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RESEARCH PAPER

Effects of fiber-type on the microstructure and mechanical properties of carbon/carbon composites

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Abstract: Two carbonized oxidized polyacrylonitrile fiber (OPF) felts and one polyacrylonitrile-based carbon fiber (CF) felt were used as preforms to prepare two kinds of carbon/carbon composites by chemical vapor infiltration,and the effect of fiber type on the microstructure and mechanical properties of the composites were investigated. The microstructure was characterized bypolarized light microscopy and Raman spectroscopy and the mechanical properties were characterized by nanoindentation and three-point bend tests. The two carbonized OPFs are surrounded by a darklaminar layer about 1.4-2.6 μm thick followed by a rough laminar layer of about 10.2-11.6μm, while the CFs are surrounded by a smooth laminar layer about 8.8 μm thick and arough laminar layer of about 4.4 μm. Nanoindentation indicates that the modulus and hardness of the carbonized OPFsare obviously lower than those of the CFs, and the modulus and hardness of the matrix decrease with increasing extinction angle. The low modulus of the matrix and the OPFsresult in a decrease of the tensile and flexural strength by about 14.5%-24.2% and 7.3%-15.4% and a decrease of the tensile and flexural modulus by about 9.7%-19.8% and 15.1%-18.6%, respectively, for the OPF-derived composites compared with the CF-derived composites. However, for the OPF-derived composites the ductility factor increases by about 224%-235% because of the high content of rough laminarcarbon and the obvious shrinkage of the OPFs after graphitization. Meanwhile, a modelinvolving the three components in the composites is proposed to predict their tensile modulus, which shows deviations between experimental and predicted results below 9.9%.

Key Words: Carbon/Carbon composites; Microstructure; Mechanical properties; Chemical vapor infiltration

1 Introduction

Carbon/carbon (C/C) composites are widely used for structural and frictional applications in aeronautic and space industries, as well as brake material for high speed vehicles owing to their high specific strength, stiffness and toughness, self-lubricating capability, low thermal expansion coefficient and outstanding refractory properties[1-3]. Chemical vapor infiltration (CVI) of carbon fiber (CF) preforms is the accepted process for mass production of the C/C composites used in the aircraft brake industry[4]. But the high cost largely limits their civil applications such as building materials, sport accessories and biological prostheses because of the expensive high modulus CFs and the long densification time[5]. A simple and effective way to cut the cost is to substitute the high modulus CFs by the cheap oxidized polyacrylonitrile fibers (OPFs) obtained by oxidation of polyacrylonitrile fibers in a temperature range of 200-300 ^{o}C in air[6]. Moreover, Jia et al[7] reported that the elongation to break of the OPFs is almost four times as high as that of the CFs, which is advantageous for weaving. Manocha et al.[8] and Ko et al.[9] have used OPF co-carbonization with resins to make the C/C composites with acceptable mechanical properties. Chen et al.[10] have studied the mechanical properties of the C/C composites from the carbonized OPF preforms with CVI/resin carbon hybrid matrix and found that the flexural strength (100-115 MPa) was low. Moreover, Su et al.[11] have used the CF cloth and the OPF felt alternately needled as preforms to prepare the C/C composites with remarkable ablative behaviors. However, the fiber-types, which are important to determine the microstructure and mechanical properties of composites, have hardly been taken into account in former studies, and the essential information related to their effects on the microstructure and mechanical properties is relatively rare.

The current work is to compare the microstructure and mechanical properties of the C/C composites prepared from carbonized OPF felts with those from CF felts. Because the carbonization of the OPFs has been highlighted by previous authors[12], this process is not discussed and taken into account here. So, the properties of the OPFs after carbonization are only monitored and used directly to compare with that of CFs.

2 Experimental

2.1 Material preparation

Needle-punched integrated felts were used as preforms and the mass ratio of non-woven cloth to short-cut fiber web was 7:3. The fiber types of the felts were OPFs (Jilin carbon plant, China), OPFs (Toho Tenax, Japan) and CFs (Jilin carbon plant, China) named as Nos. 1, 2 and 3, respectively.

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Table 1 Properties of the fibers.

