

Heredity and Difference of Multiple-Scale Microstructures in PAN-Based Carbon Fibers and Their Precursor Fibers

Meijie Yu,^{1,2} Yong Xu,³ Chengguo Wang,^{1,2} Xiuying Hu,^{1,2} Bo Zhu,^{1,2} Kun Qiao,^{1,2} Hua Yuan^{1,2}

¹Carbon Fiber Engineering Research Center of Shandong Province, Shandong University, Jinan 250061, China

²Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, China

³School of Materials Science and Engineering, Shandong Jianzhu University, Jinan 250101, China

Received 15 January 2011; accepted 15 November 2011

DOI 10.1002/app.36486

Published online 1 February 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Multiple-scale microstructures, including skin-core structure, fibril structure, lamellar structure, crystal/amorphous structure, were found co-present in the fibers during the whole production process of polyacrylonitrile (PAN)-based carbon fibers. The structural heredity and difference among them were systematically investigated for the first time by scanning electron microscope, optical microscope, transmission electron microscope, and X-ray diffraction. The relations between the four kinds of structures and their formation mechanisms were analyzed. The skin-core structure is contributed to inhomogeneous distribution of composition and chemical structure along the radial direction in oxidative stabilized fibers, which is proved different in PAN precursor fibers and carbon fibers. Fibrils are successively separated from low-temperature oxidative stabilized fibers by ultrasonic etching in dimethylsulfoxide solution. The separation of individual fibril

becomes harder and even impossible in those fibers prepared at temperatures higher than 245°C. This suggests a stronger bonding force between fibrils in high-temperature oxidative stabilized fibers and carbon fibers. The lamellar structures within fibrils are observed in all of these fibers but with thicker lamella width with increasing temperature. They are unlikely due to the alternatively alignment of crystal regions and amorphous regions as reported by many previous literature, because the oxidative stabilized fibers are amorphous but have lamellar structures. The (002) diffraction arc gives the evidence that the lamellar structure in carbon fibers is not strictly perpendicular to the fiber axis, but have an angle of about 45° with it. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 3159–3166, 2012

Key words: fibers; stabilization; structure; carbonization; fibril

INTRODUCTION

Carbon fiber is one of the most important reinforcement fibers for composites. It is widely used in many fields such as aerospace, transportation, chemical industry, sports, medical, and building areas.^{1–3} Among the precursors for carbon fibers, polyacrylonitrile (PAN) is the most popular and promising one because it has high carbon yield and is liable to produce high strength carbon fibers with good com-

prehensive performance.^{4,5} From the polymeric precursor fibers to the inorganic carbon fibers, the microstructure of fibers undergoes remarkable changes due to complicated reactions at 200–300°C under an oxidative atmosphere (in the thermal stabilization process) and 500–1400°C under an inert atmosphere (in the carbonization process).^{6–9} Various structure models have been proposed, of which fibrillar structure, lamellar structure, two phase (crystal and amorphous) structure, and skin-core structure are often mentioned in the previous literature. As for carbon fibers and graphite fibers are concerned, there are ribbon model,¹⁰ microfibrils model,¹¹ three-dimensional structure model,¹² and skin-core model.¹³ Comparatively, only one structure model was proposed for oxidative stabilized fibers.¹⁴ Warner et al.¹⁵ have proposed a structure model for oriented PAN fibers, wherein a rod-like molecular arrangement and a lamellar-like texture composed of amorphous (disordered) and partially ordered regions were first reported and are frequently quoted by many researchers now.

Because similar microstructures or morphologies are observed in PAN precursor fibers, oxidative stabilized fibers, and carbon fiber, what the difference or

Correspondence to: M. Yu (jenniferxy@gmail.com) or C. Wang (sduwangchg@gmail.com).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50902088.

Contract grant sponsor: National Basic Research Program of China; contract grant number: 2011CB605601.

Contract grant sponsor: National Natural Science Foundation of Shandong Province; contract grant number: ZR2009FQ013.

Contract grant sponsor: Postdoctoral Innovation Projects in Shandong Province; contract grant number: 200902028.

Contract grant sponsor: International Cooperation Projects; contract grant number: 2009DFR50600.

relationship between them? As multiple-scale textures including fibrils or microfibrils, lamellas, crystallites and amorphous regions, and skin-core structure are co-existed in these fibers, what the affiliation relationships among them? These questions remain unsolved and we will try to find out the correlations by giving some direct evidence through experimental data. We believe it is helpful for better understanding of the structural heredity in PAN-based carbon fibers and is advantageous for obtaining high-performance carbon fibers.

EXPERIMENTAL

Materials

PAN precursor fibers are the copolymers of acrylonitrile and itaconic acid, which were prepared using wet-spinning method. The property indexes of the PAN fibers are: average titer of single filament, 0.95 dtex; tensile strength, 7.0 cN/dtex; and elongation at break, 10.5%. For description convenience, the PAN precursor fibers are named as PF.

