



The role of impurity oxygen in hydrogen bubble nucleation in tungsten

Xiang-Shan Kong^a, Yu-Wei You^a, Q.F. Fang^a, C.S. Liu^{a,*}, Jun-Ling Chen^b, G.-N. Luo^b, B.C. Pan^c, Zhiguang Wang^d

^aKey Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, PR China

^bInstitute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, PR China

^cHefei National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei 230026, PR China

^dInstitute of Modern Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

HIGHLIGHTS

- ▶ A new impurity assistant mechanism of H bubble nucleation is proposed based on the results of O–H–V interaction.
- ▶ The interstitial O atom traps multiple H atoms to form O–H complex.
- ▶ The initial vacancy could be created at the unstable sites nearby the O–H complex to form stable V–O–H complex.
- ▶ Abundant V–O–H complexes could survive due to their lower formation energy and thus the hydrogen bubble nucleates.

ARTICLE INFO

Article history:

Received 5 August 2012

Accepted 17 October 2012

Available online 27 October 2012

ABSTRACT

The impurity role for hydrogen bubble nucleation is investigated based on first-principles studies of the interaction between impurities (oxygen and carbon), hydrogen and vacancy in tungsten. A new mechanism of hydrogen bubble nucleation is proposed: the interstitial oxygen atom traps multiple hydrogen atoms inducing the appearance of some unstable lattice sites nearby, where the initial vacancy can be created to form vacancy–oxygen–hydrogen complex, whose formation energy is so low that abundant vacancy–oxygen–hydrogen complexes could survive and thus the hydrogen bubble nucleates. This mechanism could provide a sound explanation for the hydrogen bubble nucleation in tungsten (with quite low vacancy concentration) exposed to low-energy (far lower than displacement threshold energy) deuterium ions irradiation. The proposed mechanism should be generally applicable for hydrogen bubble nucleation in other metals with low vacancy concentration.

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1. Introduction

Hydrogen bubble formation in metals is an important consideration in materials selection. The underlying reason is that bubbles can radically alter the mechanical properties of the metals, typically leading to hydrogen embrittlement and structural failure [1–3]. The hydrogen bubble formation firstly requires the existence of regions with elevated hydrogen concentration as a starting point, i.e., the nucleation point. Lattice defects, such as vacancies and impurities, could act as such nucleation points due to their ability of trapping hydrogen or impeding hydrogen diffusion. But the exact hydrogen bubble nucleation mechanism is still under debate and unclear specially for those metals with pretty low vacancy concentration.

Massive works have been done to investigate the interaction of vacancy with hydrogen in metal, such as Al [4–6], Fe [7–9], W [10–

13], and Pd [7,14–16], and reveal the crucial role of vacancies in hydrogen bubble nucleation: vacancies trap multiple hydrogen atoms to form the vacancy–hydrogen ($V-H_n$) complexes, which further aggregate to form V_m-H_n complex acting as embryos for hydrogen bubbles. No doubt, these results contribute enormously to our understanding of the hydrogen bubble nucleation process in metals with high vacancy concentration, but it is still unclear that how the hydrogen bubbles nucleate in metals with quite low vacancy concentration (for example, the vacancy concentration of iron and tungsten are $\sim 10^{-22}$ and $\sim 10^{-54}$, respectively, at room temperature). Particularly, recent experimental studies have observed hydrogen bubble formation in tungsten exposed to low-energy (far lower than displacement threshold energy) hydrogen irradiation [17–24].

In the last decade, some experimental studies found that the impurity can increase the hydrogen retention in metals [19,25–29]. Recently, a few theoretical works have focused on the role of impurities on trapping hydrogen in metals [30–33]. A weak attractive binding energy between interstitial hydrogen and carbon atom is found in bcc iron and tungsten. The hydrogen can be trapped by

* Corresponding author. Tel.: +86 551 5591062.

E-mail address: cslu@issp.ac.cn (C.S. Liu).

and accumulate around some substitutional solutes in metals. All these results reveal that the impurity may have an effect on the hydrogen retention and diffusion in metals. On the other hand, it has been known from early days of point-defect studies that impurity atoms can increase the equilibrium vacancy concentration in metals [15,34,35]. Furthermore, the concentration of the impurity is greatly larger than that of the vacancy in metals. For example, the concentration of oxygen is 30 atomic parts per million [20,36] in tungsten at room temperature, which is much larger than that of vacancy, about 10^{-54} . Therefore, some impurities could be expected to play an important role in the hydrogen bubble nucleation in metals, especially in the case with low vacancy concentration. However, until now, the interaction between the impurity and hydrogen and vacancy has not attracted extensive attention, and the microscopic atomic-level relationship between the impurity and hydrogen bubble nucleation has not been revealed.

