

# Multi-scale quantitative analysis of carbon texture and structure: II. Dark-field electron imaging analysis

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**Abstract.** The different modes in transmission electron microscopy can be used to obtain textural and structural information on carbon materials for a wide range of scales (from less than 1 nm up to several  $\mu\text{m}$ ). Specifically, 002-diffracted electron-based Dark Field (DF) imaging allows visualising, at various magnifications, the amount and extent of areas in which graphenes exhibit similar orientations.

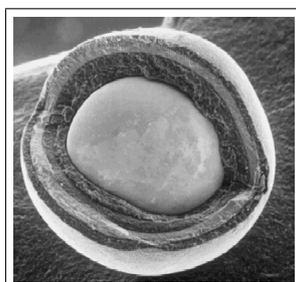
A novel procedure for extracting quantitative textural information from digital DF images is described. Software tools were developed based on standard Open Source solutions (ImageJ and Python). The principle is to binarize DF image pairs with orientations perpendicular and parallel to a reference direction, e.g. an interface plane. The objective aperture opening is chosen accordingly. The ratio  $R$  of the surface areas for the two orientations provides a measurement of the overall (an)isotropy. Beside, as the size distribution of the illuminated domains roughly follows a power law, its exponent  $\alpha$  provides a measurement of the textural organisation.  $\alpha$  correlates to the (an)isotropy measurement provided by the usual electron diffraction-based OA value [1], but also relates to the average size of the pseudo-coherent domains, and somehow relates — in some conditions — to the size of the textural entities (e.g. pores, spherulites).

This methodology was tested on different kinds of pyrocarbon deposits, including the dense, spherulitic deposits in TRISO fuel particles for HTR nuclear reactors.

This work was carried out under collaboration with CEA-Saclay/DMN/SEMI.

## 1 Introduction

The recent years have seen a renewed interest in the high temperature reactor (HTR) technology for nuclear power plants [2]. In such a reactor, the fuel is composed of small ( $\sim 1$  mm) spherical particles, with a fissile or fertile uranium core and a multi-layer protective coating (Fig. 1).



**Figure 1:** Example of TRISO HTR fuel particle. The layers are, from the core out: porous pyrocarbon (buffer), inner dense pyrocarbon (IPyC), SiC, outer dense pyrocarbon (OPyC).

This coating is deposited by fluidized bed chemical vapor deposition (CVD) and is composed of the following layers (from core to surface): (i) a porous pyrocarbon layer (buffer); (ii) an inner dense pyrocarbon layer (“IPyC”); (iii) a silicon carbide (SiC) layer; (iv) an outer dense pyrocarbon layer (“OPyC”) [3].

Each layer has a specific function. First, the buffer absorbs the gaseous fission products and allows for mechanical expansion of the core. Fission products confinement is mainly performed by the SiC layer, while the IPyC layer protects the core from the corrosive chemicals used during SiC deposition and the OPyC layer protects the SiC layer.

The dense pyrocarbon (PyC) layers also act as a mechanical reinforcement for the SiC layer: since neutron irradiation induces structural alterations in the PyC, namely an increase in anisotropy and a (anisotropic) densification, the PyC layers apply a compressive stress on the SiC, thus counteracting the outward pressure from fission products.

However, if irradiation-induced PyC densification is too important, structural weaknesses may appear and propagate to the SiC, as the PyC layers are mechanically coupled to the SiC layer, and cause confinement failures.

PyC densification is isotropy-dependent: the more anisotropic the material initially, the greater the compaction. Hence, the dense PyC layers should be as isotropic as possible at the time of deposition.

Assessment of the degree of (an)isotropy in the material is therefore of great import. Transmission electron microscopy (TEM) imaging can be used to investigate carbon materials at a variety of scales. In particular, dark field imaging using 002-diffracted electrons allows to visualize local molecular orientation domains, a.k.a. “*anisotropic domains*”, that is to say the microtexture of the material.

Furthermore, it is possible to gauge the (an)isotropy of a sample by comparing the complementary dark field images collected for two perpendicular orientations. If the sample is isotropic (at the scale considered), the arrangement of the anisotropic domains is equivalent in both images. Conversely, if the sample is anisotropic, this parameter will be orientation-dependent.

