[Article]

doi: 10.3866/PKU.WHXB201228239

www.whxb.pku.edu.cn

两步法制备具有自愈合能力的纯 SiC 涂层

陈 旻^{1,2} 王成国^{2,*} 赵 伟²⁽¹⁾ 山东大学材料液固结构演变与加工教育部重点实验室, 济南 250061; ⁽²⁾ 山东大学碳纤维工程技术研究中心, 济南 250061)

摘要: 为了提高碳/碳(C/C)复合材料的抗氧化性能, 通过两步法在基体表面制备了具有自愈合能力的纯 SiC 涂层. 首先, 通过高含氢硅油(H-PSO)的高温热解在基体表面引入 SiC 纳米线, 然后通过高温渗 Si, 在碳材料表面生成厚度约为 100–200 μm 的涂层. 通过 X 射线衍射(XRD)、扫描电子显微镜(SEM)表征了所制备的涂层形貌及相组成, 并对所制备的试样进行了氧化实验. 实验结果表明: 涂层是由纯 SiC 构成的, 且具有一定的自愈合能力; 所制备的试样在 1400 $^{\circ}\text{C}$ 下氧化 4 h, 失重仅为 0.71%, 抗氧化性能得到提高.

关键词: C/C 复合材料; SiC 纳米线; SiC 涂层; 抗氧化性能; 自愈合

中图分类号: O647

Fabrication of a Self-Healing Pure SiC Coating by a Two-Step Technique

CHEN Yang^{1,2} WANG Cheng-Guo^{2,*} ZHAO Wei²⁽¹⁾ Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, P. R. China; ⁽²⁾ Carbon Fiber Engineering Research Center, Shandong University, Jinan 250061, P. R. China)

Abstract: A self-healing pure SiC coating was prepared on a carbon/carbon (C/C) composite by a two-step technique to protect the C/C composite from oxidation. First, SiC nanowires were obtained on the substrate surface by the thermal decomposition of hydrogen silicone oil (H-PSO). Second, a coating with a thickness of 100–200 μm was produced by infiltrating with silicon at high temperature in an argon atmosphere. The morphology and phase composition of the coating were observed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Oxidation tests were carried out on specimens and the results indicated that the obtained coating consisted of pure SiC and had a certain self-healing ability. The SiC self-healing coating significantly increased the antioxidant properties of the C/C composites and it protected the C/C composites from oxidation at 1400 $^{\circ}\text{C}$ in air over 4 h with a corresponding mass loss of only 0.71%.

Key Words: C/C composite; SiC nanowire; SiC coating; Oxidation resistance; Self-healing

1 Introduction

C/C composites are widely used in many industries, including but not limited to aerospace, metallurgy, pharmaceutical, biotechnology, and chemical industries, due to their high specific strength, high specific modulus, low linear expansion coefficient, and excellent resistance to wear.^{1,2} However, C/C composites are prone to be oxidated above 370 $^{\circ}\text{C}$ and the oxi-

dation rate increases rapidly over 500 $^{\circ}\text{C}$. Oxidation mass loss makes their properties degrade substantially, which limits their broad applications at high temperatures.^{3–5} The key to solve this question lies in improving the oxidation resistance of C/C composites at high temperatures. SiC coating can cut carbon materials off from the oxygen gas, which improves oxidation resistance remarkably. Besides that, it can also prevent corro-

Received: July 18, 2011; Revised: October 19, 2011; Published on Web: October 28, 2011.

*Corresponding author. Email: sduwangchg@gmail.com; Tel/Fax: +86-531-88395322.

The project was supported by the National Key Basic Research Program of China (973) (2011CB605601) and International Technical Cooperation Projects, China (2009DFR50600).

