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Dissolution and diffusion of hydrogen in a molybdenum grain boundary: A first-principles investigation

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ABSTRACT

We have performed a first-principles investigation with a zero point energy correction on dissolution and diffusion of hydrogen (H) in a Σ5 (310)/[001] molybdenum (Mo) symmetrical tilt grain boundary (STGB). H prefers to stay at the interstitial site in the vacant space of the Mo GB with a negative solution energy (−0.42 eV) and segregation energy (−1.16 eV), which are decreased in the presence of vacancy in the GB. Furthermore, the H solution energy at the vacancy in the Mo GB is lower than that in the Mo bulk, suggesting a larger trapping capability for H of the vacancy in the Mo GB. The dissolving stability of H in the Mo GB can be explained by the low charge density that the GB provides for H. Kinetically, H prefers to easily diffuse within the vacant space along the Mo GB with a small diffusion barrier (0.04 eV), and to migrate to the GB from the bulk. These results provide a systematically exploration and analysis of H behaviors in the Mo GB at an atomic scale, which suggest that the Mo GB can serve as a trapping center for H, similar to the vacancy. In particular, a detailed comparison of H dissolution and diffusion behaviors in a Mo GB with those in a tungsten GB is performed. This can be helpful in understanding the experimentally observed H bubble formation in the Mo GB from the microscopic view.

1. Introduction

In future fusion reactors, plasma facing materials (PFMs) should withstand irradiation from low energy (0–100 eV) and high fluxes ($>10^{24}/m^2s$) of hydrogen (H) isotopes, helium plasma and neutrons with high energy of 14.2 MeV [1,2]. The plasma and neutron irradiation will initiate radiation damages such as surface blistering and displacement cascades into PFMs, leading to the property degradation [1–4]. Choice of materials for PFMs is thus a key issue for the ultimate realization of fusion energy. High-Z metal molybdenum (Mo) and its alloys, in addition to tungsten (W), are deemed as promising candidates for PFMs, because Mo is a refractory metal with good thermal property, better ductility, high sputtering threshold and most importantly, low H isotope retention [5,6]. Mo has already been applied as PFMs in EAST tokamak, and successfully used to fully cover the walls in the Alcator C-Mod tokamak [6]. In fact, during the operation of fusion reactors, Mo-based PFMs will be exposed to high fluxes of H isotopes plasma, thus the unwanted H bubble formation and blistering are key issues that influence the service performance of Mo as PFMs [4,5–8]. H bubble formation is believed to be directly associated with the accumulation of H to defects including vacancy, dislocation and grain boundary in metals [1–4], which has been tentatively reviewed in Lu et al. [9]. Vacancies in metals have already been demonstrated to be trapping centers for H by serious of experimental works [1,4,10] and theoretical studies [11–15]. Moreover, a vacancy trapping mechanism for the H bubble formation in metals has been revealed, suggesting vacancies and other vacancy-type defects can provide an isosurface to accommodate H, which leads to the preliminary stage of H bubble nucleation [14,15].

Grain boundaries (GBs), as another typical kind of defects like vacancies, play a crucial role in influencing the performance of metal materials. The atomic structure of GB and its interaction with other point defects and impurities have a great influence on the property of metals [16–18]. It is well known that the segregation of impurities such as phosphorus, nitrogen and oxygen in the GB of metals contributes to the GB embrittlement [19,20], causing drastic changes of mechanical properties of metals. While other impurities, boron and carbon for instance in GBs, act as cohesion enhancers for metals, resulting in an improvement in the GB ductility [20–22]. In particular, H bubble formation and the subsequent H-induced fracture of PFMs are close related to H behaviors in GBs [5,23–25]. It has been experimentally observed that H bubbles tend to form and grow in a W GB, and succeeding internal cracks are generated in the GB [23,24]. For a Mo GB, experimental

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work showed numerous H atoms can accumulate in the GB as a trapping site, leading to the observed H blistering and grain fracture in the GB as a result [5,25].

The H segregation behaviors in the symmetrical tilt grain boundary (STGB) of metals including Ni, Fe, Cu and Al [19,21,26] have been explored by previous first-principles studies. Geng et al. [21] studied effects of H on the Ni Σ5 (2 1 0) GB and showed that H segregates to a vacancy site in the GB, embrittling the GB due to the ionic chemical interaction of H and Ni atom. Yamaguchi et al. [19] then demonstrated that H is an embrittle on the Ni Σ5 (2 1 0) GB with a negative segregation energy. Similar results of the embrittling effects of H on GBs were reported for the Fe Σ3 (1 1 1) GB and Al/Cu Σ5 (2 1 0) GBs [26]. However, behaviors of H in GBs which are directly associated with the H bubble formation were little discussed in these studies. In the work of Zhou et al. [27], the dissolution, segregation and diffusion of H in a W GB were systematically investigated by a first-principles method, and H was found to occupy the interstitial site with an optimal charge density in the W GB. Moreover, Zhou et al. revealed the W GB can serve as a trapping center for H, and the experimentally observed H bubble formation in the W GB should rely on a vacancy trapping mechanism. For H behaviors in Mo GBs, Janisch et al. [28] determined the diverse influences of light elements including H on the cohesion of a Mo Σ5 (3 1 0) GB, but the effect of H was not fully discussed. Nevertheless, the H dissolution and diffusion in the Mo GB which are related to the experimentally observed H bubble formation in GBs have been still not well investigated so far.

