JOURNAL OF MATERIALS SCIENCE **34** (1999) 6009–6014

Oxidation behavior and mechanical properties of C/SiC composites with Si-MoSi$_2$ oxidation protection coating

YONGDONG XU, LAIFEI CHENG, LITONG ZHANG, HONGFENG YING, WANCHENG ZHOU
State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, People's Republic of China
E-mail: ydxu@nwpu.edu.cn

A new kind of oxidation protection coating of Si-MoSi$_2$ was developed for three dimensional carbon fiber reinforced silicon carbide composites which could be serviced upto 1550 °C. The overall oxidation behavior could be divided into three stages: (i) $500\,^{\circ}\mathrm{C} < T < 800\,^{\circ}\mathrm{C}$, the oxidation mechanism was considered to be controlled by the chemical reaction between carbon and oxygen; (ii) $800\,^{\circ}\mathrm{C} < T < 1100\,^{\circ}\mathrm{C}$, the oxidation of the composite was controlled by the diffusion of oxygen through the micro-cracks, and; (iii) $T > 1100\,^{\circ}\mathrm{C}$, the oxidation of SiC became significant and was controlled by oxygen diffusion through the SiC layer. Microstructural analysis revealed that the oxidation protection coating had a three-layer structure: the out layer is oxidation layer of silica glass, the media layer is Si + MoSi$_2$ layer, and the inside layer is SiC layer. The coated C/SiC composites exhibited excellent oxidation resistance and thermal shock resistance. After the composites annealed at 1550 °C for 50 h in air and $1550\,^{\circ}\mathrm{C} \Leftrightarrow 100\,^{\circ}\mathrm{C}$ thermal shock for 50 times, the flexural strength was maintained by 85% and 80% respectively. The relationship between oxidation weight change and flexural strength revealed the criteria for protection coating was that the maximum point of oxidation weight gain was the failure starting point for oxidation protection coating. *© 1999 Kluwer Academic Publishers*

1. Introduction

Carbon fiber reinforced silicon carbide composite (C/SiC) is a kind of promising thermal structure composites for use in applications requiring high strength, low density, and high fracture toughness at elevated temperatures in aero-engines and aerospace [1]. However, a severe problem is that the carbon fiber and interfacial layer of the composite are easy to be attacked by oxygen in air at the temperatures as low as 370 °C [2, 3]. The main reason is that there are many microcracks on the silicon carbide matrix resulted from the mis-match of thermal expansion coefficients between carbon fiber and silicon carbide matrix. The oxidation has a significant effect on the weakening and mechanical properties of the materials. It has been reported that the oxidation weight loss of 2 wt% resulted in the tensile strength decrease of almost 40% at medium temperature of 900 °C by oxidation treatment [4]. So far, two kinds of approaches have been developed to protect the carbon fiber and interfacial layer. The first approach is oxidation protection of interfacial layer, such composition-graded C(B) interface and BN interfacial layer [5–10]. Obviously, the effect of this approach is limited because the interfacial layer is usually very thin ($\sim 10^2$ nm). The second approach is oxidation protection coating for composite, and is considered as a promising method.

There are many issues which must be considered in the development of a successful oxidation protection system for carbon-based composite materials [2, 3]. The critical factors for oxidation protection system of carbon-based composite materials are: (i) oxygen diffusion through the coating micro-cracks; (ii) volatility of coating materials at high temperature; (iii) oxidation of coating by diffusion of oxygen through the coating layer, and; (iv) the chemical and mechanical compatibility between coating and substrate. The oxidation protection coating for composites is usually prepared by chemical vapor deposition (CVD) method which has been described elsewhere [11]. The coating has a sandwich structure which could be divided into three layers. The inner layer is CVD SiC layer, the medium layer is boron-containing layer (BN or B$_4$C), and the outer is CVD SiC layer. At high temperatures, B$_2$O$_3$-SiO$_2$ glass is formed from the oxidation of boron-containing layer and SiC and seals easily the micro-cracks to protect the composites [2, 12]. The service temperature of this kind coating is lower than 1200 °C because the borate glasses exhibit high vapor pressure at high temperature. In order to improve the service temperature of oxidation protection coating, it is necessary to develop new kind of coating materials system. This paper is a continuation of an articles published previously [12–14], and the aims are (i) develop a new kind of oxidation protection coating for C/SiC composites which could be utilized above 1200 °C; (ii) investigate the oxidation behavior of coated C/SiC composites, and; (iii) examine the effects of oxidation on the mechanical properties and failure behavior of the composites.

