

# A Comparative Study of Pyrocarbon Microstructure by Atomic Force, Transmission Electron and Polarized Light Microscopy

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## Abstract

Carbon-carbon composites are of great technological as well as scientific interest, and there is a need for a more detailed understanding of their microstructure and its implications on the resulting mechanical properties. However, when studying carbon-carbon composites with transmission electron microscopy (TEM), the interpretation of the obtained data is not clear mainly due to possible effects of sample preparation on TEM image contrast.

To study this question, we have investigated the influence of topography and heterogeneous etching behavior of different carbon microstructures due to TEM sample preparation on the resulting TEM image data. In our experiments, the pyrocarbon matrix within composites obtained by chemical vapor infiltration of carbon fiber felts was comparatively studied by atomic force microscopy (AFM), transmission electron microscopy and polarized light microscopy (PLM). The influence of mechanical polishing and ion etching on pyrocarbon with different textures is investigated. The AFM surface topography of the ion etched samples is compared with TEM image amplitude contrast and corresponding electron diffraction patterns as well as with polarized light microscopy. It is shown that the roughness value  $R_q$  and height differences extracted from AFM cross sections are correlated with amplitude contrast variations, radial broadening of the carbon 001 reflections and extinction angles.

*Keywords:* A. carbon/carbon composites; B. chemical vapor infiltration, grinding; C. atomic force microscopy, transmission electron microscopy

## 1. INTRODUCTION

Carbon-carbon (C-C) composites composed of carbon fibers embedded in a pyrolytic carbon matrix offer a unique combination of high temperature stability, wear and corrosion resistance. A thorough knowledge of the microstructure of the pyrolytic carbon matrix is essential for the understanding of their microscopic and macroscopic mechanical, adhesive and tribological properties.

Transmission Electron Microscopy (TEM) is a frequently applied tool for the investigation of pyrolytic carbon and carbon/carbon composites. However, the relationship between surface topography induced by mechanical polishing or ion milling, which are frequently applied processes for the TEM study and preparation of C-C composites, and the degree of texture has not been reported previously. This information is important for the

understanding of the interplay between mass-thickness and Bragg contrast observed by TEM.

Atomic force microscopy is a tool that allows to obtain a spatially resolved contrast between materials that exhibit different mechanical properties which has been demonstrated on carbon infiltrated carbon fiber bundles [1].

To reach these goals, a carbon felt with a matrix that contains pyrolytic carbon with three different textures obtained by chemical vapor infiltration (CVI) was comparatively studied by atomic force microscopy (AFM), transmission electron microscopy (TEM) and polarized light microscopy (PLM).

## 2. EXPERIMENTAL

The infiltration procedure of the polyacrylonitrile based fibers with pyrolytic carbon is described elsewhere [2]. In order to characterize the optical anisotropy, the extinction angle  $A_e$  was measured by polarized light microscopy according to a procedure described elsewhere [3]. The arising optical textures with a progressive degree of anisotropy are defined as low textured (LT,  $4^\circ \leq A_e < 12^\circ$ ), medium textured (MT,  $12^\circ \leq A_e < 18^\circ$ ) and highly textured pyrolytic carbon (HT,  $A_e \geq 18^\circ$ ) [4].

For TEM studies, a double-sided dimpling (Dimple Grinder, Gatan) was applied using  $3 \mu\text{m}$  and  $0.25 \mu\text{m}$  diamond pastes. Two argon ion guns (PIPS, Gatan) operating at 4 kV and a current of 12 mA at an angle of 4 degrees relative to the sample surface were operated for 30 min.

TEM was carried out in a LEO EM 912 Omega transmission electron microscope at an electron energy of 120 keV. Zero-loss filtered selected-area electron diffraction patterns were acquired to quantify the degree of texture [4].

The AFM measurements were performed with a commercial AFM (Autoprobe CP, Park Scientific Instruments) at room temperature and in air. The images were taken in the contact mode of the AFM in the repulsive force regime with a total normal force in the range of  $0.4 - 1.0 \cdot 10^{-7} \text{ N}$  including capillary forces.

## 3. RESULTS AND DISCUSSIONS

Fig. 1a is a low-magnification negative TEM image showing LT, MT and HT pyrolytic carbon layers which exhibit different contrast. The inserted zero-loss filtered selected-area electron diffraction patterns clearly illustrate

the variation of the preferential orientation of carbon layers with respect to the fiber surface. The corresponding orientation angles derived from selected-area electron diffraction are  $90^\circ$  for LT,  $70^\circ$  for MT and  $27^\circ$  for HT pyrolytic carbon, respectively.

