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# Thermodynamic properties of vacancy-hydrogen complex in tungsten

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## Abstract

Formation energies for vacancy-hydrogen (V-H) complexes in tungsten (W) are calculated in terms of first-principles calculations. The dependence of concentration of V-H complexes on temperature and local H concentration is estimated assuming thermal equilibrium. It has been reported that a maximum of 12 H atoms are accommodated in a W monovacancy at 0 K. However, major monovacancies trap six H atoms in finite temperature.

**Key words :** *hydrogen, tungsten, bcc metals, vacancy, plasma, fusion*

## 1. Introduction

Tungsten (W) is one of promising plasma-facing materials (PFMs) in future fusion reactors due to low hydrogen (H) solubility, low erosion rate, and high melting point. However, the PFMs are exposed to high energy and high flux H-isotopes (deuterium and tritium) plasma particles in actual fusion reactors. In fact, it has been reported that a large amount of deuterium were retained in W specimen by irradiation experiment <sup>1)</sup>. In particular, tritium retention in PFMs installed in the International Thermonuclear Experimental Reactor (ITER) is an important problem for the safety operation. However, tritium retention mechanism in bulk W is not sufficiently identified.

Because W as well as molybdenum (Mo) has very low H solubility in the bulk crystal due to its high heat of solution. So, it has been supposed to be prime candidate PFMs. However, the attractive interactions of W and Mo monovacancies to H atoms are considerably strong. Such low H solubility causes multiple H precipitation in a monovacancy and reduction of formation energy for V-H complexes <sup>2, 3)</sup>. In fact, it has been reported that a maximum of six H atoms are accommodated in usual bcc transition metals at 0 K in terms of first-principles calculations, while a maximum of twelve

and ten H atoms are accommodated in a W and Mo monovacancy, respectively <sup>4, 5)</sup>.

First-principles calculations are assumed to be  $T = 0\text{K}$ . However, phenomena in finite temperature are very important to investigate H retention in PFMs in actual fusion reactor and vacancy formation mechanism under irradiation condition. In the present paper, concentration of V-H complexes in W bulk crystal is calculated assuming a thermal equilibrium model and its dependence on local H concentration <sup>6, 7)</sup>. For comparison, concentration of V-H complexes in Fe is calculated as well.

## 2. Methodology

First-principles calculations based on the density functional theory <sup>8)</sup> are performed using the Vienna Ab-initio Simulation Package (VASP) <sup>9, 10)</sup> with the generalized gradient approximation <sup>11)</sup> and projected augment wave potentials <sup>12)</sup>. All supercells used in the present simulations are composed of 54 lattice points ( $3 \times 3 \times 3$  bcc lattice) containing a monovacancy. A cutoff energy is 350 eV for all metal-H systems. A Monkhorst-Pack scheme of  $5 \times 5 \times 5$  k-point mesh is used within the Brillouin-zone. <sup>13)</sup> Atomic positions and supercell size relaxations are iterated until the force acting on every atom is less than  $3 \times 10^{-3} \text{eV}/\text{\AA}$ . However, the calculation accuracy for Fe-H system is lowered because of computer performance limits. In the case of Fe-H system,  $3 \times 3 \times 3$  k-point mesh is used and convergence condition for lattice relaxation is  $5 \times 10^{-3} \text{eV}/\text{\AA}$ . Nevertheless, the results of the present simulations for Fe-H

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system are in agreement with those calculated in more accurate conditions<sup>14</sup>).

The binding energy for single and multiple H atoms to a monovacancy is defined in a total energy manner.

$$E_b(m) = E[M_{n-1}\text{Vac}] - E[M_{n-1}\text{H}_m\text{Vac}] + m(E[M_n\text{H}^T] - E[M_n]), \quad (1)$$

where the function  $E$  is the cohesive energy of the supercell. In the present simulations  $n = 54$ .  $M_{n-1}\text{Vac}$  is a supercell composed of  $(n-1)$  metal atoms and a monovacancy;  $M_{n-1}\text{H}_m\text{Vac}$  is that composed of  $(n-1)$  metal atoms,  $m$  H, and a monovacancy;  $M_n\text{H}^T$  is that composed of  $n$  metal atoms and an interstitial H embedded at a T-site because H prefers T-site in bcc bulk crystal; and  $M_n$  is perfect lattice composed of  $n$  metal atoms, respectively. Therefore, total binding energy  $E_b(m)$  in Eq. (1) gives the total energy gain of  $m$  H atoms migrating from distant T-sites and becoming trapped in a monovacancy.

