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First-principles investigation of the energetics of point defects at a grain boundary in tungsten

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ABSTRACT

Tungsten (W) and W alloys are considered as the most promising candidates for plasma facing materials in future fusion reactor. Grain boundaries (GBs) play an important role in the self-healing of irradiation defects in W. Here, we investigate the stability of point defects [vacancy and self-interstitial atoms (SIA's)] in a $\Sigma5(310)[001]$ tilt W GB by calculating the energetics using a first-principles method. It is found that both the vacancy and SIA are energetically favorable to locate at neighboring sites of the GB, suggesting the vacancy and SIA can easily segregate to the GB region with the segregation energy of 1.53 eV and 7.5 eV, respectively. This can be attributed to the special atomic configuration and large available space of the GB. The effective interaction distance between the GB and the SIA is ~6.19 Å, which is ~2 Å larger than that of the vacancy-GB, indicating the SIA are more preferable to locate at the GB in comparison with the vacancy. Further, the binding energy of di-vacancies in the W GB are much larger than that in bulk W, suggesting that the vacancy energetically prefers to congregate in the GB.

1. Introduction

As an environmentally clean and infinite energy source, nuclear fusion energy is considered as the most effective solution to the energy shortages. Fusion energy is being developed internationally via the International Thermonuclear Experimental Reactor Project, which aims to demonstrate the extended burn of deuterium-tritium (D-T) plasma in a fusion reaction [1]. The application of fusion energy is mainly dependent on the development of the key materials. Tungsten (W) is considered to be the most promising candidate for the plasma-facing material (PFM), because of its high melting temperature, high thermal conductivity and low sputtering erosion [2]. However, during its lifetime, W will be subjected to neutron irradiation, high heat flux and plasma particles bombardment. These circumstances will lead to the deterioration of the W-PFM due to defect formation and displacement damage [3–8].

Defects induced by neutron irradiation in W will lead to material failure [7,8]. Behaviors of point defects play an important role in the degradation of W macroscopic properties [9]. Great efforts have been made to investigate the defect behaviors in W, including hydrogen [10–14], helium [12,15,16], vacancy [17–19] and self-interstitials [19,20]. Grain boundaries (GBs) act as a transition region between two adjacent crystal lattices and thus the crystallographic structure and chemical composition of GBs are distinct from those of the bulk crystal. Nanocrystallized materials contain lots of GBs and interfaces, which are shown to enhance radiation tolerance in extreme environments [21–23]. The GBs and interfaces may serve as effective sinks for defects [11,19,24–26]. Experimentally, much work has been undertaken in the development and preparation of high performance radiation resistance W materials [27,28], which has demonstrated that nanostructured W has a good radiation resistance performance.

In order to understand the effects of GBs on the evolution of irradiation induced defects, a lot of studies have been made to investigate the interaction between the GB and point defects [11,19,24–26]. On the one hand, it has been demonstrated that the GB can emit the interstitials with a low energy barrier to annihilate vacancies in the bulk, which is efficient for self-healing of the radiation-induced damage [22,24]. On the other hand, it is found that the existence of GBs can reduce the formation energy and diffusion barrier of vacancy and self-interstitial atoms (SIA's) [22,24], promoting the recombination rate of Frenkel pairs via the coupling of the individual segregation process of vacancies and SIA near the GB.

Neutron irradiation will produce Frenkel defects (vacancy and SIA), which will further aggregate and form clusters, such as voids

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and dislocation loops [21]. The combination of Frenkel defects plays an important role in self-healing of radiation damage. Classical atomistic simulations are widely used to study the annihilation process of interstitials and vacancies [22,24,26] within a rather large spatial scale up to billions of atoms and temporal scale up to micro-seconds. Though these classical simulations have advantages on a larger scale and have faster computational simulation speed, they are weak in computational accuracy resulting from the lack of electronic structure information. More accurate statics property results are the basis of the dynamical study of self-healing mechanisms, so the statics study of Frenkel defects using first-principles methods is valuable. In the present work, we have systemically investigated the energetics of Frenkel defects at a W GB using a first-principles method. Our findings give insight into the basic behavior of Frenkel defects in GBs, which will provide a good reference to understand the typical experimental phenomenon related to Frenkel defects. These will be very useful for developing W-PFM for future nuclear fusion reactors.

2. Computational method

We employ a first-principles plane-wave method based on density functional theory (DFT) with generalized gradient approximation (GGA) according to Perdew and Wang [29] using VASP [30,31]. The interaction between ions and electrons is described by the projector augmented wave (PAW) potential based on GGA. The cutoff energy of plane-wave basis set was chosen to be 400 eV. The supercell contains 160 W atoms to simulate the 36.9° $\Sigma5(310)/[001]$ symmetrical title GB. The GB structure is constructed according to the coincident site lattice (CSL) theory. Specifically, two bcc grains are rotated around the [001] axis by an angle of 36.9°. The mirror-symmetric GB structure used here is quite typical in metallic GBs, which has been widely used for impurity segregation and embrittlement studies [11,32–37]. The calculated equilibrium lattice constant is 3.17 Å for bcc W, in good agreement with the corresponding experimental value of 3.16 Å. The lattice size for the W GB supercell is $10.02 \times 40.87 \times 6.31$ Å^3. In all the calculations, the integrations over the first Brillouin zone were performed by using the special k-point scheme and a $2 \times 1 \times 3$ Monkhorst-Pack k-point mesh [38] with a full relaxation of the atomic positions and volume of the supercell. The energy relaxation iterates until the forces acting on all the atoms are less than 10^{-3} eV Å^{-1}.

