Molecular Dynamics Study on the Diffusion Properties of Hydrogen Atoms in Bulk Tungsten

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Abstract Molecular dynamics simulations were performed to study the diffusion behavior of hydrogen atoms in body-centered cubic (bcc) tungsten (W). The energy distribution of a single hydrogen atom in the (001) plane of tungsten lattice was computed. The values of diffusion barriers agree well with other theoretical and experimental results. The interaction between an H atom and a vacancy was simulated, which shows evidence of strong binding effect. The temperature effect on the diffusion behavior of hydrogen atoms was investigated. The critical temperature for an H atom to diffuse in bulk W with and without vacancies were calculated to be 950 K and 450 K, respectively, which is supported by several experimental results. In addition, the diffusion coefficient of hydrogen atoms in tungsten was evaluated and analyzed.

Keywords: molecular dynamics, tungsten, hydrogen, diffusion

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1 Introduction

Apart from graphite and beryllium, the high Z material tungsten (W) has been considered as the most promising plasma facing material (PFM) for the next fusion device, the International Thermonuclear Experimental Reactor (ITER), because of its lower sputtering erosion and good thermal properties such as high thermal conductivity and high melting temperature. As a PFM, W will be subjected to high heat and fluxes of hydrogen (H) isotopes from the plasma. Being the lightest element, H atoms can easily diffuse into the bulk, become immobilized by point defects and lead to the modification of the thermal and mechanical properties of W. Therefore, the interaction between H and W atoms has been one of the most import issues for developing W as a PFM.

Previously, many experimental studies have been carried out to understand the interaction of H atoms and the W surface. Blisters were observed on the W surface after the bombardment of H and/or its isotope ions [1~4]. The formation of the blisters depends on the substrate temperature [2]. Different results about the temperature under which blisters disappear were reported [2~4]. However, the ongoing atomic level mechanism is still not well explained by experiments because the low solubility and diffusivity of H in W make the direct detection of H atoms quite difficult. Therefore, numerical methods become the most attractive tools. The first principle method based on the density functional theory (DFT), also known as ab initio, is one of the popular numerical methods. By using the DFT, HEINOLA [5] studied the diffusion properties of H atoms in a W lattice. The diffusion barrier and diffusion coefficient were computed and used to analyze the diffusion behavior of H atoms in W qualitatively, while the quantitative results, to some extent, are lower than experimental data. LIU [6] investigated the structure and solubility of H, as well as H-vacancy interaction in single crystal W by employing the DFT. It was revealed that vacancies play an important role in trapping H atoms. Despite the advantages of DFT, this method also has several limits. First of all, DFT calculations can only deal with hundreds of atoms even in a modern computing cluster environment. Moreover, the DFT cannot take into account the dynamic and temperature effects which actually have a great influence on the diffusion behavior of H atoms in a W host lattice.

Another atomic scale simulation tool is the so-called molecular dynamic (MD) method which has been successfully used to simulate the W-H system. YANG [7] modeled injection and reflection of low energy H atoms onto W surface. HENRIKSSON [8] investigated the sticking process of H atoms on a tungsten (001) surface. LI [9] studied the interaction of H and vacancy in W and proved the trapping effect of vacancy. All this work proves that the MD method is a powerful tool to study the atomic level mechanism of the interaction between H and W. The most critical issue of the MD method is the potential. For the W-H system, the most popular one is the tersoff-like bond-order potential developed by JUSLIN et al. [10]. Previous work [7~9] shows that this potential can properly describe the interaction between W-W and W-H atoms. However, Li [8] also reported that JUSLIN’s potential may have limits in describing the interaction of H atoms and vacancies in bulk W. Based on this discovery, their group recently developed a new potential [11] which is supposed to be more ac-

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curate when the simulated system contains defects like vacancies but more work needs to be done to verify the feasibility of the new potential.

The aim of this work is to study the diffusion properties of H atoms in bulk W. The MD method is employed to simulate the diffusion processes of H atoms. The trapping effect of vacancy, as well as the temperature effect, is simulated and analyzed.

