Advanced Composite Materials
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tacm20

Y2Si2O7 Whisker Reinforced MoSi2 Multi-composition Coating for SiC Pre-coated Carbon/Carbon Composites

Ya-Qin Wang [a] , Jian-Feng Huang [b] , Li-Yun Cao [c] & Xie-Rong Zeng [d]

[a] Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an Shaanxi 710021, China

[b] Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an Shaanxi 710021, China; Shenzhen Key Laboratory of Special Functional Materials, Shenzhen University, Shenzhen, Guangdong 518086, China;, Email: huangjf@sust.edu.cn

[c] Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an Shaanxi 710021, China

[d] Shenzhen Key Laboratory of Special Functional Materials, Shenzhen University, Shenzhen, Guangdong 518086, China

Version of record first published: 02 Apr 2012.

VSP

Advanced Composite Materials 20 (2011) 125–132

ADVANCED COMPOSITE MATERIALS
brill.nl/acm

$Y_2Si_2O_7$ Whisker Reinforced $MoSi_2$ Multi-composition Coating for SiC Pre-coated Carbon/Carbon Composites

Ya-Qin Wang [a], **Jian-Feng Huang** [a,b,*], **Li-Yun Cao** [a] **and Xie-Rong Zeng** [b]

[a] Key Laboratory of Auxiliary Chemistry and Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an Shaanxi 710021, China
[b] Shenzhen Key Laboratory of Special Functional Materials, Shenzhen University, Shenzhen, Guangdong 518086, China

Received 19 October 2009; accepted 8 June 2010

Abstract

$Y_2Si_2O_7$–$MoSi_2$/SiC multi-composition coatings were deposited on the surface of SiC pre-coated carbon/carbon (C/C) composites using a hydrothermal electrophoretic process. The prepared coatings were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Influences of $Y_2Si_2O_7$ whisker on the morphologies and anti-oxidation properties of coatings were particularly investigated. Results show that $Y_2Si_2O_7$ whisker has a strong influence on the microstructure and oxidation resistant performance of the coated composites. Compared with $MoSi_2$/SiC coating, $Y_2Si_2O_7$–$MoSi_2$/SiC coating exhibits dense, uniform, and homogeneous morphologies without any microcracks. $Y_2Si_2O_7$ whisker can effectively decrease the thermal expansion coefficient of $MoSi_2$ and prevent coatings from cracking, which results in improved oxidation resistant performance of the coated composites. The as-prepared multi-layer coating can protect C/C composites from oxidation for 100 h at 1773 K with a weight loss of 1.22×10^{-3} g/cm^2.

Keywords

Carbon/carbon composites, $Y_2Si_2O_7$ whisker, $MoSi_2$ coatings, oxidation

1. Introduction

The excellent ultrahigh strength of carbon/carbon (C/C) composites at temperatures above 2273 K make them the most promising candidate materials for high temperature structural applications with advanced thermal protection. However, their oxidation above 673 K limits their applications in oxygen containing atmosphere at high temperature [1, 2], which has led to research to try to improve their oxidation resistance. A multi-layer protective coating, using SiC as an internal bonding layer, has been proposed [3–5]. In the multi-layer coating, $MoSi_2$ can be a useful

* To whom correspondence should be addressed. E-mail: huangjf@sust.edu.cn
Edited by the JSCM

DOI:10.1163/092430410X523944

outer-layer material because it has a high melting point and excellent high temperature oxidation resistance. However, the coefficient of thermal expansion (CTE) mismatch between $MoSi_2$ (8.5×10^{-6}/K) outer-layer and SiC (4.5×10^{-6}/K) bonding layer causes cracks in the protection layer, and provides channels for oxygen to attach to the carbon matrix.

Therefore, pure $MoSi_2$ cannot be used as the outer layer, and a multi-composition coating might be better. The CTE of $MoSi_2$ can be decreased with enhanced toughness by adding $Y_2Si_2O_7$ whisker, which has low thermal expansion coefficient and equivalent physical and chemical adaptability to SiC [6]. To date, there are no reports of the use of $Y_2Si_2O_7$ whisker toughened $MoSi_2$ coating. In order to obtain a dense $Y_2Si_2O_7$–$MoSi_2$/SiC multi-layer coating, a novel hydrothermal electrophoretic deposition technique was used. Influences of $Y_2Si_2O_7$ whisker on the microstructure and oxidation resistance of the coated C/C composites were investigated.

