Journal of Alloys and Compounds 509 (2011) 8277–8282

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Investigating behaviors of H in a W single crystal by first-principles: From solubility to interaction with vacancy

Yue-Lin Liu[a,*], Hong-Bo Zhou[b], Ying Zhang[b]

[a] Department of Physics, Yantai University, Yantai 264005, China
[b] Department of Physics, Beihang University, Beijing 100191, China

ARTICLE INFO

Article history:
Received 31 December 2010
Received in revised form 18 March 2011
Accepted 18 March 2011
Available online 29 March 2011

PACS:
61.82.Bg
67.63.–r
61.72.jd
66.30.J–

Keywords:
Tungsten
Hydrogen
Solution
Diffusion
First-principles

ABSTRACT

We have investigated structure and solubility of H, as well as H–vacancy interaction in tungsten (W) single crystal employing a first-principles method. Single H atom is shown to be energetically favorable sitting at the tetrahedral interstitial site (TIS). The solubility of H is estimated in W according to the Sieverts' law. We found that the solution concentrations are 2.3×10^{-10} and 1.8×10^{-7} at the typical temperatures of 600 K and 1000 K, respectively. The calculated results are basically consistent with the experiments. The vacancy can be found to play a key role on the trapping of H in W. There exists a very strong binding between single H and vacancy with the binding energy of 1.18 eV. With the H atoms added, the H_nV complexes can be easily formed in the vacancy. A monovacancy is shown to be capable of trapping as many as 7 H atoms. Kinetically, we show that the H jumps into the vacancy from the first nearest neighboring TIS into vacancy with a much reduced barrier of 0.02 eV, which indicates a down-hill "drift" diffusion of H towards vacancy. The physical mechanism underlying H assisted vacancy formation is originated from that H atoms can stimulate the formation and growth of vacancy or void by binding with vacancy to decrease the effective formation energy of vacancy in W.

1. Introduction

As the lightest element in nature, hydrogen (H) has attracted many great attentions due to its chemical activity. Thus, the interaction of H with metals and metal-alloys is of great scientific and technological interest [1–7]. Especially in a fusion reactor [8] at present, metals are used as the plasma facing material (PFM) which is exposed to extremely high fluxes of H isotope [deuterium–tritium (D–T)] ions. The PFM must withstand "H" radiation damage to keep its intrinsic mechanical properties and structural strength. Hence, understanding the interaction between H and a metal PFM has a direct impact on the design and operation of a fusion reactor [8]. Tungsten (W) and W-alloys are considered as the most promising PFMs because of their low sputtering erosion and good thermal properties such as high thermal conductivity and high melting temperature. Consequently, much recent effort has been devoted to understanding the interaction of H with W between experiment [9–13] and simulation [14–16].

It is well known that the implanted H would easily diffuse into the inner of material, which could eventually find the suitable trapping sites in a material [17,18] to lead to the nucleation and growth of H blistering [19,20]. Experiments have shown that the bombardment of high flux of H isotope ions on single crystal [9,10] and polycrystalline W [11–13] can cause roughening and blistering at the W surface. Accordingly, H blistering accumulation will change the microstructures and mechanical properties of W, which is the most important issue in developing W as a PFM. On the other hand, H has been also shown to assist vacancy formation in W as well as other metals such as Mo, Ni, Cr, Pd and Al [1–3,21], which will in turn further enhance the H trapping. The relevant results have been reviewed systematically by Condon [22] and Fukai [23].

Despite many years of research, many fundamental aspects underlying the H–W interaction remains poorly understood such as the solution concentration of H and the physical mechanism as to how H can assist vacancy formation under an H-rich environment in W. In order to further understand the physical mechanism of interaction between H and W, more precise examinations should be still indispensable. We know that experimental methods for the solution of H atom in W are quite limited due to the extremely low solubility of H. Hence, computational method with accuracy would be a most promising tool to address many basical physical problems. In this paper, we thus have systematically investigated the interaction of H with W including the solubility, occupancy of H at vacancy, and physical mechanism of H assisting vacancy formation

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* Corresponding author. Tel.: +86 535 6902506; fax: +86 535 6902506.
E-mail addresses: liuyl@ytu.edu.cn, liuyuelin@ss.buaa.edu (Y.-L. Liu).

0925-8388/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2011.03.117

in a W single crystal using the first-principles method. Our calculations will provide a good reference for developing W materials as a PFM.

