Journal of
MATERIALS RESEARCH

Scanning tunneling microscope study of polyacrylonitrile-based carbon fibers

Dongxia Shi, Ning Liu, Haiqiang Yang, Juning Gao, Yueshan Jiang, and Shijin Pang
Beijing Laboratory of Vacuum Physics, Center for Condensed Matter Physics, Chinese Academy of Sciences, P.O. Box 2724, Beijing 100080, China

Xubiao Wu and Zhen Ji
University of Science and Technology Beijing, Beijing 100083, China

(Received 12 February 1996; accepted 30 April 1997)

Scanning tunneling microscopy (STM) was used to characterize the surface topography of polyacrylonitrile (PAN)-based carbon fibers before and after electrochemical treatment, stretch resistance test, and high-temperature treatment. A new kind of spiral structures was found, which was not only on the surface but also in the inner layer. The spiral structure of the fibers was caused by the spinning process. The fiber structure contained the shape of the precursor. There were some large cracks in the carbon fibers after the stretching resistance test. The large cracks can result in carbon fiber breaking under certain stress conditions. The difference in the structures of the carbon fibers before and after the high-temperature treatment was determined.

I. INTRODUCTION

Carbon fiber composites have been extensively used in industry such as aerospace, astronautical, and sporting goods because of low density, high strength and modulus, and superior strength-to-weight properties.[1] PAN-based carbon fibers are produced from polyacrylonitrile (PAN) which are more resistant to the compressive forces applied in flexure than liquid crystal-based materials such as carbon fibers from pitches or lyotropic polymers. In the past years the PAN-based carbon fibers have received much attention and have maintained their predominance as a reinforcing material. Many analytical methods have been employed to investigate the structure of the carbon fibers, such as x-ray diffraction (XRD) techniques,[2,3] scanning electron microscopy (SEM), transmission electron microscopy (TEM),[4] high-resolution electron-microscopy (HREM),[5,6] and polarized-light microscopy.[3,7] Except HREM, other analytical methods can investigate the structure of carbon fibers only on a micron scale. Although HREM can investigate the structure on a submicron scale, the sample preparation is generally sophisticated and the obtained images are not in real space. However, scanning tunneling microscopy (STM) can image the surface structure of carbon fibers down to the nanometer scale and in real space.[8–11] Sample preparation is easy and the sample can be observed nondestructively in air.

In this paper, STM was used to analyze the fiber surface structures and morphology before and after electrochemical treatment, strength resistance test, and high-temperature treatment.

II. EXPERIMENTAL

To prepare the samples, one bundle of 1K fibers was cut into four parts. The first part without treatment was directly observed with STM, the second part was for electrochemical treatment, the third part for a strength resistance test, and the last part for high-temperature treatment. The electrochemical treatment of the fibers was in 2 mol/ml NaOH solution for 2 min with starting etching current 60 μA. In the strength resistance test, the force added to the two ends of the 1K fibers was 30 N. In high-temperature treatment, the fibers were heated at 1600 °C for 15 min. The fibers after each of the above treatments were observed separately with STM.

The STM experiments were carried out with CSPM930a instrument in air at room temperature. Electrochemical-etched tungsten tips with apex radii $<$ 100 nm were employed for the STM studies. The tunneling current was between -2.0 nA and -3.0 nA, and the bias voltage was 100–300 mV. All STM images were obtained in constant current mode.

III. RESULTS AND DISCUSSION

The carbon fiber structures, similar to other carbon materials, depend on both their precursor and production. A schematic diagram of PAN-based carbon fibers is shown in Fig. 1.[12]

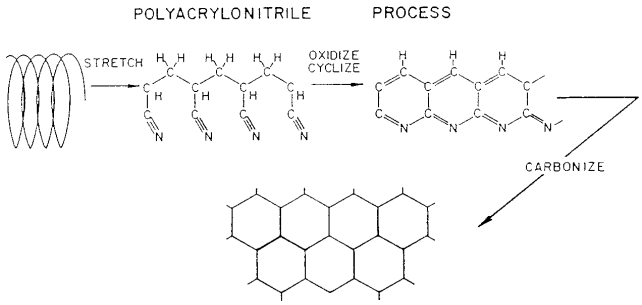


FIG. 1. Polyacrylonitrile precursor of carbon fibers. Remnants of the preferred orientation of the ladder polymer are retained in the carbon fibers.

