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First-principles study of Frenkel pair recombination in tungsten

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ABSTRACT

The recombination of one Frenkel pair in tungsten has been investigated through first-principles simulation. Two different recombination types have been identified: instantaneous and thermally activated. The small recombination barriers for thermally activated recombination cases indicate that recombination can occur easily with a slightly increased temperature. For both of the two recombination types, recombination occurs through the self-interstitial atom moving towards the vacancy. The recombination process can be direct or through replacement sequences, depending on the vertical distance between the vacancy and the ⟨1 1 1⟩ line of self-interstitial atom pair.

1. Introduction

Tungsten (W) is considered as the most promising candidate for plasma facing materials (PFMs) for the next generation of fusion devices such as ITER. The primary advantages of W are its ability to tolerate high temperatures and its high threshold for physical sputtering. W target will be exposed to high fluxes of hydrogen (H) isotope and helium (He) ions as well as neutron irradiation in the extreme fusion environment. In particular, neutron irradiation produces Frenkel defects as primary damage by displacing the atoms in fusion materials hundreds of times during service [1,2]. The Frenkel defects are composed of two elementary types of point defects, which are self-interstitial atom (SIAs) and vacancies. These point defects can develop to extended defects such as voids and interstitial clusters, resulting in hardening, swelling and embrittlement of W [3,4]. Consequently, enhancing radiation resistance of W is extremely important. GBs, interfaces and interfacial structures are speculated to enhance radiation tolerance by serving as effective sinks for defects [5–13]. However, the influence range of the GB is small (1–1.5 nm), leading to a small volume fraction of the GB region working as the sink. This indicates that GBs may play a limited role in improving radiation performance [14]. In the bulk W, it is shown that Frenkel defects can annihilate through the recombination of vacancies and SIAs. Both molecular dynamics (MD) method and density functional theory (DFT) method have been applied to calculate the recombination region of one Frenkel pair (one vacancy and one SIA) [15–17]. In MD calculation, the recombination region is an ellipse with the semi-minor axis of 5.4 Å and semi-major axis of 18 Å [15]. While, the DFT calculation figures out a smaller ellipse region with the semi-minor axis of 2.7 Å and semi-major axis of 5.5 Å [16,17]. The recombination in Refs. [16,17] is realized through the migration of vacancy. Because the migration barrier of SIA (0.005 eV) is much lower than that of vacancy (1.7 eV), which indicates that the migration of SIA is easier than vacancy [18–24], we investigate the recombination of one Frenkel pair in the bulk W through the migration of SIA using first-principles method in this paper. It is believed that these results will help to understand the recovery mechanism of Frenkel defects and provide a good reference for the design of anti-irradiation fusion materials.

2. Computational method

The first-principles calculations are performed using the VASP code [25] based on the density functional theory (DFT). The generalized gradient approximation of Perdew and Wang [26] and projector augmented wave potentials [27] with a plane wave energy cutoff of 350 eV are used. During geometry optimization, a bcc-W supercell of 128 atoms is used with the side length of 12.64 Å and the Brillouin zones are sampled with $3 \times 3 \times 3$ k-points grid according to the Monkhorst-Pack scheme [28], which is sufficient to converge the total energy with an energy convergence of 0.01 eV. During the calculation, all the supercell size, shape and atomic positions are relaxed to equilibrium, and the energy minimization is converged until the forces on all the atoms are less than

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10^{-3} eV/Å. The climbing image nudged elastic band (CI-NEB) method [29] is used to calculate the migration energy of vacancy and SIA and the energy barrier of recombination.

The formation energies of vacancy and SIA are defined as

$$E_f^V = E_{127W+V} + \frac{1}{128}E_{128W} - E_{128W} \quad (1)$$

and

$$E_f^I = E_{128W+I} - \frac{1}{128}E_{128W} - E_{128W} \quad (2)$$

respectively. E_{127W+V}, E_{128W+I} and E_{128W} is the energy of W system with 127 W atoms and a vacancy, the energy of W system with 128 W atoms and one SIA and the energy of bulk W with 128 W atoms, respectively.

3. Results and discussions

3.1. Formation and migration energies of vacancy and SIA in W

We firstly examine the formation energies and migration energies of the vacancy and SIA in W (Table 1). The calculated formation energy and migration energy of the vacancy agree with the experimental results [18] and other DFT calculation results [19–21]. SIA is demonstrated to prefer forming an SIA pair with another bulk atom along ⟨1 1 1⟩ direction in W, which is consistent with the previous DFT calculation results [22]. The formation energy and migration energy of SIA also agree with the experimental results [23] and other DFT calculations [19,22,24]. According to the results, the diffusion barrier of SIA is so small that SIA can easily diffuse along ⟨1 1 1⟩ direction, which indicates that the recombination of vacancy and SIA is mainly through the moving of SIA. Apparently, when the vacancy locates in the same ⟨1 1 1⟩ line with the SIA pair, recombination can easily occur through the diffusion of SIA towards the vacancy directly. However, for the vacancies not locating in the ⟨1 1 1⟩ line of the SIA pair, the recombination behaviors are unclear, which is the motivation of this investigation. The Frenkel pair formation energy E_f^{FP} referring to infinite separation of the defect pair equals the summation of vacancy formation energy and SIA formation energy and is 12.64 eV by our calculation.

