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Thermal shock behavior of two-dimensional C/SiC composites in controlled atmospheres

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The thermal shock behavior of a two-dimensional carbon fiber reinforced SiC matrix composite fabricated by chemical vapor infiltration technique was investigated using a quenched method. Damage to composites was assessed by fracture strength, real-time damage energy and SEM characterization. The results showed that: (1) 2D-C/SiC composites had an excellent thermal shock resistance in different atmospheres which were simulated for an aero-engine gas. After 50 quenches from 700 to 1200°C, the residual strength of the composite still retained 88.92% of the original strength in the wet oxygen atmosphere, and retained 98.90%, 96.46%, 95.82% in the argon, dry oxygen and water vapor atmosphere, respectively. (2) The real-time System of Damage Information Acquisition forecasted that the critical cycle number of thermal shock for 2D-C/SiC composite in the wet oxygen atmosphere was about 40 times, which was consistent with experimental statistical results. (3) Different atmospheres under the thermal shock affected mechanical properties of composites differently.

1. Introduction

Carbon-fiber-reinforced SiC-matrix composites (C/SiC) fabricated by the chemical vapor infiltration process (CVI) have been proposed as advanced materials suitable for aerospace and gas turbine engine parts [1, 2]. In particular, in the last years many efforts have been devoted to the high-temperature applications of C/SiC composites. These composites show some attractive properties and advantages over traditional ceramics: higher tensile and flexural strength, enhanced fracture toughness and impact resistance, lower density. The mechanical properties of C/SiC composite can be retained at high temperatures and under severe service environments. However, effects of thermal shock and thermal cycling on composites have been anticipated to be an important factor resulted in degradation of performance in many instances. Consequently, thermal shock damage must be understood well before actual use.

Thermal shock resistance of monolithic materials has been extensively studied, and some theoretical analyses have been successfully applied to explain experimental observations [3–6]. Experimental thermal shock studies also have been conducted on unidirectional, two-dimensional and three-dimensional woven-fiber composites [7–9]. However, a comprehensive understanding of the thermal shock behavior of 2D carbon-fiber-reinforced ceramic composites (CFCCs) in the different atmospheres has not been obtained, despite recent advances in the architecture design and processing of these materials. In the present study, thermal shock behavior of a 2D-C/SiC composite is investigated under the controlled atmospheres. Much of analysis and discussion will then focus on the effects of different atmospheres and quench number on the residual strength of the composites. Damage energy of 2D-C/SiC in testing was acquired in real time by win-sound card based on Matlab® DAQ toolbox.

2. Experimental

2.1. Preparation of 2D-C/SiC composite

T-300™ carbon fiber from Toray (Japan) was employed. 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 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, CH_3 $SiCl_3$) was used for the deposition of the SiC matrix. MTS vapor was carried by bubbling hydrogen. Typical conditions for deposition were 1000°C, a hydrogen: MTS ratio of 10, and a pressure of 5 kPa. Argon was employed as the dilute gas to slow down the chemical reaction rate of deposition. Finally, the substrate (Fig. 1a) was machined from C/SiC composite, and then an approximate 50 μm SiC coating was deposited on the surfaces of the substrates. The top surface of the coated specimens is shown in Fig. 1b. The dimensions of as-received specimen were

TABLE I The properties of the as-received 2D-C/SiC composites

Property	Density ($\times 10^3$ kg/m^3)	Modulus (GPa)	Strength (MPa)	Poisson's ratio	Porosity (%)	CTE* ($\times 10^{-6}$/K) 600°C	800°C	1000°C	1200°C
Value	2.0	70	248	0.32	13	4.6	6.1	5.2	5.4

*CTE (the coefficient of thermal expansion) is measured by a dilatometer (Model DIL402C from NETSZCH, in Germany).