In this paper, we investigate the influence of the impurities (oxygen and carbon) on the hydrogen, vacancy and V-H_n complex in tungsten based on a series of first-principles calculations. Our choice of choosing tungsten as a metal model system is partly because tungsten is considered to be the most promising candidate for the plasma-facing materials (PFMs) in fusion reactors and has been selected as the PFM at the divertor baffles in the ITER design [20,37]. The oxygen and carbon are chosen as the representation of the impurities in metals because they are considered as the most frequent impurities atoms in tungsten and they are also introduced in the plasma device [20,37]. In addition, some experimental studies [19,25–29] have been made to investigate the influence of oxygen and carbon on hydrogen retention and bubble formation in tungsten and suggested that the oxygen may be the primary nucleation site for hydrogen or deuterium clusters in tungsten exposed to high flux and low energy deuterium plasma, while the carbon has little effect on the hydrogen bubble formation. Our calculated results could make a comparison between the influence of oxygen and carbon and provide some explanation for the experimental results. For clarity, we use the LE (light element impurity) to denote the two impurities in the following paper.

2. Computation method

The present calculations are performed within density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) [38,39]. The interaction between ions and electrons is described by the projector augmented wave potential (PAW) method [40]. Exchange and correlation functions are taken in a form proposed by Perdew et al. within the generalized gradient approximation (GGA) [41]. The supercell composed of 128 lattice point ($4 \times 4 \times 4$) is used. The relaxations of atomic position and optimizations of the shape and size of the supercell are performed. The plane wave cutoff and *k*-point density, obtained using the Monkhorst–Pack method [42], are both checked for convergence for each system to be within 0.001 eV per atom. Following a series of test calculations a plane wave cutoff of 500 eV is used and a *k*-point grid density of $3 \times 3 \times 3$ is employed. The structural optimization is truncated when the forces converge to less than 0.1 eV/nm.

The formation energy of defect (A_1) is calculated by [43]

$$E_f^{A_1} = E_{tot}^{A_1} - E_{tot}^{bulk} - \sum_i \Delta n_i \mu_i, \quad (1)$$

where $E_{tot}^{A_1}$ is the total energy of the supercell with the defect A_1 and E_{tot}^{bulk} is the total energy of perfect tungsten bulk in supercell. The quantity μ_i is the chemical potential of element i and Δn_i is the difference in the number of element i in these two supercells. Here, the energy of a tungsten (carbon) atom in metallic bcc-W (graphite) has

been taken as the reference for the chemical potential of tungsten (carbon). It should be pointed out that the experimental value of graphite cohesive energy (7.37 eV) [44] is directly used due to the failing of DFT in reproducing Van der Waals forces (and therefore the interlayer spacing) correctly [45]. The energy of a hydrogen (oxygen) atom in the H₂ (O₂) molecule is taken as the reference for the chemical potential of hydrogen (oxygen). The equilibrium concentration of defect (A_1) can be roughly calculated from its formation energy [43]

$$c = N_{sites} N_{config} \exp \left(\frac{E_f^{A_1}}{kT} \right), \quad (2)$$

where N_{site} is the number of lattice sites on which the defect can be incorporated and N_{config} is the number of equivalent configuration per site.

The vacancy formation energy is the energy required to take an atom from inside the crystal, and place it into a reservoir of the same atoms. In the perfect supercell, it can be calculated by Eq. (1). Similarly, to characterize the energy required to take an tungsten atom from the lattice site nearby a defect (A_1), the vacancy formation energy can be defined as [46,47]:

$$E_f^{V_{A_1}} = E_{tot}^{A_1-V} - E_{tot}^{A_1} + \mu_W, \quad (3)$$

where the $E_{tot}^{A_1-V}$ is the total energy of the supercell with the defect A_1 and a vacancy nearby. Negative value of the vacancy formation energy means that the site is unstable, where the vacancy formation is exothermic.

The binding energy between two point defects (A_1, A_2) is calculated as follows:

$$E_b^{A_1-A_2} = E_{tot}^{A_1} + E_{tot}^{A_2} - E_{tot}^{A_1-A_2} - E_{tot}^{bulk}, \quad (4)$$

where $E_{tot}^{A_1-A_2}$ is the total energy of the supercell containing the stable A_1-A_2 complex. All supercells contain 128 lattice sites.

3. Results and discussion

3.1. Interstitial hydrogen, oxygen and carbon in intrinsic tungsten

In bcc tungsten, there are two possible interstitial sites, i.e., tetrahedral (*t*) and octahedral (*o*) positions for hydrogen, oxygen and carbon. These interstitial sites are illustrated in Fig. 1. The formation energies for different configurations of hydrogen, oxygen and carbon in interstitial position are determined using Eq. (1). As shown in Table 1, the hydrogen and oxygen will occupy the tetrahedral site and the carbon prefers the octahedral position, which are in agreement with the former theoretical results [48–50]. The results of interstitial hydrogen atom agrees within the experimental value 1.04 ± 0.17 eV [51].

