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Effects of chemical vapor infiltration atmosphere on the mechanical properties and microstructure of carbon fibers

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Abstract

Investigations of the effects of chemical vapor infiltration atmosphere on the mechanical properties of carbon fiber and examinations of the microstructure of the carbon fiber were carried out in the present paper. The experimental results revealed that tensile strength and fracture strain of the carbon fiber were decreased after annealing at temperatures of 850–1100°C in HCl atmosphere, but the elastic modulus was not varied. The degradation of strength and strain were responsible for the oxidation weight loss. Both oxidation weight loss and strength loss of the carbon fiber was obviously increased with the presence of HCl resulting from the by-product of MTS reaction. As oxidation weight loss was increased from 0 to 4.97%, the strength was decreased from 2850 to 1423 MPa. After oxidation, microstructure of the carbon fiber exhibited three zones: a skin outer zone, a porous thin zone, and the bulk laminated structure. During the chemical vapor infiltration process, the effects of the carbon interfacial layer lie in protecting the carbon fiber by filling the micro-depressions on the surface of the carbon fiber and by separating the carbon fiber with the oxidation atmosphere.

Keywords: C-fibres; C–SiC composites; Composites; CVI; Mechanical properties; Oxidation; SiC matrix

1. Introduction

Continuous carbon fiber reinforced silicon carbide matrix composites (C/SiC) have received considerable attention for high temperature structural applications because of their superior strength, fracture toughness, and abrasive properties.[1–3] So far, various processing methods used to produce ceramic matrix composites are divided into four categories:[4–8] the traditional mixing and slurry infiltration technique, sol–gel and polymer precursor processing, melt infiltration, and chemical vapor infiltration. Among these methods, chemical vapor infiltration (CVI) is the most promising technique for preparing C/SiC composite components with complex and near-net shape. It is especially suited for the processing of high temperature non-oxide ceramic matrix (carbide, nitride, boride, and so on) at relatively low temperature (~1000°C). In processing for silicon carbide matrix composites, SiC is deposited by the chemical reaction:[2]

$$CH_3SiCl_3 \rightarrow SiC + 3HCl \qquad (1)$$

Usually, the constituents of the C/SiC, composite materials are divided into three basic parts: the reinforcement of the carbon fiber, the matrix of silicon carbide, and the interfacial layer of the pyrolysis carbon. It is known that the interfacial layer has significant influence on the mechanical properties of the C/SiC composite materials during the service by acting as releaser of residual thermal stress, tailoring the interfacial shear or bonding strength between fiber and matrix. However, the function of the interfacial layer during the fabrication is less understood. Investigations revealed that oxidation of both the SiC matrix and the interfacial layer could not be avoided during the fabrication.[9–11] The oxidation was derived from the residual oxygen in the reaction chamber. Both the carbon fiber and the interfacial layer are easily attacked by oxygen at temperatures as low as 400°C. Consequently, the oxidation would result in the damage of mechanical properties of the C/SiC composite materials. Furthermore, it was noted that the CVI atmosphere of HCl gaseous species from chemical reaction has influence on the mechanical properties of the carbon fiber.

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The aims of the present research work are: (1) to investigate the effect of chemical vapor infiltration atmosphere on the mechanical properties of the carbon fiber; and (2) to examine the microstructure of the carbon fiber exposed in chemical vapor infiltration atmosphere.

2. Experimental procedures

2.1. Preparation of the carbon fiber yarns

The carbon fiber yarns were cut into lengths of 180 mm and placed individually into the graphite tube furnace at different atmosphere environments, which simulated the CVI SiC reaction conditions. The yarns were thermally exposed in the furnace at temperatures of 850 and 1100°C. The HCl gas was introduced into the furnace by bubbling hydrogen gas. The experiment schematic is shown in Fig. 1.

2.2. Preparation of the C/SiC composite materials

The C/SiC composites were prepared by isothermal/isobaric chemical vapor infiltration (ICVI) which has been described elsewhere in detail.[12,13] Methyltrichlorosilane (CH_3SiCl_3, MTS) was employed to deposit silicon carbide. MTS was maintained at a constant temperature and carried into the reaction chamber by bubbling hydrogen gas. In each run, the carbon fiber preforms were precleaned and preheated above the deposition temperature in hydrogen for 30 min. Typical conditions now being used for deposition were a hydrogen to MTS mole ratio of 10 and 1100°C. Argon was used as dilute gas to show the chemical reaction rate.

