MICROSTRUCTURE ANALYSIS OF A CARBON-CARBON COMPOSITE USING ARGON ION ETCHING

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Abstract

The microstructure of carbon-carbon composites obtained by chemical vapor infiltration of a carbon fiber felt was comparatively studied by reflection light microscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and laser scanning confocal microscopy (LSCM). Ar+ ion etching was used to reveal and distinguish structural units of the pyrolytic carbon matrix. Mechanically polished samples, polished and subsequently ion etched samples and fractured samples were compared. The values of surface roughness and surface height obtained after polishing and subsequent etching determined by atomic force microscopy and laser scanning confocal microscopy correlate well with the degree of texture of the matrix layers obtained by polarized light microscopy (PLM) and selected area electron diffraction (SAED). The carbon matrix is composed of structural units or “cells”, which contain a carbon fiber and a sequence of several differently textured layers around each fiber. Within high-textured layers columnar grains are well-recognizable using polarized reflection light microscopy and confocal microscopy. The size of depressions within high-textured carbon layers which are found by atomic force microscopy after ion etching correlates well with the size of differently tilted domains detected by both transmission electron microscopy and scanning electron microscopy.

Introduction

The combination of polarized light microscopy (PLM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) combined with selected area electron diffraction (SAED) allows the study of the structural characteristics and texture of pyrolytic carbon deposits in a broad range of length scales starting from the nanometer scale up to a few 100 µm. Techniques based on atomic force microscopy (AFM) not only allow the determination of the topography down to the atomic scale, but also give a spatially resolved contrast between materials that exhibit different mechanical properties. In addition, laser scanning confocal microscopy (LSCM) not only allows the acquisition of optical data with a higher resolution than conventional optical microscopy. It also provides the true *three*-dimensional surface topography and therefore a link between the three-dimensional nanometer-scale resolution AFM data and the PLM data.

A comparative study of an infiltrated carbon fiber felt was presented recently [1] which allows a more detailed understanding of the complex interplay between mass-thickness and Bragg contrast in TEM images of differently textured pyrolytic carbon layers. In this case, Ar^+ ion etching was used as a routine thinning step for obtaining thin electron transparent samples for TEM. Here, we demonstrate that one can also take advantage of this non-uniform etching: we show that Ar^+ ion etching can be used as a technique for revealing structural units within the matrix of infiltrated carbon fiber felts.

Experimental

Chemical vapor infiltration

Sample synthesis was performed by chemical vapor infiltration of a carbon fiber felt. The carbon fibers produced from polyacrilonitrile (PAN) precursor fibers had a mean diameter of 12 µm and were randomly oriented in the felt before infiltration. The mass density of the fibers was 1.76 g/cm^3. The infiltration of the fiber felt was carried out at a temperature of 1100^{o}C in a hot-wall reactor using methane as carbon source ($p_{methane}$ = 26.25 kPa, $p_{hydrogen}$ = 3.75 kPa, residence time = 0.33 s). Further details of the infiltration procedure are described elsewhere [2].

Sample preparation

For the preparation of the TEM sample, a double-sided dimpling (Dimple Grinder, Gatan) was applied using 3 µm and 0.25 µm diamond pastes. Two argon ion guns (PIPS, Gatan) operating for 30 minutes at 4 kV and a current of 12 mA were used for the final thinning of the sample from both sides. The ion beam was focused on the center of the sample at an angle of 4° relative to the sample surface. The sample was continuously rotated with respect to the ion beam during the etching process to avoid preferential etching. To ensure comparability, PLM, LSCM and AFM studies were performed on the TEM sample as well as on flat samples that were cut from the same piece of infiltrated carbon fiber felt as the TEM sample. The flat samples were prepared following the same procedure as for the TEM sample, but instead of dimpling, the flat surfaces were polished with different diamond pastes.

