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

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Version of record first published: 02 Apr 2012.

To cite this article: Satoshi Kobayashi , Shuichi Wakayama , Takuya Aoki & Hiroshi Hatta (2003): Oxidation behavior and strength degradation of CVD-SiC coated C/C composites at high temperature in air , Advanced Composite Materials, 12:2-3, 171-183

To link to this article: http://dx.doi.org/10.1163/156855103772658542

Adv. Composite Mater., Vol. 12, No. 2-3, pp. 171–183 (2003)

Also available online - www.vsppub.com

Oxidation behavior and strength degradation of CVD-SiC coated C/C composites at high temperature in air

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Received 27 June 2002; accepted 28 January 2003

Abstract—Simple tensile tests and tensile tests after high temperature exposure of carbon fiber reinforced carbon matrix (C/C) composites have been carried out at high temperature (1000–1400°C) in air. Types of specimens were bare, notched bare and CVD-SiC coated C/C composites. The CVD-SiC coated C/C composites were mechanically loaded to a strain of 0.13% and were exposed in air at the testing temperature for 10 min. Then, the specimens were subjected to tensile load to failure. The nominal tensile strength of the CVD-SiC coated C/C composite was decreased with increasing temperature due to the oxidation under the coating cracks. Two kinds of true strength were calculated using the cross-sectional area at fracture or the effective cross-sectional area. The effective strength of the CVD-SiC coated C/C composites, based on the decrease in cross-sectional area with no contribution of 90° plies to load carrying, is appropriate to characterize strength after exposure. A diffusion model was applied to predict the oxidation behavior of CVD-SiC coated C/C composite. The effectiveness of the present model was confirmed. It is possible to predict the nominal strength of C/C composites under oxidation condition using the radius of oxidation damage calculated by the diffusion model.

Keywords: C/C composites; CVD-SiC coating; high temperature strength in air.

1. INTRODUCTION

Though carbon fiber reinforced carbon matrix (C/C) composites possess excellent mechanical properties, they are seriously damaged by oxidation at high temperature. For these reasons, techniques of providing anti-oxidation ceramic coatings have been investigated [1–4]. Chemical vapor deposition (CVD) is one of the most

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promising coating techniques. However, a number of coating cracks occur due to a significant mismatch in thermal expansion coefficient between the C/C substrate and the ceramic coatings. These cracks allow oxygen diffusion toward the C/C substrate and the C/C substrate is degraded [2–4]. On the other hand, it was also reported that those cracks close at higher temperature than the coating treatment temperature, which closes the paths of oxygen penetration and suppresses the oxidation of the C/C substrate [2]. However, mechanical loading applied to the structures in service would open the cracks.

In the present study, the strengths of bare, notched bare and CVD-SiC coated C/C composites after high temperature exposure were investigated. The CVD-SiC coated C/C composites were exposed in air under constant tensile strain, then they were loaded to fracture to clarify the effect of oxidation damage on the tensile strength. It is expected that the mechanical loading during exposure, similar to the actual service condition, promotes oxidation damage by opening of the coating cracks. A diffusion model [3, 4] was used to predict the radius of the local oxidation damage, which significantly affects the tensile strength after exposure.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Materials used were $[0/90]_{4s}$ 2D cross-ply C/C composites fabricated by a preformed yarn method. Reinforcing fiber was Toray M40 and the nominal volume fraction of the fiber was 50%. Thickness of one layer was about 190 μm.

The SiC coating was made using the CVD method. After the formation of a thin conversion layer by direct chemical reaction of $SiCl_4$ gas and carbon, the SiC coating was thermally deposited on the C/C composites at 1200°C. Finally, the SiC coating with 35 μm thickness was obtained. A number of coating cracks were initiated due to a significant mismatch in thermal expansion coefficient between the C/C substrate and SiC coatings. Average coating crack spacing due to thermal stress was 250 μm and average and maximum crack opening displacements were about 1 μm and 6.5 μm, respectively.

2.2. Oxidation tests

The oxidation tests were carried out under xenon lamp heating and natural convection of air. The size of specimens is 4 mm long, 4 mm wide and 3 mm thick. Types of the specimens were bare and CVD-SiC coated C/C composites. The change in weight was monitored continuously under the constant temperature field between 700 and 1600°C. The temperatures measured by the thermo-viewer were calibrated with those by tungsten–rhenium or platinum–rhodium thermocouples.