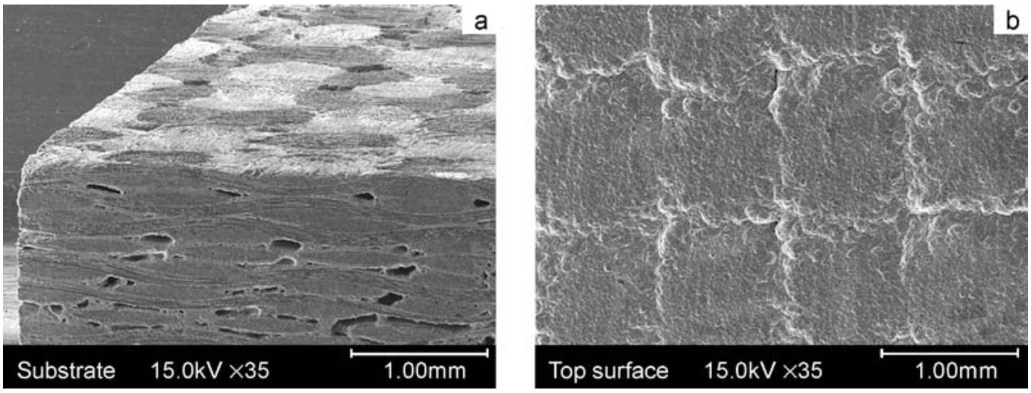


Figure 1 The substrates of 2D-C/SiC composites (a) and the top surface of the as-received specimens coated with coating (b).

3 mm ×3 mm ×185 mm. The properties of the 2D-C/SiC composites are listed in Table I.

2.2. Thermal shock tests

Thermal shock tests were conducted in a high frequency induction heating furnace fixed on a servo-hydraulic machine (Model INSTRON 8801 from INSTRON Ltd., in England). The temperature was measured by an infrared pyrometer through a small window in the wall of burner and the wall was internally cut out to enable the circulating cold water to reach all over the surfaces of the furnace. Automatic heat generation system was designed to run thermal cycles by a microprocessor controller in a programmable mode. Only the middle part of specimens (about 40 mm long, 3 mm wide and 3 mm thick) were kept in the quenching and different gas atmospheres, holding for 30 s at the lower temperature (less than 700°C), heating to 1200°C in the 60 s and holding for 30 s, then cooling in the atmospheres ($\Delta T \approx 500$°C). Flux of gases was accurately controlled by mass flow controller (5850 i series of BROOKS, in Japan) and its precision could reach 0.1 SCCM. In testing, controlled atmospheres was pure argon ($\geq 99.99\%$, 1.01×10^5 Pa), dry oxygen (8000 Pa), water-vapor (15000 Pa, about 54°C) and wet oxygen (combined above O_2 and H_2O), respectively.

The damage information of specimens in testing was real-time monitored and measured by a System of Damage Information Acquisition (SDIA). The system comprised of the following parts:

(1) Data acquisition. Create the analog input object AI for a sound card and then add one hardware channel to AI. Getdata (AI) command forced Matlab engine to collect voltage signal correlated with damage energy. Sample rate was set to 8 kHz and interval of a frame was 10 ms. Acquired results were saved as energy per frame parallel to time. Transient energy of per frame (e.g. the frame i) is given by,

$$e(i) = 20 \sum_{n=1}^{N} \log_{10} u_i^2(n) \tag{1}$$

where $e(i)$ is the energy of the frame i and its unit is dB, N, the sample number of the frame i, $u_i(n)$, voltage of the sample point n in the frame i.

(2) Data analyzer. The programme module could replay or analyze the recorded data by the functions in Matlab®, and then drew diagrams in the windows.

2.3. Measurements and observations

Maximum tensile fracture strength of the specimen after thermal shocks was measured on an INSTRON device at room temperature. The fracture surface was observed with a scanning electron microscope (SEM, HITACHI S-2700).

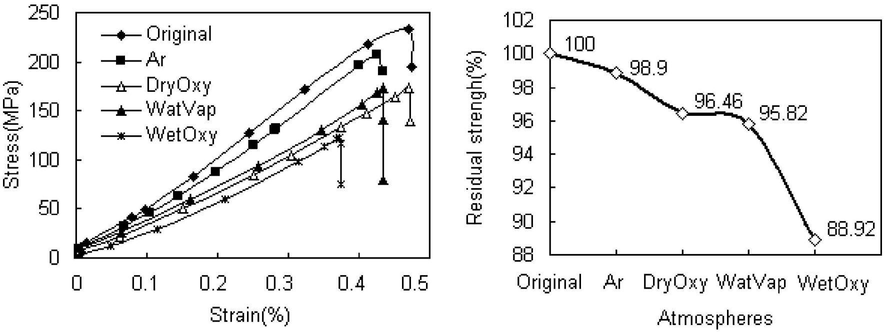
3. Results and discussion

3.1. Effect of thermal shock in the different atmospheres on the mechanical properties

These materials fail when subjected to a sudden change in temperature (thermal shock). The sudden change in the surrounding temperature generates temperature gradient, thereby, the ceramic body experiences thermal stress. The thermal stress created due to the temperature gradient is given by [8],