国家重点基础研究发展规划项目(973) (2011CB605601)和国际科技合作项目(2009DFR50600)资助

© Editorial office of *Acta Physico-Chimica Sinica*

sion and significantly increase impact strength.^{6–8} In recent years, a great deal of effort has been devoted to the preparation of SiC coatings.^{9–13} In order to decrease the mismatch of coefficient of thermal expansion (CTE) between coating and C/C substrates, researchers add heterogeneous elements in the preparation, such as Al₂O₃, CrSi₂, and MoSi₂.^{14–16} However, heterogeneous elements introduced during preparation of the SiC coating could pollute the service environment at high temperatures, thus disabling the coating in some applications. SiC nanowires have great potential as a reinforcement material in ceramics because of their excellent properties, such as high thermal stability, high strength, and high thermal conductivity.¹⁷ They are expected to provide efficient protection for SiC coated C/C composites and assure the purity of SiC coating.

In this paper, a self-healing pure SiC coating was prepared on C/C composite by a two-step technique. The SiC nanowires were first obtained on the surface of C/C substrates by thermal decomposition of hydrogen silicone oil (H-PSO), and then the specimens were coated with SiC by a simple embedding technique. The structure and resistance to oxidation in air of the as-received coating was investigated.

2 Experimental

2.1 Preparation of coating

Small C/C composites (density: 1.76 g·cm⁻³, Zhuoyuan Carbon Fiber Composite Co. Ltd., Yantai, China) specimens of 10 mm×10 mm×10 mm size were hand-polished using SiC papers, and cleaned with deionized water and dried at 60 °C for 2 h in an oven. The coating was prepared by two steps. Firstly, specimens were impregnated in H-PSO (CH₃-(SiO)_n-Si-H, hydrogen content: 0.1%–1.6%, Guobang Chemical Co. Ltd., Jinan, China) under a pressure of 0.5 MPa and subsequently solidified in the presence of catalyst-platonic chloride ethanol solution (Pt element was approximately 0.001%) at 120 °C for 6 h. The specimens were put in tube furnace, and SiC nanowires were prepared on the surface of C/C composites by pyrolytic technique at 1500 °C for 2 h in an argon protective atmosphere with the flowing flux of 150 mL·min⁻¹. Secondly, the SiC bonding layer was formed at 1600 °C for 2 h in an argon atmo-

sphere by an embedding technique with the powder mixture of Si and C. The corresponding chemical composition was 65% (w) Si (300 mesh) and 35% C (300 mesh). All the powders were analytically pure. In all the processes, the heating and cooling rates were 4 °C·min⁻¹, which decreased the residual stress caused by thermal mismatch.

2.2 Microstructure and oxidation tests of the SiC coating

The oxidation tests were carried out at 800, 1000, 1200, or 1400 °C for 4 h in a corundum tube furnace in static air flowing freely. The mass loss (Δw) is calculated by equation (1).

$$\Delta w = (m_0 - m_1) / m_0 \times 100\% \quad (1)$$

where m_0 is the mass of the specimens before oxidation and m_1 is the mass after oxidation.

Morphology and crystalline structure of the coating were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) with Cu K α radiation ($\lambda=0.154056$ nm). The chemical compositions (including the oxygen content after oxidation) were analyzed using energy dispersion spectroscopy (EDS) attached to the SEM.

3 Results and discussion

3.1 Microstructure of the coating

Fig.1 shows the surface morphologies of the coatings obtained by the first process. The orientation of the nanowires is random and the surface coverage on the C/C substrate is complete. These nanowires are generally 20–100 nm in diameter and 10–20 μ m in length with straight morphologies. Fig.2 shows a TEM image of a single nanowire. A clearly defined dark inner core and a light outer shell, which is a single crystalline core of a diameter of 30 nm coated with an amorphous silica layer, were observed. The similar core-shell heterostructure was reported by Zhou *et al.*¹⁸

Fig.3 shows the XRD pattern of SiC nanowires obtained by the first process. It can be observed that β -SiC is the main phase. The well-defined intense peaks at 35.6°, 60.0°, 71.7° correspond to (111), (220), (311) reflections and relatively weak peaks at 41.3°, 75.6° correspond to (200), (222) reflec-

Fig.1 SEM images of surface morphology of the coating obtained by the first process