3.2. The recombination behaviors of one Frenkel pair

Before investigating the recombination of one Frenkel pair (one vacancy and one SIA), we examined the possible configurations of one vacancy and one SIA in W. In the 4 * 4 * 4 supercell with 128 W atoms, one vacancy and one SIA can form 18 independent configurations, which can be classified into four kinds according to the vertical distance between the vacancy and the ⟨1 1 1⟩ line of the SIA pair. The vertical distances are 0 Å, 2.59 Å, 4.48 Å and 5.18 Å in I, II, III and IV, respectively, as shown in Fig. 1. The recombination of SIA and vacancy includes two different types: instantaneous or thermally activated. The criterion to categorize the two recombination types is whether recombination occurs at 0 K. Recombination can and cannot happen at 0 K for instantaneous and thermally activated recombination, respectively. The vacancy-SIA configurations associated to the different recombination types are shown in Table 2.

Table 1
Comparison of the results of DFT calculations with experiments: vacancy formation energy E_f^V (eV), migration energy of vacancy E_m^V (eV), SIA formation energy E_f^I (eV) and migration energy of SIA E_m^I (eV).

	Experiment	DFT	
		Other works	This work
E_f^V	3.68 ± 0.2 [18]	3.34 [19] 3.10 [20]	3.09
E_m^V	1.78 ± 0.1 [18]	1.71 [19] 1.78 [21]	1.66
E_f^I	9.06 ± 0.6 [23]	9.86 [19] 9.94 [24]	9.56
E_m^I	–	0.005 [19] 0.004 [22]	0.007

For configuration I, the vacancy locates in the ⟨1 1 1⟩ line of the SIA pair, recombination occurs instantaneously for all the three configurations. SIA can recombine with the vacancy instantaneously through diffusion along ⟨1 1 1⟩ direction directly because of the small diffusion barrier of SIA along ⟨1 1 1⟩ direction. In this calculation, instantaneous recombination still occurs for the SIA with a long distance as 8.24 Å from the vacancy (case 1), which is the maximum region within first-principles calculation. However, it is believed that the critical distance for instantaneous recombination is much larger if large-scale simulation method is applied.

In configuration II, the vacancy is located in the first closest site to the ⟨1 1 1⟩ line of SIA and with a vertical distance of 2.59 Å from the ⟨1 1 1⟩ line. Instantaneous recombination and thermally activated recombination occurs in case 1–5 and case 6–7, respectively. Analyzing from the appearance, the recombination type should depend on the vacancy-SIA separation distance. Instantaneous recombination should be associated with short separation distance and thermally activated recombination should be associated with long separation distance in general. However instantaneous recombination occurs in case 1 while fails in case 6 even if the SIA-vacancy separation distance in case 6 is smaller than that in case 1. To further analyze the difference between two recombination types, we examine the recombination process of each instantaneous recombined case. In the instantaneous recombined cases, the SIA diffuses along ⟨1 1 1⟩ direction one by one to reach reset and one atom in the line transfers the diffusion direction and moves to recombine with the vacancy. The recovery process for case 1 is illustrated as an example, which is shown in Fig. 2(a). As discussed above, the diffusion of SIA along ⟨1 1 1⟩ is quite easy, so the "transfer atom (TA)" which transfers the diffusion direction and moves towards the vacancy may play a vital role in deciding whether the instantaneous recombination will occur. As a consequence, we figure out TA in each instantaneous recombined case. Besides, we examine the distances between the TAs and the vertical point (point O) of vacancy to ⟨1 1 1⟩ line of the SIA pair, which is a simplified expression of the distances between the TAs and the vacancy. The results are shown in Table 3(a). The TAs are in the left lower and right upper side of point O for case 1–3 and case 5, respectively, indicating that TA is always on the same side with the SIA pair. In case 4, the SIA pair is around point O, TA is the one closer to point O. It can be determined that TA is the closest atom to point O on the same side with SIA pair in the ⟨1 1 1⟩ line. While for case 6 and 7, the SIA pair just makes a little rotation after relaxation and cannot recombine with the vacancy instantaneously. According to the location of SIA pairs in case 6 and 7, the expected TA should be on the right upper side of and closest to point O in case 6 and 7. Comparing with the instantaneous recombined cases, we find that the TA-O distance in case 6 and 7 is larger than that in the instantaneous recombined cases. For case 1–5, the TA-O distance ranges from 0.25 Å to 0.83 Å. While in case 6 and 7, the TA-O distance is 1.17 Å and 1.54 Å, respectively. Consequently, it is the TA-vacancy distance rather than the SIA-vacancy separation distance that decides the recombination type.

In configuration III and IV, the vacancy is no longer located in the closest site to the ⟨1 1 1⟩ line of SIA pair. Under this condition, each type of recombination will occur through a replacement sequence. The intermediate atom (IA) between TA and vacancy fills the vacancy, while TA moves to the former IA site. In configuration III, instantaneous recombination occurs in none of the three cases.