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In-situ TEM studies of ion-irradiation induced bubble development and mechanical deformation in model nuclear materials

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ABSTRACT

The MIAMI* facility at the University of Huddersfield is one of a number of facilities worldwide that permit the ion irradiation of thin foils in-situ in a transmission electron microscope. MIAMI has been developed with a particular focus on enabling the in-situ implantation of helium and hydrogen into thin electron transparent foils, necessitating ion energies in the range 1 – 10 keV. In addition, however, ions of a variety of species can be provided at energies of up to 100 keV (for singly charged ions), enabling studies to focus on the build up of radiation damage in the absence or presence of implanted gas.

This paper reports on a number of ongoing studies being carried out at MIAMI, and also at JANNuS (Orsay, France) and the IVEM / Ion Accelerator Facility (Argonne National Lab, US). This includes recent work on He bubbles in SiC and Cu; the former work concerned with modification to bubble populations by ion and electron beams and the latter project concerned with the formation of bubble super-lattices in metals.

A study is also presented consisting of experiments aimed at shedding light on the origins of the dimensional changes known to occur in nuclear graphite under irradiation with either neutrons or ions. Single crystal graphite foils have been irradiated with 60 keV Xe ions in order to create a non-uniform damage profile throughout the foil thickness. This gives rise to varying basal-plane contraction throughout the foil resulting in almost macroscopic (micron scale) deformation of the graphite. These observations are presented and discussed with a view to reconciling them with current understanding of point defect behavior in graphite.

*Microscope and Ion Accelerator for Materials Investigations

INTRODUCTION

MIAMI is a facility permitting in-situ ion irradiation of thin foils within a Transmission Electron Microscope (TEM) which has been constructed with funding from the UK Engineering and Physical Sciences Research Council (EPSRC) and which is now located at the University of Huddersfield, UK. A full description of the facility can be found elsewhere [1] and the major technical specifications are listed in Table 1. A primary focus of MIAMI is the study of candidate materials for both Generation IV fission reactors and future fusion reactors. In particular, we aim to study the combined effect of the presence of gases such as He, high temperature and displacing irradiation on the properties of a variety of potential nuclear reactor materials including steels, refractory metals and ceramics. In order to implant light elements such

Specifications	
TEM	JEOL JEM-2000FX
e-Beam Accelerating Voltage	80 to 200 kV
Ion Beam Accelerating Voltage	1 to 100 kV
Ion Species	Most ions from H to W at all energies
Ion Flux	Fluxes of up to $1.5 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ for 6 kV He (for example)
Angle between Ion and Electron Beams	30°
Temperature	100 to 370 K or RT to 1270 K
Image/Video Capture	Gatan ES500W Wide Angle CCD Gatan Orius SC200 (4 Megapixels)

Table (i): Technical specifications of MIAMI Facility

as He and H into foils of a suitable thickness for TEM (typically 50–100 nm), implantation energies of order a few keV must be employed. This requirement has led to the design of an ion accelerator consisting of a low energy ion-beam system capable of producing mass-analysed ion beams (of most ion species up to the mass of W at energies from 1 to 10 keV. Post-acceleration by means of a custom designed and built uniformly-graded acceleration stage then allows the ion beam energy to be increased to 100 keV (200 keV for doubly charged species) enabling, for instance, the use of self-ion irradiation to simulate neutron damage effects to total fluences of >100 displacements per atom (DPA).

The purpose of this paper is to present some ongoing work aimed at understanding radiation damage phenomena in model nuclear materials that has been carried out using in-situ ion irradiation in a TEM.

EXPERIMENTS

He bubbles in SiC

Materials in both nuclear fission and fusion reactors are subjected to complex environments in which high temperatures, displacing irradiation and the build up of transmutation products, such as helium, combine to produce generally deleterious effects. The aim of the experiments reported in this section is to determine the effects of displacing irradiation on helium bubbles in silicon carbide, a material of particular interest for applications in fusion reactors [2].

