ADVANCED COMPOSITE MATERIALS

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

Effect of Water on Oxidation Behavior of 3-D C/SiC Composites Coated with SiC/a-BCx/SiC Coatings

Yongsheng Liu [a], Litong Zhang [b], Laifei Cheng [c], Shengtian Zhou [d], Wenbin Yang [e], Weihua Zhang [f] & Qingfeng Zeng [g]

[a] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an Shaanxi 710072, People's Republic of China; ; yongshengliu@nwpu.edu.cn, Email: liuys99067@163.com

[b] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an Shaanxi 710072, People's Republic of China

[c] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an Shaanxi 710072, People's Republic of China

[d] Shenyang Aeroengine Research Institute, Shenyang, Liaoning 110015, China

[e] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an Shaanxi 710072, People's Republic of China

[f] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an Shaanxi 710072, People's Republic of China

[g] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an Shaanxi 710072, People's Republic of China

To cite this article: Yongsheng Liu , Litong Zhang , Laifei Cheng , Shengtian Zhou , Wenbin Yang , Weihua Zhang & Qingfeng Zeng (2010): Effect of Water on Oxidation Behavior of 3-D C/SiC Composites Coated with SiC/a-BCx/SiC Coatings, Advanced Composite Materials, 19:2, 185-196

To link to this article: http://dx.doi.org/10.1163/092430409X12605406698237

///VSP/// Advanced Composite Materials 19 (2010) 185–196 ADVANCED COMPOSITE MATERIALS brill.nl/acm

Effect of Water on Oxidation Behavior of 3-D C/SiC Composites Coated with SiC/a-BC_x/SiC Coatings

Yongsheng Liu [a,*], **Litong Zhang** [a], **Laifei Cheng** [a], **Shengtian Zhou** [b], **Wenbin Yang** [a],
Weihua Zhang [a] **and Qingfeng Zeng** [a]

[a] National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an Shaanxi 710072, People's Republic of China
[b] Shenyang Aeroengine Research Institute, Shenyang, Liaoning 110015, China

Received 21 November 2008; accepted 10 June 2009

Abstract
The oxidation behavior of 3-D C/SiC composites coated with SiC/a-BC_x/SiC coatings was investigated in wet oxygen environments. The effects of water on oxidation behaviors of the coated composites at different temperatures were discussed based on weight change, morphology change and strength change. After oxidation at 700, 1000, and 1200°C in two kinds of water atmosphere for 100 h, the high strength retained ratios of the composites with modified coatings are demonstrated, which prove the good oxidation protection of the modified coatings for 3-D C/SiC composites.

Keywords
Oxidation behavior, water partial pressure, boron carbide, C/SiC, ceramic matrix composites

1. Introduction

The oxidation of carbon fiber and pyrolytic carbon (PyC) interface in C/SiC and C/C composite limits their long-term applications in high-temperature oxidizing environments, for example, rocket nozzles and aeronautic jet engines [1, 2]. To improve oxidation resistance of C/SiC and C/C composites, boron-bearing species [3] are widely used, which include boron oxide (B_2O_3), boron carbide (B_4C) and ternary boron-bearing compound (Si–B–C).

Various boron-bearing inhibitors, coatings, and sealants have been used to protect C/SiC and C/C composites [4–7]. McKee *et al.* [4, 5] studied the oxidation behavior of graphite impregnated with aqueous solutions of boric oxide and organo-

---

[*] To whom correspondence should be addressed. E-mails: liuys99067@163.com; yongshengliu@nwpu.edu.cn
Edited by the KSCM

DOI:10.1163/092430409X12605406698237

borates, and reported a marked reduction in oxidation rate of the graphite in dry or moist air between 600°C and 1000°C. A proposed mechanism for inhibition was the formation of a glassy boron-oxide residue that blocked active sites on the carbon surface.

Non-oxide boron-bearing ceramics, such as boron [8], B–C [9] and Si–B–C [10], were considered important candidates for oxidation protection of C/SiC composites, since glassy boron oxide would be formed due to the oxidation reaction. Multilayer SiC/B/SiC [8, 11], SiC/B_4C/SiC [11] or SiC/SiBC/SiC [10] coatings can be fabricated expediently by CVD process. Labruquere *et al.* [12–14] reported oxidation protection of B–C, Si–B–C and SiC for C/C composites. Their results showed that B–C deposits could oxidize rapidly and lead to the formation of B_2O_3 film that protects carbon from oxidation at interfacial zones. The multilayer SiC/C(B)/SiC interphase was prepared by Jacques *et al.* [15]. The crack in the interphase could self-seal at 600°C in oxidation environment. The fatigue life of the composites was higher than that of composite with PyC interphase. The oxidation protection of B_4C for carbon fiber and carbon/carbon composites were also researched by Piquero *et al.* [16] and Tsou and Kowbel [17], which demonstrated the good oxidation protection of B_4C for carbon fiber and C/C composites below 900°C. B–C and Si–B–C were also used as partial matrix in C/SiC and SiC/SiC composites for improving oxidation resistance by Lamouroux *et al.* [18] and Viricelle *et al.* [19].

Boron carbide was frequently introduced into C/SiC and C/C composites by CVD methods based on the above researches. Crystal boron carbide was synthesized in almost all investigations used with the CVD method. The amorphous boron carbide was only fabricated by Berjonneau *et al.* [20]. No report about oxidation protection of amorphous boron carbide for C/SiC or C/C composites was found.

