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Effects of Displacing Radiation on Graphite Observed Using *in situ* Transmission Electron Microscopy

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ABSTRACT

Graphite is used as a moderator and structural component in the United Kingdom's fleet of Advanced Gas-Cooled Reactors (AGRs) and features in two Generation IV reactor concepts: the Very High Temperature Reactor (VHTR) and the Molten Salt Reactor (MSR). Under the temperature and neutron irradiation conditions of an AGR, nuclear-grade graphite demonstrates significant changes to it mechanical, thermal and electrical properties. These changes include considerable dimensional change with expansion in the c-direction and contraction in the a/b-directions. As the United Kingdom's AGRs approach their scheduled decommissioning dates, it is essential that this behaviour be understood in order to determine under what reactor conditions their operating lifetimes can be safely extended.

Two models have been proposed for the dimensional change in graphite due to displacing radiation: the "Standard Model" and "Ruck and Tuck". The Standard Model draws on a conventional model of Frenkel pair production, point defect migration and agglomeration but fails to explain several key experimental observations. The Ruck and Tuck model has been proposed by M.I. Heggie *et al.* and is based upon the movement of basal dislocation to create folds in the "graphene" sheets and seeks not only to account for the dimension change but also the other phenomena not explained by the Standard Model.

In order to test the validity of these models, work is underway to gather experimental evidence of the microstructural evolution of graphite under displacing radiation. One of the primary techniques for this is transmission electron microscopy with *in situ* ion irradiation. This paper presents the results of electron irradiation at a range of energies (performed in order to separate the effects of the electron and ion beams) and of combined electron and ion beam irradiation.

INTRODUCTION

In 2010, a total of 363 TWh of electricity was generated in the United Kingdom [1]. The United Kingdom's fleet of Advanced Gas-Cooled Reactors (AGRs) has a maximum capacity of 66 TWh and makes a considerable contribution to the electricity supply. However, all 14 AGRs have scheduled decommissioning dates between the 2016 and 2023 [2]. Furthermore, the United Kingdom also has two Magnox reactors at Oldbury and Wylfa which are scheduled to shutdown in 2012 taking 1.4 MW of net electricity generation off-line and the *European Large Combustion Plant Directive* (2001/80/EC) may force some coal power stations to cease operation [3]. In order to continue to meet the electricity consumption requirements of the United Kingdom, the British Government announced the approval of eight new nuclear power stations in the *National Policy Statement for Nuclear Power Generation* [4] but none of these will be operational before

2018 at the earliest. This leaves the United Kingdom with what is termed an “energy gap”. One solution to this problem is to extend the operating licences of the existing AGRs until new electricity generation capacity is brought on-line. In order to produce the safety cases for such extensions it will be necessary to be able to predict the behaviour of the AGRs under the intended operating conditions and in particular to understand the behaviour of the nuclear-grade graphite which constitutes the main structural component of the cores and also acts as the moderator. Beyond the short-term need to fill the United Kingdom’s energy gap, graphite also features in two Generation IV reactor concepts: the Very High Temperature Reactor (VHTR) and the Molten Salt Reactor (MSR).

Nuclear-grade graphite demonstrates significant changes to its mechanical, thermal and electrical properties under the temperature and neutron irradiation conditions of an AGR [5]. These changes include considerable dimensional change with expansion in the c-direction and contraction in the a/b-directions. Two models have been proposed for the dimensional change in graphite due to displacing radiation: the “Standard Model” and “Ruck and Tuck”.

The Standard Model draws on a conventional model of Frenkel pair production, point defect migration and agglomeration [6]. Neutron irradiation creates vacancies and interstitials: vacancies migrate in the basal planes and agglomerate to form vacancy-type dislocation loops which collapse causing contraction in the a/b-directions; and interstitials migrate in the regions between the basal planes and agglomerate to form new basal planes causing expansion in the c-direction.

In the Ruck and Tuck model proposed by M.I. Heggie *et al.* [7, 8], buckling of graphite can occur where one “graphene” sheet is pinned at two points to another sheet of different length or by the interaction of two dislocations of opposite sign in different sheets. Neutron collisions cause basal edge dislocations to pile-up and glide past each other on nearby sheets creating a “ruck and tuck” defect where a “graphene” sheet is buckled. In this way, the glide of basal dislocations can cause expansion in the c-direction, contraction in the a/b-directions and perform the commensurate mass-transport. This model also seeks to explain several experimental results which are not explained by the Standard Model: large energy release below the temperatures for vacancy and interstitial migration during the annealing of radiation damage created at 20 K [5, 9]; the densities of radiation-induced dislocation loops are too low to cause the dimensional changes observed [10]; and, similarly, smaller interstitial defects cannot explain the large dimensional changes. A full discussion of this theory is beyond the scope of this introduction so the interested reader is directed to [7, 8].