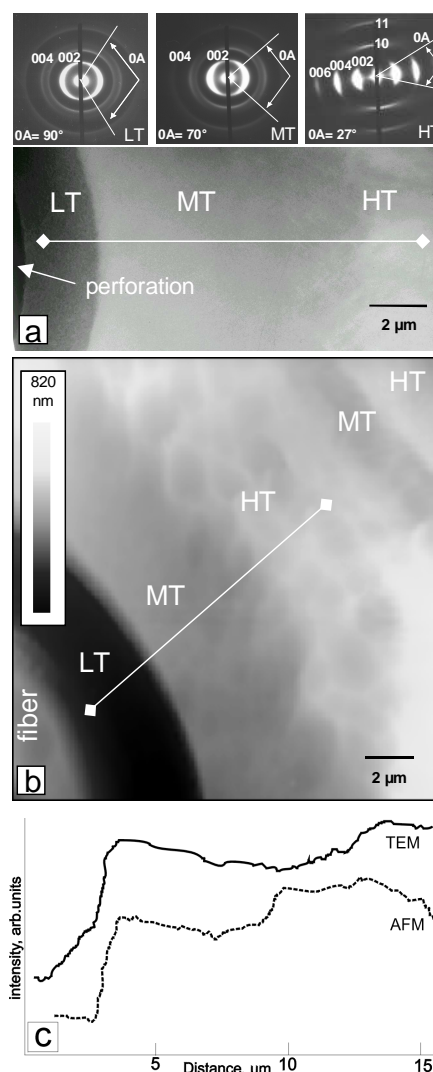


Fig. 1. Negative TEM image (a) and AFM topography (b) of an ion milled thin foil of an infiltrated carbon fiber felt. Linescans (c) of the TEM brightness along the white line in (a) and of AFM topography along the white line in (b). Insets in (a): selected area electron diffraction patterns together with the corresponding orientation angles (accuracy  $\pm 5^\circ$ ). The small white arrow in (a) marks the former position of the fiber. Note the similar contrast variation in (a) and (b).

Figure 1b shows the same TEM sample also imaged by AFM. The sequence and thickness of the imaged pyrolytic carbon layers are in good agreement with the results obtained by PLM and TEM.

The strong variation of the surface height levels after

ion milling (Table I) can be explained by the different rates at which HT, MT and LT pyrolytic carbon are thinned. The sequence of increasing surface height after ion milling: LT < Fiber < MT < HT corresponds to the expected sequence of increasing mass density [5]. However, before ion milling the sequence of increasing surface height is MT < LT < HT < Fiber. This might be due to different mechanical properties of the pyrolytic carbon microstructures, resulting in different abrasion rates during the grinding process.

Pyrocarbon texture	Low textured (LT)	Medium textured (MT)	High textured (HT)
<b>Atomic force microscopy</b>			
Height relative to fiber			
before ion milling	-45 nm	-58 nm	-30 nm
after ion milling	-264 nm	153 nm	287 nm
RMS roughness			
before ion milling	2.1 nm	1.7 nm	3.2 nm
after ion milling	4.3 nm	2.5 nm	10.3 nm
<b>Selected-area electron diffraction</b>			
Orientation angle	90°	70°	27°
<b>Polarized light microscopy</b>			
Extinction angle	<4°	12-18°	>18°

Table I. RMS roughness, layer height measured relative to the fiber level, orientation angle obtained from selected-area electron diffraction patterns and extinction angle  $A_e$  obtained from polarized light microscopy of the different pyrolytic carbons. (experimental error: orientation angle 5°, surface height 30% and RMS roughness 20%, respectively).

The roughness as determined from the AFM topographic images is also modified by ion milling. The HT material exhibited the highest RMS roughness. Significantly smoother surfaces are found for MT and LT pyrolytic carbon, the lowest surface roughness being observed for MT material.

The information about the surface height levels provided by AFM should be taken into account to interpret the TEM contrast of the differently textured layers shown in Fig. 1a. Two contributions based on elastic electron scattering can be distinguished: mass-thickness and Bragg-diffraction contrast. Even at the same sample thickness, Bragg-diffraction and mass-thickness contrast must be expected to contribute both to the contrast of differently textured pyrolytic carbon due to the different degree of crystallinity. With increasing sample thickness, inelastic scattering processes play an increasing role. The surface level profiles obtained by AFM after ion milling show that large thickness variations occur after TEM sample preparation for layers with different textures which may be as large as 1  $\mu\text{m}$  (see Table I: variation of height levels times

a factor 2 because the ion milling for TEM samples is performed from both sides). Therefore, it can be concluded that the TEM intensity variations are dominated by the large relative variation of the sample thickness in differently textured layers. This is compatible with the intensity scan of the negative TEM image displayed in Fig. 1c where a low electron density is detected for the MT and HT layers and a high electron density in LT pyrolytic carbon.

#### 4. CONCLUSION

The variation of the surface height and RMS roughness obtained by AFM are correlated with the texture measured by TEM from selected area diffraction patterns and by polarized light microscopy. The different surface height levels are due to different local etching rates resulting from different degrees of texture of the different pyrolytic carbon layers deposited on the carbon fiber surface. It is shown that TEM contrast indeed is dominated by the significant variation of sample thickness due to TEM sample preparation.

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