A comparative characterization of Highly Oriented Pyrolytic Graphite by means of diffraction topography

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ABSTRACT
Highly Oriented Pyrolytic Graphite is a very efficient and well-known x-ray and neutron monochromator. The crystal macroscopic properties are determined by its microscopic structure. Our aim is to study the crystal internal structure and correlate it with the crystal optical behavior. We studied the texture of the crystal, in particular its spatial homogeneity, for different samples using x-ray diffraction topography. The experiment was performed at the ESRF beamline BM5 using a laminar 18 keV monochromatic beam.

Several samples supplied by different manufacturers have been studied. Images of (002) reflected beam have been acquired at the Bragg angle for each sample, using a phosphor coated CCD digital detector. Contrast profiles have been obtained, and exponential fits has been performed allowing to deduce the secondary extinction coefficient.

It has been found that some samples are quite perfect and the results agree with ideally imperfect crystals model. Other samples present well defined granular macrostructures (with dimensions of tens of microns) superposed to the well-known Gaussian-like crystallite distribution. The different behavior between different samples should be explained in terms of sample internal structure, which is also related to the different graphitization process used by manufacturers.

KEYWORDS: Mosaic crystals, Highly Oriented Pyrolytic Graphite (HOPG), x-ray topography, secondary extinction, macrostructures

1. INTRODUCTION

Mosaic crystals provide an interesting choice for medical physics\(^1\) (quasi-monochromatic x-rays for mammography), astrophysics applications\(^5,6\) (polarimeters and hard x-ray concentrators), neutron monochromators, analyzers and filters; and x-ray monochromators for synchrotron radiation.\(^7,8\) Mosaic crystals are considered to be formed by a large number of small perfect crystallites of microscopical or submicroscopical size which are oriented almost but not exactly, parallel to one another. They show a much wider but lower diffraction profile as compared to perfect crystals. These diffraction profiles can be calculated using the theory in Ref. 9 or in Ref. 10 which are equivalent. They assume that the crystallites are oriented almost parallel to the crystal surface (for Bragg case) following a Gaussian distribution which full-width-at-half-maximum (FWHM) \(\tau\) is considered the mosaic spread or mosaicity.

It has been found experimentally that the reflectivity profiles of real Highly Oriented Pyrolytic Graphite (HOPG) do agree only roughly with the theory predictions. Moreover, the diffraction profiles recorded using highly collimated

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narrow beams (of micrometrical size) are very irregular, suggesting that the structure of the real mosaic crystals is much more complex than the assumptions in the theoretical models. It was suggested\(^\text{11}\) that the HOPG could be considered as a "supermosaic" structure, consisting of crystallites grouped to form blocks or layers which are independent from one to another. Detailed measurements of rocking curves as a function of the crystal depth\(^\text{12}\) showed that the HOPG can be described by two types of mosaic structures. The first type consists of macrostructures formed by relatively large tiles (about 40 \(\mu\)m-thick parallel to the \(c\)-axis and about 400 \(\mu\)m in perpendicular) which are misoriented between them by an average mosaic spread of 0.3°. The second mosaic structure on a smaller scale has a mosaic spread \(\tau\) around 0.1°. High resolution x-ray topographic investigations\(^\text{13}\) produced direct images of these macrostructures and showed the alignment between them.

The problem addressed in this work is to study whether or not these macrostructures are intrinsic to the HOPG or they are depending on the sample identity (e.g., fabrication process, size, mosaicity, etc.). We studied the mosaic crystal local structure or texture in the spatial range from few microns to several mm by means of x-ray diffraction topography. HOPG samples are produced by different companies, namely Advanced Ceramics (USA), Optigraph (Russia) and Panasonic (Japan). We have selected samples from these manufacturers to try to find differences in the mosaic crystals microstructure.

X-ray diffraction topography is one of the most used techniques to study the defects in highly perfect crystalline materials. It usually employs a large x-ray beam (projection topography) in combination with an x-ray image detector (photographic film or CCD). This standard technique is not suited for studying the HOPG crystals, because the resulting image would contain a superposition of the images produced by the many different defects, making impossible to extract any concrete information. We performed x-ray diffraction topography using a narrow incident laminar beam (section topography) to reduce this superposition effect. Section topography of imperfect crystals record information from the crystal slice that is directly illuminated by the incident beam.

We have found that the existence macrostructures and its distribution in the mosaic crystal depend on the different samples, perhaps on the particular zone of the same sample, and specially on the sample origin (fabrication process).

