Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 39 (2013) 9797–9801

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

An $AlPO_4$–SiC–$MoSi_2$/SiC oxidation protective coating on carbon/carbon composites by pulse arc discharge deposition

Hao Wei, Huang Jian-Feng*, Cao Li-Yun, Yin Li-Xiong, Wu Jian-Peng, Fei Jie, Huang Yi-Cheng, Yang Liu-Qing

Key Laboratory of Auxiliary Chemistry & Technology for Chemical Industry, Ministry of Education, School of Material Science and Engineering, Shaanxi University of Science & Technology, Xi'an 710021, Shaanxi, PR China

Received 1 April 2013; received in revised form 9 May 2013; accepted 13 May 2013
Available online 28 May 2013

Abstract

A new type of oxidation-protective $AlPO_4$–SiC–$MoSi_2$ coating for SiC pre-coated carbon/carbon composites (SiC–C/C) was prepared by a novel pulse arc discharge deposition process. XRD and EDS line scanning analyses show that the phases of the multi-layer coatings are composed of $AlPO_4$, nano-SiC, SiO_2 and $MoSi_2$ and the bonding coating between the coating and C/C composites is composed of SiC and Si. In addition, SEM images of the surface and the cross-section of the coating also display the dense microstructure. Oxidation test shows that the as-prepared multi-coating characterized by excellent thermal shock resistance on the surface of C/C composites during exposure to an oxidizing atmosphere at 1873 K can effectively protect the C/C composites from oxidation for 44 h with a weight loss of 1.57%.

Keywords: D. SiC; $AlPO_4$; $MoSi_2$; Carbon/carbon composites; Pulse arc discharge deposition

1. Introduction

Carbon/carbon (C/C) composites exhibit outstanding mechanical properties, particularly at high temperatures. However, it is oxidized dramatically above 773 K, which limits its broad applications. It is therefore important to increase the resistance of the materials towards the air oxidation at high temperature [1,2]. Coating is an effective method for protecting C/C composites from oxidation [3]. Especially, multi-layer coatings are considered as one of the best choices to protect C/C composites from oxidation at high temperature [4,5]. SiC ceramic has been widely used as the best bonding layer for C/C composites, not only because of its good compatibility with C/C composites, but also its good physical and chemical adaptability of coating to the outer ceramics layer [3,6]. Unfortunately, microcracks develop due to the mismatch of thermal expansion coefficient between SiC and C/C substrates, which cannot be self-cured by themselves [7]. A multi-layer coating is to be a feasible way to solve this problem.

So far, many multi-layer coatings, such as $MoSi_2$–$CrSi_2$–Si [8], C-$AlPO_4$–mullite [7] and $MoSi_2$–SiC–B [9] coatings have been developed by some researches. However, microcracks can be further developed due to the mismatch of thermal expansion coefficient between the SiC coating and the outer coating, which leads to the decrease in oxidation resistance of the multi-coating. In order to solve this problem, in recent papers, mullite ceramic coatings were developed to protect carbon materials and SiC by employing hydrothermal electrophoretic deposition [7,10], pack cementation [1], and plasma spraying technique [11].

In the present work, a new kind of multi-composition coating, including $AlPO_4$, nano-SiC and $MoSi_2$ on SiC–C/C composites was firstly produced by a novel method of pulse arc discharge deposition. The structure and oxidation protection properties of the coating were primarily investigated.

2. Experimental

Small specimens ($10 \times 10 \times 10\ mm^3$) used as substrates were cut from bulk 2D C/C composites with a density of 1.747 g/cm^3. The specimens were hand-polished using 300-grit SiC paper, then cleaned with distilled water and dried

---

*Corresponding author. Tel./fax: +86 29 86168802.
E-mail addresses: haoweimaster@163.com (W. Hao), huangjfsust@126.com, huangjf@sust.edu.cn (J.-F. Huang).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.05.052

at 333 K for 2 h. The SiC coating was then applied through the pack cementation procedure. Details for the preparation of the bonding SiC coating were reported in Ref. [12].

