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Carbon Fiber Surfaces Studied by STM

The STM has been applied to the surface study of various carbon fibers, thermally treated from carbonization to graphitization. The results showed that at large scales, some common features were always observed. These features are characterized by the ribbons along the fiber axis, the smaller fibriform crystallite stackings and the discontinuous boundaries. At atomic resolution, the results have shown that even at carbonization temperature, the carbon fiber exhibits a high degree of organization which is enhanced by the graphitization in a very short time. In addition, the surface heterogeneity has been directly observed, and at least, three kinds of graphitic organizations have been imagined and they are presented and discussed.

Introduction

The STM was first applied to the study of the surfaces of carbon fibers in 1988 [1], since then, only few papers have appeared in the literature [2-5]. This may be due to the experimental difficulties associated with the nature of carbon fibers (flexible and very fine diameter). But since the surface properties of carbon fibers are far from being understood and they are so important to the fiber-matrix composite materials, it is necessary to use modern techniques like STM to study systematically the carbon fiber surfaces and the possible changes induced either by thermal treatment, or by fiber precursor or by surface treatment on a nanometer scale. This report is concerning the first objective.

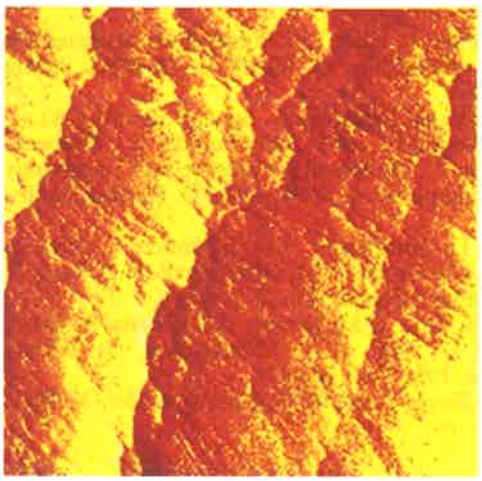

FIGURE 1a. - *Fiber A, 500*500 nm².*

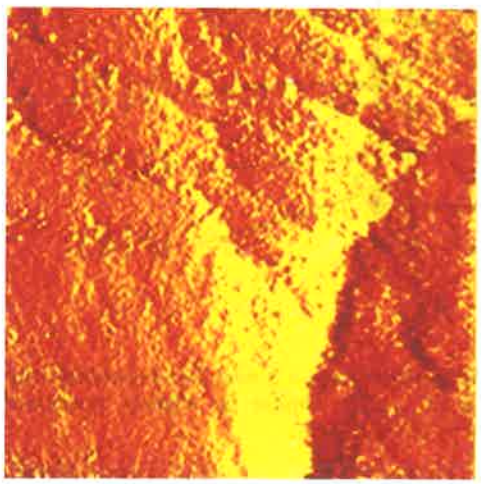

FIGURE 1b. - *Fiber A, 100*100 nm².*

FIGURE 1c. - *Fiber B, 500*500 nm².*

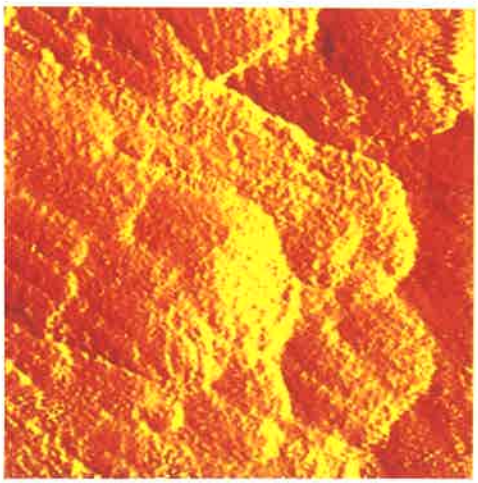

FIGURE 1d. - *Fiber B, 100*100 nm².*

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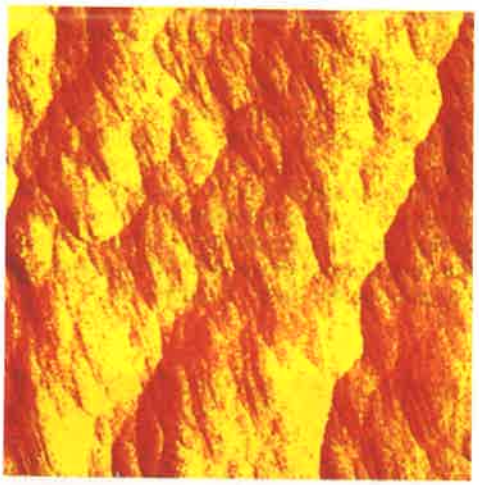