The outline of this paper is as follows. In section 2, the simulation details are presented. Section 3.1 is focused on the diffusion properties of a single H atom in intrinsic W. The vacancy effect is discussed in section 3.2. Section 3.3 demonstrates the temperature effect on the diffusion behavior of a single H atom in the W lattice. Section 3.4 covers the calculation and analysis of the diffusion coefficient.

2 Details of simulations

2.1 Computational method

Molecular dynamics simulations (MDS) were used in this paper to investigate the diffusion behavior of H atoms in W. The Tersoff-like potential developed by JUSLIN et al. [12] was employed to describe the interaction between atoms of the W-H system. The total energy is given by the sum over bond energies

\[ E = \sum_{i>j} f^C_{ij}(r_{ij})[V^R_{ij}(r_{ij}) - \frac{b_{ij} + b_{ij}}{2} V^A_{ij}(r_{ij})], \] (1)

where the pair-like attractive and repulsive terms are taken as follows

\[ V^R(r) = \frac{D_0}{S-1}\exp(-\beta\sqrt{2S}(r-r_0)), \]
\[ V^A(r) = \frac{SD_0}{S-1}\exp(-\beta\sqrt{2/S}(r-r_0)). \] (2)

The cutoff function can be written as

\[ f^C(r) = \begin{cases} 
\frac{1}{2} - \frac{1}{2} \sin[\frac{\pi}{2}(r-R)/D], & r \leq R-D \\
\frac{1}{2}, & |r-R| \leq D, \\
0, & r \geq R+D
\end{cases}, \] (3)

The bond-order parameter \( b_{ij} \) includes three-body contributions and angularity

\[ b_{ij} = (1 + \chi_{ij})^{-\frac{1}{2}}, \] (4)

\[ \chi_{ij} = \sum_{k(\neq i,j)} f^C_{ik}(r_{ik})g_ik(\theta_{ijk})\omega_{ijk}\exp[2\mu_{ik}(r_{ij} - r_{ik})], \] (5)

\[ g(\theta) = \gamma \left( 1 + \frac{\epsilon^2}{d^2} - \frac{\epsilon^2}{d^2 + (\hbar + \cos \theta)^2} \right). \] (6)

All the parameters were taken from Ref. [12].

The structure of the W lattice was taken as bcc which is the most stable one as compared with the other two structures named fcc and A15 [5]. Periodic boundary conditions were always applied in all three directions. All simulations are performed by using open source MDS code LAMMPS (Large-scale Atomic Molecular Massively Parallel Simulator) [13]. The canonical ensemble (NVT fix in LAMMPS) was used to process the system to equilibrium state.

2.2 Lattice constant of W

The lattice constant is the intrinsic physical parameter of materials. It varies with temperature due to the natural phenomenon of thermal expansion. The canonical ensemble where the volume is conserved will induce great pressure on the system as the temperature rises. LI [14] reported that stress can significantly influence the behavior of hydrogen atoms in tungsten. Therefore, a varied lattice constant of W was employed under different temperatures for the MD simulation in this work.

The relationship between the lattice constant and temperature was estimated using the molecular dynamics method. The initial value of the lattice constant was taken as 3.165 Å [15]. The pressure was controlled by using BERENDSEN barostat [16] where both the starting pressure and stopping pressure are set to 1 bar. The whole system was relaxed for 100 ps, which is long enough for the system energy to be stable, under the Nose-Hoover thermostat [17,18] at a fixed temperature. The lattice constant was calculated through the volume of the system. Fig. 1 shows the results in a wide temperature range from 0.1 K to 3000 K. It can be seen that the lattice constant of bcc tungsten increases nonlinearly with temperature. We fitted the simulated results with a 3-order polynomial equation which can be denoted by

\[ a = 3.164 + 2.149 \times 10^{-5}T + 1.939 \times 10^{-9}T^2 + 5.217 \times 10^{-13}T^3, \] (7)

where \( a \) denotes the lattice constant and \( T \) the temperature in Kelvin degree. Fig. 1 also shows the experimental results given by WORTHING [19] who measured the expansion coefficient of the tungsten filament from room temperature to 2700 K and presented the following equation:

\[ \frac{L - L_0}{L_0} = 4.44 \times 10^{-6}(T - 300) + 4.5 \times 10^{-11}(T - 300)^2 + 2.20 \times 10^{-13}(T - 300)^3, \] (8)

where \( L \) and \( L_0 \) are the sample length at temperature \( T \) (K) and 300 (K), respectively. The two curves agree well as temperature is low. However, the difference increases as the temperature rises. This means that the potential employed in this work may overestimate the coefficient of the thermal expansion of W. Nevertheless, the lattice constant of W was calculated through Eq. (7) in the following simulations of this paper to avoid the influence of the pressure caused by thermal expansion.
3 Results and discussion

