First-principle Study on Binding Energy of Vacancy-Hydrogen Cluster in Tungsten

Daiji KATO, Hirotomo IWAKIRI[1], Kazunori MORISHITA[2]

National Institute for Fusion Science, Toki, Gifu 509-5292, Japan
[1]University of the Ryukyus, Okinawa 903-0213, Japan
[2]Institute of Advanced Energy, Kyoto University, Kyoto 611-0011, Japan

Multiple-hydrogen trapping by mono-vacancies in tungsten was investigated based upon the first-principle (density functional) calculation. An equilibrium thermodynamic model is presented to describe a bulk tungsten crystal containing the mono-vacancies and hydrogen atoms by taking account of the first-principle calculations of vacancy-hydrogen interaction. The present model gives average numbers for trapped hydrogen atoms at the single mono-vacancy and the vacancy concentration as functions of local hydrogen concentrations for different temperatures. Based on the present results, we examine a speculation suggested from recent experimental observations, that new hydrogen traps may be created by super-saturated low-energy hydrogen implantation.

Keywords: hydrogen retention, vacancy, tungsten, first-principle calculation

1. Introduction

Tungsten is one of the prime candidate plasma-facing materials at ITER, which would be exposed to high flux and fluence of hydrogen. Some experimental studies [1,2] showed that the amount of retained deuterium in deuteron-implanted tungsten was of the same order of magnitude as in graphite. Trapping sites in tungsten are however not fully identified yet.

It is known that lattice displacements in the bulk by high-energy ion impact can become traps. Radiation damage by the high-energy ion irradiation would therefore generally enhance the hydrogen retention in the bulk. However, it has also been reported [3] that after low-energy deuteron irradiation of higher flux, level of retained D/W concentration in molybdenum was orders of magnitudes higher than one would expect from inherent or 'natural' traps in the bulk. It becomes an issue of study to investigate mechanisms of new trap creation during high-flux and low-energy ion implantation.

Tungsten as well as molybdenum has very low natural hydrogen solubility in the bulk crystal, because of its high heat of solution. However, it has been pointed out [4] that significantly lower heat of solution would be obtained by taking account of vacancy-hydrogen cluster formation; vacancy-hydrogen attractive interaction would reduce formation energies of the vacancies dressed with multiple hydrogen atoms. In this context, it may be noteworthy that several interesting phenomena observed under hydrogen-rich conditions have been explained by the superabundant vacancy formation induced by hydrogen, e.g. large volume contraction of some metals [5,6], enhancement of inter-diffusion at the junction of two metals [7], etc. Thus, it is intriguing to investigate enhancement of the vacancy abundance by the vacancy-hydrogen cluster formation in non-occluder metals like tungsten.

This paper is organized as follows. In Sec. 2, we study binding energies between hydrogen atoms and mono-vacancies of tungsten by means of the first principle molecular dynamics code, VASP [8]. In Sec. 3, thermodynamic properties of a bulk tungsten crystal (body-cubic-center) containing the mono-vacancies and hydrogen atoms are studied by taking account of the calculated binding energies. Average numbers for trapped hydrogen atoms at the single mono-vacancy and the vacancy concentration are presented as functions of local hydrogen concentrations for different temperatures. Sec. 4 is devoted to conclude the present work.

2. The first-principle study on binding energy of vacancy-hydrogen cluster

The first-principle calculations of the binding energies between hydrogen atoms and mono-vacancies of tungsten are preformed by using the VASP code. In the present calculations, Perdew, Burke and Ernzerhof version of generalized-gradient approximation [9] in the density functional theory was used to obtain electron density distribution.

