Texture analysis of pyrolytic carbon by polarized light microscopy, x-ray diffraction and selected area electron diffraction: A quantitative model

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INTRODUCTION

Different methods are used for the determination of the degree of texture of pyrolytic carbon: polarized light microscopy (PLM), selected area electron diffraction (SAED) in a transmission electron microscope and x-ray diffraction (XRD) are the most popular techniques.

For the relationship between orientation angle (OA) determined by SAED and extinction angle (Ae) determined by PLM, empirical data (Oberlin, 2002; Reznik, 2002) as well as a quantitative model (Pfrang, 2005) were presented. Here we present an extended quantitative model describing the relationship between SAED data, XRD data and extinction angles determined by PLM.

THEORETICAL DESCRIPTION

Pyrolytic carbon is composed of turbostratic domains of nearly parallel, slightly distorted graphene layers. In the model presented here, the distribution of twist and tilt of these turbostratic domains is determined by SAED or XRD.

The expected average optical properties of the pyrolytic carbon sample can be calculated by assuming that the reflection coefficients correspond to the sum of the reflection coefficients of all turbostratic domains. This summation is carried out by integration taking into account the orientation of the turbostratic domains. The ratio of reflection coefficients of the turbostratic domains for extraordinary and ordinary rays r_e/r_o and their relative phase shift Δ are not known a priori and are considered as fit parameters in the model.

Based on the calculated reflection coefficients the extinction angle of the sample can be calculated (Bortchagovsky, 2003; Pfrang, 2004) and compared with the extinction angle measured by PLM.

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EXPERIMENTAL

In this study pyrolytic carbon layers with high texture deposited on planar substrates (graphite foil and carbon fiber fleece) by chemical vapor deposition in a gap reactor at 1125°C, 20 kPa methane pressure, and 0.5 s residence time (Benzinger, 1999) were investigated. The samples were investigated before and after heat treatment (2900 °C, 2 h). One highly oriented pyrolytic graphite (HOPG) sample was used as reference for the high textured (HT) pyrolytic carbon.

PLM was carried out using an optical microscope equipped with a polarizer and a rotating analyser according to (Pfrang, 2004). The planar carbon samples were cut perpendicular to the pyrolytic carbon layers.
Transmission electron microscopy (TEM) was carried out using a Philips CM 200 FEG/ST electron microscope. The texture is evaluated from SAED patterns by measuring the OA value as outlined in detail by (Bourrat, 2000; De Pauw, 2003). The aperture used for the SAED patterns corresponds to a diameter of 225 nm. OA values of less than 50° were assigned to HT pyrolytic carbon according to (Reznik, 2002; Pfrang, 2005).
X-ray diffraction (XRD) measurements were carried out before and after heat treatment using a Siemens D500 diffractometer in order to characterize the influence of the heat treatment on the texture of the samples. Silicon powder was used as an internal standard (Iwashita, 2004). Both standard X-ray profiles and rocking curves were measured.

RESULTS AND DISCUSSION

Polarized Light Microscopy

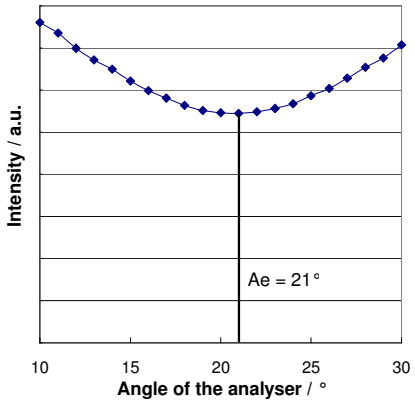

FIGURE 1: Light intensity vs. angle of the analyzer measured by polarized light microscopy. The sample (HT layer on C-fiber fleece) was cut perpendicular to the pyrolytic carbon layer followed by polishing.

All samples were investigated by polarized light microscopy and the extinction angle was determined. An example for the determination of the extinction is shown in Fig.1. The intensity is measured for different orientations of the analyser. In this case the extinction angle was 21°.

Selected Area Electron Diffraction

Fig. 2 shows an overview (left-hand side) and high-resolution (right-hand side) TEM image of a HT carbon layer after heat treatment in cross-section perspective. A small OA of 12° is deduced from the SAED pattern which is inserted in the overview image. The pronounced alignment of the graphene layers is clearly visible in HRTEM image. The orientation angles of the other samples are given in Table 1.