2. Experimental procedure

2.1. Preparation of three dimensional carbon/silicon carbide composites

PAN-based carbon fiber was employed and each yarn contained 3000 filaments. The fabric preform was prepared by three dimensional braided method, and supplied by Nanjing Institute of Glass Fiber (People's Republic of China). The fiber volume fraction was 40%. In the present experiment, isothermal/isobaric chemical vapor infiltration (ICVI) was employed to prepare C/SiC composite which has been described elsewhere in details [13–15]. In ICVI process, a thin layer of pyrolytic carbon was pre-deposited on the surface of carbon fiber as interfacial layer with butane at 850 °C prior to densification. Methytrichosilane (MTS, CH_3SiCl_3) was used for deposition of SiC and was carried by bubbling hydrogen into the reaction chamber. Typical conditions being used for deposition are 1100 °C, a hydrogen to MTS ratio of 10, and a pressure of a few kPa. Argon was used as dilute gas to slow down the chemical reaction rate of deposition. After the densification of the composites was finished, the C/SiC composites were coated with silicon-molybdenum alloy (Si-Mo) melt at temperature of 1500–1600 °C in vacuum for 0.5 h.

2.2. Oxidation tests

The oxidation tests were conducted at 400–1500 °C in air. The thermal shock experiments were conducted as follows: the samples were placed into the furnace at 1550 °C for 15 min, then drawn out from the furnace placed into the boiling water of 100 °C immediately. The oxidation weight change of the samples were measured with an analytical balance (sensitivity: 0.1 mg).

2.3. Mechanical properties measurement

Flexural strength was measured with three-point-bending method with samples 3 × 4 × 40 mm in size and the curves of loading stress vs. displacement were recorded. The loading rate for flexural strength was 0.5 $mm{\cdot}min^{-1}$. The mechanical properties was conducted on an Instron-1195 machine at room temperature.

2.4. Microstructure observation and surface analysis

The morphology of the specimens was characterized by a scanning electron microscope (SEM, JEOL 840). The microstructure of the texture was studied with a transmission electron microscope (TEM, Philips EM 400).

3. Results and Discussion

3.1. Oxidation behavior of C/SiC composite

The carbon fiber has a substantially lower thermal expansion coefficient than any of ceramic materials. The occurrence of residual mechanical stress generated by thermal expansion mis-match and the lack of plasticity of SiC matrix at the medium temperature (∼900 °C) are such that the matrix micro-cracks can not be avoided. The cracking temperature (T_c) is defined as the formation temperature of micro-cracks in SiC matrix, and is lower than the deposition temperature (T_d) of SiC matrix. The oxidation threshold temperature (T_t) for carbon-carbon composite materials is 370 °C [2, 3, 16]. This temperature can be improved by the incorporation of refractory particles as inhibitors. The instinctive protection range of the coating is defined by the micro-cracking temperature and the coating limiting-use temperature. In this temperature range, the micro-cracks can be mechanically closed and sealed by oxidation products. The range between oxidation threshold and cracking temperature is very dangerous and sealant must be employed. Fig. 1 shows the oxidation behavior of the coated C/SiC composite. The oxidation profile could be classified into three parts. The first part is located at the temperature range from 500 to 800 °C. The oxidation weight loss was increased with the increase of temperature. For the coated C/SiC composite, the oxidation threshold temperature was improved to 500 °C because the SiC matrix was incorporated into the composite as inhibitor. The second part is within the temperature range of 800–1100 °C. The weight loss is decreased with the increase of temperature. The third part is located in the temperature above 1100 °C. The oxidation weight gain rather than oxidation weight loss was observed, and the oxidation weight gain loss was increased with the increase of oxidation temperature.

