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Examination of reactor grade graphite using neutron powder diffraction

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A B S T R A C T

Graphite is of principal interest in Generation IV nuclear reactor concepts. In particular, graphite will be the moderator for the Very High Temperature Reactor. In support of experimental and computational investigations that aim at understanding the behavior of reactor grade graphite under operating conditions, neutron powder diffraction experiments have been performed at the North Carolina State University PULSTAR reactor. The collected diffraction patterns exhibit intense broadening of several of the reflections, characteristic of turbostratic stacking. In order to quantify this disorder structurally, a model combined with a Rietveld-like refinement approach was implemented, which includes several refinable parameters that aim at describing this type of structure. Stacking parameters representing the probabilities of a random and registered shift between stacking packages were defined. The results indicate that the studied reactor grade graphite specimens contain a small fraction of layer disorder. The inferred interlayer spacing for the specimens is slightly larger than the theoretical value for graphite of 0.335 nm and the lattice constant is slightly less than 0.246 nm. The developed methodology is found to be successful in fitting the neutron diffraction patterns of reactor grade graphite.

1. Introduction

Graphite has been of principal interest in nuclear reactor design since the operation of the first nuclear fission reactor (CP-1). More recently, Generation IV concepts, specifically the gas cooled Very High Temperature Reactor (VHTR), employ graphite as the moderator. In such reactors, a type of graphite known as “reactor grade graphite” is the form that will be used. This type of graphite is a polycrystalline material that exhibits a high degree of graphitization, high chemical purity to minimize the thermal neutron absorption in the moderator, and random bulk orientation. This later characteristic results in dimensional stability under high neutron fluences. The manufacturing process is discussed in great detail elsewhere [1]. Structurally, this material may be considered as multiphase and composed of a petroleum-coke filler phase and a coal-tar pitch binder phase. The petroleum-coke achieves a high level of crystallinity upon heating the material to temperatures between 2800 and 3000 °C. The density is generally less than that of single crystal graphite and is in the range of 1.5–1.8 g/cm^3, due to being a porous material.

Graphite has a crystalline structure that is composed of C atoms arranged in a hexagonal pattern and stacked in an ABABA… planar sequence. Within each plane, strong covalent bonds exist between the C atoms, while the bonds between the planes are relatively weak. Reactor grade graphite on the other hand has a less perfect structure than highly crystalline graphite [2]. The ABABA… stacking sequence is lost and the planes may exhibit a random translation or rotation relative to each other. The term “turbostratic” has been used to describe this type of disorder [3,4].

The interest in reactor grade graphite has lead to a considerable effort in the modeling of the fundamental properties of this material [5,6]. Thermal neutron scattering cross-sections, thermal expansion, thermal conductivity and heat capacity are just a few of the properties that are being investigated. All of these properties have been derived using either first principles or molecular dynamics techniques. These methods involve a detailed knowledge of the structure of the material on the atomic level. Nevertheless, so far the simulations have focused on perfect graphite structures and the effects that neutron damage may have on the properties of these structures. Thus, an experimental investigation of the atomic structure of reactor grade graphite can contribute to improving the fidelity of these computational methods and their potential impact on nuclear reactor design applications.

One technique of structure investigation is neutron powder diffraction. This technique can provide information on the crystal structure (lattice parameters, atomic species, etc.) of a material. A typical diffraction experiment (that is performed at a reactor neutron source) involves the use of monochromatic neutron beams incident on specimens that are powder-like. The neutrons scattered by the specimen are then collected by a detector and the counts (often normalized to a fixed number of beam monitor counts) are recorded as a function of the scattering angle 2θ. A diffraction pattern containing a series of peaks will then appear as a function of the scattering angle. The position of the peaks is related to the diffraction from atomic planes with different interplanar

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spacing. The collected diffraction patterns are subsequently analyzed by assuming a structural model and assessing its match to the measured data using Rietveld analysis techniques [7,8].