(a) low magnification, (b) high magnification

Fig.2 TEM image of nanowires obtained by the first process

tions of β -SiC, respectively. This indicates that β -SiC nanowires are formed on the surface of C/C substrates. The appearance of a low intensity peak at 33.6° is attributed to stacking faults. Usually, a ratio X of the intensity of the peak at 33.6° to that at 41.3° , i.e., $X=I_{33.6}/I_{41.3}$, is used to estimate the density of stacking faults.^{19–21} The value is 1.4147, which indicates that a higher density of stacking faults presents in the β -SiC nanowires. High density of stacking faults is due to thermal stress during the growth process of β -SiC nanowire. The average particle size of β -SiC crystals is 25.2 nm by the Scherrer equation $D=K\lambda/(\beta\cos\theta)$.²² Besides β -SiC, the weak peaks of carbon that comes from C/C composite are detected, which is due to the existence of spaces between SiC nanowires covering on the specimens.

During pyrolysis of H-PSO, the Si—H is considered to be a radical initiator to break CH_3-Si ²³ and the dehydrogenation occurs between Si—H bonds simultaneously. As the temperature increases (above 1200 °C), the following reaction occurs:²⁴

As shown above, H-PSO transforms from organic to inorganic. The formation of SiC nanowires is due to the gas phase reaction. The decomposed SiO and CO from H-PSO react to grow SiC nanowires gradually. Droplets are found on the tips of the present nanowires in Fig.1, suggesting that the nanowires are grown by the gas-liquid-solid reaction mechanism. SiC nanowires are prone to form by thermodynamic calculations when the pressure ratio of SiO to CO ($p_{\text{SiO}}/p_{\text{CO}}$) is higher than 1.²⁵

Fig.3 XRD pattern of the surface of SiC nanowires obtained by the first process

Fig.4 SEM image of the surface morphology of the final coating

Fig.4 shows the surface SEM image of the final SiC coating obtained by the second process. The irregular grains with micropores are generated contiguously, with a uniform surface. The energy dispersion spectroscopy reveals that the atomic ratio of Si to C, within the experimental limit, is close to 1:1. Research has shown that a certain amount of micropores in SiC coating causes not only passivation of the crack tip, but also a reduction in the stress concentration of the coating.²⁶

The peak of carbon disappears in the XRD pattern of the final coating surface produced by the two-step technique (Fig.5), which illustrates that the coatings are mainly composed of β -SiC and that the SiC coating is uniform and relatively dense. It is apparent that the peaks of β -SiC become sharper, indicating that the grain size of SiC increases⁹ and calculates to be 63.4 nm. The grains are not coarsened remarkably. The uniform distribution of SiC nanowires inhibits growth of SiC grain sequentially, so it is beneficial to improve the oxidation resistance. Additionally, the density of stacking faults can be calculated from XRD pattern and it is only 0.1945, which suggests less grain defects.

Cross-sectional image of coating is shown in Fig.6. The thickness of coating is about 100–200 μm without penetration cracks or holes. Moreover, there is no obvious interface between substrate and coating. During sintering, liquid Si is first formed and flows along the surface of substrate. Then the liquid Si coats the SiC nanowire layer and infiltrates the open

Fig.5 XRD pattern of the surface of the final coating

Fig.6 SEM image of cross-section of the final coating

pores of the substrate. The newly formed SiC originates from four formation mechanisms (Fig.7). The liquid Si reacts with C used as an embedded powder, and there are some reactions between Si and C from substrate. The two reactions make new SiC grains generate around previous SiC nanowires. On the other hand, SiC nanowires prepared by the first step have some oxycarbide phase because H-PSO does not always decompose completely. This phase would contain silica as well as oxycarbide. At the second step, the silica remained can react with C from substrate and embedded C. Newly formed SiC grains embedded in SiC nanowires previously, now cover the entire surface of the substrate and form a transition layer. The SiC nanowire layer acts as a diffusion barrier against Si transfer, causing a reduction in the excessive corrosion of C/C substrates from liquid Si. Moreover, the SiC nanowires with random orientation play an important role in avoiding the formation of cracks protruding through the coating, and improve the interface bonding between substrate and coating.