The oxidation behaviors of 3D C/SiC composites were similar to those of 2D C/SiC composites and could be illustrated by the model proposed by Lamouroux [4]. The carbon fiber and CVI SiC matrix are known to exhibit coefficients of thermal expansion that are significantly different. The T300 carbon fiber is an an-isotropic material and characterized by two CTEs: a radial CTE (-0.1–$1.1 \times 10^{-6}\,{}^{\circ}C^{-1}$) and a longitudinal CTE ($7.0 \times 10^{-6}\,{}^{\circ}C^{-1}$). The CTE of CVI SiC matrix is $4.8 \times 10^{-6}\,{}^{\circ}C^{-1}$ [17]. Hence, there are many

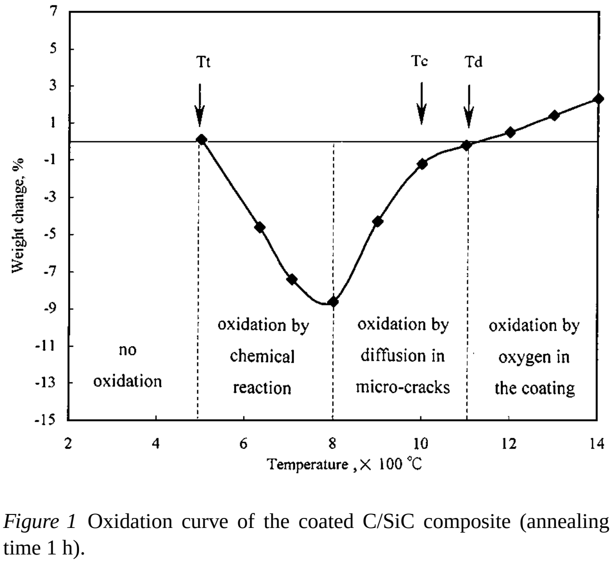


Figure 1 Oxidation curve of the coated C/SiC composite (annealing time 1 h).

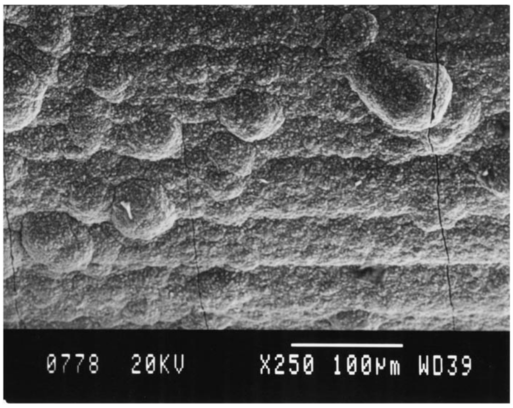


Figure 2 Micro-cracks in SiC substrate of C/SiC composite.

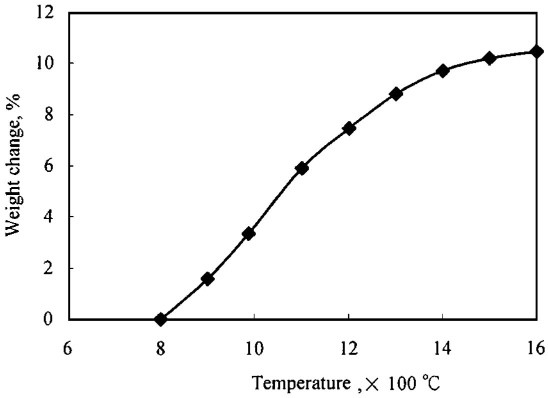


Figure 3 Oxidation of CVI SiC matrix.

micro-cracks on the SiC matrix formed perpendicular to the carbon fiber axis resulted from thermal stress (Fig. 2). During the oxidation process at the temperature of 500–800 °C, these micro-cracks play a role of transporting tunnel for oxygen diffusion inside. At this stage, the oxidation mechanism was considered to be controlled by the chemical reaction between carbon and oxygen, and oxidation rate should be obeyed Arrehnius equation. Obviously, the increase of temperature led to accelerating the rate of oxidation.