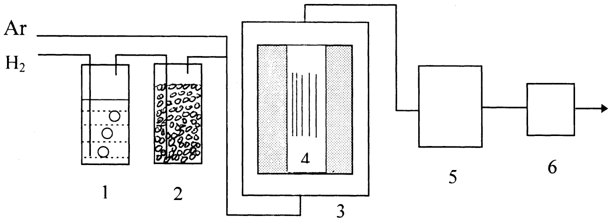


Fig. 1. Experiment schematic of simulated CVI atmosphere. 1. HCl bubbler, 2. Desiccator, 3. Reaction chamber, 4. Fiber, 5. Cold trap, 6. Rotary pump.

2.3. Mechanical properties measurement of the carbon fiber and C/SiC composites

Prior to testing, the carbon yarns were carefully infiltrated with epoxy resin and placed into an oven at the temperature of 220°C for 2 h. Then the carbon fiber yarns were mounted on the cut board frames. The yarns were sandwiched at the end portions with the use of a structural adhesive. The neck of the paperboard frame was cut after the specimen was placed in the grip holds. The tensile tests of the carbon fiber yarns were carried out at the strain rate of 100% min^{-1}. Flexural strength of C/SiC composite samples was measured by three-point bending method with the loading rate of 0.5 $\text{mm}\cdot\text{min}^{-1}$. The dimension of the samples was $3\times4\times40$ mm^3. All these tests were conducted in an Instron-1195 testing machine.

2.4. Observation of the microstructure

The microstructure of the samples was observed in a scanning electron microscope (SEM, Model JEOL 840). The surface chemical compositions were examined with a scanning multiple Auger Probe (Perkin–Elmer). Transmission electron microscope (TEM, JEOL 2000 fx) was used to characterize the crystal structure and bulk microstructure. TEM samples were prepared by cutting 300 μm thick using a low special diamond saw, then mechanically thinned to 75 μm, dimpled to a center using Ar^+ ions at an incident angle of 15°.

3. Results and discussion

3.1. Oxidation weight loss on the mechanical properties of carbon fiber

Table 1 lists the relationship between atmosphere environment and oxidation weight loss of the carbon fiber. Oxidation kinetic rate constant (k) of the carbon fiber is considered to obey an Arrhenius law:[14,15] $k = k_0 \exp(-E_a/RT)$. Where E_a is the activation energy, R is the prefect gas constant, T is the temperature, and k_0 is an experimental term. Obviously, oxidation weight loss of the carbon fiber was increased with the exposure temperature. With the view of oxidation kinetics, oxidation

Table 1
Effect of heat treatment on weight loss of the carbon fiber

Temperature (°C)	Time (min)	Atmosphere (mol ratio)	Atmosphere status	Weight loss (%)
850	5	Ar	0.1 MPa, static	0.33
1100	30	H_2:Ar = 1:1	0.1 MPa, static	1.77
1100	30	H_2:Ar = 1:1	5 Pa, flowing	4.03
1100	30	H_2:Ar:HCl = 1:1:0.016	5 Pa, flowing	4.97

of the carbon fiber involves four steps: (i) diffusion of the oxygen into the boundary layer surrounding the carbon fiber; (ii) surface diffusion of the oxygen towards the active sites which are located at the defects of the carbon fiber; (iii) chemical reaction between the oxygen and the carbon fiber with formation of the oxide gaseous species; and (iv) the diffusion of the oxide gaseous species into the boundary layer.

Under the conditions of the static atmosphere and low temperature of 850°C, oxidation of the carbon fiber yarns was limited by mass transport of the oxygen. Mass transport of the oxygen was dominated by diffusion of gaseous species. The oxidation rate was significantly increased in the flowing atmosphere environment because of the strong convection of gaseous species. Oxidation weight loss of the carbon fiber was obviously increased from 4.03 to 4.97% with the presence of HCl in the atmosphere. It was believed that the HCl acted as a catalyst during the oxidation process. Oxidation chemical reactions of the carbon fiber are usually expressed by:[16]