In order to test the validity of these models, work is underway to gather experimental evidence of the microstructural evolution of graphite under displacing radiation. One of the primary techniques for this is transmission electron microscopy (TEM) with *in situ* ion irradiation. However in order to be able to interpret these results correctly, it is important to have a careful understanding of the effects of the electron beam. Below are the results of a study into the effects of electron-beam damage on graphite and initial ion irradiation experiments.

EXPERIMENTAL

TEM Samples of graphite were produced from highly-oriented pyrolytic graphite (HOPG) via mechanical exfoliation. TEM with *in situ* ion irradiation was performed using the Microscope and Ion Accelerator for Materials Investigations (MIAMI) facility at the University of Huddersfield, United Kingdom. The facility consists of JEOL JEM-2000FX TEM interfaced with 1−100 kV ion accelerator allowing irradiation to be performed whilst the sample is under observation in the microscope. Full details of the facility can be found in reference [11].

Electron irradiation was performed at energies of 80 to 200 keV. For sequential multiple-energy irradiations of the same material, the lower energy irradiations were performed first. The experiment was then repeated on virgin material for the lowest and highest energies to rule-out cumulative effects from the intermediate irradiations. Electron flux was kept approximately constant at 1.5×10^{35} e.cm^{-2}.s^{-1}.

Ion irradiation was performed using 50 keV He^+ at a flux of 10^{13} cm^{-2}.s^{-1}. This species and energy combination was chosen so as create a smooth damage profile across the thickness of a TEM sample (< 100 nm) with relatively few of the incident ions coming to rest within the sample (< 0.001 %) to avoid the perturbing effects of introducing additional atoms and new species to the graphite. Ion ranges and damage profiles were calculated using the Stopping Ranges of Ions in Matter (SRIM) 2011 [12] with the results shown in Fig. 1.

The sample temperature in initial experiments in this study was 550°C so as to be comparable with experimental results in the literature from the 1960s as this was in the intended operating range for AGRs at the time of that historical work. However, AGRs are currently operated with their cores at around 400°C to avoid thermal oxidation of the graphite and so subsequent experiments in this study were performed at this temperature. Both of these temperatures are above that at which vacancies ($E_{\mathrm{m,V}} \cong 1.0$ eV, $T_{\mathrm{m,V}} > 80$°C) and interstitials ($E_{\mathrm{m,I}} \cong 1.2$ eV, $T_{\mathrm{m,I}} > 150$°C) are expected to be mobile [8].

