Rare Metal Materials and Engineering
Volume 45, Issue 10, October 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(10): 2543-2548.

ARTICLE

Magnetron Sputtering Preparation and Properties of SiC/MoSi$_2$ Oxidation Protective Coating for Carbon/Carbon Composites Prepared

Fu Wenbin[1,2], Dai Mingjiang[2], Wei Chunbei[2], Zhao Mingchun[1], Hu Liang[1],
Hou Huijun[2], Lin Songsheng[2]

[1] Central South University, Changsha 410083, China; [2] Guangzhou Research Institute of Non-ferrous Metals, Guangzhou 510650, China

Abstract: A SiC/MoSi$_2$ alternating multilayer coating was prepared on Carbon/Carbon (C/C) surface to protect it against oxidation by a magnetron sputtering method. The microstructural characteristic, oxidation behavior and oxidation mechanism of the SiC/MoSi$_2$ multilayer coating were investigated. The as-received coating exhibits dense columnar structure and outstanding uniformity in thickness. The coated C/C composites possesses a superior oxidation resistance, and its mass loss is only 3.2×10^{-2} g/cm^2 after oxidation at 1500 ℃ for 60 min. The mass loss of the coated C/C composites is considered to be related with the penetration crack generated during the oxidation of the coating.

Key words: Carbon/Carbon composites; mass loss; oxidation; magnetron sputtering

Carbon/Carbon(C/C) composites are noted for their high strength-to-weight ratio and low density, as well as their good mechanical properties at elevated temperature[1]. These characteristics make them appeal to the aircraft and aerospace fields as the thermal structural components[2]. However, the easy oxidation of C/C at temperatures above 454 ℃ greatly limits their applications in oxygen-containing atmosphere[3]. Much effort has been made to prevent oxidation of C/C composites. Current attempts to solve the oxidation problem of C/C composites are usually on surface protection with oxidation resistant coatings, especially multilayer coatings[1-3].

SiC is usually applied as an bonding and internal buffer layer owing to its low coefficient of thermal expansion (CET), good compatibility with C/C composites and surviving under an oxidation environment below 1600 ℃[4,5]. MoSi$_2$ is well recognized for its high melting point and outstanding corrosion resistance at high temperature[6]. Consequently, the SiC/MoSi$_2$ coating system was widely used to prevent the oxidation of C/C matrix.

Up to now, numerous ways such as pack cementation[7,8], hydrothermal electrophoretic deposition[9], supersonic plasma spraying[10], slurry[11] and chemical vapor deposition[12] have been applied to fabricate SiC/MoSi$_2$ coating on C/C surface to protect it from oxidation. All of these methods are based on a pack cementation method, thereby obtaining a gradient SiC layer with the concentration of Si element decreasing and the C element increasing gradually in the interface of C/C which can relax the thermal stress and reduce the possibility of crack generation during oxidation[13]. However, the coating thickness are difficult to control by the pack cementation method. Moreover, the experimental condition of pack cementation is so harsh (usually has to be carried out above 1800 ℃[14]) that it attenuates serious carbon fiber properties and therefore degrades the mechanical performance of C/C matrix.

Conversely, magnetron sputtering deposition has been demonstrated to be a good low-temperature and environmental method[15], which not only does less damage

---

Received date: October 15, 2015

Corresponding author: Fu Wenbin, Master, School of Materials Science and Engineering, Central South University, Changsha 410083, P. R. China, E-mail: 593760968@qq.com

to substrate but also can meet the precise requirements for the evenness and thickness of the coating by controlling deposition time. However, as far as the authors know, little work has been performed on SiC/$MoSi_2$ coating prepared on C/C surface by the magnetron sputtering method to evaluate their oxidation resistance.

According to the research of M. Lattemann and S. Ulrich[16], the alternating multilayer is beneficial to the decrease of the residual stress and the enhancement of the film toughness. Therefore, in the present work, a SiC/$MoSi_2$ coating combined in the alternating multilayer concept was prepared on the C/C composites by the magnetron sputtering method, and the microstructure, oxidation protective ability and mechanism of the coating in air at 1500 ℃ were investigated.