As the temperature was increased to 800–1100 °C, the width of the micro-cracks ($e(T)$) became narrow which was defined as a function of the temperature:

$$e(T) = e_0(1 - T/T_0) \tag{1}$$

Where e_0 is the width of micro-crack at room temperature, T is the test temperature, and T_0 is the temperature at which the micro-crack width is zero.

The decrease of width of micro-cracks resulted in the varying of oxidation mechanism under a Fick and a Knudsen regime [18, 19]. Therefore, the oxidation mechanism of the composite was controlled by the diffusion of oxygen in the micro-cracks. The oxygen diffusion control implies a crack geometry effect especially regarding the width and depth of the micro-cracks. At the temperature above 1100 °C, the width of micro-cracks became very narrow due to the thermal expansion of SiC matrix, and the oxidation of SiC became significant and was controlled by oxygen diffusion through the SiC layer. Furthermore, the volume expansion of oxidation scale of SiC would eventually enclose the micro-cracks. Consequently, the oxidation mechanism was controlled by the diffusion of oxygen in silicon carbide layer. The oxidation model of the composite was demonstrated by the oxidation behavior of CVI SiC matrix in Fig. 3. At the temperature below 800 °C, the oxidation weight change of SiC matrix was not observed. At the temperature range of 800–1400 °C, the oxidation rate was increased rapidly as the increase of temperature.

3.2. Structure characterization of oxidation protection coating of C/SiC composite

An important issue concerns the selection of the primary oxygen barriers. It is usually emphasized that the adherent *in-situ* oxide could be formed in order to getter the oxygen at the free surface of the composites. The silicon-based ceramics have the best thermal expansion comparability and exhibit the lowest oxidation rates. Therefore, they are often selected for protection of carbon-based composites. It is reported that the thin amorphous SiO_2 scale has low oxygen diffusion coefficient and can be modified with other oxides to control the viscosity of the glass. As shown in Fig. 4, the SEM observation results indicated that oxidation protection coating was consisted in three layers: (i) The out layer is oxidation layer of silica glass; (ii) The media layer is $Si + MoSi_2$ layer, and; (iii) The inside layer is SiC layer. The silica glass oxidation layer is very smooth because it was resulted from the oxidation of $Si + MoSi_2$ layer. In the $Si + MoSi_2$ layer, the $MoSi_2$ particles was dispersed in the matrix of Si. Fig. 5b, c, d show the TEM morphology and diffraction patters of media layer. The further observation of TEM on the silica glass scale revealed that this layer is mainly consisted in SiO_2, with little amount of Mo element (Fig. 5). The oxidation reactions of Si and $MoSi_2$ can be expressed as follows [20, 21]:

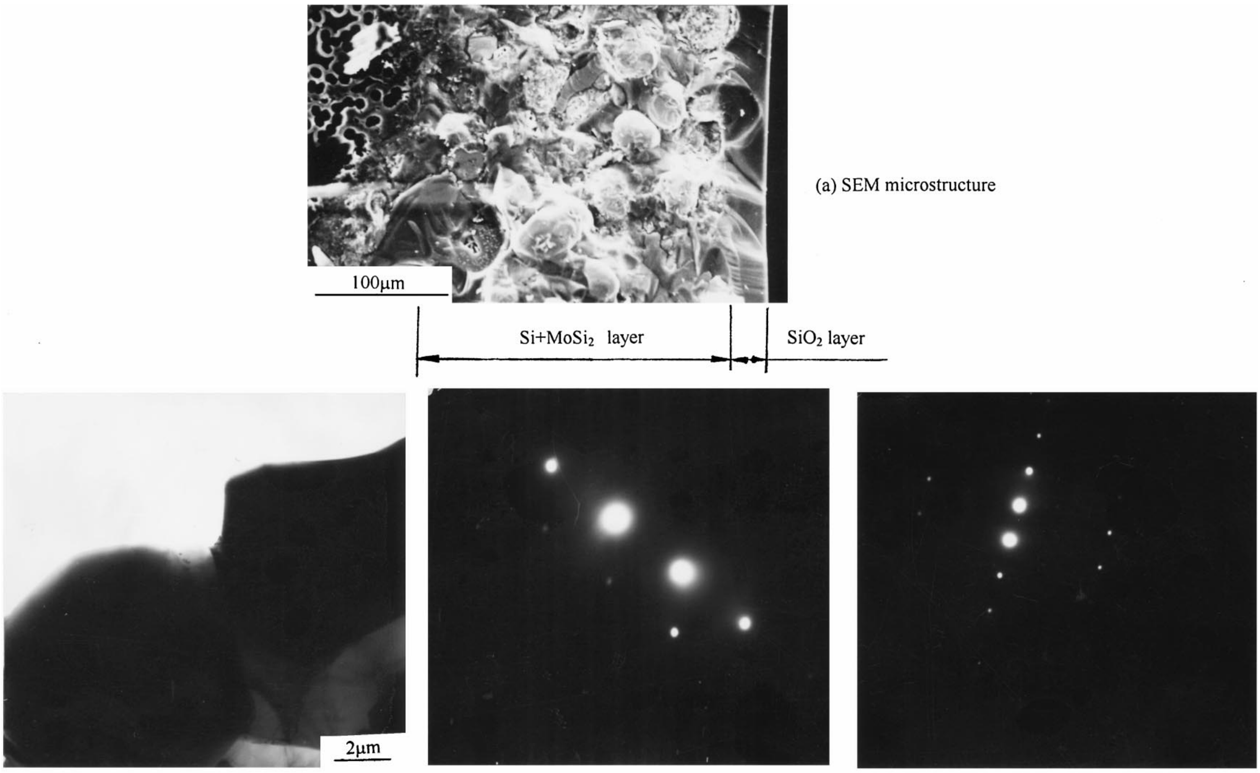
$$Si + O_2 = SiO_2 \tag{2}$$

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

MoO_3 has relatively low melting point (800 °C) and good fluidity, as a result, it could seal the micro-cracks of oxidation coating and enhance the oxidation resistance of the composite. Usually, Mo is a kind of adjusting element of network in the glass, and has no ability to form glass. But at the condition of presence of SiO_2, Mo and SiO_2 could form a kind of glass with high resistance of both crystallization and oxygen diffusion. In the glass system, Mo exists in the form of $[MoO_3]$ [22].

3.3. Effect of oxidation on the mechanical properties of coated composite

It was observed that the coated C/SiC composites exhibited oxidation weight gain during the whole oxidation. At the initial stage of oxidation, the lineal relationship is observed between oxidation weight gain and temperature. The increase rate was decreased when the oxidation time was more than 20 h. The oxidation