2. Computational method

Our first-principles calculations were performed using the VASP code [24,25] based on the density functional theory (DFT). We used the generalized gradient approximation of Perdew and Wang [26] and projector augmented wave potentials [27] with a plane wave energy cutoff of 350 eV. During geometry optimization, we used $(5 \times 5 \times 5)$ grid for 54 atoms and $(3 \times 3 \times 3)$ grid for 128 atoms of **k**-points chosen by the Monkhorst-Pack scheme [28], respectively. The calculated equilibrium lattice constant is 3.17 Å for bcc W, in good agreement with the corresponding experimental value of 3.16 Å [29]. The energy relaxation iterates until the forces acting on all the atoms are less than 10^{-3} eV/Å.

The solution energy of the interstitial H atom in the intrinsic W is defined as

$$E^{s}_{H} = E_{NW,H} - NE_{W} - \mu_{H}, \qquad (1)$$

where $E_{NW,H}$ is the energy of the supercell with N W atoms and one interstitial H atom, E_W is the energy of an ideal bulk W atom, and μ_H is the H chemical potential, which is one-half of the energy of a H_2 molecule. Here we obtained the value of −3.36 eV according to the present calculation.

The binding energy of H atoms with vacancy in H–vacancy complexes (H_nV) is defined

$$E^{b}_{H_nV} = \left[E_{(N-1)W,H_nV} - E_{(N-1)W,H_{n-1}V}\right] - \left[E_{NW,H(TIS)} - NE_{W}\right] \qquad (2)$$

where the $E_{(N-1)W,H_nV}$ and $E_{(N-1)W,H_{n-1}V}$ are the energies of the supercell with H_nV and $H_{n-1}V$ complexes, respectively. While $E_{NW,H(TIS)}$ is the energy of the supercell with a tetrahedral interstitial site (TIS) H atom. Here, negative binding energy indicates repulsion between per H and vacancy, while positive value represents attraction.

The H_nV formation energy with the presence of monovacancy is defined as

$$E^{f}_{H_nV} = E_{(N-1)W,H_nV} - (N-1)E_{W} - n\mu_{H} \qquad (3)$$

where the $E_{(N-1)W,H_nV}$ is the energy of the supercell with $N-1$ W atoms, n H atoms and one vacancy.

3. Results and discussion

3.1. The stability of single H atom in W

We first examined the stability of single H atom in the bulk W. For single H atom, we select the TIS, the octahedral interstitial site (OIS), and the diagonal interstitial site (DIS, which sits in between two nearest neighboring TISs). Single H is shown to be energetically favorable sitting in the TIS with a solution energy of 0.86 eV in reference to the H chemical potential μ_H (−3.36 eV) in comparison with 1.06 eV and 1.24 eV at the respective DIS and OIS. Our results indicate that the solution of H in W is endothermic. One sees that the value of 1.06 eV at the DIS is basically consistent with the existing experimental results of 1.10 eV [30] and 1.04 eV [31]. The possible reason might be mainly because H exhibits an obvious character of fugacity [22] even at the room temperature, while the experimental value of 1.10 eV was obtained at the temperature range of 900–1750 K. Therefore, we believe that there exists the drift instability for H at such high temperature, i.e., H might not sit in the most stable TIS but stay at the DIS or OIS.

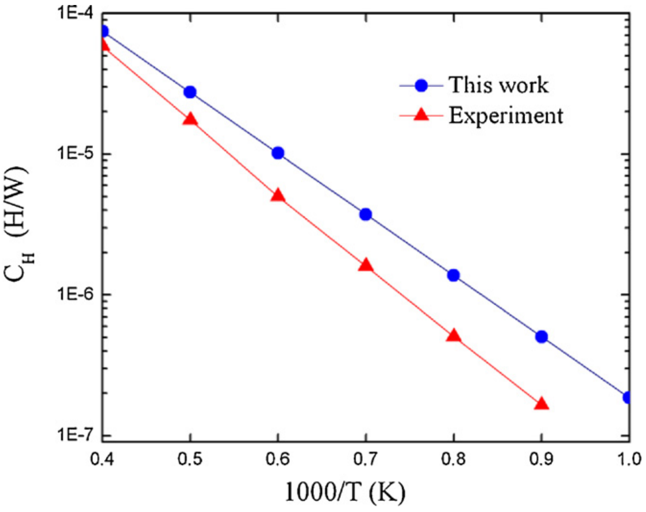

Fig. 1. The solution concentration of H in W as a function of reciprocal temperature in comparison with the previous experimental results.