In previous studies [21], an amorphous boron carbide (a-BC_x) coating was synthesized by low pressure chemical vapor deposition. The oxidation behaviors of 3-D C/SiC composites coated with SiC/a-BC_x/SiC coatings and SiC/SiC/SiC coatings were compared. The better oxidation protection of the SiC/a-BC_x/SiC coatings for C/SiC composite than that of SiC/SiC/SiC coatings was also demonstrated.

In the present work, the effect of water partial pressure on oxidation behavior of 3-D C/SiC composites coated with SiC/a-BC_x/SiC coatings was discussed. The weights, microstructure, and strengths of 3-D C/SiC composites before and after oxidation were compared. The oxidation protection mechanism of SiC/a-BC_x/SiC coatings for 3-D C/SiC composites at different water partial pressure was also discussed.

2. Experimental Procedure

2.1. Fabrication of Specimens [2]

Firstly, the preforms were fabricated in the Nanjing Institute of Glass Fibre, China, from carbon fibre (T-300, Japan Toray), which has a volume fraction in the range of 40–45 vol% and a braiding angle of 20° using a four-step three-dimensional

(4-step 3-D) braiding method. Secondly, PyC interface and the silicon carbide matrix were deposited by low pressure chemical vapor infiltration (LPCVI) process. The PyC was deposited on the carbon fibre using C_3H_6 precursor at 870°C for 1 h at a reduced pressure of 500 Pa, yielding a thickness of 200 nm. The SiC matrix was achieved at 1100°C for 120 h at reduced pressure of 2 kPa by using methyltrichlorosilane (MTS, CH_3SiCl_3) with a H_2:MTS molar ratio of 10. This was achieved by bubbling hydrogen in gas phase through the MTS. An argon dilution was used to slow down the chemical reaction rate during deposition. Then the test specimens were machined from the C/SiC composite to a size of 3.0 × 4.0 × 40.0 mm, followed by polishing. Finally, the specimens were coated with the hybrid CVD SiC/CVD a-BC_x/CVD SiC multilayer coatings. The CVD SiC were the same fabrication conditions as the SiC matrix except for the deposition time of 30 h. The deposition conditions for CVD a-BC_x coating were as follows: temperature 900°C, pressure 1.0 kPa, time 20 h, BCl_3 flow 50 ml/min, H_2 flow 60 ml/min, CH_4 flow 20 ml/min, Ar flow 60 ml/min.

2.2. Oxidation Tests

Oxidation tests were conducted in an alumina tube furnace with a purity of 99.99% in wet oxygen environments with volume ratio of 14 vol% H_2O/8 vol% O_2/78 vol% Ar (named as 14H_2O atmosphere) and 21 vol% H_2O/8 vol% O_2/78 vol% Ar (named as 21H_2O atmosphere) at 700, 1000 and 1200°C for 100 h. Five specimens were used for each experimental condition. The H_2O gas flowing rates were 14.0 ml/min and 21.0 ml/min, respectively. The weights of the specimens were recorded after they were oxidized for 0, 0.5, 1, 2, 5 and 10 h at the desired temperature. Then the recorded time sequence was 20 h, 30 h, 40 h, 50 h, 60 h, 70 h, 80 h, 90 h and 100 h. They were measured using an electronic balance (sensitivity = 0.01 mg).

2.3. Measurements of the Composites

The phase was identified by an X-ray diffraction device (XRD, Rigaku D/MAX-2400 with Cu K_α radiation). Surface and cross-section morphologies of the coating were observed using a scanning electron microscope (SEM, S-2700, Hitachi, Japan).

Flexural strengths of the composite specimens with size of 3.0 mm × 4.0 mm × 40.0 mm before and after oxidation were measured by a three-point bending method at the room temperature. The span dimension was 30.0 mm and the loading rate was 0.5 mm/min.

3. Results and Discussion

Figure 1 shows the weight change curves of C/SiC composites coated with SiC/a-BC_x/SiC coatings after oxidation within 14H_2O and 21H_2O atmospheres for 100 h at 700, 1000 and 1200°C. It is apparent that the weight change curves of the coated composites depend on oxidation temperature and water partial pressure. At 700°C, the weight loss for the coated composites increased continually

