§7. *Ab initio* Calculations of Binding Energies of Vacancy-hydrogen Clusters in Metals

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Atomic structure of vacancy-hydrogen clusters in metals is an issue of study concerning radiation effects by hydrogen of high particle fluence at divertor. As the cluster may have smaller formation energy than that of a mono-vacancy, it would have higher concentration at thermal equilibrium and enhance diffusion of metal atoms via the abundant vacancies[1]. Strong enhancement of hydrogen retention in Mo under exposure to high pressure hydrogen gas has been observed. The enhancement may be associated with formation of the vacancy-hydrogen clusters.

We investigated the formation energies of the vacancy-hydrogen clusters in ferritic iron and tungsten by means of an *ab initio* (first principle) molecular dynamics code, VASP[2]. Total energies were calculated for a body-cubic-center (bcc) super cell with 54 metal atoms, $E(M_{54})$, the super cell involving one H atom at a tetrahedral site of interstitial, $E(M_{54}H_1)$, the super cell including one mono-vacancy, $E(M_{53}V_1)$, and the super cell with a cluster of n H atoms trapped at octahedral sites of the mono-vacancy, $E(M_{53}V_1H_n)$. Using energy values of the present calculation, vacancy formation energies, $e_V = E(M_{53}V_1) - 53/54\,E(M_{54})$, were evaluated to be 2.18 eV for ferritic iron and 3.25 eV for tungsten. The present values are consistent with experimental values measured by positron annihilation method for the ferritic iron (1.4-2.0 eV) and with calculated values by Finnis and Sinclair[3] with aid of empirical interaction potentials for tungsten (3.71 eV), respectively.

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

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

Fig. 1 shows calculated values of the binding energies for ferritic iron and tungsten as functions of number of trapped H atoms. It is noted that according to the present results, a mono-vacancy would be able to trap multiple H atoms with considerable binding energies. The binding energy values for ferritic iron agree with those of other *ab initio* calculations by Tateyama and Ohno[4], and are consistent with those inferred from hydrogen retention measured by ion-beam technique[5]. Formation energies of the clusters with N H atoms are then given by,

$$E_F = e_V - \sum_{n=1}^{N} (e_B(n) - e_S), \quad (2)$$

where $e_S = E(M_{54}H_1) - E(M_{54}) - 1/2\,E(H_2)$ stands for solution energies of H atoms in metals. As seen in Fig. 1, the binding energies are larger than the solution energies for both ferritic iron and tungsten in cases that the number of trapped H atoms is less than or equals to 3 (5 for ferritic iron), i.e. the formation energies of those clusters are smaller than that of a bare mono-vacancy.

According to the present results, it is likely that the mono-vacancies would preferably form the clusters with H atoms in metals. Due to the less formation energies, concentration of the clusters would be considerably higher at thermal equilibrium. It is intriguing to investigate hydrogen retention by the clusters. Quantum properties of such the nano-scale hydrogen clusters trapped at vacancies in metals are hitherto unknown, it should be studied more thoroughly.

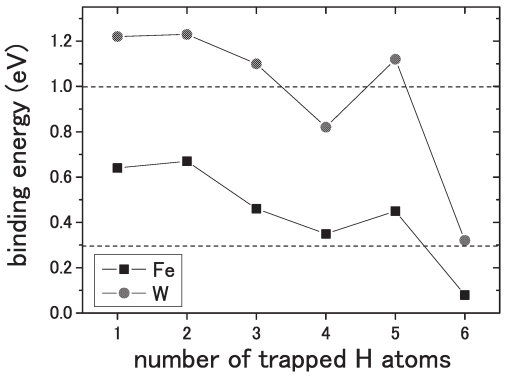

Fig.1: Binding energies of H atoms trapped octahedral sites of a mono-vacancy in metals. Correction in the zero-point energy (+0.06 eV) is taken into account for ferritic iron. Solution energies are indicated by dashed lines at 0.3 eV for ferritic iron and at 1.0 eV for tungsten, respectively. The present solution energy of tungsten includes larger uncertainty.

References

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