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Energetics of He and H atoms with vacancies in tungsten: First-principles approach

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ABSTRACT

The formation energies of various defect configurations of He and H atoms in W were estimated based on the density functional theory. A special consideration was given to the coexistence of the He and H atoms at the presence of the vacancy and vacancy cluster in W. A single He atom favors a substitutional site, while a H atom spontaneously incorporates at an interstitial site with the negative formation energy. When He and H are present close to each other, they form an interstitial pair, occupying relaxed tetrahedral sites. When He, H and a vacancy coexist within a unit cell of W, however, He occupies the vacancy site then the He_{sub}–H_{tet} pair is predicted to be the lowest energy configuration. At the presence of a nearby vacancy cluster, He atoms occupy the vacant space while H atoms move slightly toward W.

1. Introduction

Tungsten has been considered as one of the candidates for plasma-facing materials in a fusion reactor, which is exposed to high fluxes of plasma. Therefore, the accumulation and retention of helium and hydrogen in tungsten are one of the prime concerns in fusion materials research. The deleterious effects of He and H on the properties of metals and alloys have been well known and extensively documented. The degree of damage is more profound under high-energy irradiation that generates significant concentrations of transmuted H and He [1]. In the case of irradiated tungsten, the resulting damages include various microscopic defects such as surface modifications, erosions, and formations of craters, clusters and bubbles [2–10].

Numerous computational works have been also performed to understand the atomic scale phenomena such as defect configurations in W. The first-principles calculations [11–14], molecular dynamics (MD) simulations [14–16], kinetic Monte Carlo (KMC) simulations [14], and the rate theory [17] have been undertaken to investigate the vacancy, interstitial defects, cluster formation of He or H. In fact, He and H are present simultaneously in W after irradiation, however, the atomic scale simulations on the coexistence of the He and H atoms have seldom studied so far.

In the present work, we focus of the energetics of the coexistence of the He and H atoms to estimate their simultaneous behavior in W. The first-principles calculation based on the density functional theory (DFT) was performed to estimate the formation energies of various defect configurations of He and H atoms including the coexistence of He and H atoms at the presence of a vacancy or a 6-vacancy cluster in W. These results are expected to provide basic understanding of the atomic-scale behavior of He and H in W.

2. Computational method

A $4 \times 4 \times 4$ supercell of body centered cubic (bcc) W containing 128 atoms was generated as a base structure for the simulation studies to minimize the interactions with adjacent images of defects caused by the periodic boundary condition. All calculations were carried out within DFT using the Vienna Ab-initio Simulation Package (VASP) [18,19]. The electron–ion interactions were described by projector augmented wave (PAW) potentials [20,21]. To calculate the exchange-correlation energy of electrons, the Perdew–Burke–Ernzerhof (PBE) parameterization [22,23] within generalized-gradient approximation (GGA) was employed. The lattice constant of the bulk bcc W was estimated to be 3.171 Å, which agrees well with the experimental value of 3.165 Å [24].

An energy cutoff of 400 eV and the k-point meshes of $4 \times 4 \times 4$ by the Monkhorst–Pack scheme [25] were used to achieve an accuracy of total energy within 10 meV/atom. Brillouin zone integration was performed using the tetrahedron method with Blöchl corrections [26]. Spin-unpolarized calculation was performed since the spin polarization did not affect the total energy and the atomic positions. Atomic positions of each configuration were fully relaxed. When necessary, however, some calculations were also performed with a certain atomic positions fixed. The formation energies of various defect configurations, E^{f}_{defect}, were defined as

$$E^{f}_{defect} = E^{tot}_{system} - E^{128}_{W}\left(\frac{N}{128}\right) - n_{He}E_{He} - n_{H}E_{H} \quad (1)$$

where E^{tot}_{system} is the total energy of the system with defects, N, n_{He}, n_{H} are the numbers of W, He and H atoms, E^{128}_{W} is the total energy

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of a perfect $4 \times 4 \times 4$ supercell of bcc W with 128 atoms, and E_{He}, E_H are energies of He and H atom, respectively.