Vacancy formation energy  $E_v$  in metals is defined, as follows.

$$E_v = E[M_{n-1}\text{Vac}] - \frac{n-1}{n}E[M_n] \quad (2)$$

Formation energy for V-H complex trapping  $m$  H atoms is

$$E_f(m) = E_v - E_b(m). \quad (3)$$

Figure 1 shows schematic view of the bulk crystal composed of  $N_0$  metal atoms,  $N_H$  H atoms, and  $N$  monovacancies.  $n_m$  is the number of monovacancies trapping  $m$  H atoms.  $M$  is total number of H atoms trapped in monovacancies.  $\omega_m$  is multiplication of energetically degenerate atomic configurations of V-H complex trapping  $m$  H atoms. The H configurations in a  $W$  monovacancy are calculated by Ohsawa *et al.*<sup>5</sup>). As an example, V-H complex trapping two H atoms is supposed to be triplet state, as shown in Fig. 2. Therefore, multiplication  $\omega_2 = 3$ . The important parameters used in the present paper are listed, as follows.

$N_0$	total number of metal atoms
$N_H$	total number of H atoms
$N$	total number of vacancies
$n_m$	number of vacancies trapping $m$ H atoms
$M$	total number of H atoms trapped in vacancies
$\omega_m$	multiplication of degenerate H configuration

Now, we obtain trivial relation.

$$N = \sum_{m=0} n_m \quad M = \sum_{m=0} mn_m \quad (4)$$

Thermodynamic properties of metal-hydrogen systems in finite temperature are investigated by partition function. In the present work, only configurational entropy

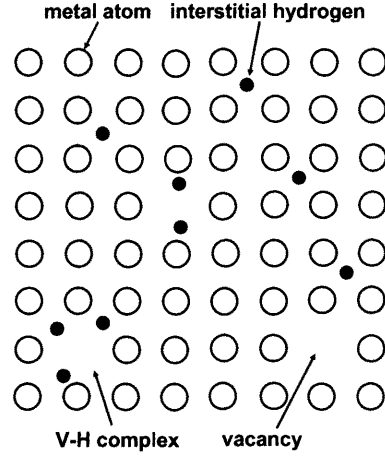


Fig. 1 Schematic view of crystal containing monovacancies and H atoms.

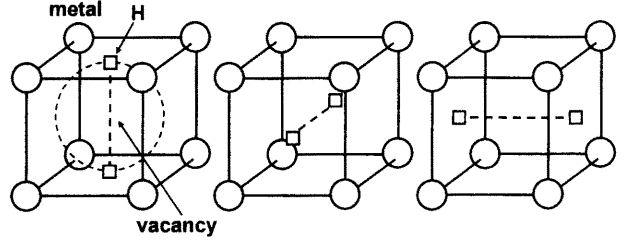


Fig. 2 Triplet stable configurations of two H atoms trapped in monovacancy.

is taken into account.  $N$  monovacancies are assumed to be formed among  $N + N_0$  lattice points.  $M$  H atoms are trapped in the  $N$  monovacancies.  $6(N_0 + N)$  T-sites exist but  $24N$  T-sites next to the monovacancies are not available for interstitial sites of H atoms, as shown in Fig 3. Therefore,  $N_H - M$  H atoms are distributed over  $6N_0 - 18N$  interstitial sites. Partition function  $Z$  is

$$Z = \binom{N_0+N}{N} \binom{6N_0-18N}{N_H-M} \frac{N!}{n_0!n_1! \dots} \omega_0^{n_0} \omega_1^{n_1} \dots \exp\left(-\sum_{m=0} n_m E_f(m)/k_B T\right) \quad (5)$$

One obtains the number of monovacancies trapping  $m$  H atoms by minimizing free energy,  $F = -k_B T \ln Z$ .

$$\frac{\partial F}{\partial n_m} = 0 \quad (6)$$

Therefore,

$$\frac{n_m}{N_0 + N} = e^{-E_f(m)/k_B T}$$

$$\frac{(6N_0 - 18N - N_H + M)^{18-m} (N_H - M)^m \omega_m}{(6N_0 - 18N)^{18}}, \quad (7)$$