1 Experiment

Small specimens (10 mm×10 mm×10 mm) used as substrates were cut from a 2D C/C composite bulk with a density of 1.60 g/cm^3. All specimens were hand-abraded using 400 grit SiC paper, then cleaned ultrasonically with acetone and dried at 100 ℃ for 2 h.

The alternating multilayer coating structure was designed as shown in Fig.1, which was prepared on C/C composites by the magnetron sputtering method. Fig.2 shows the magnetron sputtering system layout. A direct current (DC) and middle-frequency (MF) sputtering technique were used in the SiC and $MoSi_2$ coatings deposition. 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 distance between target and substrate was about 80 mm, the deposition temperature was fixed at 200 ℃ and the bias was set to 100 V. Prior to deposition, the specimens were cleaned by argon ion etching for 20 min. Sputter deposition was performed with a twin-SiC target (length of 300 mm, width of 75 mm, thickness of 8 mm, 99.99% purity) using an MF input power of 800 W and a $MoSi_2$ target (length of 300 mm, width of 75 mm, thickness of 6 mm, 99.99% purity) using an DC input power of 1200 W. The deposition gas pressure of SiC and $MoSi_2$ was 0.65 Pa and 0.55 Pa, respectively. The deposition rate of SiC and $MoSi_2$ was 1 μm/h and 7 μm/h, respectively, which was measured by cross-sectional scanning electron microscopy and ellipsometry. Therefore, we can set deposition time as follows: t_0, t_1, t_2 was 35, 1 and 1 h, respectively (t_0, the deposition time of layer 0; t_1, the deposition time of layer 1; t_2, the deposition time of layer 2). The coating cycles were 14 and the outmost layer was $MoSi_2$ as shown in Fig.1. After deposition, the specimens were processed with a sol-gel method to obtain a denser coating surface.

The oxidation behavior of specimens, with and without coatings, was evaluated by static oxidation in air at 1500 ℃ using an electrical furnace. After the furnace was heated up to 1500 ℃, the specimens were moved into the hot zone of the electrical furnace, whereafter (at the designated time 60 min) they were taken out and cooled to room temperature for weighing. Mass of the specimens was measured by an electronic precision balance with sensitivity of ±0.1 mg. The mass loss (Δw) of specimens were calculated using Eq.(1).

$$\Delta w = (m_0 - m_1)/S \qquad (1)$$

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; and S is the surface area of the sample. The final mass loss of specimens was the average oxidation rate of three specimens.

The crystalline structure of the coating was measured with X-ray diffraction (XRD). The morphologies of the specimens and the element distribution of the coatings were analyzed by scanning electron microscopy (SEM), equipped with energy dispersive spectroscopy (EDS).

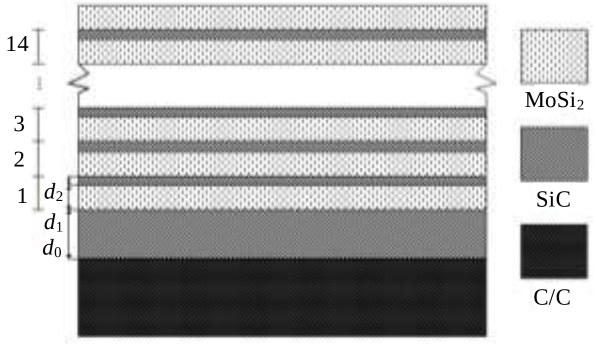

Fig.1 Schematic structure of the alternating $MoSi_2$/SiC multilayer coating (where d_i is the thickness of each layer: d_0=35 μm, d_1=7 μm, d_2=1 μm)