Samples of 4-H SiC were implanted with 160 keV He ions (ex-situ to the TEM at the Institut Pprime at the University of Poitiers) at 400°C and subsequently annealed at 1400°C for 15 minutes in an argon atmosphere. Cross-sectional specimens were then prepared for TEM by tripod polishing and ion-beam milling. The purpose of this specimen preparation methodology was to create a population of He bubbles, with a mean diameter of a few nanometers, in a defined band within the specimen in order to monitor changes in bubble size, shape and position under subsequent heavy-ion irradiation. These samples were transferred to the JANNuS Facility, Orsay, France, where they were irradiated in-situ in a Technai G2 TEM with 4 MeV Au ions with the specimen held at 700°C. The TEM was initially operated at 200 kV and the electron beam was continuously incident on the area of sample being followed during the ion irradiation. The ion flux was in the range 3 to 6×10^{11} ions/cm²/s and the specimens were irradiated to fluences in the range 5 to 10×10^{15} ions/cm². Images of helium bubbles within the sample were captured regularly throughout the experiments with the objective lens underfocused by ≈ 800 nm to obtain Fresnel contrast in the bubbles.

Figures 1a) and b) show the changes to the bubble distribution following Au ion irradiation to a fluence of 10^{15} ions/cm². It can be clearly seen that a significant reduction in bubble size has occurred. The mean bubble size changes by 21% from 4.8 nm to 3.8 nm. Qualitatively similar effects have been seen during heavy ion irradiation of He bubbles in Al [3] and in this case the changes were attributed to a ballistic scattering of the helium from the bubbles by the heavy ion irradiation coupled with a re-equilibration of the bubble pressure by interaction of the bubbles with the flux of Frenkel defects resulting from the irradiation.

During in-situ experiments carried out in a TEM, there is always the possibility that the electron beam may have an influence on observed processes. It is therefore generally necessary to carry out control experiments in which the possibility of effects due to electron irradiation are eliminated or significantly reduced. The experiment whose results are shown in Figures 1a) and b) was therefore repeated but, in this case, with the TEM operating at 80 kV and only switched on to record occasional images (thus greatly reducing the total electron fluence). It should be noted that the maximum energy that can be transferred from 200 kV electrons to Si, C and He atoms is 19.4, 43.7 and 131.2 eV, respectively. For 80 keV electrons, the equivalent values are 7.0, 15.8 and 47.3 eV, respectively.

The results of the experiments carried out under these conditions (80 keV electron beam mainly off) are shown in Figures 1c) and d). Despite the fluence of Au ions being almost 30% higher in this case compared to that for Figure 1b) it can be seen that, although some reduction of bubble size has taken place, the effect is significantly smaller than in the experiment in which the 200 keV electron beam continuously irradiates the specimen.

In order to attempt to explain these observations, we have modeled the ejection of the He out of the bubbles and into the SiC matrix by the 200 keV electrons using a combination of Monte-Carlo (MC) and Molecular Dynamics (MD) modeling. The MC calculations were performed using the PENELOPE code [4] to determine the spectrum of energy transferred to the helium atoms by the electrons. The density assumed for the He was derived from the equilibrium pressure of a bubble 4 nm in radius coupled with an equation of state due to Mills et al. [5]. The results of this calculation are shown in Figure 2a). An estimate of the probability of ejection of the He into the SiC matrix was then calculated by MD modeling the impact of several hundred individual He atoms with a SiC (010) surface at energies of 20, 40, 60, 80 and 100 eV. The simulations used a combination of Brenner potentials [6] for the C and a Tersoff potential [7] for