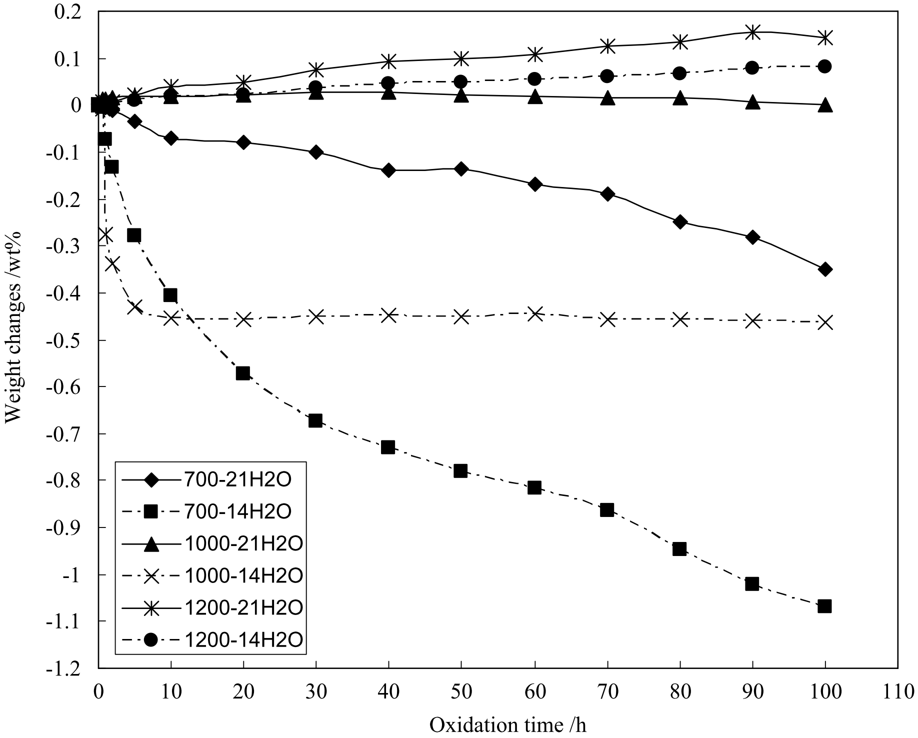


Figure 1. The weight change curves of C/SiC coated with SiC/a-BC_x/SiC coating after oxidation within $14H_2O$ and $21H_2O$ atmospheres for 100 h at 700, 1000 and 1200°C.

within $14H_2O$ and $21H_2O$ atmosphere. At 1000°C, the weight loss for the coated composites increased continually within $14H_2O$ atmosphere; however, the weight gain for the coated composites occurred within $21H_2O$. At 1200°C, the weight gain for the coated composites increased continually within $14H_2O$ and $21H_2O$ atmosphere. Figure 2 shows weight change of 3-D C/SiC composites coated with SiC/a-BC_x/SiC coatings after oxidation within $14H_2O$ and $21H_2O$ atmospheres for 100 h at different temperatures. The weight changes within $14H_2O$ are markedly larger than that within $21H_2O$, when the oxidation temperature is below 1000°C. At 1200°C, the weight change within $14H_2O$ is almost same as that within $21H_2O$. On the other hand, the discrepancies of weight changes between within-$14H_2O$ and within-$21H_2O$ decreased with increasing oxidation temperature. For example, the discrepancies are 0.7% at 700°C, 0.4% at 1000°C and less than 0.1% at 1200°C, respectively. This behavior is related to oxidation reactions between modified coating and O_2/H_2O atmosphere. This feature will be discussed combined with morphology changes and strength changes in the next part of the discussion.

Figures 3–5 show the surface and cross-sectional morphologies of 3-D C/SiC composites coated with SiC/a-BC_x/SiC coatings after oxidation within $14H_2O$ and $21H_2O$ atmospheres for 100 h at different temperature.

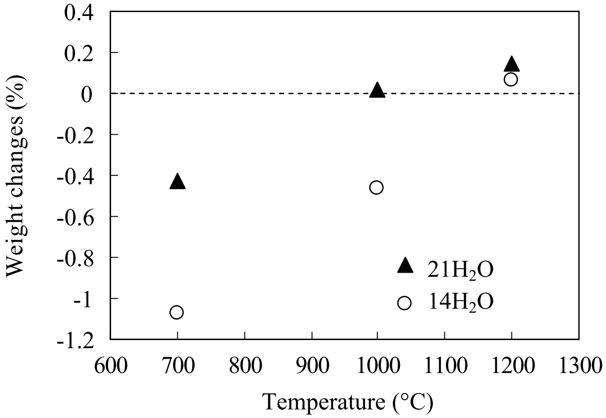
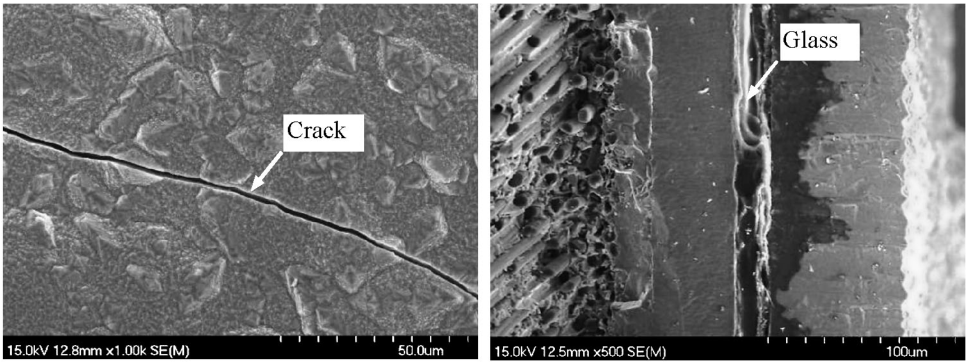
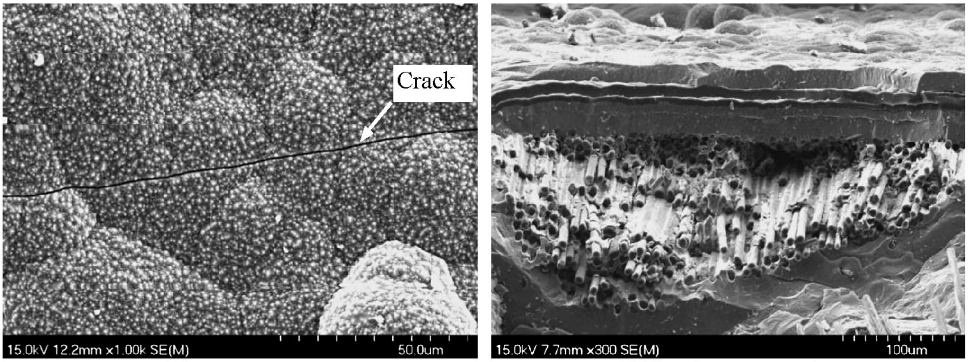