3.1 Single H atom in defect-free W

A simulation box of size $9a \times 9a \times 9a$ was set up, where $a$ is the lattice constant of W. The box contains 1459 W atoms and an H atom. All the W atoms on the surface are frozen. The H atom was fixed in the (001) plane of the central lattice of W. By moving the H atom all over the (001) plane, the full picture of the energy map of a single H atom in the (001) plane of the W lattice was drawn, as shown in Fig. 2. The 4 white corners are occupied by W atoms. The H atom can not get any closer because of the strong repulsive force.

From Fig. 2, we can see that there are three kinds of possible stable sites for H atoms where the energy shows a local minimum. They are the so-called tetrahedral interstitial site (TIS), octahedral interstitial site (OIS) and diagonal interstitial site (DIS). All of them are marked as T, O and D on the figure, respectively. Usually, DIS is defined as the center between two neighboring TISs [6]. However, according to our simulation, DIS may not locate right at the center of two neighboring TISs but a little distance away from the center toward the neighboring OIS. Fig. 3 gives a clear view of the potential profile along the surface diagonal of the (001) plane. The coordinates of DIS were $(0.4125a, 0.4125a)$. The energy gap between OIS and DIS was calculated to be 0.09 eV.

MD results suggest that TIS has the lowest energy which makes it the most stable site for an H atom. Thus, the diffusion pattern of an H atom would be the jump between adjacent TISs. According to the energy distribution shown in Fig. 2, there are two possible ways to diffuse. One is via OIS, the other is via DIS. Since the energy of DIS is 0.09 eV lower than OIS, it may be easier for H atoms to diffuse via DIS, which is consistent with other published results [5]. Fig. 4 shows the energy distribution along the two diffusion paths. Sites 1, 3 and 5 are TISs. Site 2 is an OIS and site 4 is a DIS. Path A means the H atom diffuse between two neighboring TISs via OIS and path B via DIS. The energy barrier between TIS and OIS was calculated to be 0.36 eV which is well matched with the DFT result of 0.38 eV [5]. The energy barrier between TIS and DIS is 0.27 eV which is a little higher than the DFT result of 0.21 eV [5]. The saddle-shaped curves indicate that all TIS, OIS and DIS are stable sites for H atoms and also make our results more reasonable compared with the DFT’s dome-like curves since the top of the dome-like curve is obviously unstable. It is important to note that the diffusion energy of path A is not the energy gap between TIS and OIS because the energy of OIS is not the maximum along path A. According to our simulation, the minimum energy to diffuse along path A is 0.48 eV. For path B, the diffusion barrier is 0.35 eV. This value is close to FRAUENFELDER’s experimental result of 0.39 eV [20].
3.2 Interaction of single H atom with a vacancy

According to recent research [6,21,22], vacancies play an important role in trapping H atoms in single crystalline W. To verify this point, we computed the energy profile of an H atom in (001) plane based on the process described in section 3.1. A vacancy was introduced by simply removing a W atom in the center of the simulation box, which is also adjacent to the H atom. The results are plotted in Fig. 5. It seems that all TISs and DISs shrank to OIS due to the attraction of the vacancy. The energy difference and diffusion barrier between TIS and the center OIS, as well as that between DIS and the center OIS, decreases. On the contrary, the energy gap between TIS and the far end OIS becomes bigger. Fig. 6 shows the energy distribution along the O-T-O path. Sites 1, 2 and 3 are the first nearest neighbors (1NN) to OIS, 1NN DIS and 2NN OIS respectively. The energy difference and diffusion barrier between site 1 and site 2 are 0.02 eV and 0.34 eV. Both of them are lower than that of the intrinsic W lattice. The diffusion barrier between site 2 and site 3 is 0.68 eV which is much higher than that without the vacancy. It is obvious that an H atom is easy to diffuse around but hard to get away from the vacancy.