$$\sigma_t = \frac{\alpha E \Delta T_c}{1 - \nu} \tag{2}$$

where σ_t is the thermal stress, α, the coefficient of thermal expansion, E, is the Young's modulus, ΔT_c, the temperature gradient, and ν, the Poisson's ratio.



(a) (b)

Figure 2 Typical stress vs. strain curves and statistical results of residual strength in the organ, dry oxygen, water vapor and wet oxygen atmosphere (compared with original strength which was unquenched) after 50 thermal shock cycles.

In the present paper, the tensile strength of as-received 2D-C/SiC was about 248 MPa, the value of ν approximated to 0.32, E was about 70 GPa and α was about 5.3×10^{-6}/K in average. Therefore, from Equation 2, we obtained: $\Delta T_c \approx 455°\text{C}$, which was slightly lower than temperature difference in testing of thermal shock ($\Delta T \approx 500°\text{C}$). The thermal stress produced more and more cracks on the surface of matrix, and then propagated inwards when it exceeded the strength of the matrix material.

The assessment of thermal shock damage in the different atmospheres was done by comparing tensile stress-strain curves and residual strength of 2D-C/SiC composites. The influence of thermal shock (50 thermal cycles) in the different atmospheres is shown in Fig. 2. It was apparent from these curves in Fig. 2a that the elastic modulus and fracture strength were all lower for quenched composites than unquenched because of the lower slope of the linear portion of the curve and earlier deviation from linearity, respectively. The elastic modulus ascended continuously to original unquenched composites, however, to the quenched composites, kept almost a steady value and the value was lower and lower with different atmosphere: argon, water vapor, dry oxygen and wet oxygen. Furthermore, as shown in Fig. 2a, the stress-strain curves of the composites were apparently divided into two groups according to non-oxidizing and oxidizing (i.e. water vapor, dry oxygen and wet oxygen) atmospheres: one had higher moduli, higher facture strength and larger strains, the other had lower moduli, lower facture strength and less strains. Oxidation damage of the fibers and interfaces in the oxidizing atmospheres should be considered to be responsible for this result. In addition, the maximum fracture strength (as shown in Fig. 2b), and work-of-fracture (area under the curve in Fig. 2a) were also from bad to worse with the different atmospheres order after 50 thermal shocks, compared with these of original materials which were unquenched.

The effects of thermal shock in the different atmospheres on the maximum tensile strength could result from the following three causes: (1) the oxidation of the fibers in the corrosive gas. (2) the fracture of fibers under the thermal stress. (3) the interface damage due to thermal mismatch. The decrease of modulus of composites could be ascribed to matrix cracking, fiber fracture and interface debonding.

When C/SiC composites were cooled from higher temperature to lower temperature, the tensile stress on the surface and the compressive stress in the interior are created by the thermal gradient, which caused a large quantity of matrix cracks on the surface of composites. In the present study, however, after 50 thermal shocks carbon fibers were hardly oxidized at the bottom of test temperature by dry oxygen or pure water vapor because of low temperature, protective compact oxidation film formed at high temperature and slow diffusion of corrosive gas through incompletely open micro-cracks on the surface of composites. Similarly, fibers were also rarely oxidized at the top of thermal shock temperature (1200°C) for the sake of close of matrix cracks when temperature was above fabricated temperature (1000°C). Under this condition, defects were major tunnel of oxygen. Certainly, another important cause was too short time of test (only 100 min) and no added load.

But damage and degradation of fibers was very severe in the oxygen containing water vapor (wet oxygen) after the same 50 thermal shocks. Typical morphology of fracture section of 2D-C/SiC in the dry oxygen and wet oxygen after 50 thermal cycles is presented in Fig. 3. It was indicated that water vapor could accelerate the diffusion of oxygen through the oxidation film, and then oxygen reached rapidly the surface of fiber, caused oxidation due to a large quantity of matrix cracks. Consequently, an affirmative conclusion could be drawn that the most sensitive atmosphere to 2D-C/SiC composites under the thermal shock was wet oxygen.