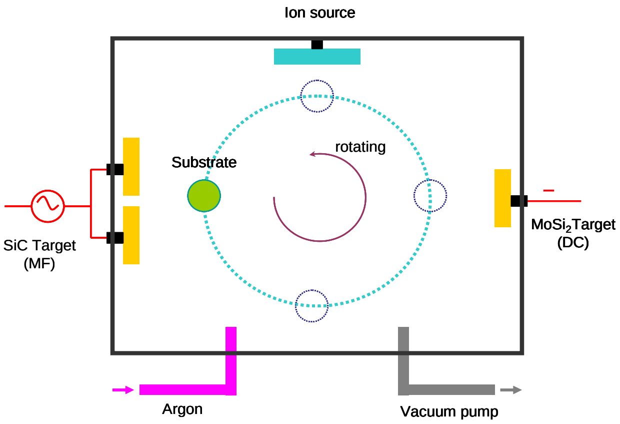

Fig.2 Schematic diagram of the deposition system

2 Results and Discussion

2.1 Microstructure of the as-received coating

A typical surface image of C/C composites is present in Fig.3. The surface of C/C composites is coarse, many grooves and big holes can been seen and some holes are even more than 50 μm in diameter, which has a great influence on the morphology of the coating.

The surface morphology of the coated C/C composites is shown in Fig.4a. It can be seen that the coating is compact and smooth, and the grains are spherical with uniform size. A few cavities resulted from those as-noted big holes of the C/C matrix surface can be observed as well, which is not favorable to protecting C/C matrix. Consequently, a sol-gel method is adopted to fill the cavities and the surface morphology of the coating after sol-gel process is shown in Fig.4b.

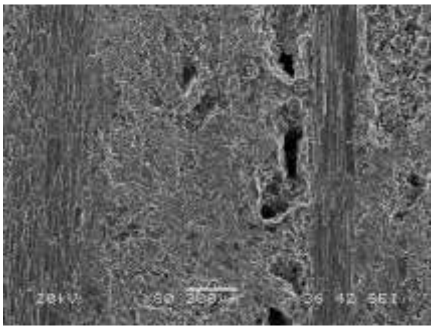

Fig.3 Surface micrograph of as-received C/C composites

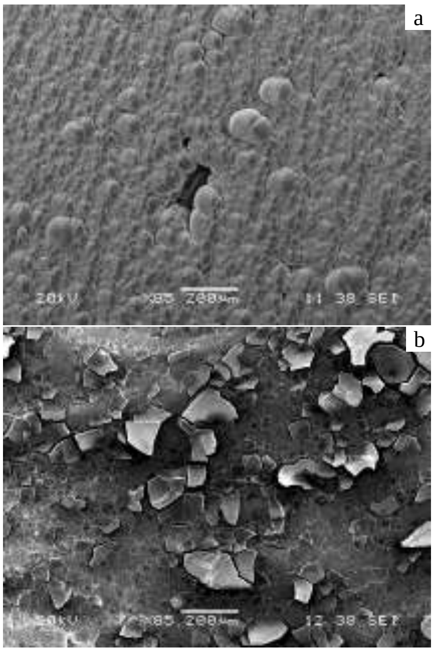

Fig.4 Surface micrographs of the coated C/C composites: (a) before sol-gel process and (b) after sol-gel process

The cross-section morphology of the coated C/C composites is shown in Fig.5. It can be found that the evenness and uniformity of the coating is very good (Fig.5a). The whole coating is about 155 μm in thickness (SiC bonding layer is about 35 μm, SiC/ $MoSi_2$ alternating multi-layer is about 120 μm), which is completely consistent with the coating thickness as we designed in