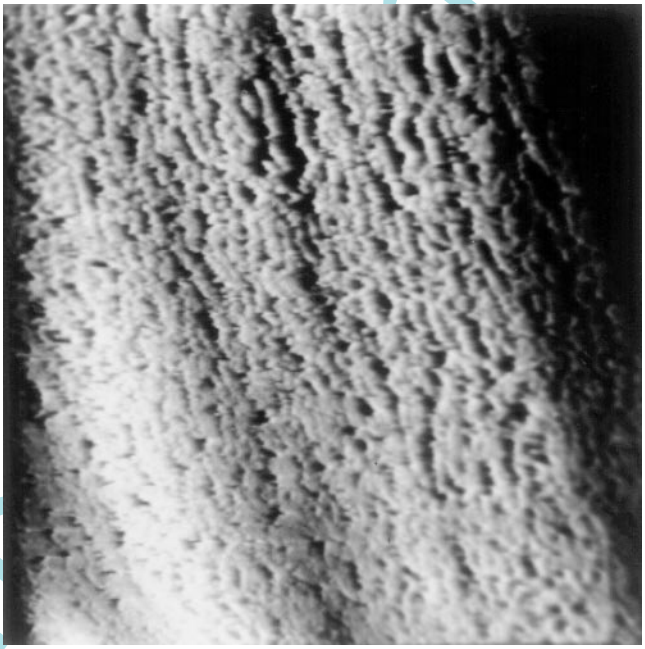
The fibers are kept under tension to maintain the alignment of the PAN polymer during oxidation. The precursor has an oriented cyclic or ladder structure after the stabilization stage. The hexagonal ribbons of carbon atoms tend toward aligning with the fiber axial during the carbonized stage. In the last heat treatment of carbon fibers, the heated temperature depends on the properties that are desired.[8] The PAN-based fibers are high tensile strength fibers with lower modulus. The last carbonized temperature is about 1000 °C.

Figure 2 shows a typical STM image obtained from untreated fibers on a large scale. The scanning region of Fig. 2 is 1200 nm × 1200 nm. From the image, it is found that the carbon fiber surface is composed of different wide ribbons that are almost along the fiber axis. These ribbons have longitudinal ridges.

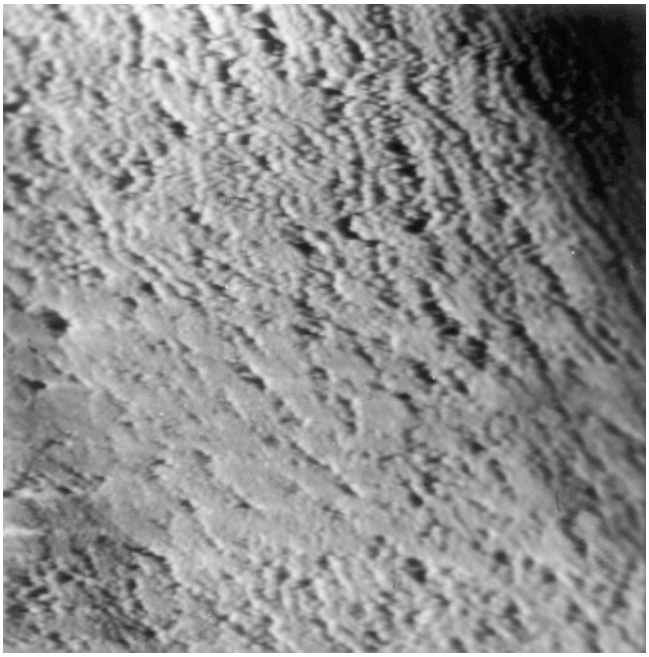
FIG. 2. STM image of PAN-based carbon fibers without treatment on submicron scale. (1200 nm × 1200 nm)

We zoomed in Fig. 2; the images are shown in Fig. 3. It is seen that the fiber surface is rough, and the ribbons are composed of small crystallized grains. The scale in Fig. 3(a) is 500 nm × 500 nm; the scale in Fig. 3(b) is 200 nm × 200 nm.