$$C + O_2 \rightarrow CO_2 \tag{2}$$

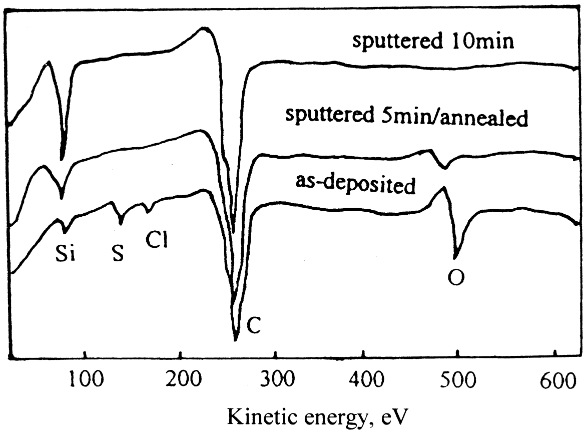


Fig. 2. Surface chemical composition of silicon carbide.

$$\Delta G_1^0 = 394133 - 0.84T(\mathrm{J}) \tag{3}$$

$$2C + O_2 \rightarrow 2CO \tag{4}$$

$$\Delta G_2^0 = -223426 - 175.3T(\mathrm{J}) \tag{5}$$

According to variation of the free energy of chemical reactions, the oxidation product of the carbon is mainly dependent on the reaction temperature. The connection point temperature for tow free energy curves of $\Delta G_1^0 \sim T$ and $\Delta G_2^0 \sim T$ is 975 K. If the oxidation temperature is higher than 975 K, the product should be CO gas because the free energy of the reaction (4) is lower than that of reaction (2). Even if there is some amount of CO_2 in the product, it should react with carbon and produce CO gas by the following reaction equation:

$$CO_2 + C \longleftrightarrow 2CO \tag{6}$$

The oxygen source is usually considered as: (1) the residual oxygen gas in the CVI reaction chamber; (2) the residual oxygen and the water in the chemical regents (such as H_2, Ar, and MTS); and (3) the residual water in the insulation materials of the carbon fiber felt because of the strong moisture absorption of MTS.

The chemical compositions on the surface of C/SiC composite materials were analyzed with an Auger probe and the results are shown in Fig. 2. Besides silicon and carbon, the elements of S, Cl, and O were also found on the surface of the composites. However, the elements of S, Cl, and O were completely disappeared after the surface of the samples was sputtered for 10 min. The results indicated that these elements were located only in a very thin layer of the composites. Cl was from the reaction gaseous species of MTS and S was a kind of impurity in MTS. O exited in the form of silica and was from the residual O_2 and H_2O in reactant system. Fig. 3 showed the distribution of elements of C, Si, and O across the

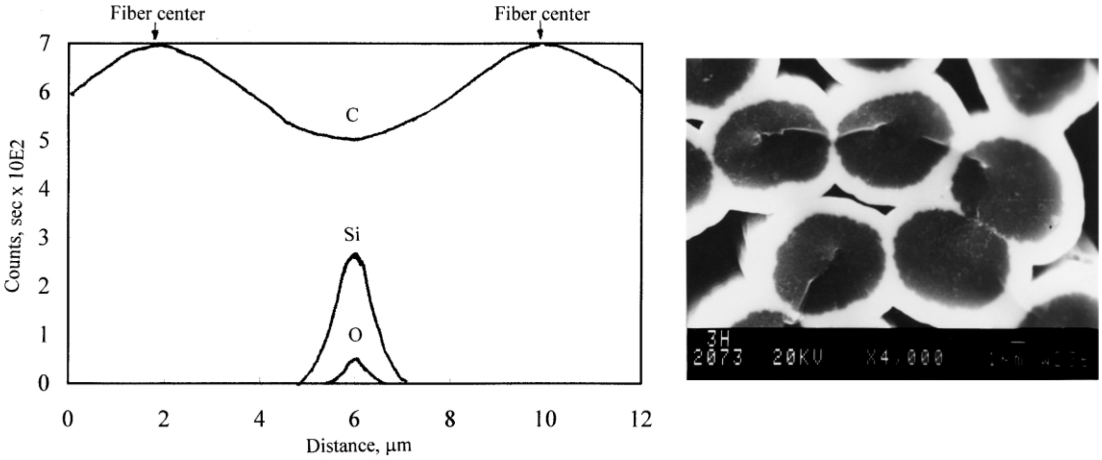


Fig. 3. Distribution of elements of Si, C, and O across the interfacial layer.

interfacial layer between the carbon fiber and the silicon carbide matrix.

