Journal of Nuclear Materials 440 (2013) 250–256

Contents lists available at SciVerse ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Energetic and kinetic behaviors of small vacancy clusters near a symmetric Σ5(310)/[001] tilt grain boundary in bcc Fe

Xiangyan Li [a], Wei liu [a], Yichun Xu [a], C.S. Liu [a,*], Q.F. Fang [a], B.C. Pan [b], Zhiguang Wang [c]

[a] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, PR China
[b] Hefei National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei 230026, PR China
[c] Institute of Modern Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

ARTICLE INFO

Article history:
Received 15 March 2013
Accepted 7 May 2013
Available online 15 May 2013

ABSTRACT

Using combined techniques of molecular dynamics, molecular statics and the temperature-accelerated dynamics, we investigate the energetic and kinetic behavior of small vacancy clusters near a symmetric tilt grain boundary (GB) Σ5(310)/[001] in bcc Fe. We find that, the formation energy of the vacancy cluster (containing 1–9 vacancies) is reduced as it approaches to the GB, which serves as an energetic driving force for the segregation of vacancy clusters. The vacancy clusters in the bulk and near the GB exhibit different configurations. As a typical example, the cluster with four vacancies (V_4) undergoes three stages corresponding to the location of the cluster in the bulk, partially at the GB and completely at the GB, indicated by twice steplike decreases in the formation energy, as it moves from the bulk to the GB. In addition, through a dynamical monitor of its transition, we find that the GB enhances the diffusion of V_4 by reducing its diffusion barrier near the GB. Meanwhile, there occurs configurational transition for V_4 both as the cluster vibrates and moves towards the GB. The present results should help understand the healing processes of radiation-induced defects near the GB in Fe.

1. Introduction

Ferritic–martensitic (F–M) steels, iron-based bcc steels, have many advantages, such as low thermal expansion coefficients and great resistance to radiation-induced voids, to act as candidate structural materials for advanced nuclear reactor systems [1,2]. As structural materials, F–M steels will be exposed to high fluxes of neutrons under irradiation. The energy transferred from neutrons to the matrix atom will displace the matrix lattice, producing point defects (such as interstitials and vacancies). These defects can further migrate and aggregate, degrading mechanical properties of materials (such as swelling and hardening) [3–6]. On the other hand, the presence of defect sinks like grain boundaries (GBs) will significantly modify the production and evolution of point defects [7–15]. Therefore, the understanding of interaction between the radiation-induced defects and GBs in bcc Fe is important due to the polycrystalline nature of structural materials.

So far, extensive experimental efforts have been devoted to radiation responses for stainless steels with matrix element Fe [16–20]. Computational investigation is mainly made of the primary radiation damage in single crystalline iron (see the review paper Ref. [21]), and also the energetic behavior of point defects near the GB in bcc Fe [22,23]. Typically, interstitials are preferentially absorbed into the GB during irradiation [24], with larger segregation energy as a driving force than that of the vacancy [22,23]. In additional, it is well established that clusters of both vacancies and interstitials are produced in displacement cascades [25–28]. Furthermore, interstitial clusters in bcc Fe also have high mobility [29–31] (the migration barrier for an interstitial is about 0.34 eV and 0.48 eV for a di-interstitial [31]), and are intended to segregate into the GB. The loss of interstitials into the GB and the resulting supersaturated vacancies near the GB are thought to be responsible for void swelling in ploycrystalline (PC) materials [32,33]. Meanwhile, large volume fractions of GBs in nanocrystalline (NC) materials are expected to be effective sinks for irradiation-generated point defects like interstitials and vacancies [22–24,34,35], and account for the good radiation performance of NC materials. Undoubtedly, the knowledge of vacancy cluster behaviors near the GB is essential to predicting microstructure evolution and understanding the resulting modifications of materials properties during irradiation.

However, it is difficult to investigate vacancy clusters behaviors near the GB. It is time consuming to use molecular statics (MS) to probe the configuration space of vacancy clusters; a cluster containing five vacancies has about 120 different configurations. Further, a vacancy cluster has multiple configurations and its migration can be complex, while the artificial mechanism generated using MS may be incorrect. The temperature-accelerated dynamics (TAD) [36,37] does not require the prior knowledge of

* Corresponding author. Tel.: +86 0551 65591062.
E-mail address: csliu@issp.ac.cn (C.S. Liu).

0022-3115/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnucmat.2013.05.021

defect migration and thus can be used to investigate the kinetic behavior of vacancy clusters. In this paper, we use MD to generate vacancy clusters, MS to investigate energetic behavior of the vacancy cluster, and TAD to investigate kinetic behavior of small vacancy clusters (containing 1–9 vacancies) near the GB in bcc Fe. Our calculations indicate that, energetically, small vacancy clusters have a tendency to locate at the GB, with the lowered formation energy as a driving force. For the cluster with four vacancies, its diffusion barrier is greatly reduced as it comes closer to the GB. Moreover, there occurs configurational transition both as the cluster vibrates and moves towards the GB.

2. Computation method

The symmetric tilt GB $\Sigma5(310)/[001]$ in bcc Fe has been selected as a model GB. The embedded-atom-method (EAM) potential developed by Mendelev et al. [38] was chosen to describe interatomic interactions. During the development of the potential, the short-range form of the potential has been splined to reproduce the high-energy empirical potential of Ziegler et al. [39] for interatomic distance less than 1.0 Å, and thus the potential can be used to simulate primary radiation damage in Fe. The potential has been used to investigate point defects segregation near the GB in bcc Fe [22,23].