We present here the image analysis method we designed in order to extract isotropy data from dark field image pairs. This algorithm was subsequently implemented in Python, with some data analysis capabilities provided by the ImageJ software.

We show that, in addition to an isotropy ratio  $R$  based on bright area surface measurements in both orientations, it is possible to extract two other quantitative parameters (namely  $\alpha$  and  $a_{50\%}$ ), characteristic of the anisotropic domains size distribution (which roughly follows a power law), and thus of the material’s textural organization.

We then apply this procedure to the investigation of the textural properties of the dense pyrolytic carbon in several TRISO fuel particle samples.

## 2 Experimental Methods

### Image analysis

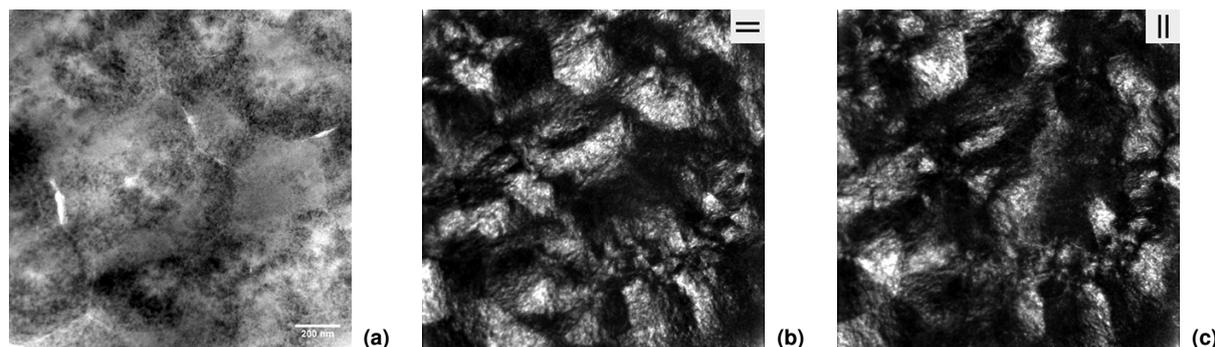
For the purposes of this study, we developed new, specific software tools. Since we wanted the programs to be easy to maintain, modify and transfer to other users, we opted for reference Open Source solutions, namely *Python* and *ImageJ*.

Python is a popular, multi-platform high-level programming language [4], and possesses easy-to-use and powerful scientific libraries (*NumPy*, *SciPy* and *Matplotlib* [5, 6, 7]). We also made use of the *Python Imaging Library* (Secret Labs AB, Sweden).

ImageJ is a scriptable image analysis software written in Java (thus also cross-platform) [8, 9]. We used it mostly as an external “engine” for particle analysis.

### Isotropy parameter

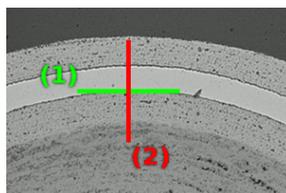
Our first objective was to extract a quantitative isotropy parameter from the dark field image pairs (e.g. Fig. 2).



**Figure 2:** Example of bright field image (a) and dark field image pair (b, c) from one of the pyrocarbons investigated. Inserts in b and c show graphene orientation.

This requires to define a common, consistent reference orientation plane for the graphenes. Typically, one uses the substrate surface, which sets the deposition plane. Here, by analogy, we chose the local tangent to the analyzed layer (i.e. parallel to the fuel particle surface) as the reference direction. Dark field image pairs were thus acquired by selecting graphene orientations parallel (*direction #1*) and perpendicular (*direction #2*) to this reference (Fig. 3).

Once acquisition conditions are standardized, it is possible to measure and compare the total areas of the bright zones in an image pair, provided both images (i) were collected with the same illumination settings and (ii) are binarized using the same threshold.



**Figure 3:** Selected directions for 002 dark field image pairs collection: parallel (#1, green) and perpendicular (#2, red) to the pyrocarbon layers.