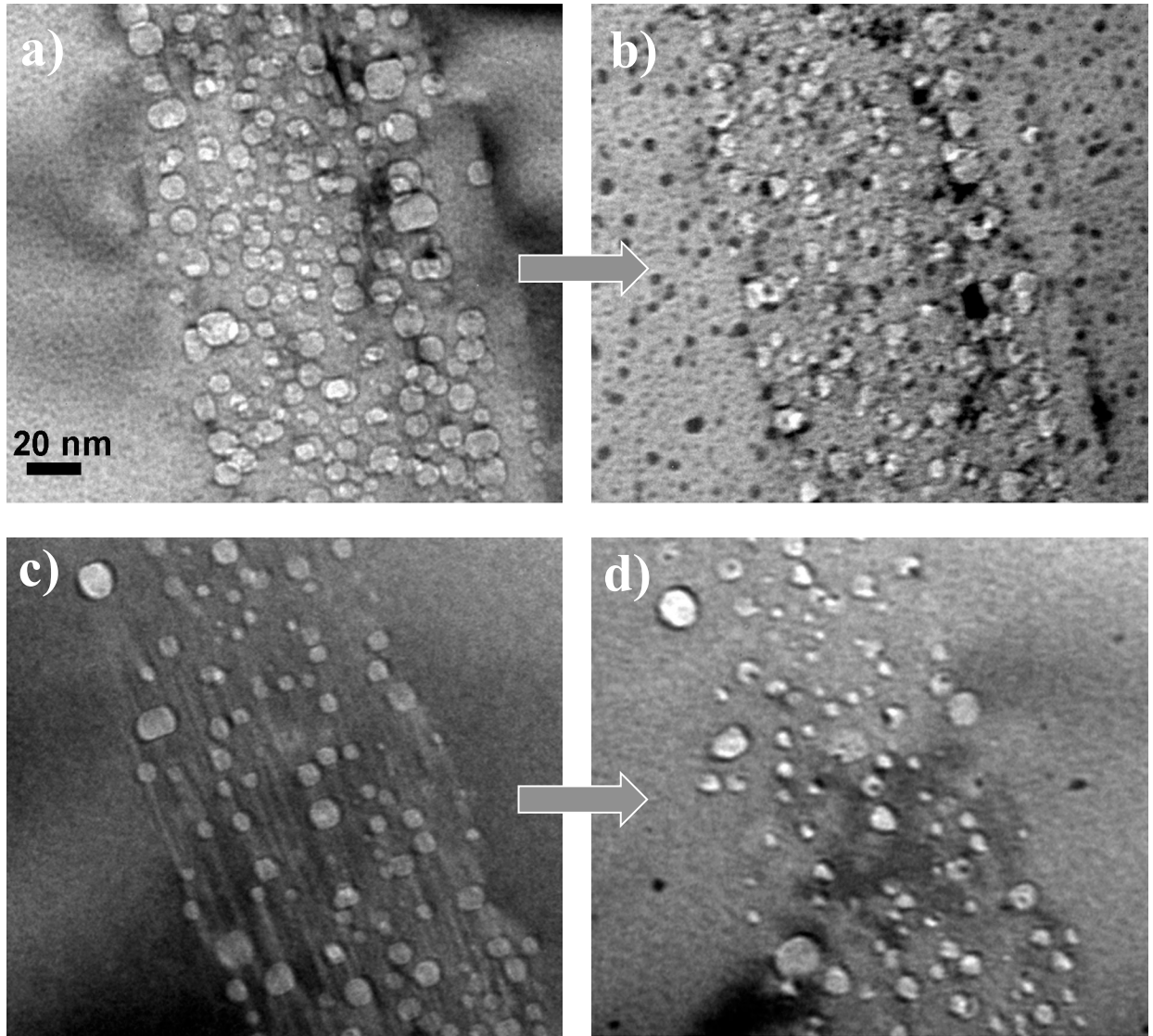


Figure 1: Bright field underfocused (≈ 800 nm) TEM micrographs: a) and c) initial He bubble distributions in two different samples of SiC prior to ion irradiation at 700°C ; b) He bubble distribution following irradiation with 4 MeV Au ions to a fluence of 5×10^{15} ions/ cm^2 with 200 keV electron beam continuously incident on the area shown; d) He bubble distribution following irradiation with 4 MeV Au ions to a fluence of 6.4×10^{15} ions/ cm^2 with 80 keV electron beam incident only for capturing of images. See text for further details. Scale marker in a) applies to all four images.

