortunately, carbon can react rapidly with oxygen above 773 K and the composites are subjected to oxidation degradation. It greatly restricts their applications in oxygen-containing environment[3,4]. Currently, applying coatings is considered as an effective solution to the oxidation problem of C/C composites[5,6].

It has been proved that silicide coatings with boron have good oxidation protective ability for C/C composites not only at high temperatures (1773~1873 K) but also at intermediate temperatures (1073~1373 K) due to the formation of SiO$_2$ and B$_2$O$_3$, which can provide good oxidation protection above 1473 K and effectively seal the cracks below 1473 K, respectively[7]. This kind of borosilicate glass layer is expected to provide good oxidation protection for C/C composites within broad temperature range[8-10]. Therefore, numerous boracic silicide coating systems, especially the SiC-MoSi$_2$-ZrB$_2$ system have been explored to protect C/C composites against oxidation in oxygen containing environment[11-13].

The existing techniques of applying SiC-MoSi$_2$-ZrB$_2$ coatings to C/C composites are based on the pack cementation[11-13]. However, the pack cementation process is always carried out at extraordinarily high temperature (1873~2573 K), which causes serious carbon fiber properties attenuation[14]. If the mechanical properties of substrate are decreased to a large extent during the process of coating preparation, service life will be shortened, even disaster. Besides, the evenness and the thickness of the coating prepared by pack cementation are difficult to control because of the effect of gravity. For some precision structural components, it would be difficult to protect them from oxidizing by anti-oxidation coating if the thickness of the coating could not be controlled accurately. Therefore, trying to use new techniques without damaging C/C composites matrix to prepare uniform coatings in thickness

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appears to be critical.

As well known, magnetron sputtering deposition has been demonstrated to be a good low-temperature and environmental method to deposit coatings on all surfaces of the sample[15], which does less damage to matrix and can meet the precise requirements for the evenness and thickness of the coating as well. However, so far, we could find seldom report about using the magnetron sputtering technique to produce a SiC-$MoSi_2$-ZrB_2 coating, especially on C/C surface.

In the present work, a SiC/$MoSi_2$-ZrB_2 coating was prepared on C/C composites by magnetron sputtering method. The deposition mechanism and microstructure of SiC/$MoSi_2$-ZrB_2 coating were discussed. The anti-oxidation properties of the as-received coating at 1273 and 1773 K in air were investigated as well.

1 Experiment

Small cubic specimens (10 mm×10 mm×10 mm) used as substrates were cut from a 2D C/C composites bulk with a density of 1.60 g/cm^3. These specimens were hand-polished using 400# and 800# SiC abrasive papers, then cleaned ultrasonically with acetone and dried at 100 ℃ for 2 h.

Fig.1 shows a scheme of the SiC/$MoSi_2$-ZrB_2 coating structure, and the thickness of SiC and $MoSi_2$-ZrB_2 coating showed in the illustration were designed for 10 and 60 μm, respectively. The coating system was prepared on C/C composites by magnetron sputtering method as follows: a middle-frequency (MF) and direct current (DC) sputtering technique were used in the SiC and $MoSi_2$-75wt%ZrB_2 coatings deposition, respectively (as shown in Fig.2). Pure argon (99.99%) was introduced into the vacuum chamber in a certain flow through a mass flow controller after the chamber was evacuated below 10^{-3} Pa. The target/substrate distance was 80 mm. The temperature during the deposition was fixed at 473 K and the substrate bias was set to 100 V. Prior to deposition, the specimens were cleaned by argon ion etching for 30 min. Sputter deposition was performed with a twin-SiC target using an MF input power of 700 W and a $MoSi_2$-75wt%ZrB_2 target (length of 300 mm, width of 75 mm, thickness of 4 mm, 99.99% purity) using a DC input power of 1200 W. The working pressure of SiC and $MoSi_2$-ZrB_2 was 1.0 Pa. The deposition rate of SiC and $MoSi_2$ was 1.5 and 6 μm/h, respectively, which was measured by cross-sectional scanning electron microscopy (SEM) and ellipsometry (Spectra Thick 2000-deluxe). Therefore, the deposition time of SiC was 7 h and the deposition time of $MoSi_2$-ZrB_2 was 10 h, thereby obtaining the coating structure as Fig.1 shows. The deposition conditions are summarized in Table 1.