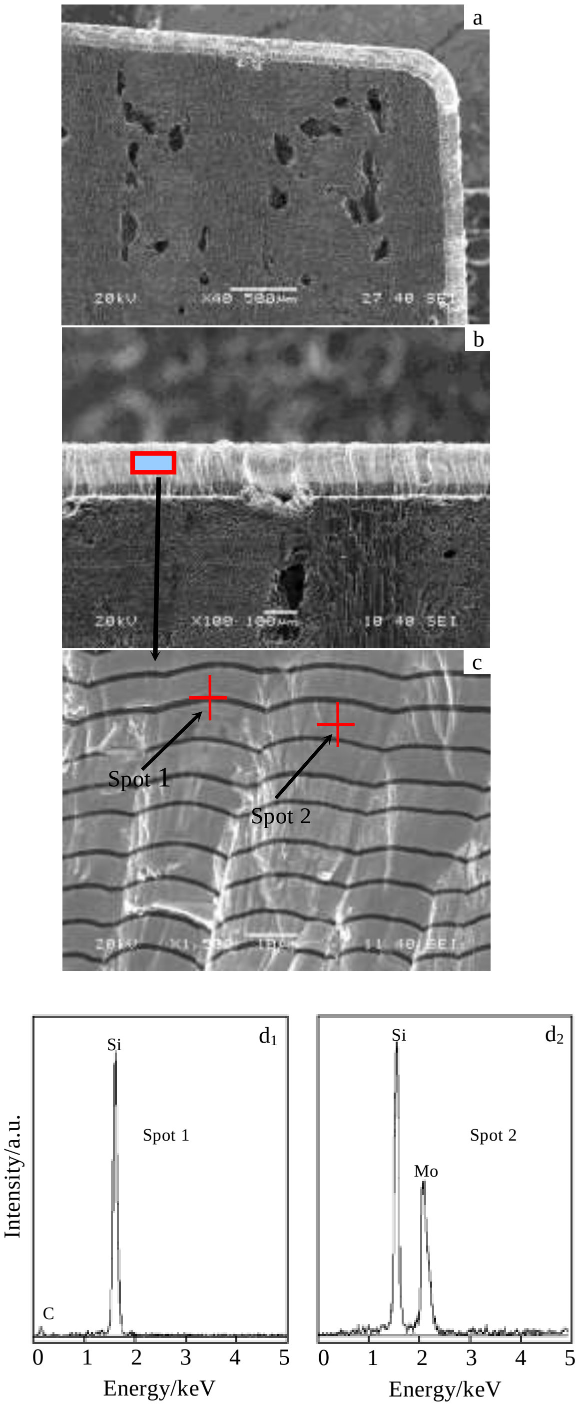

Fig.5 SEM micrographs (a~c) and EDS spectra of spot 1 (d_1) and spot 2 (d_2) of the cross-section of the coating

Fig.1, indicating that the coating thickness can be controlled precisely by setting deposition time using the magnetron sputtering method (Fig.5b). It is also clearly observed that SiC and $MoSi_2$ grains are grown into the surface normal direction, showing columnar microstructure typical for that of 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. From Fig.5c, we can find that there are two kinds of layers characterized as black (Spot 1) and grey (Spot 2). By EDS analysis (Fig.5d), the black and grey layers can be distinguished as SiC and $MoSi_2$ (thickness of SiC layer is about 1 μm, and $MoSi_2$ about 7 μm), respectively, which accords with the designed structure (Fig.1). In addition, compared with the research of Zhang et al[17], the interface between the C/C matrix and the coating is obvious, which shows that the adhesion strength of the coating is relatively poor.

XRD patterns from the sample before and after the sol-gel process are shown in Fig.6. Before the sol-gel process, no detectable typical $MoSi_2$ peaks can be seen and this indicates that the coating is amorphous or poorly crystalline, which results from the short deposition time of the outmost layer (too short to completely crystallize). After the sol-gel process, the $MoSi_2$ peak becomes broader and a weak broad SiO_2 peak appears.

2.2 Oxidation behavior

Fig.7 illustrates the oxidation resistance of C/C and coated C/C composites at 1500 ℃ in air. It can be found that the bare C/C composite has a poor oxidation resistance, and its mass loss percent is up to 28.8×10^{-2} g/cm^2 after oxidation at 1500 ℃ for 60 min. Whereas the coated C/C exhibits a superior oxidation resistance, and its mass loss is only 3.2×10^{-2}g/cm^2. Therefore, the as-prepared coating can provide oxidation protection for C/C composites at 1500 ℃ for 60 min.

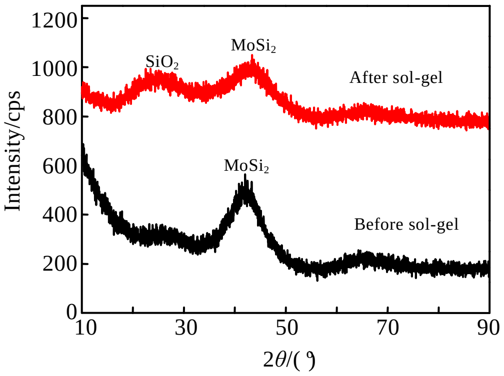

Fig.6 Surface XRD patterns of the coated C/C composites

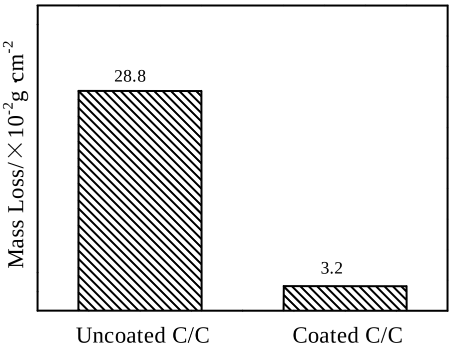

Fig.7 Oxidation resistance of C/C and coated C/C composites in air at 1500 ℃ for 60 min