the Si-C with the He modeled using a repulsive ZBL potential [8]. The He atoms were normally incident on the SiC surface and (unlike the case within a bubble) no dissipation of the energy by means of He-He collisions was included. The MD simulations thus served to maximize the probability of the ejection of the He into the SiC matrix. This data was then fitted by means of a second-order polynomial which was also used to extrapolate the data to the maximum transferred energy of 131 eV.

The total electron fluence incident on the specimen during the experiment illustrated in Figures 1 a) and c) was approximately 10^{21} electrons/ cm^2 . By combining this value with the results presented in Figures 2a) and b), the amount of helium ejected from the bubbles into the

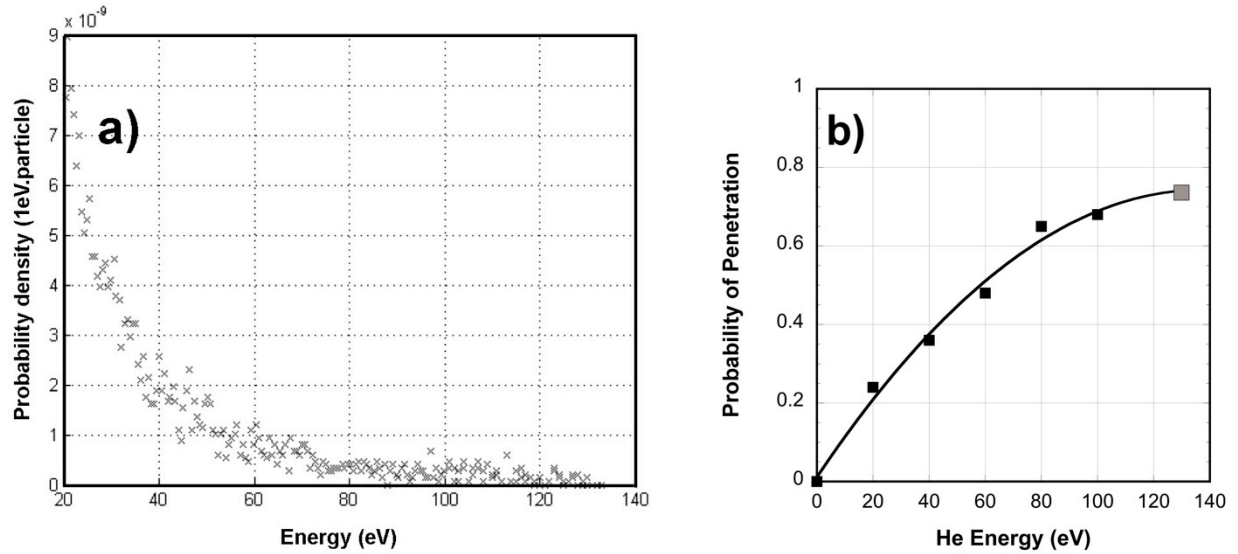


Figure 2: a) Energy transfer from 200 keV electrons to helium at a density appropriate to an equilibrium bubble with 4 nm radius calculated using the Monte-Carlo code PENELOPE [4]. b) Results of molecular dynamics simulations showing probability of penetration of a helium atom with energy in the range 0 to 100 eV into an SiC slab and extrapolated to 131 eV using a 2nd order polynomial fit shown by solid curve. See text for further details.