3.2. Effect of quench number on the fracture strength in the wet oxygen

The thermal cycling could result in a physical damage of C/SiC composites [9], while the oxidizing atmospheres were considered to be responsible for a chemical degradation (i.e., oxidation). Therefore, thermal shock damage in the wet oxygen atmosphere, actually, could be understood as a coupled effect of above two factors: a physical damage caused by thermal cycling and a chemical degradation caused by oxidizing atmospheres. Moreover, the former could also provide the latter with the oxidation channels by opening the cracks of the composite and then the latter became a dominant factor of the degradation. The energy absorbed into materials caused a physical damage of materials (such as

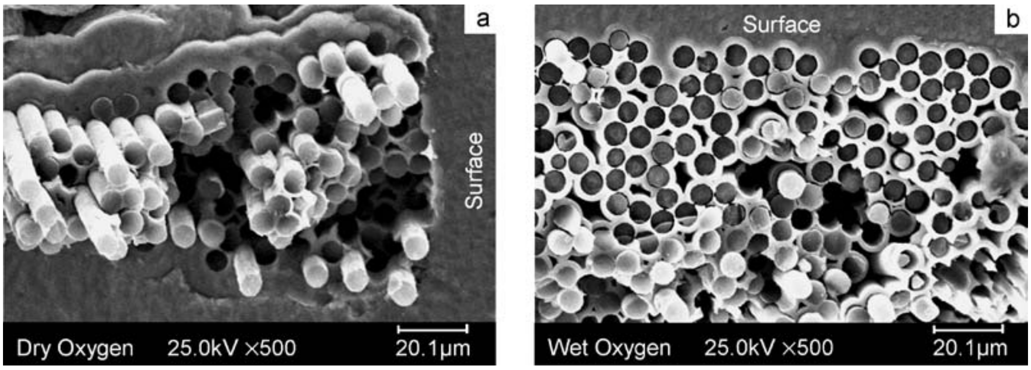


Figure 3 SEM micrograph of fracture section of 2D-C/SiC in the dry oxygen (a) and wet oxygen (b) atmosphere after 50 thermal cycles

matrix cracking, fiber fracture and interface debonding) in order to release itself while the oxidizing gas damaged the fibers and interfaces through the channels opened by thermal stress. Both physical damage and chemical corrosion were responsible for the degradation of the composites during the initial stage of thermal shock. However, when the quenching number was larger than a critical value, the crack density was saturated, and the further decrease in the strength of the composites mainly depended on oxidation, not thermal cycling. At this time, the composites hardly had response to the destructive energy of thermal cycling because macro-cracks of matrix had enough space to tolerate micro-thermal-expansion. Accordingly, damage to C/SiC composites caused by thermal cycling was limited and there existed a critical thermal cycle number.

As shown in Fig. 4, the statistical result of thermal shock tests in the wet oxygen atmosphere showed that residual strength of 2D-C/SiC composites decreased gradually and decrement was less and less with the increase of quenching times. The value of transverse axis parallel to inflexion of the curve was about 40 times and the quench number reached the critical value. After this point, the continuous and slow decrease of the strength was due to oxidation of fibers and interfaces in wet oxygen with increasing quenching time. However, after 100 thermal cycles the residual strength of the composite was still 85.69% of the as received strength. The high densification of SiC CVI matrix in the 2D woven perform (Fig. 1a) and the approximate 50 μm SiC surface coating (Fig. 1b) were helpful for understanding the thermal shock resistance of the composites.

During the initial stage of thermal shock, with increasing quench number, surface cracks propagated inwards, which led to the increase of crack density in composites. The increase of matrix crack density resulted in the rapid decrease of the mechanical properties of composites. A typical energy response curve of the specimen to thermal shock impact damage in the wet oxygen is presented in Fig. 5a. The transient energy was calculated by Equation 1 and the amplitude of voltage signal correlated with the damage energy absorbed into materials was displayed in real time on the screen (Fig. 5b). At the initial stage of the test, according to Fig. 5a, the energy absorbed into the specimen was very high and rapidly dissipated to destroy the materials. The destructive energy was less and less with the saturation of physical damage. Finally, it also remained a lower steady level at about 4500 s, which was consistent with above experimental results (40 cycles). As shown in Fig. 5b, the voltage signals changed periodically with thermal cycles and their periods were equal approximately.