Thermal oxidative stabilization and carbonization

Thermal oxidative stabilization and carbonization processes are carried out on our self-designed continuous production line. The equipments of this production line were described in detail in our previously published paper.¹⁶ The PAN fibers are thermal oxidative stabilized successively in 10 furnace zones, wherein temperatures are set as 195, 205, 215, 235, 245, 255, 265, 270, 275, and 275°C. We cut fiber from each furnace zone and named them from OF1 to OF10 in the sequence. During oxidative stabilization process, it took 6 min for the fibers passing through each furnace zone under proper stretching tension. Following stabilization, the fibers were heated continuously in low carbonization furnace (350–600°C) and high carbonization furnace (1100–1380°C) under the protection of inert atmosphere. The resultant carbon fibers were named as CF.

Characterizations

Optical microscope (OM)

Fibers cut off of 15–20 mm long were vertically embedded in acrylic resin. The cross sections were polished and then observed using a JXA-840 OM to study the skin-core structures.

Scanning electron microscope

The fibers' fracture cross sections were prepared in liquid nitrogen. They are coated with carbon film and observed using a JEOL JSM-7600F cold field emission scanning electron microscope (SEM). The

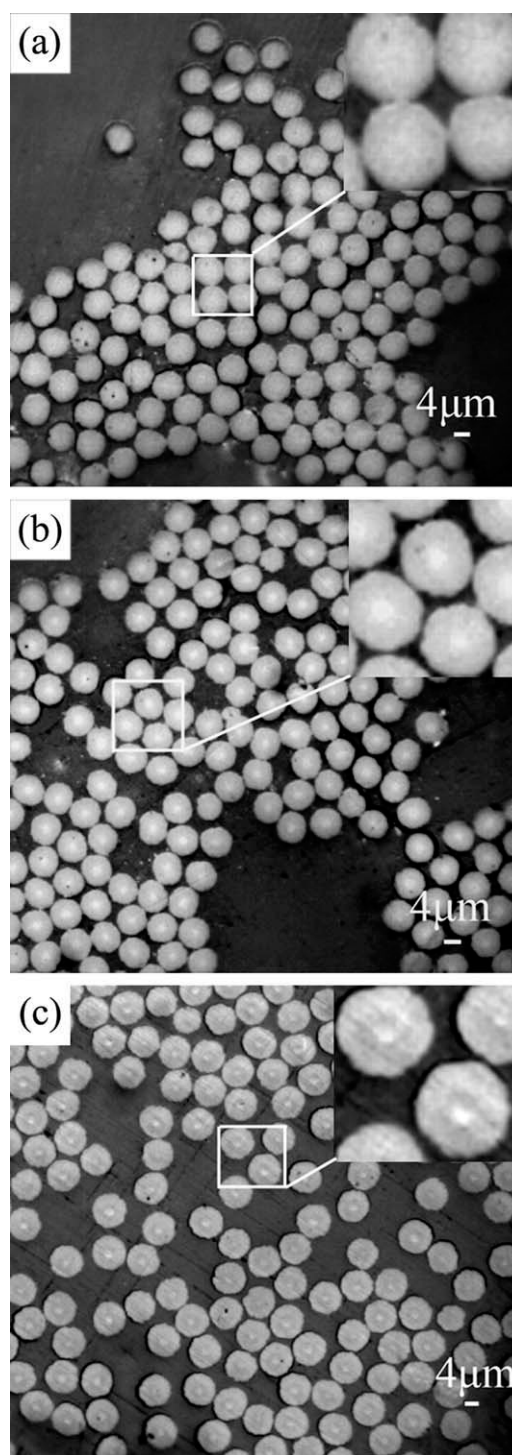


Figure 1 Cross-sectional morphologies in fibers (a) OF6, (b) OF8, and (c) OF10 observed by OM. Insets are the magnified images from the white rectangles.

surface morphologies of fibers were also investigated by SEM.

Fibrils separation method

Fibrils separation is carried out using a KQ-200KDE ultrasonic cleaner at frequency of 40 kHz through