Figure 2. The weight changes of C/SiC coated with SiC/a-BC_x/SiC coating after oxidation within $14H_2O$ and $21H_2O$ atmospheres for 100 h at 700, 1000 and 1200°C, respectively.



(a) Surface morphology

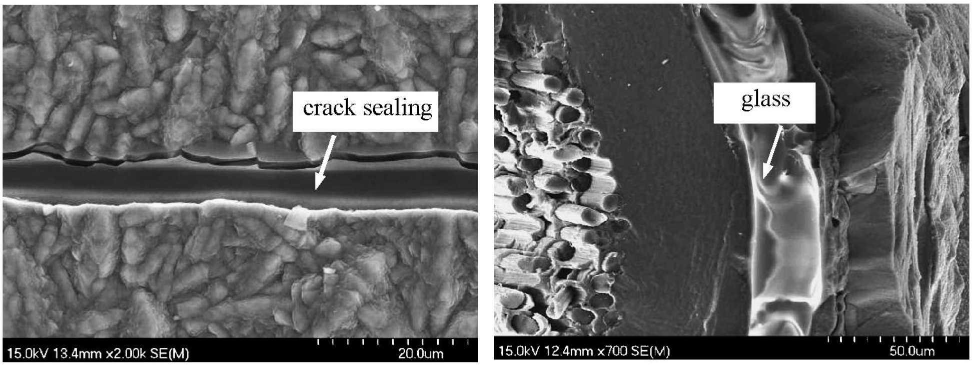
(b) Fracture morphology



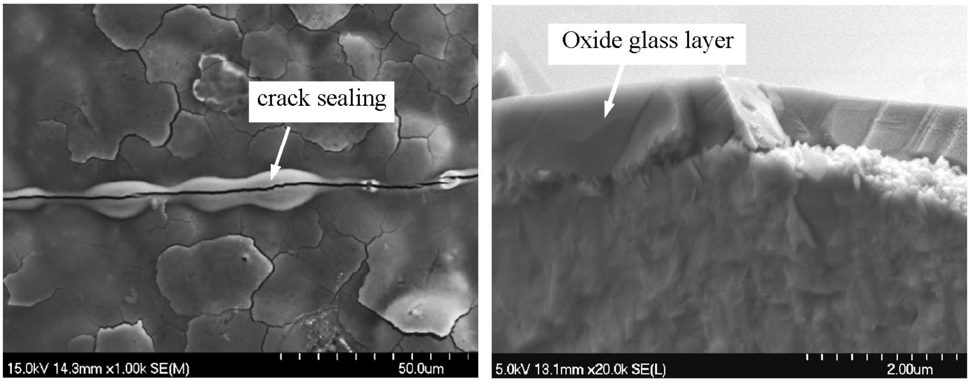
(c) Surface morphology

(d) Fracture morphology

Figure 3. SEM photos of the SiC/a-BC_x/SiC coating after oxidation at 700°C within $14H_2O$ and $21H_2O$ atmospheres for 100 h: (a) and (b) $14H_2O$; (c) and (d) $21H_2O$.