FIGURE 1e. - *Fiber C, 400*400 nm².*

FIGURE 1f. - *Fiber C, 100*100 nm².*

FIGURE 1g. - *Fiber D, 500*500 nm².*

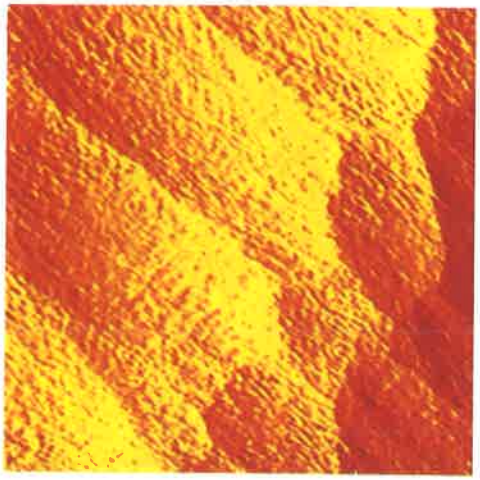

FIGURE 1h. - *Fiber D, 200*200 nm².*

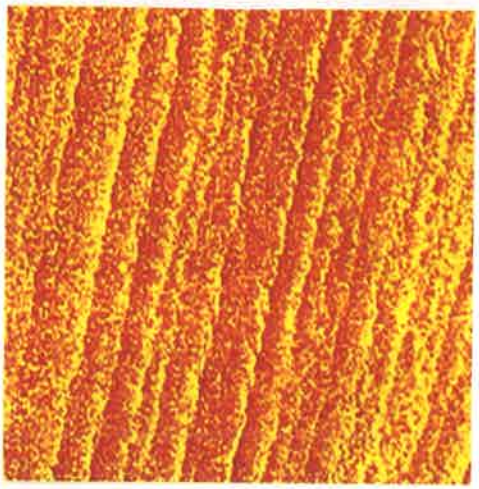

FIGURE 1i. - *Fiber E, 3000*3000 nm².*

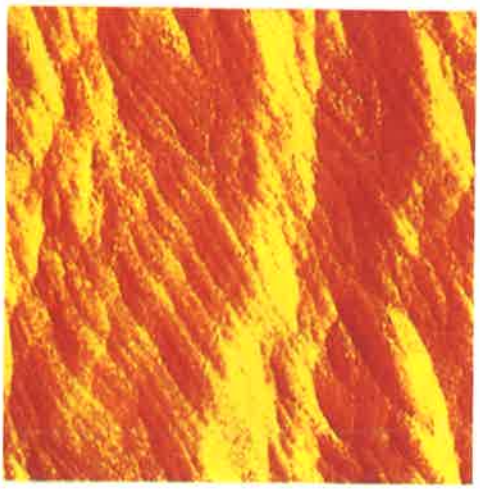

FIGURE 1j. - *Fiber E, 300*300 nm².*

Experimental

The samples marked A, B, C, D and E are all virgin carbon fibers prepared from the same precursor (petroleum mesophase pitch fiber) but submitted to thermal treatments ranging from carbonization to graphitization temperatures. The experiments were carried out with Nanoscope II (Digital Instruments Inc., Santa Barbara, Cal./USA) at ambient conditions. The principal parameters are : the setpoint current 1.0 ~ 2.0 nA and the bias voltage 10 ~ 100 mV. All images were captured in constant current mode.

