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Hydrogen-related phenomena due to decreases in lattice defect energies—Molecular dynamics simulations using the embedded atom method potential with pseudo-hydrogen effects

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ABSTRACT

Solute hydrogen atoms and lattice defects are known to have strong interactions that significantly weaken the strength of a material. Although molecular dynamics (MD) simulations can treat complicated interactions among various lattice defects, their timescales are insufficient for the treatment of hydrogen diffusion over long distances or cooperative motion of hydrogen atoms and lattice defects at room temperature. Here, we used an interatomic potential for body-centered-cubic iron (bcc Fe) including pseudo-hydrogen effects on the lattice defect energies to perform three kinds of MD simulations: crack growth, nanoindentation, and tensile loading of a polycrystalline nanorod. The simulations show that well-known hydrogen-related phenomena can occur depending on the boundary conditions and the initial conditions of the materials. Our analyses indicate that decreasing the lattice defect energies leads to typical deformation and fracture behaviors in a gaseous hydrogen environment and that these so-called defactant effects of hydrogen play a significant role in hydrogen embrittlement.

1. Introduction

It is well-known that solute hydrogen atoms in a metal weaken its strength. This phenomenon, called hydrogen embrittlement, makes it unsafe to use hydrogen in various applications. For example, much attention has been paid to hydrogen as a clean energy source to solve environmental problems, but an increase in hydrogen use would result in an increase in failure accidents related to hydrogen embrittlement. Although hydrogen embrittlement has long been known to occur, the overall embrittlement process has not yet been clarified because hydrogen atoms exist in extremely low concentrations in metals, have high diffusivity, and are difficult to measure directly on account of their atomic size. The elementary steps of the hydrogen embrittlement phenomenon are believed to involve changes in the stability and/or mobility of lattice defects due to the presence of hydrogen. In this regard, three typical mechanisms have been proposed. First, hydrogen could enhance the mobility of dislocations and induce localized ductile fracture (hydrogen-enhanced localized plasticity, or HELP) [1–3]. Second, hydrogen could enhance the formation and accumulation of vacancies through interactions between hydrogen atoms and vacancies during plastic deformation, thus promoting void formation and ductile crack growth (hydrogen-enhanced strain-induced vacancy model, or HESIV) [4,5]. Third, hydrogen accumulation in the grain boundaries (GBs), around inclusions, or at the crack tips could lead to decohesion [6–8]. As another, more general mechanism, Kirchheim referred to the elements that decrease lattice defect energies as “defactants” [9] and suggested that hydrogen has strong defactant-like effects on various lattice defects [10].

Atomistic simulations are considered to be effective for analyzing hydrogen embrittlement mechanisms. In previous research, we have analyzed the effects of hydrogen on each individual lattice defect by use of the nudged elastic band (NEB) method [11], and atomistic simulations and have shown that the aforementioned effects of hydrogen on the lattice defects (i.e., modification of the dislocation

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mobility, vacancy stabilization, and reduction of GB cohesive energy) are likely to occur within the bcc-Fe lattice [12–16].

The complicated interactions among many lattice defects and the influence of hydrogen atoms on them are also considered important factors in hydrogen embrittlement phenomena. Molecular dynamics (MD) simulations can treat complicated interactions among various lattice defects, and thus MD has been often used to study hydrogen embrittlement [17–21]. However, the effects of hydrogen mostly become large for small deformation speeds, because at low deformation rates, the hydrogen distribution can follow the stress distribution and respond to defect nucleation and motion [22–24]. Thus, the timescales of direct MD simulations are insufficient for the treatment of these phenomena, since hydrogen diffusion over long distances and cooperative motion of hydrogen atoms and lattice defects at room temperature are slow processes. For this reason, most studies have employed artificial initial hydrogen distributions and/or impractically high hydrogen concentrations. Hydrogen diffusion in materials is definitely very fast compared to the diffusion of other elements, and it is well known that the hydrogen distribution follows the motion of lattice defects and the stress distribution during deformation. Nevertheless, the diffusion is still too slow to treat by direct MD simulation.

If the speed at which the hydrogen distribution can change is not sufficient relative to the dislocation velocity, hydrogen atoms exhibit only pinning effects or drag forces on the dislocation instead of enhancing its mobility [12]. Recently, Song and Curtin performed MD simulations of tens of nanoseconds of the dragging of hydrogen by edge dislocations and concluded that hydrogen impedes the dislocation motion [25]. However, this result may have been influenced by the high shear stress and the high hydrogen concentration [26]. It should also be noted that the hydrogen diffusion becomes slower around dislocation cores [12,27,28]. Song and Curtin also performed an MD study of crack growth using an effective approach in which the loading and redistribution of hydrogen atoms are repeated after the hydrogen introduction. This technique simulates the arrival of hydrogen atoms from the far-field into the region near the crack tip [29]. However, the interactions between lattice defects and hydrogen through cooperative motion were considered to be weak in this study, because even though hydrogen was allowed to redistribute for several nanoseconds, the average strain rate was still within the typical range for MD simulations. Iterative MD and Monte Carlo (MC) schemes are also powerful methods for accessing longer timescales, but the problems that can be treated using this method are restricted because of the limitations of the MC method [30].