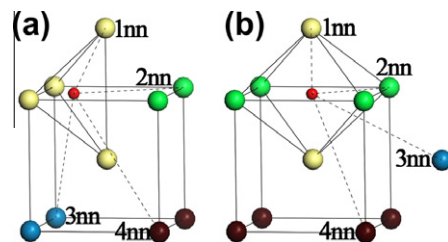


Fig. 1. The interstitial sites and their tungsten neighbor atoms. (a) Tetrahedral site and (b) octahedral site. The interstitial sites are represented by a small red ball. Their first, second, third and fourth nearest neighbors are represented by large light yellow, light green, dark cyan and dark red ball, respectively. 1nn stands for the first nearest neighbor, 2nn stands for the second nearest neighbor and so on. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Formation energies (eV), E_f^t and E_f^o , and formation-energy difference, $\Delta E = E_f^o - E_f^t$, between tetrahedral and octahedral sites for hydrogen and LE atom in tungsten. The previous DFT results ($\Delta E^{\text{Previous}}$) of formation-energy difference are listed in the fifth column for comparison.

	E_f^t	E_f^o	ΔE	$\Delta E^{\text{Previous}}$
Hydrogen	0.93	1.31	0.38	0.38 ^a
Oxygen	0.57	0.84	0.27	0.315 ^b
Carbon	1.64	0.17	−1.47	−1.46 ^c

^a Reference [48].

^b Reference [49].

^c Reference [50].

To investigate the effect of interstitial hydrogen, oxygen and carbon on the stability of the lattice sites nearby, the vacancy formation energies of their nearest-neighbors are calculated using Eq. (3) and summarized in Table 2. It is clearly seen that the vacancy formation energies of these nearest-neighbor sites are lower than that in the perfect supercell (the calculated value, 3.2 eV, and the experimental value, 3.7 eV [52]), especially for the 1nn and 2nn of oxygen (0.15 eV). This indicates that the introduction of hydrogen, oxygen and carbon in the interstitial site could decrease the stability of their nearby lattice sites. The vacancy can more easily form nearby these interstitial atoms than in perfect lattice. The decrease of vacancy formation energies may result from the lattice distortion and charge redistribution induced by these interstitial atoms [53]. Note that the 1nn vacancy formation energy of interstitial hydrogen decreases to 2.0 eV, which is still very high for the vacancy formation. The lattice sites in the vicinity of the hydrogen and LE are still stable and the vacancy formation is endothermic in these sites.

3.2. LE–H pair

From the above calculation, we know that the hydrogen and the oxygen prefer the tetrahedral site and the carbon prefers the octahedral site. After carefully checking, it has been found that these individual equilibrium sites do not change when interstitial LE and hydrogen form a stable LE–H pair. In order to determine the lowest energy configurations of LE–H pair, a number of possible configurations are investigated, which are as following: a LE atom is first placed on its most stable interstitial site and then a hydrogen atom is placed on the tetrahedral site surrounding the LE. The binding energies between the LE and the hydrogen are calculated using Eq. (4) and represented in Fig. 2. The binding energies between the LE and hydrogen are positive, except two or three special configurations, indicating that there is an attractive interaction between the LE and hydrogen for most LE–H pairs. Such attractive interaction may lead to the accumulation of hydrogen around the interstitial LE and the increase of the local hydrogen concentration. The most stable LE–H pair separation distances are ~0.240 nm for oxygen and ~0.322 nm for carbon. From the stable separation distance, on the whole, the positive binding energy between interstitial LE and hydrogen decreases with the increase of LE–H separation distance and ultimately decreases to almost

Table 2

The vacancy formation energies of lattice sites nearby the stable interstitial hydrogen, oxygen and carbon (unit in eV).

	Hydrogen	Oxygen	Carbon
1nn	2.01	0.15	1.23
2nn	2.91	0.15	2.74
3nn	3.08	3.03	2.91
4nn	3.11	2.25	2.76

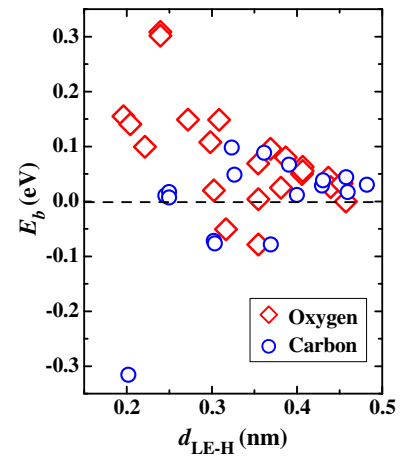


Fig. 2. Variation in the binding energy of a interstitial hydrogen atom and a stable interstitial LE atom as function of the distance between hydrogen and LE.