2.3. Tensile tests

Dog-bone shaped specimens were prepared for the tensile tests as shown in Fig. 1. The whole length was 155 mm and the gauge region was 4 mm in length, 6 mm in width and 3 mm in thickness. In the present study, 3 types of the specimens, bare, notched bare and CVD-SiC coated C/C composites, were tested. The bare and SiC coated C/C composites correspond to the specimen with and without the SiC coating, respectively. The notched bare C/C composites have notches on the surface of the bare C/C composites, which imitate the local oxidation damage under the coating crack. Notch shape is shown in Fig. 2. In the present study, notch depths were selected as 280 μm for 1000°C and 200 μm for 1200 and 1400°C, which correspond to the radius of oxidation damage.

Figure 3 shows the schematic diagram of the tensile testing instrument. Both sides of the specimen were heated by two infrared lamps and the heated area was circular with a diameter of 8 mm. The specimen grips were cooled by water. Since the heated area was small, the specimen was uniformly loaded by the actuators at both sides so that the heated area was fixed.

Testing conditions are shown in Fig. 4. The tensile tests were carried out at 1000, 1200 and 1400°C. The heating rates were 20°C/min. The simple tensile tests were conducted on the bare C/C composites. Tensile tests after exposure with loading were conducted on all types of specimens. Specimens were heated in N_2 not to be oxidized during heating. In the tensile tests after exposure with loading, specimens were exposed for 600 s at the test temperature. Exposure atmosphere

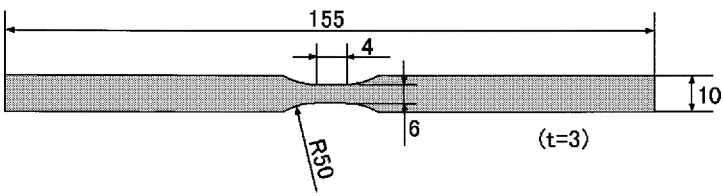

Figure 1. Size of specimens for tensile tests.

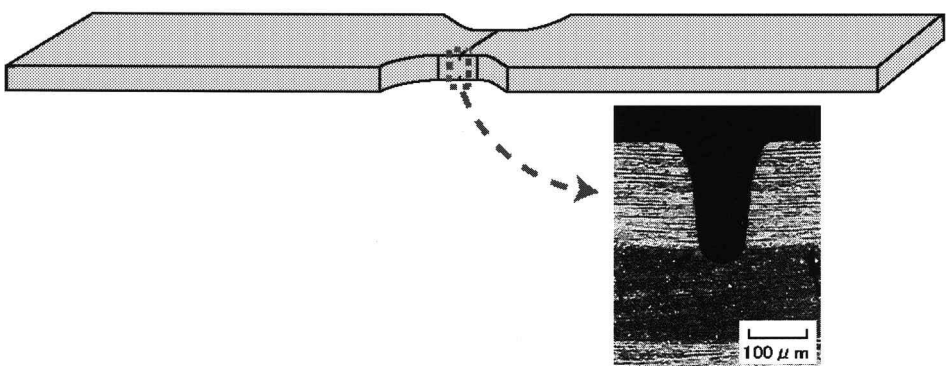

Figure 2. Notch shape of notched bare C/C composites.

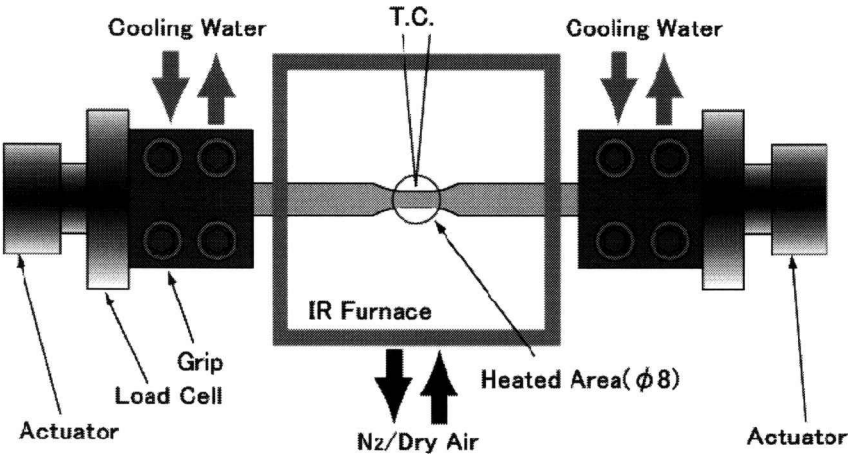

Figure 3. Schematic diagram of the tensile testing instruments.

was air for the CVD-SiC coated C/C composites. The bare and notched bare C/C composites were exposed in N_2. During exposure, the specimens were subjected to the constant tensile strain, 0.13%, to open the coating cracks at 1400°C: 0.13% strain corresponds to 0.33 μm in crack opening displacement. After exposure, the specimens were strained at 1 mm/min in N_2 until fracture.