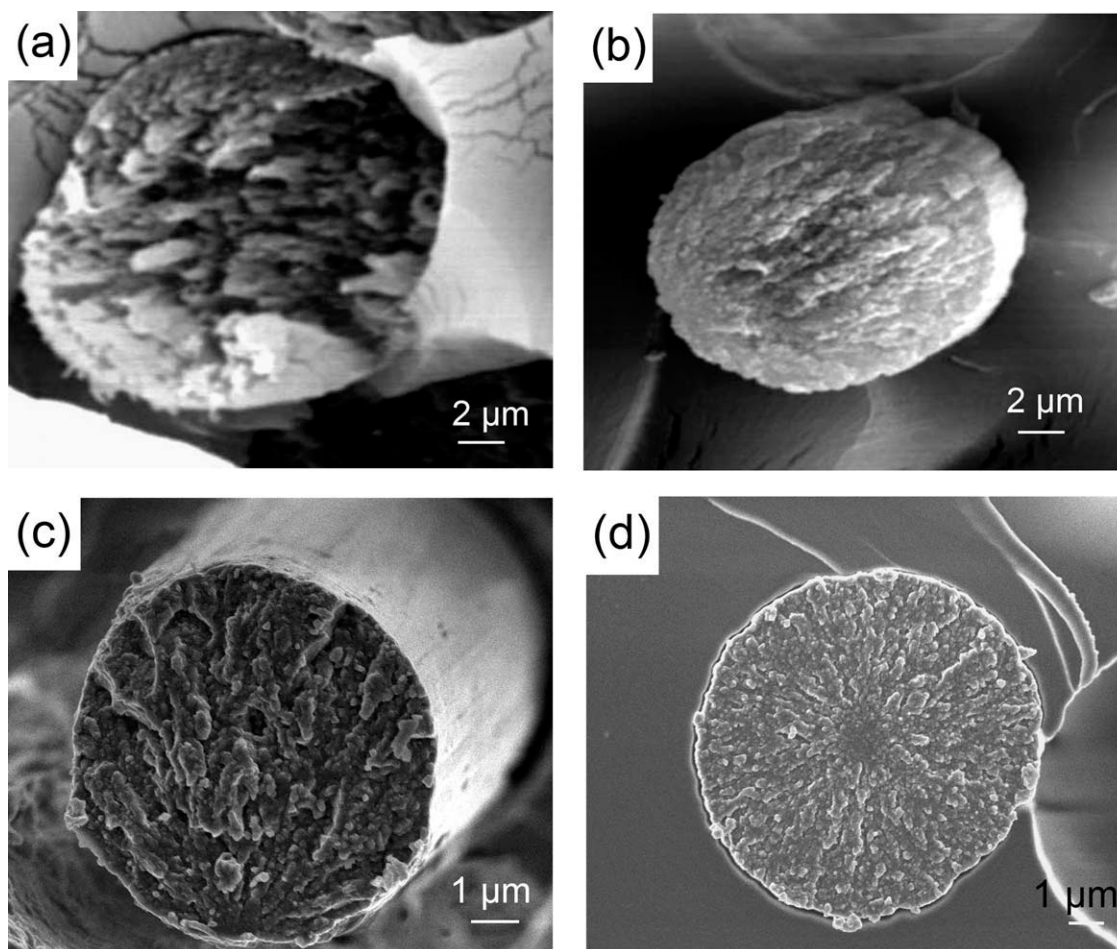


Figure 2 SEM images of fracture cross-sectional morphologies of (a) PF, (b) OF10, (c) CF, and (d) another OF10 with defects.

ultrasonically processing fibers of 2–3 mm length in the 90 wt % aqueous dimethylsulfoxide (DMSO) solution or pure DMSO at $75 \pm 2^\circ\text{C}$ for 6–10 h. The morphologies of fibrils are observed on a JEOL JSM-7600F SEM.

Transmission electron microscope

The inner structures of fibers were observed by H-800 transmission electron microscope (TEM) and Philips Tecnai 20U-TWIN high-resolution TEM (HRTEM). The samples for TEM are prepared by ion bombardment. The samples for HRTEM are ultrathin sections of about 30 nm in thickness, which are cut using an Ultracut E ultramicrotome (Reichert-Jung).

RESULTS AND DISCUSSION

Skin-core structure

The cross-sectional morphologies of PF, CF and OF1–OF10 are observed by OM and SEM. Typical images are selected and shown in Figure 1. No distinct skin-core structures are observed in PF and

CF by OM. The oxidative stabilized fibers, which were heated at temperatures lower than 265°C , also show homogeneous texture. When temperature is higher than 265°C , skin-core structures occur. The skins are dark colored and the cores are light

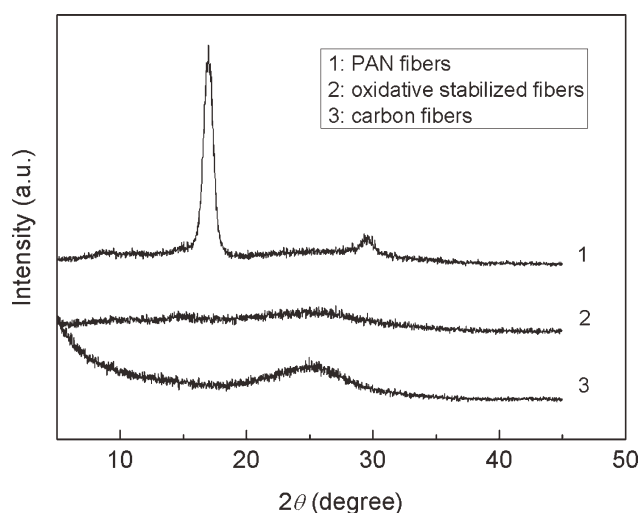


Figure 3 XRD patterns of different fibers.

colored. The thickness of the “skin” is about 4 μm . This thickness is almost unchanged, but the color difference between the skin and the core becomes more obvious as increasing treatment time at 275°C. The effects of temperature, time, as well as the titer and the cross-sectional shapes of precursor fibers on the skin-core structure of oxidative stabilized fibers are studied in our previous work.¹⁷ The results show that the oxidative stabilization temperatures and heating mode are the two essential factors that affect the skin-core structure.

The fracture cross section morphologies of PF, OF1–OF10, and CF are characterized using SEM to further investigate the skin-core structure. Some typical images are shown in Figure 2. From Figure 2(a), we can see fibril-like ribbons compactly aggregate in the skin part and loosely distribute in the core part in one of PF filaments. This kind of inhomogeneous morphology is not representative of the average. Most of the observed filaments in PF, OF, and CF show a fairly uniform structure just like the image in Figure 2(b,c). However, we observed defects as shown in Figure 2(d) in several OF9 and OF10 filaments. In brief, skin-core structures are observed by SEM in a few part of PF and OF, but not observed in CF in our present work.

