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Influence of oxidation on fatigue life of a carbon/silicon carbide composite in water vapor containing environments

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Abstract

The influence of oxidation on the fatigue life of two-dimensional carbon/silicon carbide composites in water vapor containing environments at 1300 °C was investigated. Tension–tension fatigue experiments were conducted at sinusoidal frequency of 3 Hz. Using a stress ratio ($\sigma_{min}/\sigma_{max}$) of 0.1, specimens were subjected to peak fatigue stresses of 90, 120 and 150 MPa. The mean residual strength of the specimens after survived 100,000 cycles with a peak stress of 90 MPa was 83.9% of that of the as-received composite. The mean fatigue lives of the specimens subjected to peak fatigue stresses of 120 and 150 MPa were 42,048 and 13,514 cycles, respectively. Oxidation was the dominant damage mechanism, which remarkably decreased the fatigue life. Oxidizing species diffusion within the composite defects was discussed. The higher the applied stresses, the larger the equivalent radius of the defect and the shorter the fatigue life.

Keywords: B. Composites; C. Fatigue; C. Corrosion; C. Lifetime

1. Introduction

Ceramics are one of the best material classes when they come to high temperature capabilities. Thus, the materials that are garnering much of the attention are ceramic matrix composites (CMCs). However, CMCs do have some limiting factors that affect their performance. One of these limiting factors is the oxidation that occurs within the CMC at elevated temperatures. Carbon fiber reinforced silicon carbide (C/SiC) is a CMC that succumbs to oxidation above 400 °C because of the carbon phase burn-out. Both oxygen and water vapor are able to react with the carbon and oxidize the carbon fibers within the SiC matrix. Despite this oxidation problem, C/SiC composites are considered as a composite candidate for many space and aircraft applications such as, heat exchangers, integrally bladed disks, nozzle exit ramps, un-cooled nozzles, combustors, thrust chambers, turbo pump rotors, and re-entry heat shields. These applications will involve cyclic loading with large cycle accumulation at very high temperatures.

When evaluating CMCs for potential use in high temperature structural applications, the basic material characterization obtained from mechanical and environmental testing is important to understand their fundamental properties. However, these types of tests may not be able to provide enough information on how the material will perform under working conditions. This is especially true when application conditions include variables such as high temperature, mechanical and thermal stresses, flowing gases, reactive environments, high chamber pressure, and material reactivity/recession (oxidation). The ultimate performance test is to insert a CMC component into its real application (i.e., in an engine). This is often very expensive and impractical when dealing with developmental materials. Simpler, less expensive and more practical test methods must be utilized. One type of performance test is stressed oxidation or creep-rupture testing, allowing to screen the material at controlled stress, temperature and environmental conditions similar to a real application.

Several studies have been conducted to analyze the oxidation that occurs within C/SiC composites. For example, Verilli et al. [1] studied the behavior of C/SiC during creep-rupture at temperatures of 550 and 650 °C. They concluded that oxidation was the primary damage mechanism during these

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tests. Halbig et al. [2] studied the creep-rupture behaviors of several kinds of CMCs at 1454 °C in oxidizing atmosphere. Their results showed that the rupture lives of the composites were remarkably decreased by the oxidation. However, the behaviors of CMCs subjected to cyclic loadings in water vapor containing environments were rarely reported.

The present work is to investigate the influence of oxidation on fatigue life of 2D C/SiC composites in water vapor containing environments at elevated temperatures. Effects of applied loading and gaseous diffusion within the composite on the composite fatigue life were discussed.

2. Experimental

2.1. Materials

T-300™ carbon fibers (Toray, Japan) were used. The fiber preform was prepared using a layered carbon-cloth braid method, and was supplied by the Nanjing Institute of Glass Fiber, People's Republic of China. The volume fraction of fibers was about 40%. Low pressure isothermal chemical vapor deposition (I-CVI) was employed to deposit a pyrolytic carbon layer and the silicon carbide matrix. A thin pyrolytic carbon layer was deposited on the surface of the carbon fiber as the interfacial layer with C_3H_8 at 800 °C. Methyltrichlorosilane (MTS) was used for the deposition of the SiC matrix. MTS vapor was carried by bubbling hydrogen, under typical conditions of 1000 °C, H_2:MTS ratio of 10 and pressure of 5 kPa. Argon was employed as the diluent gas to slow down the chemical reaction rate of deposition. Finally, the test specimens were machined from the fabricated composites and further coated with SiC by I-CVI under the same conditions. The density and open porosity of the as-received composite was 2.28 g/cm^3 and 8.0%, respectively. Monotonic tensile tests were conducted at room temperature on a servo-hydraulic machine (Model Instron 8801, Instron Ltd., England). The mean tensile strength of the as-received specimens is 275.0 MPa.

