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Interpretation of X-ray diffraction patterns of (nuclear) graphite

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ABSTRACT

The atomic structure of several nuclear graphite samples, an essential moderator material for nuclear reactors, has been investigated by X-ray diffraction. The patterns were analyzed by the conventional Rietveld refinement approach as well as by the CARBONXS model, which takes into account disorder and stacking faults. The refined parameters compiled with those from literature reveal a generic picture for the structure of all graphite specimens.

1. Introduction

Since the first man-made nuclear reactor, Chicago Pile 1 in 1942, several types of graphite moderated nuclear reactors have been developed. Graphite is a good moderator because it has low atomic mass, a high scattering cross section and a negligible absorption cross section for neutrons [1]. In addition graphite has excellent mechanical and physical properties, e.g., it does not melt, which make it a perfect choice for moderating neutrons in the very high temperature reactor (VHTR) or the high temperature gas-cooled Generation IV reactor (HTGR). For the safe operation of these reactors it is important to understand this moderator material with the aim of being able to predict and control the changes occurring under long term irradiation [2].

Nuclear graphite is a complex polygranular system, with a very high chemical purity and a high degree of graphitization due to its specific application requirement [3]. The crystal structure consists of series of layers of carbon atoms, which form the 2D hexagonal network of graphene layers. These layers are stacked either in the ABAB sequence leading to the hexagonal 2H structure or in the ABCABC arrangement for the rhombohedral 3R structure. Normally, highly ordered or highly oriented graphite has the 2H hexagonal structure but even high quality samples still contain a non-negligible fraction of the 3R rhombohedral phase [4–6]. This is because graphite cannot be produced out of the melt at ambient pressure.

X-ray diffraction (XRD) is the standard method for investigating the microscopic structure of bulk graphite. The analysis of XRD patterns, however, is not trivial because the Bragg peaks are asymmetric and broad due to several factors, such as the high penetration depth of X-rays, the fluctuations in lattice spacing and the stacking disorder between the carbon layers. The combination of these effects has not always been taken into account properly. In particular, earlier studies [5–15] focused only on the influence of the stacking faults and random shifts between adjacent carbon layers. This disordered layered structure was described by the term "turbostratic" and it was supposed that graphite contains nearly perfect segments of carbon layers, but without correlation between adjacent layers. The relative displacements between layers were assumed to be translations or rotations with the resulting strains leading to fluctuations of interlayer spacing.

Other studies focused on the influence of the high penetration depth of X-rays on both the positions and widths of the Bragg peaks. For this purpose samples consisting of a mixture of graphite and silicon powders were measured [16–19]. The graphite Bragg peak positions and widths were then corrected on the basis of the effects found for silicon.

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From these studies it became clear that the broadened diffraction patterns cannot be solely attributed to the penetration depth of X-rays, because in this case non-physical results such as interlayer spacing and crystallite size that depend on the specific diffraction line used are obtained [17].

It is therefore obvious that a correct analysis of graphite XRD patterns must include both disorder and the high penetration of X-rays. However, disorder in graphite is complex due to the inherent anisotropy of the layered structure, with strong covalent bonding in the (graphene) layers and weak van der Waals interactions between the layers. For this reason the standard Rietveld refinement [20], which implicitly assumes isotropic crystallite size, perfect tri-periodicity and disorder at atomic scale, cannot properly reproduce the observed broadening and intensities of the Bragg peaks and fails in giving reliable structural information [21–23]. In order to overcome these limitations Shi introduced a structural model that incorporates disorder and the anisotropy of the graphite structure [24,25]. This model has been successfully applied to both X-ray and neutron diffraction patterns of carbon materials. It will be introduced in the following section and will be used to analyze our XRD patterns of nuclear graphite. The resulting refined parameters reveal a generic picture for the structural properties of all graphites including nuclear graphites.

2. The disordered graphite model CARBONXS

Shi considered a two-layer model to describe the structure of graphitic carbon. In this model an ideal and rigid AB stacking sequence forms a primary building block of the structure as illustrated by Fig. 1. Then the blocks are stacked as follows:

(1) a random shift between adjacent blocks with probability P_{RS}, accounting for the stacking faults with a random translational component in basal plane;
(2) a registered shift between adjacent blocks leading to a local 3R rhombohedral order with probability P_{3R}, describing the ABC stacking faults with a fixed translational component;
(3) no shift at all between adjacent blocks with probability $P_{2H} = 1 - P_{3R} - P_{RS}$, giving the 2H ABAB order.