SiC matrix by the electrons can be estimated. It should be noted that this calculation should yield a maximum figure both because of the maximizing assumptions in the MD simulations and because no account is taken of diffusion of He back into the bubbles. If it is assumed that the bubbles that have lost He are able to re-equilibrate their pressure, by interaction with the flux of Frenkel defects, then the calculated reduction in He content could be used to calculate bubble size. The result of this calculation, however, is that only $\approx 0.15\%$ of helium would be displaced from a 4 nm radius bubble as a result of the energy transfer from the electron beam resulting in a negligible change in bubble size. This effect is, thus, insufficient to account for the significant differences in bubble size reduction that are observed with continuous and minimized electron irradiation in our experiments. The observed effects would, thus, appear to result from synergistic effects of combined ion and electron irradiation. Experiments involving a comparison between sequential and concurrent electron and heavy-ion beam irradiation are underway in our laboratories in order to test this hypothesis.

Bubble superlattices in metals

Superlattices of both voids [9,10] and He gas bubbles [11,12] in metals were first observed in the 1970s, with voids having a consistently larger lattice spacing than the bubbles. Although much experimental and theoretical work has been published in an attempt to explain the lattice formation mechanism(s) there is, as yet, no unequivocal identification of the mechanism in either case – although 1-D and 2-D interstitial diffusion have been considered and the latter would seem to be a strong candidate for the case of void lattices in bcc metals [13,14].

Bubble lattice (BL) formation by means of in-situ inert-gas ion implantation in a TEM would appear to offer the possibility of shedding some light on the mechanism(s) involved. We report in this section on some preliminary experiments on BL formation in metals. Further work on this topic will be reported elsewhere in these proceedings [15].