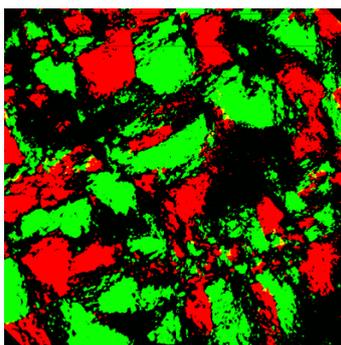
In our image analysis procedure, the threshold value is selected *concurrently* for both images in a pair, so that the area illuminated simultaneously for both orientations is no higher than 0.5% of the total field (e.g. Fig. 4). This criterion was chosen empirically in order to minimize the overlap between both orientations while limiting the erosion of the anisotropic domains. It is then possible to integrate the illuminated area for orientations #1 and #2.

We define the *isotropy ratio*  $R_{21}$  (or just  $R$ ) as:

$$R_{21} = \frac{N_2 - N_{1+2}}{N_1 - N_{1+2}} \approx \frac{N_2}{N_1} \quad (1)$$

$N_1$  and  $N_2$  are the number of bright pixels for orientations #1 and #2, respectively, and  $N_{1+2}$  is the number of pixel lit at the same time in both images (which means that the “yellow” pixels in Fig. 4 for instance are ignored).

If the sampled material is isotropic,  $N_1 \approx N_2$ , hence  $R \approx 1$ . Otherwise,  $R < 1$  or  $R > 1$  — since, as a rule, graphene layers tend to orient parallel to the deposition substrate,  $R$  values are expected to be predominantly less than 1 however.



**Figure 4:** False color superposition of the dark field images from Fig. 2b (*green*) and Fig. 2c (*red*), after binarization. Here  $R_{21} = 0.73$ .

### Domain area statistical distribution

The binarized dark field images provided by the previous procedure are well suited to the application of particle analysis algorithms such as ImageJ’s “*Analyze Particles...*” function.

This enables us to obtain the statistical distribution of the anisotropic domain surface areas in a field or a set of fields. We found that those distributions are, in a first approximation, analogous to a *power law*, that is a distribution where  $p(x) = Pr(X = x) = Cx^{-\alpha}$ , for  $x \geq x_{min}$  [10]. The probability density function  $p(x)$  is represented by a straight line in a log-log diagram, as is the cumulative distribution function  $P(x)$ .

The characteristic parameter of such a distribution is the exponent  $\alpha$ . When  $\alpha$  increases, the relative abundance of the smaller domains increases (and the abundance of the larger domains decreases). It is therefore possible to use  $\alpha$  as a criterion of organization in the material.

One should be aware that the accurate estimation of the  $\alpha$  parameter is non-trivial [10]. For instance, a simple linear regression of the data on a log-log plot may introduce an important bias. Following the recommendations of Clauset *et al.* [10], we used the Maximum Likelihood Estimator (Eq. 2) for computing the  $\alpha$  value for a given data set.

$$\hat{\alpha} = 1 + n \left[ \sum_{i=1}^n \ln \frac{x_i}{x_{min}} \right]^{-1} \quad (2)$$

## Domain size parameter

In addition to the  $\alpha$  parameter, we found it useful to also specify another parameter that would depend on the *absolute* size of the anisotropic domains.

We thus defined  $a_{50\%}$  as the threshold area value at which half the bright area in a dark field image is due to domains smaller (or larger) in surface area than  $a_{50\%}$ . This parameter increases when the domain sizes increase.

## Sample preparation

Fuel particle samples were provided by CEA (Saclay, France) and ORNL (Oak Ridge, TN, USA) either as polished half-spheres, the core having been removed, or envelope fragments. Hemispheres were favored during sample preparation as they are easier to handle.

The hemispheres were first thinned to  $\sim 15\ \mu\text{m}$  cross-sections by polishing on diamond-coated disks. The resulting ring was then glued to a single-hole TEM grid and ion-milled with argon to  $< 100\ \text{nm}$  thickness using a GATAN Precision Ion Polishing System™ (PIPS).

Two to three particle coatings were prepared for TEM observation for each fuel production investigated.