The oxidation behavior of specimens with and without coating was evaluated by static oxidation in air at 1773 K using an electrical furnace. After the furnace was heated up to 1273 or 1773 K, the specimens were moved into the hot zone of the electrical furnace directly and then kept at 1273 or 1773 K for 1 h, whereafter (at the designated time 60 min) they were cooled to room temperature with the furnace for weighting. The mass of specimens was measured by an electronic precision balance with sensitivity of ±0.1 mg. The weight loss (Δ*w*) of specimens were calculated using Eq.(1).

$$\Delta w = (m_0 - m_1)/s \tag{1}$$

where m_0 is the original mass of coated C/C composites; m_1 is the mass of coated C/C composites after oxidation at high temperature; *s* is the surface area of the sample. The final mass loss of specimens were the average oxidation rates of three specimens.

The morphologies and crystalline structure of the coating

Fig.1 Schematic of the SiC/$MoSi_2$-ZrB_2 coating structure

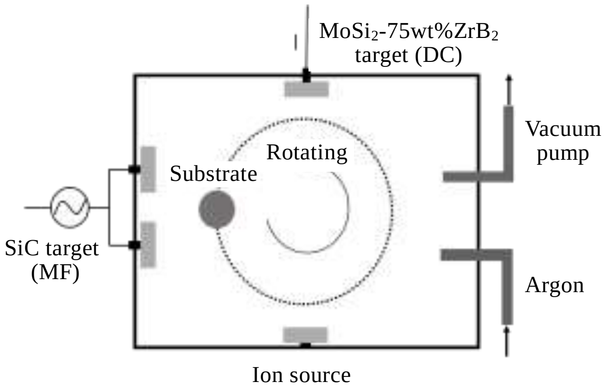

Fig.2 Schematic diagram of the deposition system

Table 1 Main deposition parameters of the coating

Parameter	Value
Base pressure/Pa	< 10^{-3}
Working pressure/Pa	1.0
Working gas	Ar
Sputtering power/W	SiC: 700; $MoSi_2$-ZrB_2: 1200
Substrate bias/V	100
Substrate temperature/K	473
Deposition time	d_0: 7 h; d_1: 10 h

were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). At the same time, the element distribution of the coatings were analyzed by energy dispersive spectroscopy (EDS).

2 Results and Discussion

2.1 Microstructure of the coating

Fig.3 shows a typical surface image of the C/C composites. It is obvious that the surface of C/C composites is coarse. Furthermore, many macro-holes are more than 50 μm in diameter. This has great influence on coating morphology.

The surface morphologies of SiC/$MoSi_2$-ZrB_2 coated C/C composites are shown in Fig.4. We can see that the coating grains are spherical with uniform size at low magnification (Fig.4a) and exhibit “cauliflower” structure to some degree at high magnification (Fig.4b). Besides, a few cavities resulted from those as-noted big holes of the C/C matrix surface and microcracks caused by the mismatch of thermal expansion coefficient (CTE) between coatings and C/C composites can be observed as well.

Fig.5a shows the cross-section of a cavity in the coating. We can find that the coating at the bottom of the observed cavity is much thinner than that of the matrix surface. It is not favorable to protecting C/C matrix from oxidation.

Fig.5b and Fig.5c illustrate the cross-section morphologies of the coated C/C composites under different magnifications. It can be observed that the evenness and uniformity of the coating is very good (Fig.5b). From Fig.5c, we can see that there are two kinds of layers characterized as black (spot 1) and grey (spot 2). By EDS analysis (Fig.4d), the grey and black layers can be distinguished as $MoSi_2$-ZrB_2 and SiC, respectively, which is consistent with the designed structure (Fig.1). According to the measurement results, the average thickness of SiC, $MoSi_2$-ZrB_2 and the whole coating is approximately 10, 59 and 69 μm, respectively, which are very close to the pre-set thickness values of the coating in Fig.1, illustrating that the coating thickness was controlled perfectly when using magnetron sputtering technique. Theoretically, the thickness of coatings can be accurately controlled by setting deposition time while the deposition rate of target atoms is constant and can be measured easily. The deposition rate of SiC and $MoSi_2$ is 1.5 and 6 μm/h, respectively, in the present study. Therefore, if we want to obtain such SiC/ $MoSi_2$-ZrB_2 coating structure shown in Fig.1, we just need to deposit SiC for 7 h at first, and then deposit $MoSi_2$-ZrB_2 for 10 h. In addition, it is manifest that SiC and $MoSi_2$-ZrB_2 grains grow into the surface normal direction of C/C substrate, showing columnar microstructure typical for films prepared by the sputtering deposition method, in the as-deposited sample, which is disadvantageous to suppress the diffusion of oxygen across the grain boundary. Obvious interface between the C/C matrix and the coating can also be observed, indicating that the bonding between them is relatively poor, which are not favorable to protecting C/C matrix from oxidation as well.

