Atomistic study of hydrogen distributions around lattice defects and defect energies under hydrogen environment

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1. Introduction

It is well known that hydrogen atoms and lattice defects have strong interactions and mechanical properties of metals are significantly changed under hydrogen environment. It has been reported that hydrogen stabilizes vacancies [1, 2], and changes the mobility of dislocations [3-5]. Furthermore, the hydrogen distribution is strongly influenced by the stress fields [3-6]. In order to advance our understanding about hydrogen related fractures of metals, it is essentially important to reveal the hydrogen distributions around various lattice defects and the hydrogen effects on defect-formation and defect-motion.

In this study, first, we analyze the distributions of hydrogen trap energy around a vacancy, edge and screw dislocations, and grain boundaries in Fe using atomistic simulations and first principles calculations. We also report the influences of hydrogen on the defect energies and the number of trapped hydrogen under a thermal equilibrium condition.

2. Analytical procedure

2.1 First principles calculation

We performed DFT calculations within the spin-polarized generalized gradient approximation (GGA) [7] for electron exchange and correlation using the Vienna ab-initio simulation package (VASP) [8]-[10]. The interactions between the ions and electrons are described by Blöchl's projector augmented wave (PAW) method [11], which has the accuracy corresponding to an all-electron method within the frozen-core approximation. The Monkhorst-Pack scheme [12] is used for defining the k-points, and the conjugate-gradient method is employed for the relaxation algorithm. Zero-point energy (ZPE) correction, calculated from the Hessian matrix, was considered for hydrogen atom. We used $30 \times 30 \times 30$ k-points per unit lattice and 425 eV cut-off energy, which is sufficient for reliable calculations.

2.2 Molecular statics analysis

Although DFT calculations can give quantitative predictions for given atomic structures, the model size is small because of the calculation costs. Therefore, for the systems that require many atoms, we used molecular statics calculations using

interatomic potential. Here we employed the embedded atom method (EAM) potential developed by Wen et al. for Fe-H system [13]. We confirmed that the EAM potential can represent the heat of solution of hydrogen and strain effect on the heat of solution [14], and the migration energy of hydrogen in bcc lattice with good accuracy.

2.3 Heat of solution of hydrogen and trap energy

The heat of solution for incorporation of hydrogen into the occupation site positioned at $\boldsymbol{x}$ is calculated as follows.

$$E^{\mathrm{HOS}}(\boldsymbol{x}) = \Phi_{\mathrm{Fe+H}}(\boldsymbol{x}) - \left(\Phi_{\mathrm{Fe}} + \frac{1}{2}\Phi_{\mathrm{H2}} \right) \tag{1}$$

Here, $\Phi_{\mathrm{Fe+H}}(\boldsymbol{x})$ is the total energy of the system with a hydrogen atom at a trap site located at $\boldsymbol{x}$. Φ_{Fe} is the energy of the system without hydrogen, and Φ_{H2} is the energy of a hydrogen molecule. We estimated the energy of the system as the total potential energy for molecular statics simulations, and grand-state energy that is defined as the absolute total energy against the origin of the total energy of free ions and electrons separated infinitely for first principles calculations.

The trap energy arisen at trap site positioned at $\boldsymbol{x}$ is estimated by

$$E^{\mathrm{Trap}}(\boldsymbol{x}) = -\left(E^{\mathrm{HOS}}(\boldsymbol{x}) - E^{\mathrm{HOS\_T-site}}\right), \tag{2}$$

where $E^{\mathrm{HOS\_T\text{-}site}}$ (= 0.28 eV) is the heat of solution of the hydrogen atom on the T site in the relaxed bcc-Fe lattice.

2.4 Hydrogen occupation frequency at trap site

We estimate the hydrogen occupancy at T site ($c_{\mathrm{T\text{-}site}}$) under hydrogen pressure p and temperature T in reference to Ref. [15] as follows.

$$c_{\mathrm{T\text{-}site}} = 0.9686 \times 10^{-6} \sqrt{p} \exp\left(-\frac{3440}{T} \right) \tag{3}$$

In this paper, we show the results for p = 70 MPa and T = 300 K ($c_{\mathrm{T\text{-}site}} = 8.49 \times 10^{-8}$). The pressure consists with the value of recent high pressure hydrogen tank. Using the hydrogen occupancy at T site $c_{\mathrm{T\text{-}site}}$, the hydrogen occupation frequency at trap site with hydrogen trap energy $E^{\mathrm{Trap}}{}_i$ under thermal equilibrium condition is estimated by

$$\frac{c_i}{1-c_i} = \frac{c_{\mathrm{T\text{-}site}}}{1-c_{\mathrm{T\text{-}site}}} \exp\left(\frac{E^{\mathrm{Trap}}{}_i}{k_{\mathrm{B}}T} \right), \tag{4}$$

where k_{B} is Boltzmann's constant.

