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Study on hydrogen-vacancy complexes in BCC metals from first-principles culculation

第一原理計算によるBCC金属中の空孔水素複合体に関する研究

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It has been reported that a maximum of six hydrogen atoms are trapped in a BCC metal monovacancy, but a maximum of twelve hydrogen atoms can be accommodated in a tungsten and molybdenum monovacancy. It is found that the stable positions of H atoms shift toward tetrahedral interstitial sites as the number of hydrogen atom increases.

1. Introduction

Plasma facing materials (PFMs) are exposed to high heat and high energy particles for a long time period in plasma confinement devices, such a fusion reactor. As a result, many lattice defects are nucleated in the PFMs by collisions of the plasma particles. In addition to the direct damage, the accumulation and retention of hydrogen (H) isotopes in metals induce embrittlement of the PFMs. We simulate stable H sites trapped in molybdenum (Mo) and tungsten (W) monovacancy in terms of first-principles calculations in order to investigate the properties of W-H and Mo-H systems. For comparison Fe-Hsystem is also examined.

In the case of BCC lattice, such as Mo and W, an interstitial atom is located at tetrahedral interstitial sites, as shown in FIG. 1 (a). On the other hand, a single H atom trapped a Mo and W monovacancy is located close to an o-site on the inner surface of the monovacancy as shown in FIG. 1 (b). Similarly, multiple H atoms ($n \leqq 6$) trapped in a monovacancy have been also assume to be located close to the o-sites. However, we are skeptical about the established assumption. In order to determine valid stable configurations of multiple H atoms in a monovacancy, a skillful calculation method was developed in the present work.

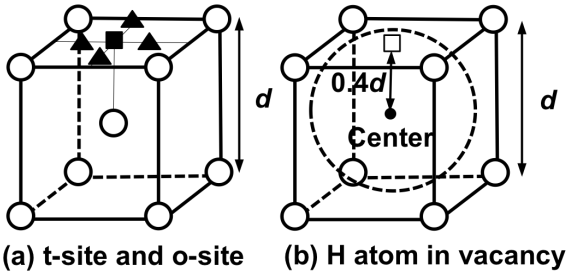

FIG. 1. (a) Schematic view of o-site (■) and t-site (▲). (b) Schematic view of a single H trapped in a vacancy in BCC lattice.

2. Calculation method

First-principles calculations based on the density functional theory are performed using the Vienna ab initio simulation package (VASP) with the generalized gradient approximation and projected augmented wave potentials. Periodic boundary condition is imposed to a BCC supercell composed of 54 lattice points. Plane-wave energy cutoff is 350 eV and 5*5*5 Brillouin zone sampling is used. The lattice relaxation is iterated until each resultant force applied on each atom becomes lower than 0.003 eV/Å.

Total binding energy is defined as

$$E_{\mathrm{total}} = E[\mathrm{M_{53}V}] - E[\mathrm{M_{53}VH}_n] + n(E[\mathrm{M_{54}H^T}] - E[\mathrm{M_{54}}]), \quad (1)$$

where the function E is the cohesive energy of the supercell. $\mathrm{M_{53}V}$ is supercell composed of 53 metal atoms and a vacancy; $\mathrm{M_{53}VH}_n$ is that composed of 53 metal atoms, a vacancy, and n H; $\mathrm{M_{54}H^T}$ is that composed of 54 metal atoms and one H embedded at a T-site; $\mathrm{M_{54}}$ is

perfect lattice composed of 54 metal atoms, respectively.

We investigated the more stable sites for the multiple H atoms using random initial distribution of n H atoms ($n \leqq 6$) in a monovacancy, as shown FIG. 2. In the case $n \geqq 7$, we located random initial distribution close to t-sites.