In oxygen-containing environment, the coated C/C samples would react with oxygen as follows:

$$2SiC_{(s)} + 3O_{2(g)} \rightarrow 2SiO_{2(s)} + 2CO_{(g)} \tag{1}$$

$$SiC_{(s)} + 2O_{2(g)} \rightarrow SiO_{2(s)} + CO_{2(g)} \tag{2}$$

$$5MoSi_{2(s)} + 7O_{2(g)} \rightarrow 2Mo_5Si_{3(s)} + 4SiO_{2(s)} \tag{3}$$

$$2MoSi_{2(s)} + 7O_{2(g)} \rightarrow 2MoO_{3(g)} + 4SiO_{2(s)} \tag{4}$$

$$2C_{(g)} + O_{2(g)} \rightarrow 2CO_{(g)} \tag{5}$$

$$C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{6}$$

Reactions (1)~(3) lead to net mass gain, and reactions (4)~(6) cause net mass loss. Therefore, the mass loss of the coated specimens during oxidation mainly results from the oxidation of the C/C substrate and the volatilization of oxidation production (SiO_2, MoO_3).

Fig.8 shows the surface image of the coated C/C composites after oxidation at 1500 ℃ in air for 60 min. It can be found that a smooth glass film is formed on the coating surface. Besides, we can also find several microcracks caused by shrinkage of amorphous silica during rapid cooling (the coating would suffer tensile stress because of its larger thermal expansion coefficient than that of C/C composites) and holes left by the escape of gases (MoO_3 with high vapor pressure at high temperatures[18]) on the surface of the coating. Holes are not considered as the main reason of the mass loss of the coated specimens, because the coating under these holes would be oxidized again and a new glass phase would be produced.

From Fig.9, the XRD pattern of the coating after oxidation at 1500 ℃ for 60 min shows that the as-noted glass layer is SiO_2 glass, which is produced due to the oxidation of SiC and $MoSi_2$ (as shown from Eqs.(1)~(4)), and can efficiently protect C/C matrix from oxidation owing to its very low oxygen permeability. Compared with the XRD patterns of the coating before oxidation (Fig.6), Mo_5Si_3, a new phase appears, which is in accordance with the reaction (4). Meanwhile, the $MoSi_2$ peak becomes sharper than that of Fig.6, indicating that the crystallinity degree of the coating increases after oxidation.

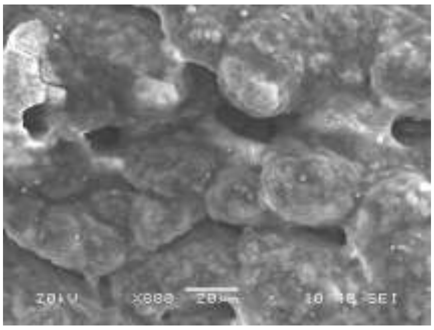

Fig.8 Surface SEM micrograph of the coated specimens after oxidation at 1500 ℃ for 60 min

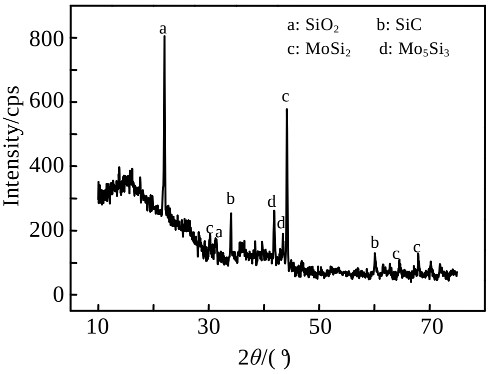

Fig.9 Surface XRD patterns of the coated C/C composites after oxidation at 1500 ℃ for 60 min