2.5 Formation energies of lattice defects

We estimate the formation energy of lattice defect under the hydrogen environment $E^{\mathrm{Def+H}}$ by neglecting the hydrogen-hydrogen interactions as follows.

$$E^{\mathrm{Def+H}} = E^{\mathrm{Def}} - \sum_i c_i E^{\mathrm{Trap}}{}_i n_i \quad (5)$$

Here, n_i is the number of trap site with trap energy $E^{\mathrm{Trap}}{}_i$ per unit amount of defect, and E^{Def} is the energy of lattice defect without hydrogen. Defects energy estimated by Eq. (5) undergoes the upper-limit of hydrogen influence, because we assumed that the maximum number of hydrogen under a thermal equilibrium condition is instantaneously trapped at the defect formation. We evaluate the number of trapped hydrogen by unit amount of defect as $N = \Sigma c_i n_i$.

3. Results and discussion

3.1 Interaction with vacancy

We treated a 2 × 2 × 2 bcc-Fe lattice with one vacancy (15 Fe atoms) by first principles calculations. Hydrogen atoms are introduced into the trap site around the vacancy in order of trap energy. In order to evaluate the accuracy of the EAM potential, we also performed the same calculations by the molecular statics simulation. Figure 1 shows the hydrogen trap energies of vacancy. We can confirm that the results agree well with reference values [2, 16]. The average number of trapped hydrogen by vacancy under the thermal equilibrium state was estimated as $N \approx 2.1$. And, whereas the energy of vacancy is 2.14 eV for without hydrogen, it is estimated as 0.82 eV under the hydrogen gaseous environment by Eq. (5). This result indicates the possibility of increase in vacancy density by plastic deformations under hydrogen environments.

3.2 Interaction with dislocations

We estimated the distributions of hydrogen trap energy around dislocations by molecular statics simulations. The estimation procedure is similar as Ref. [17]. Figure 2 (a) and (b) show the distributions of hydrogen trap energy around {112}<111> edge and {112}<111> screw dislocations, respectively. The dislocation cores that have non-bcc structure are shown in the figures by dashed lines. Trap sites distribute not only in the dislocation cores and under the edge dislocation but also on the slip plane of edge dislocation and in the elastic strain field around the screw dislocation core. The maximum hydrogen trap energy was 0.49 eV for the edge dislocation and 0.45 eV for the screw dislocation. The strong interaction between shear strain and hydrogen atom is attributed to the tetragonal strain caused by o-site occupation [14]. The average number of trapped hydrogen by 1 nm of {112}<111> edge and screw dislocation under the hydrogen environment (p = 70 MPa, T = 300 K) is about 23 and 18 atoms, respectively. The energy required to elongate 1 nm of dislocation is also reduced by 10 eV and 8 eV for the edge and screw dislocations, respectively. Here, considering the repulsive force between hydrogen atoms, we removed the weaker trap site when the distance between two trap sites are closer than 0.19 nm. The hydrogen interaction with screw dislocation is often assumed very small compare to that with edge dislocation because of the absence of hydrostatic stress component. However, our

analyses clearly showed that hydrogen has the equivalent strength of interaction with edge and screw dislocations.

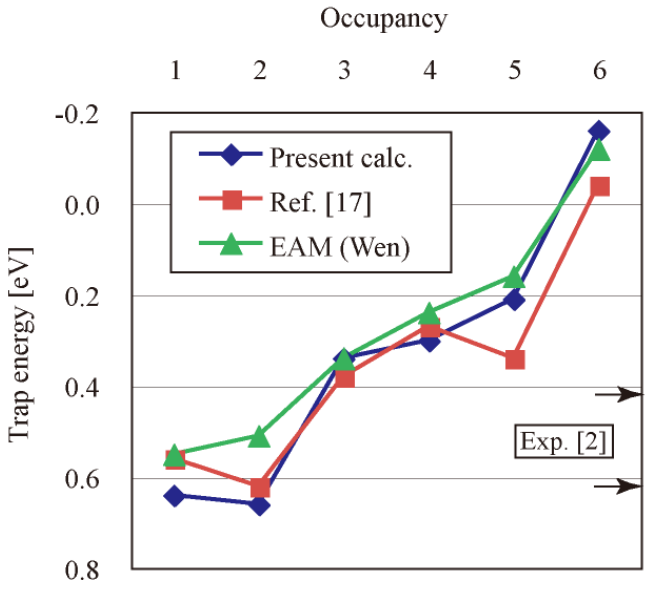

Fig. 1 Hydrogen trap energy around vacancy, estimated by DFT and molecular statics simulations.