In the present study, nominal strength, σ_n and apparent true strength, σ_{at} are defined by the relations

$$\sigma_n = \frac{P_f}{A_0}, \quad \sigma_{at} = \frac{P_f}{A_f}, \tag{1}$$

where P_f is the maximum load in the tensile tests, A_0 is nominal cross-sectional area, and A_f is minimum cross-sectional area calculated as,

$$A_f = A_0\left(1 - \frac{2r}{t}\right)\left(1 - \frac{2r}{w}\right), \tag{1'}$$

where r is the maximum radius of local oxidation damage under the coating crack observed after test and t and w are the thickness and the width of the C/C specimen, respectively.

In the present study, the radius of oxidation damage was about 200–280 μm, which means the tip of the oxidation damage reached the middle of the second (90°) layer in the thickness direction. In the C/C composite laminates, 90° layers have little load capacity because of transverse cracking, so the rest of the second layer cannot carry the load. That is, surface [0/90] layers of $[0/90]_{4s}$ laminates can be neglected as only the remaining $[0/90]_{3s}$ laminates carry the load. Therefore, we define the effective strength, σ_{eff}, as

$$\sigma_{eff} = \frac{P_f}{A'_f}, \tag{2}$$

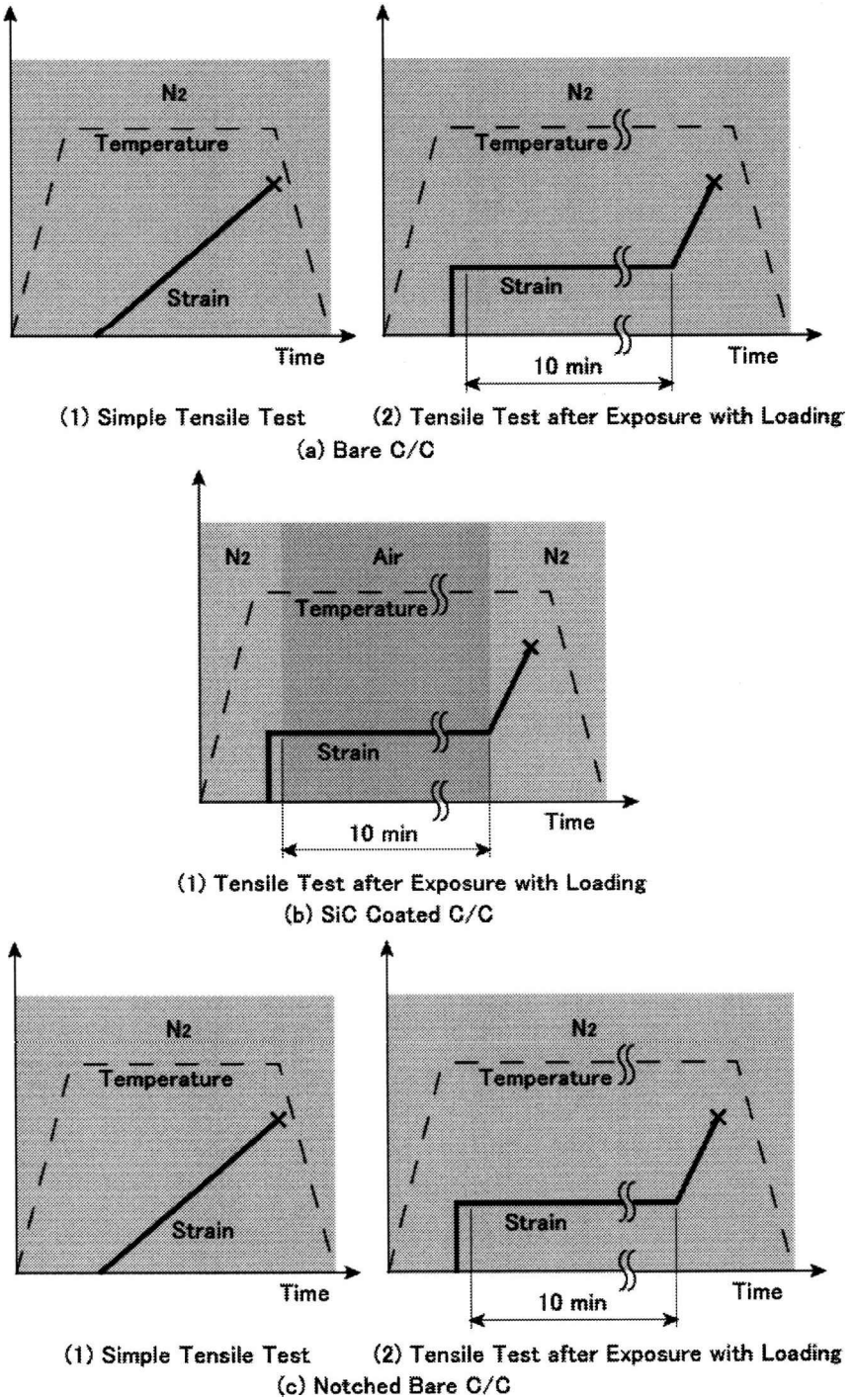

Figure 4. Test conditions of simple tensile tests and tensile tests after exposure at high temperature.