3.2 Anti-oxidation property of the coating

Fig.8 shows that the mass loss of the coated C/C composite specimens in air at different temperatures. Preparing SiC coating on C/C composites causes materials to maintain excellent oxidation resistance in an oxidative atmosphere — mass loss does not exceed 4.5%. Especially at 1400 °C, the mass loss is only 0.71%.

Fig.8 Oxidation mass loss of the coated C/C specimens prepared using the two-step process

This coating structure plays an important role in improving resistance to oxidation. Firstly, the emergence of cracks, usually generated through the coating caused by heat stress during the cooling, is prevented. Secondly, the SiC obtained by reaction of Si with C from substrate promotes interfacial chemical combinations between the coating and substrate. The coating with a transition layer greatly enhances the continuity and density of the coating, but can also improve interface adhesion by modulating CTE of carbon materials and SiC coating.

Additionally, what's even more interesting in Fig.8 is that mass loss does not increase instead falls. Regarding this, we hereby make the following explanations: the surface morphology of coatings observed by SEM after oxidation tests at different temperatures are listed in Fig.9. It can be seen that the surface porosity is reduced with increasing temperature. The entire surface is smooth when the oxidation temperature is about 1400 °C, indicating that the SiC coating has a certain self-healing ability. The oxygen spreads to the inside of specimens through uniformly distributed micropores in the oxidation process. The oxidation rate of this material is controlled by microporous diffusion.²⁶

In the process of the oxidation tests, the oxygen diffuses through the pores to the inner structure and reacts with superficial SiC to SiO₂. The bonded grains together fill the void — the

Fig.7 Schematic representation of the formation process of SiC coating

Fig.9 SEM images of the surface morphology of the coating after oxidation at different temperatures

(a) 800 °C; (b) 1000 °C; (c) 1200 °C; (d) 1400 °C

Fig.10 Oxygen content after oxidation at different temperatures

temperature is higher, the bond area is wider, and the dense coating on the surface completely cuts off oxygen from the carbon substrate. The self-healing ability of the coating is due to the existence of SiO_2 , which can be verified by elemental analysis.

It has been suggested that oxygen content increased with increasing temperature (Fig.10). The reactivity of the coating with oxygen during oxidation tests can be concluded as follows:

The above reactions also indicate the formation of SiO_2 on the coating surface. The formation of SiC/SiO_2 solid solutions on the outer surface can strengthen the grain boundaries. On the basis of the above analysis, it can be concluded that the obtained coatings show excellent oxidation resistance.

4 Conclusions

In this work, pure SiC coatings were successfully prepared on the C/C composites by a simple and low-cost technique. Especially low-cost production of SiC nanowires came true. The coating with the transition structure showed excellent oxidation resistance. In oxidation tests, the surface of coating with micropores could be healed by itself. Increasing the oxidation temperature could lead to the achievement of better antioxidant properties. The oxidation mass loss was only 0.71% at 1400 °C. Improvement of oxidation resistance by introduction of SiC nanowires may be relevant to creation of excellent high temperature antioxidation materials, on the premise of low-cost production.

References

- (1) Li, C. Y.; Li, F. A. *New Chemical Materials* **2006**, 34 (3), 18. [李翠云, 李辅安. 化工新型材料, **2006**, 34 (3), 18.]
- (2) He, F. *Carbon Fiber and Its Application Technology*; Chemical Industry Press: Beijing, 2004; pp 363–416. [贺 福. 碳纤维及其应用技术. 北京: 化学工业出版社, 2004: 363–416.]
- (3) Li, H. J. *New Carbon Mater.* **2001**, 16 (2), 79. [李贺军. 新型炭材料, **2001**, 16 (2), 79.]
- (4) Huang, J. F.; Li, H. J.; Xiong, X. B.; Zeng, X. R.; Li, K. Z.; Fu, Y. W.; Huang, M. *New Carbon Mater.* **2005**, 20 (4), 373. [黄剑锋, 李贺军, 熊信柏, 曾燮榕, 李克智, 付业伟, 黄 敏. 新型炭材料, **2005**, 20 (4), 373.]
- (5) Guo, W. M.; Xiao, H. N. *Carbon* **2007**, 45 (5), 1058.
- (6) Hu, H. F.; Li, Y. W.; Chen, Z. H.; Feng, C. X.; Zhang, C. R.;