zero at a certain distance (~0.45 nm for both oxygen and carbon), beyond which interstitial LE and hydrogen are nearly non-interactive. The hydrogen trapping radius is ~0.45 nm for both oxygen and carbon. In addition, the binding energies have different values at the same distance due to the different arrangement of interstitial LE and hydrogen atoms. The binding energy of O–H pair is much larger than that of C–H, suggesting that the ability of hydrogen trapping is greater for oxygen than for carbon. The positive binding energies of C–H_n are lower than 0.1 eV, indicating that there is a weak interaction between the interstitial carbon and hydrogen. This is consistent with the previous results [33]. The weak interaction between the carbon and hydrogen suggests that the carbon have little effect on the hydrogen retention in the tungsten. This may be one reason for the experimental results that most of the deuterium diffuses far beyond the carbon modified layer and is trapped in natural defects of pure tungsten [29].

3.3. Multiple hydrogen accumulation around LE

As mentioned above, there is an attractive interaction between the LE and hydrogen in tungsten. In order to check the possibility for multiple hydrogen aggregation around the LE (LE–H_n complex), the hydrogen atom is introduced one by one to the tetrahedral interstitial sites nearby the LE and the energy is minimized to find the most stable configuration of LE–H_n complex. In each step, we investigate up to 15 possible configurations based on the most stable configuration of LE–H_{n−1} complex. The most stable configurations for LE–H_n complexes are presented in Fig. 3 and their corresponding binding energies are calculated using Eq. (4) and showed in Fig. 4. The positive binding energy indicates that the addition of a hydrogen atom to LE–H_{n−1} complex is energetically favorable. It is clearly seen from the Fig. 4 that multiple hydrogen atoms can aggregate in the vicinity of the LE. For O–H_n complex, the binding energy decreases approximately linearly as *n* increases and decreases to a negative value when *n* = 6, suggesting that the maximum number of hydrogen atoms accumulation around the oxygen is five. The binding energy of C–H_n complex is insensitive to *n* values, and remains around 0.11 eV, indicating a weak interaction between the C–H_n complex and the interstitial hydrogen atom. The different behaviors of the binding energies of O–H_n and C–H_n complex show that there is a much larger synergistic effect between hydrogen atoms around the interstitial oxygen than the interstitial carbon. In other words, the presence of hydrogen atoms around the oxygen has a large effect on the binding of another hydrogen atom, while that has little effect for the case of carbon.

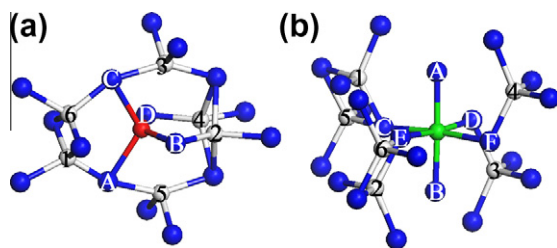


Fig. 3. The stable configurations for LE- H_n complex: (a) the LE is oxygen and (b) the LE is carbon. The tungsten, hydrogen, oxygen and carbon atoms are represented by the large blue, small white, small red and small green balls, respectively. The hydrogen atoms are indicated by numbers of 1–6. For example, the LE- H_1 consists of the LE and the hydrogen atom numbered 1, the LE- H_2 consists of the LE and the hydrogen atoms numbered 1 and 2, and so on. The lattice sites nearby LE- H_n are labeled by capital letters of A–D and A–F for oxygen and carbon, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

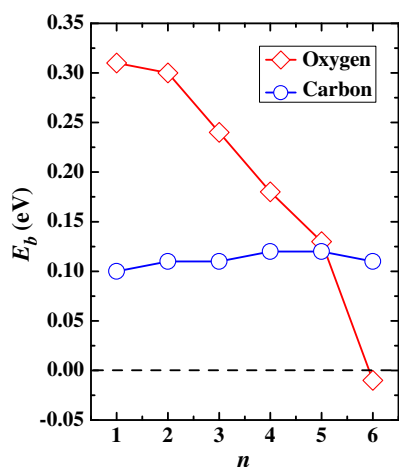


Fig. 4. The binding energy of the n th interstitial hydrogen atom with the stable LE- H_{n-1} complex. The zero point is the energy of hydrogen in the tetrahedral site far away from the LE- H_{n-1} complex.

The vacancy formation energies of lattice sites nearby LE- H_n complex are systematically calculated using Eq. (3) and summarized in Tables 3 and 4. To our surprise, the vacancy formation energies of some lattice sites in the vicinity of O- H_n complex (such as the site A in O- H_1 , sites A and B in O- H_2 , and site A in O- H_5 , Table 3) become negative, a condition sufficient for spontaneous formation of vacancy. That is, these lattice sites become unstable. Hence, it can be expected that the initial vacancy would be created on the unstable sites nearby the O- H_n in tungsten irradiated with low energy (far lower than displacement threshold energy) deuterium ions. For the case of C- H_n complex (see Table 4), the vacancy formation energies are still positive, and all of them are lower than the vacancy formation energy in pure tungsten, similarly with the case of isolated interstitial hydrogen and LE.

