

First-principles Calculation on Binding Energy of an Interstitial Hydrogen Atom around a Screw Dislocation in BCC Iron

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The binding energy of an interstitial hydrogen atom at various lattice sites around the $a_0/2[111]$ screw dislocation core in BCC iron has been determined using the first-principles calculation. The calculation was based on the core structure of a screw dislocation with symmetric displacement field, which was obtained using the large-scale supercell containing 231 atoms and $1 \times 1 \times 4$ k-point samplings. The binding or trapping energy of a hydrogen atom at both the t-site (tetrahedral site) and o-site (octahedral site) near a core is found to be approximately 0.2 eV.

Keywords: first-principles calculation, screw dislocation, BCC iron, hydrogen atom, binding energy

1. INTRODUCTION

The presence of hydrogen atoms at interstitial sites causes a significant change in mechanical properties of solids. In particular, hydrogen atoms in metals enhance plasticity, and, when a microcrack exists in steels, result finally in cleavage or grain boundary fracture depending on the concentration of hydrogen atoms. The mechanism of this embrittlement due to hydrogen is not precisely known and is of much concern to the development of, for example, materials for hydrogen containment, high-tensile structural materials, and fusion and fission nuclear materials.

Electronic and atomistic bonding states of materials containing hydrogen atoms are required to understand fundamental cause of hydrogen embrittlement, in particular, for BCC materials, such as steels, which are important for most of the structural materials. However, because of the presence of magnetism, even a pure single α -iron crystal in BCC structure is hard to understand from the standpoint of modeling and numerical simulation. The process that hydrogen atoms in metals finally lead to fracture is complex, and, from the microscopic point of view, two issues on the change of bonding states must be clarified using the first principles calculation. One is a change in the bonding strength of the grain boundary due to hydrogen segregation, and the other is the binding or trapping energy of hydrogen atoms to a dislocation and its effect on the motion of a dislocation. The latter

issue, in particular, requires a large-scale simulation because a dislocation has a long-range strain field and magnetism must be taken into account in iron. Here the binding energy of a hydrogen atom to a screw dislocation core in BCC iron is evaluated using the first principles calculation.

Before studying the interaction of a hydrogen atom and a dislocation, it is first necessary to understand behavior of a screw dislocation, in particular, the dislocation core structure and Peierls stress, which is considered to control the low temperature plasticity of BCC metals. Numerous first-principles and empirical atomistic simulation studies have been carried out so far to determine the accurate core properties, however, the results of the core structure and Peierls stress differ depending on the simulation methods. Essentially, two core structures have been proposed for a screw dislocation in BCC molybdenum by various computational approaches [1][2][3][4][5]; the threefold structure (Fig. 1(a)) is obtained using the empirical potential, while the symmetric structure (Fig. 1(b)) is obtained by the tight-binding and the density functional theory (DFT) methods. Although the DFT method gives the most accurate energy among these methods, the sizes of its supercells are severely limited, and the effects of core overlapping and image stress can be significant. Woodward and Rao [2] proposed a boundary condition for the supercell containing one screw dislocation, in which atomic displacements due to a screw