A new kind of interesting fiber structure without treatment is shown in Fig. 4. The scanning area of Fig. 4(a) is 500 nm × 500 nm. It can be observed that

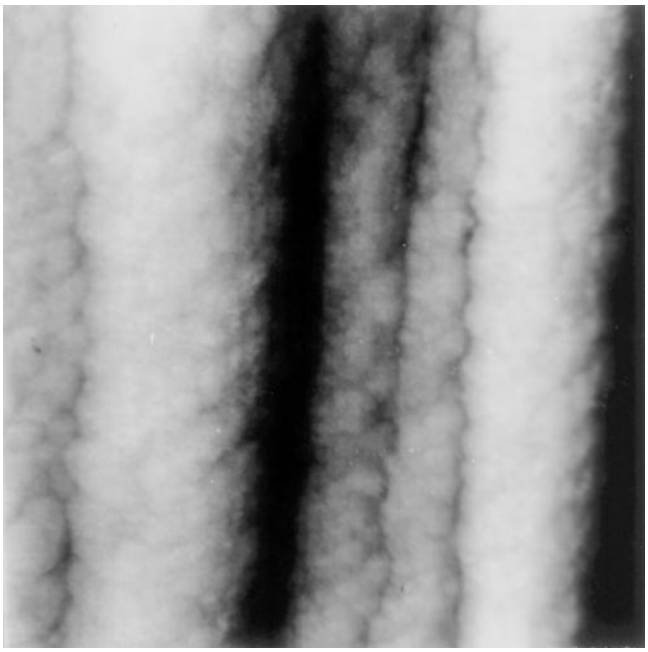


(a)

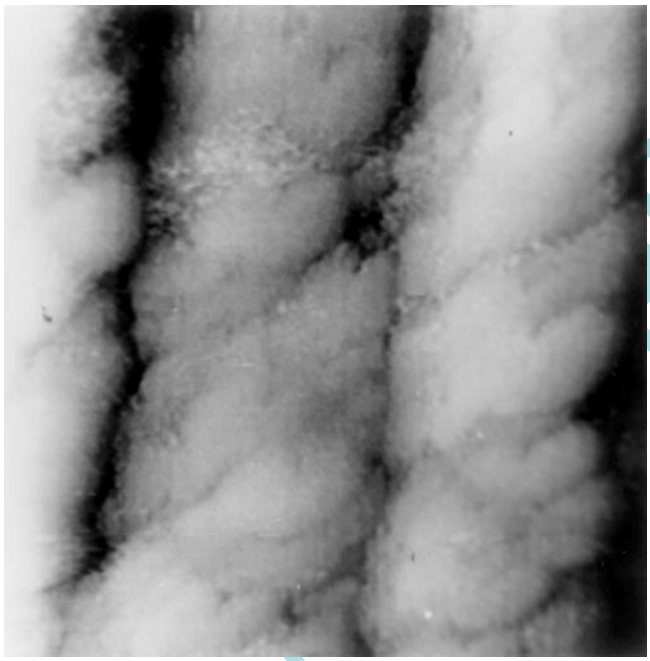


(b)

FIG. 3. STM images of PAN-based carbon fibers without treatment on nanometer scale. (a) 500 nm × 500 nm and (b) 200 nm × 200 nm.



(a)



(b)

FIG. 4. STM images of a new kind of fiber structures without treatment. (a) 500 nm × 500 nm and (b) 200 nm × 200 nm.

these ribbons have a spiral trending structure along the axial. To understand the details clearly, we zoomed in the ribbons in Fig. 4(a). The image is shown in Fig. 4(b) with the scale of 200 nm × 200 nm. It is clearly seen that each of the three ribbons has a right-spiral structure.