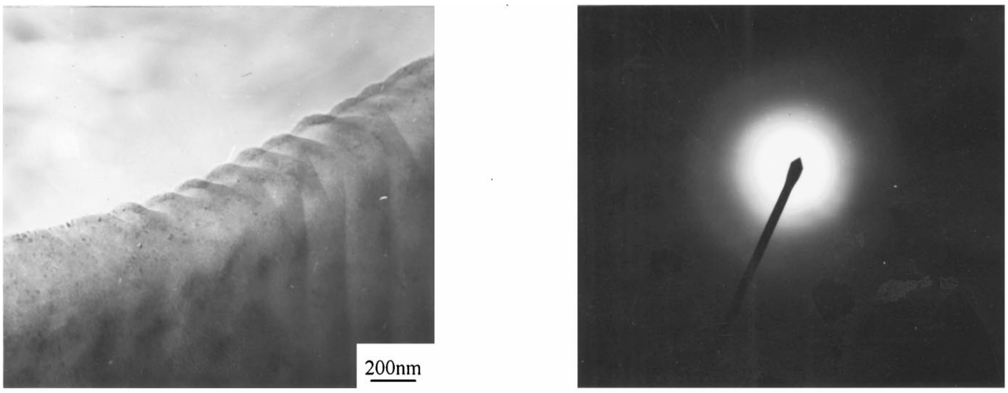
(a) SEM microstructure

(b) TEM microstructure of Si+MoSi$_2$

(c) Diffraction partten of MoSi$_2$

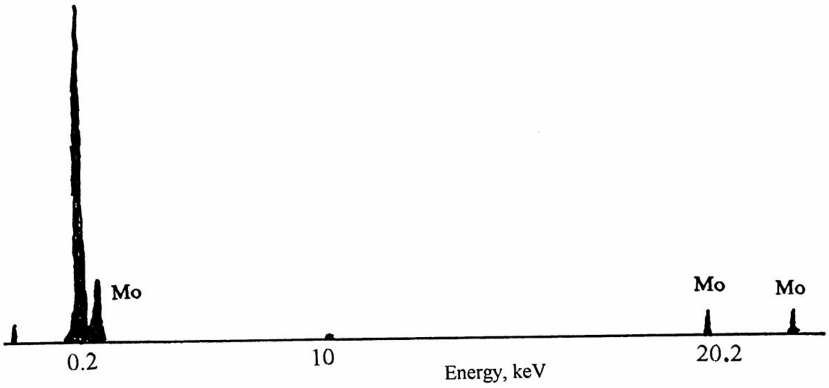
(d) Diffraction partten of Si

Figure 4 Structure analysis of oxidation protection coating of coated C/SiC composite.



(a) Microstructure of SiO$_2$ layer sealent

(b) Diffraction partten of SiO$_2$ layer sealent



(c) X-ray energy spectrum

Figure 5 Structure and chemical compositions of silica sealant.

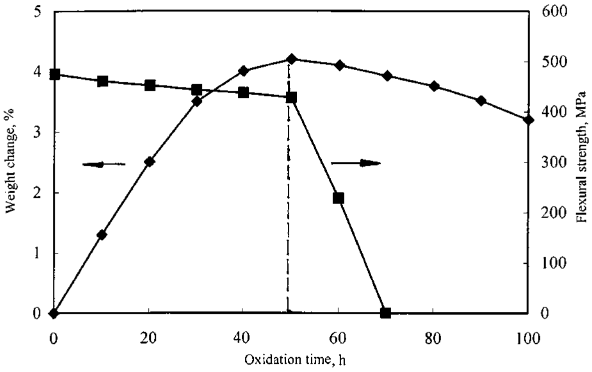


Figure 6 Relationship between oxidation and flexural strength of coated C/SiC composite.

weight gain reached the maximum value when the oxidation time was equal to 50 h, and then decreased with the increase of oxidation time. Correspondingly, the flexural strength was slightly decreased with the oxidation time within 50 h. Then, the flexural strength was dramatically decreased after 50 h, and equaled to zero when the oxidation time is 70 h (Fig. 6). Obviously, the maximum point of oxidation weight gain curve is the starting point of mechanical properties degradation for coated C/SiC composites.

The oxidation weight gain at the initial stage is attributed to the oxidation reactions of silicon and $MoSi_2$ presented by chemical reaction 2 and 3.

However, the product of MoO_3 is easily to escape from the oxidation coating because of its high vapor pressure at high temperatures. Accordingly, the oxidation weight gain rate is decreased with the temperatures. As the oxidation of silicon processes, the contents of both Si and $MoSi_2$ is decreased. If the contents of both Si and $MoSi_2$ exhausted at some localized area, the oxidation was shifted to SiC. Because the partial pressure of oxygen at localized zone was very low, the active oxidation of SiC would take place [23]:

$$SiC(s) + O_2(g) = SiO(g) + CO(g) \qquad (4)$$

If the partial pressure reached the critical value, the gaseous product will escape out and damage the glass layer of SiO_2-MoO_3. A hole was formed in the oxidation coating and became the transport tunnel for oxygen (Fig. 7). Hence, the oxidation process was enhanced and resulted in the oxidation of C interfacial layer and carbon fiber. Above all, it could be considered that the time of hole formation is the failure point of oxidation coating.