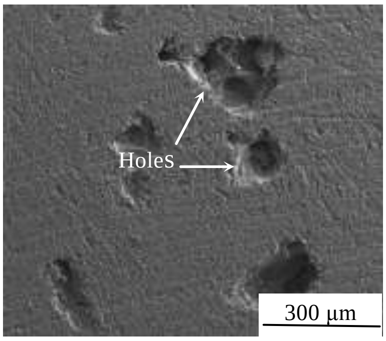

Fig.3 Surface morphology of C/C composites

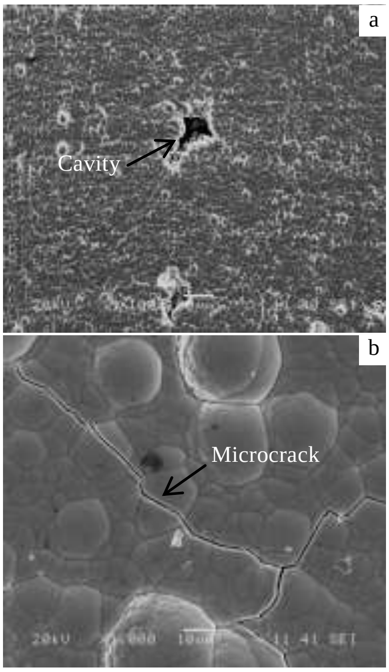

Fig.4 Surface morphologies of the as-received SiC/$MoSi_2$-ZrB_2 coating at low magnification (a) and high magnification (b)

The structure of the coating can be explained by the formation mechanism of a coating. As shown in Fig.6, in the initial deposition stage, the atoms arrive at the surface of the substrate and unite as nucleus which will grow in three-dimensional direction, then the density of nucleus on the surface of the matrix will become saturated rapidly and the growth of the coating changes into island growth model. Along with the coalescence of the islands, the single island becomes bigger and an intermittently reticular structure which contains lots of pores and vacant channels is formed between two adjacent islands, and the target atoms that

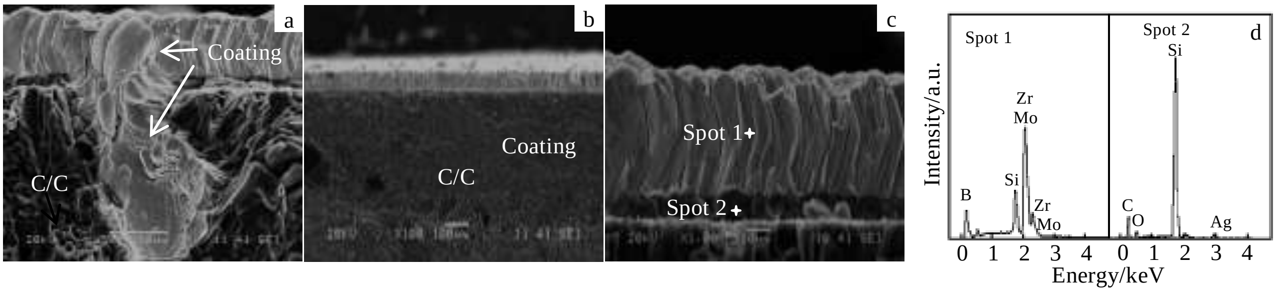

Fig.5 Cross-section morphologies of SiC/$MoSi_2$-ZrB_2 coating: (a) a cavity in the coating, (b) the coating at low magnification, and (c) the coating at high magnification; (d) EDS spectra of spot 1 and spot 2 in Fig.5c