The effect of oxidation weight loss on mechanical properties of the carbon fiber yarns was shown in Fig. 4. Oxidation of the carbon fiber, even though very limited, could result in a significant damaging on the strength of the carbon fiber. A treatment at the temperature of 850°C corresponding to 0.3% oxidation weight loss led to a tensile failure strength decrease by 30%. As oxidation weight loss increased from 0.3 to 4.03%, the curve exhibited slightly graduate slope. However, the slope of the curve became steep again when the oxidation weight loss was increased from 4.03 to 4.96 wt.%. The relationship between the fracture strain and oxidation weight loss was similar to that of strength. But the elastic modulus of the carbon fiber was not varied with increase of the oxidation weight loss. The reason is that the elastic modulus is one of the instinct properties of the carbon fiber and only dependent on the internal characteristic microstructure, and is determined by the heat treatment temperature of PAN precursor during the fabricating procedure:[17]

$$E = R_1 r_0 / S \tag{7}$$

Where E is the elastic modulus, R_1 is the tensile force constant, r_0 is the bond balance space, and S is the cross section square of the chemical bond.

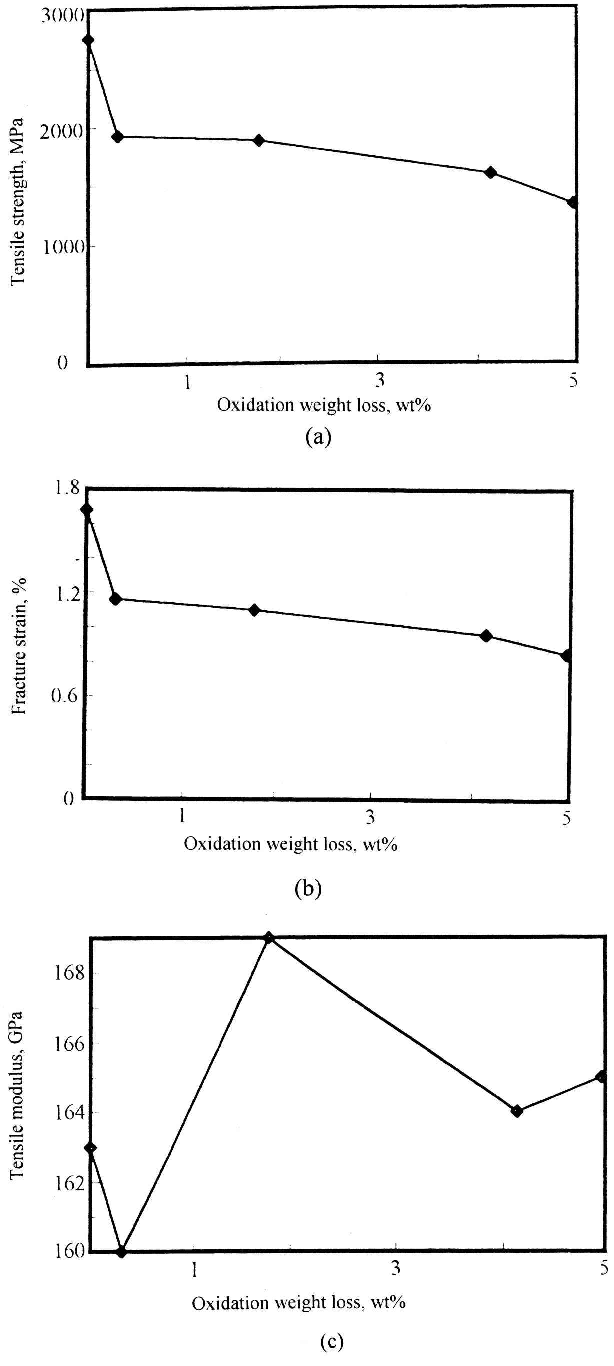


Fig. 4. Relationship between weight loss and mechanical properties of carbon fiber.