Figure 5 shows a typical STM image of the carbon fibers after electrochemical treatment. The etching layer thickness of one fiber was about 10 nm. Electrochemical

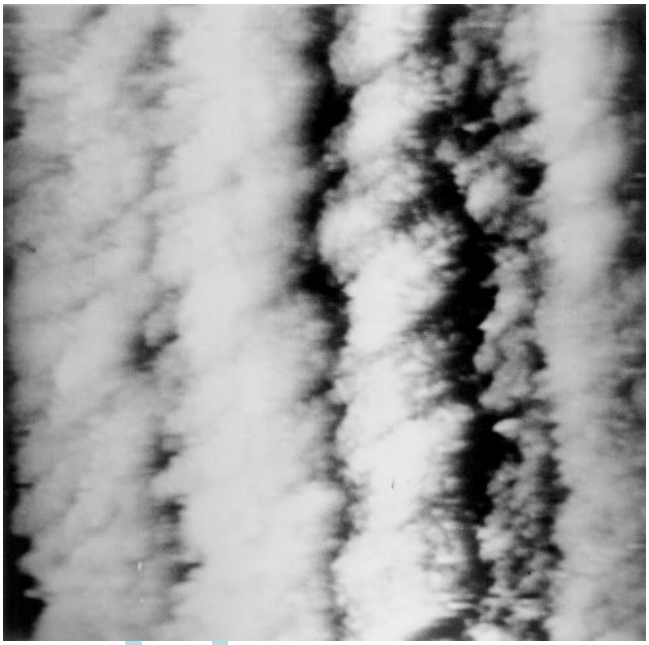


FIG. 5. STM image of PAN-based carbon fibers after electrochemical treatment. (225 nm × 225 nm)

treatment stripped the outer layer, exposing the layers in the core of the fibers. The scanning area of Fig. 5 is 225 nm × 225 nm. It is found that the right-spiral ribbon structures also exist after electrochemical treatment. So this kind of spiral structures is not only on the surface but also in the inner layer.

The spiral structures can be explained by the Diefendorf model. According to Diefendorf, the rippled ribbon can describe the PAN-based carbon fibers of lower modulus.[12] Figure 6 is a sectional, schematic diagram of the Diefendorf model. All ribbons are spiral in the diagram. Some are right spiral and others are left spiral. The precursor of PAN-based carbon fibers is spun from polyacrylonitrile polymer, with the spinning process influencing its shape. The precursor arranges as a sine wave. The wavelength of the sine wave increases and amplitude decreases in the carbonization process. Finally the rippled ribbon can be formed. These ribbons wind around each other, becoming more compact. The wound ribbon structures greatly increase the tensile strength of the carbon fibers. All ribbons in the STM images are right spiral, but not all ribbons wind around each other, which is different from the diagram of the Diefendorf model. This is probably because these STM images are of the fiber surface, and not of the fiber section. It can be said that the observed surface structures of the spiral ribbons coincide with the Diefendorf model. This kind of spiral structures was not observed in all the cases. It appeared only if the carbon fibers were observed in a suitable direction.