Nevertheless, we cannot draw a conclusion that there are no skin-core structures in other PAN fibers, oxidative stabilized fiber, and carbon fibers which are prepared by different processing, because improper technologies and parameters during each steps of the whole production process can deteriorate or give rise to defects in the microstructure of fibers. Skin-core heterogeneities have ever been found in PAN fibers¹⁸ and carbon fibers^{12,19} by SEM and TEM, which are deemed as the limiting factors for the tensile strength of fibers. Then, a question comes up: what are the differences and relationships between the skin-core structures of PAN fibers, oxidative stabilized fibers, and carbon fibers? As we know, the uneven morphologies present in OM are mainly the result of reflection of different colors. Chromogenic groups, e.g., C=C, C=N, and C=O formed during oxidative stabilization due to dehydrogenation, cyclization reactions, and uptake of oxygen. With oxygen diffusing from skin to core, the oxidation degree is higher in the skin than in the core. This leads to the uneven distribution of chromogenic groups along the radial direction of fibers, as a result, the skin-core structures are observed under OM. With the increasing of temperature, the dense skin becomes a barrier for oxygen diffusion which intensifies the content difference of oxygen functional chromogenic groups between the skin and core. Therefore, obvious skin-core structures are observed in OF8, OF9, and OF10. As for PF and CF are concerned, the results of OM characterization

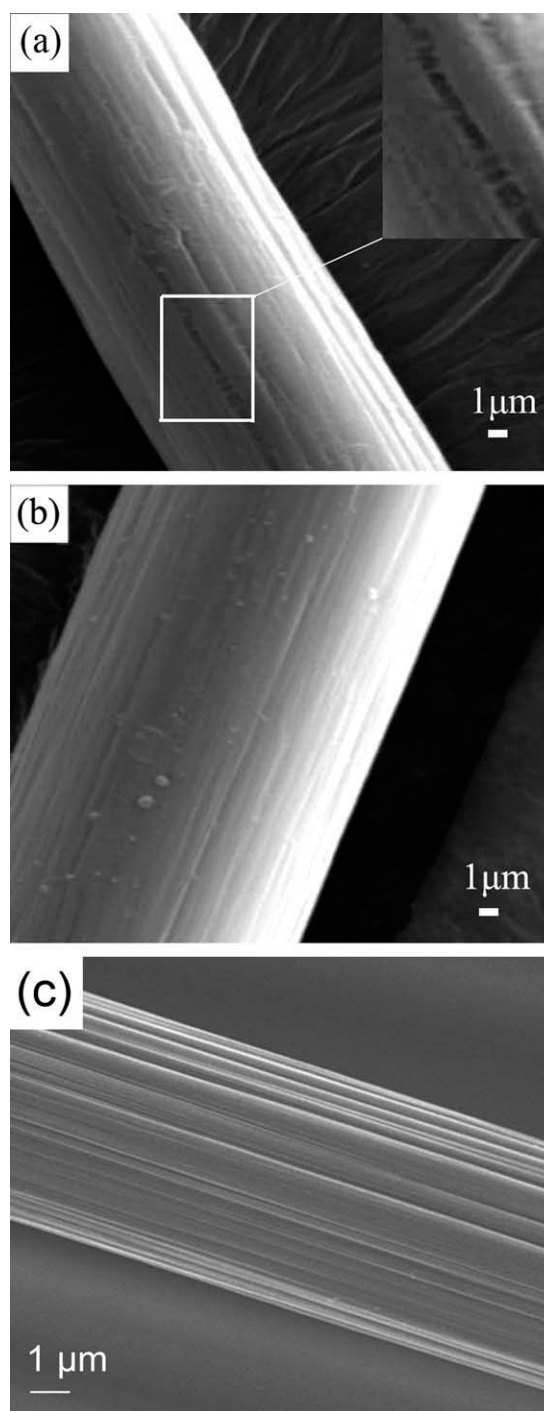


Figure 4 SEM images of surface morphologies of (a) PF, (b) OF, and (c) CF.

indicate that the chemical compositions along the radial direction are basically uniform. The skin-core structures in PAN fibers observed by other researchers were attributed to different crystallization and orientation of PAN molecule, which are higher in the skin than core.¹⁸ The skin-core structures in carbon fibers are reported attributed to two different causes. Barnett and Norr¹² proposed a three-dimensional model in which long-range crystalline

