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Morphology evolution and defect distribution in irradiated graphite from molecular dynamics

Juan Liu[a], Tongxiang Liang[b,*], Wensheng Lai[c], Yuejun Liu[a]

[a] Key Laboratory of Advanced Packaging Materials and Technology of Hunan Province, School of Packaging and Materials Engineering, Hunan University of Technology, Zhuzhou 412007, China

[b] School of Materials Science & Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

[c] Advanced Material Laboratory, School of Materials Science & Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

Molecular dynamics is carried out to study the morphology evolution and point defect distribution in irradiated graphite. Collision cascade processes are simulated in a wide PKA energy range (0.5–2.5 keV) by using the AIREBO potential. The formation process of a hillock (bump) defect that frequently observed in radiation experiments is repeated at atomic level and two formation mechanisms are proposed qualitatively. One light spot of this work is the quantitative analysis of defect distribution involving total vacancy defects and classified vacancy types (monovacancy, divacancy and vacancy loop). Our data is in good agreement with other theoretical calculations and the broadly accepted Norgett-Robinson-Torrens model. An evidence of the transform between different vacancy types is provided from a statistical view, which can be illustrated that monovacancy tends to form vacancy loops by transition of divacancy. The simulations help to provide a deep insight into the cascade procedure in graphite and associate surface features with the generation of defects due to the impact of energetic particles.

1. Introduction

Nuclear graphite, acting as a fundamental core component in high temperature gas cooled nuclear reactors (HTGR), has been studied substantially on the mechanical, chemical, and electronic properties under irradiation. Oxidation resistance of nuclear graphite which critically limits the lifetime of HTGR is also one of the key issues for improvement of the next generation of nuclear power plants (Gen IV) for lifetime extension [1–3]. Atomic scale defects in graphite have a profound influence on the overall behavior without exception of oxidation property. For example, the adsorption energy of reactive species such as O_2 on vacancy defected graphite is approximately 10 times as strong as that on a defect-free graphite surface and the occurrence of vacancy defects during irradiation significantly reduces oxidation resistance of nuclear graphite [4]. Therefore, a better understanding of defect production, evolution and distribution in graphite under irradiation damage is either as the prerequisite to explore the root cause of degradation, or as a foundation for further improvement of oxidation resistance.

In addition to vacancies and interstitials, another kind of small-scale defects has been frequently observed in numerous experimental visions on graphite surface under ion bombardment, appearing as hillocks or protrusions of a few angstroms [5–7]. Scanning tunneling microscopy (STM) images of defected graphite surfaces prepared using low-energy ions show small hillocks of 2–7 Å in diameter [8]. The density of these hillock defects is less than that of ion impacts and not linearly dependent on the dose. Bending sheet is also occurred in high resolution electron microscopy (HREM) images of graphite surface damaged by particle radiation [9]. Most of the defects are considered as a result of interstitial migrations and lattice rearrangements by cascade. Theoretical calculations reveal that surface curving occurs as a result of cross-links underneath those affected area along with atomic contractions of the surrounding atoms under continuously bombardment of energetic particles [10]. Heggie et al. give the explanation based on displacement method that the buckling is resulted from the linking between two graphene sheets with different lengths, furthermore an isolated dislocation can cause buckling as well by localize a basal dislocation core artificially through pinning points [11]. They also suggest that the permanent nano-buckling which further forms a ruck and tuck defect is intrinsic to all layered materials and account for changes in dimension. Nordlund speculates that this extraordinary defect may be resulted from a surface defect called “D3” with an extra atom on the top layer

* Corresponding author.
E-mail address: liang_tx@126.com (T. Liang).

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forming a threefold coordinated vertical ring [7]. The topmost atom is about 2 Å higher than the undisturbed lattice, and its neighboring atoms have risen significantly from the surroundings. This D3 defect is considered to be the source of hillocks higher than 2 Å. Mochiji et al. suggest that the production of surface defects is caused by the enhancement of partial charge density of state at the surface and the defect size rapidly increases with the charge state of impacting Ar ions [12]. Despite the extensive experimental work and theoretical studies on radiation defects in graphitic materials [11,13–15], there are substantial gaps in our understanding of how this special type of defects is created, evolved and interacted. In this work, a typical evolution process of graphite under energetic particle radiation is repeated in the framework of molecular dynamics simulation. Deeper insight into the atomic level of irradiation and the formation mechanisms of hillock defects will be characterized.

Radiation damage by nuclear collision causes displacement of lattice atoms which further induces vacancy and interstitial defects in the crystal structure. Vacancies have been proved to be the predominant source of defects, even though significant numbers of interstitial atoms and bond switch defects (Stone-Wales rotation) also occur [7]. The distribution of point defects in irradiated graphite bulk is not only related to oxidation behavior, but also associated with mechanical and thermal properties. Calculation method has been carried out to study material property changes to crystal dimensions, elastic moduli and thermal expansion associated with atomic scale defects created by radiation damage [16].