Fig.10 shows the cross-section images of the coated C/C composites at different magnifications after oxidation at 1500 ℃ in air for 60 min. It can be seen that the outermost layer of the coating is covered by a glass film, which is in accordance with the above description. No debonding are detected in the coating, which shows high bonding strength and good thermal compatibility between layer-to-layer. The glass film is thin and the whole coating thickness has no obvious change, which can be inferred that the depletion of the coating is slight and only the surface of the coating is oxidized. In addition, a penetration crack along the boundary of two columnar grains can be found in the coating and the oxidation attacking of C/C matrix happens beneath the cross-crack. Therefore, the penetration cracks provide a channel for the diffusion of oxygen and are the main reason for the oxidation of C/C substrate. The further research about how to eliminate the penetration cracks is needed.

2.3 Oxidation mechanism of the coated C/C composites

According to the analysis of the micro-morphology of the $SiC/MoSi_2$ multilayer coating and the oxidation behavior of the $SiC/MoSi_2$ multilayer coated C/C composites, the oxidation mechanism of the $SiC/MoSi_2$ multilayer coated C/C composites can be proposed. Fig.11 shows the oxidation mode of the coated C/C composites. When oxidation begins, both coating and substrate expand due to the thermal effect, which results in two results: On the one hand, the interaction between columnar grain boundaries weakens even therefore leading to the generation of crack along the grain boundaries; but on the other hand, the coating obtains compressive stress because of its larger CTE than that of C/C composites and the compressive stress distributes in a trend as the picture shows, which contribute to inhibit the propagating of microcrack, and the better adhesion between the coating and the C/C substrate, the better this inhibition effect. Meanwhile, the columnar grain boundaries is prone to attacking by oxygen in oxygen-containing environment, which would result in the fracture and discontinuity of the grain boundary. Despite generation only on the surface of the coating in the initial oxidation stage, the microcrack, as the oxidation proceeds, will expand along the as-noted fractured and discontinuous grain boundary and finally become a penetration crack, which provides a channel for the diffusion of oxygen. By this time, the glass layer on the surface of the coating is too thin to cover the crack completely. Consequently, C/C matrix will be oxidized by oxygen diffusing through the penetration crack at 1500 ℃ before the crack is fully sealed. After the top of has the penetration crack is blocked by SiO_2

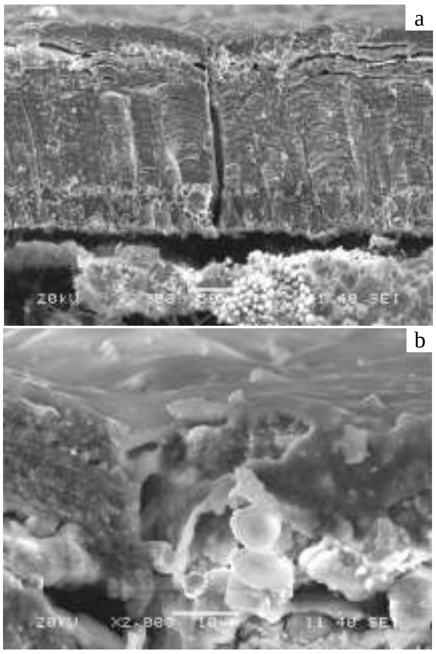

Fig.10 Cross-section SEM micrographs of the coated specimens after oxidation at 1500 ℃ for 60 min: (a) low magnification and (b) high magnification

glass, oxygen had to pass through the glass layer to reach the interface between coating and C/C matrix, so C/C matrix could be protected efficiently. However, even though the glass layer has a very low oxygen permeability, it is not so thick that a considerable number of oxygen gas could diffuse through it to reach the surface of C/C matrix with the increase of oxidation time, which causes severe oxidation of the C/C composites.