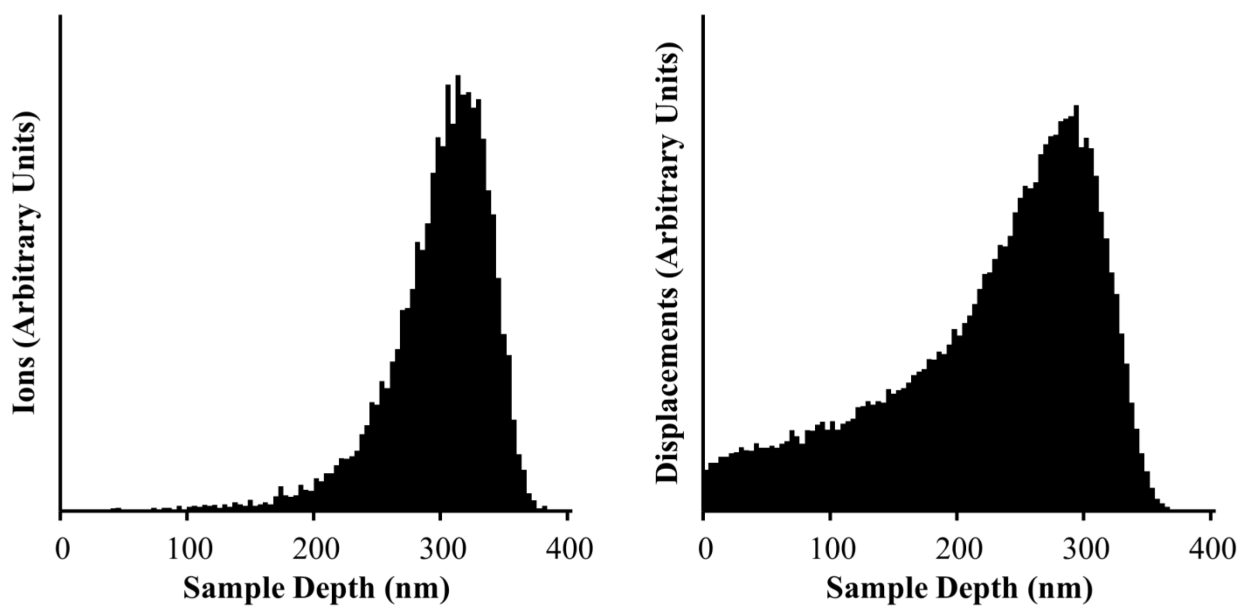

Figure 1. Results of SRIM-2011 calculation for range of and atomic displacements caused by 50 keV He^+ into carbon. The range of the ions is beyond the TEM sample thickness (< 100 nm) and a relatively-smooth damage profile is predicted across this region.

RESULTS

Transmission Electron Microscopy of Radiation Damage using Moiré Patterns

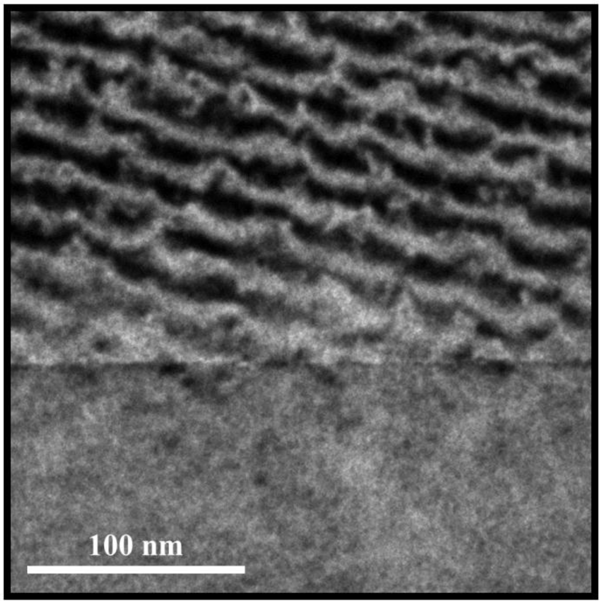

Figure 2. TEM (80 keV) underfocus bright-field micrograph showing radiation-induced disruption to a moiré pattern in HOPG irradiated at 400°C using 50 keV He^{+} to a fluence of 6.8×10^{15} ions.cm^{-2} ($\cong$ 0.45 dpa). The region imaged contains two areas with different combinations of graphite layers: the layers in the area at the top of the micrograph are correctly orientated so as to generate a moiré pattern whilst the layers in the area at the bottom are not. Note that radiation damage is not observable in the absence of a moiré pattern (i.e. it does not generate significant diffraction or structure factor contrast which can be detected in bright-field) but can be seen clearly in the moiré pattern which "magnifies" disruption to the misoriented crystals which generate the pattern.

Moiré patterns are created by the interference between diffracted beams generated by crystals of different orientations. In a layered structure such as graphite, rotational misorientations are common and therefore moiré patterns are likely to be observable over significant areas within a TEM sample.

As can be seen in Fig. 2, a moiré pattern is created where two misorientated crystals create diffraction vectors $\boldsymbol{g}_1$ and $\boldsymbol{g}_2$ which then interfere. Where these crystals are disrupted by radiation damage the vector is altered and the result is a significant change in the interference pattern. However, the radiation-induced changes to the diffraction vectors in the graphite layers present in the bottom of Fig. 2 are not sufficient to generate diffraction contrast in standard bright-field. This demonstrates the usefulness of moiré patterns for detecting radiation damage.

Electron Beam Irradiation

Fig. 3 shows a moiré pattern in HOPG at 550°C exposed to increasing electron beam energies from 80 to 200 keV for 1 h per 20 keV step. No significant disruption to the moiré pattern was observed below 200 keV. Fig. 4 is a repeat experiment (performed at the slightly lower temperature of 400°C – see Experimental section) at 80 keV and 200 keV to confirm the absence of observable damage at the lowest energy and to rule out a cumulative exposure effect in Fig. 3. As can be seen, comparable levels of disruption to the moiré patterns can be seen after exposure to 200 keV e^{-} in both cases.