3. Results and discussion

3.1. Formation of a single vacancy in the W GB

In order to find the most stable site of a single vacancy in the W GB, the formation energies of a vacancy at eleven different GB sites (see Fig. 1) have been examined. Because of symmetry and periodicity, we only consider a vacancy in the *A* layer. The vacancy formation energy E_V^f is defined as

$$E_V^f = E_{GB+V} - E_{GB} + E_{ref}, \quad (1)$$

where E_{GB+V} and E_{GB} are the total energies of W GB supercell with and without vacancy. E_{ref} is the reference energy for the W atom, which is chosen to be the energy per atom of the W atom in its ground state. Positive vacancy formation energy denotes endothermic, while negative value denotes exothermic.

Fig. 2 shows the vacancy formation energy in the W GB as a function of distance between the vacancy and the GB. It is found that the formation energies of the vacancy are positive for all cases, which indicates that the vacancy formation in the W GB is an endothermic process. Further, the vacancy formation energy at the neighboring sites of the GB (except for the vacancy at the GB plane, S_0) are lower than that in bulk W (~3.11 eV) [39]. This suggests that a vacancy has a tendency to segregate into the neighboring sites of the GB. Besides, the vacancy formation energies increase with increasing the distance between vacancy and the GB (except for the vacancy at the GB plane, S_0). At the most stable site in the GB (S_1), the vacancy formation energy is 1.58 eV. After that, the vacancy formation energy increases to 2.90 eV and 2.64 eV at the distance of 2.14 Å (S_2) and 3.19 Å (S_3), respectively. Beyond this distance, the vacancy formation energy almost converges to a constant ~2.95 eV from ~4.2 Å. Therefore, the effective interaction distance between the GB and the vacancy is approximately 4.2 Å, which is similar to that found in previous studies ~4.7 Å [24]. However, it should be noticed that the vacancy formation energy (~3.18 eV) at the GB plane (S_0 site) is larger than that in bulk W and neighboring sites of the GB. Thus, compared with the GB plane, the neighboring sites of the GB are energetically preferable for the vacancy. It also should be noticed that the vacancy formation energy decreases in the W GB by ~1.53 eV, while a reduction of 0.86 eV was found in previous atomistic simulation studies [24].

To further shed light on the physical origin underlying the stability of a single vacancy in the W GB, the vacancy formation energy is decomposed into two contributions. One is the energy release during lattice relaxation after vacancy formation, the so-called lattice-relaxation contribution. The other is the energy increase during vacancy formation (without atomic relaxation), called the bond-broken contribution. Fig. 2 shows the lattice-relaxation contribution and the bond-broken contribution for the vacancy formation energy in the W GB. Apparently, the bond-broken contribution is much larger than the lattice-relaxation contribution and is 104.2%–136.3% of the vacancy formation energy at different sites in the GB. Besides, the variation tendency of bond-broken contribution is consistent with that of the vacancy formation energy. Therefore, the bond-breaking during vacancy formation is largely responsible for the vacancy formation energy in the GB.

To understand the bond-broken contribution to the vacancy formation energy, the atomic configurations of the GB and bulk W have been investigated. For various vacancy configurations, the vacancy formation energy, the number of first nearest neighbor (1NN) atoms of the vacancy and the shortest distance between the 1NN atom and the vacancy are listed in Table 1. It can be clearly found that the number of 1NN atom for the most stable site (S_1 site) is seven, which is one less than other sites in the GB and bulk W, indicating that the interaction between W(S_1) and its surrounding atoms is weaker than other cases. Further, the shortest distance between 1NN atom and W(S_1) is 2.2 Å, which is much shorter than the optimal W-W distance in the bulk ~2.75 Å. This will also weaken the interaction between W(S_1) and its surrounding atoms. Therefore, the W atom at S_1 is easier to be removed than that at other sites, leading to the decrease of vacancy formation energy.

3.2. Interaction of di-vacancies in W GB

In order to quantify the interaction of di-vacancies, we calculate the binding energy between two vacancies. The first vacancy is set at the most stable site (S_1) in the W GB, while the second one occupies the different neighboring lattice position (S_4 and N_0-N_3, see Fig. 1). The binding energy of di-vacancies can be expressed as

$$E^b_{V_1-V_2} = 2E_{GB+V_1} - E_{GB+V_1+V_2} - E_{GB}, \quad (2)$$

where E_{GB+V_1} is the total energy of the W GB supercell containing one vacancy at S_1. $E_{GB+V_1+V_2}$ is the total energy of the W GB supercell containing di-vacancies. One vacancy is set at S_1 and the other

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