2. Experimental

Small specimens ($10 \times 10 \times 10$ mm^3) cut from bulk 2D-C/C composites with a density of 1.72 g/cm^3 were used as cathode substrates. The specimens were hand-polished using SiC paper with 200, 500 and 800 grit, and were cleaned in acetone for 10 min and then dried at 333 K for 1 h in an oven. After the preparation of the SiC bonding layer by a two-step pack cementation process [7], hydrothermal electrophoretic deposition was conducted, as shown in Fig. 1. Firstly, 50 wt% $Y_2Si_2O_7$ whiskers and 50 wt% $MoSi_2$ powders were mixed and dispersed in isopropanol with sonication for 30 min and magnetic stirring for 24 h. Then, iodine (0.06 g/l) as a charging agent was added into the above suspension, and the mixture was subjected to sonication and magnetic stirring for 12 h. The as-prepared suspension solution was put into a hydrothermal autoclave. During the deposition process, the autoclave temperature and the voltage were kept at 393 K and 210 V, respectively. After

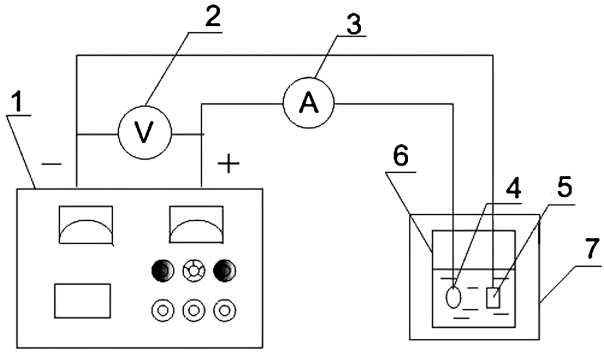

Figure 1. Schematic illustration of hydrothermal electrophoretic equipment. (1 — DC power supply, 2 — voltmeter, 3 — ammeter, 4 — anode (graphite), 5 — cathode (C/C), 6 — hydrothermal autoclave, 7 — oven.)

20 min deposition, the specimens were taken out from the autoclave and cooled naturally to room temperature. Subsequently, the samples were dried at 333 K in air for 4 h. Multi-layers were coated on the C/C–SiC substrates. The crystallite structures of the coatings were measured with Rigaku D/max-3C X-ray diffraction (XRD) equipment. The morphologies of the multi-coating were analyzed using a JSM-6400 scanning electronic microscope (SEM). The isothermal oxidation test was carried out from 773 K to 1773 K in air in an electrical furnace. The samples were weighed at room temperature by electronic balance with a sensitivity of ±0.1 mg. The $\Delta W\%$ mass loss was calculated using equation (1):

$$\Delta W\% = (m_0 - m_1)/m_0 \times 100\%, \tag{1}$$

where m_0 is the original mass of the coated C/C composites; m_1 is the mass of the coated C/C composites after oxidation at high temperature for a certain time. An Instron 1186 electron universal testing machine was used to determine the bonding strength between the multi-coating and C/C–SiC substrates.

3. Results and Discussion

Figure 2 shows the surface XRD spectrum of the as-prepared coating. It indicates that a strong peak of $MoSi_2$ and $Y_2Si_2O_7$ at 30°–50° can be observed, which is in good agreement with what would be expected from the original composition of the multi-composition coating.