where A'_f is calculated as,

$$A'_f = \frac{3}{4}A_0\left(1 - \frac{2r}{w}\right). \tag{2'}$$

The thickness of 90° layers is considered in calculating A_f, but not in A'_f.

3. EXPERIMENTAL RESULTS

3.1. Oxidation behavior

The oxidation behavior of the bare and CVD-SiC coated C/C composites is shown as the Arrhenius plots in Fig. 5. The plots of the bare C/C composites exhibit oxidation behavior consistent with conventional knowledge [3, 4], i.e. oxidation at lower temperature (<800°C) is controlled by the chemical reaction rate between carbon and oxygen and that at higher temperature is controlled by the oxygen diffusion rate through the boundary layer of air flow at the surface of the composites.

On the other hand, the oxidation rate of the CVD-SiC coated C/C composites is lower than that of the bare C/C composites. Figure 6 shows the cross-sectional view of the CVD-SiC coated C/C composites after exposure in 1200°C for 600 s. The oxidation damage regions are limited under coating cracks, which demonstrates the

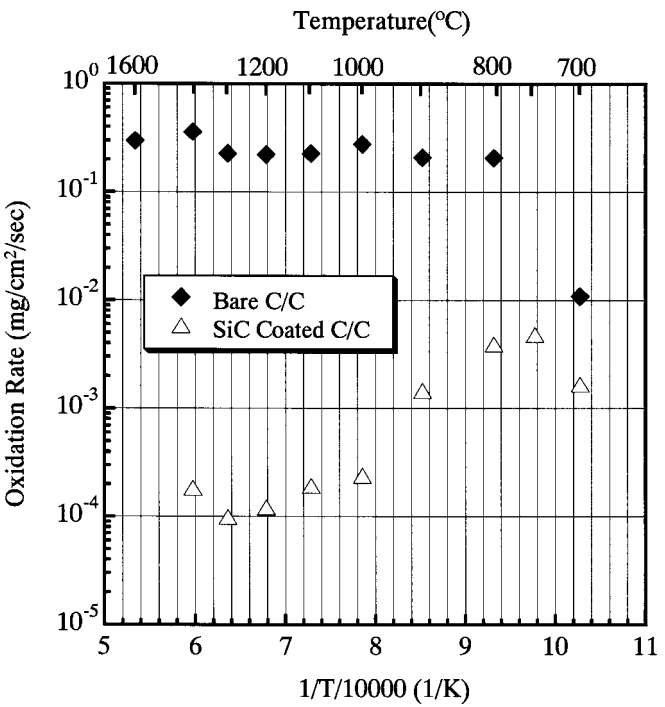

Figure 5. Arrhenius plot for bare and SiC coated C/C composites.

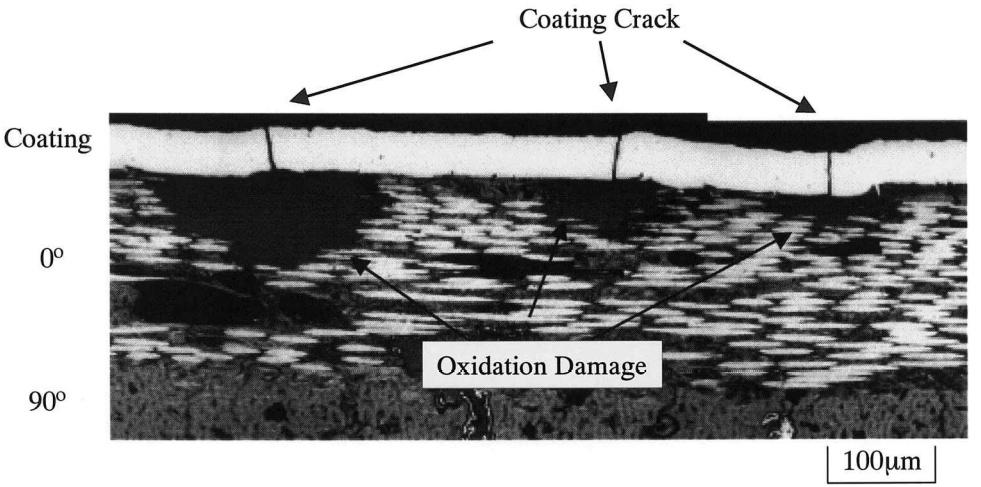

Figure 6. Cross-sectional view of SiC coated C/C composites in the tensile test after exposure for 600 s in 1200°C.