author's e-mail:kato.daiji@nifs.ac.jp

Total energies were calculated for a body-cubic-center (bcc) super cell with 54 tungsten atoms, $E(W_{54})$, the super cell involving one hydrogen atom at a tetrahedral site of interstitial, $E(W_{54}H_1)$, the super cell including one mono-vacancy, $E(W_{53}V_1)$, and the super cell with a cluster of n hydrogen atoms trapped at octahedral sites of the mono-vacancy, $E(W_{53}V_1H_n)$. In the calculations, lattice relaxation was taken into account. The cell shape and lattice configuration were relaxed until the lowest total energy was obtained for a given cell volume. By fitting Marnaghan's equation of state (EOS) to the so-obtained energy-volume curve, we determined values of the minimum total energy, the equilibrium volume and the elastic modulus of the cell. Using energy values of the present calculation, vacancy formation energies, $e_V = E(W_{53}V_1) - 53/54\,E(W_{54})$, were obtained to be 3.25 eV. The present value is consistent with calculated values by Finnis and Sinclair [10] with aid of empirical interaction potentials for tungsten (3.71 eV).

Binding energies of hydrogen atoms trapped at the octahedral sites of the vacancy are given by,

$$e_B = E(W_{53}V_1H_{n-1}) - E(W_{53}V_1H_n) + E(W_{54}H_1) - E(W_{54}). \quad (1)$$

Fig. 1 shows calculated values of the binding energies as a function of number of trapped hydrogen atoms. In the figure, results for a ferritic iron are also plotted for comparison. It is noted that the binding energy values for ferritic iron agree with those of earlier first-principle calculations by Tateyama and Ohno [11], and are consistent with those inferred from hydrogen retention measured by ion-beam technique [12]. Variations of the binding energies along the number of the trapped hydrogen atoms are similar for both cases. The first and second hydrogen atoms are trapped with almost the same binding energies, indicating that the two hydrogen atoms influence little each other. The third and subsequent hydrogen atoms have significantly smaller binding energies due to mutual repulsion of the hydrogen atoms in the cluster. The vacancies dressed with three or more hydrogen atoms would be less abundant at ambient condition of hydrogen pressure, since the binding energies are not substantially larger than the hydrogen solution energy.

Stability of the hydrogen atoms trapped at the vacancies is described in terms of the electronic states. Fig. 2 shows partial densities of states (DOS) projected to the hydrogen atom and its nearest-neighbor tungsten atom for two cases: a VH cluster and an interstitial hydrogen atom in the tungsten super-cell, respectively. The DOS for the VH cluster indicates that a broad hydrogen induced states are appeared overlapping largely with the 5d band of tungsten. The induced state has a covalent bonding character via a strong hybridization of H-1s orbital and 5d orbital of the nearest-neighbor tungsten atom. This hybridization may be responsible for the large binding energies of the VH cluster. In contrast to this, the induced state of the interstitial hydrogen atom is localized
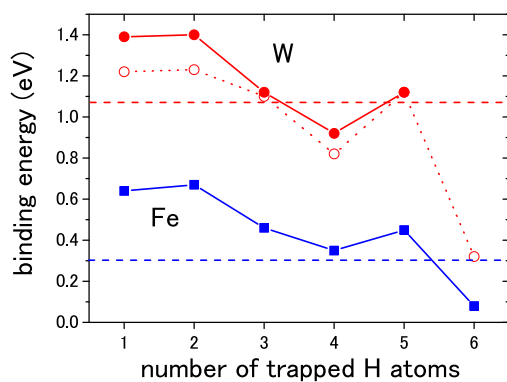