Table 3

The tungsten vacancy formation energies ($E_f^{V_{O-H_n}}$) of lattice sites nearby the O- H_n complex (unit in eV). Configuration of O- H_n complex is shown in Fig. 4a and positions of tungsten vacancies are indicated by A–D.

n	A	B	C	D
1	−0.64	0.37	0.56	0.37
2	−0.41	−0.41	0.78	0.77
3	−0.10	−0.28	−0.07	0.88
4	0.06	−0.09	0.09	−0.09
5	−0.85	−0.08	0.31	−0.08

Table 4

The tungsten vacancy formation energies ($E_f^{V_{C-H_n}}$) of lattice sites nearby the C- H_n complex (unit in eV). Configuration of C- H_n complex is shown in Fig. 4b and positions of tungsten vacancies are indicated by A–F.

n	A	B	C	D	E	F
1	1.04	1.11	1.63	2.69	2.65	2.72
2	0.93	0.93	1.56	2.68	1.56	2.68
3	0.84	0.74	1.53	1.60	1.58	2.62
4	0.66	0.66	1.55	1.55	1.55	1.55
5	0.60	0.57	0.55	1.50	1.53	1.56

3.4. Hydrogen trapping in the V-LE complex

It has been found that a vacancy can trap multiple hydrogen atoms in tungsten [11,12]. If one LE atom is trapped in a vacancy, do hydrogen atoms still accumulate in this vacancy trapped a LE atom (V-LE complex)? The effects of LE on the hydrogen trapping in vacancy have been studied. For comparison, we firstly calculate the binding energy of the n th interstitial hydrogen atom with the stable V- H_{n-1} complex as a function of the number of hydrogen trapped sequentially in a single vacancy (see Fig. 5). With increasing number of H atoms in a single vacancy, the binding energy shows a generally decreasing trend, and its occasional fluctuations originate from the presence of H configurations with high symmetry. One vacancy can trap as many as 12 hydrogen atoms and the atomic configurations of 1–12 hydrogen in the vacancy are in good agreement with the results reported by Ohsawa et al. [12]. The binding energy of a first and second hydrogen atom at the vacancy is consistent with the experimental results given by Poon et al. [36]. And then, the most stable configuration of V-LE complex is determined. The preferable position for an oxygen (carbon) atom in vacancy is 0.124 nm (0.131 nm) off the vacancy center close to an octahedral interstitial site. Based on the above results, the binding energy of the n th interstitial hydrogen atom with the stable V-LE- H_{n-1} complex (see Fig. 5) and their corresponding stable configurations (see Fig. 6) are obtained as follows: the hydrogen atoms are brought to the V-LE complex one by one and the energies are minimized to identify the optimal dissolving site at each step. As shown in Fig. 5, comparing with the pure vacancy, the binding energies are slightly decreased due to the introduction of the LE, and the maximum numbers of hydrogen atoms are decreased to 8 and 9 by the introduction of the oxygen and carbon, respectively. These results indicate that the LE slightly weakens the hydrogen-trapping efficiency of vacancy. Further calculations reveal that

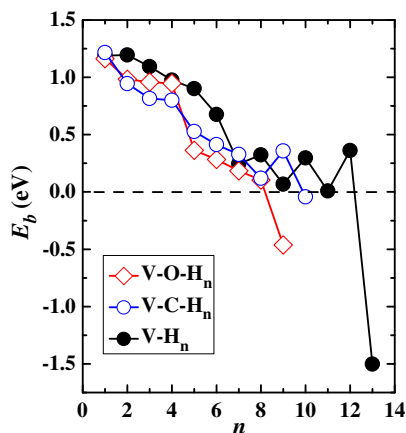


Fig. 5. The binding energy of the n th interstitial hydrogen atom with the stable V-LE- H_{n-1} complex. The zero point is the energy of hydrogen in the tetrahedral site far away from the V- H_{n-1} or V-LE- H_{n-1} complex.