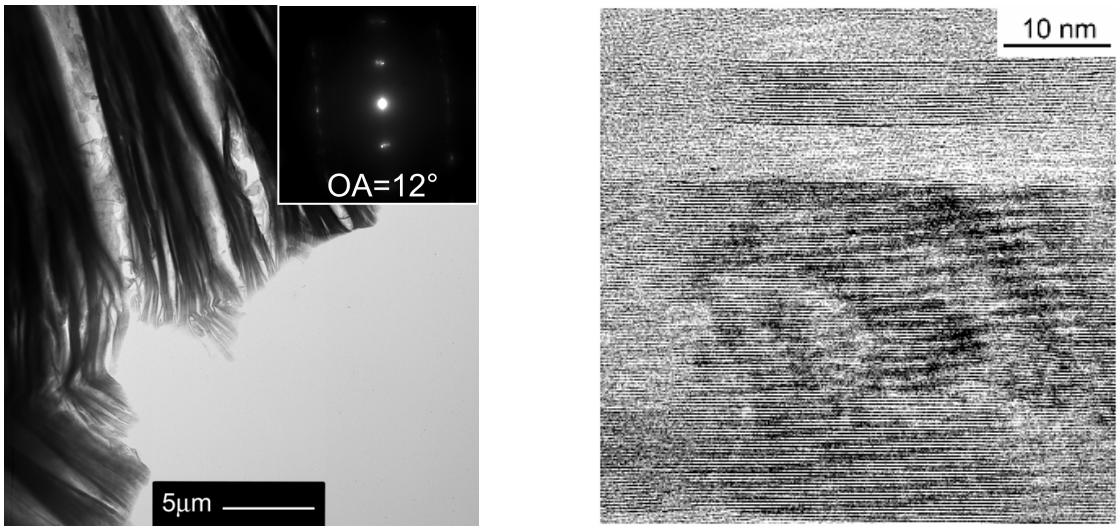

FIGURE 2: TEM micrographs of a high textured pyrolytic carbon layer deposited on a C-fiber fleece after heat treatment (2900°C for 2 hours). Left: overview, right: high-resolution image. Inset: corresponding SAED image, with an orientation angle of 12°.

Sample	Substrate	Heat treatment	Orientation angle
HT layer	Graphite foil	-	26° ± 5°
HT layer	Graphite foil	2900°C / 2h	13° ± 9°
HT layer	C fiber fleece	-	26° ± 4°
HT layer	C fiber fleece	2900°C / 2h	14° ± 9°
HOPG	-	-	7° ± 4°

Table 1: Investigated samples together with the orientation angles determined by SAED. The HOPG sample was investigated as received from the manufacturer and was used as reference.

The orientation angles do not differ significantly for the two different substrates. For both substrates, the values of 26° are typical for high textured layers. After heat treatment, the orientation angles are much lower (13° and 14°, respectively). But these values are still higher than the value of 7° found for HOPG.
Obviously, the heat treatment has a strong influence on the degree of texture as expected.

X-Ray Diffraction

Fig. 3 shows X-ray diffraction patterns acquired on a heat treated pyrolytic carbon layer on a C-fiber fleece.

From the (002) diffraction peak the apparent layer stack height L_c and the interlayer spacing d_{002} were calculated using the modified Scherrer and the Bragg Formula, respectively. The

rocking curve characterizes the distribution of the orientation of the domains relatively to the deposition surface. The full width of the curve at half maximum (mosaic spread) is a parameter describing the texture of the sample (Moore, 1973).

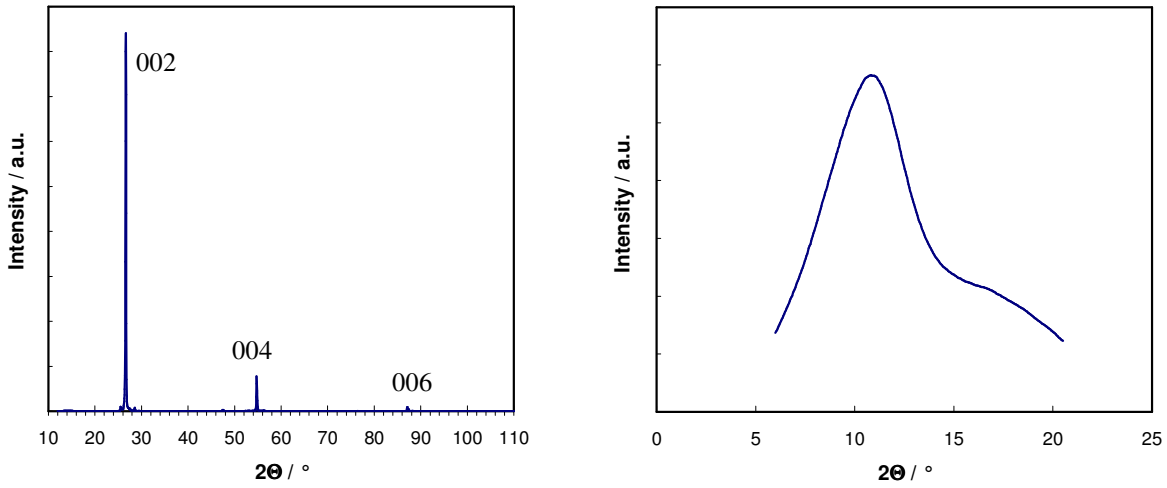

FIGURE 3: X-ray diffraction patterns of a high-textured pyrolytic carbon layer deposited on a carbon fiber fleece. The sample was heat treated at 2900°C for 2 hours. Standard X-ray profile (left) and rocking curve (right). The distribution of the orientation of the domains can be derived from the rocking curve shown on the right.

CONCLUSIONS

A quantitative model for the relationship between different techniques for the characterization of the degree of texture of pyrolytic carbon, namely PLM, SAED and XRD, was suggested. In order to test this model, different pyrolytic carbon samples were investigated by PLM, SAED and XRD and compared with HOPG.

The model is based on the assumption that the distribution of the orientation of turbostratic domains can be derived from the SAED azimuthal intensity distribution or the XRD rocking curve. Furthermore the reflection coefficients of pyrolytic carbon are considered as the sum of reflection coefficients of the turbostratic domains taking into account their orientation. The described model represents the first quantitative description of the relationship between extinction angle, orientation angle and the XRD rocking curve measured for pyrolytic carbon.

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