The microstructure of the typical as-manufactured composite is shown in Fig. 1. The composite contains microcracks and pores within the matrix-rich regions and the carbon fiber plies and individual tows. These types of microcracks and pores in C/SiC have been well documented [3].

2.2. Fatigue tests and measurements

The integrated system and specimen set-up is schematically shown in Fig. 2. The chamber temperature was firstly heated to 1300 °C with specimen protected by pure argon. After keeping the temperature for 10 min, the atmosphere in the chamber was changed to 81.2% argon, 12.8% water vapor and 6.0% oxygen. The atmosphere was changed to pure argon immediately the specimen failed.

Fatigue tests were performed on the aforementioned servo-hydraulic machine under load control at stress ratio ($\sigma_{min}/\sigma_{max}$) of 0.1 and sinusoidal frequency of 3 Hz. Maximum stress levels of 90, 120 and 150 MPa were selected. Tests were interrupted either the number of cycles reached 100,000 or the specimen fractured. Tensile tests were conducted for the survived specimens at room temperature to examine the residual strength. The number of specimens for each test was three. The specimen microstructures were observed by scanning electron microscopy (SEM, JSM-6700F).

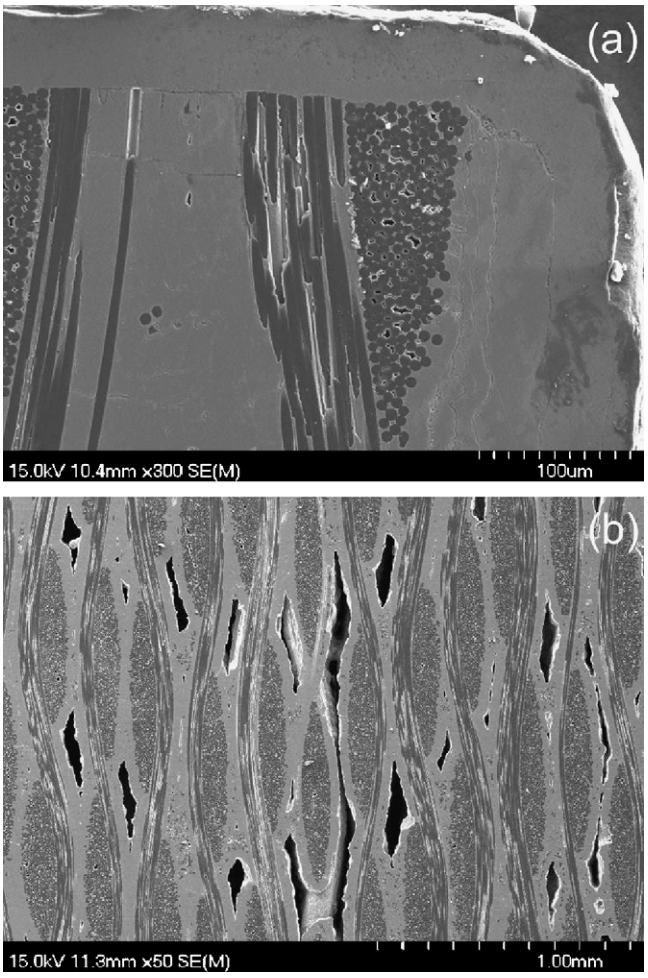

Fig. 1. Polished sections of the as-received composite: (a) micrograph of the SiC coating and pores within carbon fibers and (b) morphology of pores within bundles.

3. Results and discussion

3.1. Fatigue lives of the 2D C/SiC specimens

The fatigue lives and residual strengths of the specimens cycled at different peak stresses are listed in Table 1. The mean residual strength of the specimens after survived 100,000 cycles with a peak stress of 90 MPa was 230.6 ± 4.4 MPa, which was 83.9% of that of the as-received composite. The average lives of specimens cycled at 120 and 150 MPa were 42,048 and 13,514 cycles, respectively. The specimen life decreases as the applied stress increases.

