First-principles Calculation on the Diffusion of Hydrogen along a Screw Dislocation Core in BCC Iron

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The new boundary condition for a single screw dislocation core in BCC iron has been devised to calculate the diffusion of hydrogen using the first principles calculation. It is found that the core structure of a screw dislocation changes drastically by extension due to the presence of high density hydrogen atoms in the core region. Also, we searched the diffusion path of a hydrogen atom from the surrounding trapping lattice site to the core of a screw dislocation, and found that there is the large energy barrier of 0.25eV. We conclude that the diffusion of hydrogen atoms along the core of a screw dislocation is very unlikely to occur in BCC iron.

Keywords: first-principles calculation, screw dislocation, BCC iron, hydrogen atom, diffusion.

1. INTRODUCTION

Hydrogen in metals is known to cause a significant change in mechanical properties of solids, in particular for example, embrittlement [1]. Hydrogen in pure iron materials diffuses easily between neighboring lattice t-sites [2]. The presence of dislocations influences significantly the behavior of hydrogen in metals, because dislocations are the strong trapping sites for hydrogen atoms [3]. It is also believed that diffusion of hydrogen is increased through the core region of dislocations. The understanding of the mechanism of hydrogen embrittlement in metals, which is still elusive at present, depends crucially on the resolution of these processes. However, it is generally difficult to predict experimentally and numerically the interaction of hydrogen atoms with defects in metals, let alone the core structures of a dislocation, in particular, for BCC iron [3, 4, 5]. The difficulty arises from the inadequacy of the dependable empirical potential [6] for use in molecular dynamics simulations, where dynamics of more than a million atoms can be tracked. The first principles calculation based on the density functional theory is the most reliable method for predicting the total energy of the system consisting of a mixture of different atoms. This method is particularly required for the accurate calculation of iron materials and the core region of a dislocation where the arrangement of atoms is largely disordered. However, this method is restricted to clarify the static properties for the system of less than nearly one hundred atoms. Therefore, for the problem of the interaction of a dislocation core with a hydrogen atom, a lot of effort should be put into the improvement of the boundary condition.

In this paper, we apply the first principles method to the diffusion of hydrogen along the core of a screw dislocation in iron. We also employed the molecular dynamics method with the newly developed Fe-H empirical EAM (embedded atom model) potential [6] to predict the general behavior of the system and to evaluate the differences from the first principles results. A new boundary condition for a single dislocation core has been developed to incorporate at least two unit layers of atoms along the dislocation core for the diffusion of hydrogen. Also, we searched the possible diffusion path from the nearby lattice site into the core and estimated the energy barrier of that path.

2. COMPUTATIONAL METHOD

We have employed the VASP (Vienna *ab-initio* simulation package) code with Projector Augmented Wave (PAW) method [7-9] for the electronic structure calculations and the atomic structure relaxations by force minimizations. The generalized gradient approximation by Perdew, Burke, and Ernzerhof (PBE) is used [10]. All calculations are performed in spin-polarized state. The cutoff energy for the plane wave basis set is 280 eV for Fe systems. The Monkhorst Pack k-point mesh is 1x1x8 for the unit cell as shown in Fig. 1 (b). The Methfessel-Paxton

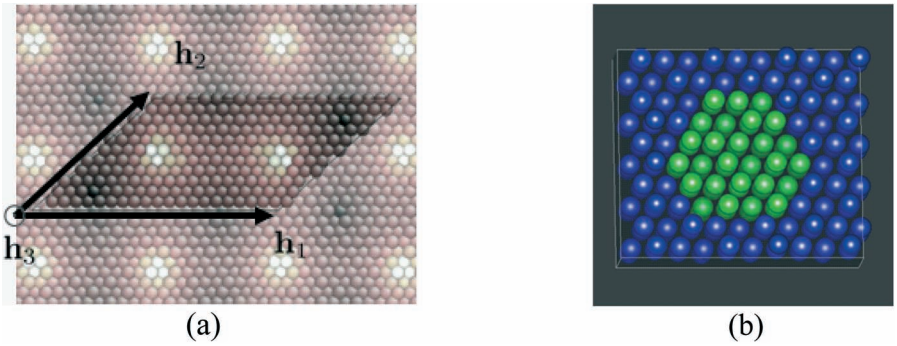

Fig. 1 A system for calculating the core of a screw dislocation.
(a) The previous system containing a pair of dislocations with one unit layer of atoms.
(b) The present system containing a single dislocation with two unit layers of atoms.

smearing method with 0.1-eV width is used.

The calculation system is changed from the previous dislocation-dipole arrangement [3,4,5] (Fig. 1(a)) to the single-dislocation arrangement (Fig. 1(b)), for the prediction of diffusion of hydrogen along the dislocation. The previous 231-atom system contains a pair of screw dislocations with the periodic boundary condition and the one unit layer of atoms along the dislocation core. On the other hand, the present 200-atom system contains only one screw dislocation with the surrounding atoms displaced and fixed according to the displacement solution of the elasticity equation for a single screw dislocation. This system contains the two unit layers of the BCC iron crystal along the dislocation core. Although the previous system has the advantage of canceling the strain field of a dislocation at the boundary, the single dislocation arrangement is employed to enlarge the system along the dislocation with nearly the same number of atoms. The results of the atomic structure relaxation reveal that the atoms on the outer edge are exerted by the artificial forces induced by the mismatch of atomic configurations at the boundaries. However, these artificial forces are shown to decrease on the next line of atoms down to 0.1eV/Å, so that the boundary effects on the core region are small even with the present size of the system.