Reflection light microscopy

Polarized reflection light microscopy was carried out using a Leica DM LM optical microscope. In order to characterize the optical anisotropy**,** the extinction angle Ae was measured.

Transmission and scanning electron microscopy

TEM was carried out using a LEO EM 912 Omega transmission electron microscope at an electron energy of 120 keV. Zero-loss filtered selected area electron diffraction (SAED) patterns were acquired to quantify the degree of texture by the orientation angle (OA).

Freshly fractured surfaces were examined by scanning electron microscopy (SEM) in a LEO 1530 microscope without evaporating conductive layers prior to investigation. Details of SEM observations are given elsewhere [3].

Atomic force microscopy
The AFM investigations were performed with a commercial AFM (Autoprobe CP, Park Scientific Instruments) at ambient conditions. Commercially available V-shaped silicon cantilevers with force constants between 0.2 and 0.4 N/m were used. 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 ·10^{-7} N including capillary forces.

Laser scanning confocal microscopy
Laser scanning confocal microscopy was performed with a Leica TCS SP2/X1. Polarized light with a wavelength of 458 nm from an Ar^+ ion laser was used for illumination. The focus of the laser beam was scanned two-dimensionally parallel to the plane of the sample surface (xy-plane) and the sample was moved in the direction perpendicular to the sample surface (z direction) to acquire images. *Topography images* were generated by using the z coordinate with the highest measured intensity for each xy-position. *Maximum intensity images* were generated by plotting the highest measured intensity for each xy-position.

Results

Figure 1 shows a representative PLM image of a polished section of the infiltrated carbon fiber felt. The carbon fibers are randomly oriented within the composite. The deposited matrix material replicates the cylindrical shape of the fibers. A structural unit which in the following will be called a '*cell*' is defined as the volume of one fiber plus the

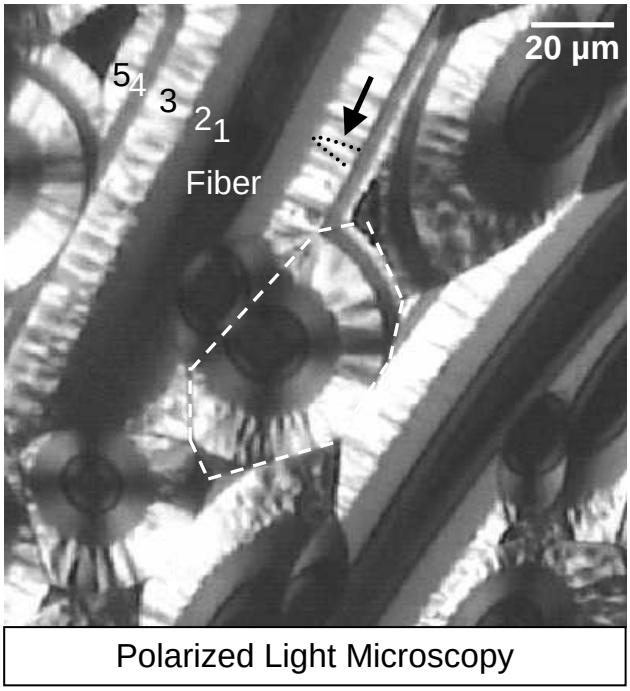

Figure 1. PLM micrograph of a polished section of an infiltrated carbon fiber felt. The matrix material consists of "cells" (one cell is marked by the dashed polygon) consisting of five ring-shaped layers (1-5) around one carbon fiber.

matrix material deposited on this fiber (dashed polygon). Therefore, the infiltrated felt can be considered to be composed of a number of cells corresponding to the number of fibers in the carbon fiber preform. The matrix in each cell consists of up to five concentric *layers* (labeled 1 to 5 in Figure 1) exhibiting different optical anisotropy. Based on the measurements of the extinction angle Ae the texture degrees of the layers are: low- (LT, Ae ~ 10°, layer 1), medium- (MT, Ae ~ 15°, layers 2 and 4) and high-textured (HT, Ae > 18°, layers 3 and 5).