3.2. Microstructural observations

The typical fracture section of the specimen fractured during cyclic loading at peak stress of 120 MPa is shown in Fig. 3. Fig. 3(a) shows the oxidation morphology beneath the SiC

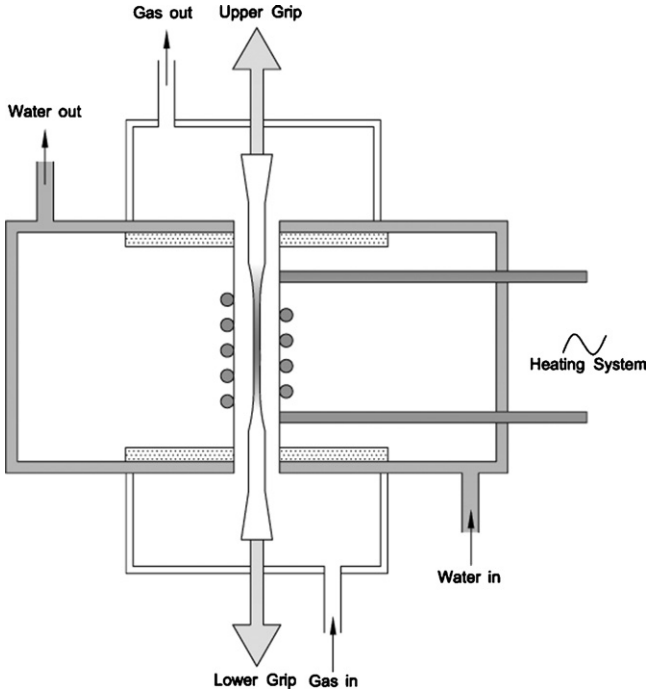

Fig. 2. Schematic of test equipment and specimen set-up.

Table 1
Fatigue lives of specimens cycled at different peak stresses

Lifetime/cycle	Peak stress (MPa)		
	90	120	150
Average	>100,000[a]	42,047	13,514
Deviation	/	6,784	8,137

[a] No failure after 100,000 cycles.

coating, clear fiber oxidation can be observed. Fig. 3(b) shows the near-centre region morphology of the fracture section, where oxidation is much less than that of the superficial region.

Pointed fiber morphology was observed at the outer region of each fiber bundle (Fig. 4). Non-uniform oxidation of the fiber bundles was presented. These pointed fiber tips were less noticeable at the superficial region because the fibers were almost completely oxidized. Moreover, this oxidation morphology could also be found at the centre regions of the fracture surface, which indicated that the oxidizing species diffused throughout the specimen cross section.

In order to clarify the gaseous diffusion paths, the SiC coating surface and cross section were polished and then observed by SEM. The morphology of polished SiC coating surface is shown in Fig. 5. After fatigue, new cracks which are perpendicular to the loading axis emerge on the coating surface (see Fig. 5(a)), which has been previously reported by Shuler et al. [4]. The authors [4] investigated the room-temperature fatigue behavior of a 2D C/SiC composite and found that the crack spacing decreased rapidly within the first 100 cycles and remained constant as the loading cycling continued. It is seen from Fig. 5(b) that the processing pores of the composite were sealed by crystalline silica. Direct oxidation took place once the oxidizing species diffuse through the cracks (see Fig. 3(a)).