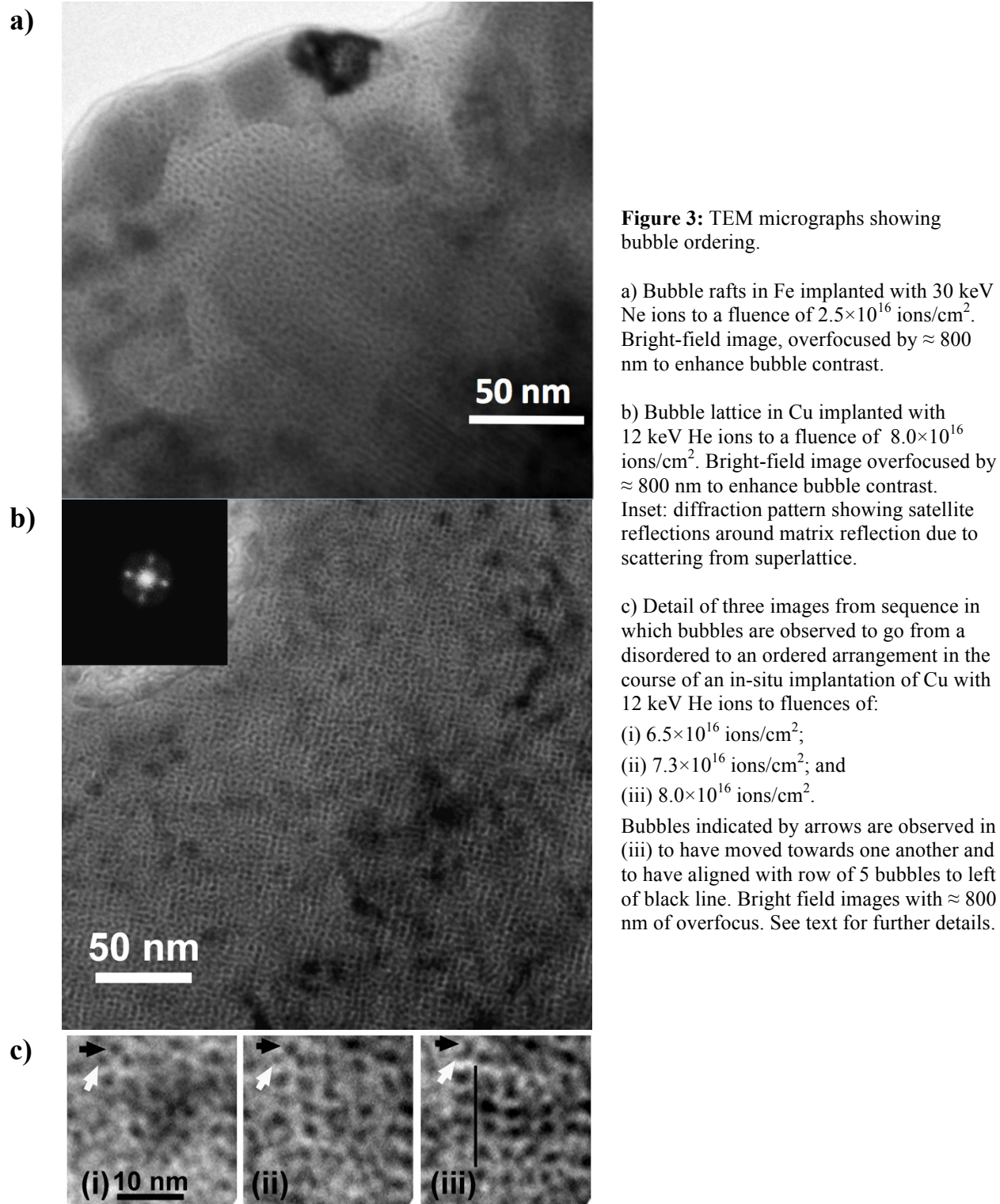


Figure 1a) shows a ≥ 1 -dimensional ordering of bubbles discovered in a single grain of polycrystalline Fe implanted with 30 keV Ne ions. To our knowledge this is the only example of the ordering of Ne bubbles. Although He bubble ordering has been observed in a range of metal lattices (fcc, bcc and hcp), lattices of bubbles involving the heavier inert gases have been much

less frequently reported in the literature, e.g. by Mazey and Evans [16] and more recently by Gan et al. [17]. In general, bubble lattices have been formed by implantation into bulk materials which were subsequently back-thinned to prepare TEM foils. Following the serendipitous observation of the Ne bubble rafts we carried out a number of experiments aimed at determining whether it was possible to form bubble lattices by direct implantation into TEM foils – a fundamental requirement for in-situ experiments.

The in-situ experiments consisted of He implantation at room temperature into TEM foils of single crystal Cu that were prepared using a Focused Ion Beam (FIB) system. The foils were prepared so as to have a thick “frame” around the electron transparent region in order to minimize localized tilting of the foils that we had previously observed to occur when using larger, electrochemically-thinned foils. The absence of localized tilting facilitates the tracking of the motion of individual bubbles in the course of the experiments

Figure 3b shows the result of an experiment in which a single-crystal Cu foil (with a $\langle 100 \rangle$ surface normal) has been implanted with 12 keV He at room temperature. The bubble lattice can be clearly seen and closely resembles those reported by Johnson and Mazey for He implanted into bulk copper at 30 keV [12]. The in-situ experiments also confirm that the bubbles first nucleate in a disordered arrangement which changes to an ordered one under continued irradiation. This process can be seen in Figure 3c) where a degree of ordering can be seen to develop on progressing to higher fluences (panel (i) to panel (iii)). The ordering can be seen as an alignment of bubbles approximately parallel to the black line in panel (iii). In this image sequence, the two bubbles indicated by the arrows can be seen to move closer to alignment with five bubbles below them in the image that have become aligned by the fluence in panel (iii). The analysis of many such image sequences is currently underway in our laboratories and will be compared with images generated from software such as that developed by Evans [13,14] to model the effects of 1-D and 2-D interstitial diffusion on bubble ordering. By direct comparison of the experimental and theoretical dynamics of bubble lattice formation we thus hope to determine the operational mechanism(s).

Ion-beam induced mechanical deformation of single-crystal graphite

Graphite is known to undergo dimensional change when subjected to displacing irradiation [18]. In particular, graphite crystals are observed to undergo a contraction of the basal planes coupled with an expansion along the c-axis. This has important implications for nuclear fission reactors that employ graphite as a structural component and moderator and also potentially to graphene-silicon hybrid electronic devices. Although this phenomenon is well documented, the underlying mechanisms are not well understood.