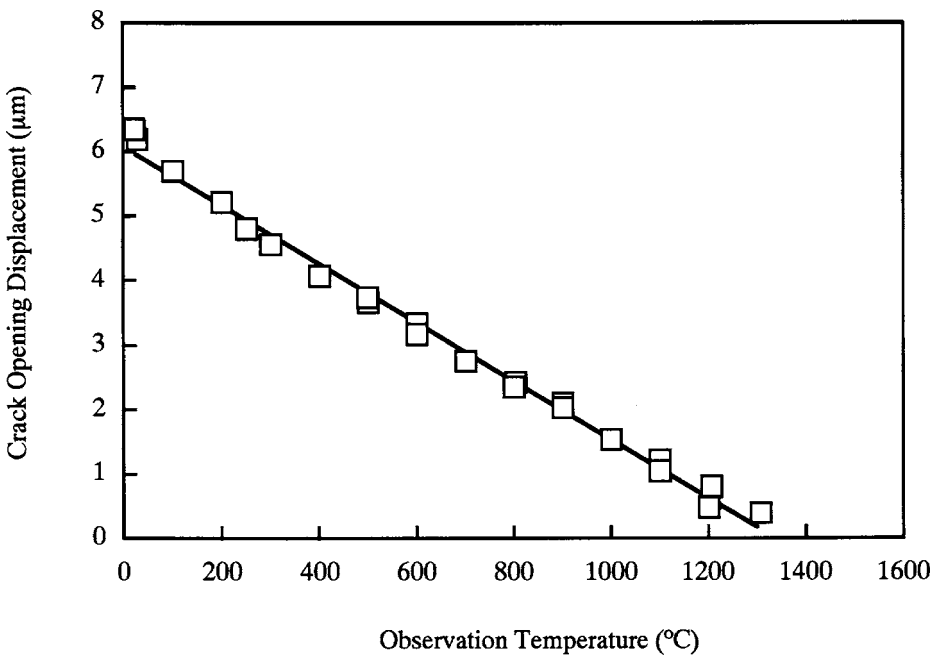

Figure 7. Coating crack opening displacement as a function of temperature.

effect of the CVD-SiC coating. It is characteristic for the CVD-SiC coating that the oxidation rate decreases as the temperature increases in the temperature range between 800°C and 1300°C. Figure 7 shows coating crack opening displacements as a function of temperature. The coating crack closes linearly with increasing

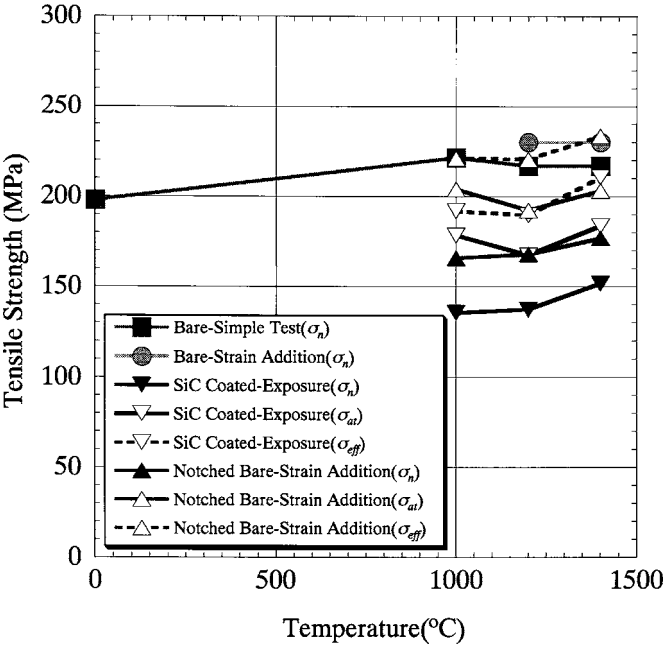

Figure 8. Tensile strength of bare, notched bare and SiC coated C/C composites.

temperature due to the relaxation of the thermal mismatch, which results in the decrease in the oxidation rates.