3. Results and discussion

The formation energies of various single defects in W are summarized in Table 1. The bulk bcc W was taken as the reference state for the calculations of all single-defect systems. For calculating defect formation energies, all atomic positions were fully relaxed except the He and H atoms at the octahedral sites. The full relaxation with He or H atom at the octahedral site did not converge. The results are in good agreement with other calculation results [11,13] and in fair agreement with experiments [27].

For He, the substitutional site is the most favorable over the tetrahedral and octahedral sites. For H, on the contrary, the tetrahedral interstitial is the most preferred site over the substitutional and octahedral sites. It is noteworthy that the formation energy of H_{tet} and H_{oct} is negative, which implies the formation of a bond between H and W. As far as the authors' knowledge, the study on the defect formation energy of H in W has seldom reported.

In order to find a stable configuration of interstitial He and H when their distance is less than the length of the unit cell of W, eight symmetrically different initial configurations (not shown) were tested. In all cases, both He and H atom were relaxed in the adjacent tetrahedral sites with each other regardless of their initial configurations of the tetrahedral or octahedral site. The equilibrium bond distance and the formation energy of He_{tet}–H_{tet} pair were estimated to be 1.65 Å and 3.66 eV, respectively. Note that this formation energy is lower than that of the isolated He in W, which suggests that the existence of He in the vicinity of H is more favorable. In fact, the affinity of He and H in W was confirmed by the binding energy of He_{tet}–H_{tet}, which was estimated to be 0.14 eV. This binding energy was obtained from the difference between the total energy of the system when the distance between the He_{tet} and H_{tet} was the half of the body-diagonal of the $4 \times 4 \times 4$ supercell (the maximum distance in this supercell) and that when the He_{tet}–H_{tet} pair was formed.

The configurations of He–H pair in the presence of nearby vacancy are shown in Fig. 1. The open and filled circles represent W vacancies and W atoms, while the open and filled squares and triangles denote the initial and final positions of He and H atoms, respectively.

Fig. 1(a) shows the relaxed configuration of H–He-vacancy complex when the three defects are located in a unit cell of W. The results indicate that, if He atom and H atom are in the same unit cell at the presence of nearby vacancy, He atom relaxes into the vacancy while H atom prefers to stay in the relaxed tetrahedral site close to the He atom. The final configuration is a He_{sub}–H_{tet} pair occupying the vacancy site. The formation of this relaxed He_{sub}–H_{tet} pair, which started from the He_{tet}–H_{tet}-vacancy, was regarded as the lowest energy configuration and their formation energy was estimated to be 1.48 eV. In addition, the binding energy of He_{sub}–H_{tet} pair was calculated to be 1.03 eV, which is more than 7 times higher than that of He_{tet}–H_{tet} pair, supporting that this configuration is more stable.

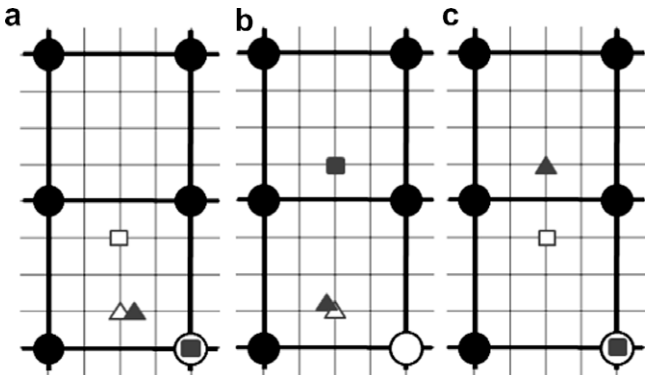

Fig. 1. Two-dimensional schematics on the atomic relaxations of the He_{tet}–H_{tet}-vacancy in W. Open and filled circles are W vacancies and W atoms. Open and filled squares and triangles are the initial and final position of He and H, respectively. The positions of the initial and final He are identical in (b) and those of H are identical in (c), respectively.