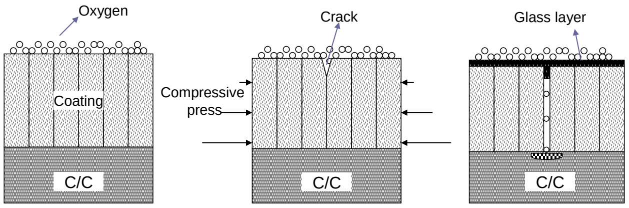

Fig.11 Oxidation mode of the coated C/C composites

3 Conclusions

1) The $SiC/MoSi_2$ alternating multilayer coating is prepared on C/C composites by a magnetron sputtering method. The as-received coating exhibits compact and columnar structure, outstanding evenness and uniformity and its thickness could be effectively controlled by setting deposition time.

2) After oxidation at 1500 ℃ for 60 min, the mass loss of the C/C sample with this coating is only 3.2×10^{-2} g/cm^2. The oxidation of C/C matrix is considered to be caused by the formation of penetration cracks along the columnar grain boundaries during the oxidation of the coating.

References

1 Golecki I, Morris R C, Narasimhan D *et al. Applied Physics Letters*[J], 1995, 66: 2334
2 Webster J D, Westwood M E, Hayes F H *et al. Journal of the European Ceramic Society*[J], 1998, 16: 2345
3 Huang J F, Zeng X R, Li H J *et al. Carbon*[J], 2004, 42: 1517
4 Nathan S Jacobson. *Journal of the American Ceramic Society*[J], 1993, 76: 3
5 Zhu Q S, Qiu X L, Ma C W *et al. Carbon*[J], 1999, 37: 1475
6 Li H J, Zhang Y L, Fu Q G *et al. Carbon*[J], 2007, 45: 2692
7 Fu Q G, Li H J, Wang Y J *et al. Corrosion Science*[J], 2009, 51: 2450
8 Zhang Y L, Li H J, Qiang X F *et al. Corrosion Science*[J], 2011, 53: 3840
9 Fu Q G, Li H J, Zhang Z Z *et al. Corrosion Science*[J], 2010, 52: 1879
10 Wu H, Li H J, Ma C *et al. Journal of the European Ceramic Society*[J], 2010, 30: 3267
11 Huang M, Li K Z, Li H J *et al. Carbon*[J], 2007, 45: 1105
12 Wu H, Li H J, Wang Y J *et al. Journal of Inorganic Materials*[J], 2009, 24: 392
13 Fu Q G, Li K Z, Li H J *et al. Carbon*[J], 2006, 44: 3348
14 Qiang X F, Li H J, Zhang Y L *et al. Corrosion Science*[J], 2011, 53: 523
15 Brauer G, Szyszka B, Vergohl M *et al. Vacuum*[J], 2010, 84: 1354
16 Lattemann M, Ulrich S. *Surface & Coatings Technology*[J], 2007, 201: 5564
17 Zhang Y L, Li H J, Yao X Y *et al. Corrosion Science*[J], 2011, 53: 207
18 Zhang Y L, Li H J, Hu Z X *et al. Corrosion Science*[J], 2013, 72: 150

$SiC/MoSi_2$高温抗氧化涂层的制备及性能探究

符文彬 [1,2]，代明江 [2]，韦春贝 [2]，赵明纯 [1]，胡 亮 [1]，侯惠君 [2]，林松盛 [2]
(1. 中南大学，湖南 长沙 410083)
(2. 广州有色金属研究院，广东 广州 510650)

摘 要：采用磁控溅射法在 C/C 复合材料表面制备 $SiC/MoSi_2$ 抗氧化涂层，并利用 SEM、XRD 以及 EDS 等测试手段对抗氧化涂层的组织结构、抗氧化性能和抗氧化机制进行了研究。结果表明，用磁控溅射法制得的涂层结构致密、厚度均匀可控，呈柱状晶。在 1500 ℃静态氧化 60 min 后涂层试样的氧化质量损失为 3.2×10^{-2} g·cm^{-2}，涂层表现出优异的抗氧化保护性能。导致 C/C 基体被氧化失重的主要原因是涂层中沿晶界产生的贯穿裂纹为氧气进入基体表面提供了通道。

关键词：C/C 复合材料；质量损失；氧化；磁控溅射

作者简介：符文彬，男，1988 年生，硕士，中南大学材料科学与工程学院，湖南 长沙 410083，E-mail: 593760968@qq.com