Fig. 1 The first-principle calculation of binding energies for tungsten and ferritic iron. Open circles with dotted line indicate the results for tungsten neglecting the zero-point energy correction, and dashed lines the solution energies.
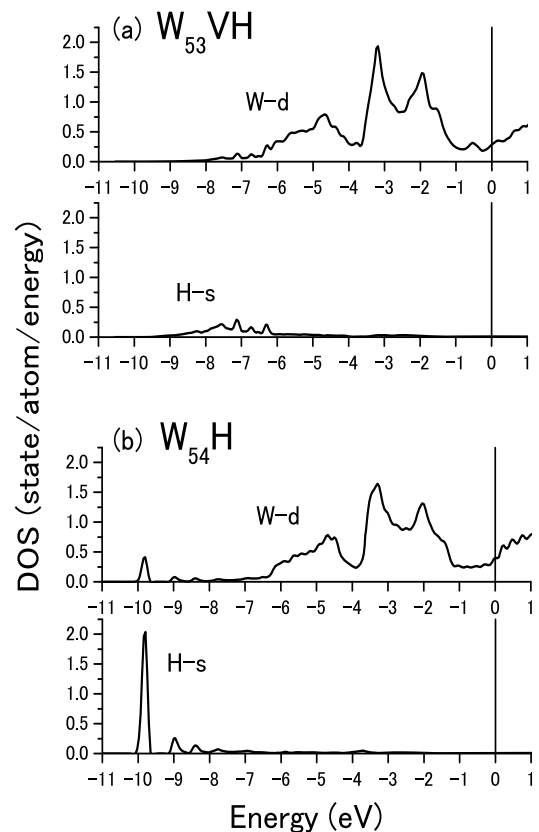

Fig. 2 Site-projected partial densities of states (DOS) for (a) the VH cluster and (b) the interstitial (tetrahedral site) hydrogen atom in the tungsten crystal (bcc). The origin of energy values is the Fermi level.

with a narrow distribution just below the 5d band of tungsten, indicating less hybridization of the orbital with a specific tungsten atom. The electronic state of the interstitial hydrogen atoms may therefore be described as that of the hydrogen atoms being embedded in high density conduction electrons of tungsten, to which the effective medium theory [13] can be applied.

3. Thermodynamic properties of vacancy-hydrogen cluster

Thermodynamic properties of a bulk tungsten crystal (bcc) containing the mono-vacancies and hydrogen atoms were studied by taking account of the calculated binding energies.

Fig. 3 illustrates the bulk tungsten crystal containing N_0 tungsten atoms, N_H hydrogen atoms, and n mono-vacancies. rn hydrogen atoms are trapped among $6n$ octahedral sites of the mono-vacancies, and residual $N_H - rn$ hydrogen atoms are distributed over $6N_0$ interstitial (tetrahedral) sites. Partition functions Z of this system at a given temperature T are approximated by,

$$Z = Z_M \times Z_I,$$
$$Z_M = \frac{(N_0 + n)!}{N_0! n!} \exp(-n f_f / kT),$$
$$Z_I = \frac{(6N_0)!}{(N_H - rn)!(6N_0 - N_H + rn)!} \exp\left[-(N_H - rn)f_s / kT\right] \times$$
$$\frac{(6n)!}{(rn)!(6n - rn)!} \exp(-n f_s' / kT),$$

(2)

where f_f, f_s and f'_s are the formation energy of the bare mono-vacancy, the solution energies of the interstitial hydrogen atom and the hydrogen atom trapped at the mono-vacancy, respectively. Those energies were obtained from the present first principle calculations. The average number of hydrogen atoms trapped by one mono-vacancy, i.e. r, is obtained under the condition that the free energy of the partition function, $F = -kT \ln Z$, has the minimum value.
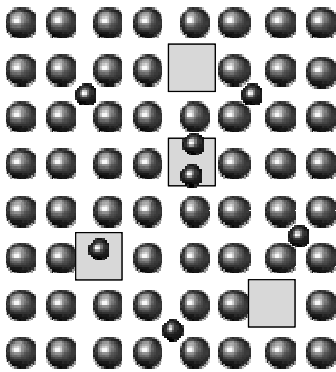
$$\frac{\partial F}{\partial r} = \frac{\partial F}{\partial n} = 0,$$
$$x_v = n/N_0, x_i = N_H / N_0,$$
(3)
$$x_{i0} = (x_i - r x_v)/6,$$
$$\frac{6}{r} = 1 + \frac{1 - x_{i0}}{x_{i0}} \exp\left[-\frac{\partial}{\partial r} \sum_r f_b(r) \Big/ kT\right],$$

where $f_b(r)$ is the binding energy of the cluster as a function of r. In this work, for the sake of simplicity, we use a constant binding energy $f_b(r) = 1$ eV for all r values, because the least square fitting of the cluster formation energy with a straight line as a function of r gives the constant binding energy of about 1 eV. As a result, the vacancy concentration is approximated as,

$$\frac{x_v}{1 + x_v} = \left(\frac{x_{i0}}{1 - x_{i0}} \frac{6}{r}\right)^6 \exp\left[-(f_f - 6 f_b)/kT\right].$$
(4)