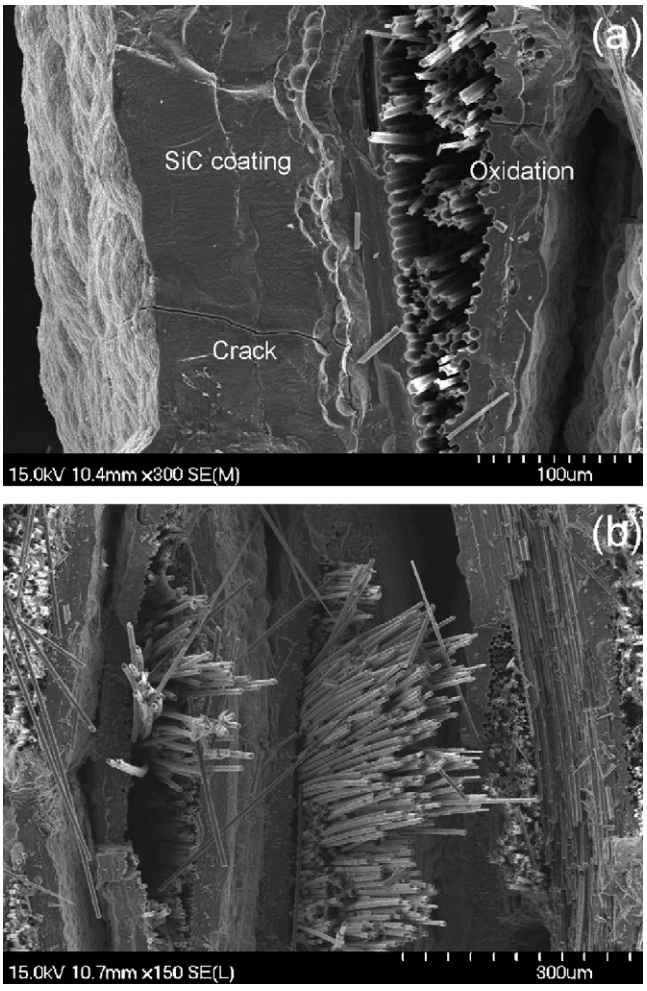

Fig. 3. Oxidation morphology of the fracture section. (a) Superficial region and (b) centre region.

Oxidation of the composite centre region could be attributed to the diffusion of the oxidizing species within the composite defects. Closer observations of the oxidized fiber bundles at the composite centre region are shown in Fig. 6. Cracks between neighboring bundles (Fig. 6(a)) and cracks of the SiC matrix around each bundle (Fig. 6(b)) provided paths for oxidizing species to diffuse to the fibers.

3.3. Damage mechanisms

Carbon fiber oxidation within the C/SiC composites is the dominant damage mechanism in the present experiments. Both oxygen and water vapor can oxidize carbon fibers, thus induce a diameter reduction. The composite loading bearing capacity is decreased by progressive loss of fibers. Oxidation firstly starts from the SiC coating. The major reactions of SiC in water vapor containing environments are [5]:

$$SiC(s) + 3H_2O = SiO_2(s) + CO(g) + 3H_2 \quad (1)$$

$$SiC(s) + (3/2)O_2 = SiO_2(s) + CO(g) \quad (2)$$

Although the viscous silica layer can seal the coating cracks, water vapor may react with silica and forms SiOH group,