3.2. Solubility of H in W

As to the fusion application, H atoms are easily trapped directly into PFM such as W and Mo. The solubility of H in the PFM not only plays a key role on determining the recombination rate coefficient [17], but also should be directly associated with the H trapping and blistering formation in W.

We can roughly calculate the solution concentration of H in W according to the Sieverts' law. The equilibrium concentration of H in a material is defined as

$$C_H = \sqrt{\frac{p}{p_0}} \exp\left(\frac{\Delta S}{k}\right) \exp\left(\frac{-E^{s}_{H}}{kT}\right), \qquad (4)$$

where p and p_0 are the background pressure and the reference pressure (here we choose standard pressure in order to make a comparison with the experimental results), respectively. ΔS is the solution (formation) entropy in reference to the H_2 gas of the standard pressure, which is chosen as $-5.5\,k$ for H in W [32]. E^{s}_{H} is the solution energy of H in the TIS in W, and k and T are the Boltzmann constant and the absolute temperature, respectively. Using the calculated H solution energy of 0.86 eV and the experimental background pressure of $\sim 10^5$ Pa, we can thus give the solution concentration of H in W.

Fig. 1 plots the solution concentration of H in W as a function of reciprocal temperature with respect to the unit of the atomic fraction of H (H/W). It is important to note that the solubility of H in W strongly depends on the temperature and increases with the increasing of temperature, suggesting an endothermic reaction for the H solution in W. In order to make a comparison with the present calculations, we also show the experimental values measured by Frauenfelder et al. in the earlier studies [31]. One sees that the present results exhibit the similar trend to and are basically consistent with those from the experiment, although the absolute values are slightly different. The concrete values of the H solution concentration at the typical temperatures (ranging from 600 K to 2000 K) are listed in Table 1. For example, the solution concentration is 2.3×10^{-10} at 600 K and 1.8×10^{-7} at 1000 K, respectively.

According to the Table 1, we can note that the actual concentration of H in the bulk W (e.g., only 2.3×10^{-10} at 600 K) is very low. This suggests that the defect-free W can not effectively trap H. Consequently, H will be difficult to accumulate and form blistering, different from experimentally observed H blistering in W at ∼500 K [9–13]. The reason lies in that here we have not taken into account

Table 1
Solution concentration of H in W (C_H) at the different temperatures ranging from 600 K to 2000 K.

Temperature (K)	600	800	1000	1200	1400	1600	1800	2000
C_H (H/W)	2.3×10^{-10}	1.5×10^{-8}	1.8×10^{-7}	1.1×10^{-6}	3.4×10^{-6}	7.8×10^{-6}	1.6×10^{-5}	2.7×10^{-5}

the defects such as vacancy and grain boundary in W. Generally, a large amount of defects will be generated under H irradiation. In the previous studies, we have investigated the role of grain boundary on the H trapping in W [15]. The grain boundary is shown to act as the trapping centers which can drive H to segregate towards these defects, leading to a large amount of H accumulation surrounding these defects.

In Fig. 2, we show the solution concentration of H in W as a function of pressure (p) at the different temperature. One can see that the solubility of H in W increases slightly with the increasing pressure at the same temperature. However, for the same pressure, the solubility of H increases obviously with the increasing temperature (e.g., the H concentration can be increased by 7 orders of magnitude at the 60 P_0 from 500 K to 2000 K). Thus, we can conclude that the H concentration has stronger dependence on the temperature as mentioned above in comparison with pressure.

3.3. The interaction of H with vacancy in W

Apparently, defect-free W can not effectively trap H atoms due to the lower concentration in the bulk W as suggested above. We now turn our attention to other possible defects that might trap H atoms relative easier. Here, vacancy comes into picture because it is one of the most common defects and it is generally considered as the trapping sites in their vicinity. Below, we thus calculate the H binding energy in the vicinity of single vacancy.

3.3.1. The interaction of single H atom with vacancy in W

We first investigate how single H atom would interact with vacancy in the vicinity of single vacancy. Fig. 3 shows six high-symmetric sites for single H atom at a monovacancy. Site 1 is the substitutional center. Site 2 and 5 are the face OIS center and the side OIS center, respectively. Both Site 3 and 4 are the TIS's, and site 4 is outside the vacancy. Site 6 is the mid-point between the substitutional center and its nearest neighboring W atom. We calculate the binding energy of H at these high-symmetric sites as well as other possible sites. The energy minimization shows that there exists a strong attraction between H and vacancy with a large binding energy of 1.18 eV, as shown in Table 2. This agrees very well with the experimentally binding energy measured between H and vacancy in W of 1.16 eV [33] and 1.07 ± 0.03 eV [34]. We further found that the most stable site for H can not sit in the center of the vacancy, but be at an off-vacancy-center position (~1.28 Å from the vacancy center) close to an OIS [Fig. 4(a)], similar to the behaviors of H isotope ion at other metals [4]. Moreover, there exists 6 same most stable sites very close to the 6 OIS's next to the vacancy center in the vicinity of the vacancy, as indicated in Fig. 4(a).