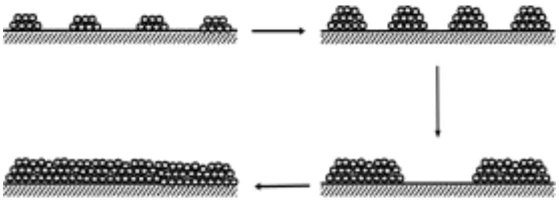

Fig.6 Schematic diagram of the initial growth progress of the film

reach the substrate subsequently will “connect” this reticular structure directly or fill the pores and vacant channel until a consecutive film is generated. According to Thornton model, when the working pressure and temperature is 1.0 Pa and 473 K, respectively, the diffusion of target atoms on the surface of the coating is not quick enough to diffuse at a long distance; in this case, the coating presents columnar structure as shown in Fig.5c.

2.2 Oxidation resistance of coated C/C composites

Fig.7 shows the oxidation resistance of C/C and coated C/C composites at middle temperature (1273 K) and high temperature (1773 K) in air. It can be found that bare C/C composites specimen has a poor oxidation resistance, and its mass loss is up to 28.8×10^{-2} g/cm^2 after oxidation at 1273 K for 60 min. Whereas the SiC/$MoSi_2$-ZrB_2 multilayer coated C/C composites exhibits better oxidation resistance, and the weight loss of the C/C sample with this coating at 1273 and 1773 K is only 5.6×10^{-2} and 6.3×10^{-2} g/cm^2, respectively. Therefore, the as-prepared coating could provide oxidation protection for C/C composites both at 1273 and 1773 K.

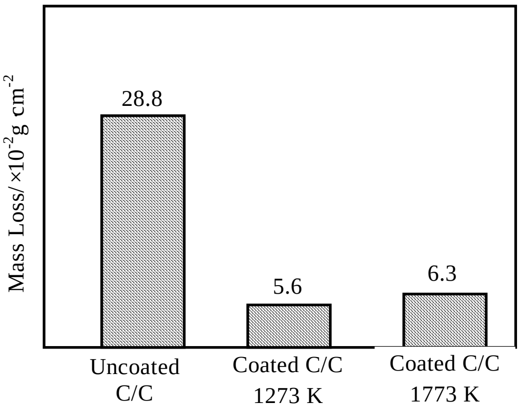

Fig.7 Mass loss of uncoated and coated C/C composites at 1273 and 1773 K for 60 min

In oxygen-containing environment at high temperature, the coated sample will react with oxygen as follows:

$$2ZrB_2(s)+5O_2(g)\rightarrow2ZrO_2+2B_2O_3(l) \tag{2}$$

$$SiC(s)+2O_2(g)\rightarrow SiO_2(l)+CO_2(g) \tag{3}$$

$$2SiC(s)+3O_2(g)\rightarrow2SiO_2(l)+2CO(g) \tag{4}$$

$$2MoSi_2(s)+7O_2(g)\rightarrow2MoO_3(g)+4SiO_2(l) \tag{5}$$

$$2C(s)+O_2(g)\rightarrow2CO(g) \tag{6}$$

$$C(s)+O_2(g)\rightarrow CO_2(g) \tag{7}$$

It is obvious that Eqs.(2)~(4) would cause a net mass gain and reaction (5)~(7) would lead to a net mass loss. Consequently, the mass loss of the coated C/C sample during oxidation at high temperature in oxygen-containing atmosphere is mainly resulted from the oxidation of C/C matrix and the volatilization of SiO_2 and MoO_3.

Fig.8 illustrate the SEM micrograph and X-ray pattern of the coating after oxidation at 1273 K for 60 min. Fig.8b is the magnification of the circled area in Fig.8a, from which we can observe that a thin smooth glassy film is formed on the surface of the coating, and this glassy substance is tend to gathering in cavities and microcracks. Besides, the crystalline grain and cavities can be observed as well, which suggests that the coating is not be oxidized completely.

As revealed by the X-ray pattern of the oxidized surface of the coating in Fig.8c after oxidation at 1273 K for 60 min, the exterior coating is composed of B_2O_3, ZrO_2, SiO_2 and some remaining ZrB_2 and $MoSi_2$ that do not react with oxygen. It suggests that the as-noted glassy film in Fig.8a is consisted of B_2O_3 and SiO_2, which are produced from the oxidation of ZrB_2 and $MoSi_2$, respectively.