In order to shed some light on the atomistic details of this effect, we have carried out a series of ion irradiation experiments on monocrystalline graphite in-situ in a TEM. We have reported recently on the deformation produced in thin single-crystal graphite TEM foils when irradiated with 60 keV Xe ions to low fluences at room temperature [19]. In films approximately 25 nm in thickness, this irradiation produces a damage profile that is calculated, using the Monte-Carlo code SRIM [8], to be peaked in the lower part of the film (where the top surface is defined as the one on which the ion beam is incident), at a depth of around 17.5 nm. Irradiation thus results in an inhomogeneous accumulation of atomic displacements that was observed to give rise to the formation of basal-plane dislocations and their propagation across the film leading to the formation of kink-bands at a fluence of only 1.2×10^{13} ions/cm². The kink bands

are a mechanical deformation of the film into ridges that form in order to accommodate the non-uniform contraction of the basal planes.

Contraction of the basal sheets of graphite is likely to occur due to the formation of vacancies by the displacing irradiation, and their agglomeration in a basal sheet to form a 1 or 2-dimensional extended defect. Rebonding of the carbon atoms “across the gap” will then result in a contraction of the basal sheets [20]. A fundamental requirement is thus that the vacancies produced within the collision cascade have a sufficient degree of mobility to agglomerate in this way. However; values for the vacancy migration energy from current literature are in the range 1.0 – 1.1 eV [21,22] with historical values never below 1 eV. For a migration energy of 1 eV (and a rate constant of 10^{14} Hz) a vacancy would make only one jump every 10 minutes at room temperature. Even during the thermal spike phase following an atomic collision cascade, the dilute nature of the cascade in graphite coupled with the short duration ($\approx 10^{-11}$ s) of the spike makes it unlikely that any significant motion would take place of a defect whose migration energy were ≥ 1 eV. In order to carry out experiments in which there is a higher degree of certainty that vacancy motion does not occur, we carried out a series of experiments in which the graphite was irradiated at a temperature of 20 – 25 K. At this temperature there will be no thermal migration of vacancies.

Samples of thin graphite were produced by mechanical exfoliation [23] and were mounted on Formvar microgrids on copper mesh TEM grids using techniques reported previously [19]. In-situ irradiations were performed using 60 keV Xe ions at 20–25 K at the IVEM / Ion Accelerator Facility at Argonne National Laboratory which has been described in detail elsewhere [24]. A liquid-helium cooled specimen rod is available on this facility and was used to cool the graphite specimens to 20–25 K during our experiments. As in our earlier experiments, a low ion beam flux of $\approx 10^{11}$ ions/cm²/s was used to prevent any sample heating.

