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# Simulating Neutron Radiation Damage of Graphite by In-situ Electron Irradiation

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**Abstract.** Radiation damage in nuclear grade graphite has been investigated using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Changes in the structure on the atomic scale and chemical bonding, and the relationship between each were of particular interest. TEM was used to study damage in nuclear grade graphite on the atomic scale following  $1.92 \times 10^8$  electrons  $\text{nm}^{-2}$  of electron beam exposure. During these experiments EELS spectra were also collected periodically to record changes in chemical bonding and structural disorder, by analysing the changes of the carbon K-edge. Image analysis software from the 'PyroMaN' research group provides further information, based on (002) fringe analysis. The software was applied to the micrographs of electron irradiated virgin 'Pile Grade A' (PGA) graphite to quantify the extent of damage from electron beam exposure.

## 1. Introduction

Around 90% of the UK's current nuclear reactors are graphite-moderated generation II Advanced Gas Cooled Reactors. As well as moderating the energies of fission neutrons, the graphite core provides structural support, contains the fuel and control rods and allows for coolant flow. Graphite blocks in these reactors are subject to high levels of radiation and as a result they experience chemical and physical property changes which can affect other reactor components. The lifetime of such reactors is therefore primarily governed by the performance of the graphite moderator so an accurate estimation of its condition is essential for economic success and plant safety.

Since the 1960s much effort has been made to understand the behaviour of irradiated graphite [1-5]. Despite the wide knowledge base achieved to date there are significant gaps in understanding at the atomic level. The bulk properties of damage features have been thoroughly experimented upon and theoretical models have been derived. Although this has allowed behavioural changes in the irradiated bulk to be accounted for to some extent, in current and future graphite -based reactor designs, the mechanisms of such processes on the nanoscale still remain uncertain. This work investigates the effect of electron irradiation on nuclear grade graphites to understand the fundamental processes involved in radiation damage.

## 2. Experimental Details

Virgin PGA graphite sourced from the University of Manchester was chosen for inspection. Samples were crushed using a marble pestle and mortar and mixed with acetone before being dispersed onto a holey carbon coated copper grid (3mm).

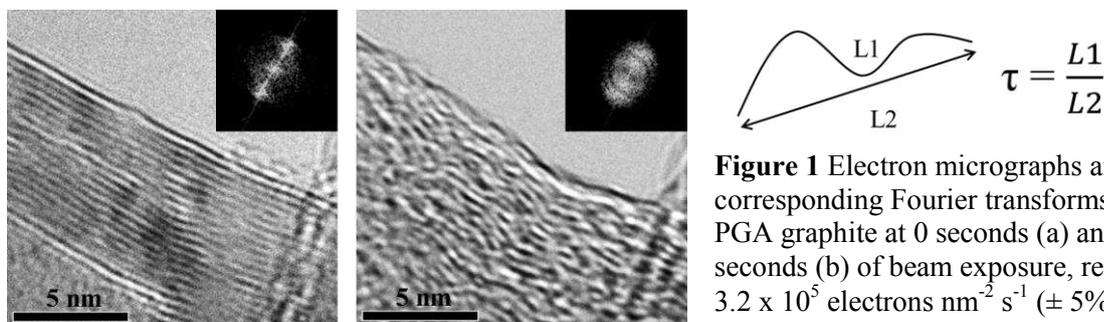


TEM investigations were performed on an FEI CM200 field emission TEM operated at 197 kV with a tip extraction bias of 3.21 kV routinely providing an electron flux of approximately  $3.2 \times 10^5$  electrons  $\text{nm}^{-2} \text{s}^{-1}$  and an electron energy loss spectroscopy (EELS) energy resolution of 0.7–0.8 eV. For EELS, the microscope was operated in diffraction mode with a collection semi-angle of 6 mrad and a convergence semi-angle of approximately 1 mrad, using a 115mm camera length (corresponding to the magic angle [6]). Digital images and energy loss spectra were captured using a Gatan imaging filter (GIF) 200 with a 1 megapixel slow scan CCD array. Data from the array (i.e. images and spectra) were processed using Gatan's Digital Micrograph (DM) software.