For the pulse arc discharge deposition process, cristobalite type of $AlPO_4$ (C-$AlPO_4$), nanometer SiC powders (nano-SiC) and $MoSi_2$ powders with 1:1:1 of the mass ratio of $AlPO_4$/SiC/$MoSi_2$ were dispersed in 170 ml isopropanol with an ultrasonic bath for 30 min (the ultrasonic power was kept at 100 W) with a later magnetic stirring for 24 h. Iodine used as a charging agent was added into the suspension with another ultrasonic bath for 30 min (the ultrasonic power was kept at 100 W) followed by the constant magnetic stirring for 24 h. Next, the above suspension was transferred into a hydrothermal autoclave reported in Refs. [7,12]. The anode of the autoclaves was a graphite substrate ($20 \times 10 \times 3\ mm^3$) and the SiC–C/C substrate was fixed to the cathode of the autoclave. After being sealed, the autoclave was put into a furnace and the pulse deposition voltage, the pulse frequency and the pulse duty ratio were kept at 380 V, 1000 Hz, and 70% respectively. During the deposition process, the temperature was kept at 393 K. After 30 min of deposition, the autoclave was taken out of the furnace and cooled down naturally to room temperature. Then, the samples were dried at 333 K in air for 2 h. Finally, the homogeneous $AlPO_4$–SiC–$MoSi_2$ coating with SiC–C/C composites was obtained.

The as-coated specimens were heated at 1873 K in air in an electrical furnace to investigate the isothermal and thermal cycling oxidation behavior. The morphology, the crystalline structure, and the element composition of the multi-composition coatings were evaluated using a scanning electron microscope (SEM, JSM-6390A), an X-ray diffractometer (XRD, Rigaku D/max-3C) and an energy-dispersive spectroscopy (EDS). The isothermal oxidation tests of the coated samples were carried out at 1873 K in an electrical furnace. The cumulative weight change of the group of five samples after each thermal cycle was measured by an electrical balance with a sensitivity of ±0.1 mg. The mass loss was calculated by the following equations. The end mass loss is from average value of the group of five samples after oxidation at high temperature for a certain time.

$$WL\% = (m_0 - m_i)/m_0 \times 100\% \qquad (A.1)$$

$$WL = (m_0 - m_i)/s \times 100\% \qquad (A.2)$$

$$WLR = (m_0 - m_i)/(st) \times 100\% \qquad (A.3)$$

Among which m_0 is the original mass of the coated C/C composites, m_i is the mass of the coated C/C composites after oxidation at high temperature for a certain time, t is the oxidation time and s is the surface area of the specimen. $WL\%$ is weight loss, WL is weight loss per unit area, and WLR is weight loss rate.

3. Results and discussion

3.1. XRD analysis of the coating

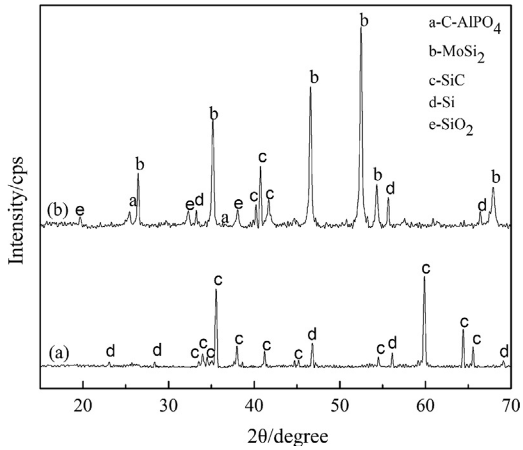

Fig. 1. XRD patterns of the bonding layer surface (a) and the multi-composition coating (b).

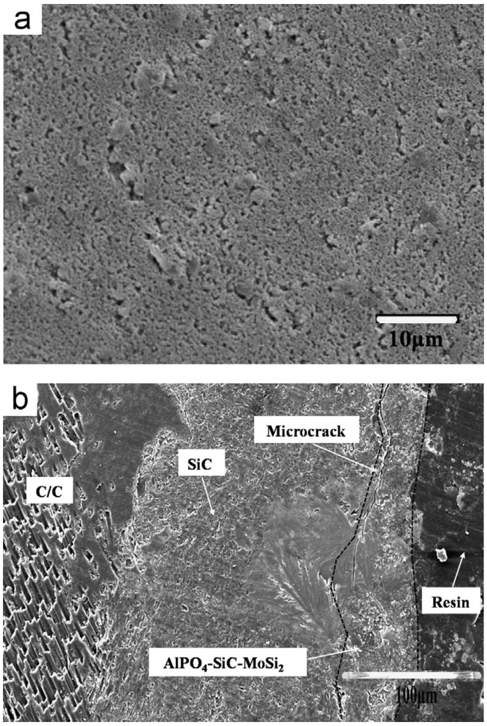

Fig. 2. SEM images of the multi-composition coating of surface (a) and cross-section (b).