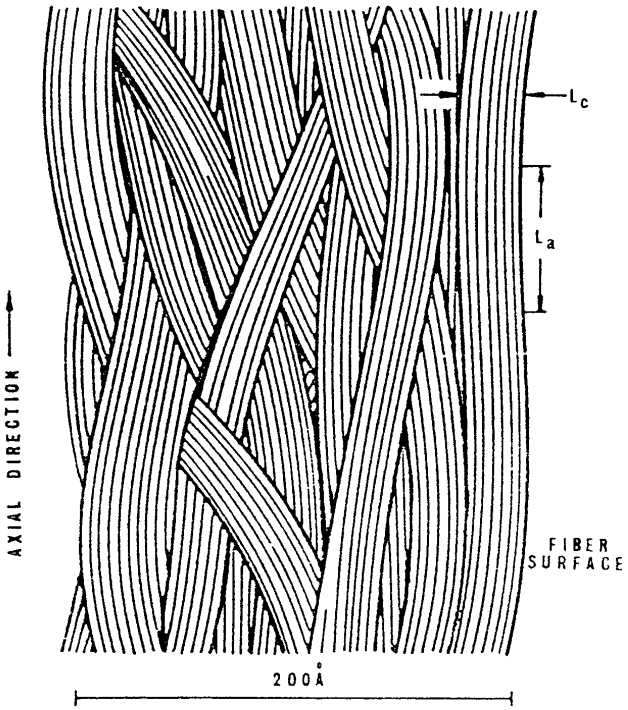


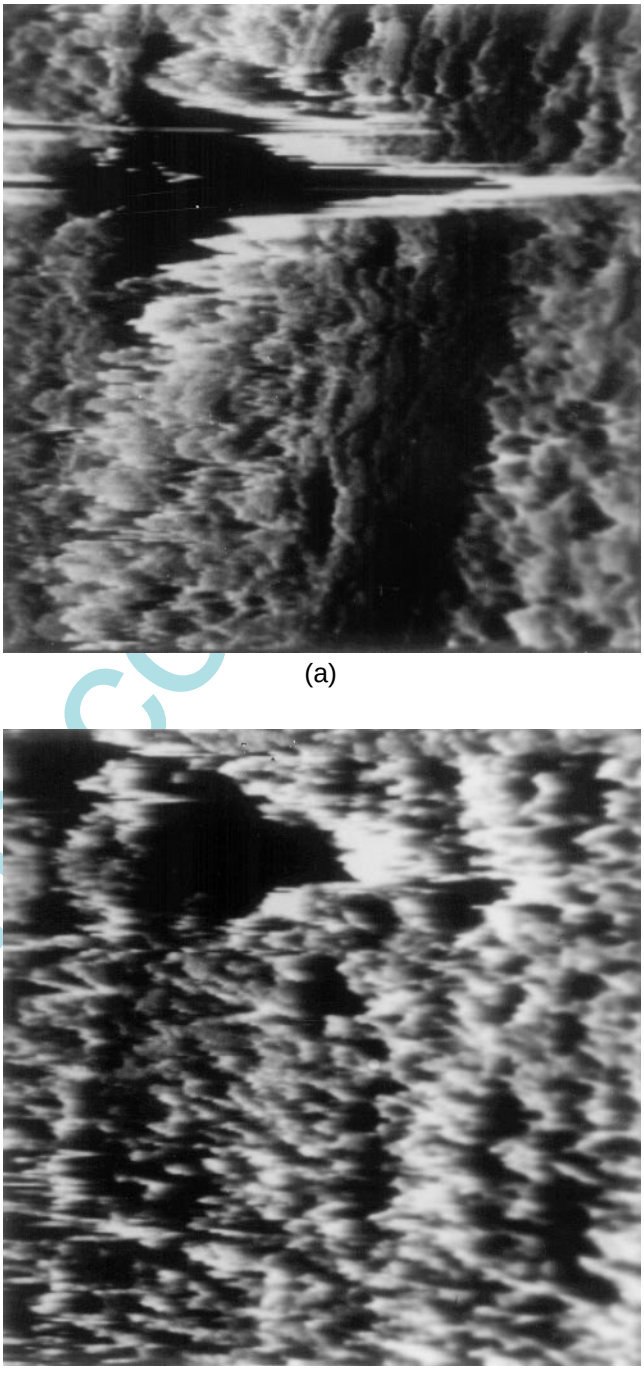
FIG. 6. Schematic diagram of ribbon structure model for carbon fibers.

STM images of the fibers after the strength resistance test are shown in Fig. 7. The scanning area is 200 nm × 200 nm. It can be observed that fibers after the strength resistance test contain some large cracks, which are not observed in fibers before the test [Fig. 3(b)] on the same scale.

From the images of Fig. 7, it can be seen that the crack in Fig. 7(a) is different from the crack in Fig. 7(b). The crack in Fig. 7(a) is wedge-shaped, the explanation being that the small crack on the fiber surface expanded along the direction perpendicular to the surface when the fiber was under stress, thus generating a wedge crack. Otherwise, the crack in Fig. 7(b) is circular, and the edge around the crack is rougher than that shown in Fig. 7(a). All these large cracks were the result of the small cracks expanding under a stress in the fibers.

The major limitation of tensile strength is gross flaws or defects.[13] Defects are small cracks in fibers, which act as stress concentrators. They expand or enlarge under stress. When the grown cracks are large enough and have an excess of stress over a specified range, the carbon fibers will break.

The structure change of the carbon fibers was also observed after high-temperature treatment. Figure 8 is an STM image, scanning area, 500 nm × 500 nm. Compared with fibers before treatment [Fig. 3(a)], it is clearly observed that the surface of the fibers is smoother after high-temperature treatment. It can also be seen that the



(a)

(b)

FIG. 7. STM images of PAN-based carbon fibers after strength resistance test. (a) 200 nm × 200 nm, wedge crack, and (b) 200 nm × 200 nm, circular crack.

grains grow large after high-temperature treatment, and the grains arrange more regularly in a certain direction.