It is difficult to determine the distribution of vacancy defects directly by experimental measurements due to the complicated and disordered graphite structure. Theoretical models relying on LSS theory have been developed to associate the implanted ions with the graphite damage, and the damage degree along depth is predicted by the concentration of implanted carbon and damage energy density indirectly [17]. Calculation simulation has shown that the maximum implanted carbon concentration locates at the depth of 47 nm with a relative atomic density of 0.35‰ under $^{12}C^{+}$ ions implantation for a fluence of 1×10^{14} ions/cm^2 [18]. In graphite, the number of defects created within the cascade is related to the amount of energy received by the target through nuclear interactions. The damage energy density as a function of depth under bombardment of $^{12}C^{+}$ with energy of 20 keV indicates that the maximum damage is not located at the surface, but at a depth of about 30 nm [8]. An increase in the number of defects up to a critical value is considered as the reason for the amorphization of graphite [19,20].

A number of theoretical models have been used to estimate the number of atomic displacements produced by a collision of a neutron and a carbon nucleus, which then permits calculations of the number of atomic displacements in a neutron spectrum, knowing the cross-sections for energy transfer [21,22]. A Kinchin and Pease (KP) model has been applied to estimate the number of displaced atoms generated by a primary knock-on atom (PKA) of known energy [23]. Considering the recombination of Frenkel defect pairs, a modified KP formula called Norgett-Robinson-Torrens (NRT) model has been constructed based on binary collision simulations [24]. The NRT model has been proved to obtain reasonable agreement with molecular dynamical models by a suitable choice of the displacement threshold. For example, by choosing an average displacement threshold of 37 eV, the numbers of Frenkel pairs predicted by NRT model is considerably matched molecular dynamics results for bcc iron [25]. Christie et al. have reported that damage defect number is consistent with the KP and NRT model with the choice of displacement efficiency of 0.8 and $E_d = 25$ eV by simulating radiation damage cascade in graphite using environment dependent interaction potential (EDIP) [26]. A further modified new damage function in the threshold region is suggested by Heggie et al. that the average number of Frenkel defects depends on the square root of the PKA energy in excess of the threshold [27].

Molecular dynamics simulations are the most realistic methods available for studying radiation processes dynamically. Compared with computational simulations for radiation process in metals and oxides [28,29], there are only a handful of simulations carried out for graphite due to the strong anisotropy structure which complicates the computational study by requiring that the methodology used adequately describe both strong covalent bonds and weak van der Waals bonds [27,30,31]. The first reported simulation of radiation cascade effects in graphite was performed in 1990 by Smith to study self-sputtering and related phenomena by using the Tersoff potential [32]. Further work by Smith and Beardmore investigated sputtering of carbon using classical molecular dynamics with a Tersoff and Brenner interatomic potential [30]. They reported a value for Ed of 34.5 eV for graphite and 34.0 eV for AA-stacked graphite. The Reactive Empirical Bond-Order (REBO) potential was employed to study temperature dependence of E_d, giving values of 44.5 eV at 300 K and 42.0 eV at 1800 K [33]. Cascade collision in graphite has been simulated under the Environment Dependent Interaction Potential (EDIP) coupled with the standard Ziegler-Biersack-Littmack (ZBL) potential to describe close-range pair interactions [26]. A displacement threshold of 25 eV is reported at room temperature and 30 eV at 900 K under the same interaction potential [27].

Here we report graphite cascade simulations using the Adaptive Intermolecular Reactive Empirical Bond-Order (AIREBO) potential with PKA in a wide energy range at room temperature. AIREBO potential [34–36], regarded as the most advanced potential for carbon and hydrocarbon materials at present, is adequate in describing both long-range intermolecular interactions and short-range atomic collision which will be analyzed in detail in the next section. The present work has two aims: the first one is to figure out the probable factors that accounts for the appearance of hillocks on irradiated graphite surface and the second is to explore the distribution of vacancy defect in damaged graphite bulk which provides theoretical foundation for further investigation of oxidation resistance property of nuclear graphite. The paper is structured as follows: Section 2 describes the technical part of our calculations. We compare the AIREBO and ZBL in describing short-range potential and outline our procedure for performing simulations and defect analysis. In Section 3 we consider qualitative behavior of the morphology evolution of graphite during irradiation, considering specific examples of cascade processes which illustrate the causes of surface hillocks. This is followed by quantitatively analysis of vacancy defects distributions in a relatively low energy range in Section 4. We conclude in Section 5 with a discussion of our results relative to macroscopic properties such as c-dimensional expansion and oxidation behavior of graphite.

2. Simulation method

All calculations are carried out by using the Large-scale Atomic/Molecular Massively Parrallel Simulator (LAMMPS) code developed by Sandia National Laboratory [37]. Adaptive Intermolecular Reactive Empirical Bond-Order (AIREBO) potential extended from Reactive Empirical Bond-Order (REBO) is chosen to describe the atomic interaction [34]. It is implanted with intermolecular interaction potential so as to simulate the inter-layer bonding more accurately. At present the AIREBO potential is regarded as the most advanced potential in describing intramolecular interactions in carbon and hydrocarbon materials [35,36].

Collision cascade process includes strong interaction of energetic atoms that are extremely close to each other. In order to affirm the accuracy of AIREBO potential in describing cascade process, short-range potential of AIREBO is compared with the widely accepted Ziegler-Biersack-Littmack (ZBL) as shown in Fig. 1. Both potentials describe intense interactions between two approaching nuclei because of coulomb repulsion and tend to converge at a distance larger than 0.7 Å. AIREBO gives much larger interaction energy than that of ZBL when two atoms infinitely close to each other. We know that it can never been infinitely approach for two nuclei, a distance about 0.7 Å is