### 3. Results and Discussion

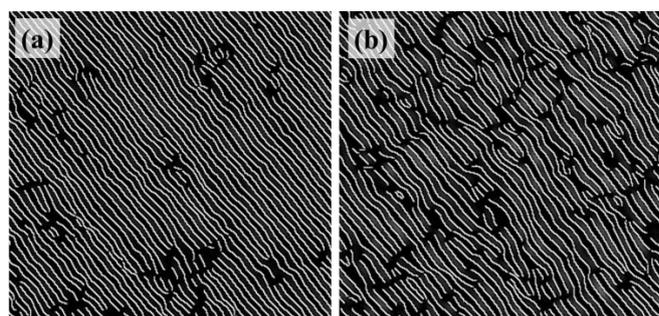
#### 3.1 TEM

PGA graphite was exposed to the electron beam for 600 seconds, corresponding to a flux of  $1.92 \times 10^8$  electrons  $\text{nm}^{-2}$ . Electron micrographs and energy loss spectra were recorded periodically throughout. It can be seen in figure 1 that electron radiation causes damage to the atomic structure of graphite. The tortuosity (or curvature,  $\tau$ ) of planes increases and fringe length decreases.



**Figure 1** Electron micrographs and their corresponding Fourier transforms of PGA graphite at 0 seconds (a) and 600 seconds (b) of beam exposure, receiving  $3.2 \times 10^5$  electrons  $\text{nm}^{-2} \text{s}^{-1}$  ( $\pm 5\%$ ).

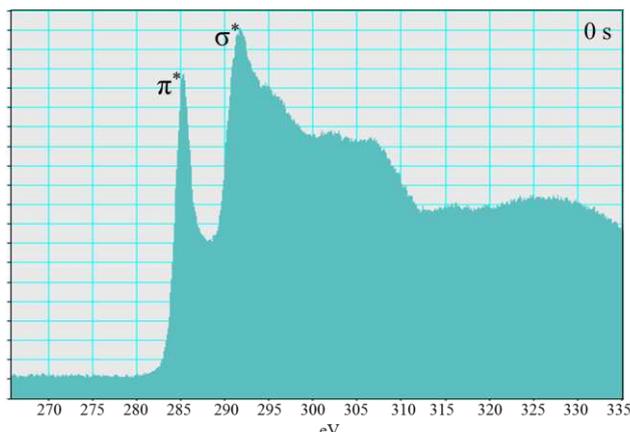
The use of image analysis software (provided by the 'PyroMaN' research group [7]) revealed that 600 seconds of beam exposure broke up fringes; reducing fringe length by approximately 68% (figure 2, figure 6). Based on 002 fringe analysis, the software masks a manually selected area and applies a grey scale pixel selector to detect fringes. Once detected, information about their length and tortuosity can be extracted.



**Figure 2** Application of PyroMaN image analysis software provides information on tortuosity (a measure of curvature) and fringe length before (a) and after (b) 600 s of beam exposure.

#### 3.2 EELS

The carbon K-edge was collected for the area presented in figure 1(a) corresponding to the EELS spectrum shown in figure 3. The image was recorded after approximately 1 second of beam exposure, and represents highly ordered graphite. The on-set energy of the carbon K-edge for all the collected EELS spectra was around 285 eV, and a spectrum of the carbon K-edge was collected each 90-100 seconds (figure 4 (a)-(e)) along with the zero loss peak.