In this paper, we choose a Σ5 (3 1 0)/[0 0 1] Mo STGB, which is a typical STGB for body centered cubic (bcc) metals. The Σ5 (3 1 0)/[0 0 1] Mo STGB can be well presented by atomistic simulations using interatomic potentials based on the model generalized pseudopotential theory (MGPT), and is proved to be a low energy configuration [29]. Experimentally, on the other hand, the Σ5 (3 1 0)/[0 0 1] Mo STGB can also be fabricated and characterized by high-resolution transmission electron microscopy (HRTEM), in agreement with atomistic simulations [28,29]. Employing the first-principles method, we calculate H dissolution behaviors at both interstitial and vacant sites (vacancies) in a Σ5 (3 1 0)/[0 0 1] Mo STGB, and further explore the diffusion properties of H among these sites along the Mo GB. Moreover, we consider zero point energies (ZPEs) of H in the Mo GB, which reflect the important quantum-mechanical vibration effects of H in metals, both for dissolution and diffusion cases. Finally, a detailed comparison of H dissolution and diffusion in the Mo GB with those in the W GB is performed. These results provide a systematically analysis of H behaviors dissolving and diffusing in the Mo GB at an atomic scale, which will be helpful in understanding the experimentally observed H bubble formation in a Mo GB from the microscopic view.

2. Methodology

The present first-principles calculations were performed using the pseudopotential plane wave method as implemented in the Vienna ab initio simulation package (VASP) code [30] based on the density-functional theory. The electronic ground state of the present grain boundary system was calculated using the projector-augmented wave (PAW) potential provided in VASP [31,32]. The electron exchange and correlation were treated with generalized gradient approximation (GGA) by Perdew–Burke–Ernzerhof (PBE) functional [33]. The energy cutoff for the plane wave basis was set to be 400 eV. The Methfessel–Paxton (MP) smearing method [34] was employed to integrate the partial occupancies of metals with a smearing width of 0.2 eV. The Brillouin zone is sampled with

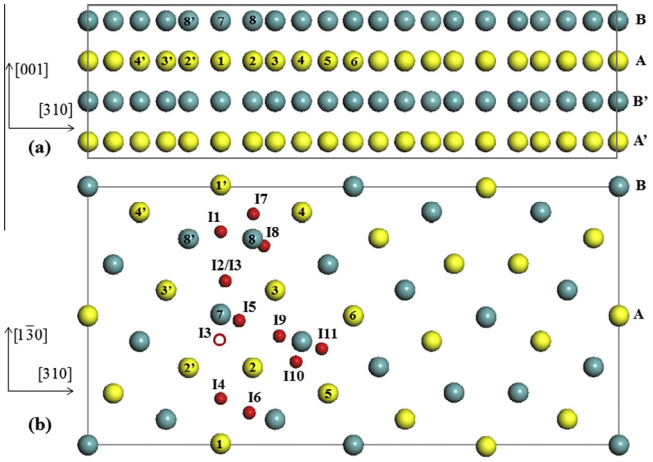

Fig. 1. Model of the Σ5 (3 1 0)/[0 0 1] Mo STGB supercell. (a) Side view of the Mo GB supercell. The yellow and blue spheres represent the Mo atoms of A(A') and B(B') layers, respectively. (b) Top view of the Mo GB supercell. The yellow spheres numbered with 1-6 represent the Mo GB atoms of A layer that serve as substitutional site or vacant site for H. The red spheres numbered with I1–I11 represent the H atoms at the interstitial sites after structure optimization. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$1 \times 2 \times 3$ *k*-points mesh by the Monkhorst–Pack scheme [35]. The structure of the system was considered fully relaxed until the forces on all atoms were less than 0.01 eV/Å.

A supercell containing 80 atoms was employed as a model for the Σ5 (3 1 0)/[0 0 1] Mo STGB, as shown in Fig. 1. The STGB was structured based on a coincident site lattice (CSL) construction [36], with the tilt angle and rotation axis of 36.9° and [0 0 1] axis, respectively. The calculated equilibrium lattice constant is 3.151 Å for bcc Mo, in good agreement with the experimental value of 3.15 Å. Therefore, the lattice constants for the Mo GB supercell were 20.50 Å × 9.92 Å × 6.26 Å, along the $[3\,1\,0]$, $[1\,\bar{3}\,0]$ and $[0\,0\,1]$ direction, respectively.

For the diffusion of H along the Mo GB in the present calculation, the minimum energy pathways were determined by the climbing-image nudged elastic band (CI-NEB) method [37]. Images were linearly interpolated along the pathway connecting by springs to construct a band, which was then optimized to determine the minimum and saddle points. ZPE corrections for both dissolution and diffusion behaviors of H in the Mo GB were taken into account. ZPEs of H, i.e., vibrational frequencies of H in the Mo GB were calculated from the Hessian matrix of H atoms with finite displacements of ±0.015 Å applied on each H atom and direction. Here, Mo GB atoms were kept fixed, only the relaxations of H atoms were allowed [13].

3. Results and discussions

3.1. H dissolution in the Mo GB

We first examine the H dissolution at different possible sites in the Mo GB, including interstitial, substitutional and vacant sites (vacancies). In Fig. 1, the calculated Mo GB model contains 4 atom layers, among which A and B layers are symmetrically equivalent with each other, A′ and B′ layers are the same as A and B layers, respectively, due to the periodicity. Therefore, we explore the H dissolution only at A layer of the Mo GB as an example [Fig. 1(b)]. For the interstitial cases, totally eleven possible sites are considered, and the finial positions of H dissolving at these sites after structure optimization (defined as I1–I11) are shown as red small spheres in Fig. 1(b). It should be noted that the initially