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Atomic scale mechanisms for the amorphisation of irradiated graphite

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ABSTRACT

Molecular dynamics simulations using empirical potentials reveal HOPG graphite's response to irradiations. Two different methodologies: displacement cascades and Frenkel pair accumulations, probe the primary damage and dose effect, respectively. This work reveals that in HOPG graphite primary knock-on atoms with initial energies less than 40 keV do not induce amorphisation by direct impact. Rather, defects stabilise and persist after a single irradiation event. However, amorphisation occurs via the accumulation of defects mimicking multiple events. Before amorphisation the graphite structure undergoes three stages of evolution characterised by (i) an increase in point defects; (ii) a wrinkling of graphene layers pinned by small amorphous pockets; and (iii) a full amorphisation of the structure via percolation of the small amorphous pockets. This structural evolution gives way to an irradiation induced volume change of the HOPG graphite. In the first stage, interstitials contribute, as expected, to c-axis swelling, while vacancies contribute to basal plane shrinkage. Subsequently, rippling of the graphene layers induces the overall volume to change. A power law relation illustrates the relation between the c-axis swelling and the basal-plane shrinkage as a function of the irradiation dose.

1. Introduction

In the early age of the nuclear industry, graphite was widely used as a neutron moderator in gas-cooled reactors [1,2]. Since then, new nuclear applications came about for graphite with high temperature gas-cooled reactors or for fusion reactors [3]. Graphite is the first and one of the most extensively studied nuclear material. Recent reviews [1,2,4–6] provide an overview of the research's current knowledge on nuclear graphites. These reviews describe a plethora of data with a variability connected to the structures of different grades of nuclear graphite. Literature exemplifies various reasons for these discrepancies. First, virgin nuclear graphites (i.e. before introduction in nuclear power plants) depend strongly on the fabrication cokes and synthesis routes [5]. These two parameters radically drive the microstructure and the impurities of nuclear virgin graphites. The second explanation comes from the operating conditions of the nuclear power plants, which vary from one site to another. This includes varying working temperatures and neutrons fluxes between different sites. Moreover, these variables fluctuate within single reactor during its lifetime. These huge differences indeed drastically alter the response of graphite to neutron irradiation [6]. Rationalising the behaviour of "nuclear graphite" under

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neutron irradiation is therefore not straightforward. Some studies [7] strive to understand polycrystalline nuclear graphite in terms of the effect on individual crystallites, using a close relative of the single crystal: Highly Oriented Pyrolytic Graphite (HOPG). Literature exemplifies the advantages of HOPG under specific irradiations [8], which provide a detailed insight. In the studies presented in this article, we take the same approach. This reduces the domain of validity of the results proposed herein. Yet, it helps in rationalising the main behaviour of "nuclear graphite" under irradiation by comparing and contrasting results in HOPG with experimental data.

Recalling, fast neutrons passing through graphite slow down via elastic collisions with carbon atoms (C-atoms) present in the matrix. These elastic collisions cause the acceleration of the primary knocked C-atoms (PKAs). Subsequently, theses PKAs interact with other C-atoms via electronic or nuclear interactions. This reduces their velocity, which drops until they finally stabilise in the graphite matrix. Numerous defects are created along the PKA trajectories, hence along the trajectories of neutrons. Some defects are simply point defects such as vacancies and interstitials [9,10] others extend to more complex defects such as prismatic dislocations [9–12].

At the macroscopic scale, irradiated HOPG swells and shrinks perpendicular and parallel, respectively, to the graphene layers [13]. Irradiations below 250–300 °C have drastic consequences on the thermal expansion [2,14,15], the thermal conductivity [16], and the mechanical behaviour [5] of the irradiated graphite. Defects produced by irradiation also act as energy reservoirs. The annealing of these defects is activated at high temperature and was observed years ago by Wigner [19].

