The Pretreatment of Carbon Fibres for 3D C/SiC Composites

Yan Liansheng, Song Maili, Wang Tao and Zou Wu

Shaanxi Non-Metallic Material and Technology Institute
P.O. Box 101 Xi'an,Shaanxi 710025 P.R. China

ABSTRACT

A hybrid pretreatment of the carbon fibers, consistingf of coating the fibers with pyrolytic carbon by the CVD process and then heating at 1500°C in N_2, has been introduced. The results show that the residual tensile strength of heat-treated fibers is merely 37% of the initial strength, while the residual tensile strength of the hybrid-treated fibers increases to 50% - 80% of the initial strength. The influence of the coating thickness on the residual fiber strength has also been investigated. The flexural strength and fracture toughness of the composites reinforced by the hybrid-treated carbon fibers improved in contrast to the composites reinforced with heated fibers. SEM microstructure analysis indicated that the increase in the strength of the carbon fibers and the reinforced composite is due to the healing of natural defects and cracks on the surface of the carbon fibers and protecting the fibers from being eroded by impurities at elevated temperatures.

INTRODUCTION

Continuous fiber reinforced ceramic matrix composites have a potential application in the high-temperature thermal structure of aerospace vehicles and propulsion systems, since they offer high strength and toughness properties along with low density /1,2/. CVI-SiC matrix composites offer many advantages, such as high strength and toughness and improvement in resistance to oxidation as compared to other ceramics and C/C composites, and they have been successfully applied in the liquid propellant booster engines by SEP /3/. Ceramic fibers (such as Nicalon fibers) lose their strength beyond 1200°C because of inherent crystallization, which leads to decreased mechanical properties of the composites. The carbon fibers are the best candidate material for the ceramic matrix composites due to their high stability at elevated temperatures. The common fabrication procedure of C/SiC composites is as follows:

$$C_f \xrightarrow[\text{laminate}]{\text{weave or wind}} \text{perform} \xrightarrow[\text{heating}]{\text{pretreatment}} \xrightarrow[\text{CVD}]{\text{interphase coating}} \xrightarrow[\text{CVI}]{\text{densification}} \text{C/SiC composites}$$

The aim of the pretreatment is to improve the thermal stability of the carbon fiber at elevated temperatures in the procedure and applications and to decrease the thermal stress at the fiber/matrix interface. The common pre-treatment is heating in inert gases (N_2) at a high temperature from 1500°C to 2500°C. However, the heat treatment severely decreases the fiber and composite strength. The aim of the interphase coating is to facilitate fiber/matrix debonding and/or sliding and fiber pull-out and to improve the fracture toughness of composites; pyrolytic carbon is usually used as the coating material.

In this work we combined interphase coating and heat stabilization treatment so as to decrease fiber strength loss in the heat treatment procedure and to improve the mechanical properties of C/SiC composites. The influence of coating thickness and heat treatment temperature on the fiber residual strength and composite mechanical properties has also been investigated. The microstructure of the treated fiber surface and the fracture cross section of the composite was characterized by scanning electron microscopy.

EXPERIMENTAL

J1 carbon fibers (3K) were used in the experiments. Three different temperatures (1500°C, 2000°C and 2500°C) were employed in the fiber heat treatment process. The hybrid pretreatment included two steps; in the first step, carbon fibers were coated with pyrolytic carbon by the CVD process from the C_3H_6-N_2 system at 900°C, the deposition thickness varying from 0.1 μm to 1.0 μm; in the second step, the coated fibers were heat-treated at 1500°C in N_2 for 30 minutes. The procedure of composites production included three steps. In the first step, carbon fibers were woven into a 3D preform with a fiber content of 50%. In the second step, the fiber preform was pretreated by the above hybrid process, coated and heated. In the third step, the pretreated preform was densified with a SiC matrix by the CVI + PIP hybrid process /4/. The effect of heat treatment temperature and coating thickness on the mechanical properties of the fiber and composite was also studied by testing the single fiber strength and the composite flexural strength and fracture toughness. The microstructure of the treated fiber surface and the fracture cross section of the composite was characterized by SEM.

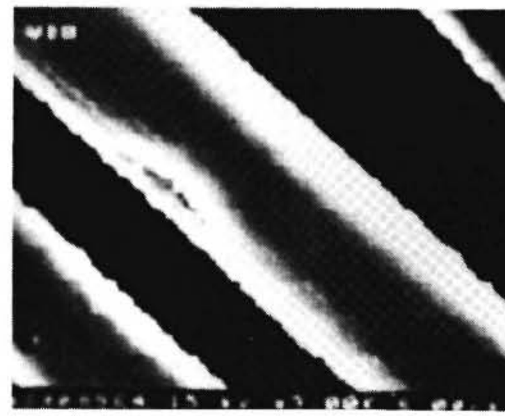
RESULTS AND DISCUSSION

The Effects of Heat Treatment

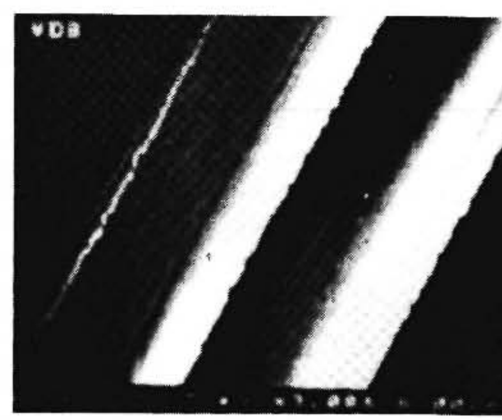
Heat treatment changed the strength and modulus of the carbon fibers: strength decreased and modulus increased. An increase in the treatment temperature led to a greater change in the fiber mechanical properties, as presented in Table 1. This is caused by changes in the structure of the carbon fibers. On the one hand, heat treatment caused growth of the crystal grains and increased axial crystal orientation in the fibers, thus enhancing the modulus and the heat stability of the carbon fibers. On the other hand, erosion of the fibers by impurities in the treatment atmosphere and volatilization of the non-carbon substances in the fibers at high temperatures produced defects and grooves in the fiber surface (see Figure 1), which caused a decrease in the fiber diameter and strength.

