

COMPUTER SIMULATION OF HYDROGEN-AFFECTED DISLOCATION MOVEMENT

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ABSTRACT

H affects dislocation mobility in bcc and fcc materials. In the present work, atomistic simulations on the H-affected kinking process of a screw dislocation in Fe and the H-affected cross-slip process of a dissociated screw dislocation in Ni are conducted by the nudged elastic band method. H binding at the dislocation cores is simulated by the conjugate gradient method. In Fe, the maximum binding energy of H at the screw dislocation is 0.449 eV. We find that when a kink pair nucleates at H, the activation energy is decreased by the transition of H to a stronger binding site, while it is increased by the transition to a weaker binding site. When a kink pair meets H during expanding, the sideward motion of the kink pair is impeded by H. We thus conclude that H-induced softening occurs as the results of H jumping out of the strongest binding site and kink-pair nucleation at the jumped H where the transition of H back to the strongest binding site occurs during kinking. H-induced hardening occurs as the results of kink-pair nucleation at the site where H is in the strongest binding and the transition of H to a weaker binding site during kinking and/or H-impeded sideward motion of kinks. In Ni, we find that the maximum binding energy of H is strongly dependent on the edge components of the partial dislocations. H binding in the stacking fault exerts no effect on the activation energy of cross-slip. H that is bound to the cores of the partial dislocations and moves with the dislocations during cross-slip leads to an increase of the activation energy and thus induces slip planarity. The increase of the activation energy for cross-slip is due to a net decrease of the H binding energy at the curved dislocations in the cross-slip process.

1 INTRODUCTION

One of the predominant factors causing H embrittlement is the interaction of H with dislocations, which leads to enhanced fracture and has received increasing attention recently (Myers [1]). Extensive evidences have shown that H affects dislocation mobility in bcc and fcc materials. In bcc Fe, it was showed experimentally that H-induced softening occurs at temperatures between 200 and 300 K, while H-induced hardening occurs below 200 K (Matsui [2] and Kimura [3]). It was interpreted that the softening is due to enhanced kink-pair nucleation on screw dislocations, while hardening is due to reduced kink mobility. However, it has not been clarified how H decreases the activation energy of kink-pair nucleation, until now. In fcc Ni, it has been observed that H can inhibit cross-slip (McInteer [4]), inducing slip planarity. The slip planarity was originally explained to be due to the reduction of stacking-fault energy by H (Windle [5]). However, the mechanism is discredited because even in Al, in which the stacking-fault energy is so high that dislocations do not dissociate, slip planarity can occur (Ferreira [6]).

In the present atomistic simulations, we study the H-affected kinking process of a screw dislocation in Fe and the H-affected cross-slip process of a dissociated screw dislocation in Ni by atomistic simulations using the nudged elastic band method (NEB) (Mills [7,8]). H binding at the dislocation cores is simulated by the conjugate gradient method. H-induced softening and hardening in Fe and H-induced slip planarity are then discussed and atomistic mechanisms are proposed on the basis of the simulation results.

2 METHOD OF SIMULATIONS

The atomic interaction for the bcc Fe/H system is described by our newly developed embedded-atom-method (EAM) potential (Wen [9]), and for the fcc Ni/H system it is described by the EAM potential developed by Angelo *et al.* (Angelo [10] and Baskes [11]). For bcc Fe, atomistic simulations are conducted on a supercell with 12 repeated cells along the $[\bar{1}\bar{2}1]$ direction, 19 repeated cells along the $[\bar{1}01]$ direction and 20 repeated cells along the $[111]$ direction. The periodic boundary conditions are used along $[111]$, and free boundary conditions are used along $[\bar{1}\bar{2}1]$ and $[\bar{1}01]$. For fcc Ni, atomistic simulations are conducted using a cylindrical cell. The cylinder has a radius of 7.5 nm and a length of 52 repeated units along the line direction $[\bar{1}\bar{1}0]$ with the periodic unit of $1/2[110]$. For Fe a $1/2[111]$ screw dislocation is inserted and for Ni a $1/2[110]$ screw dislocation is inserted. Relaxations by the conjugate gradient method are conducted to determine the equilibrium state of the supercells. The binding energy of H at the dislocation is then calculated as the difference in energy between the state with the H atom near the dislocation and the state with the H atom in the solution state. The kinking process of the $1/2[111]$ screw dislocation in Fe and the cross-slip process of the $1/2[110]$ screw dislocation in Ni are then simulated by the NEB method [7,8].