2. Model of reactor grade graphite structure

X-ray powder diffraction patterns of graphitic carbons can be calculated by assuming that the basic structure of the carbon is a two layer package with finite lateral extent and AB-registered stacking, which is the basis of the model introduced by Shi et al. [9]. In our work, this model has been adapted for the calculation of neutron powder diffraction patterns of reactor grade graphite.

In this model [9], the stacking of the two layer packages is controlled by introducing two layer disorder parameters, P and P_t. The parameter P represents the probability of finding a random shift between adjacent packages. A registered shift between the packages is determined by the probability P_t. This probability determines if the local order is AB/CA/BC etc. The probability that there is no shift is then given by $(1 - P - P_t)$. Setting $P = 0$ and $P_t = 0$ results in the ABAB stacking found in perfect graphite (see Fig. 1). If $P_t = 1$ and $P = 0$ then the ABC form is obtained.

In order to deal with fluctuations in layer spacing, a parameter corresponding to the average fluctuation in this spacing is introduced. The layer spacing is then given by $d_{002} + \delta$ where $<\delta> = 0$ and $<\delta^2> \neq 0$. In the two layer model it is assumed that there are no interlayer spacing fluctuations within the packages but only between them. The probability of a given fluctuation is described by a Gaussian function given by:

$$p(\delta) = \frac{1}{\sqrt{2\pi\langle\delta^2\rangle}} e^{-\delta^2/\left(2\langle\delta^2\rangle\right)} \tag{1}$$

where $\sqrt{\langle\delta\rangle^2}$ describes the fluctuation in the layer spacing. The quantity $\left(\langle\delta\rangle^2\right)^{1/2}/2$ represents the average layer fluctuation because half of the layer groups have no fluctuation. In the model, the number of two layer stacks is given by M. Therefore the number of layers in a crystallite is given by $2M$. Also since half of the layers are assumed to have AB stacking, the probability of finding a random shift between any two carbon layers is $P/2$.

3. Analysis of neutron powder diffraction patterns for disordered structures

Based on the structural model presented above, the diffraction intensity can be calculated by considering the reciprocal lattice for an ideal two dimensional graphite layer with finite extent. The reciprocal lattice is a series of rods which intersect the stacking plane. The calculation of the intensity at a certain scattering angle is a sum of all the contributions, averaged over all orientations in three-dimensions, from each hk rod in reciprocal space. The final intensity within an arbitrary scale factor can be calculated by:

$$y_{ci} = s\sum\left(I(\theta)_{00} + 6I(\theta)_{10} + 6I(\theta)_{11} + \ldots\right) + I_b, \tag{2}$$

where s is the scale factor, I_b is the background correction, and $I(\theta)_{hk}$ is the calculated intensity due to an hk reciprocal space rod. Since the highest scattering angle in most diffraction experiments never exceeds 150°, only the rods with max h or $k = 3$ are considered during the calculation. The calculated intensity can be directly compared to the counts (typically per a set number of monitor counts) measured in the detectors.

The average diffraction intensity due to a stack of graphite layers can be described by [10]:

$$i(s) = M|\Phi(\vec{s})|^2 G(\vec{s}), \tag{3}$$

where $\Phi(\vec{s})$ is the scattering amplitude of a two layer package and $G(\vec{s})$ is known as the modulation function and represents the effects of the layer stacking on the diffracted intensity. The modulation function can be written in terms of the average phase factor between two layers and is given as:

$$G(\vec{s}) = \mathrm{Re}\left[\frac{1+q}{1-q} + \frac{2}{M}\frac{q^{M+1} - q}{(1-q)^2}\right], \tag{4}$$

where q is the average phase factor. For a two layer package this factor can be written in terms of the various stacking probabilities and is given by:

$$q = \left\{P\delta_{h0}\delta_{k0} + 1 - P + P_t\left[\exp\left(\pi 4i\left(\frac{1}{3}h + \frac{2}{3}k\right)\right) - 1\right]\right\} \times \exp\left(\pi 4iZd_{002} - 2\pi^2\langle\delta^2\rangle Z^2\right), \tag{5}$$