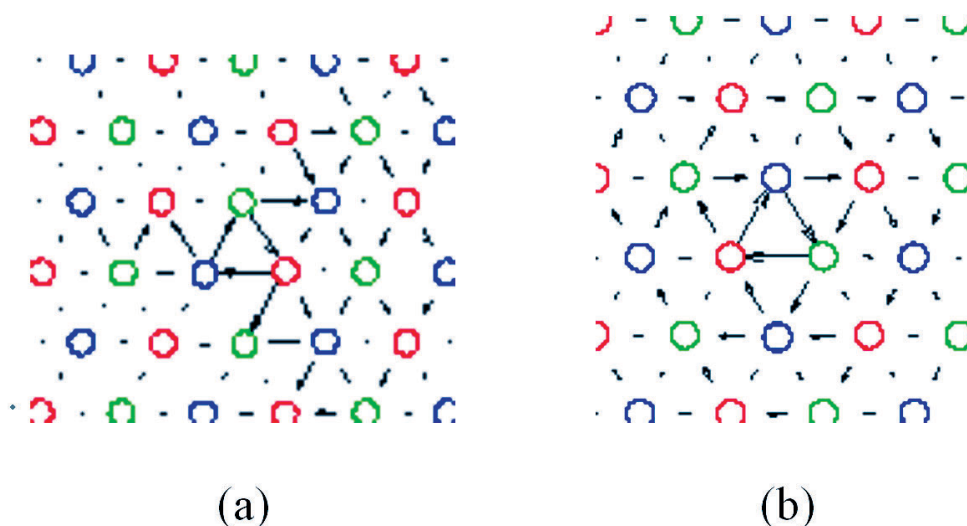


Fig. 1 Differential displacement map of (a) threefold degenerate core structure and (b) symmetric non-degenerate core structure for a screw dislocation in BCC iron.

dislocation in the cell are allotted by the Green function method. Li *et al.* [4] introduced a pair of screw dislocations in the supercell and proposed a shape of the supercell in such a way as to cancel the strains among supercells. They evaluated the accuracy of the core energy by changing the size of the supercell, and concluded that the supercell containing 231 atoms is good enough. We performed the most accurate DFT calculations using the supercell of this size by confirming the convergence on the number of k-point samplings, and concluded that the core of the $a_0/2[111]$ screw dislocation in BCC molybdenum has a symmetric non-degenerate structure [6].

The core structure of a screw dislocation for BCC iron is predicted by starting with the threefold degenerate structure and relaxing the structure. The result is found to be a symmetric non-degenerate structure with no preferential spreading along the $(-1-12)$ directions [10], as shown in Fig. 1(b), which is in agreement with the results of the previous calculations using equal to or less than 100 atoms [3][8]. It is probable that a symmetric non-degenerate core structure is obtained for a screw dislocation in BCC iron using the first principles calculations, however, the convergence of the k-point samplings must be critically checked for a final determination. Moreover, the Peierls stress for BCC iron is evaluated to be $\tau_p \approx 1.1\text{GPa}$ by applying the shear stress to the system [10]. This result is the first direct determination of the Peierls stress of a screw dislocation in BCC iron.

In this paper, we report the accurate determination of the binding energy of a hydrogen atom to a screw dislocation core in BCC iron. The calculation is based on the core structure for a screw dislocation in BCC iron using the supercell containing 231 atoms with $1 \times 1 \times 4$ k-sampling points.

2. COMPUTATIONAL METHOD

We have employed the VASP (Vienna *ab-initio* simulation package) code [9], which implements the density functional theory with the ultrasoft pseudopotential and the generalized gradient approximation (GGA) for the exchange correlation energy, for calculating accurately the total energy of the system. In order to exploit the vector processors on the ES system, we have tuned the code by using the one-dimensional FFT routine in the numerical library ASL/ES. For the problem with the supercell containing 231 atoms, the VASP code achieved 66.4% of the peak performance on the ES.

Using the configuration of the symmetric non-degenerate core structure obtained by the previous work as an initial condition, we place one hydrogen atom at the o-site or t-site near the core of a screw dislocation and the whole system is relaxed to a minimum energy state by the conjugate gradient or the quasi Newton algorithm. Using the supercell consisting of 231 atoms with various k-point samplings, this procedure requires considerable amounts of calculation time, which invalidates the original implementation of parallel coding on the VASP code. To overcome this situation, we have re-parallelized the code in terms of k-point samplings. The result shows that the parallel code achieves almost linear speedup. Analyzing the detailed profile data of the code, we found that the k-point parallelization has almost no influence on the average vector length. We have obtained the average vector length of 229.3 with 8 processors (1 node) and 229.1 with 80 processors (10 nodes), and the vectorization ratio of 99.3% and 99.1%, respectively. In the case of iron, spin polarization must be taken into consideration, and the convergence of the iterative electronic structure calculation is found to be degraded compared to the molybdenum case. The number of iterations for the iron case requires approximately five times more than that for the molybdenum