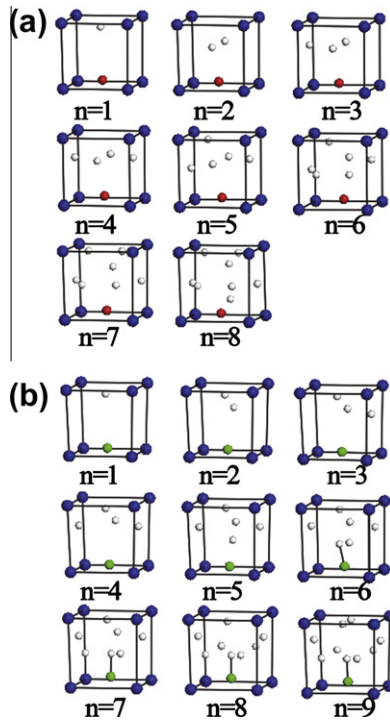


Fig. 6. The stable configurations for V-LE- H_n complex: (a) the LE is oxygen and (b) the LE is carbon. The tungsten, hydrogen, oxygen and carbon atoms are represented by the large blue, small white, small red and small green balls, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the interaction between saturated V-LE- H_n complex and additional hydrogen atoms nearby is attractive, implying that hydrogen atoms can still accumulate around the saturated V-LE- H_n complex. This is in contrast with the case of saturated V- H_n complex, where additional hydrogen atoms cannot accumulate nearby. Hence, comparing with the pure vacancy, although the maximum number of hydrogen trapped in vacancy are reduced, the local concentration of hydrogen around the vacancy may be increased due to the additional interstitial hydrogen atoms aggregation around the saturated V-LE- H_n complex.

To investigate the effect of LE on the stability of vacancy and V- H_n complex, the energetics of V- H_n and V-LE- H_n complexes are investigated. As shown in Fig. 7, the formation energy of V- H_n complex firstly decreases and then increases as n increases. The minimum formation energy is 2.45 eV occurring at $n = 4$. The formation energy of V- H_n complex is slightly lower than that of pure vacancy when $n \leq 6$, while if $n > 6$ the vacancy formation energy is larger than that of pure vacancy. The change of vacancy formation energy due to V- H_n complex formation suggests that hydrogen would modify the vacancy concentration in tungsten. According to Eq. (2), the equilibrium vacancy concentration at 300 K increases to 10^{-39} from 10^{-54} due to the hydrogen absorption into tungsten. It can be clearly seen that the formation energy of V-O- H_n complex is greatly lower than that of V- H_n complex. The formation energies of V-O- H_n ($1 \leq n \leq 4$) complexes are around 0.45 eV, which is so small that the V-O- H_n complex has high stability and may form and survive in the normal conditions. Besides, all V-O- H_n complex formation energies are smaller than the vacancy formation energy in pure tungsten, inducing a significant increase of the vacancy concentration. The concentration of V-O- H_n complex is around 10^{-7} at room temperature, which is much larger than that of both pure vacancy and V- H_n complex in tungsten. This may be responsible for the sudden significant increase in trapping

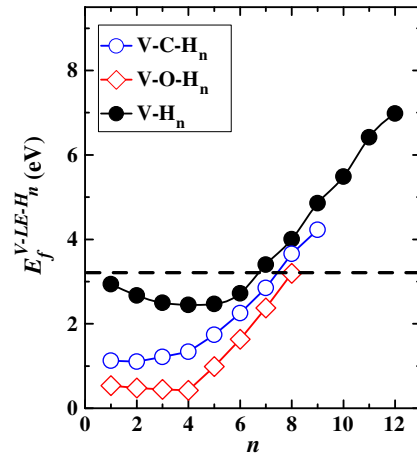


Fig. 7. The formation energy of V- H_n and V-LE- H_n complex. The dashed line is the vacancy formation energy in pure tungsten (3.2 eV).

sites for deuterium in tungsten irradiated with low energy deuterium ions. For the case of carbon, the value of V-C- H_n complexes formation energies are lower than that of V- H_n and larger than that of V-O- H_n complexes. This implies that the carbon has a smaller effect on the stability of vacancy and V- H_n complex than oxygen.

3.5. Quantum effects

Quantum effects (e.g. zero-point energy) are important for the energetic of H solution. The zero-point energy (ZPE) correction for H formation energy is 0.260 eV, which is consistent with other calculated result [12]. According to the Eq. (4), the ZPE correction of the binding energy, $\Delta ZPE^{A_1-A_2}$, can be calculated as follows:

$$\Delta ZPE^{A_1-A_2} = ZPE^{A_1} + ZPE^{A_2} - ZPE^{A_1-A_2}, \quad (5)$$

where ZPE^{A_1} , ZPE^{A_2} , and $ZPE^{A_1-A_2}$ are the zero-point energy (ZPE) correction of the supercell containing the A_1 , A_2 , and A_1-A_2 defect, respectively. The corresponding ZPE corrected binding energy yields $E_b^{ZPEc} = E_b^{A_1-A_2} + \Delta ZPE^{A_1-A_2}$. The ZPE correction of the V- H_n , O- H_n , and V-LE- H_n binding energy are calculated and summarized in the Table 5. Compared with their corresponding binding energy, the ZPE corrections of the LE- H_n , V-LE- H_n , and V- H_n binding energies are so low as to be negligible. In addition, the results of the ZPE corrections of the V- H_n binding energy are consistent with the former results [13].