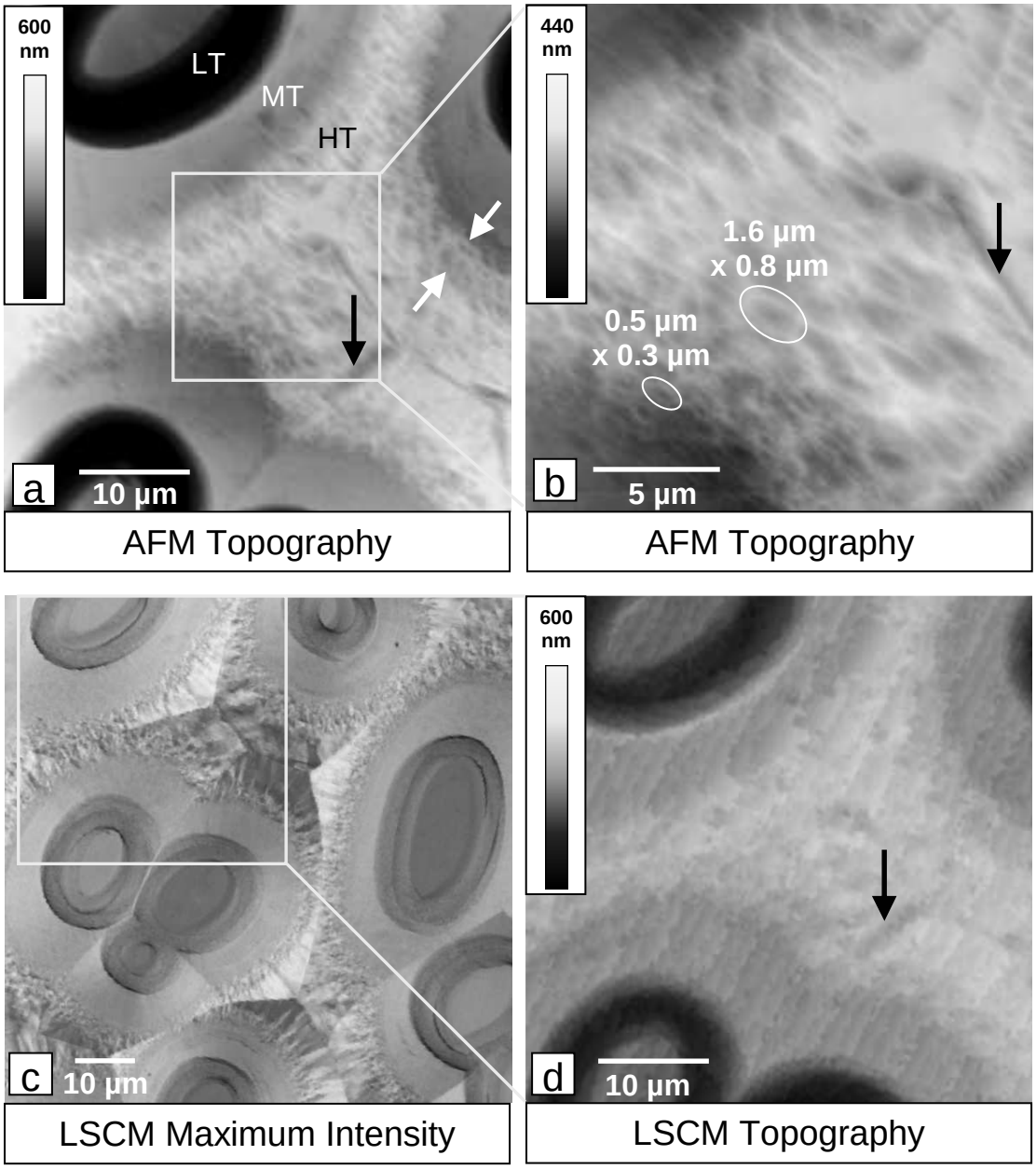

Figure 2. (a, b) AFM topography and (c, d) laser scanning confocal microscopy (LSCM) images of an infiltrated carbon felt after ion etching, (c) LSCM maximum intensity image, (d) LSCM topography image of the same region as shown in (a).