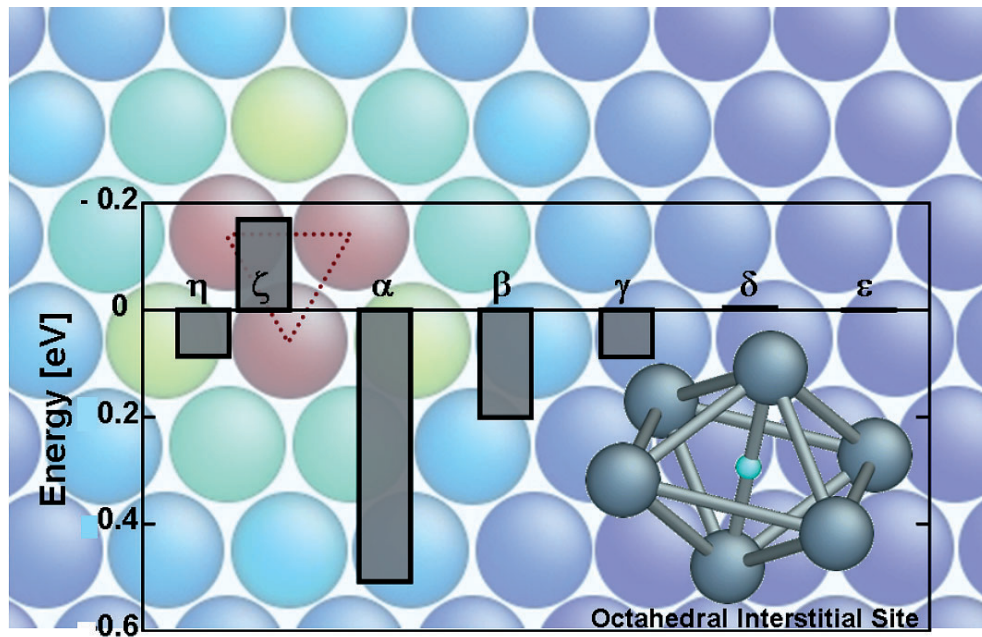


Fig. 2 The binding energy of a hydrogen atom at the different octahedral interstitial sites from a screw dislocation core. The binding energy is obtained without the relaxation procedure.

case. Therefore, the numerical condition for the supercell containing 231 iron atoms with the $1 \times 1 \times 4$ k-point samplings is adopted as a first trial numerical simulation.

3. RESULTS AND DISCUSSION

The binding energy of a hydrogen atom at the different interstitial sites from a screw dislocation core is evaluated based on the symmetric displacement field in BCC iron, which was obtained using the large-scale supercell containing 231 atoms and $1 \times 1 \times 4$ k-point samplings. Figure 2 shows the results of the binding energy of a hydrogen atom placed at different octahedral sites (o-sites) from a screw dislocation core. The binding energy of a hydrogen atom is derived by taking the difference from the energy in the bulk. In this case, the total energy is calculated by just placing a hydrogen atom without relaxing the whole system. The result shows that a large binding energy of approximately 0.6eV is obtained at the α site and decreases greatly at the fourth or fifth o-sites from the core. The effect of the relaxation procedure on the binding energy is checked by relaxing the whole system. It is found that the effect of the relaxation process is significant, and the values at the α and β o-sites reduce to those between 0.2 and 0.25eV, as shown in Fig. 3. Comparing with other binding energy data, such as a grain boundary, these data are considered to be reasonable. Along with the o-sites, the binding energy of a hydrogen atom at the interstitial tetrahedral sites (t-sites) is calculated by following the same procedure. We select two t-sites, Tb1 and Tb2, near the dislocation core, as shown in Fig. 4. It is shown in Fig. 4 that the values of t-sites are almost the same with those at o-sites. It is found that the binding energy of a