For further understanding of the H trapping effect of a vacancy, we also calculated the binding energy of an H atom to a vacancy which can be calculated through the following equation [23]:

$$E_b (H-V) = E_f (H) + E_f (V) - E_f (HV),$$

(9)

where $E_b (H-V)$ is the binding energy of an H atom to a vacancy, $E_f (H)$, $E_f (b)$ and $E_f (HV)$ are the formation energy of an interstitial H atom, an isolated vacancy and an H-vacancy pair, respectively. The formation energy is defined as the difference between a crystal which contains a defect and a crystal with the same number of atoms in their perfect lattice sites. The formation energy satisfies the following equations [24]:

$$E_f (H) = E_{tot} (NW + H) - NE_{ref} (W) - E_{ref} (H),$$

$$E_f (V) = E_{tot} ((N-1)W + V) - (N-1)E_{ref} (W),$$

$$E_f (H - V) = E_{tot} ((N-1)W + H + V) - (N-1)E_{ref} (W) - E_{ref} (H).$$

(10)

where $E_{ref} (W)$ and $E_{ref} (H)$ means the reference energy of the W and H atoms, which are equal to the cohesive energy here, $E_{tot} (NA + MB)$ is the total energy of a system containing $N$ A atoms and $M$ B atoms, e.g. $E_{tot} (NW + H)$ represents the total energy of a system containing $N$ W atoms and an H atom.

The binding energy between an H atom and a vacancy in W was computed to be 0.747 eV for OIS and 0.595 eV for TIS. Compared with the experimental result of 1.16 eV [25], our MD simulation gives a lower estimation. It could be the expression of the potential which needs to be improved. Anyway, the positive values still suggest an attraction between an H atom and a vacancy, which makes a vacancy trap site for H atoms in W.

3.3 Temperature effect

MD simulations under various temperatures were performed to study the temperature effect on the diffusion behavior of a single H atom in a W lattice. It was found that H atoms behave differently under different temperatures. The mean square displacement (MSD) of the H atoms is shown in Fig. 7. Each stair of the curve means that an H atom jumped to an adjacent interstitial site. It can be read that the jumps start at a temperature of 450 K. Therefore, 450 K should be the critical temperature for an H atom to diffuse in single crystal W. This explains the experimental mismatch of the blister size on the W surface. LUO [26] performed experiments by exposing tungsten to a deuterium plasma beam at near room temperature. Only 2–3 µm blisters on the W surface were observed. OHNO [27] performed the same experiments at a temperature of 550 K. The maximum diameter of the blisters was over 10 µm which is much bigger than LUO’s values. This is because H atoms have very low mobility in W when the temperature is below 450 K. They will
not move without external activation. As the temperature reaches 450 K, the interstitial sites become unstable for H atoms. They diffuse and congregate at other more stable trapping sites. Therefore bigger blisters will be formed. Moreover, SHU [2] also reported that bombardment of low energy and high flux deuterium ions causes small blisters on the W surface when temperature is below 500 K. It is 500 K when big blisters appear, and deuterium retention is maximum, which is also consistent with our MD result.

Fig.7 MSD of an H atom in W without vacancies (color online)

Furthermore, we introduced a vacancy into the simulation box by removing a W atom next to the H atom to study the influence of a vacancy on the diffusion temperature. Fig. 8 shows the results. The diffusion temperature increased to 950 K. Here we assume that the critical distance for an H atom free from a vacancy is the lattice constant, i.e. 3.165 (Å), which implies that the critical value for MSD is about 10.02 (Å$^2$). It was 950 K when the H atom’s MSD exceeds the critical value (the dash line in Fig. 8). Below this temperature, the H atom keeps moving around the vacancy and is unable to get away. When the temperature is above 950 K, the vacancy is no longer the nucleation of blisters. H atoms can either diffuse into deep W bulk or diffuse to the surface and be released. If there were no other more stable trapping sites for H atoms, the blisters on the W surface will finally disappear. LUO [3] reported that no blisters were observed on the W surface under H ion bombardment when the temperature reaches 900 K. YE [4] also did a lot of experiments and found that the critical temperature to avoid blisters was 950 K. SHU’s [2] experimental result is 1000 K. All the data from these studies agree with our results.