Moreover, elongated grains with growth direction perpendicular to the direction of the layer (area marked by the black arrow and the dotted black line in Figure 1) are clearly visible within HT layers. These grains will be denoted in the following as *columnar grains*.

AFM topography after polishing and subsequent ion etching (Fig. 2a, b) shows that the surfaces of the MT and HT layers are elevated with respect to the fiber and LT layer. The root mean square (RMS) surface roughness and differences in topographic height as determined by AFM as a function of the distance to the center of an ion etched composite sample are shown in [4].

Trenches along *cell boundaries* are found frequently (arrows in Figs. 2a and b). These trenches are especially pronounced at boundaries between adjacent HT layers. However, no evident etching effect is observed at the boundaries between adjacent differently textured layers *within* one cell.

Within the area of the HT carbon layers, many elliptical depressions are observed. A zoom-in is shown in Fig. 2b. The region shown in Fig. 2b is marked by the white square in Fig. 2a. Between the MT and the HT layer, a transition zone with a thickness of about 4 µm can be recognized (see white arrows in Fig. 2a). By comparing the layer thicknesses as determined by AFM and PLM this transition zone can be identified as a sublayer of the HT pyrolytic carbon layer. In the following, this sublayer will be called inner HT layer according to the distance to the fiber, the second sublayer will be called outer HT layer. In the inner HT layer the depressions are significantly smaller (typical size 0.3 µm x 0.5 µm) than in the outer HT layer (typical size 0.8 µm x 1.6 µm). The structure of the columnar grains can not be detected by AFM.

The laser scanning confocal microscopy (LSCM) maximum intensity image displayed in Fig. 2c was taken using polarized light. The depressions found by AFM in the main part of the HT layer can not be identified in the maximum intensity image of Fig. 2c. Instead columnar grains with a typical width of 5 µm are visible (compare also PLM image of Fig. 1). In addition, structures are found by LSCM in the inner HT layer that are clearly smaller (diameter below 1 µm). Fig. 2d shows the topography plot derived from LSCM of the same sample area as shown in Fig. 2a. The height differences determined from LSCM are in agreement with the AFM data. The trenches between HT layers belonging to different cells are also visible (arrow in Fig. 2d).

Fig. 3 shows TEM images of the interface region between the MT and HT layers. The TEM analysis is performed close to the perforation of the ion-thinned foil. Fig. 3a is taken under conventional bright-field conditions where the objective aperture only transmits the (000) beam whereas Fig. 3b is a (002) dark-field image. The bright-field micrograph (Fig. 4a) shows that the MT layer appears homogeneous and brighter than the HT layer. Within the HT layer elongated domains (two typical domains are marked by 1 and 2) exhibiting different contrast are observed. The typical size of the domains is about 0.5 µm x 0.3 µm. After sample tilting (about 10°) the contrast of such domains is reversed. This indicates that Bragg diffraction contrast plays a dominant role within this

sample region. The domain extensions correspond to those of the elongated depressions observed by AFM in the inner HT layer (0.5 µm x 0.3 µm, Fig. 2b).

The zero-loss filtered SAED patterns, inserted in Fig. 3b, illustrate the difference in texture between the MT and the HT layer, which is determined by the degree of preferential orientation of the (002) carbon planes with respect to the fiber surface. The ring-shaped (002) reflections of the MT layer exhibit a considerable azimutal broadening (OA = 70°). In contrast, in the case of the HT layer the azimutal broadening of the (002) reflections is smaller (OA = 27°) and (00l) reflections of higher order are present indicating a higher degree of texture of the turbostratic basal planes [3]. In addition, finely dispersed grains (diameter ~ 20 nm) with a weak contrast are observed in the MT layer. In the domains of the HT layer (e.g. marked by 1 and 2 in Fig. 3b), smaller elongated grains (dimensions ~ 20 nm x 150 nm) exhibiting a strong Bragg contrast are visible. Note that the TEM contrast between differently textured layers varies considerably.