Table 5

The ZPE correction of the LE- H_n , V-LE- H_n , and V- H_n binding energy (unit in eV).

n	O- H_n	C- H_n	V-O- H_n	V-C- H_n	V- H_n
1	0.01	0.01	0.10	0.11	0.15
2	0.01	0.01	0.01	0.03	0.14
3	0.02	0.01	0.04	0.06	-0.02
4	0.03	0.01	0.04	0.04	0.05
5	0.02	0.01	0.05	0.03	0.04
6	0.00	0.00	-0.01	-0.09	0.03
7			-0.02	-0.01	-0.03
8			0.02	-0.03	-0.01
9				0.02	0.00
10				0.02	0.01
11					0.02
12					0.03

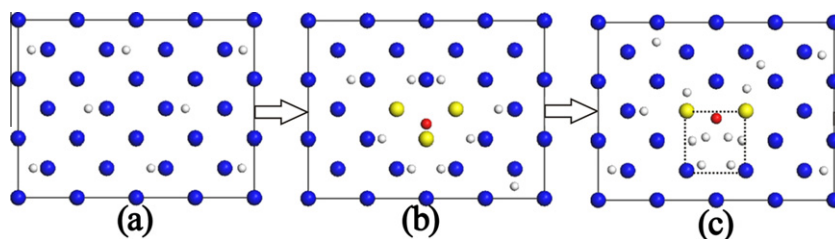


Fig. 8. One possible mechanism of bubble nucleation by hydrogen accumulation around the oxygen impurity: (a) The hydrogen atoms (small white ball) do not aggregate to form clusters in perfect tungsten; (b) Multiple hydrogen atoms accumulate around the interstitial oxygen atom (small red ball), inducing the appearance of unstable lattice sites (large yellow balls) and (c) A vacancy is formed on a unstable lattice site, and then multiple hydrogen atoms are trapped in this vacancy to form stable V–O–H_n complex; The tungsten atoms are represented by large balls. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.6. Discussions of hydrogen bubble nucleation

According to the above results, the LE can affect the hydrogen retention and the stability of vacancy in tungsten. On the one hand, the LE can trap multiple hydrogen atoms to form LE–H_n complex, which decreases the stability of lattice sites nearby. On the other hand, the introduction of LE in vacancy can enhance the local concentration and strengthen the stability of vacancy. Particularly, for the case of oxygen, the formation of O–H_n complex leads to the appearance of unstable sites nearby and the formation energy of the V–O–H_n complex is so small that it should form and survive in the normal conditions, inducing the significant increase of the vacancy concentration. So the oxygen may play an important role in the initial vacancy formation and hydrogen bubble nucleation and is suggested as the primary nucleation site for hydrogen clusters in tungsten. Comparing to the oxygen, the carbon has a little effect on the hydrogen retention and the vacancy stability in tungsten. This may be the reason for the results of the depth profiles of impurities in the deuterium implanted single crystal tungsten, i.e., the peak in the oxygen concentration corresponds to the peak in the deuterium concentration, while the peak in carbon concentration is beneath the deuterium peaks [19,25–28].

Based on these results, we propose a possible mechanism for the hydrogen bubble nucleation by hydrogen accumulation around the oxygen impurity (see Fig. 8). In normal condition, the hydrogen atoms cannot aggregate to form clusters in the perfect tungsten due to the repulsive interaction between interstitial hydrogen atoms. Once there is an interstitial oxygen atom, the uniformly distributed hydrogen atoms aggregate around the interstitial oxygen atom to form O–H_n complex, leading to the appearance of unstable lattice sites. The initial vacancy can be created on the unstable lattice sites, and then the hydrogen atoms nearby are trapped by this vacancy to form stable V–O–H_n complex. Due to its high stability, the V–O–H_n complex can survive and widely distribute in tungsten in the right condition. Thus the hydrogen bubble nucleates. Then, these abundant V–O–H_n complexes may diffuse and agglomerate, resulting in microscopic cavities and bubble formation. In this mechanism, the impurity oxygen plays two key roles: (i) the aggregation of multiple hydrogen atoms around the oxygen leads to the appearance of unstable sites nearby, sufficing for a condition of spontaneous vacancy formation; (ii) the incorporation of oxygen into vacancy can strengthen the stability of the vacancy, resulting in the significant increase of vacancy concentration in tungsten. If one impurity has a similar role as oxygen in tungsten, it can be expected as the nucleation point and promote hydrogen bubble formation in metals. Hence, this mechanism should be generally applicable for hydrogen bubble nucleation in metals, such as iron, with low vacancy concentration.