Figure 3(a) shows the surface SEM image of the $MoSi_2$/SiC coating. It indicates that some propagation of microcracks in the surface of coating has occurred, which may have resulted from the thermal stress caused by the CTE mismatch between the $MoSi_2$ outer layer and the SiC inner layer [8]. By adding 50% $Y_2Si_2O_7$

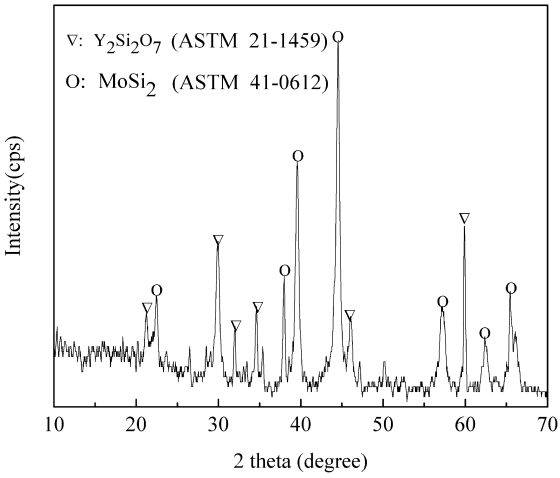

Figure 2. XRD pattern of $Y_2Si_2O_7$–$MoSi_2$/SiC coating obtained by hydrothermal electrophoretic deposition process.

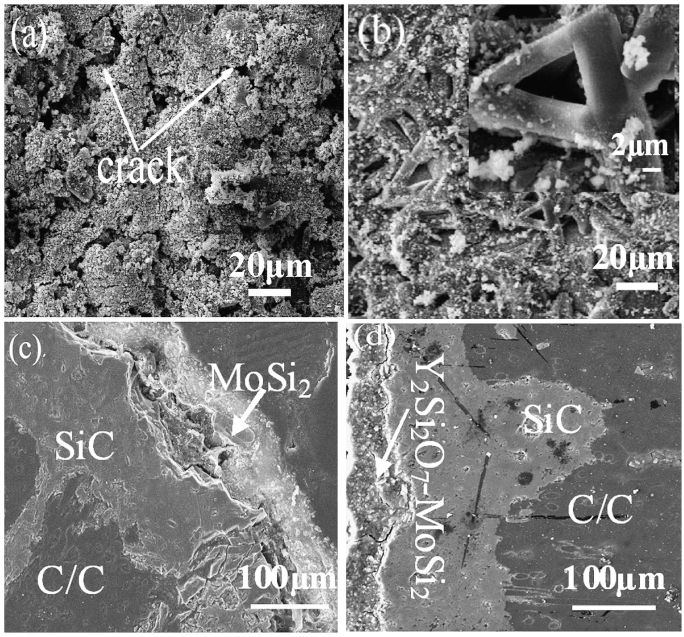

Figure 3. Surface and cross-section SEM images of the coatings: (a, c) $MoSi_2$/SiC coating and (b, d) $Y_2Si_2O_7$–$MoSi_2$/SiC coating.

Table 1.
Results of the bonding strength test of $MoSi_2$/SiC coating and $Y_2Si_2O_7$–$MoSi_2$/SiC coating

Test material	Bonding strength (MPa)	Average bonding strength (MPa)
$MoSi_2$/SiC coating	15.6; 17.4; 13.9; 16.0	15.7
$Y_2Si_2O_7$–$MoSi_2$/SiC coating	30.8; 30.3; 27.9; 29.5	27.1

whiskers into the coating, crack deflection and a decreased number of cracks around the $Y_2Si_2O_7$ whisker is observed, and a dense and crack-free coating is achieved (Fig. 3(b)). Compared with the $MoSi_2$/SiC coating (Fig. 3(c)), not only do the cracks between the internal and external coating disappear (Fig. 3(d)) but also the bonding strength between the inner and outer layers of $Y_2Si_2O_7$–$MoSi_2$/SiC coating has been notably enhanced, as shown in Table 1; this may be related to the decrease in CTE of the multi-composition coating. According to Hwang and Fergus's theories [9], the matching of CTE is one of the main influences that affect the state of thermal stress between the coating and matrix in ceramic fiber reinforced composite silicon–silicon–oxygen composite materials. The CTE of the outer layer should be as close as possible to that of the matrix, which may reduce cracking of coatings caused by thermal stress.