The effect of thermal shock (100 °C ⇔ 1550 °C) on the flexural strength was shown in Fig. 8. As the amount of thermal shock increases, the flexural strength was slightly decreased. The flexural strength was maintained to 420 MPa after 50 times of thermal shock, but the failure behavior of the coated C/SiC composites was similar to that of as-prepared composites (Fig. 9). It was indicated that the coated C/SiC composite exhibits excellent resistance of thermal shock.

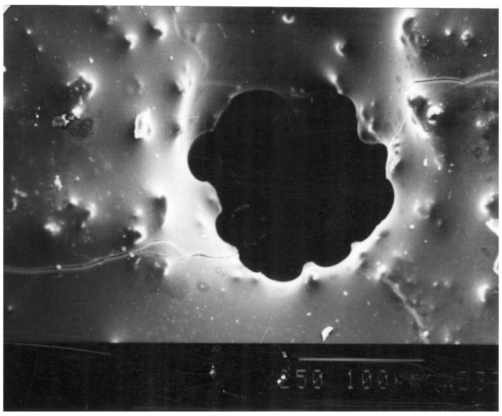


Figure 7 Hole on the oxidation protection coating.

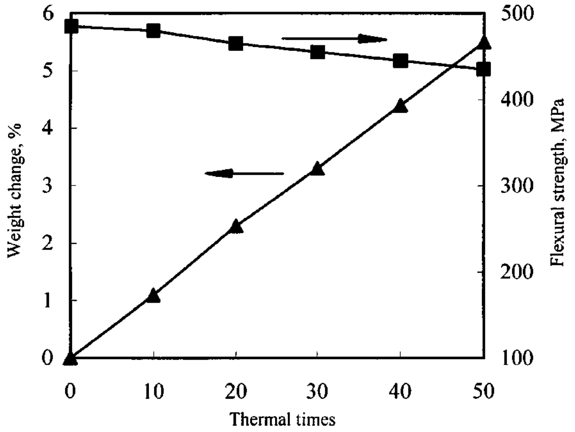


Figure 8 Relationship between thermal shock and flexural strength.

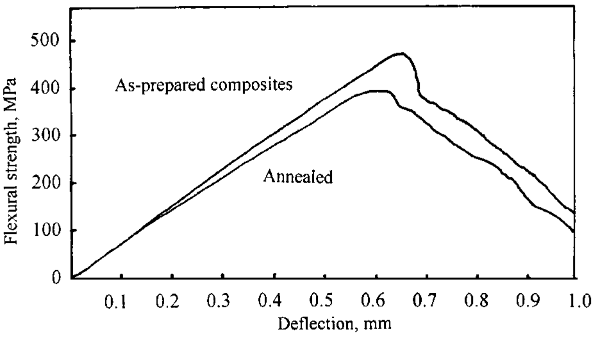


Figure 9 Failure behavior of coated C/SiC composite.

4. Conclusions

1. A new kind of oxidation protection coating of Si-$MoSi_2$ was developed for three dimensional carbon fiber reinforced silicon carbide composites which could be serviced upto 1550 °C. The oxidation protection coating had a three-layer structure: the out layer is oxidation layer of silica glass, the media layer is Si + $MoSi_2$ layer, and the inside layer is SiC layer.

2. The oxidation behaviors were investigated for the coated C/SiC composite at the temperature ranged from 500–1400 °C. The overall oxidation behavior could be divided into three stages: (i) 500 °C $< T <$ 800 °C, the oxidation mechanism was considered to be controlled by the chemical reaction between carbon and oxygen; (ii) 800 °C $< T <$ 1100 °C, the oxidation of the composite was controlled by the diffusion of oxygen through the micro-cracks, and; (iii) $T >$ 1100 °C, the oxidation of SiC became significant and was controlled by oxygen diffusion through the SiC layer.