Results and Discussions

Figure 1 shows the images obtained at large scales and *figures 2 ~ 4* present some atomic resolution images. From *figures 1a ~ j*, we can find that regardless of the fibers examined, the carbon fiber surfaces are composed of ribbons along the fiber axis. These ribbons are again constituted of the smaller fibriform crystallites stacked nearly perpendicularly to the fiber axis, sometimes at an angle less than perpendicular (see *figures 1f and j*). The discontinuous boundaries could always be observed parallel to the rib-

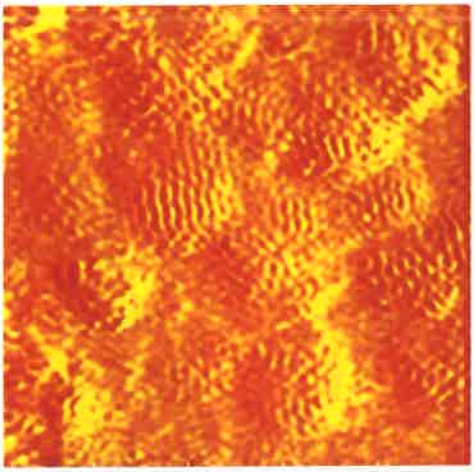

FIGURE 2a. - *Fiber A, 10*10 nm².*

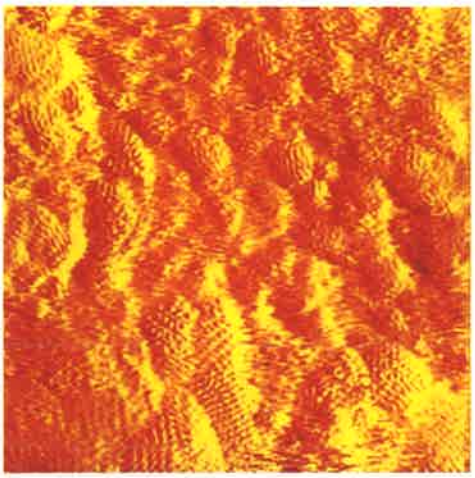

FIGURE 2b. - *Fiber C, 20*20 nm².*

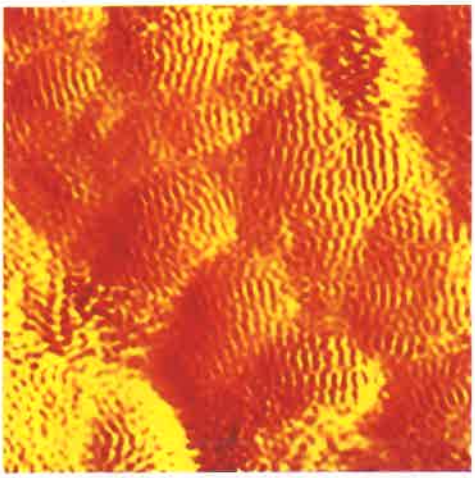

FIGURE 2c. - *Fiber E, 10*10 nm².*

bons (fiber axis). These surface features may be due to the mesophase pitch spinning process. The extruding shear force, the spinneret structure and the filament speed are the most probable factors. *Figure 1i* is the microscopic picture, showing the extruding lines along the fiber axis, which is in good agreement with the results obtained by the classic scanning electron microscopy, the only difference being that the former exhibits some "flattening effect" because of the image mode used.

At the atomic resolution, more detailed informations can be obtained, first the surface heterogeneity. At least three kinds of graphitic organisations have been observed : the modular micro-texture *(figures 2a ~ c)* which constitutes the greater part of the surface examined : the "step-like" micro-texture *(figures 3a ~ c)* and the graphenes *(figures 4a ~ b)*. From *figure 2* and *3*, it can be seen that the organised patches have been developped considerably from carbonized fiber to graphitized fiber. The two images in *figure 4* indicate that even at carbonization temperature, the carbon fiber exhibits already a high degree of organisation which is enhanced by the graphitization in few minutes. The measurement of the structural parameters of Fiber E *(figure 4b)* shows that they are very close to those of HOPG (perfect graphite), which is not the case for the Fiber A *(figure 4a)*.