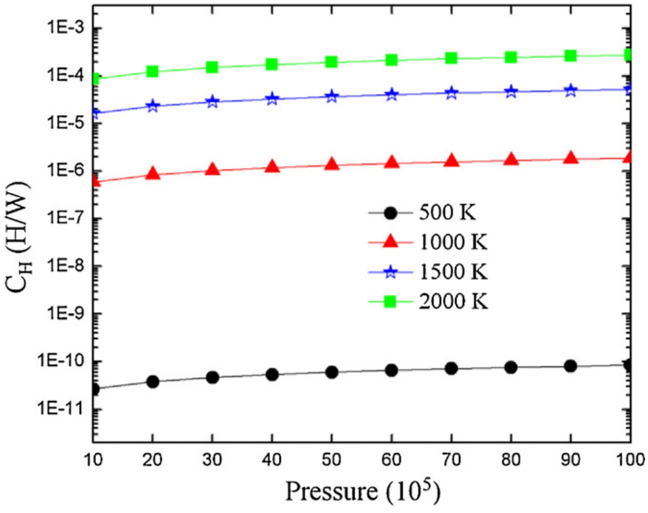

Fig. 2. The solution concentration of H in W as a function of pressure at the different temperature.

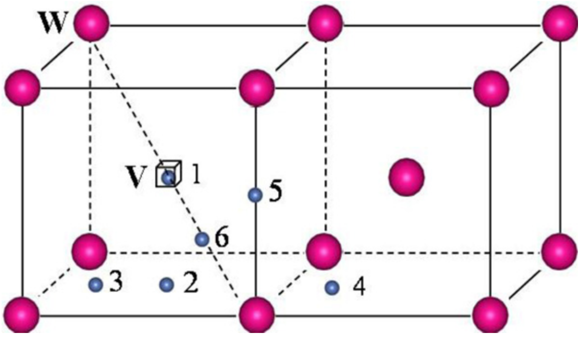

Fig. 3. Six possible sites for single H atom at one vacancy. The large red and small grey balls represent W and H atoms, respectively. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.ss.)

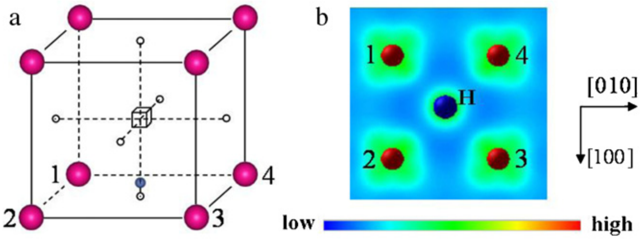

Fig. 4. Schematic illustration of single H at vacancy in W. (a) The most stable geometrical configuration for H. (b) The charge density distribution map of the most stable configuration. The red and grey balls represent W and H atoms, respectively. The cubic and open circles represent vacancy and the OIS, respectively. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.)

Table 2
The binding energy (eV) and the final distance (Å) between H and vacancy using a 54 atoms supercell.

Configuration	Binding energy	The final distance between H and vacancy center
1	−0.10	0
2	1.18	1.28
3	1.17	1.29
4	0.27	2.22
5	0.98	1.22
6	0.71	0.94
Fransens[a]	1.16	
Poon[b]	1.07±0.03	

[a] Experimental value from Ref. [33].
[b] Experimental value from Ref. [34].

