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

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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.

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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 trap-ping 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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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

$$E_H^s = E_{NW,H} - NE_W - \mu_H, \tag{1}$$

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

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

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

$$E_{H_nV}^f = E_{(N-1)W,H_nV} - (N-1)E_W - n\mu_H \tag{3}$$

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.
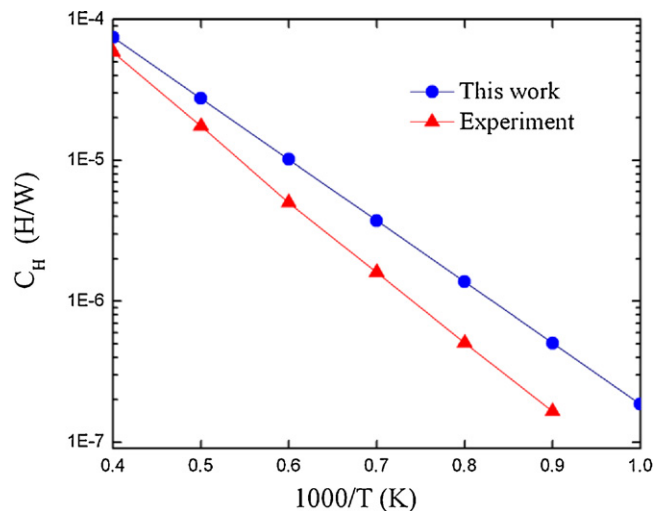

Fig. 1. The solution concentration of H in W as a function of reciprocal temperature in comparison with the previous experimental results.

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

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

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_H^s 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 $\sim10^5$ 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 $\sim$500 K [9–13]. The reason lies in that here we have not taken into account