- Song, Y. C. *Material Engineering* **1997**, No. 3, 7. [胡海峰, 李彦武, 陈朝辉, 冯春祥, 张长瑞, 宋永才. 材料工程, **1997**, No. 3, 7.]
- (7) Yeo, S.; Kim, D. J.; Park, J. W. *Int. J. Refract. Met. Hard Mat.* **2011**, 29 (5), 582.
- (8) Joinet, M. J.; Pouliquen, L.; Teyssandier, F.; Aliaga, D. *Surf. Coat. Tech.* **2008**, 202 (11), 2252.
- (9) Fu, Z. Q.; Tang, C. H.; Liang, T. X. *Surf. Coat. Tech.* **2006**, 200 (12/13), 3950.
- (10) Li, C. H.; Huang, K. L.; Li, X. D.; Cao, F.; Yu, Y. X. *Mater. Sci. Technol.* **2005**, 13 (2), 222. [李春华, 黄可龙, 李效东, 曹峰, 余煜玺. 材料科学与工艺, **2005**, 13 (2), 222.]
- (11) Liu, Z. J.; Guo, Q. G.; Liu, L.; Shi, J. L.; Zhai, G. T. *Surf. Coat. Tech.* **2008**, 202 (13), 3094.
- (12) Tang, C. H.; Guan, J. J. *Nucl. Mater.* **1995**, 224 (1), 103.
- (13) Zhao, J.; Wang, G.; Guo, Q. G.; Liu, L. *Fusion Eng. Des.* **2007**, 82 (4), 363.
- (14) Huang, J. F.; Li, H. J.; Zeng, X. R.; Xiong, X. B.; Li, K. Z. *Appl. Surf. Sci.* **2006**, 252 (12), 4244.
- (15) Fu, Q. G.; Li, H. J.; Shi, X. H.; Liao, X. L.; Li, K. Z.; Huang, M. *Appl. Surf. Sci.* **2006**, 252 (10), 3475.
- (16) Smeacetto, F.; Ferraris, M.; Salvo, M. *Carbon* **2003**, 41 (11), 2105.
- (17) Wang, Z.; Dai, Z.; Gao, R.; Gole, J. L. *Appl. Phys. Lett.* **2000**, 77 (21), 3349.
- (18) Zhou, W. M.; Yang, B.; Yang, Z. X.; Zhu, F.; Yan, L. J.; Zhang, Y. F. *Appl. Surf. Sci.* **2006**, 252 (14), 5143.
- (19) Yang, W. Y.; Miao, H. Z.; Xie, Z. P.; Zhang, L. G.; An, L. N. *Chem. Phys. Lett.* **2004**, 383 (5/6), 441.
- (20) Koumoto, K.; Takeda, S.; Pai, C. H.; Sato, T.; Yanagida, H. *J. Am. Ceram. Soc.* **1989**, 72 (10), 1985.
- (21) Seo, W. S.; Koumoto, K. *J. Am. Ceram. Soc.* **1998**, 81 (5), 1255.
- (22) Raman, V.; Bahl, O. P.; Dhawan, U. *J. Mater. Sci.* **1995**, 30 (10), 2686.
- (23) Hourlier, D. B.; Latournerie, J.; Dempsey, P. J. *Eur. Ceram. Soc.* **2005**, 25 (7), 979.
- (24) Ma, Q. S.; Chen, Z. H.; Zheng, W. W.; Hu, H. F. *Journal of National University of Defense Technology* **2001**, 23 (5), 40. [马青松, 陈朝辉, 郑文伟, 胡海峰. 国防科技大学学报, **2001**, 23 (5), 40.]
- (25) Choi, H. J.; Lee, J. G. *J. Mater. Sci.* **1995**, 30 (8), 1982.
- (26) Zhao, J.; Wang, G.; Liu, L.; Guo, Q. G. *Atomic Energy Science and Technology* **2008**, 42 (4), 353. [赵娟, 王贵, 刘朗, 郭全贵. 原子能科学技术, **2008**, 42 (4), 353.]