Fig. 5 illustrates the failure behavior of three different kinds of composites. The composites with a pyrolysis carbon interfacial layer (C/PyC/SiC) showed the typical composite failure behavior. This material exhibited the gradual and tough fracture even though it failed at the maximum stress of 460 MPa and fracture deflection of 1.0 mm. Unfortunately, the composites without a pyrolysis carbon interfacial layer (C/SiC) showed obviously brittle failure behavior, very low flexural strength and failure deflection. It was noted that both of C/PyC/SiC and C/SiC composite materials were prepared at the same conditions of reduced pressure atmosphere. For the composites prepared at normal atmosphere (0.1 MPa) even without pyrolysis carbon interfacial layer (C/SiC), the material exhibited high flexural strength (520 MPa) but brittle failure behavior. By comparing the flexural strength and failure behavior of three kinds of composites, it was found that flexural strength of the composites was dependent on the strength damage of the carbon fiber in CVI process. The interfacial layer was responsible for failure behavior of the composites. Mechanical properties results also indicated that the carbon fiber could be protected by the carbon interfacial layer against oxidation and damaging during the fabrication process.

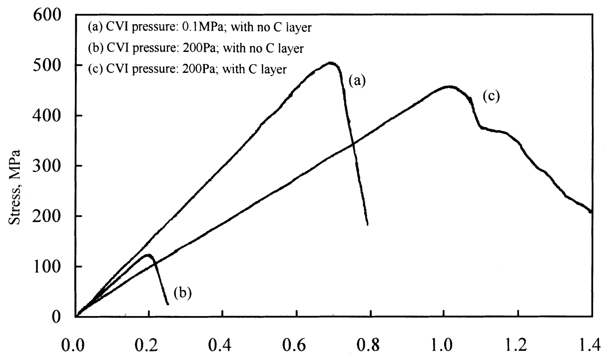


Fig. 5. Stress–displacement curves of three different kinds of composites.

3.2. Influence of oxidation on the microstructure of carbon fiber

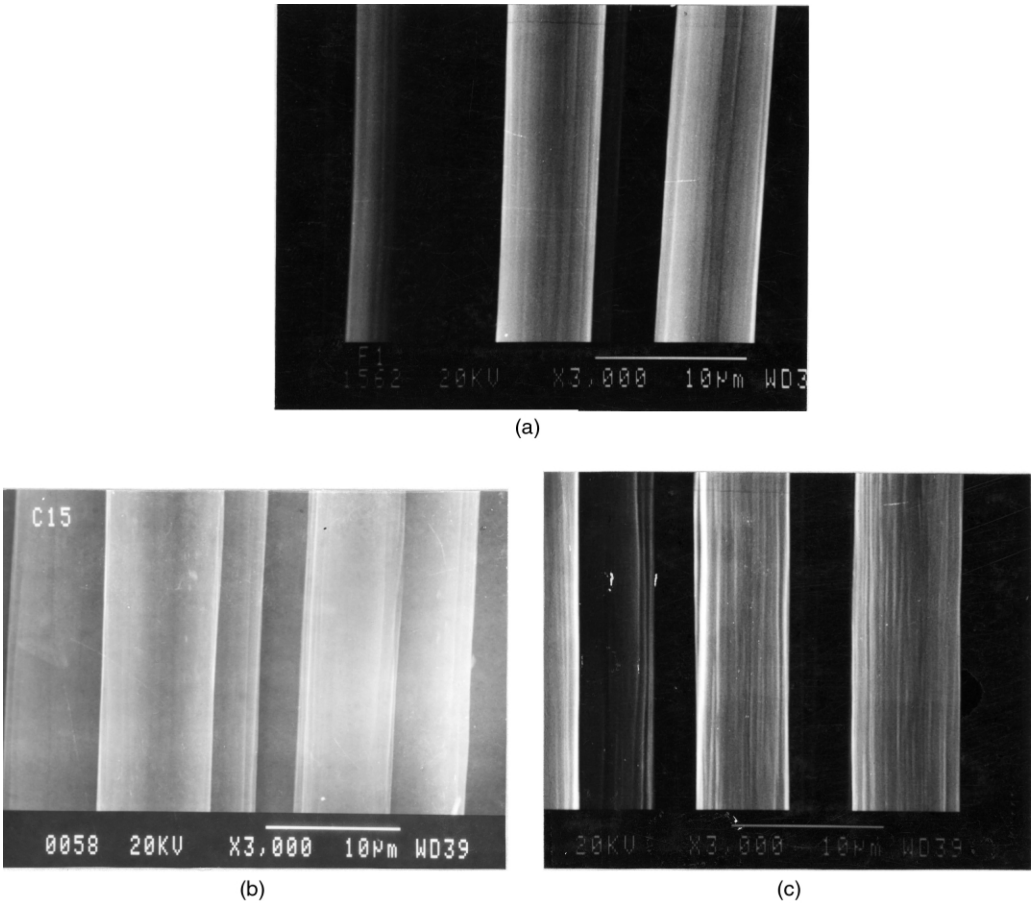
The interfacial layer is very important for ceramic matrix composites. In order to achieve high strength and high toughness, the interfacial bonding between the fiber and matrix should be strong enough to allow load transfer from the matrix to the fibers under stress, but weak enough to deflect the cracks.[18,19] In the present research, it was found that the interfacial layer could protect the carbon fiber during the CVI process. On one hand, the micro-depressions on the surface of the carbon fiber could be filled by pyrolysis carbon layer. On the other hand, the fiber damaging resulted from oxidation could be avoided because the carbon fiber was separated with the oxidation atmosphere by the interfacial layer.