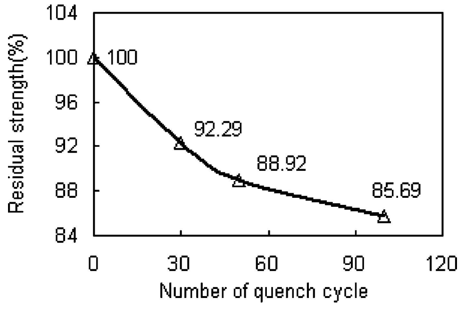


Figure 4 Effect of thermal shock cycle number on the residual strength of 2D-C/SiC in the wet oxygen.

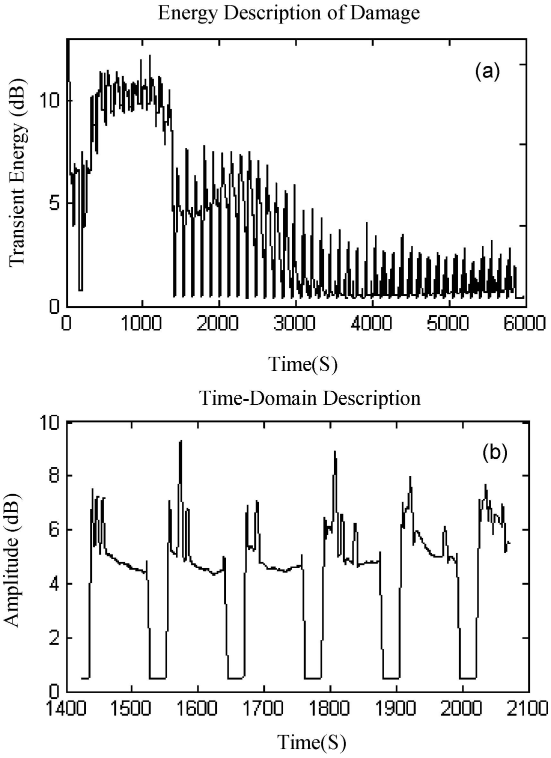


Figure 5 Typical curve of transient energy (a) recorded by SDIA and time-domain analysis (b) of voltage signal under the thermal shocks in the wet oxygen atmosphere.

4. Conclusions

1. 2D-C/SiC composites had a good thermal shock resistance in the different atmospheres including argon, water vapor, dry oxygen and wet oxygen. After the composite was quenched more than 100 times in the wet oxygen, the residual tensile strength was still 85.69% of the as-received strength.
2. Fibers of 2D-C/SiC composites during the thermal shock tests were hardly oxidized in the dry oxygen or the pure water vapor atmosphere. However, in the wet oxygen, oxidation resistance of the composites decreased greatly.
3. The thermal shock damage to 2D-C/SiC composites caused by thermal cycling was limited. The critical number of the thermal shock in the wet oxygen was about 40 times and this result had been reliably forecasted by the real-time System of Damage Information Acquisition.

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References

1. F. LAMOUROUX, X. BOURRAT, J. SEVELY and R. NASLAIN, *Carbon* **31** (1993) 1273.
2. J. CAVALIER, A. LACOMBE and J. ROUGES, in "Developments in the Science and Technology of Composite Materials" (Elsevier, London, UK, 1989) p. 99.
3. B. S. HAHN and H. L. LEE, *J. Mater. Sci.* **34** (1999) 3623.
4. W. D. KINGERY, *J. Am. Ceram. Soc.* **38** (1955) 3.
5. D. P. H. HASSELMAN, *J. Am. Ceram. Soc. Bull.* **49** (1970) 1033.
6. D. P. H. HASSELMAN, *Mater. Sci. Eng.* **71** (1985) 251.
7. J. E. WEBB and R. N. SINGH, *J. Am. Ceram. Soc.* **79** (1996) 2857.
8. R. N. SINGH and H. WANG, *Compo. Eng.* **5** (1995) 1287.
9. X. W. YIN and L. F. CHENG, *Carbon* **40** (2002) 905.

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