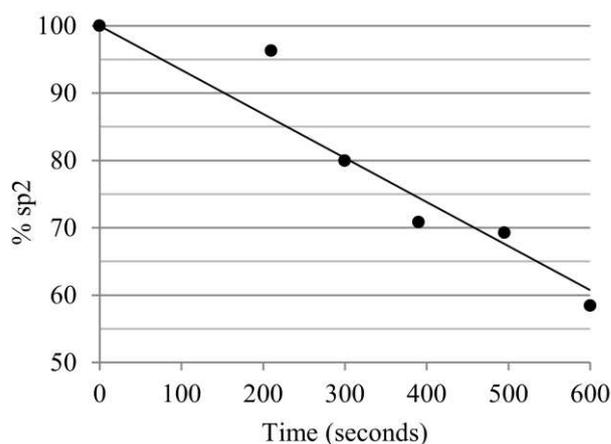


**Figure 3** EELS spectrum for highly ordered graphite.

To characterise the ratio of order to disorder ( $sp^2$  bound carbon to total carbon) the “two window method” was used [8]. It relates graphite’s two core-loss peak intensities, for  $\pi^*(sp^2)$  and  $\sigma^*(sp^3)$  peaks, as follows:

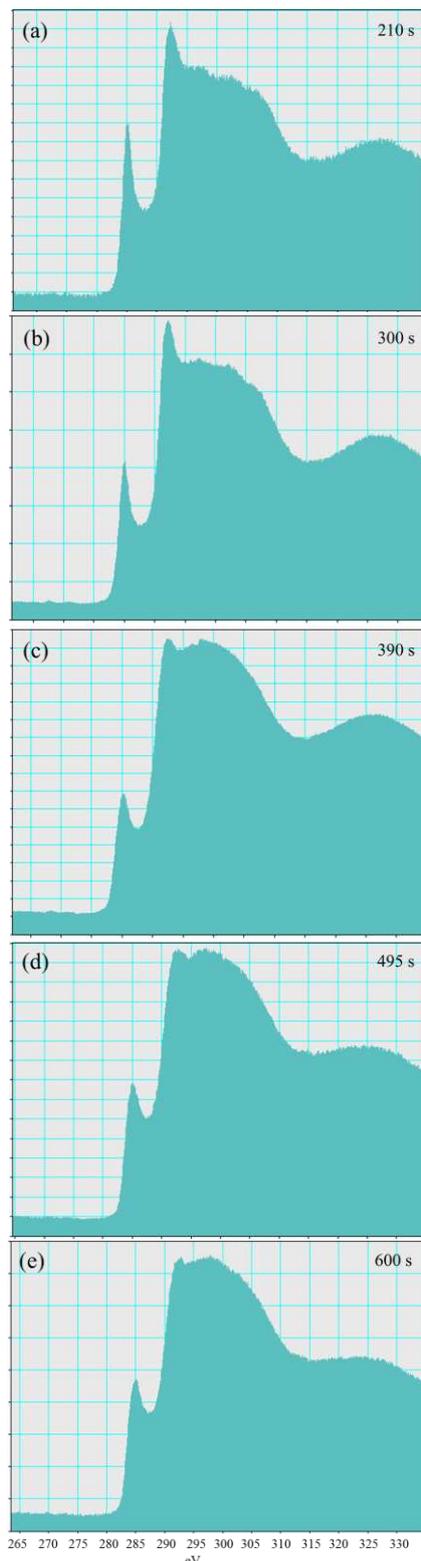
$$\%sp^2 = [(I_{\pi^*} / I_{(\pi^*+\sigma^*)}) / (I_{\pi^*} / I_{(\pi^*+\sigma^*)})_{gr}] \times 100\%$$

where the intensity values from the EELS of the highly ordered virgin graphite were used to calculate  $(I_{\pi^*} / I_{(\pi^*+\sigma^*)})_{gr}$  since this provides the best available approximation to perfect graphite (100%  $sp^2$ ). The degree of disorder changed approximately linearly with respect to electron beam exposure time (figure 5).