3.4 Diffusion coefficient of H atoms

The diffusion coefficient $D$ indicates the diffusion velocity of H atoms, which is very important for us to understand the diffusion behavior of H atoms in W. In this work, the diffusion coefficient was computed using the MD method. A simulation box containing 6750 W atoms and 100 H atoms was modeled. H atoms were randomly put into the simulation box. The time step was chosen to be 0.1 fs. During the 100 ps thermostat relax, the MSD of H atoms was computed and recorded. $D$ was calculated through Einstein relation:

$$D = \lim_{t \to \infty} \frac{\langle |r(t) - r(0)|^2 \rangle}{6t} = \lim_{t \to \infty} \frac{\text{MSD}}{6t},$$  \hspace{1cm} (11)

where $r(t)$ is the position vector of H atoms at time $t$ and $r(0)$ is the initial position vector of H atoms. Fig. 9 shows the MSD of H atoms under different temperatures. It is clear that MSD is approximately linear with time from 20 ps onward, which guarantees a good estimation of $D$.

Fig.9 MSD of H atoms in W under different temperatures (color online)

The diffusion coefficient $D$ was calculated in a wide temperature range from 300 K to 3000 K. When the temperature is lower than 450 K, $D$ is zero. This result is consistent with the conclusion drawn in section 3.3 which says that the critical temperature for an H atom to diffuse in W is 450 K. Above this temperature, $D$ increases with temperature. The Arrhenius plot with temperature ranging from 800 K to 3000 K is shown in Fig. 10 implying the following relationship between the diffusion coefficient and temperature:

$$D = D_0 e^{-\frac{E_m}{kT}}.$$  \hspace{1cm} (12)

Here $D_0$ is the pre-exponential factor, $E_m$ the migration energy and $k$ the Boltzmann constant. By linearly fitting the Arrhenius plot, as shown in Fig. 10, the
temperature independent pre-exponential factor and migration energy were calculated to be \( D_0 = 4.13 \times 10^{-8} \text{ m}^2/\text{s} \) and \( E_m = 0.38 \text{ eV} \), respectively. The value of \( E_m \) is quite close to FRAUNFELDER’s experimental data \(^{20}(0.39 \text{ eV})\) which is believed to be the most reliable data. However, the value of \( D_0 \) is far lower than FRAUNFELDER’s result \(^{20}(4.1 \times 10^{-7} \text{ m}^2/\text{s})\) but is close to HEINOLA’s DFT result \(^5(5.2 \times 10^{-8} \text{ m}^2/\text{s})\). In fact, published data about \( D_0 \) are extremely scattering. the values of \( D_0 \) vary from \( 3.5 \times 10^{-11} \text{ m}^2/\text{s} \) \(^{28}\) to \( 6.0 \times 10^{-4} \text{ m}^2/\text{s} \) \(^{29}\). This is because the diffusion coefficient is very sensitive to the microstructure of tungsten. The defects inside the W bulk will significantly influence the macro diffusion properties. There are many uncontrollable processes that may well cause different microstructure in specimens which leads to the scattered value of \( D \).

![Fig.10 Arrhenius plot of the diffusion coefficient VS the inverse surface temperature](image-url)

4 Summary and conclusions

Molecular dynamics simulations were performed to study the diffusion properties of H atoms in W. The energy map of an H atom in the (001) plane of an intrinsic W lattice was given, which shows that there are only three kinds of interstitial sites for an H atom to stay stably, i.e. TIS, OIS and DIS. The favorite diffusion path for an H atom is to jump between TISs via DIS. The diffusion barrier is not the energy difference between TIS and DIS but the energy gap between TIS and the energy peak around DIS which was computed to be 0.35 eV which is close to FRAUNFELDER’s experimental result of 0.39 eV.

The critical temperature for an H atom to diffuse in the W lattice with and without vacancies are computed to be 950 K and 450 K. These results can be used to explain the experimental phenomenon that the size of blisters on W surface irradiated by H ions differs notably under different temperatures.

References


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