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Heat-induced Internal Strain Relaxation and its Effect on the Microstructure of Polyacrylonitrile-based Carbon Fiber

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The transformation of the internal strain and its effect on the microstructure of polyacrylonitrile-based carbon fiber during the high-temperature graphitization were investigated. The internal compressive strain within the carbon turbostratic structure was confirmed through a careful analysis by wide-angle X-ray diffraction and Raman spectroscopy. Heat-induced strain/stress relaxation along the fiber axis was observed and was found to have a profound effect on the structure of both the crystallites and microvoids. The results indicated that, the relaxation of residual strain changed the graphite layers from a wrinkled and distorted morphology to a straight and smooth one, and consequently led the crystallites to stack closely and orderly with increasing stack height. The strain relaxation also changed the morphology of crystallites and microvoids, resulting in an anisotropic growth for the latters.

KEY WORDS: Graphitization; Internal strain; Microstructures; Nanocrystalline; Carbon fiber

1. Introduction

Carbon fibers are strategic engineering materials which are greatly successful to be commercialized over the past decades. Their high strength and stiffness, combined with light weight, make these fibers be widely used as reinforcement in carbon fiber reinforced plastics, metals, ceramics and carbon−carbon composites[1−5]. Polyacrylonitrile (PAN)-based carbon fiber is produced by the oxidative stabilization of polyacrylonitrile precursor fiber[6], normally followed by a two-stage carbonization process, with an added graphitization stage to manufacture high modulus fiber[7,8]. Graphitization, during which profound structural evolution occurs for carbon fiber, is an important methodology for modifying the property of fibers[7].

In fact, thermal residual strain has attracted much attention in the past decades and was well discussed in composite patch materials[9]. As reported by Findik et al.[10,11], residual strain distribution in the patched specimen can be determined generally as a function of temperature by using a strain indicator. However, in spite of the similar basic stress development theory, the internal strain in carbon materials themselves is of difference from these materials. Transmission electron microscopy (TEM) and X-ray diffraction data always show that, non-graphitized PAN-based carbon fibers contain extensively folded and interlinked turbostratic layers[12−15] with the interlayer spacing significantly larger than that of crystalline graphite[16−20]. Franklin[21] once speculated that, between each of the small crystalline regions, these unorganized carbons can be highly strained. Such a "turbostratic stacking" is accordingly unstable if it was heat-treated at high temperature or under applied stress. Warner et al.[22] determined the strain field maps on the lattice structure of graphene, and found that the strain fields generally concentrated on the dislocation cores and weaken outward from the core in graphene. Sarian and Strong[23] reported that stress in graphitized carbon fiber relaxed when the fiber was annealed to 1100 °C under zero external stress. And it was further confirmed that the driving force for the relaxation was the internal strain energy release. Rennhofer et al.[16] reported a further but less pronounced development towards a more ordered structure for carbon fiber after the main part of the heat-induced or stress-induced structural changes. Perret and Ruland[24] further

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reported that the internal strain of stress-graphitized carbon fiber was also partially released by mechanically grinding the fibers to a powder. The above studies verify our assumption, i.e., there is internal strain in the local place of carbon materials, and it will relax under certain heat or stress conditions. However, in order to measure the local strain condition, a quantitative technique is still needed.

Most of the current work concerning the characterization of the strain condition within carbon turbostratic layers tend to focus on the strain/stress distribution during the tensile deformation of carbon fibers. Wide-angle X-ray diffraction (WAXD) was well discussed in this field. Loidl et al.[20] estimated the strain of the crystalline graphite lattices and found the X-ray peak shifts were different depending on the type of carbon fibers during the tensile deformation. Shioya et al.[25] reported that the orientation parameters increased linearly with increasing tensile stress for a series of carbon fibers. And the increase of orientation parameters was attributed to the rotation and extension of crystallites. Kobayashi et al.[26] also measured the stress-induced structural changes and evaluated the stress distribution at various parts of carbon fiber monofilament[27]. Besides WAXD, Raman spectroscopy is another effective method to measure the response of carbon fiber to applied stress at the molecular level. In this field, continuous researches confirmed: (1) the application of uniaxial stress along the fiber axis could cause polarization-dependent splitting and shift of the Raman peaks[28]; (2) the shift of the Raman peaks, was basically caused by the elongation of C−C bonds in the uniaxial stretching experiment[28]; (3) the band shift caused by an application of per unit tensile stress was larger for the higher modulus fibers[29]; (4) the higher modulus fibers tended to have a lower initial Raman peak wavenumber on the tensile deformation[30]. Beyssac et al.[31] related the graphitization of carbonaceous material with high-pressure metamorphic gradient and observed the *G* band changes with regard to the ambient pressure. From their work, though nothing more was announced, red shift of *G* band was precisely observed and could be attributed to the increase of the pressure. In conclusion, the previous studies though failed to discuss the influence of heat effect on the strain condition, clearly showed that the microstrain within carbon materials can be detected by WAXD, Raman spectrum and TEM.