Obviously, for $P_{RS} = 0$, $P_{3R} = 0$, $P_{2H} = 1$, this model produces the 2H ABAB stacking sequence of perfect graphite, whereas when $P_{RS} = 0$, $P_{2H} = 0$, $P_{3R} = 1$, a perfect rhombohedral 3R ABCABC sequence is obtained.

As already mentioned, the stacking faults result in strains and thus fluctuations of the interlayer spacing, which lead to a broadening of all (00l) peaks. The model assumes a GAUSSIAN distribution of the lattice parameter along the c-axis around the mean value $\langle d_{002}\rangle$, as illustrated by Fig. 1, with $\delta = d_{002} - \langle d_{002}\rangle$ and characterized by the standard deviation $\sigma = \sqrt{\langle\delta\rangle^2}$:

$$P(\delta) = \frac{1}{\sqrt{2\pi}\sigma}\exp(-\delta^2/2\sigma^2) \quad (1)$$

According to [15,21], the probability of random shift stacking faults P_{RS} is directly related to δ_a, the fluctuations of the in-plane lattice constant a, through the GAUSSIAN:

$$1 - P_{RS} = \exp\left[-2\left(\frac{\delta_a}{\langle a\rangle/2\pi}\right)^2\right] \quad (2)$$

This expression appears slightly different from the one in [21] because here the d_{110} is substituted by $\langle a\rangle/2$. Note that because of the presence of the fluctuations in the in-plane lattice parameter a, we have used $\langle a\rangle$ to make it consistent with $\langle d_{002}\rangle$.

Besides the average lattice constants $\langle d_{002}\rangle$ along the c-axis and $\langle a\rangle$ for the hexagonal network in the planes, the model introduces two different characteristic lengths, one along the c-axis L_c and one in the plane L_a, to quantify the volumes over which X-rays (or neutrons) are diffracted coherently. This assumption is justified by the anisotropy of the graphite structure and thus offers additional flexibility as compared to the Rietveld method, which provides only one average crystallite size. We note that the coherent lengths (crystallite size), which are calculated from the widths of the diffraction peaks, are often confused with the grain size. Indeed the coherent lengths are typically of the order of several nanometers, whereas the grain size seen by optical or electron microscopy is several orders of magnitudes larger, typically of the orders of tens of micrometers (see e.g., Table 1). Thus, as pointed out in [26] and illustrated by Fig. 2 (after [13]), each

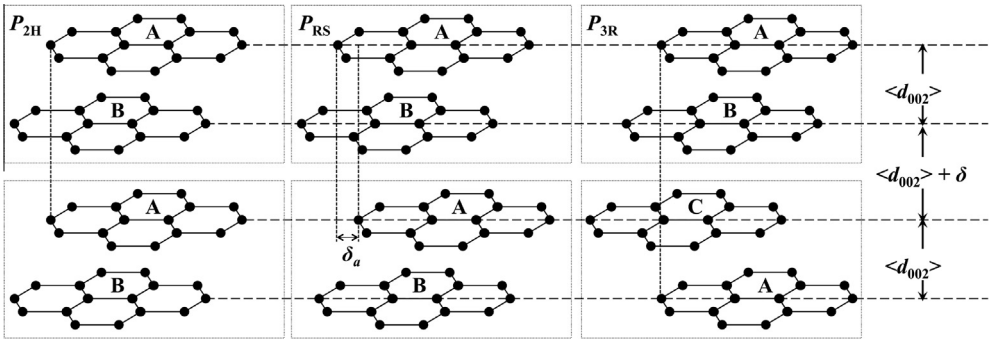

Fig. 1 – Schematic drawing of three stacking sequences of hexagonal carbon planes characteristic graphite structure. The dotted squares illustrate the two-layer units assumed by the model of Shi et al. [24]. The parameter δ is defined as $\delta = d_{002} - \langle d_{002}\rangle$ and can take positive or negative values (see text). The parameter δ_a; is related to the probability of random shift stacking faults P_{RS} (see text).