3. RESULTS AND DISCUSSION

The effect of the new boundary condition is checked by relaxing the system with a single screw dislocation without

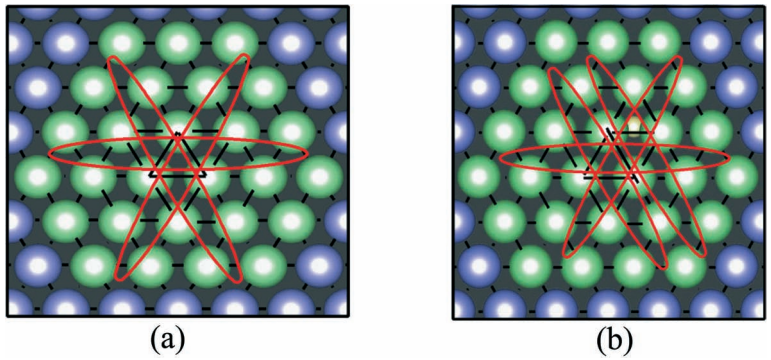

Fig. 2 The relaxed core structure of a screw dislocation without (a) and with one hydrogen atom (b).

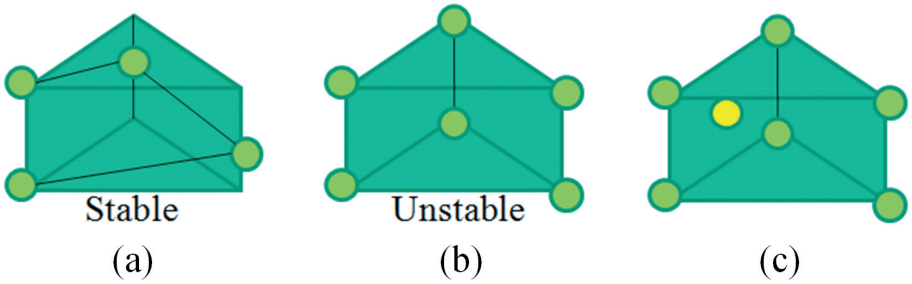

Fig. 3 Atomic configurations of one unit layer for the core region of a screw dislocation.
(a) Stable core structure for a perfect screw dislocation.
(b) Unstable structure corresponding to the structure (a).
(c) The unstable structure is realized when one hydrogen atom is present in the core.

hydrogen. The result shows that the core structure is a symmetric non-degenerate 6-fold structure which is similar to the one obtained in the previous dislocation-dipole arrangement [5]. Next, one hydrogen atom is placed in the core region. It is shown in Fig. 2(b) that the core of a screw dislocation is extended due to the presence of one hydrogen in the system. The atomic configuration of the core of a screw dislocation is shown in Fig. 3(a). The atoms are spirally displaced with one-third of the unit length along the vertical dislocation line. When the hydrogen atom is placed in the core region, the unstable configuration (Fig. 3(b)) is shown to be realized corresponding to the extended structure of Fig. 2(b). This structure is realized because a hydrogen atom prefers an extended space compensating for the high energy unstable iron configuration. It should be emphasized that this result corresponds to the high hydrogen density limit due to the periodic boundary condition in the direction of the dislocation line. Molecular dynamics method is employed to estimate the number of unit layers along the dislocation line, which is required for one hydrogen atom to be isolated. With the system consisting of more than ten unit layers of atoms along the dislocation line, it is found that the dislocation is not extended or the extension is localized to form a kink near the hydrogen atom. The first principles calculation for this system size is intractable at present. However, using the system consisting of the two unit layers, we found in Fig. 4 that, if we fix the z-displacements of three core atoms on the upper and lower boundary surface, the extension of the dislocation core can be prevented to realize the low density limit of hydrogen. The binding energy of hydrogen in the core region is evaluated using the first principles (DFT) calculation and the molecular dynamics method (EAM) as a function of the number of hydrogen atoms per unit layer (Fig. 5). It is seen that the molecular dynamics results overestimate the binding energy systematically compared with the first principles results. However, the trends are found to be very similar. Finally, a diffusion path of one hydrogen atom from the surrounding trapping lattice site into the core of a screw dislocation is searched firstly by the molecular dynamics method (Fig. 6). When the diffusion path is found, the first principles method is employed to evaluate quantitatively the energy barrier along this path. As shown in Fig. 6, it is found that there is a large energy barrier of 0.25eV from the trapping lattice site into the core of a screw dislocation. Once a hydrogen atom is in the core, the energy barrier along the dislocation core is approximately 0.04eV. However, this in-core state is found to be unstable and the temperature of 50K is sufficient for a hydrogen atom to be easily emitted back to the lattice site. Therefore, it is concluded that the diffusion inside the core region of a screw dislocation in BCC iron is unlikely to occur.