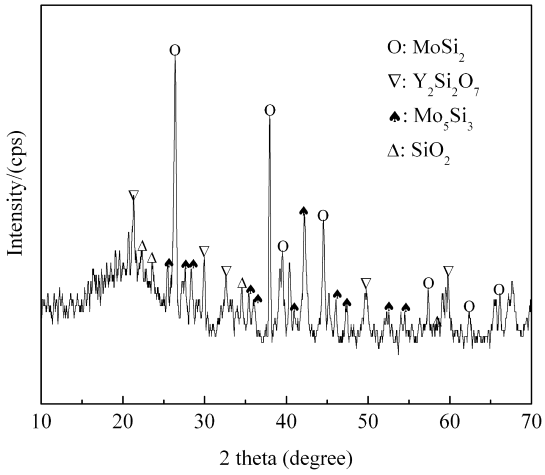

Figure 4. XRD pattern of $Y_2Si_2O_7$–$MoSi_2$/SiC coating after oxidation in air for 100 h.

The bonding strength test results between the outer layer coatings and C/C–SiC substrate are shown in Table 1. The $Y_2Si_2O_7$–$MoSi_2$/SiC coating's average bonding strength reaches 27.1 MPa compared with that of $MoSi_2$/SiC coating which is only 15.7 MPa. The bonding strength between the inner and outer layer is improved as a result of the decrease in CTE of multi-composition coating by adding $Y_2Si_2O_7$ whisker.

Figure 4 shows the XRD patterns of the coating after oxidation at 1773 K in air for 100 h. It can be seen that two new phases of Mo_5Si_3 and SiO_2 are detected in the coating, which may due to the oxidation reactions shown in equations (2)–(4):

$$SiC + 2O_2 \longrightarrow CO_2 + SiO_2 \tag{2}$$

$$2MoSi_2 + 7O_2 \longrightarrow 2MoO_3 + 4SiO_2 \tag{3}$$

$$5MoSi_2 + 7O_2 \longrightarrow Mo_5Si_3 + 7SiO_2 \tag{4}$$

The results of the isothermal oxidation test in air from 773 K to 1773 K are shown in Figs 5 and 6. Compared with the $MoSi_2$/SiC coated C/C composites (Fig. 5), the $Y_2Si_2O_7$–$MoSi_2$/SiC coated C/C composites show better anti-oxidation properties (Fig. 6). There is hardly any weight loss of $Y_2Si_2O_7$–$MoSi_2$/SiC coated sample in air at 1373 K after 100 h. However, the weight loss of $MoSi_2$/SiC coated sample reaches 0.75×10^{-3} g/cm^2 under the same conditions. Moreover, the $Y_2Si_2O_7$–$MoSi_2$/SiC multi-layer coatings can protect C/C composites from oxidation in air with only 1.22×10^{-3} g/cm^2 weight loss at 1773 K for 100 h. It is also better than that of the SiC whisker-toughened SiC oxidation protective coating [10], whose weight loss is 2.83×10^{-3} g/cm^2 after oxidation at 1773 K for 48 h. The as-prepared $Y_2Si_2O_7$–$MoSi_2$/SiC coating displays better oxidation protection ability.

Figure 7 shows the surface and cross-section SEM images of the prepared coatings after oxidation in air at 1773 K for 100 h. Figure 7(a) and 7(b) illustrates that

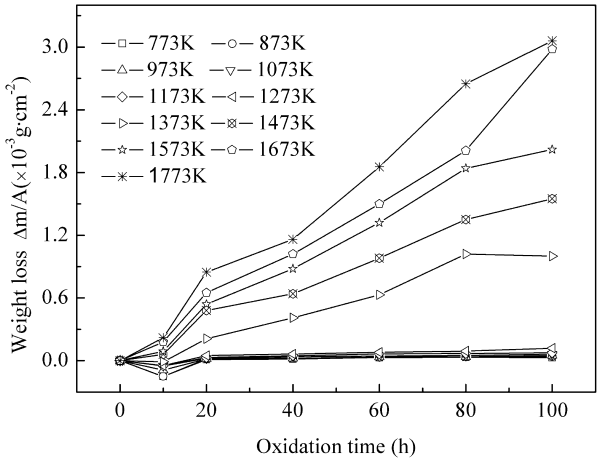

Figure 5. Isothermal oxidation curves of $MoSi_2$/SiC coated C/C samples from 773 K to 1773 K in air for 100 h.