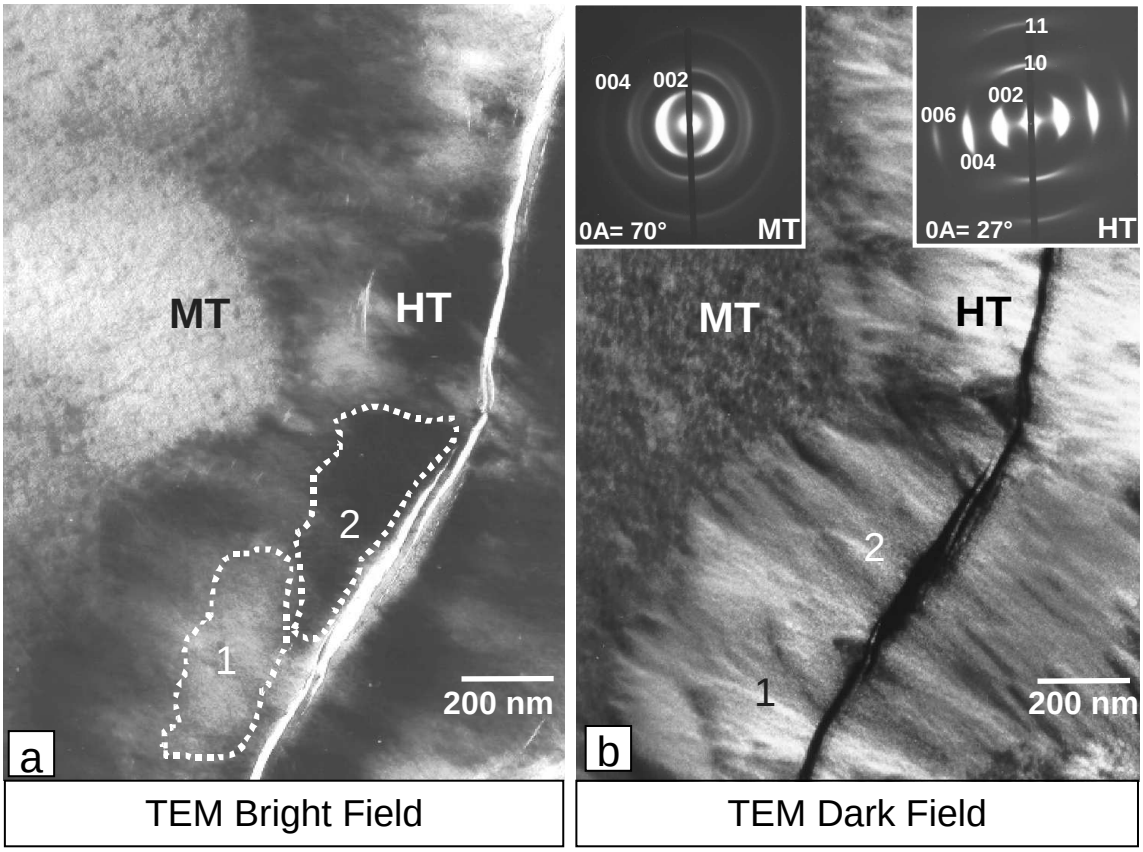

Figure 3. Microstructure of a TEM foil (after polishing, dimpling and ion etching) of the interfacial area between MT and HT layer: (a) TEM bright field image, (b) TEM (00.2) dark-field image (with SAED patterns derived from the MT and HT layers as insets) of the interfacial area between MT and HT layers. The white dotted lines in (a) mark two differently oriented domains.