2. EXPERIMENTAL

Experiments were carried out at the beamline BM5 at the ESRF. A schematic setup of the experiment is shown in Fig. 1. The source was a bending magnet with a critical energy of 20 keV. The beamline was equipped with a double crystal flat \(Si(1,1,1)\) monochromator, placed at 30 m from the source. The sample was mounted at 40 m from the source on a 3-axes diffractometer using the horizontal plane as diffracting plane. A lamellar beam was produced using a slit of 40 \(\mu\)m (horizontal) and 4.5 mm (vertical). The beam divergence is about 5 arcsec in the diffraction plane (horizontal). Beam cross sections were imaged using a position-sensitive digital detector. Aluminium filters of different thicknesses were used to attenuate the beam to match the dynamic range of the detector. The digital detector was based on a direct deposition of a gadolinium oxysulphide powder onto a CCD surface. The CCD had a pixel pitch of 22.5 \(\mu\)m and 770 \(\times\) 1152 pixels. All CCD operations were driven by means of an electronic unit which provided slow-scan readout and inverted mode operation for dark current reduction. The analog signal was digitized by means of a 12-bits data acquisition board. The evaluation of the phosphor-coated CCD showed high spatial resolution performance.\(^\text{14,15}\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{experimental_setup.png}
\caption{Schematic draw of the experimental setup at ESRF BM5 beamline.}
\end{figure}
Table 1. Parameters of the studied samples.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Manufacturer</th>
<th>thickness [mm]</th>
<th>Mosaicity FWHM[degrees]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Optigraph</td>
<td>1.0</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>Optigraph</td>
<td>1.4</td>
<td>0.28</td>
</tr>
<tr>
<td>2b</td>
<td>Optigraph (backside of 2)</td>
<td>1.4</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>Advanced Ceramics (ZYA)</td>
<td>1.8</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>Panasonic</td>
<td>3.0</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>Advanced Ceramics (ZYB)</td>
<td>1.1</td>
<td>0.67</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

3.1. Analysis of the topographs

Different section topographies were recorded for the different samples using a 18 keV laminar beam (0.040 mm × 3 mm) when the crystals were aligned at the Bragg angle for the HOPG(0,0,2) reflection (θB = 5.9°). A total of 90 good quality topographies were recorded. A selected set of images are shown in Fig. 2. These images (150 × 200 pixels, 3.375 mm × 4.5 mm) are extracted from the corresponding CCD images.

For an ideal mosaic crystal, the images should present a vertical line (the lamellar beam diffracted near the crystal surface) and then a blur (shaped exponentially) on one of the sides of the peak, due to the photons diffracted inside the crystal bulk. If a crystal presents a different pattern, this is due to the existence of structures or grains that alter the ideal pattern.

From direct observation of these images it is possible to extract a valuable information. Some crystals (e.g., sample 1) present a very homogeneous path, corresponding to a crystal which internal structure is highly perfect. Some others (e.g., sample 3) present topographies with large number of structures, showing that the crystal is made by different grains slightly misaligned one from the others. When scanning the angle around the Bragg position, it is possible to see how grains are illuminated and darkened as a function of the scanning angle. It should be possible from here to determine the mosaicity of an individual grain or macrostructure inside the crystal bulk. We also studied the dependence of crystal structure as a function of the crystal position (i.e., the position where the x-ray beam impinges on the crystal). We made few tens of images for each sample and the conclusion is that for homogeneous crystals the topographies change very little. For crystals presenting high number of inhomogeneities, the positions of these grains change from one topography to another, but maintain constant the texture or the statistical properties like mean grain size, etc. (This conclusion is obtained from simple ocular inspection of the topographies.)

In order to obtain quantitative values from these topographies, additional data analysis should be done. Work is in progress to describe the quality of the crystal by a numerical parameter and to obtain statistical values of mosaicity, peak reflectivity and integrated reflectivity from the topographies.

Another important application of this technique is to obtain a three-dimensional mapping of the crystal structure, by means of analyzing a complete set of topographies obtaining by scanning the Bragg angle and the position where the x-ray impinges the beam (see Ref. 16).

3.2. Secondary extinction

When a monochromatic collimated beam hits a crystal at the Bragg angle, it is reflected due to the co-operative effect of several atomic layers at the crystal surface. In a perfect crystal like Si, a 18 keV photon beam penetrates into the crystal a distance of about 40 μm in the direction of the incident beam until its extinction. This distance is called primary extinction length. It is a function of the grazing angle (the primary extinction is very small at the Bragg angle because the beam is fully reflected). In a mosaic crystal, primary extinction occurs inside the individual crystallites. Crystallites are oriented following an angular distribution (often Gaussian) with a given mosaicity. The crystallites that are not exactly oriented at the Bragg angle are transparent to the x-rays. This effects leads to the definition of a new extinction parameters related to mosaic crystals: the secondary extinction. It can be defined as the fractional power loss due to diffraction per unit length of path through the mosaic crystal. The secondary extinction depends on both the primary extinction and on the mosaic distribution (mosaicity).
We assume that the conditions for the mosaic crystal theory of Zachariasen\textsuperscript{6} hold in our case: i) the crystallite thicknesses is much smaller than the primary extinction length (i.e., thin crystallites), ii) there are no phase relationships between blocks, and iii) the mosaicity $\tau$ is much larger than the Darwin width. For our particular setup using a sample of 1 mm thickness, mosaicity 0.22° FWHM, and HOPG(002) reflection at 18 keV, the primary extinction is negligible (i.e., crystallites are thin) and the secondary extinction larger than true absorption. The true absorption coefficient is 0.67 cm\(^{-1}\) (therefore the related extinction length is $\lambda_{\text{true}} = 1/\mu_{\text{true}} \sim 15$ mm), the secondary extinction length is $\lambda_{\text{sec}} = 1.4$ mm, thus $\mu_{\text{sec}} = 7.25$ cm\(^{-1}\)), and the primary extinction length is $\lambda_{\text{prim}} \sim 10$ $\mu$m, thus $\mu_{\text{prim}} = 940$ cm\(^{-1}\). In our experimental conditions we can assume that homogeneous HOPG could be explained using the Zachariasen theory.