Fig. 6 showed the SEM microstructure of the carbon fibers. Microstructure observation revealed that the surface of as-received T-300 carbon fiber was not smooth but there were many micro-depressions (Fig. 6a). The feature is related with the shape of spinneret employed for spinning the PAN precursor. It has been reported that the carbon fiber is not uniform within the texture. Consequently, the oxidation rate of the carbon fiber is also not uniform. After oxidation, the surface of the carbon fiber became much rougher than that of the as-received fiber (Fig. 6c). The carbon fiber is a typical brittle material and its tensile strength can be expressed by Griffith Equation:[7,20]

$$\sigma = \sqrt{E\gamma/\pi c} \tag{8}$$

Where γ is the fracture energy and c is length of the crack.

Obviously, the tensile strength of the carbon fiber was significantly decreased because both the length and depth of defects were increased after oxidation. However, these micro-depressions of the defects on the surface could be filled with the pyrolysis carbon layer (Fig. 6b). The interfacial layer played two important roles in the processing of composites: (i) to protect the carbon fiber from attacking by oxygen and chemical reaction; (ii) to decrease the sensitivity to crack by filling the micro-depressions with of the pyrolysis carbon coating. During the oxidation, the chemical reactions would take place at the perfect points of structure defects both on the surface and within the fiber. In order to examine the effect of oxidation on the microstructure within the carbon fiber,



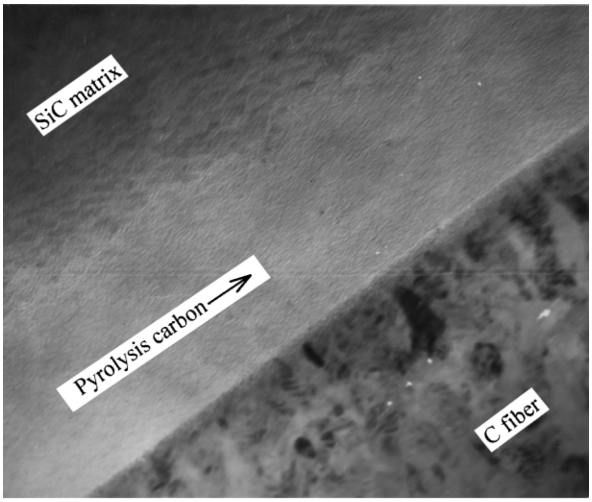
(a)

(b)

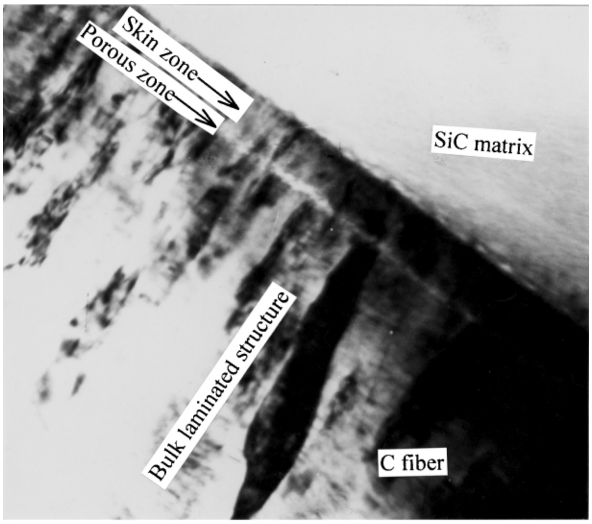
(c)

Fig. 6. SEM microstructures of carbon fibers treated at different conditions. (a) As received. (b) Coated with pyrolysis carbon layer. (c) Annealed.