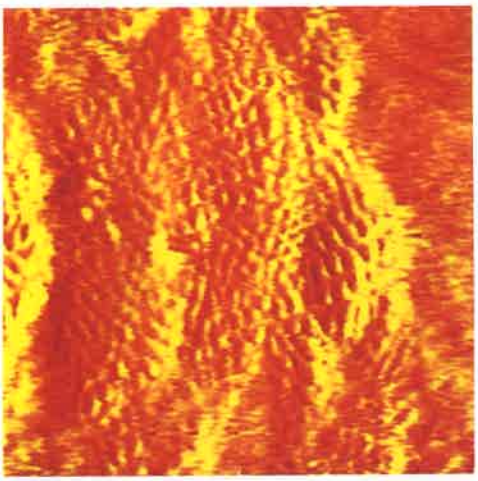

FIGURE 3a. - *Fiber B, 10*10 nm².*

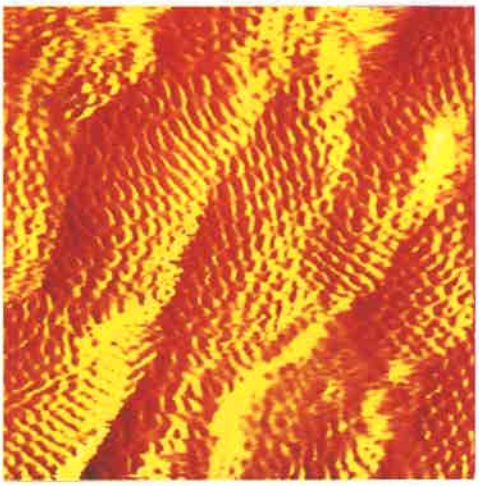

FIGURE 3b. - *Fiber C, 10*10 nm².*

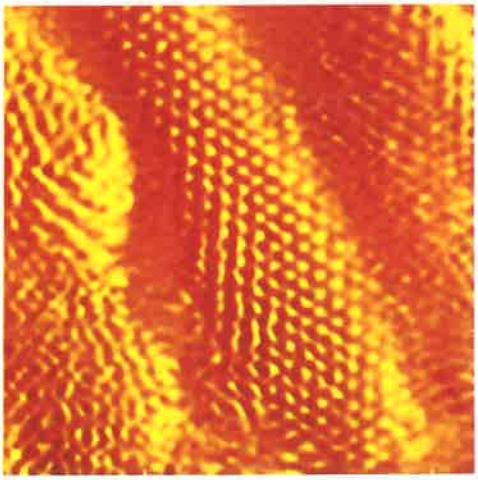

FIGURE 3c. - *Fiber E, 6.4*6.4 nm².*

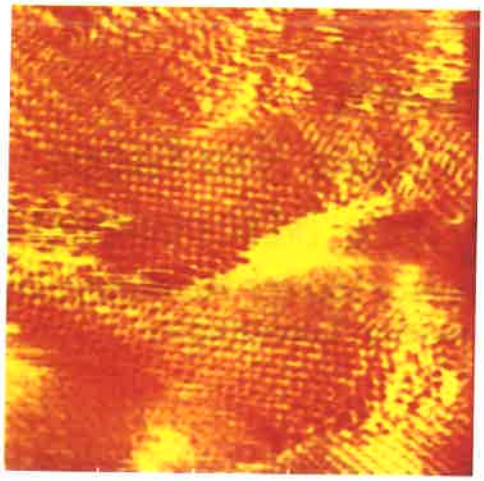

FIGURE 4a. - *Fiber A, 10*10 nm².*

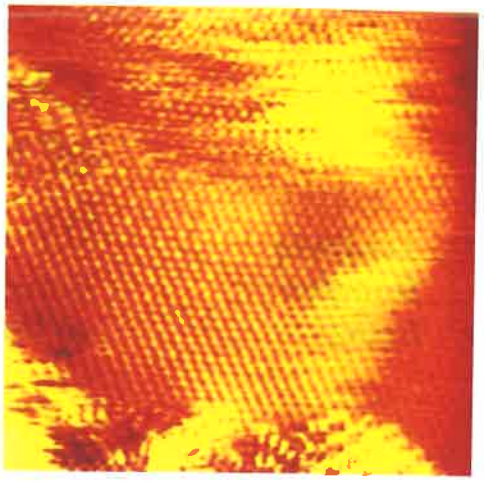

FIGURE 4b. - *Fiber E, 10*10 nm².*

References

[1] W.P. Hoffman, V.B. Elings and J.A. Gurley, *Carbon*, **1988**, *26*, 754.
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[4] W.P. Hoffman, W.C. Hurley, P.M. Liu and T.W. Owens, Carbon '90, Paris, **1990**, 166.
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