From the recorded topographies it is then possible to extract quantitative information on the value of the secondary extinction by looking at the intensity profiles in the diffraction plane. In the case of HOPG samples we observe that the beam profiles decay exponentially, with a measured mean free path (MPF) $\lambda_{\text{exp}}$ which is the projection on the image plane of the MFP inside the crystal due to secondary extinction plus the true absorption:

$$\frac{1}{\lambda_{\text{sec}}} = \frac{1}{\lambda_{\text{exp}}/\sin(2\theta_B)} - \frac{1}{\lambda_{\text{true}}}$$

being $\lambda_{\text{true}} = 1/\mu_{\text{true}}$. At the top of the rocking curve, where the topographies have been recorded, the true absorption is negligible compared to the absorption due to secondary extinction ($\lambda_{\text{true}} \gg \lambda_{\text{sec}}$), thus we can assume that the measured exponential decay profiles depend only on the secondary extinction: $\lambda_{\text{sec}} \approx \lambda_{\text{exp}}/\sin(2\theta_B)$. Intensity irregularities are observed in some profiles due to macrostructures. These irregularities can, in some cases, completely mask the exponential decay due to secondary extinction.

We have analysed all the topographies following the following steps: i) extraction of the transversal transmission profile in the up-down direction after having binned and averaged the registered counts over 10 pixels (225 $\mu$m) around the central spot, ii) normalization of the data to the maximum peak value for each profile, iii) fitting of these profiles with the function $e^{-x/\lambda_{\text{sec}}}$, iv) calculation of the average and standard deviation values from the fits of the averaged profiles, and iv) calculate the secondary extinction length $\lambda_{\text{sec}} = \lambda_{\text{exp}}/\sin(2\theta_B)$ and secondary extinction coefficient $\mu_{\text{sec}} = 1/\lambda_{\text{sec}}$. The fitting results for the two more homogeneous samples are shown in Table 2. Some plots of the profiles and fitted values are in Fig. 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Manufacturer</th>
<th>$\lambda_{\text{exp}}$ [mm]</th>
<th>$\lambda_{\text{sec}}$ [mm]</th>
<th>$\mu_{\text{sec}}$ [mm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Optigraph</td>
<td>0.30 $\pm$ 0.02</td>
<td>1.47</td>
<td>0.68</td>
</tr>
<tr>
<td>4</td>
<td>Panasonic</td>
<td>0.34 $\pm$ 0.03</td>
<td>1.66</td>
<td>0.60</td>
</tr>
</tbody>
</table>

From the fits we can observe that the secondary extinction length increases as mosaicity increases, as it is expected from the theory\textsuperscript{9}: $\lambda_{\text{sec}} \propto \tau$. Therefore, supposing all samples have the same structure factor, the ratio between $\lambda_{\text{sec}}$ and $\tau$ should be constant over all samples. We found some discrepancies that are being studied in more detail. We believe that these discrepancies are due to several experimental. A first factor is the inaccuracy of the $\lambda_{\text{sec}}$ (table 2) and $\tau$ (table 1) values. The latter was estimated by direct comparison with numerical simulations done with the XOP\textsuperscript{17} code, but no fit has been done. A possible chance in the structure factor value originated by the different manufacturing techniques employed is also expected. The most important factor is that rocking curves and topographies were not recorded at the same points on the crystal surface. We have seen that different points on the crystal surface may present different characteristics from the topographic point of view. Work is in progress to measure a collection of rocking curves and topographies at well defined points on the crystal surface for different Miller indices and apply a simultaneous fitting routine that will obtain secondary extinction factors in a simultaneous process from topographies and rocking curves.
SUMMARY AND CONCLUSIONS

It has been experimentally shown the evidence that the mosaic crystal microstructure for the HOPG can present a granular texture with grains or macrostructures of dimensions of tens of microns. The degree of presence of these grains is a measure of the quality of the crystals. It has been shown how to obtain the secondary extinction coefficient by fitting profiles from he topographies.

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REFERENCES

Figure 2. Section topographies for the different samples. See Table 1 for sample description.
Figure 3. Profiles and exponential fits for the topographies show in Fig. 2 (bottom row). From the fitted MFP value it is obtained the secondary extinction coefficient $\lambda_{sec}$ shown in Table 2.