However, besides some valuable works mentioned above, less work has been carried out to investigate the strain condition within carbon materials, especially the internal strain within carbon turbostratic layers as well as its influence on the microstructure of carbon fibers. Nowadays, continuous researches have realized PAN-based carbon fibers with tensile strength over 7.0 GPa (Toray T-1000G). The most featuring aspect of such a fiber is its higher ratio of strain to failure of 2.4% with comparing to that of 1.5% which could be normally achieved in ordinary carbon fibers[8]. A relationship between tensile strength and breaking elongation, i.e., the response of internal strain to applied stress, is thus of great interest and importance for carbon fiber production. Furthermore, high performance carbon fibers are still the primary strategic issue in China, though great breakthroughs have been made in recent years. In this sense, fundamental researches concerning the basic processes and technologies during the high-temperature graphitization are of urgent importance. Aiming to gain a better understanding of the strain conditions within turbostratic carbons, this present work for the first time is concentrated on the investigation of the relaxation of residual strain and its effect on the microstructure of carbon fibers during the high-temperature graphitization. The present work will bring us a better understanding for the carbonization and the graphitization process of carbon fibers as well as other carbon materials.

2. Experimental

2.1. Materials

All experiments in this study were performed on PAN-based carbon fiber, with typical values of 221 GPa, 3.96 GPa and 1.78% for Young's modulus, tensile strength and breaking elongation, respectively. The density of as-received carbon fiber is 1.772 g/cm^3.

2.2. Graphitization

The graphitization was carried out in a graphite element resistance furnace (Tongxin Electric Heating Apparatus Co., Ltd, Xi'an, China). The carbon fiber tow was carefully fixed without applied stress onto a graphite plate, and then placed in the constant-temperature zone of the furnace tube. The procedure for each processing run was to heat up a tow of fibers to the desired temperature at the rate of 5 °C/min in a helium atmosphere until the set heat treatment temperature (HTT) was reached, and then held at that temperature for 1 h. To ensure that the structural transformation and the strain relaxation were completely finished at the desired temperature, the holding time was thus set far longer than that in the industrial production. In this study, four final HTT points, i.e., 1800, 2000, 2300, and 2500 °C were chosen and were used to note the corresponding graphitized samples.

2.3. Characterization

Crystalline parameters were investigated by using an X-ray diffractometer (PANalytical X'Pert PRO, Cu$K\alpha$, $\lambda = 0.154$ nm, 40 kV, 40 mA) with a fiber specimen attachment. Measurements were made by performing equatorial scan, meridian scan, as well as azimuthal scan at the fixed Bragg position. The step size was about 0.05° and the scan time was set as 30 s per step for the equatorial and meridian scans. Silicon powder was pasted onto the samples as a standard for peak position correction. The measurement was carried out three times for samples in every single scan mode for error analysis and the confirmation of experimental reproducibility. The diffraction scan curves were fitted with MDI Jade 5.0, and the structural parameters were obtained according to Bragg equation and Scherrer formula[13].

The strain of the graphite planes was also measured by X-ray diffraction using the shift of the 100/101 reflection in the meridional direction of carbon fibers. The 100 and 101 reflections, which come from the lattice spacings of carbon network along the fiber axis, overlap each other and they are treated as a united 10 reflection for simplicity[1,26]. The scan step size in the experiment was about 0.016° and the scan time was set as 60 s per step. The observed d(l0) values were corrected for the asymmetry of the 10 reflection[32,33] according to the method suggested by Northolt et al.[19]. And then the accurate value of the strain within d(l0) planes, ε_{10}, was evaluated by the equation suggested by Loidl et al.[20]: $\varepsilon_{10} = \Delta d(10)/d(10)$.