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First principles investigation of cluster consisting of hydrogen–helium atoms interstitially-trapped in tungsten

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ABSTRACT

We evaluate the binding energies of mixed helium and hydrogen clusters consisted of interstitially trapped atoms in bcc tungsten by first-principles calculations based on density functional theories. It is shown that helium-rich interstitially-trapped clusters have the positive binding energies and the low electron-density region expand as the number of helium in the cluster increase. Thus, the helium-rich interstitially trapped clusters can act as a trapping site for hydrogen, and interstitially trapped helium interrupts or disturbs the hydrogen diffusion in tungsten.

1. Introduction

As tungsten has strong hardness, a high melting point, and high resistivity to surface chemical erosion, tungsten is employed as a plasma facing material of inside walls in magnetic confinement nuclear fusion reactors. In the surface of plasma facing materials, high concentrations of hydrogen, hydrogen isotopes and helium can build up and interact with the materials. These interactions will induce changes in the microstructure and thus in the mechanical properties. Therefore, the mechanical properties and the structural strength of W under exposure to plasma irradiation have been intensively investigated both experimentally [1,2] and theoretically [3–14].

Becquart et al. [6] studied the clustering behavior of He and H in tungsten by density functional theory based calculations, where they treated mixed He and H clusters in the presence of a single vacancy. Jiang et al. [8] investigated hydrogen trapping around the substitutional helium in tungsten and electronic structure around H and He. Recently, Tamura et al. [13] reported the first-principles investigation of possible clustering of noble gas atoms in bcc tungsten, where they analyzed electronic structures of single noble gas atoms and dimer of noble gas atoms in detail.

In the present study, mixed He and H clusters consisted of interstitially trapped atoms in tungsten are investigated by first principles calculations based on density functional theories (DFTs) [15,16]. It is stressed that the present study considers the case with interstitially trapped helium/hydrogen in perfect crystalline tungsten, while both the prior works by Becquart et al. [6] and Jiang et al. [8] consider the case with tungsten mono-vacancy. It is important whether interstitially trapped helium/hydrogen form cluster structure, because it implies that the diffusion behavior of helium/hydrogen in tungsten can be altered without vacancy formation such as low temperature condition.

2. Numerical methods

The calculations in this study are carried out with the "OpenMX" code package [17], which stands for "Open source package for Material eXplorer" and is designed for nanoscale material simulations based on DFTs. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional [18] is used for the exchange–correlation potential. Linear combinations of pseudo-atomic localized orbitals [19,20], norm-conserving pseudo-potentials [21], and projector expansions [22] are employed for core Coulomb potential. Bcc W supercells composed of 128 tungsten atoms ($4 \times 4 \times 4$ unit cells; each unit cell consists of two W atoms) containing interstitial atom(s) and the Brillouin zones with $4 \times 4 \times 4$ k-points for sampling using the Monkhorst–Pack method [23] are used. OpenMX uses numerical pseudo-atomic orbitals (PAOs) as the basis function to expand one-particle Kohn–Sham wave functions. We employ the 3s-, 2p-, 2d-, and 1f-state radial functions with a cut-off radius of 7.0 a.u. for tungsten, the 2s-, 2p-, and 1d-state with 8.0 a.u. for helium, the 3s-, 2p-, and 1d-state with 6.0 a.u. for hydrogen. The equilibrium lattice parameter is calculated to be 3.186 Å, although this value is slightly larger than that in the literature, 3.165 Å (at 298 K) [24].

All the calculations are carried out at constant volume with the atomic positions in the supercells fully relaxed with use of the

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Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [25–28]. It should be noted that in order to efficiently search for the most probable configurations, the initial positions of both the tungsten atoms and interstitially trapped atoms (helium and/or hydrogen) are randomized.

3. Results and discussion

First of all, the solution energies E^{sol} of single hydrogen atom and helium atom into bcc tungsten are evaluated. The solution energies are evaluated by

$$E^{\mathrm{sol}}[A] = E_{\mathrm{tot}}[W_{128}A_1] - E_{\mathrm{tot}}[W_{128}] - E_{\mathrm{tot}}[A_1],$$

where $E_{\mathrm{tot}}[X]$ is the total energy of the supercell containing the entity X, and the entity A represents either H or He in this study. The evaluated value of solution energies of H and He into tungsten are $E^{\mathrm{sol}}[\mathrm{H}] = -1.46[\mathrm{eV}]$ and $E^{\mathrm{sol}}[\mathrm{He}] = 6.17[\mathrm{eV}]$, respectively. If H_2 molecule is taken as the reference state for H, solution energy of hydrogen is $E^{\mathrm{sol}}\left[\frac{1}{2}\mathrm{H}_2\right] = E_{\mathrm{tot}}[W_{128}\mathrm{H}] - E_{\mathrm{tot}}[W_{128}] - \frac{1}{2}E_{\mathrm{tot}}[\mathrm{H}_2] = 0.843$ [eV]. In both cases, H and He atoms are relaxed at tetrahedral sites as shown in Fig. 1. These results are consistent with previous studies [13]. A negative or positive solution energy means that the reaction is exoergic or endoergic, respectively. The calculated results imply that hydrogen is easy to solve in tungsten, while energy is required for helium to solve in tungsten.