TEM analysis was performed on thin foil samples cut parallel to the carbon fiber axis. By comparing the microstructure of the C/PyC/SiC composites (Fig. 7a), the carbon fiber of C/SiC was severely damaged. Microstructure observation revealed that there were three zones in the carbon fiber: a skin outer zone, a porous thin zone, and the bulk laminated structure as shown in Fig. 7b. In TEM analysis (Fig. 7c), a small amount of Cl and O was detected in the carbon fiber. Investigation indicated that Cl has strong infiltration ability in the carbon fiber and reacts with C to form a sandwich compound.[16] As a result, the formation of the sandwich compound destroyed the original structure of the carbon fiber and provided the tunnel for the oxygen transporting into the fiber. Oxidation of the carbon fiber could be divided into two stages. At first, the oxygen penetrated into the skin of the carbon fiber. At this stage, even a small amount of oxidation weight loss (0.3%) would result in the significant decrease of strength. Then, the oxygen penetrated in two directions along the axis to form the porous zone and perpendicular to the axis to form bulk laminated structure zone with cracks perpendicular to fiber axis. If the oxidation took place perpendicular to the axis corresponding to weight loss of 4.97%, the microstructure of the carbon fiber was catastrophically damaged.



(a)



(b)

Fig. 7. Microstructure of carbon fiber annealed in CVI atmosphere. (a) With and (b) without pyrolysis carbon layer (TEM). (c) CI in the carbon fiber.

Fig. 8 showed the microstructure of interfacial layer between fiber and matrix. For the composites with pyrolysis carbon layer (Fig. 7a), the interface was very smooth and distinct. However, the interface between the carbon fiber and silicon carbide matrix was rough for the composites without pyrolysis carbon layer. The results indicated that there were some chemical reactions at the interface. The deposition of silicon carbide from MTS was very complex and the main chemical reactions were involved:[21]

$$\mathrm{CH_3SiCl_3} \longleftrightarrow \mathrm{C-H_m + Si-Cl_n + HCl} \quad (9)$$

$$\mathrm{C-H_m} \longleftrightarrow \mathrm{C-H}_x + \mathrm{C + H} \quad (10)$$

$$\mathrm{H_2} \longleftrightarrow \mathrm{2H} \quad (11)$$

$$\mathrm{C-H}_x \longleftrightarrow \mathrm{C + xH} \quad (12)$$

$$\mathrm{Si-Cl}_n \longleftrightarrow \mathrm{Si} + n\mathrm{Cl} \quad (13)$$

$$\mathrm{H + Cl} \longleftrightarrow \mathrm{HCl} \quad (14)$$

$$\mathrm{Si + C} \longrightarrow \mathrm{SiC} \quad (15)$$

where $m, n, x = 0, 1, 2, 3$.

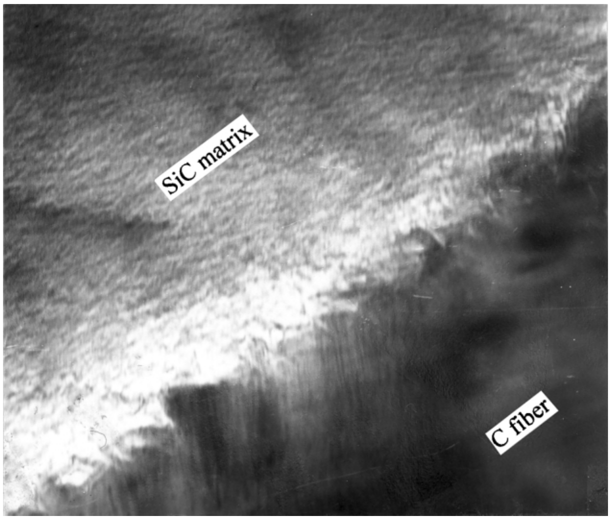


Fig. 8. Microstructure of interfacial layer of composites without pyrolysis carbon interfacial layer.