Fig. 1 displays the XRD patterns of the bonding layer surface (Fig. 1(a)) and the outer coating (Fig. 1(b)) obtained by pack cementation and pulse arc discharge deposition, respectively. It shows that SiC and Si are generated in the bonding layer. In addition, the peak intensity of SiC is stronger than that of Si, indicating that the SiC is the main phase of the coating with good crystallization. Fig. 1(b) shows that the outer coating is composed of $AlPO_4$, SiC and $MoSi_2$ with a little SiO_2. $AlPO_4$, nano-SiC and $MoSi_2$ from the suspension and the Si phase comes from the bonding layer. The formation of SiO_2 in the coating may be due to the oxidation of Si or SiC during the arc discharge sintering process.

3.2. Morphologies of the multi-composition coating

The surface image of the as-prepared coating is shown in Fig. 2(a). It shows that a very dense and homogenous coating that composed of some small particles is achieved. No clear cracks and holes are observed on the multi-layer coating surface. This may be due to the arc discharge sintering process, which provides the sufficient energy with sintering for the densification of the as-prepared $AlPO_4$–SiC–$MoSi_2$ coating. Through SEM image of the cross-section shown in Fig. 2(b), we can find a dense cross-section and an obvious two-layer structure without microholes and penetrative cracks, which may be due to the good match in thermal expansion coefficient between the SiC bonding layer and the as-prepared coating. But the microcrack between the outer coating and the bonding layer is observed, which may be caused by the arc discharge sintering process leading to the generation of thermal stress between the two layers. The thickness of the as-prepared $AlPO_4$–SiC–$MoSi_2$ coating is about 90 μm.

Fig. 3 displays EDS element line scan analysis of the cross-section of the $AlPO_4$–SiC–$MoSi_2$/SiC multi-composition coating, showing the concentration distributions of C, O, Al, Si, P and Mo elements along the coating cross direction. It shows that the multi-composition coating could be divided into three parts, designated as A, B and C. Part A is the carbon/carbon composites matrix infiltrated by some Si element, attributing to the pack cementation process. Part B is the SiC bonding layer, and part C is the $AlPO_4$–SiC–$MoSi_2$ coating that well agrees with the experimental designation and XRD and SEM analyses.

3.3. Oxidation test of the coated C/C composites

The results of the isothermal oxidation test in air at 1873 K are shown in Fig. 4. After oxidation in air for 44 h, the weight