The binding energies E^{bin} are evaluated by

$$E^{\mathrm{bin}}[A, B] = E_{\mathrm{tot}}[W_{128}A] + E_{\mathrm{tot}}[W_{128}B] - E_{\mathrm{tot}}[W_{128}AB] - E_{\mathrm{tot}}[W_{128}],$$

where entities A and B represent two different entities He_mH_n and $He_{m'}H_{n'}$. A positive binding energy means that the entity A and the entity B are attractive. The results are presented in Fig. 2 in the perspective of H trapping and in Fig. 3 in the perspective of He trapping.

Fig. 2 shows that the binding energy $E^{\mathrm{bin}}[He_mH_n, H]$ becomes negative or almost zero without helium ($m = 0$) or when $n \geqslant 4$ and $m = 1$. This implies that hydrogen atoms are repulsive and do not form a cluster constituting of interstitially trapped atoms by themselves, and that they can interstitially aggregate with the help of helium atom(s). In Fig. 2, $E^{\mathrm{bin}}[\mathrm{He}, \mathrm{H}]$ has positive finite value of 0.06 eV, that is, He–H pair is attractive. These results are consistent with the previous results by Becuqart et al. [6].

Fig. 4(a)–(d) shows the final atomic configurations and the low electron-density isosurfaces for the systems with (a) He–He pair, (b) He–H pair, (c) 2He–H cluster, and (d) He–2H cluster. Comparing these figures with Figs. 1(a) and (b), low electron-density regions expand as these pair or cluster are formed. This expansion of low electron-density region implies that such configuration can also act as a trapping site for He and H. It is explained as follows: the behavior of H in a metal can be understood via the optimal charge density [9]; furthermore, since a He atom has a closed-shell structure, the low electron-density region can act as a preferable site for He.

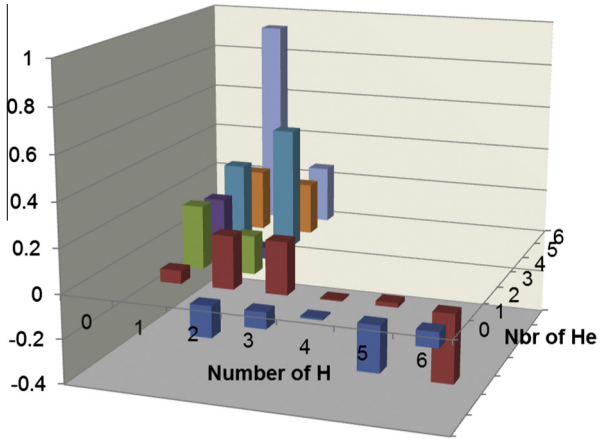

Fig. 2. Binding energies for the reaction: $He_mH_n + H \rightarrow He_mH_{n+1}$. The unit is electron volt (eV).

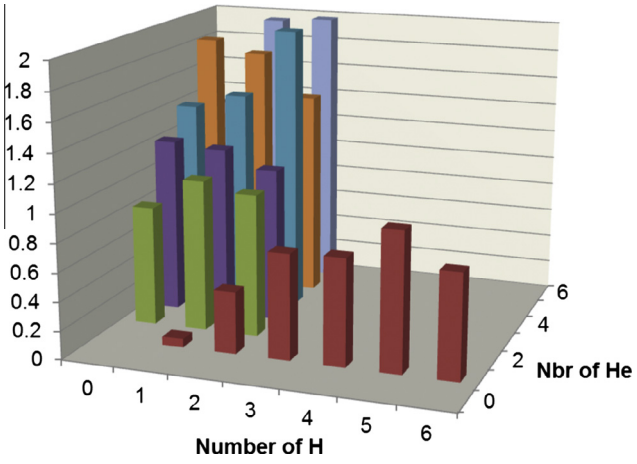

Fig. 3. Binding energies for the reaction: $He_mH_n + He \rightarrow He_{m+1}H_n$. The unit is electron volt (eV).

The binding energies $E^{\mathrm{bin}}[He_mH_n, He]$ shown in Fig. 3 are 1–2 eV, while the binding energies $E^{\mathrm{bin}}[He_mH_n, H]$ in Fig. 2 are 0.25–0.5 eV when n/m is about or less than unity. Here, m and n are the number of He and H in the cluster. Thus, it is inferred that aggregation of interstitially trapped helium dominates and helium

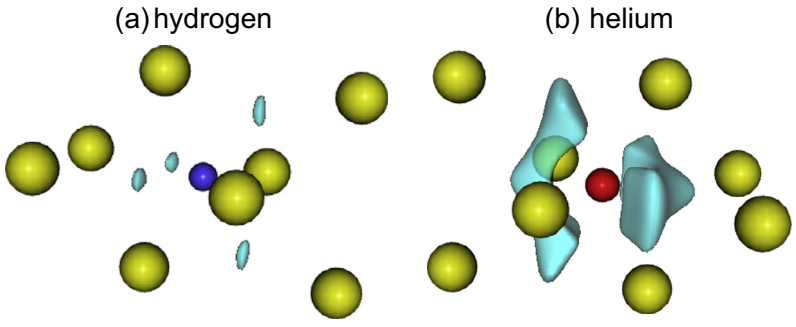

Fig. 1. Final atomic configurations and the low electron-density isosurfaces for the systems with (a) hydrogen and (b) helium, respectively. The yellow spheres represent W atoms. Both hydrogen and helium are relaxed at tetrahedral sites. The isosurfaces indicate 0.036 electrons a.u.$^{-3}$, which shows a low electron density region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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