When the coated sample is exposed in oxygen-containing atmosphere at intermediate temperature (1073~1473 K), ZrB_2 in the out-layer will directly react with oxygen and generate molten B_2O_3 with low viscosity and high wettability according to Eq.(2). This molten B_2O_3 will protect C/C substrate from being oxidized by sealing the cavities and microcracks in the coating so that preventing oxygen to contact with C/C substrate through these nature path. Therefore, it is ZrB_2 that plays the foremost role on protecting the C/C substrate under 1273 K in air (the generation of SiO_2 is considerably finite and its viscosity is too high to healing the defect in the coating under such temperature conditions). Consequently, the weight loss of the coated sample at 1273 K is mainly resulted from the oxidation of C/C matrix before the penetrating cavities and microcracks were sealed entirely by the glass phase.

Fig.9 shows the SEM image, X-ray pattern and EDS analysis of the coating after oxidation at 1773 K in air for 60 min. It can be seen that a smooth glassy film characterized as charcoal grey, gray and white was formed on the surface of the coating. By EDS and XRD analysis, the charcoal gray, gray and white phases marked by spot A, spot B and spot C can be distinguished as SiO_2, ZrO_2 and $ZrSiO_4$, respectively. Besides, microcracks that resulted from the mismatch of CTE between the coating and C/C composites when cooling down from 1773 K to room temperature can be observed, but the crystalline grain and cavities in the coating disappear, which suggest that the coating is oxidized completely.

The SiO_2-riched glass film noted above has played an important role in sealing cavities and microcracks in the coating and limiting the inward diffusion of oxygen into the inner bulk at high temperature due to its low viscosity and oxygen permeability. In addition, microcracks in Fig.8b will be sealed by the SiO_2 glass when the coated sample is heated to 1773 K again. The ZrB_2 in the exterior coating has been exhausted (reaction (2)), resulting in that ZrB_2 cannot be detected (Fig.9b). Furthermore, B_2O_3 cannot be detected as well due to its high evaporation above 1373 K and SiO_2 substituted as the protective role for C/C substrate during the statics oxidation process at 1773 K.

The $ZrSiO_4$ dispersed in SiO_2 film was formed by Eqs.(8)~(10) as follows:

$$SiC(s)+O_2(g)\rightarrow SiO(g)+CO(g) \quad (8)$$

$$2ZrO_2(s)+2SiO(g)+O_2(g)\rightarrow 2\ ZrSiO_4\,(s) \quad (9)$$

$$ZrO_2(s)+SiO_2(s)\rightarrow ZrSiO_4(s) \quad (10)$$

This high-thermally stable $ZrSiO_4$ phase could improve the stability of SiO_2 at high temperature[16]; simultaneously, the formation of continuous SiO_2 glass layer with $ZrSiO_4$ dispersants could decrease the diffusion rate of oxygen[17,18]. The dispersed $ZrSiO_4$ is conducive to the oxidation protection of SiO_2 glass. Nevertheless, it is significant to control the amount of ZrB_2 in case of the excessive consume of SiO_2 so that not enough molten SiO_2 remains to protect the matrix, since the formation of $ZrSiO_4$ is reposed on the consuming of SiO_2.

