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Irradiation damage in nuclear graphite at the atomic scale

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ABSTRACT

Microstructures of nuclear graphite have been investigated based on the analysis of both X-ray diffraction patterns and High Resolution Transmission Electron Microscopy images (HRTEM) from experiments and from molecular dynamics simulations. One filler particle – composed of almost aligned crystallites separated by Mrozowski cracks – and the whole sequence of single crystal graphite irradiated from its virgin state up to highly damaged (64.5% of defects) have been simulated. Simulations are assessed against experiments based on the analysis of its microstructures extracted with Bragg's law and Scherrer's equation applied to simulated X-ray diffraction patterns. In particular, the evolution of cell parameters with defect concentration generated by irradiation agrees well with experimental observations. Simulated HRTEM images show many features observed in experimental images in both virgin and irradiated French nuclear graphite. Some of these features can be linked unequivocally to defined atomistic configurations. Basal grain boundaries (GBs), Mrozowski cracks, graphene sheets and their folding belong to this category. Conversely, some patterns in simulated HRTEM cannot be related to a unique atomistic configuration and might eventually give rise to misleading interpretation. This is evidenced for edge dislocations in virgin nuclear graphite as well as for residues of graphene layers in highly damaged graphite.

1. Introduction

Graphite is both an historical and an up-to date material for nuclear industry. It has been extensively used as a neutron moderator [1] in early gas-cooled reactors and it is still nowadays envisioned as a choice material in high temperature gas-cooled reactors [2] as well as in fusion reactors [3]. Graphite is one of the most extensively scrutinized material in nuclear industry and numerous reviews provide overviews of the current knowledge. It is a very complex material [4] and its microstructure strongly depends upon synthesis routes and operating conditions during in-pile lifetime [5]. In addition, it contains long-life radionuclides like ^{36}Cl, ^{14}C and ^{3}H produced by in-pile neutron irradiations [6–8].

Virgin nuclear graphite is mainly composed of filler particles and binder phase [9,10]. Filler particles contain domains of aligned individual crystallites separated by micrometer pores. Individual crystallites (single crystal graphite) of each domain are stacked along the c-axis. They exhibit Mrozowski cracks in between basal planes [9]. After in-pile neutron irradiation, one observes both highly damaged zones of few hundred of nanometers and almost perfect crystallites.

Microstructure of nuclear graphite is commonly evaluated by using X-ray diffraction pattern (XRD), Raman micro-spectrometry (μ-Raman) or High Resolution Transmission Electron Microscopy images (HRTEM). Each of these techniques provides valuable information at different scales. Indeed, a global characterization is easily extracted from XRD. One can derive cell parameters and mean crystallite sizes. Data at the atomic scale are obtained from the analysis of μ-Raman spectra [11–13]. Raman signature of defects is then related to microstructure derived from XRD. This approach is relevant as long as damage is homogeneous at the μ-Raman scale [11]. However, damaged zones of irradiated nuclear graphite are far smaller than the resolution scale of μ-Raman of micrometers. It is therefore very likely that μ-Raman spectra probe crystalline zones *and* damaged zones as well. Linking damaged zones of neutron irradiated graphite with quantification of defects using μ-Raman is therefore challenging.

HRTEM appears to be the relevant tool for the characterization

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of nuclear graphite at the nanoscale. It is suitable to extract structural or atomic scale data from this technique. Two methodologies can be found in the literature to achieve this goal. The one developed by Leyssale et al. [14] uses experimental HRTEM images of irradiated graphite [15] as the starting point. Applying a reverse Monte-Carlo procedure to these images, authors are able to reconstruct the very details – at the atomistic scale – of irradiated graphite observed experimentally. Alternatively, some authors adopt atomistic calculations as starting points [16–18]. They explore different types of defects (in graphite or in graphene) that are hypothesized from experimental observations [19]. From the atomistic description of these defects, they generate HRTEM images and draw conclusions by comparison with experimental images. Yet, these studies are dedicated to few defects, neglecting abundance of stable defects in irradiated graphite.

The aim of the present work is to improve the understanding of HRTEM images of nuclear graphite, starting from different types of atomic scale configurations obtained by Molecular Dynamics (MD) simulations. We explore one domain of the filler particle composed of almost aligned crystallites separated by microcracks and the entire sequence of single crystal graphite irradiated from its virgin state up to highly damaged (see our previous work [20]). In each case, we use MD simulation snapshots to extract topological information at the atomic scale and to construct XRD patterns and HRTEM images. XRD patterns are analyzed in term of microstructure, i.e. cell parameters and crystallite sizes and subsequently assessed against experimental data, in order to check the relevancy of our MD simulations. Simulated HRTEM images are then analyzed and compared with our experimental HRTEM images. Typical features like basic structural units (BSU – meant as residues of graphene layers) or like dislocations are observed in both simulated and experimental images [6,21]. The interpretation of these features are revisited based on the direct link between atomic scale configurations from MD snapshots and their corresponding simulated HRTEM.