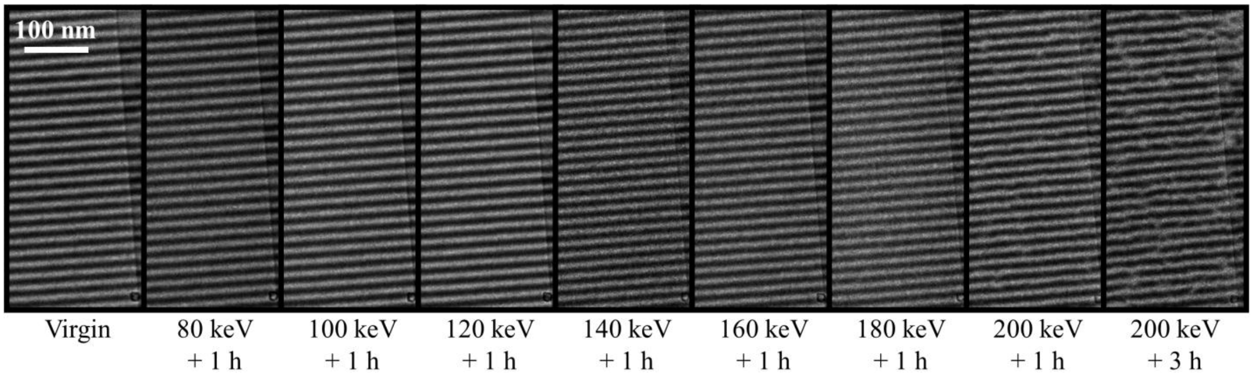

Figure 3. TEM underfocus bright-field micrograph series of a moiré pattern in HOPG at 550°C exposed to sequential electron irradiation steps at increasing energies to explore the threshold at which radiation damage becomes evident in this contrast mechanism. The circular feature in bottom right of each micrograph is a surface feature on the TEM sample used as a fiducial marker to ensure the same area is being imaged throughout the experiment.

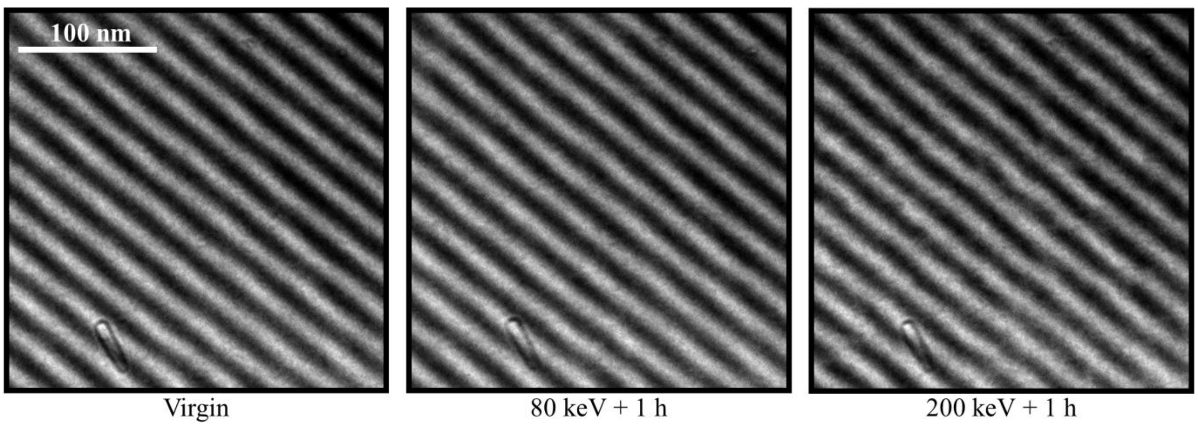

Figure 4. TEM underfocus bright-field micrograph series of a moiré pattern in HOPG at 400°C exposed to electron irradiation at 80 and 200 keV to confirm that equivalent damage would be generated above the threshold energy identified in Fig. 2 without the intermediate irradiation steps and thus demonstrate that the observed effects were not purely cumulative. The elongated feature in the bottom left of each micrograph is a surface feature on the TEM sample used as a fiducial marker to ensure the same area is being imaged throughout the experiment.

<u>Ion Beam Irradiation</u>

Fig. 5 shows the same area of a moiré pattern in HOPG before and after irradiation with 50 keV He^+ at 400°C with the electron beam operated at 80 keV. Disruption to the moiré pattern is clearly evident and appears similar in nature to that observed in the 200 keV e^- case.