(a) Surface morphology (b) Fracture morphologies

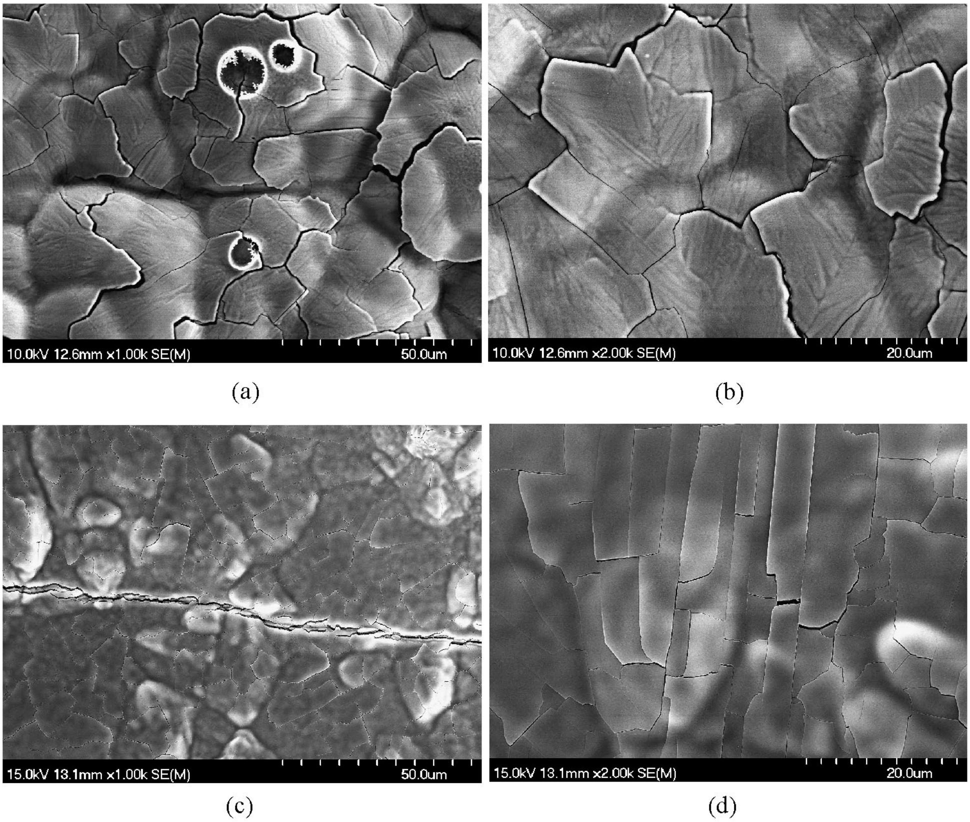


(c) Surface morphology (d) Fracture morphology of the glass layer

Figure 4. SEM photos of the SiC/a-BC_x/SiC coating after oxidation at 1000°C within $14H_2O$ and $21H_2O$ atmosphere for 100 h: (a) and (b) $14H_2O$; (c) and (d) $21H_2O$.

At 700°C, the surface of CVD SiC coating was not oxidized within $14H_2O$ and $21H_2O$ atmospheres for 100 h. No glass phase or oxidation layer was found. The cracks remained open and were not filled by glass phase. The oxidation of CVD SiC cross-sectional area of the coating was also not found from fracture morphologies. However, the oxidation of CVD a-BC_x layer and carbon fiber of the composite were found from the fracture morphologies within $14H_2O$ and $21H_2O$ atmospheres for 100 h. The oxidation within $14H_2O$ atmosphere was more serious than that within $21H_2O$ atmosphere from the fracture morphologies. The obvious glass phase was found after it had been oxidized within $14H_2O$ atmosphere.

At 1000°C, the oxidation of CVD SiC was found within both $14H_2O$ and $21H_2O$ atmospheres for 100 h. The cracks were filled by the glass. Within $14H_2O$ atmosphere, the oxidation of CVD SiC coating was not obvious; however, the oxidation of CVD a-BC_x coating was very obvious and a large amount of glass phase existed, as shown in Fig. 4(b). Within $21H_2O$ atmosphere, the oxidation of coating was more serious than that within $14H_2O$ atmosphere, which resulted in the thick



(a) (b)

(c) (d)

Figure 5. SEM photos shows the surface morphologies of the SiC/a-BC$_x$/SiC coating after oxidation at 1200°C within 14H_2O and 21H_2O atmospheres for 100 h: (a) and (b) 14H_2O; (c) and (d) 21H_2O.

oxide glass layer shown in Fig. 4(d). The glass phase was found in the coating surface, and the thickness of the glass layer reached 1.0 μm, as shown in Fig. 4(d), which demonstrated that the CVD SiC coating was oxidized within 21H_2O atmosphere. The crack in glass occurred due to the different thermo-expansion coefficient between glass and CVD SiC coating, as shown in Fig. 4(c). Few carbon fiber were oxidized within different atmospheres.

At 1200°C, the oxidation of CVD SiC was more serious within both 14H_2O and 21H_2O atmospheres for 100 h. There were a large number of cracks in glass due to the thermo-expansion coefficient mismatch between glass and CVD SiC coating, as shown in Fig. 5. Within 14H_2O atmosphere, pores were found that had resulted from the glass volatilization and the crystallization of the surface glass. This phenomenon has been discussed in previous studies [21]. Within 21H_2O atmosphere, no pores and glass crystallization were found. However, there were more cracks in the surface glass layer, which had also resulted from thermo-expansion coefficient mismatch between the glass layer and CVD SiC coating.

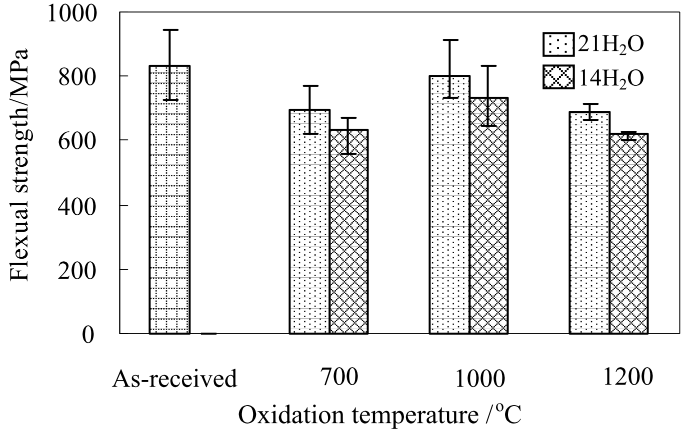


Figure 6. The residual flexural strength of C/SiC coated with SiC/a-BC_x/SiC coating after oxidation within $14H_2O$ and $21H_2O$ atmospheres for 100 h, respectively.