Fig. 4 shows SEM images of an area of the fracture surface of the composite where the failure took place predominately perpendicular to the fiber axis. An intensive fragmentation in the form of *zig-zag shaped lamellae* parallel to the fiber surface within the HT layer is shown in Fig. 4a (see for example white zig-zag line plotted along such a fragmentation line). The thickness of a lamella lies between 0.5 µm and approximately 1 µm whereas the average distance between sharp bends is about 1 µm. Two typical fragments are marked by dashed ellipses in Fig. 4a. Moreover, areas with different roughness can be seen within zig-zag shaped lamella (Fig. 4b): smooth cone-shaped areas (area between the dashed lines) are surrounded by relatively rough areas (areas above the upper and below the lower dashed line). Note that such areas are typical for the entire HT layer.

Discussion

Atomic force microscopy, light microscopy, laser scanning confocal microscopy, scanning electron microscopy and transmission electron microscopy (combined with selected area electron diffraction) yield complementary information on the complex microstructure of the pyrolytic carbon matrix.
Cells. The infiltrated felt is composed of cells exhibiting sharp cell boundaries, each cell containing one carbon fiber and the pyrolytic carbon deposited on this fiber. During ion etching, material is preferentially removed at boundaries between different cells and especially between adjacent HT layers (Fig. 2b, d). The observation of trenches at cell boundaries can be interpreted either in terms of a lower material density and reduced structural order or in terms of a different orientation of matrix structural units in relation to the Ar^+ ion beam.

Layers. Different surface height levels and surface roughness values after polishing and subsequent additional Ar^+ ion etching are associated with differently textured regions (for details see [1, 4]).

Elliptical depressions. Depressions are found within the entire HT layer by AFM (Fig. 2b). The depressions found in the outer HT layer by AFM are not visible in the LSCM maximum intensity image (Fig. 2c). This indicates that the smaller depressions found by AFM in the inner HT layer also do not result in a contrast in the LSCM maximum intensity image. This means that the contrast observed in the inner HT layer in Fig. 2c arises from changes in the reflectivity, i.e. a different local orientation of the carbon layers relative to the polarized light results in a different brightness.

Zig-zag shaped lamellae. SEM images of fractured surfaces (Fig. 4) show zig-zag shaped lamellae. The thickness of a lamella lies between about 0.5 µm in the inner HT layer and approximately 1 µm in the outer HT layer whereas the average distance between sharp bends is about 1 µm. These dimensions correlate well with the dimensions of the depressions mentioned above, which are found by AFM (Fig. 2b).
The varying roughness observed on fracture surfaces (Fig. 4b) might result from different local orientations (tilting and twisting) of carbon layers (shown schematically by the stacked hexagons in Fig. 4b). The basal planes above the upper and below the lower dashed line are expected to be almost perpendicular to the sample surface

whereas the carbon basal planes between the two dashed lines are supposed to be more parallel to the surface). This explanation is in accordance both with TEM observations (Fig. 3) showing altered Bragg contrast between domains and with the detection of differently oriented small structures in the inner HT layer in LSCM maximum intensity images (Fig. 2c). These differences in the local orientation of these small structures in the inner HT layer might well result in different etching rates. This, in turn, could explain the AFM observation (Fig. 2a and b) of depressions within the HT layers.