3. The coated C/SiC composites exhibited excellent oxidation resistance and thermal shock resistance. After the composites annealed at 1550 °C for 50 h in air and 1550 °C ⇔ 100 °C thermal shock for 50 times, the flexural strength was maintained by 85% and 80% respectively.

4. The relationship between oxidation weight change and flexural strength revealed the criteria for protection coating was that the maximum point of oxidation weight gain was the failure starting point for oxidation protection coating.

Acknowledgements

This research work has been supported by National Natural Scientific Foundation (NNSF), Nation Aviation Scientific Foundation (NASF) and Nation Defense Scientific Foundation (NDSF).

References

1. J. D. BUCKELY, *Amer. Ceram. Soc. Bull* **67**(2) (1988) 364.
2. J. R. STRIFE and J. E. SHEEHAN, *ibid.* **67**(2) (1988) 369.
3. M. E. WESTWOOD, J. D. WEBSTER, R. J. DAY, F. H. HAYES and R. TAYLOR, *J. Mater. Sci.* **31** (1997) 1389.
4. F. LAMOUROUX, X. BOURRAT and R. NASLAIN, *Carbon* **31**(8) (1993) 1273.
5. S. JACQUES, A. GUETTE, F. LANGLAIS and R. NASLAIN, *J. Mater. Sci.* **32** (1997) 983.
6. S. JACQUES, A. GUETTE, F. LANGLAIS and X. BOURRAT, *ibid.* **32** (1997) 2969.
7. R. NASLAIN, O. DUGNE and A. GUETTE, *J. Amer. Ceram. Soc.* **74**(10) (1991) 2482.
8. S. RICCITIELLO and M. K. MARSHALL, *Ad. Mater.* **7** (1994) 22.
9. M. A. KMETZE, J. M. LALIBERTZ, W. S. WILLIS and S. L. SUIB, *Ceram. Eng. Sci. Proc.* **12**(9–10) (1991) 2167.
10. C. G. COFER, J. ECONOMY, Y. XU, A. ZANGVIL and E. L. CURZIO, *Comp. Sci. Tech.* **56** (1996) 967.
11. D. P. STINTON, T. M. BESMANN and R. A. LOWDEN, *Amer. Ceram. Soc. Bull* **67**(2) (1988) 369.
12. S. COURTOIS, J. DESMAISON and H. TAWIL, *J. Phys*, II, **1** (1991) 657.
13. Y. D. XU and L. T. ZHANG, *J. Amer. Ceram. Soc.* **80**(7) (1997) 1897.
14. Y. D. XU, L. T. ZHANG, L. F. CHENG and D. T. YAN, *Carbon* **36**(7) (1998) 1051.
15. Y. D. XU, L. F. CHENG, L. T. ZHANG and W. C. ZHOU, *ibid.* in press.
16. G. SAVAGE, "Carbon-Carbon Composites," 1st ed. (Chapman & Hall, London, 1992) p. 193.
17. Y. K. KIM and J. Y. LEE, *Carbon* **31**(7) (1993) 1031.
18. L. FILIPUZZI, G. CAMUS and R. NASLAIN, *J. Amer. Ceram. Soc.* **77**(2) (1994) 459.
19. L. FILIPUZZI and R. NASLAIN, *ibid.* **77**(2) (1994) 467.
20. D. L. DAUGLASS, "Oxidation of Metal and Alloys" (Metal Park, Ohio, Amer. Soc. Metal, 1971) p. 71.
21. L. NORTHCOTT, "Molybdenum" (Butterworths, London, 1956) p. 16.
22. S. Q. PAN, "Special Glass" (Tongji University, Shanghai, China, 1992) p. 52.
23. N. S. JACOBSON, *J. Amer. Ceram. Soc.* **76**(1) (1993) 3.

Received 10 December 1998
and accepted 30 April 1999