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Strong trapping and slow diffusion of helium in a tungsten grain boundary

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ABSTRACT

We have investigated the segregation, trapping and diffusion of He in a $\sum$3<110>{111} W grain boundary (GB) using combined techniques of *ab initio* and classical atomistic simulations. We show that, with an average segregation energy of −3.20 eV, the strong He trapping can be attributed to a GB interstitial trapping or a vacancy trapping mechanism, while an average energy barrier of 1.97 eV leads to a slow diffusion of He in the GB plane. We further reveal by molecular dynamics simulations that the He diffusion will be dictated by GB migration through the motion of GB disconnections. Interestingly, we also observe a He-induced GB structural transition in classical simulations. The present work suggests that the GB does not provide fast transport channel for He, providing useful reference for the possible application of polycrystalline W under He irradiation in advanced nuclear fusion reactors.

1. Introduction

Tungsten (W) is seen as the leading candidate for plasma-facing materials (PFMs) in future fusion reactors because of its high melting point, high thermal conductivity, low sputtering yield and low tritium retention [1]. As a PFM, large amounts of helium (He) impurities will be introduced through direct He plasma implantation and (n, α) transmutation reaction. It is well known that He possesses the characters of low solubility, high mobility and self-trapping in metals [2–6]. Rapid He migration and aggregation can lead to the nucleation and growth of He clusters, thus severely degrading the physical and mechanical properties of W [7–10]. Recent experimental studies also demonstrated the formation of 'fuzz' nanoscale structures on W surface under He-ion irradiation at 1000–2000 K [9,11–17]. The thermal conductivity of W near surface can drop several orders of magnitude due to the presence of these structures, thus aggravating heat load erosion and surface exfoliation [9].

As a common feature in polycrystalline materials, grain boundary (GB) is directly associated with the formation of He bubbles [18,19], which may lead to high-temperature embrittlement [20]. Most recently, El-Atwani and coworkers [21] evaluated the performance of GBs in ultrafine-grained and nanocrystalline W as He sinks under various He ion irradiation energy and temperature. Their experimental results showed that He bubbles are preferentially formed in the GBs only when the energy of He ions are high enough to cause displacement damage and the temperature is high enough that vacancies are mobile. The size of the He bubbles has been demonstrated to increase with increasing GB energy [19]. Using a bicrystal model, a large body of *ab initio* calculations [22–27] and atomistic simulations have been [28–34] dedicated to understanding, on the one side, the segregation and diffusion of He in metallic GBs, and on the other side, the nucleation and growth He clusters. The behaviors of He and He clusters have been revealed to be heavily influenced by GB characters. Interestingly, GB reconstruction induced by He cluster growth [32] has also been observed.

A quantitative picture of defect segregation energetics and diffusion kinetics of He in W GBs is essential to the understanding of dynamic processes of He cluster evolution in W under irradiation. Generally, a single hydrogen (H) or He atom prefers to occupy the tetrahedral interstitial site [35–37] and diffuses by an interstitial mechanism [36,38]. Up to now, it is well-established that the

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diffusion of light impurities such as H and He to the GBs is enhanced and GBs effectively trap them [39,40], which are governed by the physical mechanisms of optimal charge density [41] and electrophobicity [6], respectively. However, numerous inconsistent results have been reported. For example, on the specific values of segregation energy, first-principles calculations performed by Zhou et al. [39] gave a H segregation energy of −1.11 eV to the ∑5(310) GB, while Yu et al. [42] reported a segregation energy as low as −2.5 eV for H segregation to the same GB using atomistic simulations based on an empirical potential. The origin for this seems to be that the GB structure used by Zhou et al. is perfectly symmetric to the GB plane, while the mirror symmetry of that adopted by Yu et al. is broken due to a slight translation along the tilt axis [42]. Another example is the controversy surrounding H diffusion in metallic GBs that both enhanced and inhibited diffusion results have been reported [39,42–46]. It is thus of great significance to find out whether GBs indeed inhibit He diffusion in the GBs as reported earlier [25,40]. In the present work, combined techniques of *ab initio* and classical atomistic simulations have been used to investigate the segregation energetics and diffusion kinetics of He in a W ∑3<110>{111} GB. Systematic comparisons have been made between different methods and also with previous works.