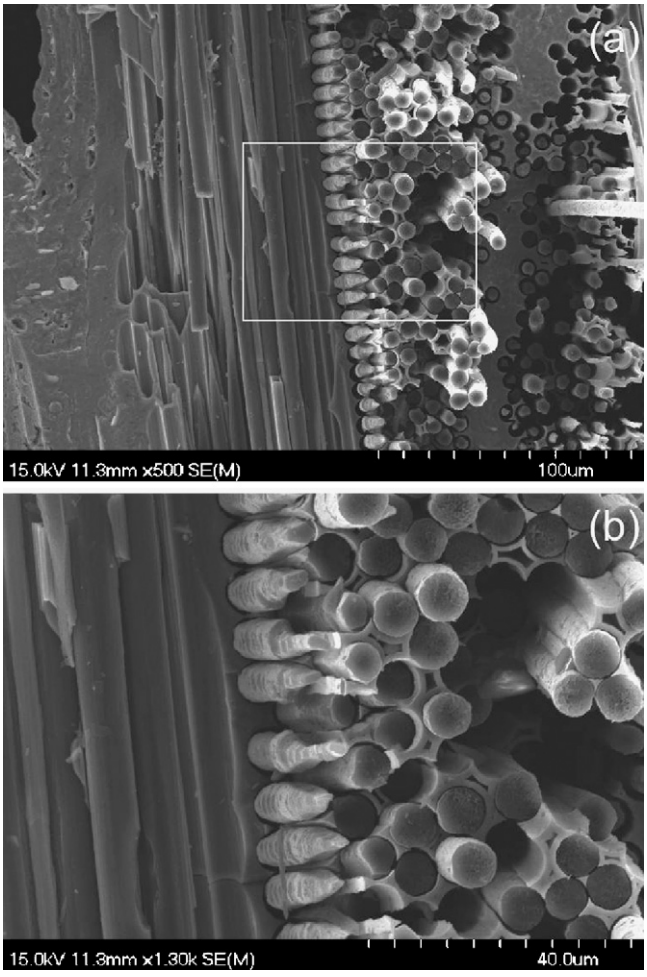

Fig. 4. (a) Morphology of pointed fiber tips near the centre region of the fracture section and (b) a magnified view. Non-uniform oxidation morphology within a single bundle is observed.

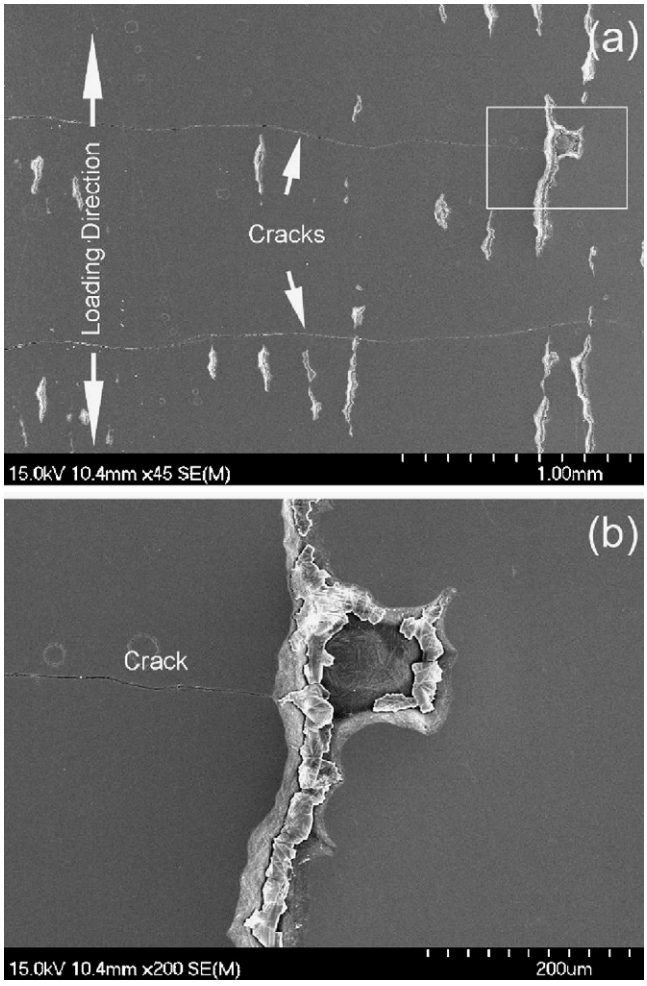

Fig. 5. (a) Morphology of polished SiC coating after experiment and (b) a magnified view.

which interrupts the SiO_2 network [6]. The destroyed SiO_2 network makes water vapor diffuse more quickly, and thereby increases the oxidation of SiC. Furthermore, once the composite is exposed to water vapor containing environments with sufficient stresses, the oxidation rate is predicted to be much higher [7].

It is accepted that during cyclic loading the processing-related matrix cracks will extend and new cracks will form [4]. The higher the peak fatigue stress, the higher the crack density. Under tensile load, the cracks are large and gaseous diffusion is less affected by the growth of silica layer.

Gaseous diffusion through the cracks within the composite is responsible for the non-uniform oxidation of the fiber bundles at the centre region. Basically, there are two kinds of defects, which together provide pathways for gaseous diffusion: pores between fiber bundles and cracks of the SiC matrix. The former provides pathways for the oxidizing species to diffuse in to the inner region of the composite, the latter enables the oxidizing species to get to and subsequently react with the fibers. The oxidation process in the C/SiC substrate with a SiC coating was controlled by the rate of gaseous diffusion through the defects. The diffusivity through the defects could be described by the Knudsen diffusivity [8]:

$$D_k = \frac{4}{3}\left(\frac{8RT}{\pi M}\right)\frac{r}{2} \quad (3)$$

where r is the equivalent radius of the defect and M is the mean molecular weight of the diffusing species. When the applied load exceeds the matrix cracking stress of the composite, pre-existing cracks start to grow and new cracks starts to form, the equivalent radius r become larger than that of non-stressed composite. Hence the oxidizing species diffuse through the pores and cracks and attack the fibers at the inner region.

