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Evolution of microstructure and electrical property in the conversion of high strength carbon fiber to high modulus and ultrahigh modulus carbon fiber

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ABSTRACT

Evolution of microstructure and electrical property in the conversion of high strength carbon fiber (HSCF) to high modulus carbon fiber (HMCF) and ultrahigh modulus carbon fiber (UHMCF) was investigated. Longitudinal grooves on fiber surfaces became less well-defined during high temperature graphitization. The tensile modulus of carbon fibers was affected by fiber crystalline structure and it increased with decreases in the value of interlayer spacing and improvements in the value of crystallite thickness. Increases in the crystallite size almost had little effect on the tensile strength. However, a lower interlayer spacing and a higher preferred orientation could result in a higher tensile strength. The crystal structure of carbon fibers became much more ordered during high temperature graphitization. It was found that the electrical resistivity gradually decreased from 14.69×10^{-4} Ω·cm to 9.70×10^{-4} Ω·cm and 8.80×10^{-4} Ω·cm, respectively, in the conversion of HSCF to HMCF and UHMCF.

1. Introduction

Carbon fibers are widely used as reinforcements of advanced composites due to light weight, high tensile strength and modulus, excellent temperature and chemical resistance, high electrical and thermal conductivity [1–3]. Carbon fibers are generally typed by precursor such as polyacrylonitrile (PAN), pitch, rayon, etc. However, the majority of carbon fibers are made from PAN precursor because of its higher melting point, greater carbon yield, and excellent properties [4,5]. According to the tensile modulus, PAN-based carbon fibers can be roughly classified into standard grade (230–240 GPa), high strength and intermediate modulus carbon fibers (HSCFs, 280–300 GPa), high strength and high modulus carbon fibers (HMCFs, 350–480 GPa) and ultrahigh modulus carbon fibers (UHMCFs, 500–600 GPa) [6]. Generally speaking, the manufacture of HSCF consists of stabilization, low-temperature carbonization and high-temperature carbonization. In order to obtain HMCF and UHMCF, further heat treatment in excess of 2000 °C known as graphitization is necessary. In the process of high temperature graphitization, the fiber structure begins to approach a truly graphitic structure with three-dimensional order. Typically, fiber strain to failure decreases as the carbonization temperature exceeds 1500 °C because of reaction of impurities with the carbon fiber and the development of an increasingly flaw-sensitive graphitic structure [7].

Great changes in physical and chemical structures happen to the fibers in the process of graphitization. Increases in the tensile modulus, electrical conductivity and thermal conductivity of PAN-based carbon fibers can be achieved by increasing the final heat treatment temperature [8,9]. This can result in commercially available PAN-based carbon fibers with tensile modulus values ranging from 230 GPa to 588 GPa, electrical conductivities of 55–143 kS/m, and thermal conductivities of 5–156 W/m/K [10]. The tensile modulus monotonically increases with heat-treatment temperature, while maximum tensile strength is obtained at about 1500 °C [11,12]. Sauder et al. [13,14] studied thermomechanical properties of carbon fibers up to 2000 °C and 2400 °C. The results revealed that there was an essentially linear elastic behavior at room temperature and intermediate temperatures up to 1400–1800 °C, then a nonlinear elastic delayed response at higher temperatures and ultimately an inelastic response with permanent deformations at very high temperatures. Li et al. [15] and Liu et al. [16] investigated the evolution of microstructure and mechanical properties in continuous graphitization, and HMCFs with modulus range from 340 GPa to 430 GPa were obtained through hot stretching graphitization. Besides preferred orientation, the crystallite size was found to be another factor which could affect fibers tensile modulus. In the research by Guigon et al. [17], HSCFs were heat-treated up to 2800 °C. The results showed that atom ratio of N/C could affect the mechanical properties, and both the tensile strength and the tensile modulus of nitrogen-rich HSCFs increased in the process of graphitization.

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PAN-based HSCFs, HMCFs and UHMCFs have been commercially available for many years. However, structural and electrical evolution in the conversion of HSCF to HMCF and UHMCF has not been well-documented yet, and there are also few studies on the structural and electrical analysis of PAN-based UHMCFs. In the present work, PAN-based HSCFs underwent a high-temperature graphitization with the temperature up to 2400–2800 °C. HMCFs and UHMCFs were obtained through accurate control of the crucial process parameters. Structural and electrical evolution in the conversion of HSCF to HMCF and UHMCF was investigated through scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy (Raman) and electrical resistivity testing apparatus. In particular, a relationship between the mechanical properties of carbon fibers and the microstructure parameters such as crystallite size, as well as the degree of preferred orientation, was also researched.

2. Experimental

2.1. Materials

HSCFs researched in this paper were produced in our laboratory and they were made from PAN precursors according to a continuous process including stabilization, low-temperature carbonization and high-temperature carbonization. The tensile strength and tensile modulus of HSCFs were 5.60 GPa and 293 GPa, respectively. There were 6000 filaments in per tow and the density of as-received HSCFs was 1.78 g/cm^3.