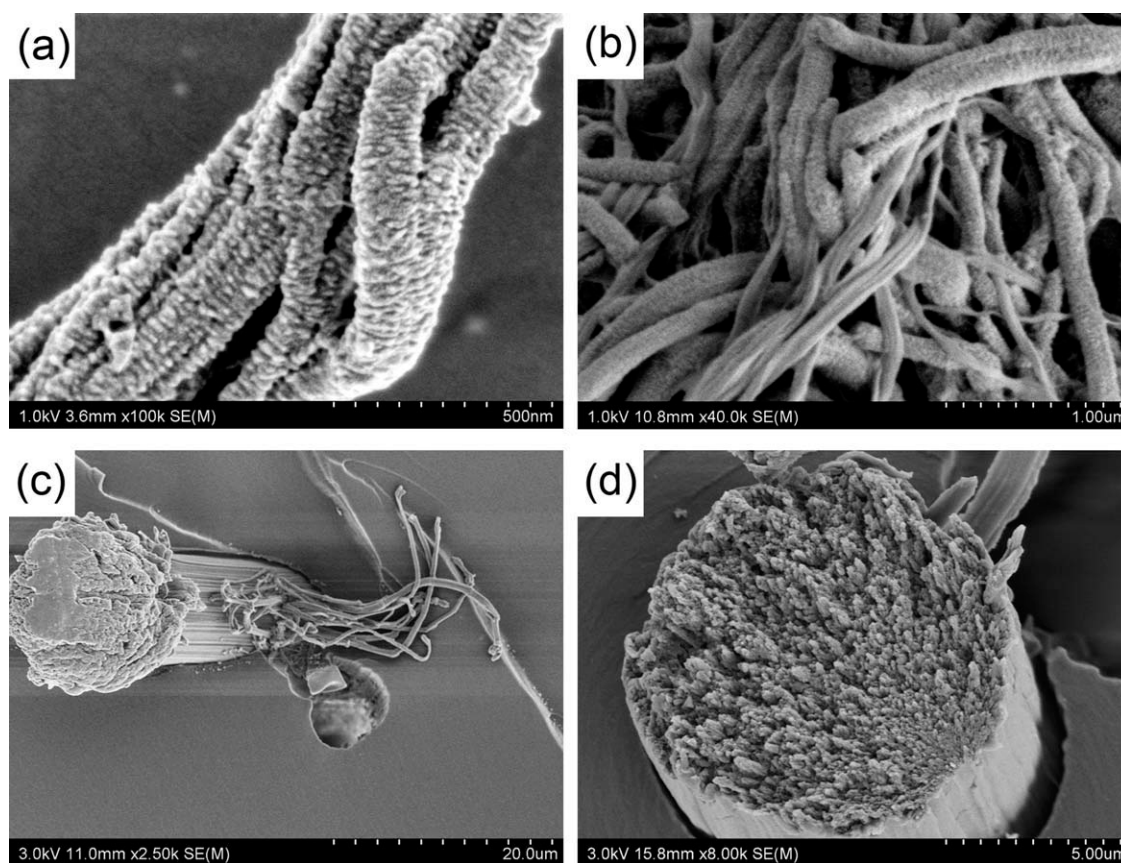


Figure 5 SEM images of fibrillar structures in (a) PF, (b) OF3, (c) OF4, and (d) OF5.

macrostructure is circumferentially oriented in the outer shell and connected to a central core by a honeycombed radial continuum. Bennet and Johnson¹⁹ pointed out that they did not find the evidence for this kind of morphology, but found that the graphite layer plane in the surface of carbon fibers have slightly improved orientation and lattice order.

It has been proved by our present work (see Fig. 3) and many other X-ray diffraction (XRD) studies that the crystal structure in PAN precursor fibers was destroyed during the oxidative stabilization process, and the stabilized fibers are almost amorphous.^{20–22} Therefore, the skin-core structures in OF is not probably due to the difference of crystallization. Watt and Johnson²³ found that the brown outer zone is relatively rich in oxygen compared with the light yellow core. Moreover, the skin zone is composed of a stable chemical structure, which is sulfuric acid resistant and flame resistant.²⁴ Our previous works also show that the initial rapid oxygen uptake and the subsequent intense aromatization are responsible for the formation of the skin-core structure.²⁵ After carbonization, this kind of heterogeneous structure will even enhance and an internal cavity is developed in the carbon fibers.²⁶ To sum up, the nature of skin-core structures are different in PF, OF and CF. Our present work indicates that the

skin-core structure is a kind of heterogeneity in composition and chemical structure along the radial direction in OF. It is attributed to difference crystallization and difference orientation in PF in CF, respectively, by other researches.

Fibrillar structure

The surface morphology of PF, OF, and CF are shown in Figure 4. Stripe-like textures are obvious on all the three types of fibers. The following analysis will give evidences that they are composed of fibrils and microfibrils. To obtain direct evidence for fibril structure, we try to separate individual fibrils from various fibers using ultrasonic etching method. The results as shown in Figure 5 suggest that it is easy to separate fibrils from PF and OF3–OF5. The separation becomes harder and even impossible with increasing temperature. When temperature is higher than 245°C, no distinct fibrils are obtained in spite of increasing the concentration of DMSO solvent and prolonging the etching time. The diameters of fibrils range from 50 to 300 nm in PF, from 100 to 400 nm in OF3, 100–300 nm in OF4 and 500–1000 nm in OF5, respectively. When temperature is up to 265°C, the cross sections of the fibers remain compact and no single fibrils can be distinguished.