Fig. 1(b) indicates that He atom does not move toward a vacancy when its distance from the vacancy is larger than the length of the unit cell. In this case one can distinguish three point defects; single vacancy and tetrahedral He and tetrahedral H, respectively. Since He atom occupies tetrahedral site and its interaction with H is small, the formation energy of this configuration is 5.76 eV that is 4.28 eV higher than that for the configuration presented in Fig. 1(a). The He atom should overcome the energy barrier generated by neighboring W atoms in order to occupy the vacancy site from this initial configuration. On the contrary, if the distance between He and the vacancy is smaller than the unit cell length, He atom spontaneously occupies the vacancy site even when H atom is located farther than the unit cell length as shown in Fig. 1(c). The formation energy of this configuration is estimated to be 2.43 eV which is 0.95 eV higher than that of Fig. 1(a). The formation energy of He–H-vacancy complex is critically determined by whether the He atom occupies the vacancy site or not. In all cases, H atom prefers to stay at a tetrahedral site even when a vacancy is present within the unit cell length of W. They could provide the general tendency about the relative movement of He and H atoms with each other and their preference toward vacancy.

To clarify the above tendency further with more complex situation, a $4 \times 4 \times 4$ supercell of W with octahedral 6-vacancy cluster surrounded by 4 He atoms and 4 H atoms was constructed as shown in Fig. 2(a). He and H atoms are positioned at the face centers in order to have an equal probability to move with respect to the location of vacancies. In this configuration, the number of vacancies was set less than the total number of He and H atoms to create some competition between He and H atoms. Fig. 2(b) shows the configuration after the full relaxation. All four He atoms moved toward the vacancy cluster and formed a 4-atom cluster of a square shape, while all four H atoms stayed away from the vacancies and relaxed slightly toward W atoms. Note that He atoms do not occupy the vacancy sites but are located at the inter-vacancy positions. The formation energy of this relaxed configuration is 3.44 eV, which is comparable with that of single vacancy shown in Table 1. In consistent with the results of the He and H with one vacancy in Fig. 1, the results clearly demonstrated the quite different behavior between He and H atoms toward vacancies. In this study, the behavior of He and H atoms at the presence of vacancies in W was explained only in terms of energetic

Table 1
Summary of the formation energies of the single defects in W

Configuration	Formation energy (eV/defect)		
	This study	Other study	Experimental
v	3.36	3.40 [11] 3.11 [13]	3.6 [27]
He_{sub}	5.00	4.70 [13]	NA
He_{tet}	6.23	6.16 [13]	NA
He_{oct}(F)	6.48	6.38 [13]	NA
H_{sub}	0.92	NA	NA
H_{tet}	−2.47	NA	NA
H_{oct}(F)	−2.07	NA	NA

v; vacancy, sub; substitutional site, tet; tetrahedral site, oct; octahedral site, F; Only the octahedral atomic position is fixed, and NA; not available.

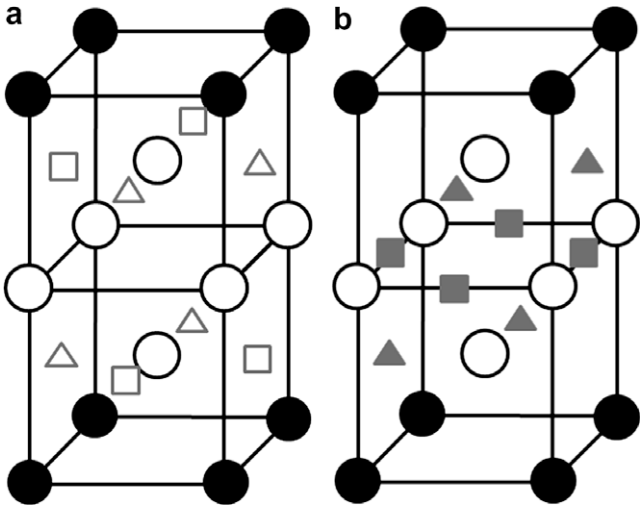

Fig. 2. Schematics of a part of $4 \times 4 \times 4$ supercell of W with 6-vacancy cluster, 4 He, and 4 H; (a) unrelaxed (b) relaxed.

consideration. Further studies such as electron density consideration, path search by the nudged elastic band (NEB) method [28] are needed to have better understanding.