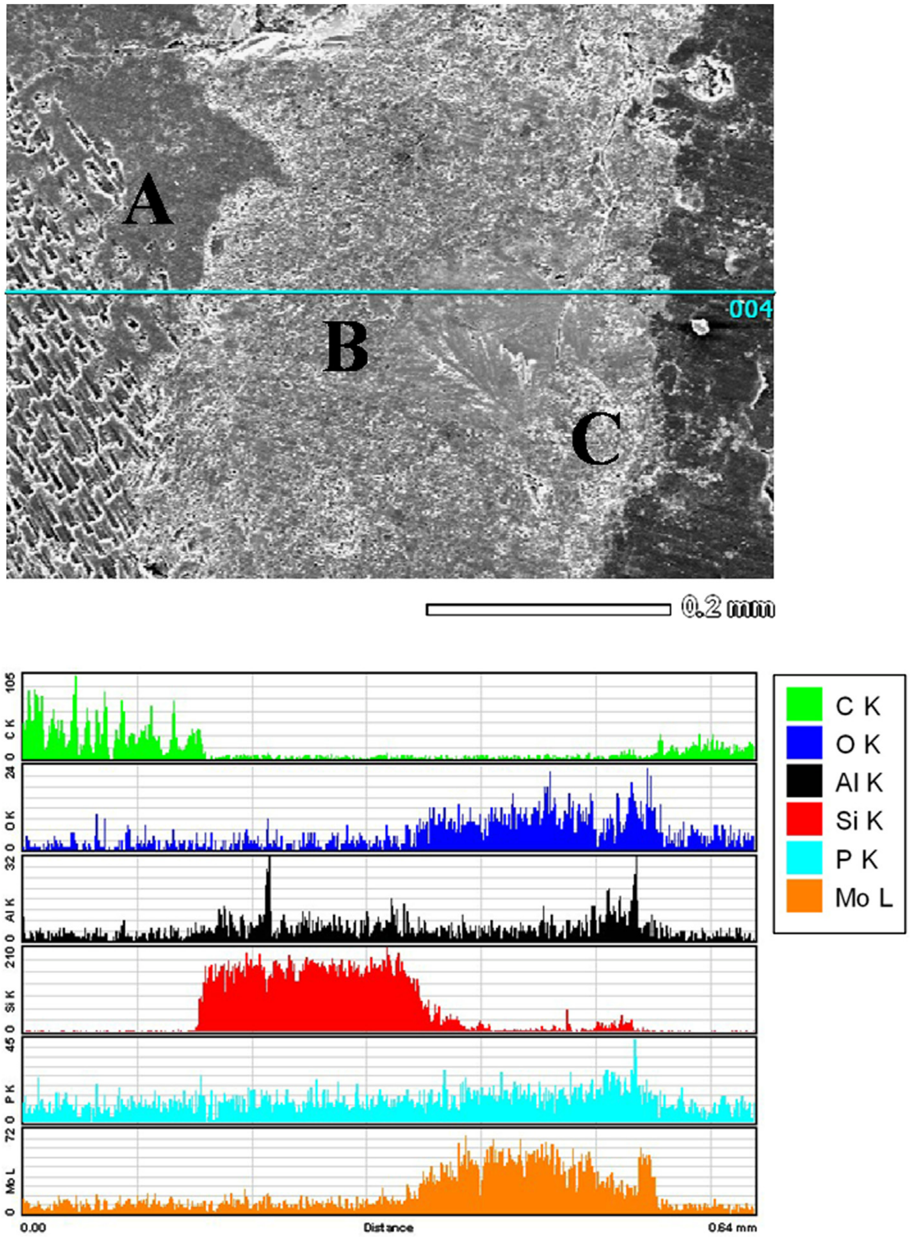

Fig. 3. EDS element line scan analysis of the cross-section of $AlPO_4$–SiC–$MoSi_2$/SiC multi-composition coating according to Fig. 2(b).

loss of the coated C/C composites is only 1.57% with the corresponding weight loss rate of 0.70×10^{-4} g/cm^2 h. The oxidation behavior of the coated C/C composites could be divided into four processes marked as A, B, C and D according to the oxidation curves (Fig. 4(a) and (b)). The weight loss equations for the oxidation curve (Fig. 4(a)) are shown as

$$WL = 0.00167 + 0.48835t - 0.05409t^2 \quad (\text{Process A}:\ 0 < t \le 4) \tag{A.4}$$

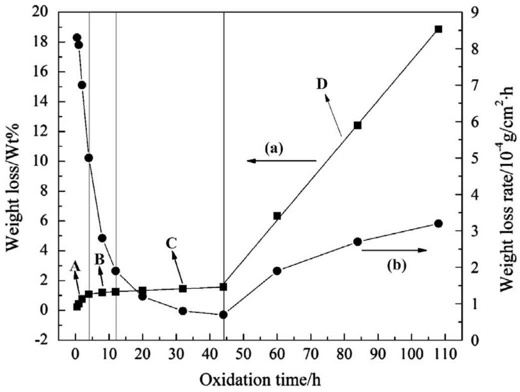

Fig. 4. Isothermal oxidation curves of the C/C composites with a multi-composition coating in air at 1873 K: (a) the relationship between weight loss and oxidation time; (b) the relationship between weight loss rate and oxidation time.

$$WL = 0.96 + 0.03625t - 9.375 \times 10^{-4}t^2 \quad (\text{Process B}:\ 4 < t \le 12) \tag{A.5}$$

$$WL = 1.1451 + 0.00963t \quad (\text{Process } C:\ 12 < t \le 44) \tag{A.6}$$

$$WL = -10.01697 + 0.2677t \quad (\text{Process } D:\ 44 < t \le 108) \tag{A.7}$$

where WL (g/cm^2) is the weight loss of the coated sample and t (h) is the oxidation time.