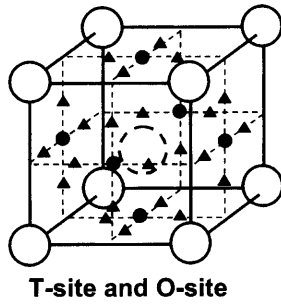


Fig. 3 Closed circles and closed triangles are O-sites and T-sites next to monovacancy, respectively.

where Stirling's formula is used. Using Eq. (4), this multiple simultaneous equation with respect to  $n_m$  becomes simple non-linear simultaneous equation with respect to  $N$  and  $M$ .

$$\frac{N}{N_0 + N} = \sum_{m=0} e^{-E_f(m)/k_B T} \frac{(6N_0 - 18N - N_H + M)^{18-m} (N_H - M)^m \omega_m}{(6N_0 - 18N)^{18}}$$

$$\frac{M}{N_0 + N} = \sum_{m=0} m e^{-E_f(m)/k_B T} \frac{(6N_0 - 18N - N_H + M)^{18-m} (N_H - M)^m \omega_m}{(6N_0 - 18N)^{18}} \quad (8)$$

### 3. Results and Discussion

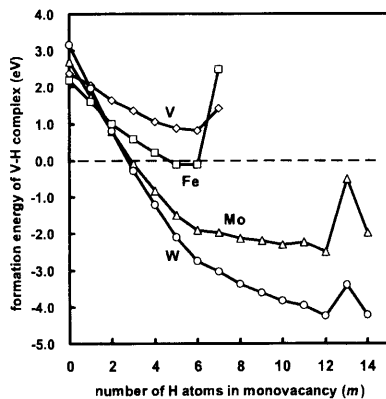


Fig. 4 Formation energy for V-H complex in bcc transition metals.

Formation energies for V-H complexes in bcc transition metals are calculated as a function of the number of H atoms trapped in the monovacancy  $m$ , as shown in Fig. 4. In particular, the V-H complex formation ener-

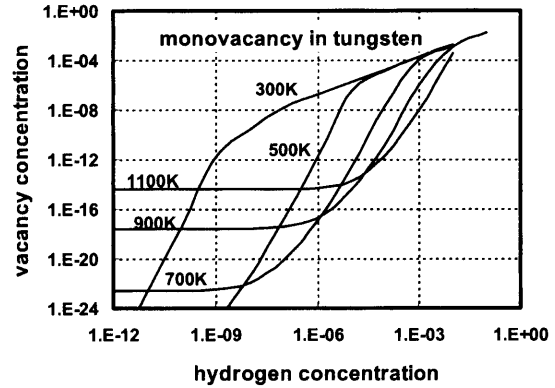


Fig. 5 Vacancy (V-H complex) concentration in W in local H concentration.

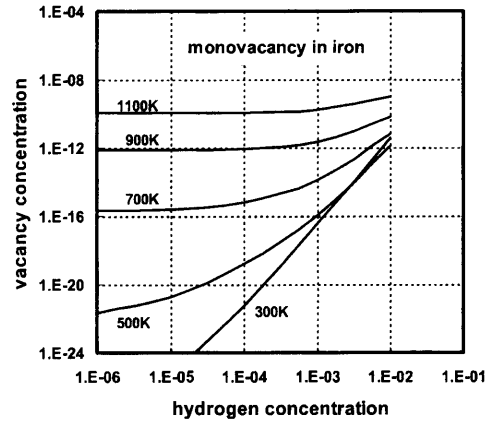


Fig. 6 Vacancy (V-H complex) concentration in Fe in local H concentration.

gies are negative in the case of W and Mo for  $m \geq 3$ , i.e., exothermic reaction. If local H concentration are sufficiently high, superabundant V-H complexes creation will be observed in thermal equilibrium<sup>2, 3)</sup>. One obtains dependence of vacancy (V-H complex) concentration on H concentration and temperature by solving Eq. (8). Table 1 shows parameter values to solve Eq. (8), i.e., formation energies for V-H complexes  $E_f(m)$  defined in Eq. (3) and multiplication of energetically degenerate ground states  $\omega_m$  for W and Fe systems. Figures 5 and 6 show vacancy concentration in bulk W and Fe in a finite temperature, respectively. Vacancy formation energies are lowered by H trapping. So, the vacancy concentration increases as H concentration increases in thermal equilibrium. In particular, vacancy concentration in bulk W rapidly increases above some threshold values of H concentration, as shown in Fig. 5. While, vacancy concentration in bulk Fe moderately increases, as shown in Fig. 6.