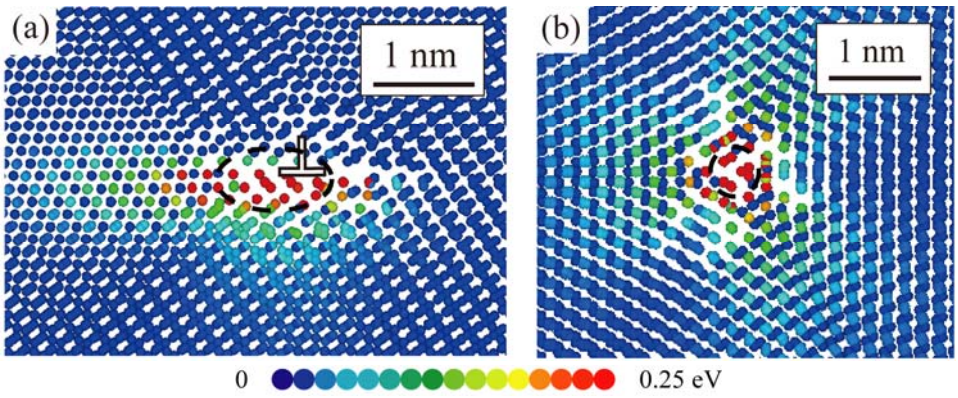

Fig. 2 Distribution of hydrogen trap energy around dislocations in bcc Fe: (a) and (b) show the distribution around {112}<111> edge and {112}<111> screw dislocations, respectively.

3.3 Interaction with grain boundaries

Figure 3 shows the relationship between the grain boundary property and number of trapped hydrogen estimated by molecular statics simulations. The estimated maximum hydrogen trap energy was about 0.55 ~ 0.6 eV for grain boundaries with large free volume, and 0.45 ~ 0.5 eV for those with small free volume. We

can confirm strong correlation among the grain boundary energy, grain boundary free volume and the number of trapped hydrogen.

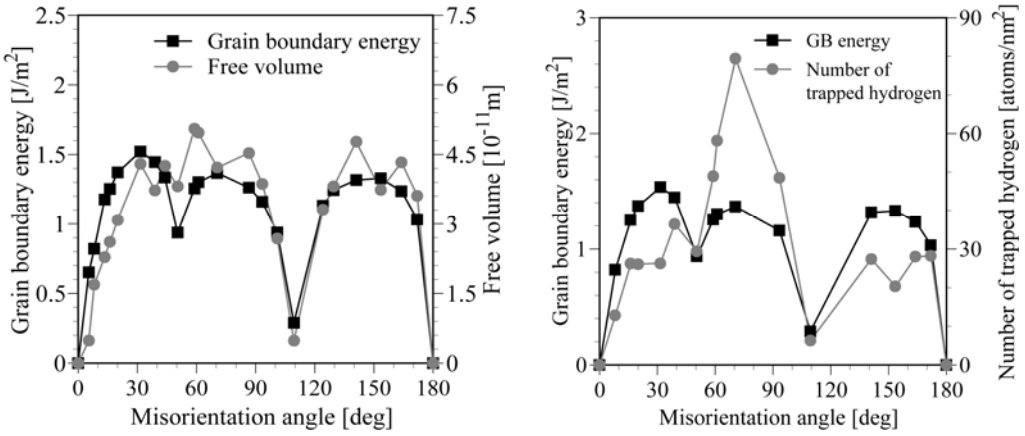

Fig. 3 Influence of misorientation angle of <110> symmetrical tilt grain boundary on the free volume (a) and number of trapped hydrogen (b).

4. Conclusion

In this paper, we estimated the hydrogen trap energies of various lattice defects in bcc-Fe using the first principles calculations and molecular statics simulations. It is demonstrated that the energy of vacancy and dislocations are significantly reduced by hydrogen. We also indicated that edge and screw dislocations have the equivalent strength of interaction with hydrogen. Finally, we showed that high energy grain boundaries trap many hydrogen atoms compare to low energy grain boundaries.

Acknowledgements

This research has been conducted as a part of ‘‘Fundamental Research Project on Advanced Hydrogen Science’’ funded by New Energy and Industrial Technology Development Organization (NEDO).

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