In the past decade, experimental results have shown that the minimum energy of deuterium ions for producing displacement damage in tungsten is calculated to be 940 eV from the displacement threshold energy of 40 eV [54], whereas deuterium plasmas

with energy of tens of eV definitely produce blisters [17–24]. Until now, three possible mechanisms have been proposed to explain this question. Alimov et al. [18] argued that the mechanism of plastic deformation could be used to give an interpretation for the sudden increase in trapping sites for deuterium and the concurrent accumulation of deuterium in tungsten irradiated with 200 eV deuterium ions. However, the details of how the initial vacancy is generated have not been given. Poon et al. [19] proposed that the recoil implantation of carbon and oxygen impurities in the background gas arriving at the surface created vacancies in tungsten, which can be centers of deuterium inventory and, consequently, for deuterium agglomeration in clusters. While this mechanism cannot explain the results using deuterium plasma with energy of tens of eV, such as 38 eV in Ref. [20]. Shu et al. [20] guessed that the mechanism of formation of superabundant vacancies [14,53] may be valid for the abundant vacancies formation in tungsten exposed to high flux and low energy (38 eV) deuterium plasma and these abundant vacancy–deuterium clusters may diffuse deeply into the bulk and agglomerate, resulting in microscopic cavities. As suggested by Fukai et al. [14,15] it is a mechanism behind the creation of superabundant vacancies in metals that the vacancy formation energy will be decreased by V–H_n complex formation. In the tungsten, the vacancy formation energy is decreased to ~2.45 eV by the V–H_n complex formation, which is still very high, suggesting that the vacancy concentration remains extremely low (10^{-39} at room temperature). Moreover, the vacancy formation energies of the lattice sites nearby the interstitial hydrogen are larger than 2.0 eV, which are still very high for the initial vacancy formation. So the mechanism of abundant vacancy formation due to the lowering of the vacancy formation energy by trapping hydrogen cannot be used to explain the sudden significant increase of trapping sites for hydrogen in tungsten irradiated with low energy hydrogen ions. Hence, it is still an open question that how hydrogen bubble nucleates in tungsten exposed to low-energy hydrogen irradiation. Based on these reported results, it could be concluded that, to explain this question, there are two key points must be addressed: the initial vacancy formation and the survivability of abundant vacancies in tungsten. The above proposed impurity trapping mechanism for hydrogen nucleate fully addresses these two key points: (i) the initial vacancy can be created on the unstable lattice sites nearby the O–H_n complex; (ii) the vacancy concentration are increased to 10^{-7} at room temperature by the formation of V–O–H_n complex. Therefore, this mechanism can give a reasonable explanation for this long-standing problem.

4. Conclusions

We have systematically investigated the interaction between the LE and hydrogen and the effect of the LE on the hydrogen trapping ability and stability of vacancy in tungsten. The hydrogen and oxygen prefer to occupy the tetrahedral site and carbon prefers the

octahedral position. There is an attractive interaction between the LE and hydrogen, which is larger for oxygen than carbon. Multiple hydrogen atoms can accumulate around the LE to form LE–H_n complex. The maximum number of hydrogen atoms around the interstitial oxygen is five. The formation of LE–H_n complex reduces the stability of lattice sites nearby, and some unstable sites are observed in the vicinity of O–H_n. The vacancy would be created on these unstable sites. The introduction of LE into vacancy slightly decreases the vacancy hydrogen trapping ability. However, the local concentration of hydrogen nearby vacancy would be increased due to the additional interstitial hydrogen atoms aggregation around the saturated V–LE–H_n complex. The most important point is that oxygen can significantly strengthen the vacancy stability and increase the equilibrium concentration of vacancy in tungsten. Based on these results, a new mechanism of bubble nucleation by hydrogen accumulation around oxygen impurity in tungsten is proposed: multiple hydrogen atoms aggregate around the oxygen inducing that some lattice sites nearby become unstable, where the initial vacancy can be created to form stable V–LE–H_n complex. The formation energy of the complex is so low that abundant V–LE–H_n complexes may survive in the right conditions and thus the hydrogen bubble nucleates. This mechanism provide a reasonable explanation for the long-standing problem of how hydrogen bubble nucleates in tungsten exposed to low-energy (far lower than displacement threshold energy) deuterium ions irradiation. It is expected that this mechanism could be generally applicable for hydrogen bubble nucleation in metals with low vacancy concentration.

Acknowledgements

This work was supported by the National Magnetic Confinement Fusion Program (Grant Nos.: 2011GB108004 and 2010GB109004), the National Natural Science Foundation of China (Nos.: 91026002 and 91126002) and the Strategic Priority Research Program of Chinese Academy of Sciences (Grant Nos.: KJJCX2-YW-N35 and XDA03010303), and by the Center for Computation Science, Hefei Institutes of Physical Sciences.

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