Eq. (9) described are the thermal decomposition step. The primary molecules carrying silicon are polar chlorides, and the primary molecules carrying carbon are simple non-polar hydrocarbons. The adsorption of gases on to the substrate surface is represented by Eqs. (10)–(12), and the chemical reactions of the adsorbed species, or of adsorbed gaseous species are depicted as in Eqs. (13)–(15). In these equations, the chloride atom is completely desorbed from the surface to the bulk gas. The hydrogen atom in the adsorbed hydrocarbon is not entirely detached from the main flow gas. Finally, the adsorbed species of silicon, carbon, and trapped hydrogen diffusing to the most preferential sites are incorporated into the crystal by surface diffusion. The silicon carbide crystal would then grow by the formation of adsorbed species on the basal surface.

It should be pointed out that chemical reactions (9)–(14) are reversible. During the CVI process, the local segregation of gaseous species would be formed in the fiber preform because it was very difficult for the reaction species to be transported to substrate and for by-products to be removed from the substrate immediately. If the local segregation reached a certain critical level, some reactions would be restrained or enhanced. As a result, the mixture of the silicon carbide containing the free carbon or the free silicon would be co-deposited. If the free silicon were present, it would react with the carbon fiber to form the tough interphase and result in strong interfacial bonding. Furthermore, the thermal cracks were observed in the silicon carbide matrix attributed to the mis-match of thermal expansion coefficients between the carbon fiber and the silicon carbide matrix. It was reported that the thermal expansion coefficients of T-300 carbon fiber along axis and chemical vapor deposited silicon carbide were 0.93×10^{-6} K^{-1} and 4.8×10^{-6} K^{-1}, respectively.[14,22] For C/SiC composites with strong bonding between the carbon fiber and silicon carbide matrix, the cracks could not be deflected at the interface (Fig. 9). Accordingly, the fiber damage resulted in low strength of the composites.

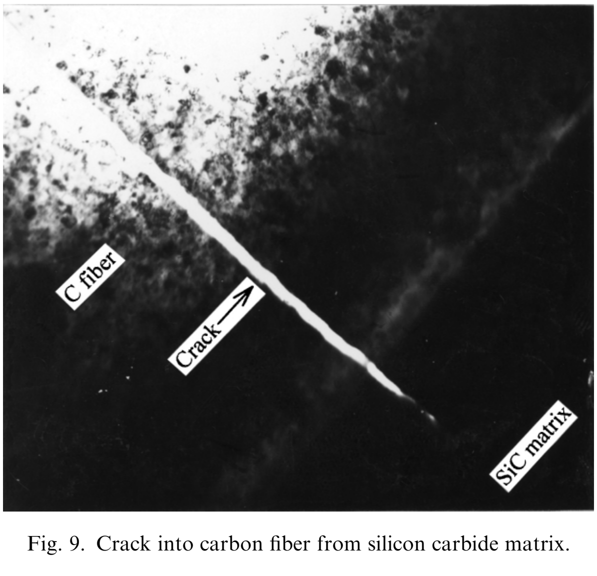


Fig. 9. Crack into carbon fiber from silicon carbide matrix.

4. Conclusions

Chemical vapor infiltration atmosphere had significant influence on the mechanical properties of carbon fiber and examine the microstructure of carbon fiber at temperature of 850–1100°C. Both tensile strength and fracture strain of the carbon fiber were dramatically decreased with the increase of oxidation weight loss of the carbon fiber. As oxidation weight loss was increased from 0 to 4.97%, the strength was decreased from 2850 to 1423 MPa. In CVI atmosphere, the oxidation weight loss and strength degradation of the carbon fiber were significantly increased with the presence of HCl. After oxidation, microstructure of the carbon fiber exhibited three zones: a skin outer zone, a porous thin zone, and the bulk laminated structure. During the chemical vapor infiltration process, the effects of the carbon interfacial layer lie in protecting the carbon fiber by filling the micro-depressions on the surface of the carbon fiber and by separating the carbon fiber with the oxidation atmosphere.

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