3 RESULTS

3.1 H effect on kink-pair mechanism in Fe

The differential displacement map of the screw dislocation core structure and the stable binding sites of H at the core are shown in Figure 1. The corresponding binding energies of H at these sites are listed in Table 1. It is clear that the structure of the $1/2[111]$ screw core has threefold symmetry, and the two degenerate cores A and B are related by the $[\bar{1}01]$ diad axis normal to the dislocation line.

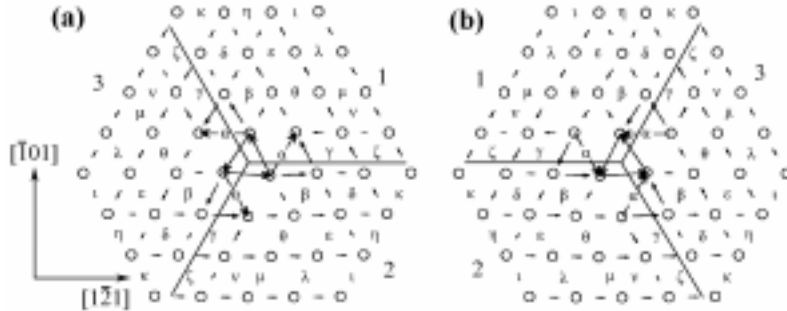


Figure 1: Differential displacement maps of dislocation cores A in (a) and B in (b) together with the stable H binding sites.

Table 1: H binding sites and energies at the $1/2[111]$ screw dislocation core.

site	α	β	γ	δ	ϵ	ζ	η	θ	ι	κ	λ	μ	ν
$E_b(\text{eV})$	0.449	0.293	0.285	0.196	0.192	0.156	0.142	0.132	0.130	0.127	0.098	0.057	0.045

To simulate the kink-pair mechanism, the straight screw dislocation with core B is assumed to be the reactant state, and the straight dislocation with core A after a step of the $1/3[1\bar{2}1]$ transition from the reactant is assumed to be the product state. H effects are simulated by adding a H atom to one of the binding sites for the reactant shown in Figure 1(b) and the corresponding site for the product shown in Figure 1(a). The binding site of H is described by Xn , where X represents the binding state and n the region of the H atom, as shown in Figure 1.

Configurations along the located minimum energy path (MEP) are obtained by the NEB method. Figure 2 shows the transition state with a H atom binding at the $\alpha 1$ site for both the reactant and the product and at the midpoint of the dislocation line. The two $(\bar{1}01)$ planes sandwiching the dislocation are also shown. The Fe atoms with energies higher than -4.22 eV are shown as large black spheres, and the H atom is shown as a small black sphere.

The effect of H on the energy change of the $1/2[111]$ screw dislocation along the MEP is shown in Figure 3. In (a), a H atom, binding at $\alpha 1$ for both the reactant and the product, is placed at the midpoint of the dislocation line or at the site one-quarter of the dislocation length of the dislocation line. No difference between the activation energy of “H free” and that of “H ($\alpha 1$ - $\alpha 1$) at the midpoint” is observed, indicating that H exerts no effect on the kinking process when the binding state does not change during kinking. However, the activation energy of “H ($\alpha 1$ - $\alpha 1$) at the one-quarter point” is higher than that of “H free”, indicating that H impedes the sideward motion of the kink pair. Effects of the transition of the binding site of H, where the H atom is placed at the midpoint of the dislocation line, on kink-pair nucleation are shown in (b) and (c). The energy difference between the reactant and the product is due to the difference in H binding states described in Figure 1 and Table 1. In (b), the binding state of H changes from a higher energy site to a lower energy site during kinking. It is clear that the nucleation energy and the activation energy of the kink pair are decreased upon the transition of H to a more stable site. In (c), the binding state of H changes from a lower energy site to a higher energy site during kinking. This clarifies also that the nucleation energy and the activation energy of the kink pair are increased upon the transition of H to the higher energy site.