Figure 6 shows the residual flexural strength of 3-D C/SiC composites after oxidation within $14H_2O$ and $21H_2O$ atmosphere for 100 h. The average strength of as-received composite was 833 MPa. After oxidation within $14H_2O$ and $21H_2O$ atmospheres for 100 h at different temperatures, the flexural strengths all decreased. The residual strengths within $21H_2O$ atmosphere were higher than that within $14H_2O$ atmosphere. Within $21H_2O$ atmosphere, the residual strengths were 693 MPa, 803 MPa and 688 MPa, respectively, and strength retained ratios were residual 83.2%, 96.4%, 82.6% after oxidation at 700°C, 1000°C and 1200°C, respectively. Within $14H_2O$ atmosphere, the residual strengths were 631 MPa, 734 MPa and 620 MPa, respectively, and strength retained ratios were residual 75.8%, 88.1%, 74.4% after oxidation at 700°C, 1000°C and 1200°C, respectively.

4. Discussion

Based on the above results, the oxidation behavior and protection mechanisms can be discussed as follows. In 3-D C/SiC composites coated with SiC/a-BC_x/SiC coatings, the carbon fiber, PyC interphase, SiC matrix and coating and BC_x coating were all oxidized within water–oxygen atmosphere from 700 to 1000°C. The melting point of B_2O_3 is 450°C and the volatilization point is 900°C [22]. Furthermore, the volatilization temperature would decrease when H_2O was present [3, 22]. Due to the H_2O effect, the volatilization of SiO_2 was also more easily achieved. In wet oxygen atmosphere, the oxidation behavior of composite was controlled by the following oxidation reactions:

$$\text{a-BC}_x\ (s) + O_2\ (g) \xrightarrow{600°C} B_2O_3\ (l) + CO_2\ (g) + CO\ (g) \quad (1)$$

$$B_2O_3\ (l) + H_2O\ (g) \longrightarrow 2HBO_2\ (g) \quad (2)$$

$$\text{a-BC}_x\ (s) + H_2O\ (g) \longrightarrow B_2O_3\ (l) + CO_2\ (g) + CO\ (g) + H_2\ (g) \quad (3)$$

$$B_2O_3\ (l) + 3H_2O\ (g) \longrightarrow 2H_3BO_3\ (g) \tag{4}$$

$$C\ (s) + O_2\ (g) \longrightarrow CO_2\ (g) \tag{5}$$

$$2SiC\ (s) + 3O_2\ (g) \longrightarrow 2SiO_2\ (s) + 2CO\ (g) \tag{6}$$

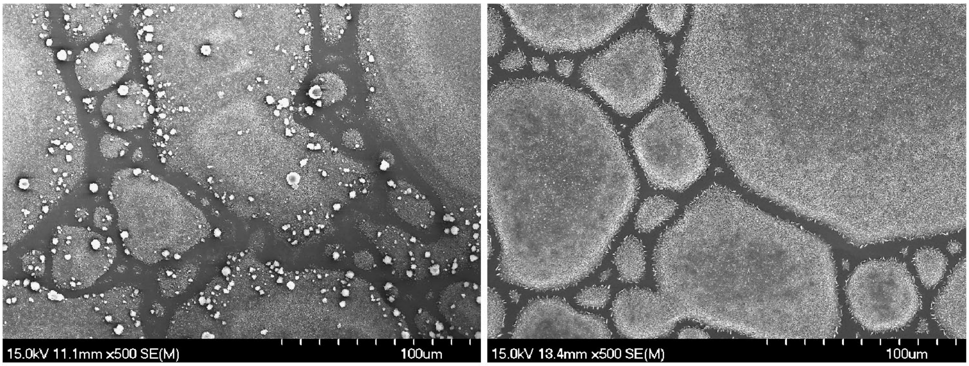
$$SiC\ (s) + 3H_2O\ (g) \longrightarrow SiO_2\ (s) + CO\ (g) + 3H_2\ (g) \tag{7}$$

$$SiO_2\ (s) + 2H_2O\ (g) \longrightarrow SiO(OH)_4\ (g) \tag{8}$$

Reactions (1)–(5) would occur below 700°C, and these led to the weight loss of the composites. Reaction (8) also led to the weight loss. Reactions (6)–(7) would occur above 700°C, and led to the weight gain of the composites.

From the above results of weight change, morphology changes and strength changes, it is apparent that the H_2O partial pressure and temperature were the main controlling factors for oxidation behaviors of 3-D C/SiC composites. Therefore, the oxidation mechanism should be discussed according to different temperature and H_2O partial pressure.

At 700°C, the reactions (6) and (7) were very slow, which led to the oxidation of CVD SiC layer that was very weak in wet oxygen atmospheres [23]. Therefore, the oxidations of SiC layer were not found within $14H_2O$ and $21H_2O$ atmospheres. However, the CVD a-BC_x layer was seriously oxidized in $14H_2O$ and $21H_2O$ atmospheres, as shown in Fig. 7. Due to the thermo-expansion coefficient mismatch between multilayer coating and 3-D C/SiC composites, unavoidable cracks exist in the multilayer coatings. The oxygen and water would intrude into composites, which led to some PyC and carbon fibers being oxidized. The oxidation of PyC interface and carbon fiber made the strength of composite decrease. On the other hand, CVD a-BC_x would react with oxygen and water as shown in reactions (1) and (3), and led to coating cracks that were partially sealed, as shown in Fig. 3(b). Therefore, the composites showed weight loss, un-oxidized CVD SiC surface, partial sealing of crack and strength decrease. The difference in the results between



(a) $21H_2O$ (b) $14H_2O$

Figure 7. Surface morphologies and EDS of CVD a-BC_x layer after oxidation for 10 h at 700°C within different water partial pressure.