Wigner [19] hypothesized that the key to understand graphite under irradiation is the kinetics of point defects (interstitials and vacancies). Although originally proposed in the sixties the idea stands nowadays, yet the very details of the underlying mechanisms remain under debate [1,5]. Marsden [2] provides a recent review of the historical first scenario referred as the standard model. The standard model theorizes point defects of the same type aggregate during irradiations forming dislocation loops. Interstitials form dislocation loops with a component of its Burger vector parallel to the *c*-axis whereas vacancies form dislocation loops with a component of its Burger vector in the basal plane. These aggregations rely on the diffusion of (i) interstitials between the graphene layers and (ii) vacancies. In the standard model, variation in the lattice dimension in irradiated graphite arises from the strain induced by point defects [20,21]. Some authors believe interstitials located between graphene layers increase the lattice parameter and promote the swelling along the *c*-axis [17] while others suggest the clusters of n carbon atoms where $n = 4 \pm 2$ perform this role [18]. The overwhelming majority of *c*-axis lattice parameter changes with irradiation disappears at about 300 °C. Similarly, vacancies help shrinkage along the basal planes. Niwase [22,23] uses Raman spectra to study the creation of extended defects in relation to the standard model. This research leads to an alternative interpretation where dislocation dipoles nucleate by reconstruction of di-vacancies. Subsequently, these dislocation lines grow by knock-ons at the ends of the dislocations lines.

Recent works [4,13,24] show that the behaviour of interstitials determined by modern theory (e.g. Density Functional Theory) is hardly compatible with the roles assigned to them in the literature, particularly in works which assume a non-bonded interstitial [17]. Irradiation induced interstitials are not mobile at low temperatures; therefore, (i) they cannot aggregate into new graphene sheets; and (ii) they cannot release Wigner energy above 300 °C. Heggie et al. [13] propose an alternative scenario (henceforth called the Heggie model) based on the buckling of graphene layers at the nanometer scale. The seeds for plane buckling depend on spiro-interstitials, which in turn hinge on temperature. Below 250 °C, spiro-interstitials lock the basal dislocations provoking buckling of the graphene layers. Above 250 °C, basal dislocations of opposite signs freely evolve and build up, which causes folding of the graphene layers. The authors of the Heggie model claim a better comparison between experimental data and their model [13]. In particular, this model anneals graphene folds rather than point defects (i.e. standard model) at low temperatures to explain Wigner energy release. Despite the apparent paradox, these models do not completely oppose one another. Both models explain parts of TEM experimental observations and propose explanations of the dimensional changes of irradiated graphite. Moreover, atomistic calculations (*ab initio* [25–29] or molecular dynamics using empirical potentials [30–32]) collaborate parts of both models. Surprisingly, atomistic calculations infer more or less the existence and more importantly the configurations of defects created by irradiation. For example, Gulans et al. hypothesize the role of bound and free interstitials [26], yet to date, no data concerning the primary damages could support the hypothesis. Formation energies and activation energies for the migration of point defects feed mesoscopic models or correlate with specific experiments [2,4,13,22–24]. But, point defect formation energies concern systems close to thermodynamic equilibrium. Activation energies also concern isolated defects in perfect graphite. Hence, the model description seldom reflects the out-of-equilibrium nature of irradiation.

In summary, the models for the evolution of the irradiation damages in graphite rely on the assumption that primary damages produced by irradiation are point defects. To our knowledge, few direct atomic scale data are available on the primary damages induced by irradiation in graphite. For example, Pregler and coworkers [31] investigated low energy (50 eV) displacement cascades. The knowledge of the primary damage state is drastically missing to robustly build the models mentioned above. We therefore address this point in the present work. We investigate in the first part the primary damages produced by single irradiation events at the atomic scale in HOPG graphite by means of displacement cascades [36]. And additionally, we tackle the effect of the irradiation dose in the second part by applying the Frenkel pair accumulation methodology [38,39]. The next section of the paper (Section 2) summarises technical details. More precisely, this section recaps the graphite structure, the huge variety of possible point defects, the displacement cascade, and Frenkel pair methodologies. Section 2 further details a novel specific