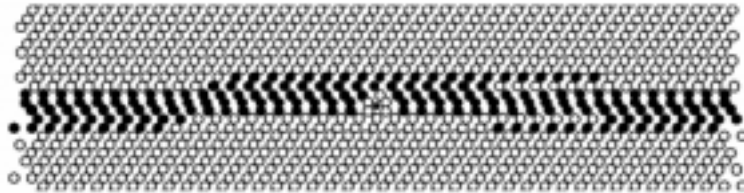


Figure 2: Transition state with H in the kinking process.

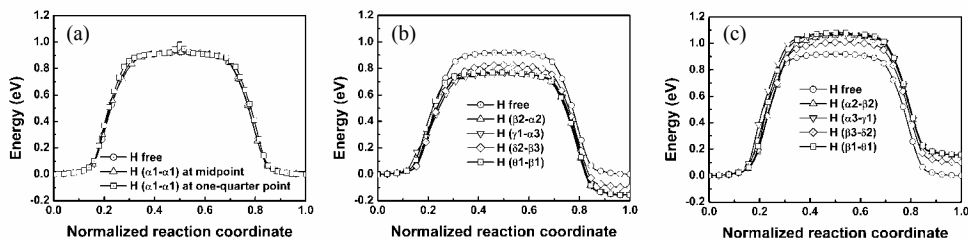


Figure 3: Effect of H on the energy change of $1/2[111]$ screw dislocation along the MEP.

3.2 H effect on cross-slip process of Ni

The cross-slip process of the $1/2[110]$ screw dislocation in Ni is also simulated by the NEB method. The straight screw dislocation dissociated on the primary slip plane $(\bar{1}11)$ is assumed to be the reactant state, and the one on the cross-slip plane $(\bar{1}\bar{1}\bar{1})$ is assumed to be the product state. The obtained transition states of “H free” and “H at DC” (H binding at dislocation cores, each partial with 26 H atoms) are shown in figure 4. Ni atoms are colored according to the maximum value of their absolute relative displacement to nearest neighbors, and mapped corresponding to the color bar indicated (range of $1/2\sqrt{6}$ to $1/2\sqrt{6}$, bottom to top). The H atoms are shown as the small black spheres.

A schematic of the cross-slip process is shown in Figure 5. The Burgers vectors are shown by arrows. E indicates edgewise and S indicates screwlike constrictions. It is clearly shown in (b) that the partials become screwlike on the lower side of the constriction, while they become edgewise on the upper side, due to curving of the partials. The two constrictions shown in (c) are not equivalent, due to the characteristics of the partials near the constrictions.

The effects of H on the energetics of cross-slip of the $1/2[110]$ screw dislocation are shown in Figure 6. The activation energy of both “H free” and “H in SF” is 3.07 eV. It is clear that H in the stacking fault exerts no effect on the cross-slip process. The activation energy of the cross-slip process of H at DC is 3.30 eV, which is around 7 % higher than that of the H free model.

To provide insight into the energetics of H-affected cross-slip, we define the energy of a constriction as the difference in energy between the constriction and its corresponding part in the unconstricted state. Table 2 lists the constriction energies and constriction energy changes. To further clarify the contribution of H binding to the activation energy of cross-slip, we calculate the binding energy of H at the dislocation core. As listed in Table 3, the decrease of the binding energy of H ΔE_b is twice the increase from 30° to 60° partials. This is the same as the increase of the screwlike constriction energy due to the presence of H (0.46 eV) being twice the decrease of the edgewise constriction energy resulting from the presence of H (0.23 eV), as listed in Table 2. Thus, the increase in the activation energy when H is present is only due to the net decrease of the binding energies during cross-slip.

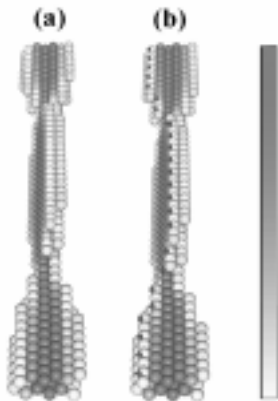


Figure 4: Transition states of the cross-slip process (a) without and (b) with H at partial cores.