In low H concentration limit, the vacancy concen-

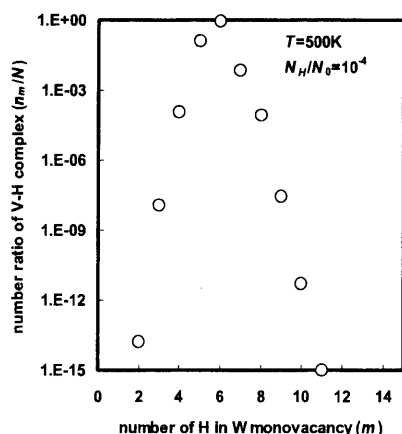


Fig. 7 Number ratio of V-H complexes in bulk W.

tration is determined by bare vacancy formation energy

$$N/N_0 \sim e^{-E_v/k_B T}. \quad (9)$$

At lower temperatures, H presence remarkably enhances V-H complex creation. Figures 5 and 6 sometimes show that vacancy concentration in lower temperature is higher than that in higher temperature. At higher temperatures, large amount of H atoms are accommodated in the interstitial sites (T-sites) because such H increases entropy and free energy is effectively lowered. However, vacancy concentration is kept at lower levels because less H atoms are trapped in vacancies.

As an example, distribution of number ratio of V-H complexes is shown in Fig. 7 in the case of  $T = 500\text{K}$  and H concentration  $10^{-4}$ . A maximum of 12 H atoms can be accommodated in a W monovacancy at 0 K<sup>4, 5)</sup>. However, it is interesting that almost all monovacancies trap only six H atoms assuming the thermal equilibrium model. This result can be explained, as follows. According to Table 1, V-H complex formation energies are estimated to be  $-2.742\text{ eV}$  and  $-4.245\text{ eV}$  for the number of H atoms of  $m = 6$  and  $m = 12$ , respectively. The absolute value of total formation energy for two V-H complexes trapping six H atoms is larger than that for one V-H complex trapping 12 H atoms, that is,  $2.742 \times 2\text{ eV} > 4.245\text{ eV}$ .

## References

1) V. Kh. Alimov, J. Roth, R. A. Causey, D. A. Komarov, Ch. Linsmeier, A. Wiltner, F. Kost, and S. Lindig, *J. Nucl. Mater.* **375**, 192 (2008).

Table 1 V-H complex formation energy  $E_f$  trapping  $m$  H atoms in W and Fe, and multiplication of degenerate ground states  $\omega_m$ .

$m$	W		Fe	
	$E_f$	$\omega_m$	$E_f$	$\omega_m$
0	3.145	1	2.172	1
1	1.962	6	1.596	6
2	0.792	3	0.987	3
3	-0.277	12	0.587	12
4	-1.223	12	0.221	12
5	-2.110	6	-0.099	6
6	-2.742	6	-0.112	6
7	-3.027	24	2.490	1
8	-3.386	24		
9	-3.624	12		
10	-3.834	6		
11	-3.955	24		
12	-4.245	2		
13	-3.396	2		
14	-4.219	2		

2) Y. Fukai and N. Okuma, *Phys. Rev. Lett.* **73**, 1640 (1994).

3) Y. Fukai, *Phys. Scr.* **T103**, 11 (2003).

4) K. Ohsawa, J. Goto, M. Yamakami, M. Yamaguchi, and M. Yagi, *Phys. Rev. B* **82**, 184117 (2010).

5) K. Ohsawa, K. Eguchi, H. Watanabe, M. Yamaguchi, and M. Yagi, *Phys. Rev. B* **85**, 094102 (2012).

6) D. Kato, H. Iwakiri, and K. Morishita, *J. Plasma Fusion Res. SERIES.* **8**, 404 (2009).

7) D. Kato, H. Iwakiri, and K. Morishita, *J. Nucl. Mater.* **417**, 1115 (2011).

8) P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, 864 (1964).

9) G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993).

10) G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).

11) J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).

12) P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).

13) H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).

14) R. Matsumoto, S. Taketomi, N. Miyazaki, proceedings of 12th International Conference on Fracture T19-012 (2009).