Here, we employ another approach by performing MD simulations using an interatomic potential with pseudo-hydrogen effects for bcc Fe [31]. The interatomic potential incorporates the thermodynamic effects of hydrogen on the lattice defect energies, and thus a calculation of the hydrogen motion is not required. We recognize that the kinetics of hydrogen and time-dependent phenomena related to hydrogen diffusion are important in some cases [12,22–25,29,32,33], but in this study, as a limiting case, we focus on the hydrogen-related phenomena appearing under the equilibrium hydrogen distribution. We perform MD simulations of crack propagation, nanoindentation, and tensile loading of a polycrystalline nanorod and discuss the effects of hydrogen on the deformation and fracture behaviors under three kinds of boundary conditions.

2. Interatomic potential for bcc-Fe with pseudo-hydrogen effects

In this section, we describe the interatomic potential employed for the MD simulations. Details of the first-principles calculations of hydrogen-lattice-defect interactions were reported by Seki et al. [31]. Here, we describe the fitting properties selected to develop the potential in Section 2.1; the conditions for the first-principles calculation in Section 2.2; the calculated lattice defect energies and hydrogen-trapping energies for vacancies, free surfaces, and stacking faults in Section 2.3; the apparent lattice defect energies in gaseous hydrogen environments in Section 2.4; and the fitting procedure and results in Section 2.5.

2.1. Fitting properties

As the fundamental material properties, we adopted the cohesive energies of diamond, simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp) structures; the lattice constants of the bcc and fcc structures; and the elastic constants of the bcc structure. We corrected the target values of the above properties from first-principles calculations [34,35] and experiment [36]. As the lattice defect energies, we adopted the vacancy formation energy; surface energies for the {1 0 0}, {1 1 0}, and {1 1 2} surfaces; and stacking fault energies for the {1 1 0}⟨1 1 1⟩ and {1 1 2}⟨1 1 1⟩ slip systems. Although there is much research on various lattice defect energies and interaction energies between the lattice defects and hydrogen atoms in the bcc Fe lattice, these values vary in the literature. Thus, we reevaluated these values by improving the precision of the calculation.

2.2. Analysis conditions

We used the Vienna ab initio simulation package (VASP) [37–39] to perform density functional theory (DFT) calculations within the spin-polarized generalized gradient approximation (GGA) [40] for electron exchange and correlation. The interactions between the ions and electrons were described by Blöchl's projector-augmented wave (PAW) method [41], which has an accuracy corresponding to the all-electron method within the frozen-core approximation. The Monkhorst–Pack scheme [42] was used for defining the k-points, and the conjugate-gradient method was employed for the relaxation algorithm. A supercell (three-dimensional periodic boundary conditions) was applied to all of the first-principles calculations as part of the calculation method.

A cut-off energy of 425 eV and a smearing width of 0.2 eV were employed. The number of k-points was determined to be $(30 \times L_0/L_x) \times (30 \times L_0/L_y) \times (30 \times L_0/L_z)$, where L_x, L_y, and L_z are the lengths of the supercell in the x, y, and z directions, respectively, and L_0 (0.2832 nm) is the lattice constant of a conventional bcc-Fe lattice containing two atoms. We used $\Phi_0 = -16.416$ eV as the ground-state energy of the unit lattice of bcc Fe, where the ground-state energy is defined as the absolute total energy relative to the total energy of free ions and electrons separated infinitely.

We calculated the zero-point energy (ZPE) of the hydrogen atom and added it to the ground-state energy of the system. We constructed a Hessian matrix by minutely displacing (0.01 nm) the hydrogen atom in the x, y, or z direction and estimated ZPE by summing the vibrational energies of the normal modes of the hydrogen atom.

2.3. Lattice defect energies and hydrogen-trapping energies

2.3.1. Vacancy

Our simulation model was constructed from $N = 15$ Fe atoms by subtracting an atom from the $2 \times 2 \times 2$ bcc structure. The vacancy formation energy was evaluated as the difference in ground-state energy between the vacancy model and the bcc structure constructed from the same number of atoms ($=\Phi_0/2 \times N$). During the first-principles calculation, both the atom positions and the supercell size were relaxed. We obtained 2.14 eV as the vacancy