$14H_2O$ and $21H_2O$ atmospheres should be attributed to the different reaction degree of reactions (1) and (3) within different water partial pressure atmosphere. Within $14H_2O$, reactions (1) and (3) are weaker than that within $21H_2O$ atmosphere. Less B_2O_3 glass was formed within $14H_2O$ atmosphere than that within $21H_2O$: so fewer cracks were sealed after oxidation within $14H_2O$ atmosphere than $21H_2O$ atmosphere, which resulted in more PyC and carbon fiber being oxidized within $14H_2O$ than $21H_2O$ atmospheres. Therefore, the weight change within $14H_2O$ atmosphere is larger than that within $21H_2O$ atmosphere, as shown as the weight change curves in Figs 1 and 2.

At 1000°C, the oxidations of CVD SiC and CVD a-BC_x were more severe than that at 700°C, because all oxidation reactions would be more vigorous. Reactions (6) and (7) become stronger. Especially the B_2O_3 glass could promote the solution of SiC and the formation of SiO_2 as shown in following reaction [24, 25].

$$7SiC\ (s) + 6B_2O_3\ (l) \longrightarrow 7SiO_2\ (s) + 3B_4C\ (s) + 4CO\ (g) \tag{9}$$

After oxidation for 10 h, the cracks were sealed rapidly, as shown by the weight changes in Fig. 1; therefore, the weight change of the composites was smaller than that at 700°C. The oxidations of SiC layer and a-BC_x layer were found within $14H_2O$ and $21H_2O$ atmospheres. The cracks were fully sealed and a large amount of glass exists between CVD SiC layers, as shown in Fig. 4(b). The effect of water partial pressure on the oxidation behavior of the coated composites was very obvious. Within $21H_2O$ atmosphere, reactions (3) and (7) were more vigorous than that within $14H_2O$ atmosphere, which led to a large amount of glass formation. The speed with which cracks were sealed in coatings was faster in $21H_2O$ atmosphere than that in $14H_2O$ atmosphere, which lead to smaller weight change within $14H_2O$ atmosphere than $21H_2O$ atmosphere, as shown by the weight change curves in Figs 1 and 2. Therefore, the composites showed lower weight change, thicker oxide layer, and higher residual strength within $21H_2O$ atmosphere than that within $14H_2O$ atmosphere.

At 1200°C, the oxidations of CVD SiC and CVD a-BC_x were more severe than that at 1000°C. The more severe reaction led to the fewer weight changes, and extensive oxidation in the surface. The cracks were all sealed rapidly within $14H_2O$ and $21H_2O$, which led to the similar weight changes within $14H_2O$ and $21H_2O$, as shown by the weight change curves in Figs 1 and 2. Therefore, there was no obvious difference on the oxidation behaviors of the coated composites in $14H_2O$ and $21H_2O$ atmospheres.

5. Conclusions

We have demonstrated the oxidation behavior of 3-D C/SiC composites coated with SiC/a-BC_x/SiC coatings in different water partial pressure. The weight change curves were controlled by oxidation temperature and water partial pressure. The weight changes decreased with increasing oxidation temperature within $14H_2O$ and

$21H_2O$ atmospheres. The weight changes within $14H_2O$ atmosphere were larger than those in $21H_2O$ atmosphere. The oxide glass occurred within $14H_2O$ and $21H_2O$ atmospheres at all oxidation temperatures. With increasing oxidation temperature, the oxidation of coating and composites became more pronounced, and the amount of glass increased. Above 1000°C, the cracks in the coating were full sealed. The high strength retained ratios of the composites with modified coatings are demonstrated, which proves the good oxidation protection of modified coatings for 3-D C/SiC composites.

Acknowledgements

This work was supported by the National Science Foundation in China (No. 90405015, No. 50672076, No. 50425208, No. 50642039). This work was also supported by the Doctorate Foundation of Northwestern Polytechnical University (CX200505). Project supported by the Research Fund of the State Key Laboratory of Solidification Processing (NWPU), China (Grant No. 45-QP-2010).

