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Dynamic microstructural evolution of graphite under displacing irradiation

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ABSTRACT

Graphitic materials and graphite composites experience dimensional change when exposed to radiation-induced atomic displacements. This has major implications for current and future technological ranging from nuclear fission reactors to the processing of graphene–silicon hybrid devices. Dimensional change in nuclear graphites is a complex problem involving the filler, binder, porosity, cracks and atomic-level effects all interacting within the polygranular structure. An improved understanding of the atomistic mechanisms which drive dimensional change within individual graphitic crystals is required to feed into the multiscale modelling of this system.

In this study, micromechanically exfoliated samples of highly oriented pyrolytic graphite have been ion irradiated and studied *in situ* using transmission electron microscopy (TEM) in order to gain insights into the response of single graphitic crystals to displacing radiation. Under continuous ion bombardment, a complex dynamic sequence of deformation evolves featuring several distinct stages from the inducement of strain, the creation of dislocations leading to dislocation arrays, the formation of kink band networks and localised doming of the sample. Observing these ion irradiation-induced processes using *in situ* TEM reveals previously unknown details of the sequence of microstructural developments and physics driving these phenomena. A mechanistic model consistent with the microstructural changes observed is presented.

1. Introduction

The response of graphene and other graphitic materials to radiation-induced atomic displacements is poorly understood despite the large number of technological and industrial applications upon which it impacts. For example, polycrystalline graphite composite materials are used in current nuclear fission reactors such as Advanced Gas-cooled Reactors (AGRs) [1] and are proposed for use in Generation IV (GenIV) reactor designs including the Very-High Temperature Reactor (VHTR) and Molten Salt Reactor (MSR) [2]. Current nuclear fission reactors typically expose core components to radiation damage levels up to the order of 10 Displacements Per Atom (DPA) [3] with GenIV increasing this up to 200 DPA over the expected operational lifetimes [2]. In order to produce the safety case for the extension of the operational lifetime of existing nuclear power stations and to develop materials for future reactor designs, it is important that the effects of displacing radiation be

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better understood. The deployment of graphene nanocomposite materials [4–6] in extreme environments is highly desirable but their safe use will require an understanding of the damage mechanisms in these materials. Furthermore, the successful development of graphene-based heterostructures for integrated electronics [6–8] will rely on the radiation stability of these devices both during processing and whilst in service.

One of the key challenges for both functional and structural applications of graphitic materials is radiation damage and in particular the known phenomenon of dimensional change under displacing irradiation. In nuclear graphite, this is a multiscale problem requiring the consideration of atomic-level effects as well as the filler, binder, porosity and cracks all interacting within the polygranular structure. In both the polygranular and single-crystal cases, the resulting dimensional changes can be significant in terms of the magnitude and the implications for materials applications.

At the single-crystal level, dimensional change consists of a contraction in the *a*/*b*-directions (i.e. in the basal planes) and an expansion in the *c*-direction (i.e. normal to the basal planes) [9–13]. The atomistic mechanisms which give rise to these changes are the subject of debate and the focus of considerable on-going scientific research [14–16]. One proposed theoretical model, which we refer to as the "point defect" model, suggests that radiation-induced vacancies agglomerate in the basal planes to form small dislocation loops. These then collapse causing contraction in the *a*/*b*-directions with expansion in the *c*-direction attributed to the agglomeration of interstitials between the basal planes to form new layers [17,18]. More recent atomic-level models of defects in graphite and graphene offer alternative possibilities for the contraction of the basal plane in the form of 5- and 7-member rings [19–24] or the rucking of the basal planes due to dislocation motion [14]. However, none of these models has been conclusively verified by experiment.

Considerable insight into the response of a material to displacing irradiation and, in particular, into the formation, evolving morphology and behaviour of extended defects can be obtained by performing *in situ* ion and/or electron irradiation studies within a transmission electron microscope (TEM). The use of such techniques has made important contributions to understanding in areas such as the effects of ion-induced collision cascades on extended defects [25] and surfaces [26], the effects of fluxes of point defects on precipitates in metals [27], nanocluster ejection [28,29] and the development of amorphous zones in silicon [30].

To date, however, the majority of work on microstructural radiation damage in graphite has been confined to *ex situ* analysis of neutron (for examples see [31–35]) and ion (for examples see [36–40]) irradiated material with only a small number of studies using TEM with *in situ* ion [41–45] and electron [15,46–48] irradiation. Radiation damage is a complex dynamic process in which multiple mechanisms compete to determine the ultimate outcome. It is necessary to observe the system *in situ* whilst under irradiation in order to capture its evolution rather than to examine only the end-state accessible in *ex situ* studies. In this paper we report *in situ* TEM observation of the dynamic sequence of structural changes that occur as a result of ion irradiation induced mechanical deformation behaviour of a single graphitic crystal.

The purpose of this work is to provide a better understanding of the underlying mechanisms that give rise to the known phenomenon of dimensional change in single-crystal graphite. This would provide useful knowledge to inform a full multi-scale model of polygranular nuclear graphite, which would also need to consider the behaviour of grain boundaries, filler, binder, cracks and porosity under displacing irradiation. The work has direct application to the understanding of radiation damage in graphene–silicon heterostructures.

2. Experimental methods

2.1. Sample preparation

Samples of thin graphite were produced by micromechanical cleavage of highly-orientated pyrolytic graphite (HOPG). Suitable flakes were identified using an optical microscope to observe the contrast produced by the flakes deposited on a silicon wafer with a ~90 nm SiO_2 surface oxide [49,50]. A 200 nm poly(methyl methacrylate) (PMMA) layer was then spin-coated on top. The flakes were detached from the silicon substrate by soaking in 3% potassium hydroxide for a few hours at room temperature to dissolve the SiO_2. The samples were then rinsed in deionised water and transferred to TEM grids. Finally, the PMMA was dissolved with acetone and the TEM grids with free-standing graphite were dried in a critical-point dryer. Further details of the sample preparation techniques have been reported previously [51,52].

The TEM samples produced in this way featured electron-transparent large single crystals of graphite with lateral dimensions typically of 10–100 μm. The single crystal TEM diffraction data and lack of Moiré fringes under TEM observation indicated the absence of rotational misorientation between the basal planes. Raman spectroscopy was performed on some samples using a Renishaw 1000 Raman Spectrometer with a 514 nm wavelength laser and ~2 μm spot size. The samples were found typically to be free from significant levels of defects and dopants as indicated by the absence of a prominent D peak in the Raman spectra [53–55].

It was vital to use high quality single crystals for this work to allow the clear observation and interpretation of features such as diffraction contrast due to the strain fields around dislocations. In more-polycrystalline graphite samples the contrast can be dominated by twist dislocations and/or Moiré patterns due to rotational misorientation between the basal planes. In nuclear graphites, the inhomogeneous polygranular structure of those materials similarly makes definitive identification and analysis of defects problematic in many cases. Whilst the single crystals used in this work offer the clear advantage of suitable crystallographic orientation and the absence of obfuscating contrast in the TEM, they are relatively-simple systems and thus extrapolation to the more complex case of nuclear graphite must be undertaken with caution. These are good model systems in which to explore the dynamic processes which can occur in single crystallites but do not contain features such as filler and binder phases, cracks and porosity which play significant roles in radiation induced dimension change in polygranular nuclear graphite. Therefore it is the aim of the current study to explore the atomistic and single-crystal level effects to feed into a better