2.2. The graphitization process of HSCFs

The continuous graphitization of HSCFs was carried out through a graphitization furnace and the hot-zone length of the graphitization furnace was 200 cm. The experiment was carried out in an inert environment. Nitrogen couldn't be used in the graphitization process as it might react with the carbon to form nitrides [12]. Therefore, argon atmosphere was chosen. The residence time of HSCFs in high temperature zone was about 70 s. In order to prevent thermal shrinkage and obtain high-performance HMCFs and UHMCFs, hot stretching was necessary and performed by stretching machines during high temperature graphitization. The percentage of stretching was defined as the following formula:

$$S = (V_a - V_b)/V_b \quad (1)$$

where V_a is the running speed of fibers after graphitization (m/min), and V_b is the running speed of fibers before graphitization (m/min) [15]. HSCFs were heat-treated up to 2400 °C and 2800 °C, and the percentages of stretching in graphitization progress were 3% and 5%, respectively. The as-received samples were denoted in the following by HMCF and UHMCF and their properties were tabulated to Table 1. The tensile strength and tensile modulus of as-received carbon fibers were evaluated according to ASTM D4018-99. The specimens were tested by a universal testing machine (model 5569A, Instron Corp.) at a cross-head speed of 10.0 mm/min with the gage length of 150 mm. As a contrast, a commercial product M55J fiber supplied by Torayca Co., Ltd., with the tensile strength and tensile modulus of 4.02 GPa and 540 GPa, respectively, was also researched in the present paper.

Table 1
Mechanical properties of as-received carbon fibers.

Sample	Graphitization temperature (°C)	Percentage of stretching (%)	Tensile strength (GPa)	Tensile modulus (GPa)
HSCF	0	–	5.60	293
HMCF	2400	3	5.07	482
UHMCF	2800	5	4.86	544

2.3. Characterization of physicochemical structure

Carbon fiber surface and transverse cross-section morphologies were characterized by a Quanta FEG250 model scanning electron microscopy (SEM). The acceleration voltage was 5 kV with an amplification of 10,000 times in the scanning mode. The samples of HSCFs, HMCFs, UHMCFs and M55J fibers were secured on a metal mount by conducting tape. After that, the samples were coated with gold prior to examination.

Wide angle X-ray diffraction (XRD) patterns of all samples were obtained in a D8 Advance Davinci diffractometer (CuKa, 0.15418 nm, 40 kV, 40 mA). The samples parallel to each other were fastened on a specimen attachment and examined in the form of equatorial scan, meridian scan and azimuthal scan. In order to obtain the detailed parameters of different peaks, the diffraction scan curves were analyzed by Jade 5.0. The value of the average interlayer spacing d_{002} was calculated using Bragg's law, and the crystallite thickness (L_c) and layer plane length (L_a) were determined using the Scherrer equation from the positions of the diffraction maxima and the width at half-maximum intensity of the (0 0 2) and (1 0 0) peaks [15,18]. Azimuthal scan was used to analyze the degree of preferred orientation of graphite layer planes parallel to the fiber axis.

Raman spectroscopy was carried out using a Renishaw in Via-reflex spectrometer. It was performed at room temperature under a nitrogen atmosphere, which was with a green 532 nm line of an argon ion laser as the incident radiation. A research grade Leica DM2700M microscope with a 50× objective was utilized to detect the Raman radiation. The laser beam was polarized parallel to the fiber axis and focused to give a spot size of 2 μm diameter on the fiber surface. The Raman spectrometer was operated in a continuous scanning mode and typical exposure time for carbon fibers ranged from 10 s to 30 s. The instrument was calibrated using an internal Si reference sample. The band position, band intensity and band width were obtained using a Lorentzian or mixed Gaussian–Lorentzian curve-fitting procedure [19,20]. The Raman spectrum was collected at different positions on the surface of each fiber in order to ensure the reliability of the results.

The electrical resistivity of as-received fibers was measured by a testing apparatus made in our laboratory. The testing apparatus is shown in Fig. 1. During the test, carbon fiber sample with the length of 300 mm was fixed on the specimen holder under certain tension. The distance between two detection electrodes could be adjusted through the moving slider, and the distance was set at 85.04 mm according to the scale line of the ruler on the platen. The rotating nut was adjusted so that the platen gradually descended until the detection electrode contacted the sample on the specimen holder. After that, the electrical current of the fiber sample was stabilized at 0.05 A, and the value of voltage was recorded at this time. The electrical resistivity was calculated based on the following formula:

$$R_f = \frac{U}{I} \times \frac{t}{\rho_f} \times L^{-1} \times 10^{-5} \quad (2)$$

where R_f is the electrical resistivity (Ω·cm), U is value of voltage (V), I is value of electrical current (A), t is linear density of carbon fiber (tex), ρ_f is the density (g/cm^3) of carbon fiber and L is fiber length. Each sample was tested by three times and the average value was finally used.

3. Results and discussion

3.1. SEM analysis of fiber surface morphology

Surface SEM photographs of HSCFs, HMCFs, UHMCFs and M55J fibers are shown in Fig. 2. Well-defined longitudinal grooves running along the length of fibers could be observed on the surfaces of HSCFs (shown in Fig. 2a). The characteristic striated topography inherited from PAN-precursor as a result of its wet spinning process [5,21]. In the