References

1. R. Naslain, Design, preparation and properties of non-oxide CMCs for application in engines and nuclear reactors: an overview, *Compos. Sci. Technol.* **64**, 155–170 (2004).
2. Y. S. Liu, Preparation and application bases of B–C ceramic by CVD/CVI, *PhD Thesis*, North Western Polytechnical University, Xi'an, China (2008). (In Chinese.)
3. R. Naslain, A. Guette, F. Rebillat, R. Pailler, F. Langlais and X. Bourrat, Boron-bearing species in ceramic matrix composites for long-term aerospace applications, *J. Solid State Chem.* **117**, 449–456 (2004).
4. D. W. Mckee, Borate treatment of carbon fibers and carbon/carbon composites for improved oxidation resistance, *Carbon* **24**, 737–741 (1986).
5. D. W. Mckee, C. L. Spiro and E. J. Lamby, The effects of boron additives on the oxidation behavior of carbons, *Carbon* **22**, 507–511 (1984).
6. P. Ehrburger, P. Baranne and J. Lahaye, Inhibition of the oxidation of carbon/carbon composite by boron oxide, *Carbon* **24**, 495–499 (1986).
7. A. Derre, L. Filipozzi and F. Peron, High temperature behaviour and oxidation resistance of carbon–boron–nitrogen compounds obtained by LPCVD, *J. Phys. IV* **3**, 195–202 (1993).
8. Y. S. Liu, L. F. Cheng, L. T. Zhang, S. J. Wu, D. Li and Y. D. Xu, Oxidation protection of multilayer CVD SiC/B/SiC coatings for 3D C/SiC composite, *Mater. Sci. Engng A* **466**, 172–177 (2007).
9. S. J. Wu, L. F. Cheng, W. B. Yang, Y. S. Liu, L. T. Zhang and Y. D. Xu, Oxidation protective multilayer CVD SiC coatings modified by a graphitic B–C interlayer for 3D C/SiC composite, *Appl. Compos. Mater.* **13**, 397–406 (2006).
10. S. Goujard and L. Vandenbulcke, Oxidation tests of carbonaceous composite materials protected by Si–B–C CVD coatings, *Thin Solid Films* **245**, 86–97 (1994).
11. S. Goujard and L. Vandenbulcke, The oxidation behaviour of two- and three-dimensational C/SiC thermostructural materials protected by chemical-vapour-deposition polylayers coatings, *J. Mater. Sci.* **29**, 6212–6220 (1994).

12. S. Labruquere, H. Blanchard, R. Pailler and R. Naslain, Enhancement of the oxidation resistance of interfacial area in C/C composites. Part I: Oxidation resistance of B–C, Si–B–C and Si–C coated carbon fibres, *J. Eur. Ceramic Soc.* **22**, 1001–1009 (2002).
13. S. Labruquere, H. Blanchard, R. Pailler and R. Naslain, Enhancement of the oxidation resistance of interfacial area in C/C composites. Part II: Oxidation resistance of B–C, Si–B–C and Si–C coated carbon preforms densified with carbon, *J. Eur. Ceramic Soc.* **22**, 1011–1021 (2002).
14. S. Labruquere, H. Blanchard, R. Pailler and R. Naslain, Enhancement of the oxidation resistance of interfacial area in C/C composites. Part III: The effect of oxidation in dry or wet air on mechanical properties of C/C composites with internal protections, *J. Eur. Ceramic Soc.* **22**, 1023–1030 (2002).
15. S. Jacques, A. Guette, F. Langlais and R. Naslain, Preparation and characterization of SiC/SiC micro-composites with composition graded C(B) interphases, *Key Engng Mater.* **127**, 543–550 (1997).
16. T. Piquero, H. Vincent, C. Vincent and J. Bouix, Influence of carbide coatings on the oxidation behavior of carbon fibers, *Carbon* **33**, 455–467 (1995).
17. H. T. Tsou and W. Kowbel, Design of multilayer plasma-assisted CVD coatings for the oxidation protection of composite materials, *Surf. Coatings Technol.* **79**, 139–150 (1996).
18. F. Lamouroux, S. Bertrand, R. Pailler, R. Naslain and M. Cataldi, Oxidation-resistant carbon fiber reinforced ceramic–matrix composites, *Compos. Sci. Technol.* **59**, 1073–1085 (1999).
19. J. P. Viricelle, P. Goursat and D. Bahloul-Hourlier, Oxidation behavior of a multi-layered ceramic matrix composite $(SiC)_f/C/(SiBC)_m$, *Compos. Sci. Technol.* **61**, 607–614 (2001).
20. J. Berjonneau, G. Chollon and F. Langlais, Deposition process of amorphous boron carbide from $CH_4/BCl_3/H_2$ precursor, *J. Electrochem. Soc.* **153**, C795–C800 (2006).
21. Y. S. Liu, L. T. Zhang, L. F. Cheng, W. B. Yang and W. H. Zhang, Preparation and oxidation protection of CVD SiC/a-BC_x/SiC coatings for 3D C/SiC composites, *Corros. Sci.* **51**, 820–826 (2009).
22. J. P. Viricelle, P. Goursat and D. Bahloul-Hourlier, Oxidation behaviour of a boron carbide based material in dry and wet oxygen, *J. Therm. Anal. Calorim.* **63**, 507–515 (2001).
23. W. H. Zhang, Self-healing mechanisms of binary-component layered BC_x–SiC coatings, *Master Thesis*, Northwestern Polytechnical University, Xi'an, China (2008). (In Chinese.)
24. H. Hatta, T. Sohtome, Y. Sawada and A. Shida, High temperature crack sealant based SiO_2–B_2O_3 for SiC coating on carbon–carbon composites, *Adv. Compos. Mater.* **12**, 93–106 (2003).
25. J. W. Fergus and W. L. Worrell, Effect of carbon and boron on the high-temperature oxidation of silicon carbide, *J. Amer. Ceramic Soc.* **78**, 1961–1964 (1995).