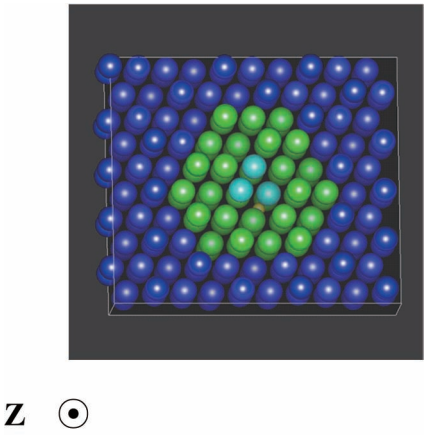

Fig. 4 The boundary condition to realize the low hydrogen density limit by preventing the extension of the core. (The dislocation line is in the z-direction.)

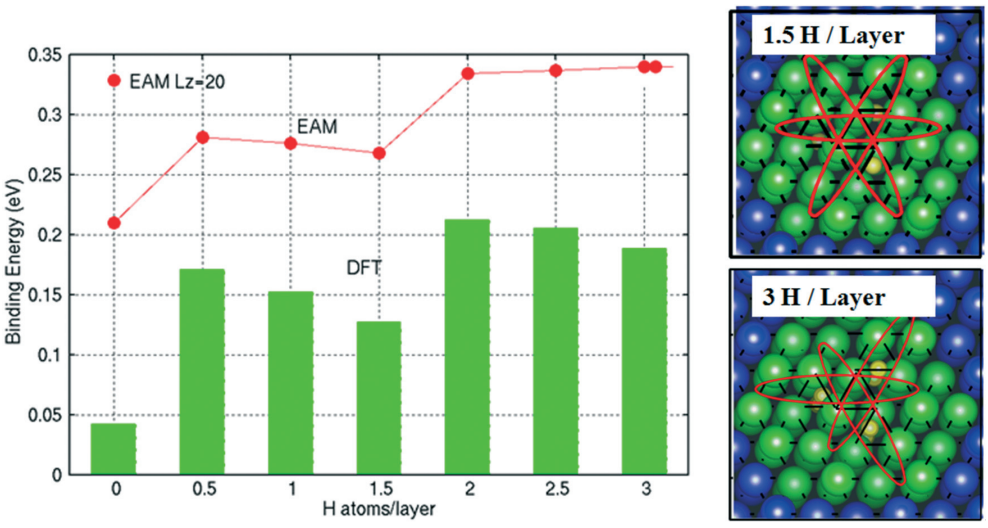

Fig. 5 The binding energy of hydrogen as a function of the number of hydrogen atoms per unit layer.

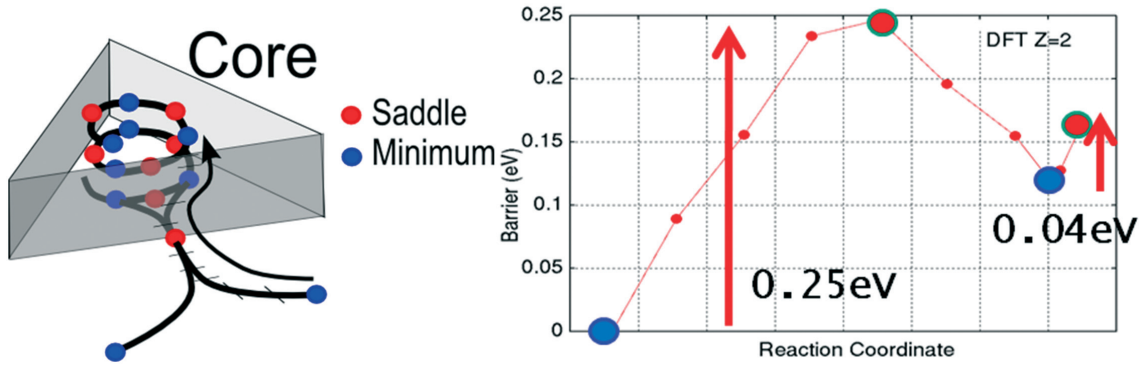

Fig. 6 A diffusion path and its energy landscape from the trapping lattice site to the core of a screw dislocation.

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第一原理計算による BCC 鉄中らせん転位芯への水素拡散経路

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第一原理計算により BCC 鉄中の一本のらせん転位芯への水素の拡散経路を調べるために新しい境界条件を提案した。この境界条件を用いて転位芯に水素を一個入れると転位芯は大きく変化して拡張することが分かった。更に転位周囲の水素の捕獲格子サイトから転位芯への拡散経路を見出し、この経路には 0.25eV の大きなエネルギー障壁があることが明らかになった。この結果 BCC 鉄中の転位芯に沿った水素の拡散は起こりにくいことが明らかになった。

キーワード: 第一原理計算, らせん転位, BCC 鉄, 水素原子, 拡散経路