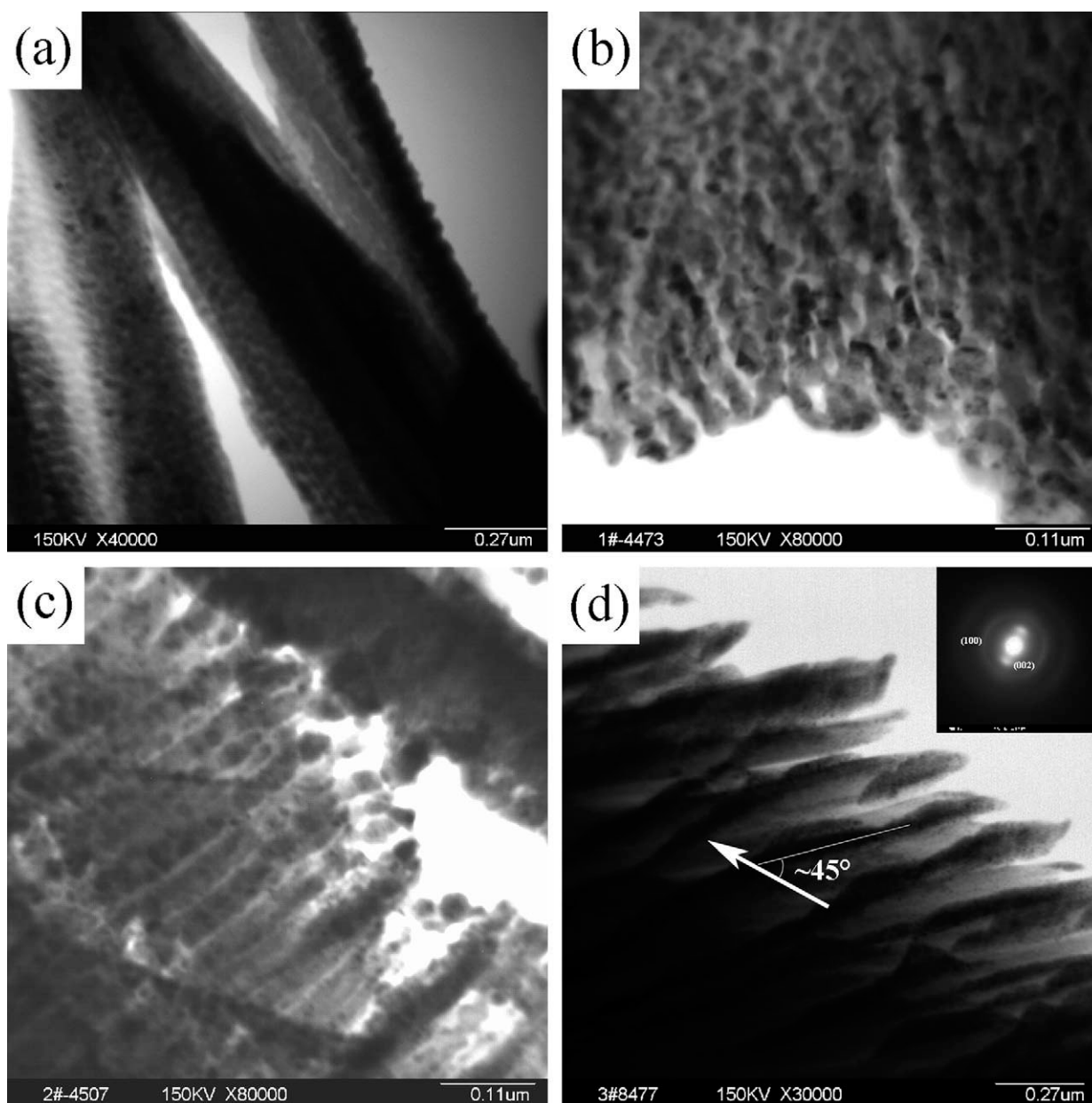


Figure 6 TEM images of lamellar structures in (a) PF, (b) OF4, (c) OF6, and (d) CF.

This result means that the interfibrils bond force gets stronger through the development of cyclization and crosslinking reactions with increasing temperature. Other technologies, like atomic force microscopy or scanning tunnel microscopy, need to find in our future work to study the fibrillar structure for high-temperature-treated oxidative stabilized fibers and carbon fibers.

Where does the fibrillar structure originated from? Fibrils have been found in both wet-spun and dry-spun PAN fibers.^{26–29} They originate from coagulation process and followed through stretching and collapsing.^{26,27} Similar morphology is typically for highly oriented polymers, e.g., polyethylene.³⁰ It is now generally accepted that fibrils in PAN precursor

fibers are consist of microfibrils, but different researchers give different sizes for them.^{15,26,29} Till now, it is the first time to report separated fibrillar structures in the oxidative stabilized fibers.

Lamellar structure

From Figure 5(a,b), lamellas of 10–20-nm thick are found inside the fibrils. More detail lamellar structures were characterized by TEM as shown in Figure 6. Figure 6(a) gives the TEM image of PAN fiber. The lamella thickness is about 20 nm, and the distance between the cores of neighbor layers is about 30–50 nm. It seems that the lamellas are not strictly perpendicular to the fiber axis, but have an

angle with it. Figure 6(b,c) shows the lamellar structure in OF4 and OF6. The orientation of the lamellas cannot be determined because the images are not from complete filaments or fibrils. The lamella thickness is about 25 nm and 35 nm, respectively. The similar lamellar structure is also found in CF, as shown in Figure 6(d). The interlayer distance is 50–200 nm, which is much larger than those in oxidative stabilized fibers and PAN fibers. Inset is the electron diffraction pattern of the carbon fiber, of which (002) represents graphite basal plane. From the direction of (002) diffraction arc, we can determine the direction of fiber axis marked by the white arrow in Figure 6(d). It can be seen that the lamellas in carbon fibers are not perpendicular to the fiber axis, but about 45° with it.