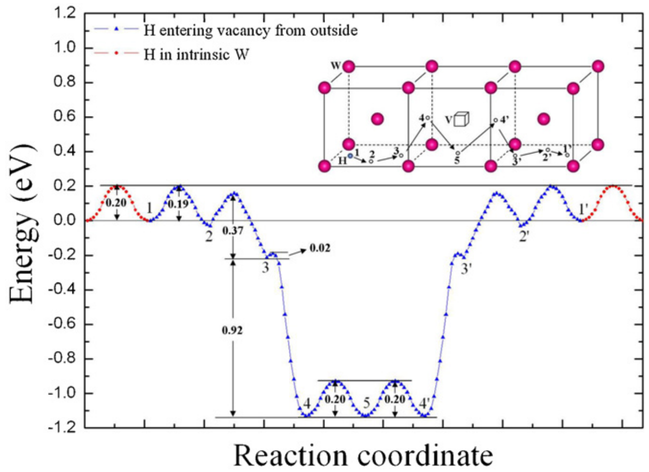

Fig. 5. Diffusion energy profile and the corresponding diffusion paths for H surrounding the vacancy in W. Site 1 (1′), 2 (2′) and 3 (3′) represent the TIS's outside of the vacancy, respectively. Site 4 (4′) and 5 represent the most stable sites of H at vacancy. The larger red and the smaller blue balls represent W and H atoms, respectively. The arrows show the corresponding diffusion paths. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.)

Also, the charge density distribution map shows that H atom is negatively charged [see Fig. 4(b)], which is consistent with the previous studies from jellium model [35]. Generally, H atom can be considered as a screened H^- ion in a homogeneous electron gas model. The charge density reduces surrounding the nearest neighboring W atoms, however, the electrons of the H^- ion buildup a lot. H atom thus attracts more conduction electrons from the vicinity of the vacancy, weakening the bonding character between W atoms, which in turn may drive the formation of divacancy or multivacancies. This is generally believed H-induced embrittlement phenomena.

Considering the kinetics of H in W, we use a drag method at a fixed volume and constrain the atomic positions to relax in a hyperplane perpendicular to the vector from the initial to finial positions [36]. In the bulk W without vacancy, H jumps from one TIS to another nearest neighboring TIS via a mediate transition state configuration. The diffusion barrier is calculated to be 0.20 eV in our previous study [14] via the optimal diffusion path, as shown in Fig. 5.

We further turn to the case of presence of vacancy. First, we calculate the diffusion barrier concerning a single H atom moving into the vacancy. The optimal diffusion path is determined by the calculated energetically favorable sites, i.e., site 1, 2 and 3 in Fig. 5, which are the third-nearest-neighbor (3NN), 2NN and 1NN TISs of the vacancy, respectively. It can be seen that the energy barrier from site 1 to site 2 is 0.19 eV, while the value further decreases to 0.18 eV from site 2 to site 3 due to the presence of the vacancy. However, the H atom can diffuse into the vacancy with an energy barrier as low as 0.02 eV from site 3, with the same magnitude as the thermal energy of 0.026 eV at the room temperature. More importantly, as long as H jumps into the vacancy, i.e., site 4, it has to overcome a barrier of 0.94 eV to go back to the bulk interstital site. Therefore, once H can be trapped by vacancy, it is impossible to escape away from the vacancy due to the larger detrapping energy barrier at the lower temperature. As to the diffusion case of H at the inner of vacancy. Site 4 (4′) and 5 are one of the six most stable sites of H at vacancy, respectively. Although the H atom is constrained in the inner of vacancy, it only overcomes an energy barrier of 0.20 eV (Fig. 5) from one stable site such as site 4 to another stable site 5. This value is the same as the case (0.20 eV) of H in the intrinsic W, implying that it is easy for single H atom to jump in the inner of vacancy.

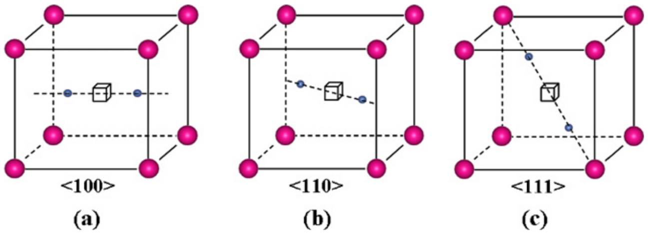

Fig. 6. (a)–(c) show the ⟨1 0 0⟩, ⟨1 1 0⟩ and ⟨1 1 1⟩ dumbbells of double H atoms at vacancy, respectively. The large red and small grey balls represent W and H atoms, respectively. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.)

3.3.2. *The interaction of double H atoms with single vacancy in W*

We further investigate the interaction of double H atoms with single vacancy. This is worth focusing on because it is related to H blistering formation. In the following description, we call H_2V about double H atoms at single vacancy. Here, we only consider ⟨1 0 0⟩, ⟨1 1 0⟩ and ⟨1 1 1⟩ three obvious dumbbell configurations for H_2V complex as shown in Fig. 6. These correspond to three high symmetric configurations for the two H atoms sitting at the both sides of the center of vacancy.