To construct the GB structure, a GB was initially created by aligning crystallographic planes (310) parallel to the desired GB plane, followed by a 180° rotation of one grain relative to the other about the direction normal to the GB plane. A stable structure at 0 K was then sought by applying a rigid-body translation parallel to the GB plane and then performing a steepest descent minimization with respect to local displacements of free atoms and rigid translations of the slabs normal to the GB plane. Periodic boundary conditions were applied in the directions parallel to the GB plane, but fixed boundary condition in the direction normal to the GB plane. The obtained stable structure of $\Sigma5(310)/[001]$ symmetric tilt GB in Fe at 0 K is shown in Fig. 1a with the energy of 0.989 J/m^2. We find that the mirror symmetry of the GB is not broken after the optimization of the structure. The core GB structure and the GB energy are in agreement with previous results [22]. Most of the atomic energies that differ from the bulk occur within about 5 Å from the boundary center. Thus, the influence range of the GB is about 10 Å.

For different purposes, two simulation cells with different sizes have been constructed. A large cell consisting of 95,520 atoms with a size of about $180 \times 70 \times 90$ Å^3 was used in simulating radiation damage and producing vacancy clusters. A small cell having 3792 atoms with a size of about $70 \times 30 \times 20$ Å^3 was used for calculating energetic and kinetic properties of vacancy clusters, considering the computational efficiency. These calculated properties include vacancy cluster formation energies and migration barriers near the GB. The size of the small cell is large enough for investigating the energetic and kinetic behavior of small vacancy clusters. We have checked that the maximal size of the vacancy cluster is less than half the size of the cell and there is no interaction between the cluster located at the two neighboring cells.

For MD simulations, a block with a slab geometry was used as illustrated in Fig. 1b. The thickness of each slab was at least twice the cutoff radius of atomic interaction. The dimensions of the free region were approximately equal in all three directions. The fixed atoms were allowed to move rigidly during the structural relaxation. The free atoms were sandwiched between two slabs of fixed atoms on each side of the GB plane. The atoms in the outmost three layers of the moving region were coupled with a velocity-rescaling thermostat to extract the cascade energy and maintain the cell temperature at 1000 K. The velocity-Verlet method was used for the numerical integration. The volume of the cell was expanded to the appropriate volume for 1000 K.

3. Results and discussion

3.1. Energetic behaviors of vacancy clusters near the GB

To generate vacancy clusters, we perform MD simulations of primary radiation damage at 1000 K in the large cell for 470.2 picoseconds (ps). Initially, the cell was relaxed at 1000 K for 10 ps to reach thermal equilibrium, with a time step of 2 femtoseconds (fs). After the relaxation, an atom at about 23 Å on one side of the GB and located at the center of the plane parallel to the GB plane was selected as the primary knock-on atom (PKA). The atom was given 3 keV of kinetic energy with its velocity directed perpendicularly toward the GB. A smaller time step of 0.1 fs was used for an additional 2 ps after which the time step was increased back to 2 fs for about 170 ps. Then we run MD for another 300 ps until the vacancies near the GB were completely removed.

To visualize the defect evolution near the GB in the MD simulations, atoms are colored with their potential energy; atoms with energy deviation from the bulk value less than 0.1 eV are treated as non-defective and are not shown. A vacancy is characterized

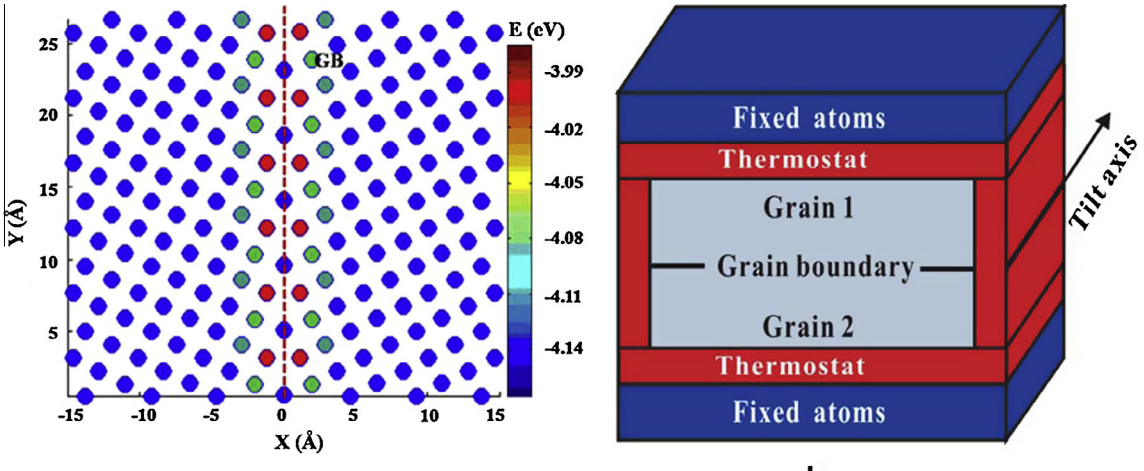

Fig. 1. The stable structure of $\Sigma5(310)/[001]$ symmetric tilt GB in bcc Fe (a) and schematic geometry and boundary conditions in GBs (b). Here atoms are colored with their potential energies and the corresponding colors are shown in the color bar in (a). The axes *X* and *Y* are along [310] and [$\bar{1}$30], respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)