## Image acquisition

Dark field images were collected on a Philips CM20 TEM, operated at 120 kV accelerating voltage and equipped with a  $2048 \times 2048$  CCD camera. The objective aperture was covering a  $44^\circ$ -wide arc on the 002 diffraction ring.

All images were acquired at 15,000 magnification — corresponding to a field of view on the CCD of  $1.6\ \mu\text{m}$  on a side, i.e.  $\approx 2.5\ \mu\text{m}^2$  — with similar illumination. With a view to the image analysis, great care was taken to have exactly the same illumination conditions for associated image pairs.

In order to have significant statistics, especially considering the great heterogeneity of our samples at that scale, twenty image pairs were typically acquired per pyrocarbon layer for each sample series.

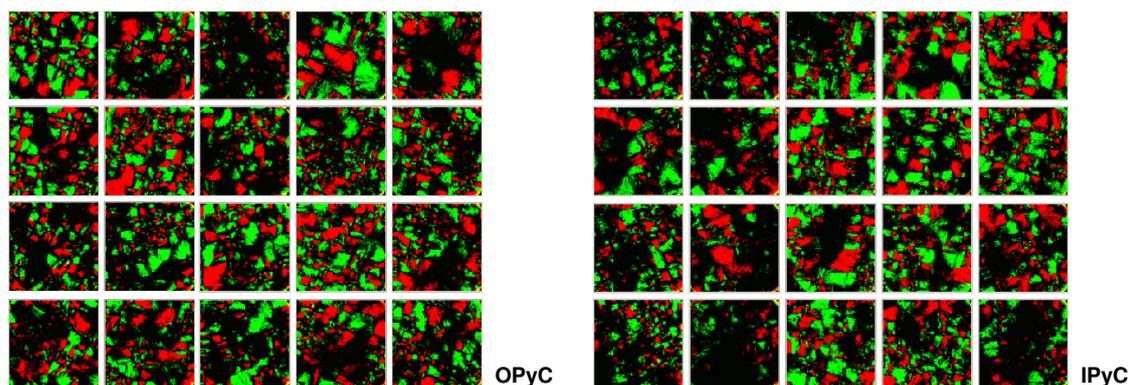
For distribution analysis purposes, the minimum domain size parameter ( $x_{min}$ ) was fixed at  $2\ \text{nm}^2$ .

## 3 Results and Discussion

The methodology described previously has been applied to various TRISO particle productions. We present here some of our results.

Samples *A* and *B* are American and French (resp.) reference productions (see also associated abstract in this issue [11]). *A/1800* is a subset of *A* that has been annealed at  $1800^\circ\text{C}$  in order to simulate the embedding in a graphite matrix and compaction in blocks or pebbles of the fuel particles [2].

Dark field images for sample *A* are displayed on Figure 5. They show the complex, heterogeneous microtexture of these spherulitic carbon materials [11]. The degree of isotropy in the sample is not obvious.



**Figure 5:** Example of dark field image pairs (sample ‘A’), after binarization. On these false-color, composite images, orientation #1 (parallel to the pyrocarbon layer) is green, orientation #2 (perpendicular) red.

On the other hand, image analysis yields a *quantitative* isotropy criterion.  $R_{21}$  ratio values are given in Figure 6a. All values are high ( $> 0.75$ ), but remain (on average) less than unity. The dispersion of individual values for a given sample is quite large, confirmation of the heterogeneity noted earlier (Fig. 5).

The dense pyrocarbon in these particles thus exhibits little anisotropy (at this scale), which is consistent with the high OA values found in SAED [11], though orientation #1 — i.e. parallel to the deposition surface — still dominates. It suggests that the spherules, following their condensation in the homogeneous phase, retain some plasticity when they are deposited on the particle growth surface.

$R_{21}$  is also moderately sensitive to the material’s thermal history. We notice that the isotropy ratio decreases from  $\sim 1.0$  to  $\sim 0.8$  between *A* and *A/1800*, a significant difference that is not apparent on diffraction OA measurements alone (*not shown*).