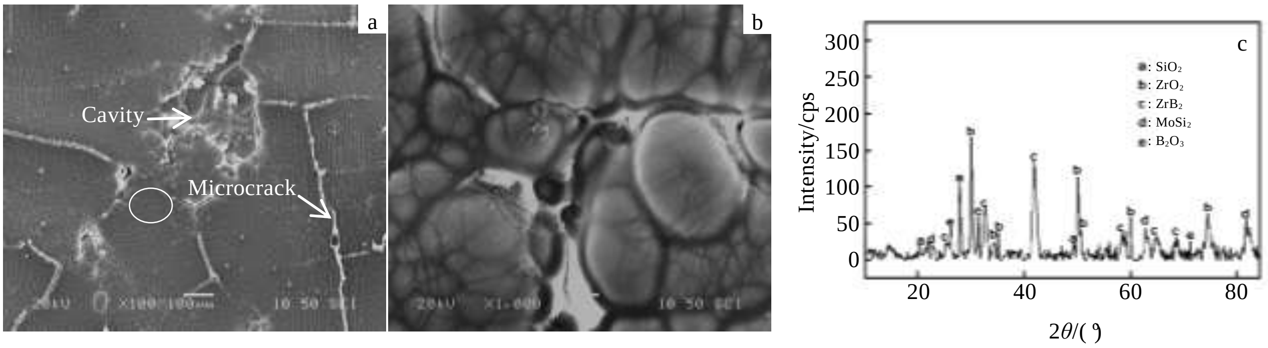

Fig.8 SEM micrograph (a, b) and XRD pattern (c) of the coating after oxidation at 1273 K for 60 min

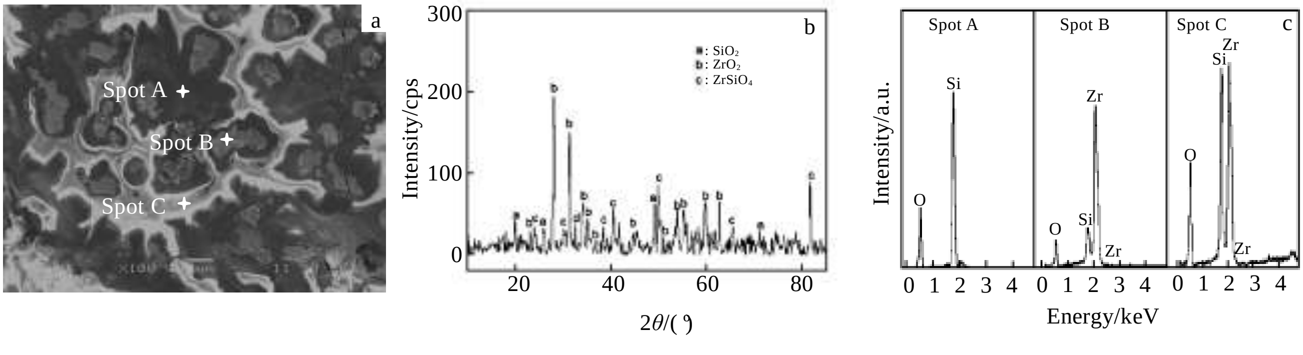

Fig.9 SEM micrograph (a) and XRD pattern (b) of the coating after oxidation at 1773 K for 60 min; (c) EDS spectra of spot A, spot B and spot C in Fig.9a

The SiC/$MoSi_2$-ZrB_2 multilayer coating prepared by magnetron sputtering method can protect C/C composite from oxidation at high temperature. The generation of B_2O_3 effectively seal the cracks below 1273 K and the formation of SiO_2 can provide good oxidation protection at 1773 K. However, compared with the research of Li et al[11,13], the oxidation resistance of the coating prepared in the present work is relatively poor, which may be related to the coating structure (the formation of cavities in the coating). Further research about how to enhance the anti-oxidation resistance properties of the coating is needed.

3 Conclusions

1) The thickness of SiC and $MoSi_2$-ZrB_2, which can be effectively and precisely controlled by setting deposition time, is 10 and 59 μm, respectively.

2) The as-received coating exhibits columnar structure and outstanding evenness and uniformity.

3) After coating, the oxidation resistance of C/C composites is significantly enhanced. The mass loss of the coated C/C sample is 5.6×10^{-2} and 6.3×10^{-2} g/cm^2 after oxidation at 1273 and 1773 K for 60 min, respectively.

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磁控溅射法制备碳/碳复合材料SiC/$MoSi_2$-ZrB_2涂层的结构及抗氧化性能研究

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摘 要：通过磁控溅射法在碳/碳复合材料表面成功制得了SiC/$MoSi_2$-ZrB_2陶瓷涂层并对其结构及其在高温有氧环境中的抗氧化性能进行了研究。结果表明制备的SiC/$MoSi_2$-ZrB_2陶瓷涂层呈柱状晶结构且均匀性良好，其在1273和1773 K的有氧环境中氧化60 min失重率分别是5.6×10^{-2}和 6.3×10^{-2} g/cm^2。

关键词：碳/碳复合材料；SiC/$MoSi_2$-ZrB_2涂层；显微结构；氧化；磁控溅射

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