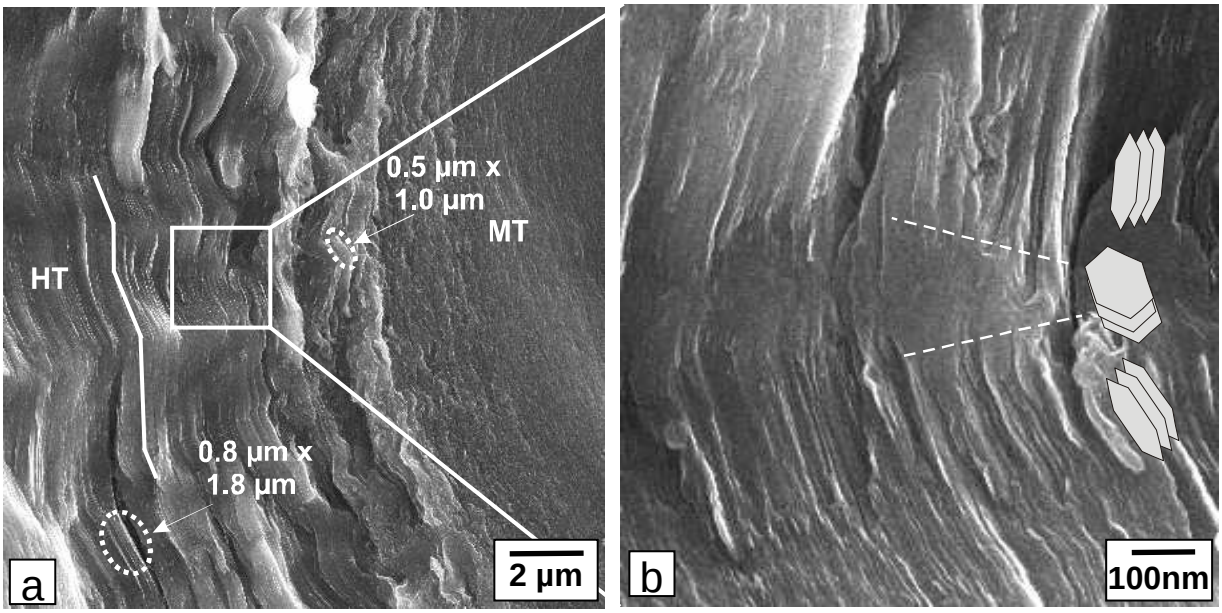

Figure 4. SEM micrographs of the fracture surface of the composite showing (a) zig-zag shaped lamellae within the HT layer and (b) regions with varying roughness within a lamellae. The two dashed ellipses in (a) show sections without bends within a lamellae.

Columnar grains. Columnar grains could only be observed by using polarized light: by PLM (Fig. 1) and LSCM (Fig. 2c). The large columnar grains in the HT layers are not visible in AFM (Fig. 2a) and LSCM (Fig. 2d) topography. However, depressions were observed in AFM topography (Fig. 2b) in the HT layer, which might result from differences in the local orientation of the carbon layers. This may be interpreted as an indirect observation of columnar grains by AFM.

Conclusions

The microstructure of a C-C composite obtained by chemical vapor infiltration of a carbon fiber felt was comparatively studied by light microscopy, laser scanning confocal microscopy, atomic force microscopy, transmission electron microscopy and scanning electron microscopy. Ar+ ion etching was used as a technique to enhance and generate topographic contrast between differently textured areas and layers. AFM in combination with previous ion etching of the polished surfaces allows the characterization of the

hierarchical structure of C-C composites ranging from structures on the length scale of less than 10 nm up to structures on the length scale of a few 10 µm.

The obtained results can be summarized as follows:

- Cell boundaries are predefined by the geometrical orientation of the fibers and are not significantly affected by the presence of differently textured layers. Cell boundaries are sensitive to Ar+ ion etching especially within regions of adjacent HT layers, indicating a lower mass density of the interfacial regions between neighboring cells.
- Boundaries between pyrolytic carbon layers with different texture within one cell and between columnar grains frequently observed within HT pyrolytic carbon layers appear not to be sensitive to the applied low energy Ar+ ion etching process.
- Zig-zag shaped lamellae were observed within the HT layer by SEM. TEM and LSCM measurements suggest that the orientation of the carbon layers changes within these lamellae. This might result in different ion etching rates that could explain the depressions observed by AFM after ion etching within the HT layer.

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