Fiber	OPFs				CFs
	No. 1		No. 2		No. 3
	Before carbonization	After carbonization	Before carbonization	After carbonization	
Density (g/cm^3)	1.36	1.73	1.42	1.75	1.76
Fiber diameter (μm)	15.37	10.67	13.56	7.95	7.00
Carbon content (%)	62.53	90.46	60.47	89.83	92.50
Tensile strength (GPa)	0.23	1.87	0.33	2.03	3.53
Tensile modulus (GPa)	5.35	163.00	8.96	212.00	230.00
Elongation (%)	14.80	1.38	15.20	1.45	1.51

Moreover, the obtained C/C composites were denoted using the same names as their preforms. The CF felt was used for comparison purpose and the two OPF felts were used to confirm the conclusion. The thickness of OPF and CF felts was about 25 and 20 mm, respectively. The density of OPF and CF felts was 0.60 and 0.45 g/cm^3, respectively. It is necessary for the OPF felts to be carbonized before densification because the two OPF felts exhibit high shrinkages in cross-section and length when used for CVI directly[10,13]. To characterize the performance of the OPFs after carbonization, 6 K OPFs the same as the OPFs for the felts were selected for this work. The carbonization was as follows: room temperature-200 ^{o}C for 5 h; 200-550 ^{o}C for 20 h; 550-700 ^{o}C for 10 h; 700-900 ^{o}C for 10 h; 900-1000 ^{o}C for 10 h; 1000 ^{o}C for 2 h. Both the OPFs and their felts were carbonized in an N_2 (purity ≧ 99.99%) environment in carbonization furnace without stretching. The density of the OPF felts after carbonization was about 0.45 g/cm^3. The felts were directly used as preforms after carbonization without high-temperature treatment. The CF preforms were heat-treated at 2300 ^{o}C for 2 h. After all of the preforms were machined to the size of Φ 200×20 mm^2, they were densified by isothermal CVI, using natural gas as pyrocarbon precursor, hydrogen as dilute and carrier gas at a temperature of 1050-1080 ^{o}C under a pressure of 1-5 kPa. The volume ratio of natural gas/hydrogen was 2/1. The three kinds of preforms were infiltrated about for 400 h and the crust was removed by machining every 50 h in the last 200 h. The final bulk density of the three preforms was 1.722, 1.718 and 1.715 g/cm^3 for Nos. 1, 2 and 3, respectively, and then they were graphitized at 2100 ^{o}C for 2 h.

2.2 Characterization of the fibers

The density of the fibers was obtained at 25 ^{o}C by the density gradient column method. The cross section of the fibers was observed by an optical microscope JXA-840 and the average diameter was calculated by the statistical software nano measurer®. The tensile strength of the fibers was measured on an Instron 5565-5KN tester using a fiber filament with a gauge length of 150 mm and a loading speed of 1 mm/min. The properties of the fibers are listed in Table 1.

Table 2 The textures of the pyrocarbon and the corresponding extinction angles [14].

Textures	Extinction angle (Ae)
Rough laminar	Ae≥18°
Smooth laminar	12°≤Ae≤18°
Dark laminar	4°≤Ae≤12°
Isotropic	Ae<4°

2.3 Characterization of the composites

The microstructure of the composites perpendicular to needle punched surface was determined on polished cross-sections under a polarized light microscope (PLM, Neophot21). The distinction of the different pyrocarbon layer was made by measuring the extinction angles. The optical textures are determined by their relationship to extinction angle (Ae). The classification of the texture of pyrocarbon is made as suggested by Duppel et al.[14] and is given in Table 2. The thicknesses of the pyrocarbon layers were measured on polished samples. The reported figures are mean values of at least 15 measurements. The polished surfaces of the C/C composites were analyzed by Raman spectrometry (AvaRaman-532) in the range from 1000 to 2000 cm^{-1}. The laser power was approximately 10 mW at a wavelength of 514 nm.

The elastic modulus and hardness of the fibers and pyrocarbon matrix were measured by the nanoindentation measurements using Nanoindenter XP system with a Berkovich-type-pyramid shape diamond indenter. The displacement resolution for the nanoindenter was 0.01 nm, and the load resolution was 50 nN. Before beginning the nanoindentation tests, the system was calibrated using the fused silica. The 2000 nm depth indentation was conducted while the indentation load, F, and displacement, h, were continuously recorded during one complete cycle of loading and unloading. The hardness of nanoindentation was determined from the load-displacement (F-h) curve (Fig. 1). The hardness value, H, is defined according to the following Eq. (1):

$$H = \frac{F_{\max}}{A} \tag{1}$$