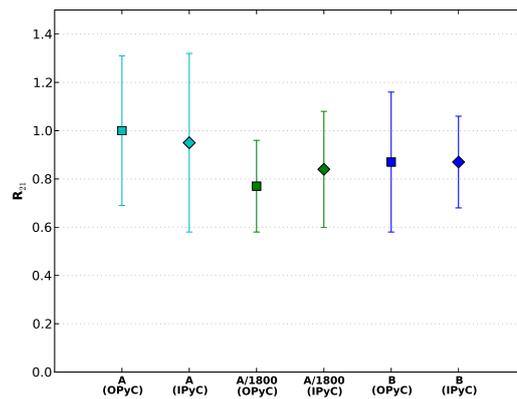
here) and supports the idea that the pyrocarbon deposited should be as isotropic as possible, as structural evolution towards greater anisotropy occurs even before irradiation.

As can be seen in Figure 6b,  $\alpha$  is more sensitive than  $R$  to the thermal history of the pyrocarbon. We note a significant decrease of  $\alpha$  between the OPyC and IPyC layers for A and B, which means the larger anisotropic domains become more abundant.  $\alpha$  is even lower for A/1800.

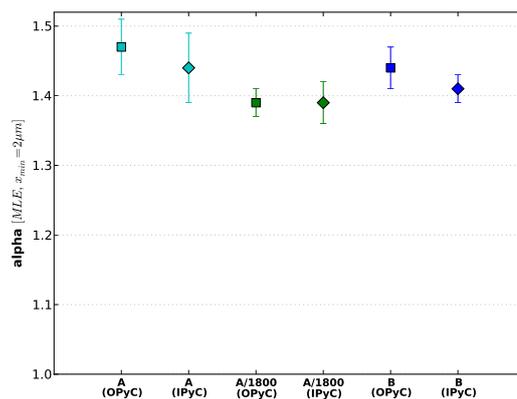
We thus observe the expected “maturation”, i.e. the increase of the degree of organization, of the carbon material with successive heat treatments (SiC deposition, then “compaction”).

$\alpha$  appears as a good characterization parameter, somewhat more sensitive than  $R$  or OA.

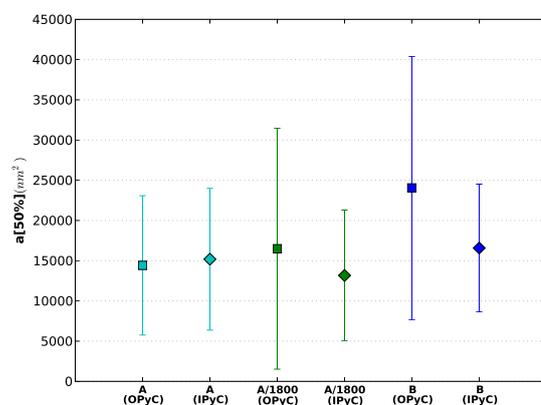
Lastly, we do not observe any significant variation of  $a_{50\%}$  for samples A and A/1800 (Fig. 6c). By contrast, this parameter reveals a definite contraction (and possibly some homogenization) of the anisotropic domains between OPyC and IPyC in sample B, domains that are larger overall than in sample A.



(a)



(b)



(c)

**Figure 6:** Isotropy ratio  $R_{21}$  (a),  $\alpha$  parameter (b) and  $a_{50\%}$  parameter (c) values for samples A, A/1800 and B [marker: mean value, bars:  $\pm 1\sigma$ ].

## 4 Conclusions

In this work, we designed and implemented original image analysis tools for 002 dark field imaging. These tools provide several useful quantitative parameters ( $R_{21}$ ,  $\alpha$ ,  $a_{50\%}$ ) for the characterization of the microtexture in pyrolytic carbons, complementary to the information supplied by electron diffraction [11].

We were thus able for instance to confirm the good conformity of the TRISO fuel particle productions ‘A’ and ‘B’ to reactor use requirements (isotropy, limited sensitivity to heat treatment. . .).

These tools are to be subsequently validated on laminar pyrocarbon samples and complemented by 002-lattice fringe image analysis in a multi-scale strategy, prior to application to a wider variety of carbon materials.

## Acknowledgements

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