3.2. Fracture behavior of C/C composite at high temperature in air

The results of tensile tests are summarized in Fig. 8. Comparing to the result of room temperature, σ_n of the bare C/C composites in the simple tensile tests became larger at high temperature. However, there were no differences in the 1000–1400°C range.

σ_n of the bare C/C composites in the exposure tests were almost the same value as those of the simple tensile tests, which means there is no effect of exposure in N_2 on strength. σ_{at} values of the notched bare C/C composites were smaller than σ_n of the bare C/C composites. This result shows less load capacity of 90° layers. On the other hand, σ_{eff} were almost the same value, which means no stress concentration at the tips of the notches in the C/C composites. σ_{at} overestimates the residual thickness of the damaged C/C composites and the strength will be underestimated. That is, σ_{eff} is more effective to evaluate the damaged C/C composite than σ_{at}.

σ_n of the CVD-SiC coated C/C composites in the exposure tests were much smaller than that of the bare C/C composites because of the oxidation, and σ_{at} is also much lower, as shown in Fig. 6. Figure 9 shows the histogram of pore radius observed after the tensile tests. Number of pores becomes smaller with increasing temperature because of the coating crack closure, as shown in Fig. 7. As a whole, the pore radius becomes smaller with increasing temperature. However, the maximum

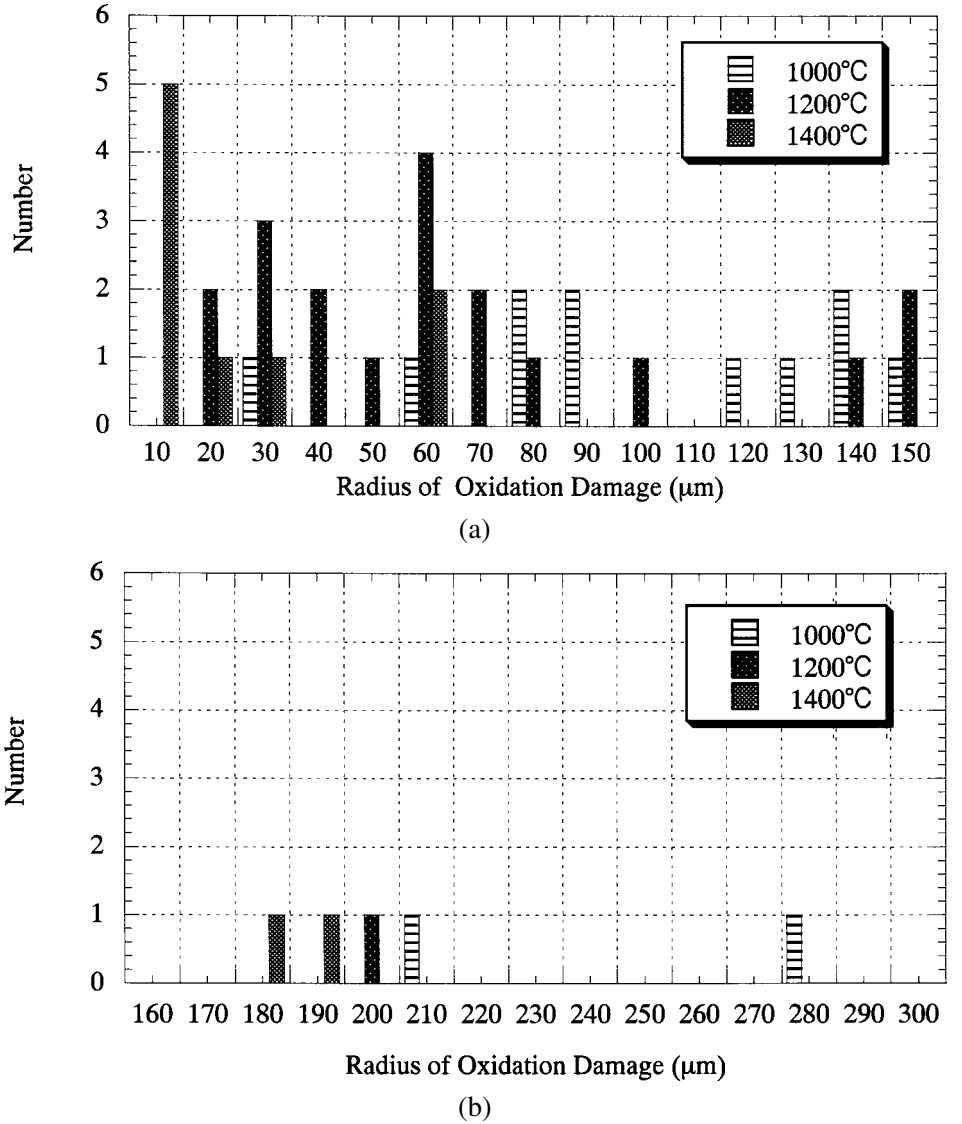

Figure 9. Histogram of radius of oxidation damage observed after tensile tests. (a) 10 μm–150 μm; (b) 160 μm–300 μm.

pore radiuses at 1200 and 1400°C were almost the same value, 200–210 μm. Although the maximum pore radius was 280 μm at 1000°C, there was no difference in σ_n of the CVD-SiC coated C/C composites in all conditions because of little load capacity of the second (90°) layer.