The widening of pores between fiber bundles is largely ascribed to the non-uniform stress distribution, which has been pointed out by Shuler et al. [4]. At the macroscopic scale, the 2D woven fiber bundles configurations produce non-uniform stress distribution along the axial and width directions within individual plies. The random stacking of the plies produces a non-uniform stress distribution in the thickness direction of the specimen. Non-uniform stretching of plies produces a shear stress and contact pressure at the contact points between plies. This phenomenon would lead to asymmetric elongation of each ply and consequently generate larger pores between bundles.

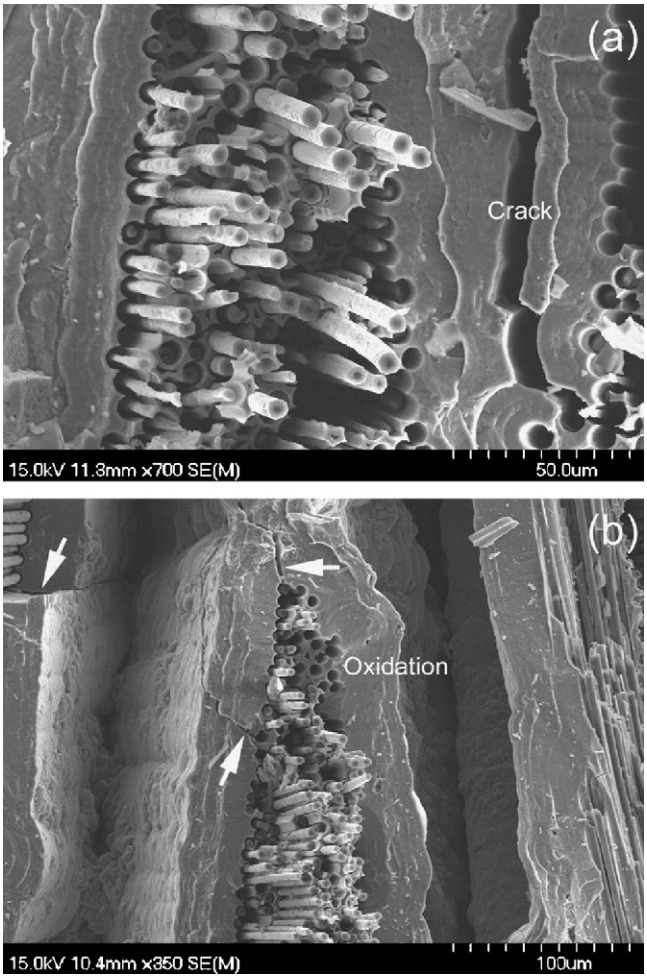

Fig. 6. Micrographs showing (a) crack between neighboring bundles and (b) crack of the SiC around a single fiber bundle.

Both the crack density (D) and the crack opening width also have contributions to the variation of r. Since the crack opening width is closely related to the applied stress, its more practical to discuss the effect of crack density on r. Ogin et al. [9] have proposed a Paris-law-type model for predicting the damage growth in cross-ply PMCs. This model considers only transverse cracking mode. The analysis suggests that the rate of crack density increase is directly proportional to the applied stress and inversely proportional to the current crack density:

$$\frac{\mathrm{d}D}{\mathrm{d}N} \propto \left(\frac{\sigma_{\max}^2}{D}\right)^n \tag{4}$$

Here, $\sigma_{\max}$ is the maximum stress, N is the number of loading cycles, and n is a constant. It is derived from Eq. (4) that, the higher the maximum applied stress, the higher the rate of crack density increase. The specimens subjected to peak stress of 150 MPa had greater number of cracks within the matrix than that of specimens cycled at lower stresses. As a result, higher stress would lead to remarkably lower fatigue lives.