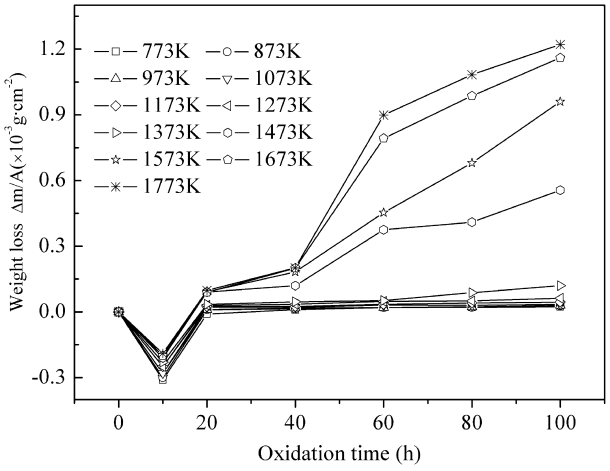

Figure 6. Isothermal oxidation curves of $Y_2Si_2O_7$–$MoSi_2$/SiC coated C/C samples from 773 K to 1773 K in air for 100 h.

smooth glass layers are formed on the samples' surface. According to XRD analysis shown in Fig. 4, the glass phase is SiO_2, which may come from the oxidation of $MoSi_2$ and SiC during the extended oxidation period. This SiO_2 glass layer can prevent the direct attack of oxygen on the C/C substrates, because the diffusion coefficient of oxygen through the SiO_2 glass layer is very low [11]. Some holes are also observed on the surface of the coating (Fig. 7(a) and 7(b)), which may have been generated by the escape of the oxidation gases. In addition, some penetrating cross-cracks can be found on the coating surface from Fig. 7(a). This may be the result of the mismatch of CTE between the $MoSi_2$ outer-layer and the SiC bonding

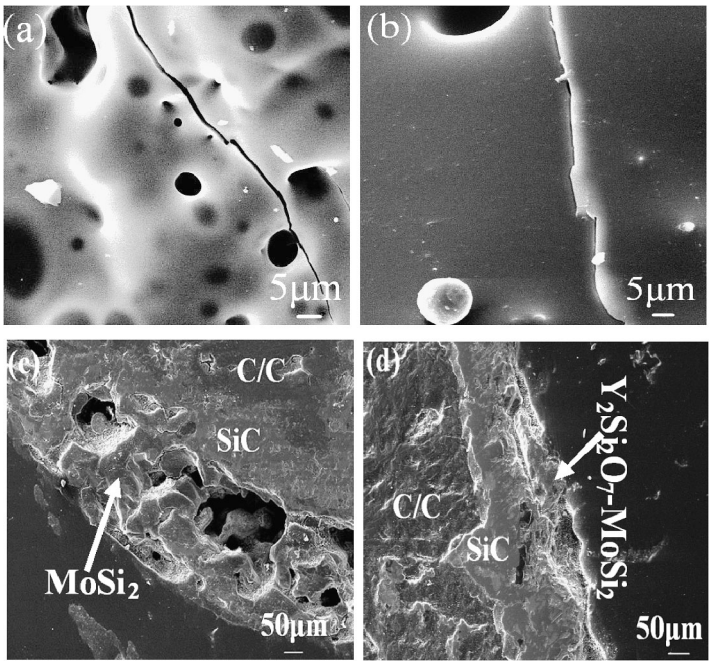

Figure 7. Surface and cross-section SEM images of the prepared coatings after oxidation at 1773 K in air for 100 h: (a, c) $MoSi_2$/SiC coating and (b, d) $Y_2Si_2O_7$–$MoSi_2$/SiC coating.

layer [12]. These cracks might not be self-sealed because the fluidity of the SiO_2 glass is poor at 1673 K. Compared with Fig. 7(a), the crack size in the coating is obviously reduced because $Y_2Si_2O_7$ whiskers decrease the CTE of $MoSi_2$ coating and effectively enhance the bonding strength between the outer layer coating and C/C–SiC substrate. The results are also verified by the cross-section SEM images observation of coatings shown in Fig. 7(c) and 7(d). Therefore, it can be deduced that oxidation protection ability of the $Y_2Si_2O_7$–$MoSi_2$/SiC coating is better than that of $MoSi_2$ coating as a result of the smaller microcracks in the former case (Fig. 6).