In this study, the low modulus PAN-based carbon fibers without the graphitization have no regular three-dimensional arrangement. The structures are turbostratic in organization. The carbonized temperature of PAN-

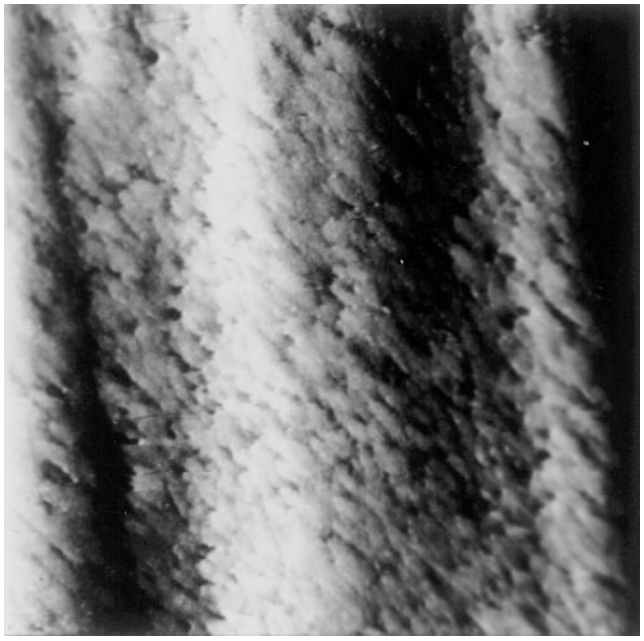


FIG. 8. STM image of carbon fibers after high-temperature treatment. (500 nm × 500 nm)

based carbon fibers is about 1000 °C. When the high temperature of treatment is 1600 °C, the grain will grow and the structure will become more regular than before the treatment. Otherwise the tensile strength will decrease.

IV. CONCLUSIONS

Investigation of the high-strength PAN-based carbon fibers on both submicron scale and nanometer scale has been carried out before and after electrochemical etching, stretch resistance test, and high-temperature treatment. The following conclusion can be drawn. On the micron scale, the surface of the carbon fibers was composed of ribbons along the fiber axis; on the nanometer scale, the surface became rough. There was a new kind of spiral structure, and the spiral structure was also observed after electrochemical treatment. The results indicate that the nanotopography of carbon fibers depends on the spinning procedure. There were some larger cracks on the fiber surface after the strength resistance test. This was the result of expansion of the small cracks in the fibers. The small cracks and the rough edge would allow the fibers to break. The fiber surface became smoother. The crystalline grain grew larger and arranged regularly in a fixed direction after high-temperature treatment.

ACKNOWLEDGMENTS

The authors are very grateful to Yuan Lei, Zengquan Xue, and Hongjun Gao for their support in sample preparation and result analyses.

REFERENCES

1. R. J. Smelly and W. N. Delgass, J. Mater. Sci. **28**, 3601 (1993).
2. M. Guigon, A. Oberlin, and G. Desarmot, Fiber Sci. Technol. **20**, 565 (1984).
3. M. Endo, J. Mater. Sci. **23**, 598 (1988).
4. G. M. Pennock and E. O. Gara, J. Mater. Sci. Lett. **9**, 847 (1990).
5. D. Crawford and D. J. Johnson, J. Microscopy **94**, 51 (1971).
6. D. L. Vezie, J. Mater. Sci. Lett. **9**, 883 (1990).
7. D. J. Johnson, Chem. Indust. **22**, 692 (1982).
8. G. Krekel and K. J. Huttinger, J. Mater. Sci. **29**, 2968 (1994).
9. W. P. Hoffman, W. C. Hurley, P. M. Liu, and T. W. Owens, J. Mater. Res. **6**, 1685 (1991).
10. J. B. Donnet and R. Y. Qin, Carbon **30**, 787 (1992).
11. P. A. Zhdan, D. Grey, and J. E. Casatle, Surf. Interface Analyses **22**, 290 (1994).
12. R. J. Diefendorf and E. Tokarsky, Polym. Eng. Sci. **15**, 150 (1975).
13. D. J. Johnson, J. Phys. D: Appl. Phys. **20**, 286 (1987).