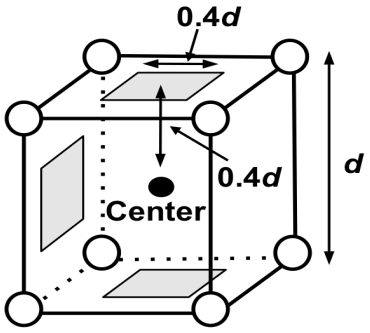

FIG. 2. Schematic view of initial distribution of n H atoms in a metal vacancy. Random placement of an H atom is uniformly distributed in each gray square. Center of square is close to the o-site.

3. Results

It is found that the stable sites of multiple H atoms trapped in Mo, W and Fe monovacancy are shifted toward tetrahedral interstitial sites as the number of H atoms increases. H configurations in a Mo monovacancy are shown in FIG.3 as an example.

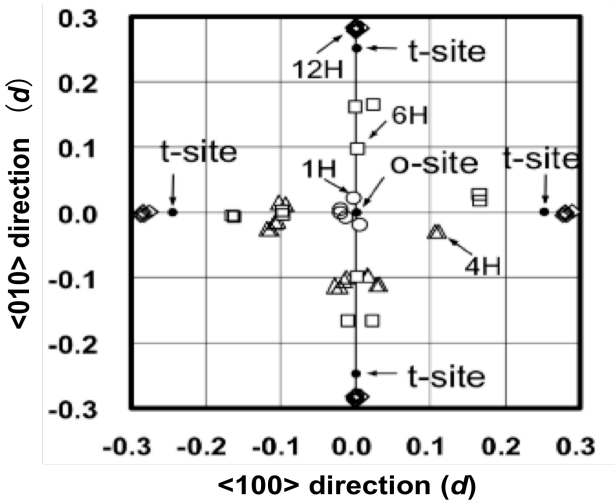

FIG. 3. Stable points of H atoms projected onto the {001} plane. Circle, triangle, square, and diamond systems correspond to the cases where one, four, six, and twelve H atoms are trapped in a monovacancy in Mo lattice, respectively. O-site is located at the center of figure.

It is understood that a maximum of twelve H atoms is trapped in a W and Mo monovacancy, as shown in FIG. 4. While, an Fe monovacancy can accommodate only six H atoms.

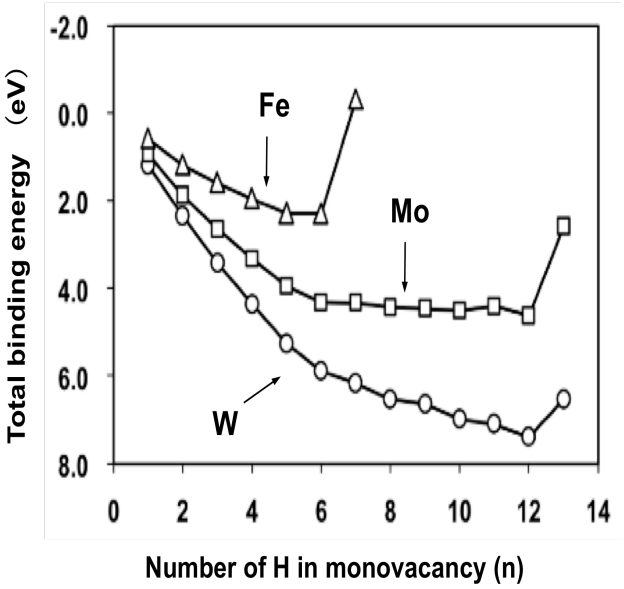

FIG. 4. Total binding energy as function of H atom number trapped in W, Mo and Fe vacancy.

4. Discussion

The H solubility for Mo and W is lower than that for Fe. However, too many H atoms are trapped in their monovacancy compared with other BCC metals. We suppose the reason is that the H atoms are strongry segregated to the vacancy-type lattice defects to reduce the high solution energy.

Zero point energy (ZPE) corrections for Metal-H systems are not necessarily negligible compared with their binding energies. However, ZPE do not play an essential role to determine the important and fundamental properties of the systems, e.g. ground-state configurations of H atoms in a monovacancy etc.

References

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