The binding energies of per H atom with vacancy for H_2V are summarized in Table 3. One can see that ⟨1 0 0⟩ dumbbell structure for H_2V is shown to be energetically favorable with a binding energy of 1.15 eV for per H atom in comparison with ⟨1 1 0⟩ and ⟨1 1 1⟩ dumbbell with the respective binding energies of 0.96 eV and 0.57 eV. We can also see that the equilibrium distance of double H atoms at vacancy is 2.55 Å for the most stable ⟨1 0 0⟩ dumbbell configuration, much longer than that of the H_2 bond length with the value of ~0.75 Å. This implies that two H atoms cannot bind together to directly form an H_2 molecule in the vacancy.

Fig. 7(b) shows the charge density distribution for the ⟨1 0 0⟩ dumbbell configuration of H_2V. We see that there exists the stronger repulsive interaction for two H atoms due to the lower charge density between them, although the larger binding energy between per H and vacancy. This suggests that double H atoms do not prefer to interact with each other to form H_2 molecule at vacancy center. Finally, we directly try to put an H_2 molecule into the vacancy center, however, the H_2 molecule dissociates and moves to the two respective stable sites.

3.3.3. *The interaction of multi-H atoms with single vacancy in W*

The above results indicate that H and vacancy is strongly attractive in W. Such strong binding between H and vacancy implies that the vacancies might act as trapping centers which drive the H atoms to go into the vacancies providing the prerequisite step for H blistering formation, i.e., H_nV complexes. To investigate this possibility, we have calculated the binding energies of additional H atoms segregating to the vacancy.

We bring the H atom one by one into the vacancy and minimize the energy to find the optimal embedding site at each step, as

Table 3
The binding energy (eV) of per H atom with vacancy and H–H equilibrium distance (Å) using a 128 atoms supercell.

Configuration	Binding energy	H–H equilibrium distance
⟨0 0 1⟩	1.15	2.55
⟨1 1 0⟩	0.96	2.44
⟨1 1 1⟩	0.57	1.91

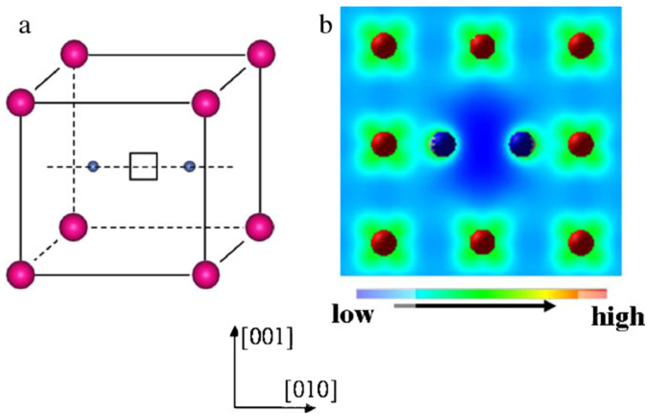

Fig. 7. The valence charge density distribution map of the ⟨1 0 0⟩ dumbbell structure at the (1 0 0) plane for H_2V. The red and blue balls represent W atoms and H atoms, respectively. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.)

illustrated in Fig. 8. For three H atoms, we found that the most stable configuration is an equilateral triangle lying {1 0 0} plane. While for four and five H atoms, the most stable configurations are square and rectangular pyramid, respectively. The six H atoms occupy the six "close-to-OISs" surrounding the vacancy to form an octahedron. In order to further determine how many H atoms a vacancy may accommodate, we plot the H binding energy for per H as a function of the number of H inside the vacancy, as shown in Fig. 9. We may understand the binding of H and vacancy as the following. The first H gains a binding energy of 1.18 eV as it sits on the most stable site. As more H atoms are added, they experience a repulsive interaction with each other. The binding energy (1.15 eV) becomes lower when the second H atom is added in comparison with the first one (1.18 eV), suggesting that such H_2V is not more stable than the H_1V in W. However, the formation of the H_2V induces large energy release of 1.15 eV. With the increasing number of H atoms added, the energy release decreases. One sees that the formation of H_3V from $H_2V + H$ can induce an energy release of 1.04 eV, and the formation of H_4V from $H_3V + H$ is also exothermic with energy release of 0.70 eV. The blistering reaction is still exothermic with the formation of H_7V. Eventually, when H atoms are beyond a critical number $n = 8$, there exists no more additional energy release, and the energy becomes negative. Thus, it is energetically favorable for single vacancy to trap as many as 7 H.