It must be noted that the specimens cycled at maximum stress of 90 MPa would fail if the experiment had continued. Since the silica layer on the coating is viscous and able to seal the cracks and pores, the sealing effect will not fail unless sufficient high stress is applied. According to the results, the maximum stress of 90 MPa is considered to be not sufficient to weaken the sealing. Still, the oxidizing species could diffuse through the silica layer, as mentioned at the beginning of this section, and then oxidize the fibers. The diffusion rate of the oxidizing species through the silica is much lower than that of the species through the open coating cracks, thus much longer fatigue lives of the specimens cycled at 9–90 MPa can be deduced.

Although the influence of cyclic loading on oxidation of C/SiC composites were discussed, there are still issues remain unsolved. In particular, the effect gas-flow velocity on the vaporization of the silica sealant was not concerned. In real aeroengine conditions, the gas-flow velocity accelerates the consumption (or vaporization) of silica [5,10–11]. More close-to-reality experiments can be conducted in high-velocity combustion wind tunnels, which are much more expensive. The relationship between the simulated aeroengine environment and a combustion wind tunnel environment on the performance of C/SiC composites was discussed by Mei et al. [12].

4. Conclusions

Sufficiently high stress under cyclic loading will weaken the sealing effect of silica layer, which are formed by oxidation of SiC coating in water vapor containing environment at elevated temperatures, and subsequently provide pathways for oxidizing species to diffuse through the coating. Oxidizing species can diffuse through the pores and cracks within the composite and attack the fibers at the inner regions of the composite. Higher loadings will lead to larger pores and higher crack density of the composite, resulting in shorter fatigue life. If the maximum stress applied is not high enough to weaken the sealing effect, much higher fatigue lives can be deduced.

Acknowledgements

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References

[1] M.J. Verilli, E.J. Opila, A. Calomino, J.D. Kiser, Effect of environment on the stress-rupture behavior of a carbon-fiber-reinforced silicon carbide ceramic matrix composite, J. Am. Ceram. Soc. 87 (8) (2004) 1536–1542.
[2] M.C. Halbig, D.N. Brewer, A.J. Eckel, Degradation of Continuous Fiber Ceramic Matrix Composites Under Constant Load Conditions, vol. 1392, ASTM Special Technical Publication, 2001, pp. 290–305.
[3] F. Lamouroux, G. Camus, Oxidation effects on the mechanical properties of 2D woven C/SiC composites, J. Eur. Ceram. Soc. 14 (2) (1994) 177–188.
[4] S.F. Shuler, J.W. Holmes, X. Wu, D. Roach, Influence of loading frequency on the room-temperature fatigue of a carbon-fiber/SiC-matrix composite, J. Am. Ceram. Soc. 76 (9) (1993) 2327–2336.
[5] N.S. Jacobson, Corrosion of silicon based ceramics in combustion environments, J. Am. Ceram. Soc. 76 (1) (1993) 3–28.

[6] E.A. Irene, R. Ghez, Silicon oxidation studies: the role of H_2O, J. Electrochem. Soc. 124 (11) (1977) 1757–1761.
[7] F. Lamourroux, R. Naslain, Kinetics and mechanisms of oxidation of 2D woven C/SiC composites. II. Theoretical approach, J. Am. Ceram. Soc. 77 (8) (1994) 2058–2068.
[8] J. Szekely, Gas Solid Reactions, Academic Press, New York, 1976 .
[9] S.L. Ogin, P.A. Smith, P. Beaumont, Matrix cracking and stiffness reduction during the fatigue of a $(0/90)_s$ GFRP laminat, Compos. Sci. Technol. 24 (1) (1985) 23–31.
[10] R.C. Robinson, J.L. Smialek, SiC recession caused by SiO_2 scale volatility under combustion conditions. I. Experimental results and empirical model, J. Am. Ceram. Soc. 82 (7) (1999) 1817–1825.
[11] E.J. Opila, J.L. Smialek, R.C. Robinson, D.S. Fox, N.S. Jacobson, SiC recession caused by SiO_2 scale volatility under combustion conditions. II. Thermodynamics and gaseous-diffusion model, J. Am. Ceram. Soc. 82 (7) (1999) 1826–1834.
[12] H. Mei, L.F. Cheng, X.G. Luan, L.T. Zhang, Y.D. Xu, D. Wang, Simulated environments testing system for advanced ceramic matrix composites, Int. J. Appl. Ceram. Technol. 3 (3) (2006) 252–257.