In less than 4 h, the weight loss of the samples with time follows a parabolic law and the obvious weight loss of 1.09% is detected (Process A) with corresponding weight loss rate of 5.00×10^{-4} g/cm^2 h. Additionally, SEM images reveal that the surface of the coating is harsh and rough with many micro-holes (Fig. 5(a)). The samples gain the weight due to the formation of SiO_2 phase [1]. As the increase of oxidation time, from 4 to 12 h (Process B), the sample loses weight slowly with passing time for the $AlPO_4$–SiC–$MoSi_2$ outer layer, which is found to gradually transform into the metaphosphate and silicate glass layer [7]. After 12 h oxidation at 1873 K, the surface of the coating is smooth (Fig. 5(b)). From 12 to 44 h (Process C), the weight loss rate of the sample is almost constant, which is due to the low oxygen permeation constant and the good self-cure ability of the thicker metaphosphate and silicate glass layer. However, microcracks and oxidation holes (Fig. 5(c)) are found generating in the coating at the oxidation time of 44 h, which may be due to the frequent

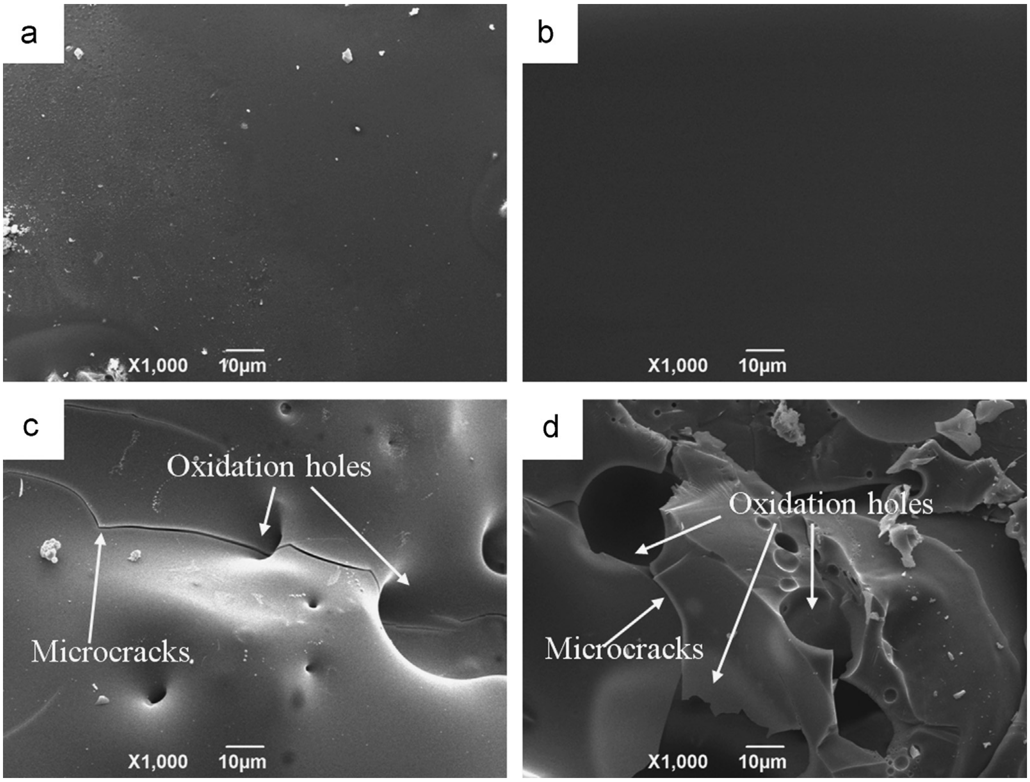

Fig. 5. Morphology images of $AlPO_4$–SiC–$MoSi_2$/SiC multi-composition coating surface after oxidation at 1873 K in air for different hours: (a) 4 h; (b) 12 h; (c) 44 h; (d) 108 h.

thermal shocks from high temperature to room temperature. Above 44 h (Process D), the as-generated microholes, micro-cracks and oxidation holes provide the channels for oxygen to attack the C/C matrix, which leads to the decrease in oxidation resistance of the coated sample (Fig. 5(d)). Additionally, the sample has endured thermal cycling between 1873 K and room temperature for 9 times without finding cracks and holes on the sample surface, indicating the excellent thermal shock resistance of the coating. The good oxidation resistance is attributed to the dense structure and the multi-composition of the coating.