σ_{eff} of the CVD-SiC coated C/C composites was about 10% lower than that of the bare C/C composites. In the coating process, the conversion treatments, which include direct chemical reaction of $SiCl_4$ with near surface carbon in the substrate C/C composite, were applied at first. $SiCl_4$ gas reaches the inside of the

composite through the transverse cracks. Reinforcing carbon fibers are attacked by $SiCl_4$ gas and SiC is formed [6]. Since the reinforcements were damaged by $SiCl_4$, σ_{eff} became a little lower in the SiC coated C/C composites. These results indicate that σ_n of the CVD-SiC coated C/C composites can be predicted when the strength reduction due to the conversion treatments and the maximum pore radius are determined successfully.

4. DISCUSSION

In the present temperature range, 1000–1400°C, the oxidation rate of the CVD-SiC coated C/C composite is controlled by oxygen diffusion through the coating cracks. To predict the radius of the oxidation damages under mechanical loading, the oxygen diffusion rate through the coating cracks was calculated [3, 4]. The diffusion model is based on the following assumptions:

(i) All the oxygen that arrives at the substrate surface is immediately converted to CO gas.

(ii) The oxygen consumption by the oxidation of SiC to SiO_2 is neglected.

(iii) The opening of coating cracks linearly decreases with temperature and becomes zero at the coating treatment temperature.

(iv) The closure of crack opening due to the silica growth at crack wall is taken into account.

The oxygen diffusion rate, J_{O_2} ($kg\,m^{-2}\,s^{-1}$), through a representative coating crack is given in terms of the concentration gradient of oxygen, dC_{O_2}/dx, and the outward diffusion of CO, J_{O_2}:

$$J_{O_2} = -D_c \frac{dC_{O_2}}{dx} + \frac{C_{O_2}}{C_T}\left(J_{O_2} + J_{CO}\right), \tag{3}$$

where D_c (m^2/s) is the effective diffusion coefficient of oxygen, C_T (kg/m^3) is the total concentration of gases that is constant at any point. In the diffusion-controlling temperature range, CO gas is the main product of oxidation reaction. Thus, the flux difference between inward O_2 and outward CO can be expressed as $J_{CO} = -J_{O_2}$, rearranging equation (3).

$$J_{O_2} = -\frac{D_c}{1 + \dfrac{C_{O_2}}{C_T}} \frac{dC_{O_2}}{dx}. \tag{4}$$

The effective diffusion coefficient D_c is divided into the molecular (D_b) and Knudsen (D_k) diffusion coefficients.

$$\frac{1}{D_c} = \frac{1}{D_b} + \frac{1}{D_k}, \tag{5}$$

$$D_{\mathrm{b}} = 5.95 \times 10^{-24} \frac{\sqrt{T^3\left(\frac{1}{M_{\mathrm{Air}}} + \frac{1}{M_{\mathrm{CO}}}\right)}}{P\sigma^3_{\mathrm{Air-CO}}\Omega_{\mathrm{Air-CO}}}, \tag{6}$$

$$D_{\mathrm{k}} = \frac{2}{3}\left(\frac{8RT}{\pi M_{\mathrm{O_2}}}\right)^{0.5} W, \tag{7}$$

where T (K) is the oxidation temperature, M_{i} (kg/mol) is the molecular mass of gases, P (Pa) is the total pressure, σ (m) is the collision diameter, Ω is the collision integral, R (J mol^{-1} K^{-1}) is the gas constant and W (m) is the crack opening displacement at the oxidation temperature. In the present study, the values of W were evaluated from the sum of the crack opening displacements caused by the mechanical loading, corresponding to 0.33 μm in the present study, and by thermal stress given in Fig. 7.

Equation (4) can be integrated under the following boundary conditions and the total amount of oxygen diffusing through the coating crack, $N_{\mathrm{O_2}}$ (kg/s), is given by equations (8) and (9).

At the coating surface ($x = 0$) $\quad C_{\mathrm{O_2}} = C^{\mathrm{S}}_{\mathrm{O_2}}$.