4. Conclusions

Based on the above research, a dense and homogeneous $Y_2Si_2O_7$ whisker reinforced $MoSi_2$ multi-composition coating was prepared on SiC–C/C composites surface by a hydrothermal electrophoretic deposition process. Compared with $MoSi_2$ coating, $Y_2Si_2O_7$–$MoSi_2$/SiC multi-layer coating possessed better oxidation protection ability for C/C composites because $Y_2Si_2O_7$ whiskers played an obvious role in decreasing the thermal expansion of $MoSi_2$ coating and increasing the toughness between the outer layer and the inner layer more effectively. The as-prepared multi-composition coating can protect C/C composites from oxidation for 100 h at 1773 K with a weight loss of 1.22×10^{-3} g/cm^2.

Acknowledgements

The present work was supported by the National Natural Science Foundation of China (50772063), Natural Science Foundation of Shaanxi Province in China (SJ08-ZT05), Foundation of New Century Excellent Talent in University of China (NCET-06-0893), Doctorate Research Foundation of SUST (20070708001) and Graduate Innovation Foundation of SUST, respectively.

References

1. H. J. Li, Carbon/carbon composites, *New Carbon Mater.* **16**, 79–80 (2001) (in Chinese).
2. J. F. Huang, H. J. Li, X. B. Xiong, X. R. Zeng, K. Zh. Li, Y. W. Fu and M. Huang, Protective coating for carbon–carbon composites, *New Carbon Mater.* **20**, 373–379 (2005) (in Chinese).
3. C. Isola, P. Appendina, F. Bosco, M. Ferraris and M. Salvo, Protective coating for carbon–carbon composites, *Carbon* **36**, 1213–1218 (1998).
4. L. F. Cheng, Y. D. Xu, L. T. Zhang and X. W. Yin, Oxidation behavior of carbon–carbon composites with a three-layer coating from room temperature to 1700°C, *Carbon* **37**, 977–981 (1999).
5. Q. G. Fu, H. J. Li, X. H. Shi and G. D. Sun, Silicon carbide coating to protect carbon/carbon composites against oxidation, *Scripta Mater.* **52**, 923–927 (2005).
6. Y. Ogura, M. Kondo, T. Morimoto and T. Sekigawa, Oxygen permeability of Y_2SiO_5, *Mater. Trans.* **42**, 1124–1130 (2001).
7. J. F. Huang, X. R. Zeng, H. J. Li and X. B. Xiong, Influence of the preparation temperature on the phase, microstructure and anti-oxidation property of a SiC coating for C/C composites, *Carbon* **42**, 1517–1521 (2004).
8. J. Zhao, L. Liu, Q. Cao, J. L. Shi and G. T. Zhai, Oxidation protective behavior of SiC/Si–$MoSi_2$ coating for different graphite matrix, *Mater. Lett.* **60**, 1964–1967 (2006).
9. L. R. Hwang and J. W. Fergus, Interface compatibility in ceramic–matrix composites, *Compos. Sci. Technol.* **56**, 1341 (1996).
10. Q. G. Fu, H. J. Li, K. Zh. Li, X. H. Shi, Zh. B. Hu and M. Huang, SiC whisker-toughened $MoSi_2$–SiC–Si coating to protect carbon/carbon composites against oxidation, *Carbon* **44**, 602–605 (2006).
11. G. Sh. Jiao, H. J. Li, K. Zh. Li, Ch. Wang and D. Sh. Hou, SiC–$MoSi_2$–$(Ti_{0.8}M_{0.2})Si_2$ multi-composition coating for carbon/carbon composites, *Surf. Coat. Technol.* **6**, 3452–3456 (2006).
12. H. J. Li, H. Xue, Y. J. Wang, Q. G. Fu and D. Y. Yao, A $MoSi_2$–SiC–Si oxidation protective coating for carbon/carbon composites, *Surf. Coat. Technol.* **24**, 9444–9447 (2007).