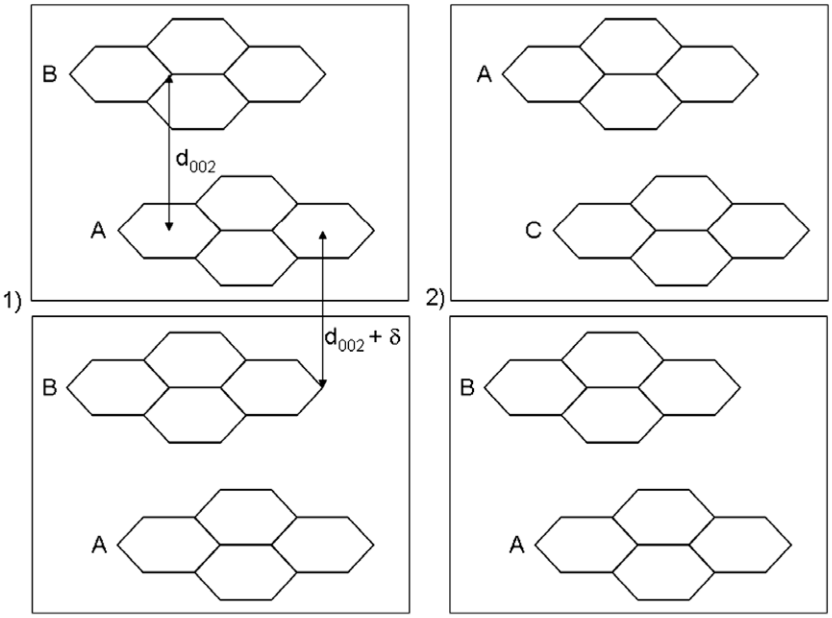

Fig. 1. Schematic showing the stacking sequence for (1) ABAB stacking and (2) ABC stacking in graphite. The boxed regions are two layer stacking packages.

where Z is the component of the scattering vector in the direction of $\hat{u}_z$, the unit vector perpendicular to the layer plane [9].

Since reactor grade graphite is a polycrystalline material, the powder average of Eq. (2) needs to be calculated in order to make comparisons with experiment. The integral is an angular average in reciprocal space and is calculated using the tangent cylinder approximation [10]. The intensity $I(\theta)_{hk}$ due to an hk rod is then given by:

$$I_{hk}(\theta) = \frac{M}{4\pi \cdot s} \cdot F_{hk}^2 \cdot \frac{L_a^4}{a^4} \cdot w \cdot I_{hk}(\vec{s}) \cdot B_{th}, \qquad (6)$$

where $I_{hk}(\vec{s})$ is the powder averaged intensity calculated with the tangent cylinder approximation, $\vec{s}$ is the scattering vector, B_{th} is the thermal parameter, a is the lattice parameter, L_a is the lateral dimension of the crystallite, F_{hk} is the structure factor for a single carbon layer, w is given by $w = 2/L_a\sqrt{3\pi}$, and s is the magnitude of the scattering vector given by $s = 2\sin(\theta)/\lambda$.

In order to convert from an X-ray specific to a neutron specific formulation several modifications were made. The atomic scattering factor for X-rays, included in the structure factor (F_{hk} in Eq. (6)), was replaced by the neutron scattering length for carbon [11]. The polarization correction for X-rays was also removed. In addition, because of the small absorption cross section of thermal neutrons in carbon, the analysis assumed that neutron absorption in the graphite specimens was negligible.