4. Summary

Energetics of various defect configurations of He and H atoms with the presence of a vacancy or a vacancy cluster in W were examined by using the first-principles calculations based on DFT.

1. A single He atom favors the substitutional site to the interstitial site in W, while a single H atom spontaneously occupies a relaxed interstitial site with the negative formation energies. For H atom, the tetrahedral site is the most favorable.
2. When He and H are present within the same unit cell of W, both atoms relax to occupy the adjacent tetrahedral sites with each other.
3. If He atom and H atom are located in the same unit cell with the presence of a nearby single vacancy, He atom readily occupies the vacancy site, while H atom prefers to stay in the relaxed tetrahedral site.
4. At the presence of a nearby vacancy cluster, He atoms readily occupy the vacant space while H atoms move slightly toward W.

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References

[1] S.T. Picraux, F.L. Vook, J. Nucl. Mater. 53 (1974) 246.
[2] S. Nagata, K. Takahiro, J. Nucl. Mater. 283–287 (2000) 1038.
[3] T.I. Mazilova, I.M. Mikhailovskii, Tech. Phys. 47 (2002) 910.
[4] K. Katayama, K. Imaoka, T. Okamura, M. Nishikawa, Fusion Eng. Des. 82 (2007) 1645.
[5] N. Yoshida, H. Iwakiri, K. Tokunaga, T. Baba, J. Nucl. Mater. 337–339 (2005) 946.
[6] H.T. Lee, A.A. Haasz, J.W. Davis, R.G. Macaulay-Newcombe, J. Nucl. Mater. 360 (2007) 196.
[7] H.T. Lee, A.A. Haasz, J.W. Davis, R.G. Macaulay-Newcombe, D.G. Whyte, G.M. Wright, J. Nucl. Mater. 363–365 (2007) 898.
[8] M.Y. Ye, H. Kanehara, S. Fukuta, N. Ohno, S. Takamura, J. Nucl. Mater. 313–316 (2003) 72.
[9] K. Heinola, T. Ahlgren, E. Vainonen-Ahlgren, J. Likonen, J. Keinonen, Phys. Scr. T128 (2007) 91.
[10] O.V. Ogorodnikova, J. Roth, M. Mayer, J. Nucl. Mater. 373 (2008) 254.
[11] K. Heinola, T. Ahlgren, A. Kuronen, K. Nordlund, Tungsten properties and defects studied by computational methods, Accelerator Laboratory, Department of Physical Sciences, University of Helsinki, The Second German-Finnish Workshop on Material Migration in Fusion Devices – Measurements and Modelling, Tervaniemi, Finland, 26–27 February 2007.
[12] D. Nguyen-Manh, A.P. Horsfield, S.L. Dudarev, Phys. Rev. B 73 (2006) 020101.
[13] C.S. Becquart, C. Domain, Nucl. Instrum. and Meth. B 255 (2007) 23.
[14] K.O.E. Henriksson, K. Nordlund, A. Krasheninnikov, J. Keinonen, Appl. Phys. Lett. 87 (2005) 163113.
[15] K.O.E. Henriksson, K. Nordlund, J. Keinonen, D. Sundholm, M. Patzschke, Phys. Scr. T108 (2004) 95.
[16] K.O.E. Henriksson, K. Nordlund, J. Keinonen, Nucl. Instrum. and Meth. B 244 (2006) 377.
[17] Y. Watanabe, H. Iwakiri, N. Yoshida, K. Morishita, A. Kohyama, Nucl. Instrum. and Meth. B 255 (2007) 32.
[18] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[19] G. Kresse, Vienna Ab-initio Simulation Package (VASP), <http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html>, 2007.
[20] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[21] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
[22] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[23] Y. Zhang, W. Yang, Phys. Rev. Lett. 80 (1998) 890.
[24] P.E. Tomaszewski, Phase Transit. 38 (1992) 127.
[25] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[26] P.E. Blöchl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 16223.
[27] P. Ehrhart, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, vol. III/25, Springer, Heidelberg, 1991.
[28] G. Henkelman, H. Jónsson, J. Chem. Phys. 113 (2000) 9978.