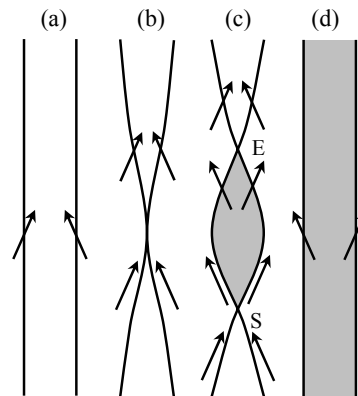


Figure 5: Schematic of the cross-slip process (a) the reactant, (b) recombination into a constriction, (c) the transition state, and (d) the product.

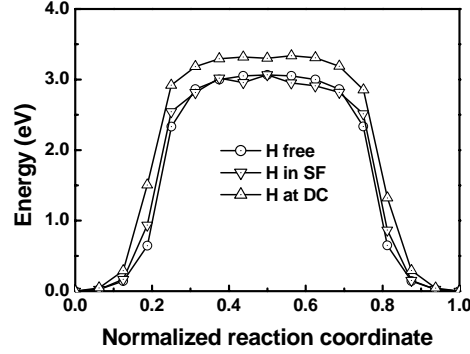


Figure 6: Effects of H on the energy change of the $1/2[110]$ screw dislocation along the MEP.

Table 2: Constriction energies, and constriction energy changes ΔE .

	H-free (eV)	H at DC (eV)	ΔE (eV)
Edgelike	3.82	3.59	-0.23
Screwlike	-0.75	-0.29	0.46

Table 3: Binding energies E_b of H and binding energy decrements ΔE_b .

	E_b (eV)			ΔE_b (eV/degree)		
	Screw	30°	60°	Edge	30°→Screw	30°→60°
	0.04	0.10	0.13	0.13	-0.002	0.001

4 DISCUSSION

On the basis of the results for Fe, the transition of the H binding state at the dislocation core alters the activation energy of kink-pair nucleation. The atomistic process for H-induced softening and hardening is thus identified. At high temperatures, H is highly mobile and jumps frequently to the weaker binding site. The activation energy of kink-pair nucleation at this site is then decreased by the transition of the jumped H to a stronger binding site during kinking, and the softening occurs. This means that only a few H atoms on a typical dislocation segment are required to increase the kink-pair nucleation. At low temperatures, H will bind to the strongest binding site at the dislocation core and not jump away. On one hand, kink pairs have to nucleate with the transition of H to a weaker binding site, which increases the activation energy of kink-pair nucleation. On the other hand, due to the strong binding, the H concentration at the dislocation core is high; hence it is impossible for screw dislocations to overcome H by the pinning/unpinning process that kink pairs have to nucleate between H atoms. Also, H may act as dragging points to impede the sideward motion of kinks. The mobility of screw dislocations is thus decreased and the hardening occurs. In general, the softening occurs at high temperatures and at low H concentration, while hardening occurs at low temperatures and at high H concentration, as argued (Hirth [12] and Matsui [2]).

The slip planarity in Ni can be understood as follows. During cross-slip, the two parallel partials of the screw dislocation bow towards each other and become curved. The character of the partials changes towards a more screwlike character in one part, and towards a more edgelike

character in the other. When two constrictions form, one constriction is screwlike and the other is edgelike. The binding energy of H is then decreased at the screwlike segments, and increased at the edgelike segments. Because the decrease of the binding energy of H at the screwlike segments is larger than the increase at the edgelike segments, the total binding energy is decreased. The activation energy of cross-slip is thus increased. Details are cited from (Wen [13,14]).

5 CONCLUSIONS

Atomistic simulations are conducted on the H-affected screw dislocation motion in Fe and Ni. In Fe, we find that the transition of the H binding state at the dislocation core alters the activation energy of kink-pair nucleation. The softening is due to the transition of H to a stronger binding site during kinking, while the hardening is due to the transition of H to a weaker binding site during kinking and the impeded sideward motion of the kink pair. In Ni, we find that H in the stacking fault exerts no effect on the activation energy of cross-slip. H that is bound at the partial dislocation cores and moves with partials during cross-slip increases the activation energy. The H-induced slip planarity is due to the net decrease of the binding energy of H during cross-slip.

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