Once the model is defined as described above and a diffraction pattern is calculated, a Rietveld-like method is employed, where a non-linear least squares refinement technique is applied to minimize the difference between a calculated and measured diffraction pattern. The method considers the entire collected diffraction pattern. During the calculation of the diffraction intensity several intensity correction factors are also considered. These correction factors may include the peak shape function, the Lorentz correction, and the preferred orientation correction for example. By taking into account an arbitrary scale factor and the background noise at a given location in the diffraction pattern, the calculated intensity can be directly compared to the collected data. In order to successfully employ this method, approximate values of the input parameters must be known before hand. These values are then adjusted to achieve the best fit (between the predicted and collected patterns) as defined by a statistical criterion such as Chi-squared (χ^2) and its minimization.

Based on the above approach, a refinement computer program has been developed for calculating neutron diffraction patterns of reactor grade graphite. The program is written in FORTRAN and the model has been integrated with a non-linear least squares adjustment routine [12]. In addition to the parameters listed above, further factors are incorporated in the North Carolina State University (NCSU) program. This includes the layer spacing and lattice constant, the lateral size of a crystallite, an overall scale factor, an isotropic temperature factor (which accounts for the effects of thermal motion,) a background function to account for background noise, a preferred orientation function which may be necessary if the crystallites do not orient themselves randomly, and a diffractometer zero correction to account for the zero angle of the diffractometer being off during the measurement of the diffraction patterns.

4. Diffraction pattern measurement and analysis

Neutron diffraction measurements were carried out at NCSU using the recently completed PULSTAR Neutron Powder Diffractometer [13,14]. The facility is located at beam tube 4 of the reactor. Six inches of sapphire provide the fast neutron filtration and a focusing monochromator that consists of nine perfectly bent single crystal silicon blades is employed in the facility. These features along with the relatively high thermal neutron flux ($\sim 3 \times 10^{12}$ n cm^2/s) at the entrance to the beam tube result in a thermal neutron flux of about 0.5×10^5 n cm^2/s at the specimen location. The detector array contains 15 linear position sensitive elements, which are each approximately 61 cm in length and 2.5 cm in diameter, and filled with six atmospheres (0.61 MPa) of ^{3}He and four atmospheres (0.41 MPa) of Ar + 0.5% CO_2. The detector array is attached to a movable cassette which allows it to be placed between 1.1 and 1.6 m from the specimen. Fig. 2 shows the current setup of the PULSTAR diffractometer facility. For the measurements described in this paper, the detector has been positioned at 1.6 m, to allow for the greatest possible resolution. The detector spans 20° and is placed at several locations around the specimen in order to measure the entire diffraction pattern. For

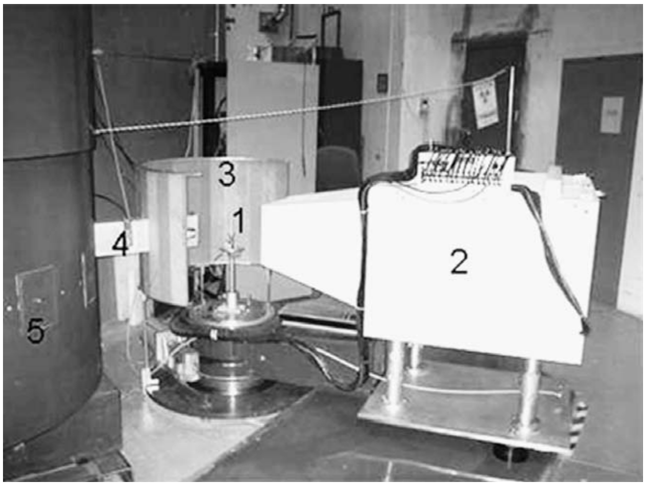

Fig. 2. The current setup of the Neutron Powder Diffractometer at the PULSTAR reactor of NCSU. The various components are labeled; (1) Specimen, (2) Large area position sensitive detector array, (3) Arc-shield, (4) Exit slit extension and (5) Monochromator shielding.