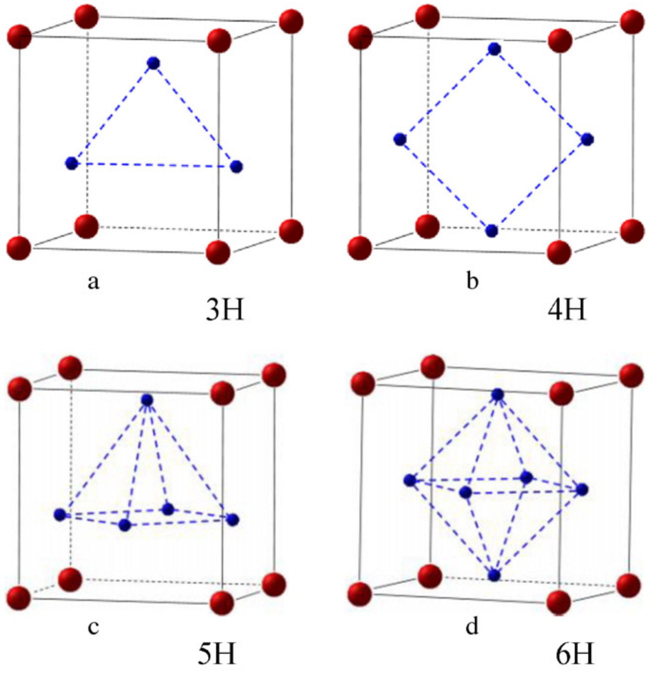

Fig. 8. Atomic structures with respect to three, four, five and six H atoms at the vacancy. The large red and smaller blue balls represent W and H atom, respectively. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.)

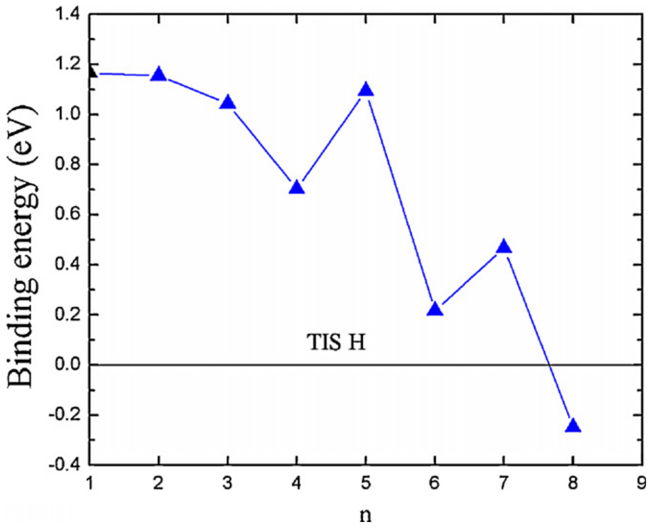

Fig. 9. The H binding energy per H with vacancy as a function of the number of H at the mono-vacancy in W. The zero-point energy is the energy of H in the TIS far away from the vacancy.

3.3.4. *How to induce abundant vacancies by H in W*

By the above analysis, we indicate that vacancy can be regarded as the trapping site for H atoms with larger binding energy. However, the H in turn may enhance the possibility of vacancy formation by binding with vacancy to add extra stability. Moreover, the recent TDS spectra results show that vacancies could be generated by the H isotope ions in the surface region of W due to lowering of effective formation energy of vacancy [37]. The similar experimental results have been also reported before in many metals such as Ni, Cr, and Pd [1,2,22].

Following the above question, we investigate the energetics of pure vacancy and H_nV complex formation in H–W system. Generally, it was believed that H–vacancy binding should be responsible for the physical mechanism of abundant vacancy formation in metals [22,23,38]. In the earlier studies, the intensive studies of plasma wall interactions in fusion reactor have shown that implanted H isotope ions are trapped by implantation-induced vacancies with very large binding energies [39,40]. In particular, Fukai et al. [1] have found superabundant vacancies formation in metals by exposing metals to H atmosphere with high pressure (e.g., 5 GPa) and high temperature ($\sim$1000 K). They believe this phenomenon is originated from that the formation energy of vacancy will be decreased by H–vacancy blistering formation at high H concentrations [1,23]. We are wondering whether this mechanism is also valid or not in the present case of H–W system. We first calculated the formation energy of pure vacancy in W. The value is shown to be 3.14 eV, consistent with previous calculated value of 3.17 eV [41]. With the H atoms entering the vacancy, the formation energy of H_nV complexes can be determined by Eq. (3).