The results indicate that lamellar structures exist in the fibers throughout the production process of carbon fibers. With increasing temperature, the lamella thickness increases from 20 nm to 200 nm. Until now, there are no public reports on this change.

Crystal/amorphous structure

When compared with the fibril structure and the lamellar structure, crystal/amorphous structures have smaller size order. PAN fiber is a kind of semicrystal polymer. From the HRTEM image in Figure 7(a), these two phases are clearly identified. The lattice fringes represent the PAN crystal region and the point-like disorder matrix is the amorphous region. The stacking thickness and width of the lattice fringes are about 0.6–6 nm and tens of nanometers, respectively, in PF. During oxidative stabilization, the ordered crystal structure of PF is destroyed; as a result, entirely amorphous structure is formed in OF10 as shown in Figure 7(b). After carbonization, turbostratic graphite structure comes into being in CF, as shown in Figure 7(c). The L_c and L_a (the stacking thickness and width of the graphite layers) of the imperfect graphite crystallites are about 0.6–1.7 nm and 2.0–3.0 nm, respectively.

Relationships between the multiple-scale structures

As one filament is concerned, skin core structure is a kind of heterogeneity at the radial direction, fibril structure is a kind of orientation texture at the axial direction, and lamellar structure is within fibrils aligning by an angle with fiber axis. These three are in fact different kinds of morphologies or texture. By contrast, crystal/amorphous structure is the “real structure,” which reflects the long-range order or disorder arrangement of atoms.

As fibril structure and skin-core structure are considered together, we believe that the outside fibrils

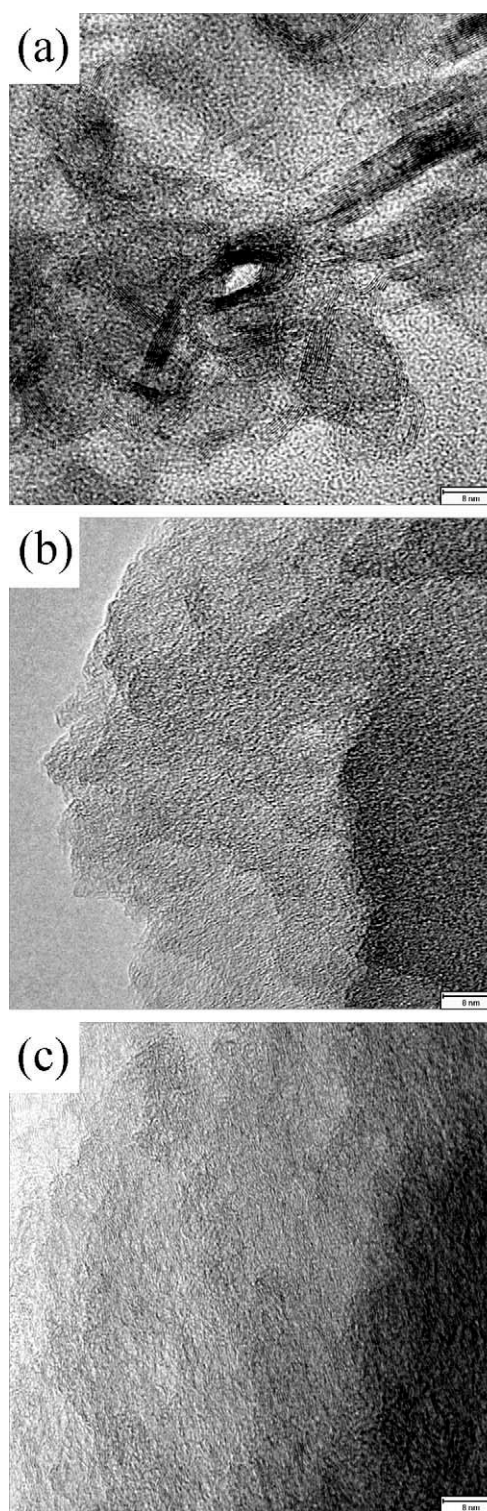


Figure 7 HRTEM images of crystal/amorphous structures in (a) PF, (b) OF10, and (c) CF.

are different with the inside ones in different aspects such as composition, crystallization, chemical structure, and orientation for different fibers.

Like other researchers, we have ever thought that lamellar structure is the alternate arrangement by crystal and amorphous region. The XRD patterns

(Fig. 3) prove that is wrong, because the oxidative stabilized fibers which are wholly amorphous also have lamellar structure. This indicates lamellar structure has little relations with crystal/amorphous structure. A lot of literature suggests that it probably due to stretching or drawing during the production process, because similar lamellar structure was also found by earlier investigators in drawn polymers under conditions of flow.^{31–33} In addition, because the lamellar structure is nearly perpendicular to the fiber axis, it is disadvantageous to the tensile strength of carbon fibers. Deeply investigations about the formation mechanism of fibrillar and lamellar structure and their effects on the mechanical properties of carbon fibers will be carried out in our future work.

CONCLUSIONS

Multiple-scale microstructures, including skin-core structure, fibrillar structure, lamellar structure and crystal/amorphous structure, are observed in not only PF but also OF and CF. On the one hand, strong structural heredity are demonstrated by the results; on the other hand, there are obvious differences which are summaries as followed.