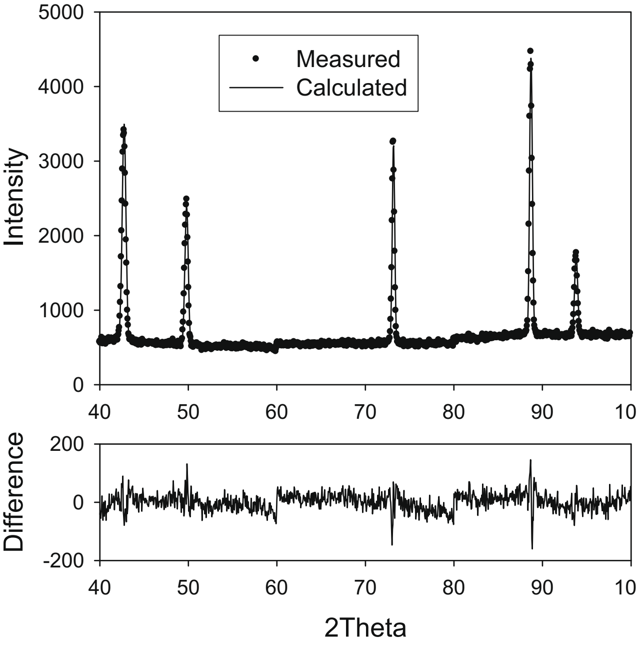

Fig. 3. Ni powder diffraction calibration pattern fitted with GSAS and EXPGUI.

the measurements of the diffraction pattern of reactor grade graphite the detector was placed at scattering angles of 20, 40, 60, 80, and 100° allowing for the collection of data covering scattering angles of 10–110°. The detector collected data for a fixed number of neutrons emerging from the secondary collimator at each location before moving to its next location. Due to complications in correcting for the curvature of the Debye-Scherrer cones, only the counts from the central detector element were considered in the analysis of the reactor grade graphite. This measured intensity can be directly compared to the calculated intensity from either the standard Rietveld approach or the approach implemented in this work.

A Ni calibration specimen was first used to measure the wavelength at the position of the specimen [15]. Fig. 3 shows the calculated diffraction pattern, analyzed with the Rietveld Analysis code package GSAS and EXPGUI [16,17] The measured thermal neutron wavelength at the specimen location was found to be 0.1485 nm (corresponding to approximately 0.037 eV).

Specimens of reactor grade graphite were cut from a large rectangular block of this material that was originally used as part of a reactor thermal column. The density of the specimens was measured to be 1.65 ± 0.05 g/cm^3. The elemental impurity content was estimated using glow-discharge mass spectrometry. In particular, the boron content was estimated to be less than 0.005 ppm by weight. The specimens were cut perpendicular in orientation with respect to each other. The dimensions of the specimens were

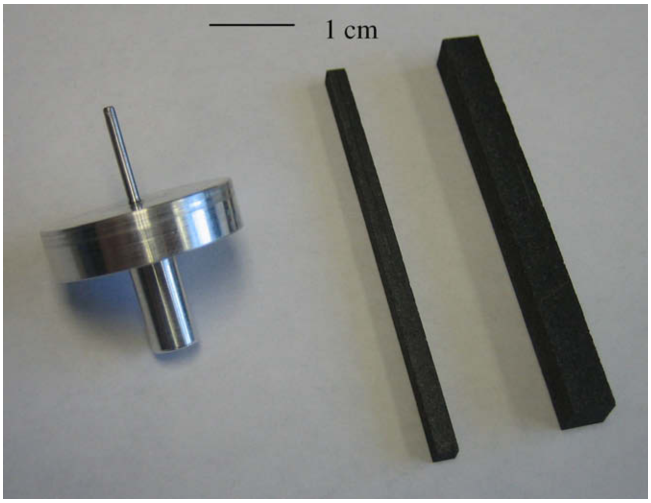

Fig. 4. Al specimen holder and two different size reactor grade graphite specimens.

