



Atomistic simulation of hydrogen dynamics near dislocations in vanadium hydrides



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ABSTRACT

Kinetics of interstitial hydrogen atoms near dislocation cores were analyzed by atomistic simulation. Classical molecular dynamics method was applied to model structures of edge and screw dislocations in α -phase vanadium hydride. Simulation showed that hydrogen atoms aggregate near dislocation cores. The spatial distribution of hydrogen has a planar shape at edge dislocation due to dislocation partialization, and a cylindrical shape at screw dislocation. Simulated self-diffusion coefficients of hydrogen atoms in dislocation models were a half- to one-order lower than that of dislocation-free model. Arrhenius plot of self-diffusivity showed slightly different activation energies for edge and screw dislocations. Directional dependency of hydrogen diffusion near dislocation showed high and low diffusivity along edge and screw dislocation lines, respectively, hence so called 'pipe diffusion' possibly occur at edge dislocation but does not at screw dislocation.

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1. Introduction

Lattice defects are known to play important roles on materials property of metals. They are inevitably generated during hydrogen adsorption and desorption processes, and possibly affect hydrogen storage property. Hydrogen atoms firstly adsorb on metallic surface (planar defect) and migrate via subsurface layer into bulk region by accompanying dislocation (line defect) or point defects at the phase boundary. Some of these defects works as a hydrogen trap and possibly affect hydrogen diffusivity. Dynamical feature of hydrogen atoms in lattice defects is one of the important issues to understand hydrogen storage processes. Relation between lattice defects and hydrogen storage property has been extensively studied. Pundt and Kirchheim [1] reviewed such studies and showed that hydrogen solubility and other properties of thin films or nanoparticles are strongly affected by lattice defects. However, effects of lattice defects, especially dislocation, in bulk region to hydrogen storage property are not fully understood yet.

Relation between hydrogen and dislocation has also been studied in aspect of hydrogen embrittlement. It is known that segregation of hydrogen atoms at defects causes degradation of structural materials. One of the interesting topics in this field is so called 'pipe diffusion' [2,3] which denotes high diffusivity of atoms along dislocation line. Experimental data of hydrogen diffusivity, however, exhibit large scattering due to incompleteness of the samples such

as surface [4]. Hence it is difficult to clarify the pure effect of dislocation among several types of lattice defects.

Atomistic simulation is useful to understand the individual effect of each defect structure. In the previous study [5], the present author simulated point, line, and planar defects in vanadium hydride by using density functional theory and classical molecular dynamics (MD). Kim et al. [6] recently observed the structure variation of vanadium hydride during hydrogen sorption cycles by X-ray total scattering. They suggested by comparing the observed and simulated values that damping of pair correlation in middle and long ranges after repeated hydrogen sorption could be explained by dislocation pileup. In the present study, effect of dislocation on static and dynamic features of hydrogen in α -vanadium hydride was analyzed by classical MD simulation.

2. Modeling and simulation of dislocation

The most fundamental property of dislocation geometry is the Burgers vector \mathbf{b} . Depending on the angle between \mathbf{b} and dislocation line vector \mathbf{d} , dislocation is classified into three types: edge (\mathbf{b} is perpendicular to \mathbf{d}), screw (\mathbf{b} is parallel to \mathbf{d}), and mix (others). All types of dislocation can be modeled within a rectangular MD cell with three-dimensional periodic boundary conditions by introducing pairs of positive and negative dislocations having the Burgers vectors $+\mathbf{b}$ and $-\mathbf{b}$, respectively. Java applet *DLstudio* [7] was designed to construct such periodic models for arbitrary dislocation in arbitrary crystal. In this study, we deal with two representative dislocations of b.c.c. metal: edge dislocation with $\mathbf{d}||$

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$[\bar{2}11]$ and $\mathbf{b} = [111]\mathbf{a}/2$ on the slip plane $(01\bar{1})$, and screw dislocation with $\mathbf{d}/\mathbf{b} = [111]\mathbf{a}/2$. Detailed settings of the models are given in Table 1. In both models, dislocation line extends toward z infinitely and the dislocation cores initially locate on a rectangular grid on xy plane with about 3 nm spacing. Assumed dislocation density in these models is about $10^5 \mu\text{m}^{-2}$. Number of dislocation cores and their arrangement in periodic cell are different between edge and screw models. The edge dislocation model has two cores in a periodic cell, and their replica images of the same sign align toward y direction. This arrangement corresponds to dislocation array on very small angle, tilt grain boundary. In the case of screw dislocation model, two positive and two negative cores locate alternatively on a rectangular grid in periodic cell. This arrangement is equivalent to the periodic, two core model with slant y -axis which is frequently used for screw dislocation calculation [8].

Cell thickness toward z -axis is related to the degree of static and kinetic freedom of atoms along dislocation line. A very thin models having very few atomic layers, which is inevitably adopted in first-principles calculation, will lead artificial results on dynamics of hydrogen atoms and dislocation motion by closely neighbored replica images. Thickness of present dislocation models is about 3 nm which is fairly large to reduce the effects from neighboring replica images. A dislocation-free, single crystal model was also calculated for comparison. Appropriate numbers of hydrogen atoms were initially added to the models randomly and homogeneously to the interstitial T-sites. Assumed hydride composition is $\alpha\text{-VH}_{0.0625}$.