2. Methodology

2.1. Ab initio methods

Ab initio calculations were performed using two methods: CP2K package [47] with a mixed Gaussian and plane wave basis, and the pseudopotential plane-wave method implemented within the VASP code [48,49] based on density functional theory. For the former method, we used the spin-polarized PBE functional [50] with Goedecker-Teter-Hutter (GTH) pseudopotentials [51,52]. The Kohn-Sham matrix diagonalization method was utilized for an efficient wave function optimization. The outer 14 electrons of W and the outer 2 electrons of He were treated as valence electrons. Contracted Gaussian basis sets of DZVP quality were employed with a grid cutoff of 350 hartree. For the latter method, the generalized gradient approximation of Perdew and Wang [51] and projected augmented wave potentials [53] with a plane wave energy cutoff of 400 eV were used. For summation over the Brillouin zone, the uniform grids of k-points were set as $3 \times 3 \times 3$ according to the Monkhorst–Pack scheme with a full relaxation of the atomic positions and supercell volume [54]. The energy relaxation continues until the forces on all the atoms are less than 10^{-3} eVÅ^{-1}. Periodic boundary condition was applied in all three dimensions.

Using the CP2K package, we conducted *ab initio* molecular dynamics (MD) simulations in the Born-Oppenheimer approximation using the always stable predictor-corrector method [55] in a NVT ensemble (the number of atoms, volume and temperature remain constant) with a time step of 1 fs. The canonical sampling through velocity rescaling thermostat–barostat [56] was used with a time constant of 10 fs for system equilibration and 1000 fs for He diffusion simulations. As diffusion is a relatively slow process at the time scales accessible to atomistic modeling, which is especially true for the *ab initio* methods, it is necessary to accelerate the simulated dynamics. We thus employed the metadynamics [57,58] method available in CP2K to force the He atom out of the equilibrium positions in the GB. The collective variables used for the metadynamics were the distances along the Cartesian *x*, *y* and *z* directions between the He atom and the center defined as the average of all W atoms. During the metadynamics simulations, Gaussian potentials were added every five steps (5 fs) of the simulations and this potential gradually builds up until it is sufficient to force the He atom out of an energy minimum, such that the He atom was able to explore the GB landscape.

2.2. Classical methods

Classical atomistic simulations were performed using two kinds of potential formalisms: an embedded-atom method (EAM) potential and a bond-order potential (BOP). The EAM potential for W-He system comes from recent work by Juslin and Wirth [59], while the BOP potential for W-H-He system was developed by Li et al. [60]. Using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [61] package, we constructed the ∑3<110>{111} bicrystal following Refs. [62,63]. We first brought two differently oriented grains together to obtain the bicrystal based on the coincident site lattice model. The two grains were then translated rigidly relative to each other in the GB plane, followed by an atom elimination process once atoms were too close to each other. The conjugate gradient energy minimization was subsequently performed for each translation and elimination. The open software Ovito [64] was used for structural visualization. Note that the interstitial He in the GB was created following a similar procedure as that adopted in Ref. [65]. Classical MD simulations based on the EAM potential were performed within the NPT (the number of atoms, pressure and temperature remain constant) ensemble for equilibration, followed by He diffusion simulations within the NVT ensemble at a temperature interval of 100–2500 K for up to 20 ns. The time step of the MD simulations is 1 fs. Both three-dimensional periodic boundary condition and a free boundary condition (with two free surfaces parallel to the GB plane) have been used to evaluate the effect of GB migration on He diffusion. Note that the boundary conditions are the only factors that differ in the simulation setups.

2.3. General simulation setups and basic properties

It can be seen from Table 1 that the calculated equilibrium lattice constants from these four methods are in good agreement with the corresponding experimental value of 3.17 Å. The two interatomic potentials well reproduce the He formation energies in W as compared to *ab initio* values. The small values of migration barriers indicate the high mobility of interstitial He in bulk W. Therefore, only interstitial He formation and diffusion have been considered in this study. Due to the high computational cost of *ab initio* calculations, much smaller bicrystal models were used in comparison with classical methods. By testing the effect of system size on GB energy, we show that the cell sizes adopted in the present study is overall satisfactory for single-He simulations. Segregation energy was utilized to quantify the segregation tendency of an interstitial He to the GB, which can be simply expressed as

$$E_{He}^{S} = E_{He}^{f}(GB) - E_{He}^{f}(bulk), \tag{1}$$

where $E_{He}^{f}(bulk)$ and $E_{He}^{f}(GB)$ denote the formation energy of interstitial He in a perfect bcc bulk lattice and in a crystal with a GB, respectively. Thus, a negative segregation energy indicates attraction between the He and the GB. Notably, the equilibrium GB structures obtained by these four methods are exactly the same. For the statics simulations at 0 K, 35 initial He placements were chosen in the *ab initio* calculations, and 930 positions were used in the classical simulations. While for MD simulations, a single He was placed at the most stable site at the plane.