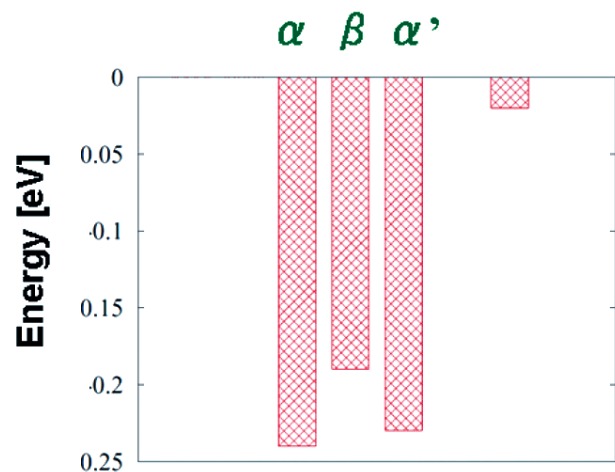


Fig. 3 The binding energy of a hydrogen atom at the octahedral sites near a screw dislocation core. The result is obtained by relaxing the system.

hydrogen atom to a screw dislocation is reasonably high, even though a screw dislocation does not have a hydrostatic stress field around the core.

A further study for the effect of hydrogen atoms on the motion of a screw dislocation is required to determine the plastic behavior of BCC iron containing hydrogen.

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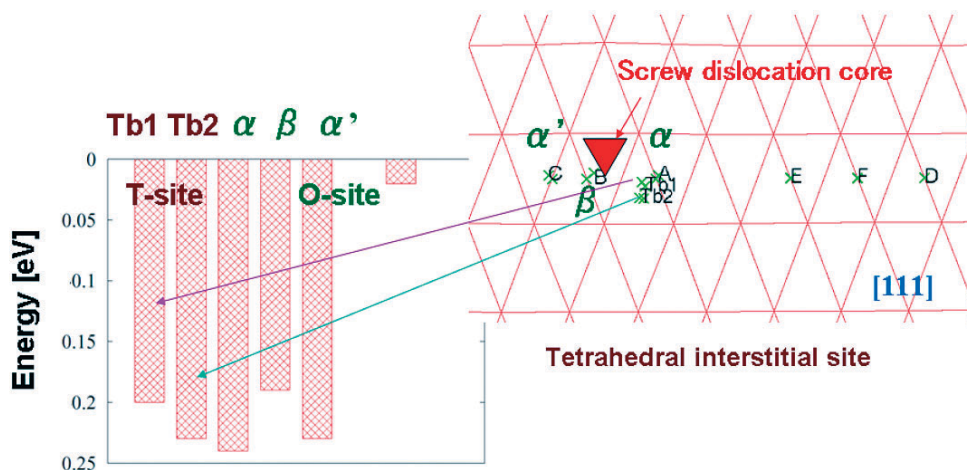


Fig. 4 The binding energy of a hydrogen atom at the tetrahedral site near a screw dislocation core. The result is obtained by relaxing the system.

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第一原理計算によるBCC鉄中らせん転位と格子間水素原子の結合エネルギーの計算

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BCC鉄中の $a_0/2[111]$ のらせん転位周辺の色々な格子間原子サイトにおける水素原子の結合エネルギーを第一原理計算により求めた。本結合エネルギーの計算は、231個の原子からなる大規模なスーパーセルと $1 \times 1 \times 4$ のk点サンプリングにより得られた対称的な変位場を持つらせん転位芯構造の結果を用いて行った。転位芯近傍のt-サイト(四面体格子間サイト)及びo-サイト(八面体格子間サイト)両方において、水素原子の結合(トラップ)エネルギーは約0.2eVであった。

キーワード：第一原理計算, らせん転位, BCC鉄, 水素原子, 結合エネルギー