Many-body and pairwise potentials were assumed for V–V, V–H and H–H interactions. Pair potential of V–H was calculated by fitting the potential energy surface of H atom at more than 100 interstitial points in b.c.c. vanadium [5] by using the VASP code [9,10], and the other terms were assumed the literature values [11,12]. By these potential functions, experimental data [13–17] of α , β and γ phases of vanadium hydrides were successfully reproduced as shown in Table 2. At the beginning of simulation, all atoms were freely relaxed from the initial configuration. MD simulation was carried out as constant- NPT ensemble at 0.1 MPa for up to 2 ns at each target temperatures from 150 K to 600 K.

3. Results and discussion

3.1. Simulated core structure and hydrogen atom distribution near dislocation

As in real metals, dislocation in MD simulation is movable and possibly causes pair annihilation [5]. In the present models

Table 1

Settings of the edge and screw dislocation models. Vectors \mathbf{a} and \mathbf{b} denote the cubic lattice vector and Burgers vector, respectively, L_x , L_y and L_z are the edge vectors of the periodic cell, and core(+) and core(–) denote the positive and negative dislocation, respectively. Dislocation line vector \mathbf{d} is parallel to L_z in both models.

Property	Unit	Edge	Screw
\mathbf{b}	\mathbf{a}	$1/2 [111]$	$1/2 [111]$
L_x	\mathbf{a}	$12 [111]$	$8 [\bar{2}1\bar{1}]$
L_y	\mathbf{a}	$8 [01\bar{1}]$	$14 [01\bar{1}]$
L_z	\mathbf{a}	$4 [\bar{2}11]$	$6 [111]$
$ L_x $	nm	6.31	5.96
$ L_y $	nm	3.45	6.02
$ L_z $	nm	2.98	3.16
N_V	/cell	4608	8064
N_H	/cell	288	504
N_{core}	/cell	2	4
ρ_{dist}	$10^5 \mu\text{m}^{-2}$	0.92	1.11
$(x, y)_{\text{core}(+)}$	(L_x, L_y)	$(1/4, 1/2)$	$(1/4, 1/4),$ $(3/4, 3/4)$
$(x, y)_{\text{core}(–)}$	(L_x, L_y)	$(3/4, 1/2)$	$(3/4, 1/4),$ $(1/4, 3/4)$

Table 2

Comparison of simulated and experimental value at 300 K on lattice constants a and c , surface tension γ , and hydrogen diffusion coefficient D_H of vanadium and its hydride.

Property	Phase	MD	Exp.
a (nm)	α	.304	.303 [13]
a (nm)	β	.579	.600 [14]
c (nm)	β	.682	.662 [14]
a (nm)	γ	.418	.428 [13]
$\gamma\{100\}$ (J m^{-2})	pure V	3.23	3.18 [15] ^a
$\gamma\{110\}$ (J m^{-2})	pure V	2.55	2.55 [16]
D_H ($10^{-9} \text{m}^2 \text{s}^{-1}$)	α	6.1	6 [17]

^a Calculation.

including small amount of hydrogen, both edge and screw dislocations remained during the simulation. Firstly, core structure of each dislocation type was examined. The relaxed positions of vanadium atoms on the slip plane of edge dislocation show small displacements from the straight line along the Burgers vector as shown in Fig. 1. The trace of dislocated atoms resembles to the extension of edge dislocation suggested by Cohen et al. [18] for b.c.c. metals by combination of three partials as $\mathbf{b} = \{[011] + 2[\bar{2}11] + [01\bar{1}]\}\mathbf{a}/8$. In the case of screw dislocation, on the other hand, two types are known for the candidate core structure for b.c.c. metals as *hard* and *easy* [19]. Simulated core structure in this study was *easy*-type. Formation of *easy*-type core is consistent with experimental [20] and simulation [21] results on b.c.c. transition metals.

During the initial relaxation, hydrogen atoms aggregated in the vicinity of dislocation lines. Fig. 2 shows the number density profiles of hydrogen atoms after relaxation as functions of distance from dislocation core. Both edge and screw dislocations attract hydrogen atoms to their core regions by about 4 times of that at far from dislocation. The average profiles (solid line) in both dislocation models show similar Gaussian-like curves with half-height radius of about 0.5 nm from core centers. Hydrogen trapping at dislocation was observed by small angle neutron scattering experiment [22,23] and the radius of segregated region was estimated to be about 1 nm [24].

Anisotropic distribution of hydrogen atoms toward x and y direction (dashed lines) was found in edge dislocation model: aggregated region extends up to about 1 nm toward x (along the slip plane) but about a half toward y (perpendicular to the slip plane). This anisotropy is probably cause by the dislocation partialization mentioned above. Similar anisotropic distribution in site energies was calculated for edge dislocation in b.c.c. iron [25]. In

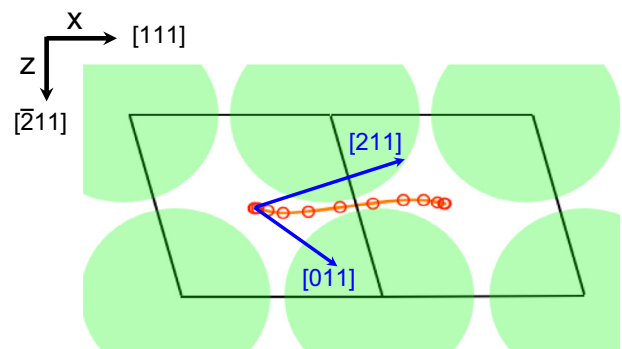


Fig. 1. Positions of vanadium atoms (small red circles) on a slip plane relative to the $(01\bar{1})$ lattice under the plane (large green circles) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

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