Table 1
Effects of Heat Treatment on Mechanical Properties and Structural Properties of Carbon Fibers

Heating Temperature, °C	Untreated	1500°C	2500°C
Tensile Strength, MPa	4200	2562	1554
Tensile Modulus, Gpa	202	262	354
Tensile Elongation, %	2.06	–	0.56



(a) heated only



(b) coated and heated

Fig. 1: Microstructure of Carbon Surface (SEM)

The Effects of Pyrolytic Carbon Coating

As described in Table 2, carbon fibers with different coating thicknesses, heated at 1500°C, have different residual strengths. The residual strengths of fibers increased as the coating thickness was increased from 0.1 μm to 1.0 μm. This can be explained by the fact that the coating filled and/or healed the inherent defects and cracks and protected the fibers from being eroded by the treatment impurities (see Figure 1), which enhanced the fiber residual strength.

Table 2
Single Strength of Carbon Fibers (MPa)

Untreated	Heat-Treated	Coated and Heat-Treated (Coating Thickness)		
		0.3 μm	0.7 μm	1.0 μm
3280	1220	1640	1680	2010

The Effects of Pretreatment on Composite Properties

The effects of pretreatment on the mechanical properties of 3D C/SiC composites have been studied. The results show that the mechanical properties of 3D C/SiC composites reinforced with heated fibers were poor, with flexural strength and fracture toughness reaching merely 386 MPa and 9.6 MPa•m$^{1/2}$, respectively. In contrast, the mechanical properties of 3D C/SiC composites reinforced with coated and heated fibers improved to a large extent, the flexural strength being between 456 MPa and 586 MPa and the fracture toughness between 12.6 MPa•m$^{1/2}$ and 16.8 MPa•m$^{1/2}$. The flexural strength reached the maximum at a coating thickness of about 0.7 μm. Therefore, the selected optimum coating thickness in the hybrid pre-treatment process was 0.7 μm (Tables 3 and 4). The SEM analysis indicated that the fracture mode of the composite was tough failure with many pulled-out fibers in the fracture cross section (Figure 2, the density of the composite was 0.2 g/cm^3).

Table 3
The Influence of Coating Thickness on the Composite Flexural Strength

	0.30 μm	0.39 μm	0.51 μm	0.61 um	0.71 um	1.0 μm
Flexural Strength, MPa	543	529	523	550	571	586

Table 4
The Influence of Coating Thickness on the Composite Fracture Toughness

	0.32 μm	0.39 μm	0.47 μm	0.61 μm	0.68 μm	1.03 μm
Fracture Toughness, MPa•m$^{1/2}$	10.0	12.1	15.2	15.9	16.8	16.1

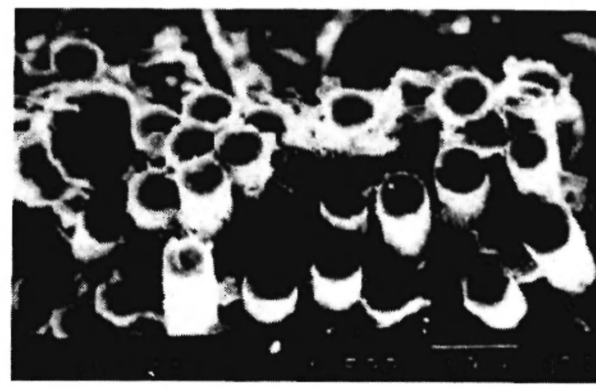


Fig. 2: Cross-section microstructure (SEM) of the fracture composites.

CONCLUSION

Heat treatment in the C/SiC composite fabrication process can improve the fiber thermal stability; however, it also leads to a heavy decrease in fiber strength. Coating the fiber with pyrolytic carbon before heat treatment can enhance the fiber residual strength. This can be explained by the fact that the coating filled and/or healed the inherent defects and cracks and protected the fibers from being eroded by the impurities. It was noted that coating and heating hybrid pre-treatment can improve the composite strength and toughness in the mean time. The composite reinforced with carbon fiber at a coating thickness of about 0.7 μm exhibited the best overall mechanical properties.

REFERENCES

1. T. Mah et al. Recent developments in fiber reinforced high temperature ceramic composites, *Am. Ceram. Soc. Bull.*, 66 (2), 304 (1987).

2. K.M. Prewo. Fiber reinforced ceramics: new opportunities for composite materials, *Am. Ceram. Soc. Bull.*, **68** (2), 395 (1989).
3. A. Lacombe and C. Bonnet. Ceramic matrix composites, key materials for future space plane technologies, AIAA-90-5208, in: *AIAA Second International Aerospace Planes Conference*, Orlando, FL, 29-31 Oct., 1990.
4. L. Yan. Rapid fabrication of carbon fiber reinforced silicon carbide composites, *24th Biennial Conference on Carbon – CARBON'99*, Charleston, South Carolina, USA, July 11-16, 1999; p. 406.