In Fig. 10, we plot the formation energies from H_1V to H_7V. It is important to note that the formation energy of H_nV complexes decreases with the number of H atoms increasing at the beginning. The formation energies of the H_1V, H_2V, and H_3V drop

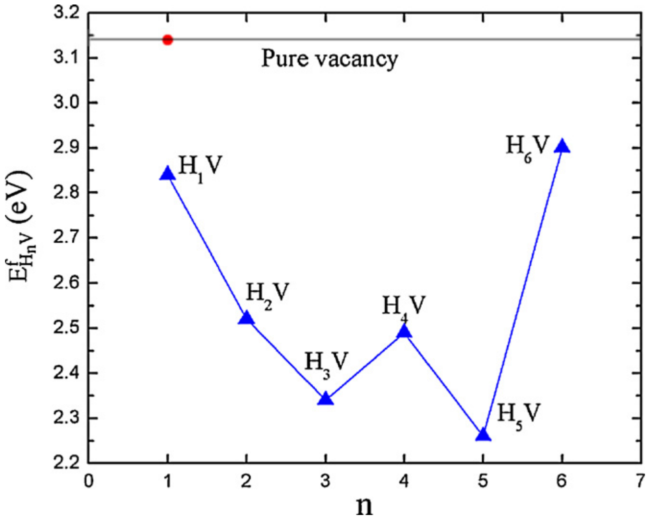

Fig. 10. The formation energy of H_nV complex in W as a function of the number of H at vacancy.

to 2.84 eV, 2.52 eV, and 2.34 eV in comparison with that of pure vacancy of 3.14 eV, respectively. For the H_4V, the formation energy increases slightly with the value of 2.49 eV compared with that of H_3V. While for the H_5V, the formation energy decreases again. When the H atom adds up to six in vacancy, i.e., H_6V, the formation energy becomes larger with the value of 2.90 eV than that of other H_nV ($n < 6$), however, it is still lower than that of pure vacancy (3.14 eV). Therefore, vacancies should easily exist with the form of H–vacancy blistering due to the presence of H atoms in comparison with that in the bulk W because their formation energy can be reduced. The presence of H stimulates the formation and growth of vacancy. The present calculated results, to a certain extent, can well explain the experimental observation of H assisted abundant vacancy formation in various metals [1–3,21–23] and provide the physical mechanism for H-induced vacancies formation. Although our calculations are only for the H–monovacancy complexes, such physical mechanism for H-induced vacancies formation can be generalized to H-mutivacancies (void) in W as well as other metals and metal alloys. This is because the presence of H can also decrease formation energy of mutivacancies (void) in W as well as other metals and metal alloys.

In addition, the diffusion generally occurs for H atom in W or other metals via vacancy. Since vacancies or void can absorb a large number of H atoms, the formation of abundant vacancies will in turn affect the diffusivity of W and H atoms in H–W system or H–other metal system [22]. Iida and co-workers found that the diffusion coefficient of Nb in the H–Nb alloys is close to six orders of magnitude larger than that of Nb in the pure Nb system [42].

4. Conclusions

Using a first-principles method based on density functional theory, we have investigated structure and solubility of H, as well as H–vacancy interaction in a tungsten (W) single crystal. The solution energy of single H at the tetrahedral interstitial site (TIS) is shown to be 0.86 eV in comparison with 1.06 eV and 1.24 eV at the diagonal interstitial site (DIS) and the octahedral interstitial site (OIS), respectively, which demonstrates the endothermic reactions for all three cases. According to the Sieverts' law, we have estimated the solution concentration of H in W, which are 2.3×10^{-10} and 1.8×10^{-7} at the typical temperatures of 600 K and 1000 K, respectively. The present calculated results are basically consistent with the experiments. We found that vacancy plays a key role on the trapping of H in W. There exists a very strong binding between single H and vacancy with the binding energy of 1.18 eV. With the H atoms added, the H_nV complexes can be easily formed in the vacancy. A monovacancy is shown to be capable of trapping as many as 7 H atoms. Kinetically, we show that the H atom moves easily towards a vacancy and its diffusion barrier is reduced gradually in comparison with that of the intrinsic case. The H jumps into the vacancy from the 1NN TIS into vacancy with a much reduced barrier of 0.02 eV, which indicates a down-hill "drift" diffusion of H towards vacancy. We further investigate the physical mechanism of H assisted vacancy formation in W. The H atoms stimulate the formation and growth of vacancy or void by binding with vacancy to decrease the effective formation energy of vacancy in W.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (NSFC) Grant No. 50871009 and National Magnetic Confinement Fusion Program with Grant No. 2009GB106003.

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