4. Conclusions

Based on this work, it can be concluded that the $AlPO_4$–SiC–$MoSi_2$ multi-composition coating with a thickness of around 90 μm could be produced by pulse arc discharge deposition. The bonding phases between the coating and C/C composites are SiC and Si. The multi-composite coating characterized by excellent thermal shock resistance could effectively protect the C/C composites from oxidation at 1873 K for 44 h, and the corresponding weight loss rate of the coated C/C composites is only 0.70×10^{-4} g/cm^2 h.

Acknowledgments

This work has been supported by the National Natural Science Foundation of China (51272146 and 51172134), Natural Science Foundation of Shaanxi Province Educational Department (2010JK444 and 2010JM6017) and the Graduate Innovation Foundation of Shaanxi University of Science and Technology. The authors are also grateful to Mrs. Ren Huijun from Shaanxi University of Science and Technology for polishing the paper writing.

References

[1] J.F. Huang, X.R. Zeng, H.J. Li, X.B. Xiong, M. Huang, Al_2O_3–mullite–SiC–Al_4SiC_4 multi-composition coating for carbon/carbon composites, Materials Letters 58 (2004) 2627–2630.

[2] J. Zhao, L. Liu, Q.G. Guo, J.L. Shi, G.T. Zhai, Oxidation protective behavior of SiC/Si–$MoSi_2$ coating for different graphite matrix, Materials Letters 60 (2006) 1964–1967.

[3] Y.H. Chu, Q.G. Fu, H.J. Li, K.Z. Li, X. Zou, C.G. Gu, Influence of SiC nanowires on the properties of SiC coating for C/C composites between room temperature and 1500 °C, Corrosion Science 53 (2011) 3048–3053.

[4] James E. Sheehan, Oxidation protection for carbon fiber composites, Carbon 27 (1989) 709–715.

[5] X.F. Qiang, H.J. Li, Y.L. Zhang, Q.G. Fu, J.F. Wei, S. Tian, A modified dual-layer SiC oxidation protective coating for carbon/carbon composites prepared by one-step pack cementation, Corrosion Science 53 (2011) 523–527.

[6] X.Y. Yao, H.Y. Li, Y.L. Zhang, J.J. Ren, D.J. Yao, J. Tao, A SiC/ZrB_2–SiC/SiC oxidation resistance multilayer coating for carbon/carbon composites, Corrosion Science 57 (2012) 148–153.

[7] K.T. Wang, L.Y. Cao, J.F. Huang, J. Fei, B.Y. Zhang, Microstructure and oxidation resistance of C–$AlPO_4$–mullite coating prepared by hydrothermal electrophoretic deposition for SiC–C/C composites, Ceramics International 39 (2013) 1037–1044.

[8] H.J. Li, T. Feng, Q.G. Fu, H. Wu, X.T. Shen, Oxidation and erosion resistance of $MoSi_2$–$CrSi_2$–Si/SiC coated C/C composites in static and aerodynamic oxidation environment, Carbon 48 (2010) 1636–1642.

[9] Q.G. Fu, X. Zou, Y.H. Chu, H.J. Li, J.Z. Zou, C.G. Gu, A multi-layer $MoSi_2$–SiC–B coating to protect SiC-coated carbon/carbon composites against oxidation, Vacuum 86 (2012) 1960–1963.

[10] T. Damjanovic, Chr. Argirusis, B. Jokanovic, G. Borchardt, K. Moritz, E. Müller, R. Herbig, R. Weiss, Oxidation protection of C/C–SiC composites by an electrophoretically deposited mullite precursor: cyclic thermogravimetric analysis, Journal of the European Ceramic Society 27 (2007) 1299–1302.

[11] Y.R. Niu, X.B. Zheng, C.X. Ding, H. Li, C. Hu, M.S. Ren, J.L Sun, Microstructure characteristics of silicon carbide coatings fabricated on C/C composites by plasma spraying technology, Ceramics International 37 (2011) 1675–1680.

[12] J.F. Huang, M. Liu, B. Wang, L.Y. Cao, C.K. Xia, J.P. Wu, SiC_n/SiC oxidation protective coating for carbon/carbon composites, Carbon 4 (2009) 1198–1201.