Fig. 4 shows variation of the mono-vacancy concentration in the bulk tungsten crystal as functions of the hydrogen concentration. For low hydrogen concentration, the vacancy concentration at a given temperature has a certain value determined by the formation energy of the bare mono-vacancy. Above some threshold values of the hydrogen concentration, the vacancy concentration shows rapid increase. It turns out that the rapid increase of the vacancy concentration is associated with increase in the average number of the hydrogen atoms trapped by the vacancy.

According to the present results, higher the material temperature, enhancement of vacancy concentration sets in at higher H concentration values. It may be understood as followings. When the level of hydrogen concentration becomes too high to be accommodated in the interstitial sites for a given temperature, the vacancy-hydrogen

Fig. 3   Illustration of the bulk tungsten (larger balls) crystal containing mono-vacancies (squares) and hydrogen atoms (smaller balls).
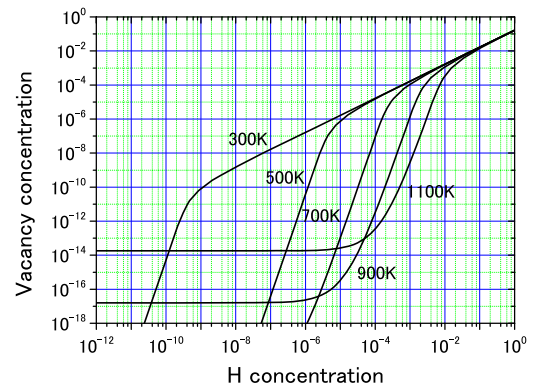

Fig. 4   Vacancy concentration at thermal equilibrium as functions of hydrogen concentration at five temperatures for 300-1100K.

cluster formation is enhanced and then it increases rapidly the vacancy concentration. At higher temperatures, larger amount of hydrogen atoms can be accommodated in the interstitial sites (mobile hydrogen atoms) for a given hydrogen concentration, which therefore gives less vacancy-hydrogen cluster formation and keeps the vacancy concentration at lower levels. It is noted that mitigation of plasma-driven trap production in tungsten at elevated temperatures has been reported in recent Pilot-PSI experiments [3]. The present model gives consistent results with this observation.

4. Conclusion

In this paper, we presented a thermodynamic model to describe the superabundant vacancy (hydrogen trap) creation under hydrogen-rich conditions by taking account of the first-principle calculations of the vacancy-hydrogen interaction. The present model does not conflict with a speculation suggested from the DIONISOS experiments [3], that new hydrogen traps may be created by the super-saturated low-energy hydrogen implantation.

However, the present study is not yet enough to tell us whether such the super-saturated hydrogen condition would be realized in tungsten. To answer this, dynamic transport, i.e. the implantation (source) and the diffusion/surface-recombination (sink), of the mutually interacting high-density hydrogen must be also studied. Recalling large uncertainties remained in published data of the diffusion and surface-recombination coefficients in tungsten, we may readily understand difficulties in accurately modeling the transport of the hydrogen in tungsten. In natural conditions of hydrogen concentration, the large uncertainties in the transport coefficients may be ascribed solely to different abundance of the natural traps inherent in the low-solubility materials. However, in the present work we showed that at elevated hydrogen concentrations, the vacancy concentration itself could depend on the hydrogen concentration strongly. Comprehensive studies on the hydrogen transport taking this into account are an important issue of study to understand the hydrogen retention in tungsten irradiated by high-flux ions of divertor plasmas.

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