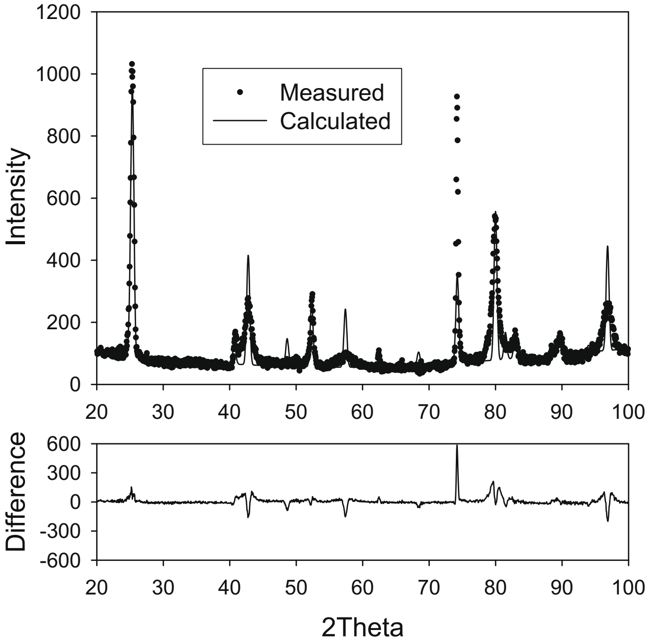

Fig. 5. Attempt to fit reactor grade graphite diffraction patterns using standard Rietveld procedures and the codes GSAS and EXPGUI. The resulting χ^2 is 8.8.

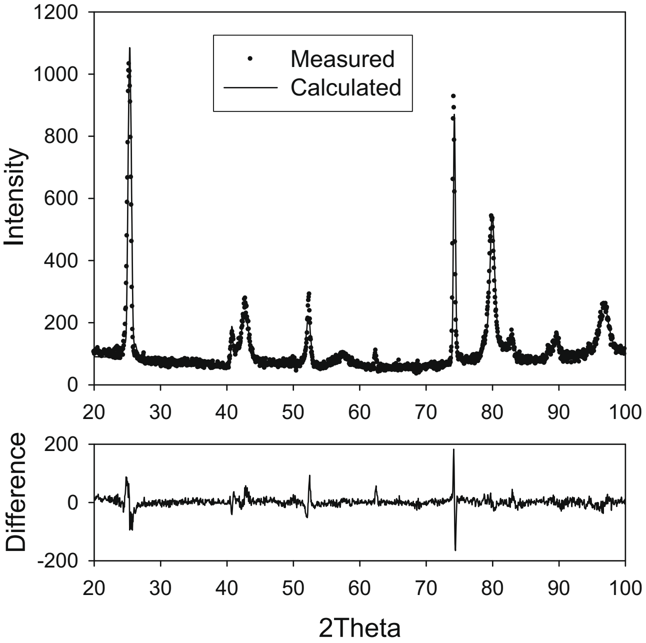

Fig. 6. Measured and calculated diffraction pattern for reactor grade graphite specimen #1. The resulting χ^2 is 1.7.

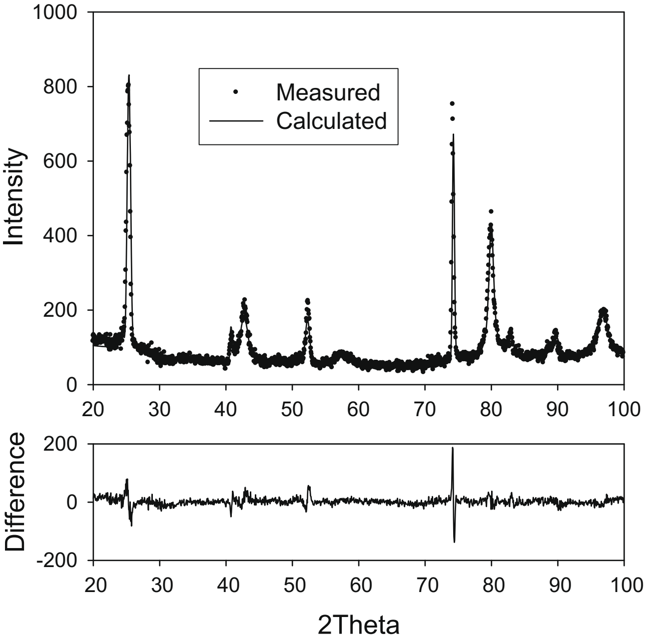

Fig. 7. Measured and calculated diffraction pattern for reactor grade graphite specimen #2. The specimen is cut from the sample block of graphite with a direction that is perpendicular to specimen #1. The resulting χ^2 is 1.6.