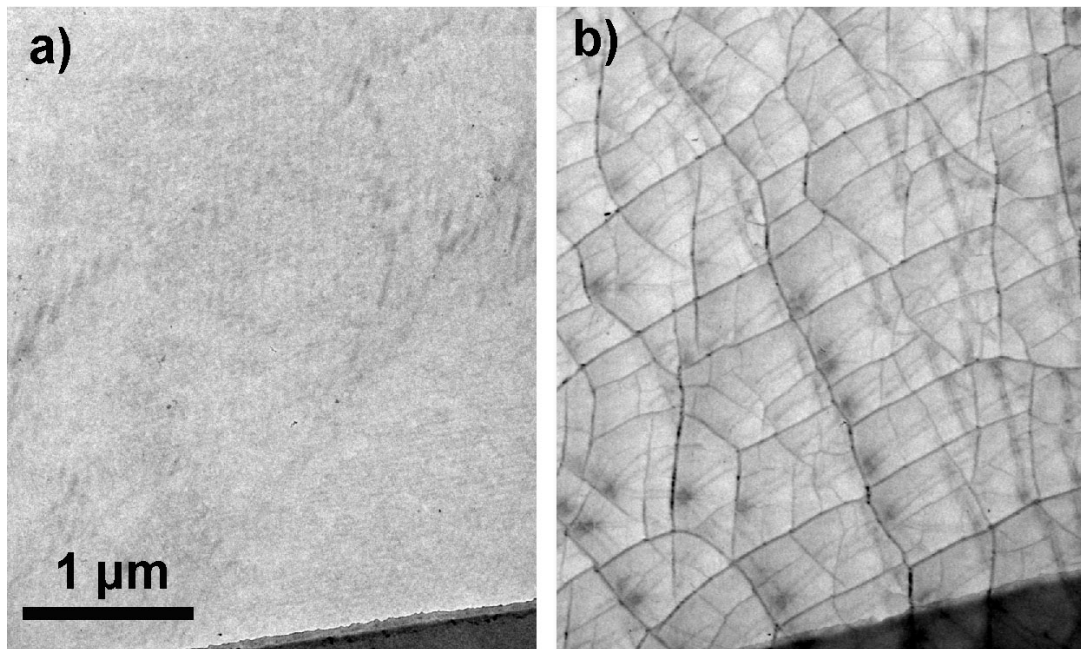


Figure 4: Bright-field images of a single-crystal graphite film a) prior to ion irradiation and b) following irradiation at a temperature of 24 K with 60 keV Xe ions to a fluence of 1×10^{14} ions/cm² with a flux of $\approx 1 \times 10^{11}$ ions/cm²/s. Scale marker on a) applies to both images. Bar of Formvar micro-grid is visible in the lower part of the micrographs.

The Hitachi H-9000NAR TEM used for the in-situ observations was operated at 100 kV to minimize the known damaging effects of electron-beam irradiation of graphitic materials [25].

Note that any significant perturbation of the observed effects by the electron beam was ruled-out by a comparison of the electron irradiated areas of the samples to those outside of the electron beam. Video was captured at a frame rate of 8 s^{-1} and recorded digitally using a frame size of 1000×736 pixels. Images were also recorded at the beginning and end of each experiment with a frame size of 2004×1336 pixels.

In all experiments conducted with the specimen cooled to a temperature in the range 20–25 K, behavior similar to that observed for irradiations at room temperature were observed. In particular, at fluences of $\approx 10^{13}$ ions/cm², kink band formation was observed to begin, leading to a complex network of kink bands and doming of the film between the bands at the final fluences used of 10^{14} ions/cm². This can be seen clearly in Figure 4 where an area of graphite film before and after irradiation to a fluence of 10^{14} ions/cm² is shown. Detailed comparison of this and similar images with those obtained for room temperature irradiations reveal differences in the separation and apparent symmetry of the kink-band network which we are attempting to understand in the light of the mechanical properties of graphite at the two temperatures. However, the major and significant finding of these experiments is that basal-plane contraction clearly occurs at 25 K. As this effect is believed to be due to vacancy agglomeration coupled with reconstruction of the resulting extended defect, it is difficult to understand how it is able to occur at a temperature where negligible vacancy motion would be expected with any reasonable estimate of migration energy. In fact, in order to make on the order of one thermally activated jump per second at 25 K, the migration barrier would have to be as low as 0.07 eV. These experimental results thus pose challenges for our understanding of radiation damage processes in graphite and attempts are currently underway to model them using multiscale modeling.

CONCLUSIONS

This paper has presented experimental work carried out using in-situ ion accelerator / TEM facilities in which the access to real-time observations of radiation damage / implantation processes has yielded significant insights into the atomistics of the processes taking place. In He bubbles in SiC, the formation of inert gas bubble lattices in metals and radiation induced mechanical deformation of graphite, the results have raised new questions which themselves are leading to further lines of investigation – experimental, theoretical and through modeling. The progress made in all three examples would have been unlikely to have occurred without the use of the in-situ technique.

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