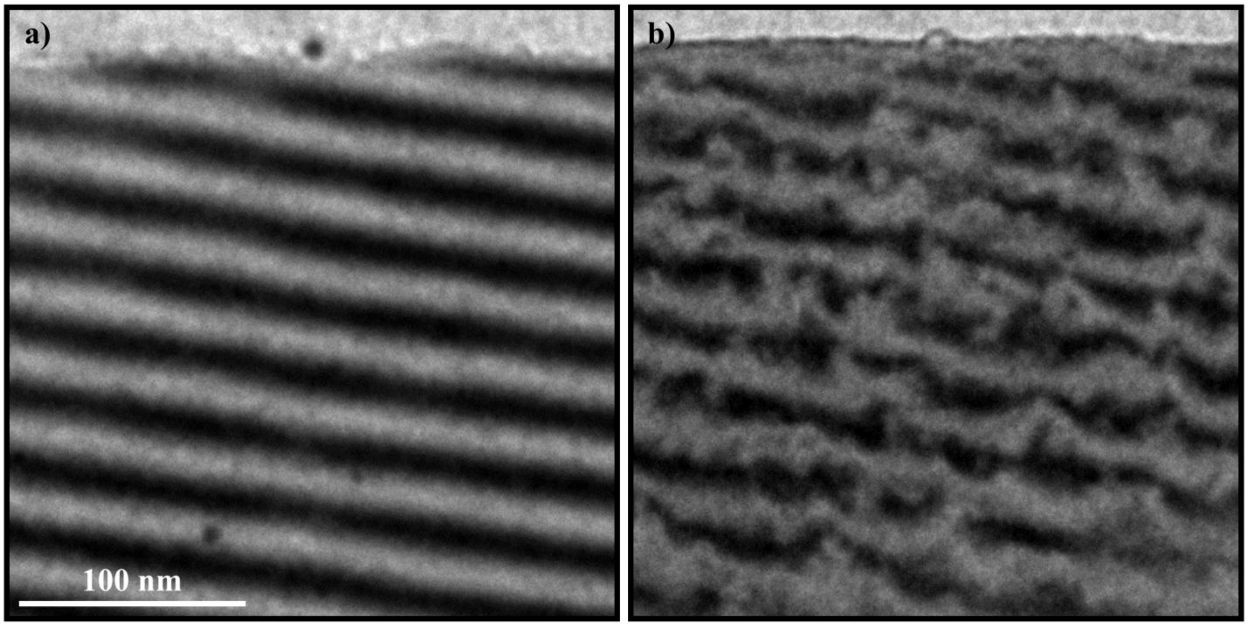

Figure 5. TEM (80 keV) underfocus bright-field micrograph showing: a) virgin HOPG with moiré pattern; and b) radiation-induced disruption to a moiré pattern irradiated at 400°C using 50 keV He^+ to a fluence of 6.8×10^{15} ions.cm^{-2} ($\cong$ 0.45 dpa). The circular feature in the top middle of each micrograph is a surface feature of the TEM sample used as a fiducial marker to ensure the same area is being imaged throughout the experiment – the contrast reversal demonstrated by this feature between a) and b) is due to sputtering by the ion beam rather than a change in defocus.

DISCUSSION

No radiation damage was detected in moiré patterns in HOPG with electron beam energies below 200 keV at the electron flux and temperatures used over the duration of the experiments. However, it cannot be concluded that damage was not introduced below this energy as point defects could have still been produced but at too slow a rate to agglomerate into sufficiently large structures to be detected on the timescales over which observations were made. It is therefore advisable to operate a TEM at the lowest electron beam energy possible so as to avoid such effects.

In both the 200 keV e^- and 50 keV He^+ irradiations damage has been observed to occur through disruption to moiré patterns in HOPG above the temperature for interstitial and vacancy migration. In both cases the damage appears to have structure as indicated by localised disruption to the moiré patterns rather than a global diffusive effect on the pattern which would be consistent with homogeneous damage accumulation. In the electron case this could only arise through the agglomeration of point defects into larger defect structures as electrons will generate only isolated Frenkel pairs and not collision cascades as in the 50 keV He^+ case.

However it is not possible on the basis of this evidence to distinguish between the Standard Model and Ruck and Tuck. Although the former model is based on an agglomeration of point defects into larger defect structures, Ruck and Tuck could also occur through the agglomeration of point defects into dislocations which then facilitate the mechanisms in that theory. Furthermore, although it would appear likely to be the case, it cannot be definitively concluded that the displacing-radiation induced structural damage detected in the moiré patterns of HOPG in these experiments is responsible for dimensional change in nuclear graphite.

SUMMARY

Moiré patterns are a useful contrast mechanism for the detection of radiation damage especially in layered materials where they are likely to be observed. It is advisable to perform TEM observations at the lowest electron beam energy possible to avoid sample damage. Both 200 keV e^- and 50 keV He^+ irradiation at 400°C and above created radiation damage in HOPG which was observable in the moiré patterns. In both cases this damage appeared to be structured and can be concluded to arise, at least in part, through the agglomeration of point defects. Further work is required to explore the nature of the damage observed and the conditions under which it is generated.

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