Table 1
Fitted parameters for graphite specimen #1 and #2. The number of layers is equal to 2 M.

Specimen	P	P_t	d_{002} (nm)	a (nm)	$\frac{1}{2}(\langle\delta\rangle^2)^{1/2}$ (nm)	L_a (nm)	Number of layers
Graphite #1	0.29	0.18	0.3362	0.2457	0.0059	23.379	41.51
Graphite #2	0.28	0.18	0.3361	0.2456	0.0055	23.889	39.72

$0.3 \times 0.3 \times 5$ cm^3 and $0.6 \times 0.6 \times 5$ cm^3. Fig. 4 shows the specimen holder and two specimens. The smaller specimens were used during the measurement and they were rotated about their axis during the collection of the data.

The diffraction patterns of the specimens were first analyzed using standard Rietveld analysis procedures and the code package GSAS and EXPGUI. The results of an attempted fit to reactor grade graphite specimen #1 using the standard Rietveld approach is shown in Fig. 5. It can be seen in the figure that the standard method has difficulty in reproducing the peak shapes of many of the reflections. Several of the reflections, for example the 102, 103, and 104, show characteristic broadening due to turbostratic stacking disorder. The difference curve also appears very jagged and the reduced χ^2 for specimen #1 is 8.8.

The reactor grade graphite neutron diffraction patterns were then fit using the refinement technique developed in this work. The results of the fits for the two reactor grade graphite specimens are shown in Figs. 6 and 7. The reduced χ^2 for specimen #1 is 1.7 and for specimen #2 is 1.6 indicating a significantly improved fit over the standard Rietveld approach. This improvement is attributed to the improved model that is implemented in this work (i.e., Sections 2 and 3). The present model also allows for quantification of the stacking disorder in reactor grade graphite and several other important structural parameters. The results for the reactor grade graphite specimens are shown in Table 1. The agreement between the two different cuts is very good. The stacking probabilities P and P_t indicate that the reactor grade graphite specimens contain a small fraction of layer disorder. The measured interlayer spacing (d_{002}) for the specimens is larger than the theoretical value of 0.335 nm and the lattice constant is slightly less than of 0.246 nm. The increased interlayer spacing is a characteristic of graphites which exhibit disorder of this type [2]. These results could be used to investigate the effect that layer disorder has on the neutron scattering properties of the material. A representative structure of reactor grade graphite on the atomic level could be adjusted based on the parameters in Table 1. This information could then be used as input for computational simulations (e.g., first principles or molecular dynamics techniques).

Several other factors are still being investigated in the refinement procedure. The effects of preferred orientation and inadequate powder average (graininess) on the values of the parameters need to be investigated in greater detail. Also, in order to calculate more accurate parameters, the instrumental resolution needs to be included in the calculation of the diffraction pattern. However, as it stands the model appears to provide a solid foundation for the analysis of stacking disorder in reactor grade graphite.

5. Conclusions

A model has been implemented for calculating neutron powder diffraction patterns for reactor grade graphite. The model takes into account parameters which are related to the probability of stacking disorder within the crystal structure. It has been demonstrated that the model offers a significant improvement in the fitting results when compared with the standard Rietveld refinement approach. The ability to quantify the disorder in the atomic structure provides an essential starting point for the investigation of the structure of reactor grade graphite, especially upon exposure to neutron irradiation.

Acknowledgements

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