2. Technical details

Nuclear graphite has been investigated by means of molecular dynamics (MD) simulations, using LCBOP empirical potentials with the LAMMPS code [22,23] to keep consistency with our previous work [20].

We have generated one domain of aligned crystallites [9] of the filler particle by building a cubic supercell of size $69.84 \times 69.84 \times 69.84$ nm and composed of 20 crystallites (single crystal graphite); with a total of 36 059 062 atoms (see Fig. 1). Each crystallite (single crystal graphite) is a rectangular parallelepiped of 35×35 nm^2 in the basal plane and 15 nm along the c-axis. Crystallites are stacked along the c-axis, and randomly tilted from each other with angles ranging between 0 and 20° without any weighting function. This microstructure – called hereafter nanocrystalline graphite (NCG) – is relaxed at 300 K in the NVT ensemble (constant volume and constant temperature ensemble with N carbon atoms) for 20 ps.

Irradiated single crystal graphite is examined with a supercell containing 102 400 atoms (called hereafter SCG). Radiation damages are mimicked by performing Frenkel pair accumulation (FPA). FPA methodology [20] operates by periodically creating Frenkel pairs (every 1 ps) with careful control of pressure and temperature. FPA has proven to be able to reproduce the evolution of graphite under irradiation from virgin state until complete amorphization [20]. It includes the very details of the three stages of amorphization by irradiation: (i) progressive increase of isolated point defects; (ii) wrinkling of graphene layers pinned on amorphous pockets; and, (iii) percolation of the amorphous pockets until full amorphization. Snapshot of each stage has been carefully chosen such that it gives the opportunity to examine three typical configurations of irradiated graphite.

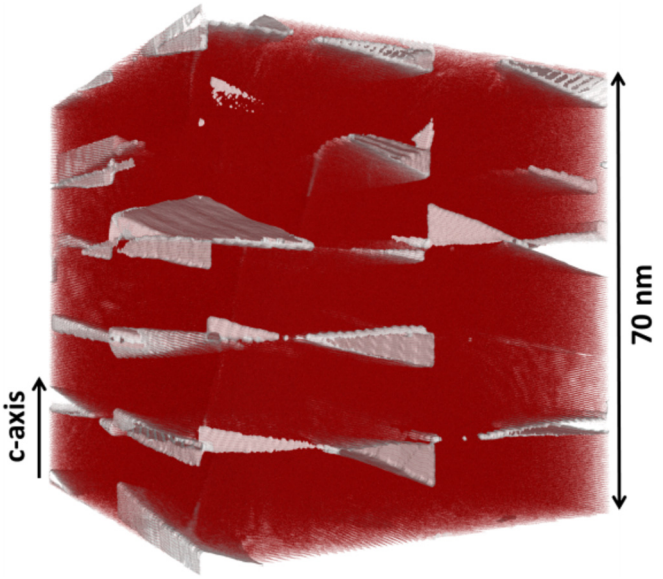

Fig. 1. 3D view of nano-crystalline graphite obtained by MD simulations and displayed with OVITO software [34,35]. Red points represent carbon atoms while white surfaces delimit nano-scale porosity, i.e. Mrozowski cracks. (A colour version of this figure can be viewed online.)

We evaluate the number of defects in our simulations by using a dedicated curvature criterion. The procedure operates in two steps. We first remove carbon atoms departing from their ideal coordination (CN) of 3 with cutoff distance of 1.8 Å. We secondly calculate a local curvature for each carbon remaining, and keep those having curvature angle higher than 32°. This criterion is detailed in Ref. [20] and is able to discriminate defects which keep their initial CN – like grafted interstitials for example.

HRTEM images are generated from MD snapshots with the Multislice code [24] wherein is implemented the eponymous methodology [25–27]. Incident beam energy is set to 300 kV and a thickness of 1 Å is chosen for each slice for diffraction/diffusion throughout the sample. Images are then generated with a spherical aberration of 2.2 nm and an objective aperture of 10 mrad.

X-ray diffraction patterns (with the $K\alpha_1$ emission of copper $\lambda = 1.54056$ Å) are calculated from snapshots of MD calculations using the Debyer code [28] wherein is implemented Debye scattering formulas [29]. We set the cutoff radius of the Fourier transform to 10 nm for SCG and 15 nm for NCG. XRD patterns are calculated in a 2θ domain ranging from 10° to 90° with a 0.005° step. We derive cell parameters using the Bragg's law, respectively from (100) and (002) peak for intra- and interlayer lengths. Average width L_a and height L_c of crystallites are also determined with the Scherrer's formula:

$$L = \frac{K \times \lambda}{B \times cos\theta} \quad (1)$$

K is set to 0.886 for the (002) peak (L_c length) and 1.84 for the (100) peak (L_a length) after Fujimoto [30]. B is evaluated for each peak from the ratio between its area and its height. They are extracted from XRD peaks fitted with a Pseudo-Voigt function using Fityk [31,32]. Note that strain broadening is not removed from XRD, leading to an underestimation of crystallite sizes L [33].

For our experimental characterizations, graphite samples originate from French Natural Uranium Graphite Gas, SLA2 (EDF