1. The skin-core structure with thickness of about 4 μm is a kind of heterogeneity in composition and chemical structure along the radial direction of OF. The OM and SEM images indicate no such kind of structure in most of the PF and CF filaments.
2. Fibrils are successively separated from some oxidative stabilized fibers for the first time by ultrasonic etching in DMSO solution. The difficulty level of separation suggests a stronger bonding between fibrils with increasing temperature in OF and CF.
3. Lamellar structures are within fibrils. It evolves from PF to CF with increasing thickness. The direction of (002) diffraction arc and the direction of lamellae give the evidence that the lamellae structure in carbon fibers is not strictly perpendicular to the fiber axis, but have an angle of about 45° with it.
4. The crystallites in PF are destroyed, during oxidative stabilization, and new crystal structure, turbostratic graphite, forms in CF. The whole amorphous structure in OF give an indirect

evidence that lamellar structure is not consisted by such alternative alignment of crystal and amorphous regions as reported by many previous studies.

References

1. Chand, S. *J Mater Sci* 2000, 35, 1303.
2. Kobets, L. P.; Deev, I. S. *Compos Sci Technol* 1998, 57, 1571.
3. Walsh, P. J. in *ASM... ASM International: the United States of America*. 2001; Vol. 21.
4. Zhang, W. X.; Liu, J.; Wu, G. *Carbon* 2003, 41, 2805.
5. Liu, J.; Zhang, W. X. *J Appl Polym Sci* 2005, 97, 2047.
6. Ji, M. X.; Wang, C. G.; Bai, Y. J.; Yu, M. J.; Wang, Y. X. *Polym Bull* 2007, 59, 527.
7. Rahaman, M. S. A.; Ismail, A. F.; Mustafa, A. *Polym Degrad Stab* 2007, 92, 1421.
8. Dalton, S.; Heatley, F.; Budd, P. M. *Polymer* 1999, 40, 5531.
9. Bashir, Z. *Carbon* 1991, 29, 1081.
10. Perret, R.; Ruland, W. *J Appl Crystallogr* 1970, 3, 525.
11. Diefendorf, R. J.; Tokarsky, E. *Polym Eng Sci* 1975, 15, 150.
12. Barnett, F. R.; Norr, M. K. *Composites* 1976, 7, 93.
13. Bennett, S. E.; Johnson, D. J. *Carbon* 1979, 17, 25.
14. Ko, T. H.; Ting, H. Y.; Lin, C. H. *J Appl Polym Sci* 1988, 35, 863.
15. Warner, S. B.; Uhlmann, D. R.; Peebles, L. H. *J Mater Sci* 1979, 14, 1893.
16. Yu, M.; Wang, C.; Bai, Y.; Wang, Y.; Wang, Q.; Liu, H. *Polym Bull* 2006, 57, 525.
17. Yu, M.-J.; Wang, C.-G.; Bai, Y.-J.; Ji, M.-X.; Xu, Y. *Polym Bull* 2007, 58, 933.
18. Ge, H.; Liu, H.; Chen, J.; Wang, C. *J Appl Polym Sci* 2008, 108, 947.
19. Bennett, S. C.; Johnson, D. J. *Carbon* 1979, 17, 25.
20. Yu, M.-J.; Bai, Y.-J.; Wang, C.-G.; Xu, Y.; Guo, P.-Z. *Mater Lett* 2007, 61, 2292.
21. Jain, M. K.; Balasubramanian, M.; Desai, P.; Abhiraman, A. S. *J Mater Sci* 1987, 22, 301.
22. Jiang, H.; Wu, C.; Zhang, A.; Yang, P. *Compos Sci Technol* 1987, 29, 33.
23. Watt, W.; Johnson, W. *Nature* 1975, 257, 210.
24. Ko, T.-H.; Ting, H.-Y.; Lin, C.-H.; Chen, J.-C. *J Appl Polym Sci* 1988, 35, 863.
25. Yu, M. J.; Wang, C. G.; Bai, Y. J.; Xu, Y.; Zhu, B. *J Appl Polym Sci* 2008, 107, 1939.
26. Wang, Q.; Wang, C.; Bai, Y.; Yu, M.; Wang, Y.; Zhu, B.; Jing, M.; Ma, J.; Hu, X.; Zhao, Y.; Zhang, M. *J Polym Sci Part B: Polym Phys* 2010, 48, 617.
27. Craig, J. P.; Knudsen, J. P.; Holland, V. F. *Text Res J* 1962, 32, 435.
28. Dobretsov, S. L.; Lomonosova, N. V.; Stelmakh, V. P.; Frenkel, S. Y. *Polym Sci USSR* 1972, 14, 1278.
29. Tucker, P.; George, W. *Polym Eng Sci* 1972, 12, 364.
30. Sheiko, S. S.; Moller, M.; Cantow, H. J.; Magonov, S. N. *Polym Bull* 1993, 31, 693.
31. Bezruk, L. I.; Lipatov, Y. S. *J Polym Sci Part C: Polym Symp* 1972, 38, 337.
32. Steidl, J.; Pelzbauer, Z. *J Polym Sci Part C: Polym Symp* 1972, 38, 345.
33. Dees, J. R.; Spruiell, J. E. *J Appl Polym Sci* 1974, 18, 1053.