At the crack bottom ($x = \delta$) $\quad C_{\mathrm{O_2}} = 0$.

$$N_{\mathrm{O_2}} = \frac{W D_{\mathrm{c}} C^{\mathrm{S}}_{\mathrm{O_2}}}{y\delta}, \tag{8}$$

$$y = \frac{\frac{C^{\mathrm{S}}_{\mathrm{O_2}}}{C_{\mathrm{T}}}}{\ln\left(1 + \frac{C^{\mathrm{S}}_{\mathrm{O_2}}}{C_{\mathrm{T}}}\right)}. \tag{9}$$

The values of $C^{\mathrm{S}}_{\mathrm{O_2}}$ and δ are the oxygen concentration in air and the thickness of the SiC coating, respectively.

Finally, by assuming that semi-circular oxidative damage will appear in the C/C substrate, the radius of the oxidation damage, r (m), can be calculated as:

$$r = \sqrt{\frac{2 \times \frac{24}{32} N_{\mathrm{O_2}} t}{\pi\rho}}, \tag{10}$$

where t (s) is the oxidation time and ρ (kg/m^3) is the density of the C/C substrate, respectively.

Figure 10 shows the radius of the oxidation damage calculated as a function of time. Bold and fine lines correspond to with and without mechanical loading, respectively. At 1400°C, the coating cracks closed perfectly without mechanical loading, which results in no oxidation. The radius of the oxidation damage becomes smaller with increasing temperature because of crack closure due to

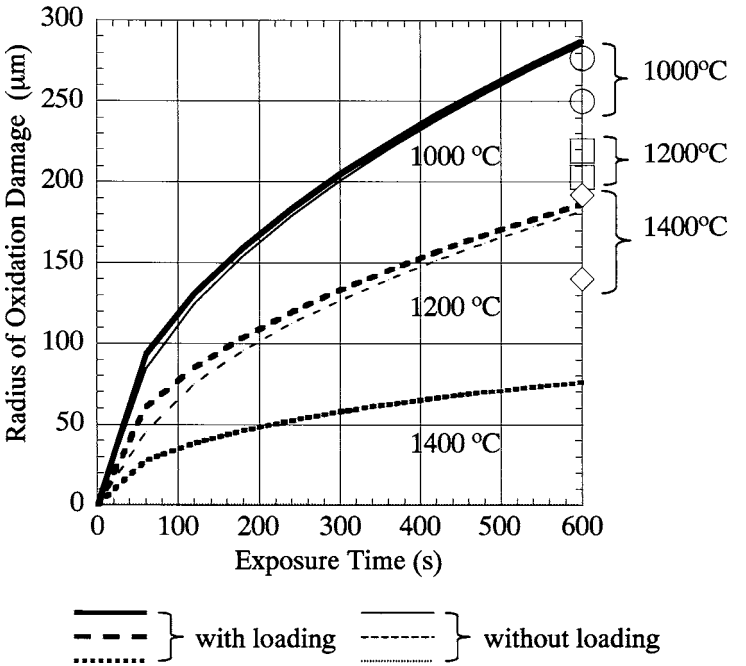

Figure 10. Maximum radius of oxidation damages as a function of exposure time (with and without mechanical loading).

the release of thermal stress. At the same temperature conditions, the amounts of oxidation become larger with mechanical loading, and the difference between with and without mechanical loading increase with increasing temperature. This indicates that the mechanical loading must be an important factor for evaluating the characteristics of the SiC coating, especially at high temperature. Though prediction for 1400°C is smaller than the experimental results, predictions for 1000°C and 1200°C are in good agreement with the experimental results. Once the radius of the oxidation damage is predicted, residual strength can be estimated, as discussed in Section 3.2. The present model is also available for evaluating residual strength of the CVD-SiC coated C/C composites at high temperature in air under mechanical loading, which is the condition expected for the structures in service.

5. CONCLUSION

Tensile strength of the bare and CVD-SiC coated C/C composites were investigated at high temperature in air. Especially, the coated materials were exposed in air under mechanical loading. Consequently, the following conclusions were reached.

(1) The CVD-SiC coating could suppress the oxidation rate of C/C composite, effectively.

(2) From the results of the bare and notched bare C/C composites, there are no effects of exposure in N_2 and stress concentration by the notches on the effective strength of the C/C composites.

(3) The effective strength of the CVD-SiC coated C/C composites, based on the decrease in cross-sectional area with no contribution of 90° plies to load carrying, is appropriate to characterize the strength after exposure at high temperature in air under mechanical loading.

(4) A diffusion model [3, 4] was found to be effective under mechanical loading. It is possible to predict nominal strength of C/C composites under oxidation condition using the radius of the oxidation damage calculated by diffusion model.

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