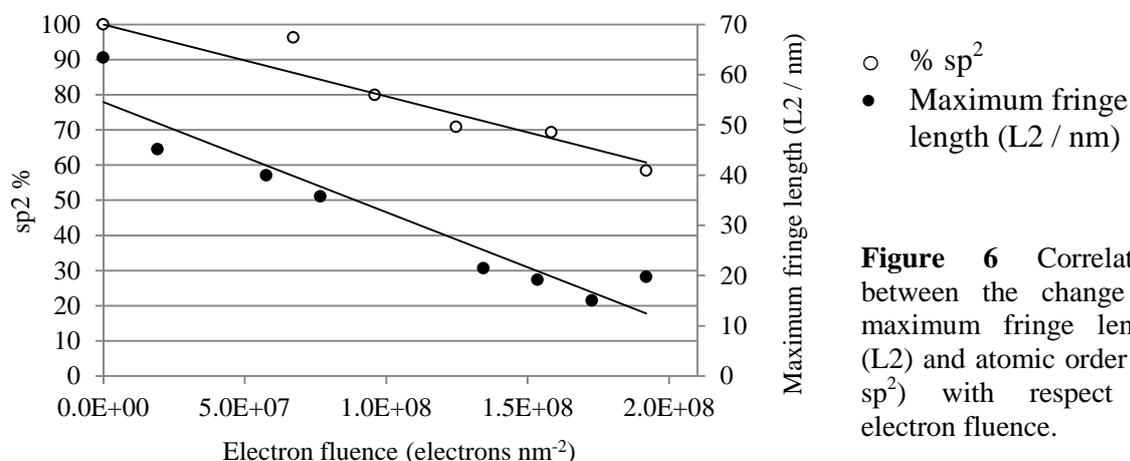


**Figure 5** Correlation between the sample’s degree of order ( $\%sp^2$ ) and electron irradiation time.

The  $sp^2$  percentage in figure 5 dropped from 100% to below 60% after 600 seconds of beam exposure, showing that electron irradiation introduces atomic disorder. In figure 6 it can be seen that the rate in maximum fringe length reduction follows a similar path.



**Figure 4** EELS spectra following various durations of electron beam exposure at a flux of  $3.2 \times 10^5$  electrons  $nm^{-2} s^{-1}$ .



**Figure 6** Correlation between the change in maximum fringe length (L2) and atomic order (% sp<sup>2</sup>) with respect to electron fluence.

#### 4. Summary

It has been shown that in-situ electron irradiation at room temperature damages PGA graphite at the atomic level. This can be used to better understand the behaviour of graphite moderators inside a nuclear reactor. The electron flux in the TEM can be easily controlled allowing for the observation of radiation damage mechanisms. Future work is in progress using in-situ heating to observe the effects of electron beam irradiation at elevated temperatures. Samples of neutron irradiated graphites are also being investigated.

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#### References

- [1] Hennig G R 1962 Vacancies and Dislocation Loops in Graphite *J. Appl. Phys. Lett.* **1** 55
- [2] Nightingale R E 1962 *Nuclear Graphite*. vol. 1 (New York: Academic Press)
- [3] Reynolds W N and Thrower P A 1963 The Flux Level Effect in Radiation Damage in Graphite *J. Nucl. Mater.* **10** 209
- [4] Bollmann W and Hennig G R 1964 Electron Microscope Observations of Irradiated Graphite Single Crystals *Carbon* **1** 525
- [5] Gray B S, Brocklehurst J E, Kelly B T, Sorenson H and Dietrich O W 1969 Irradiation Damage in Solids and Reactor Materials (Vienna: IEAEA)
- [6] Daniels H, Brown A, Scott A, Nichells T, Rand B and Brydson R M D 2003 Experimental and Theoretical Evidence for the Magic Angle in Transmission Electron Energy Loss Spectroscopy *Ultramicroscopy* **96** 523
- [7] Raynal P I, Monthieux M, Da Costa J P, Dugne O 2010 Multi-Scale Quantitative Analysis of Carbon Structure and Texture: iii. Lattice fringe imaging analysis. *Proc. Int. Carbon conf. (USA)*
- [8] Zhang Z, Brydson R M D, Aslam Z, Reddy S, Brown A, Westwood A and Rand B 2011 Investigating the structure of non-graphitising carbons using electron energy loss spectroscopy in the transmission electron microscope *Carbon* **49** 5049