Three-dimensional molecular dynamics simulation of hydrogen-enhanced dislocation emission and crack propagation*

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Abstract A three-dimensional molecular dynamics simulation using the embedded atom method (EAM) potentials shows that for both pure Ni and Ni + H, dislocations are firstly emitted during loading and the crack propagates after enough dislocations are emitted. In the case of hydrogen embrittlement, local plastic deformation is a precondition for crack propagation. For the crack along the $(1\bar{1}1)$ slip plane, one atom fraction in percent of hydrogen can decrease the critical stress intensity for dislocation emission K_{Ie} from 0.42 to 0.36 $MPam^{1/2}$, and that for crack propagation K_{Ip} from 0.80 to 0.76 $MPam^{1/2}$. Therefore, hydrogen enhances dislocation emission and crack propagation.

Keywords: molecular dynamics simulation, hydrogen, dislocation emission, crack propagation, nickel.

Molecular dynamics simulation (MDS) has been used to study dislocation emission and crack propagation[1~6]. In the beginning, a two-dimensional or quasi three-dimensional MDS was used[1~3]. Recently, three-dimensional (3-D) MDS has been developed[4~6]. In a quasi three-dimensional simulation, periodic boundary condition is applied along the thickness. The obtained results using the quasi three-dimensional MDS indicated that the ductile and brittle behavior of fcc metals depended upon the orientations of the crack plane relative to the slip plane[1~3]. When the inclination angles between the crack plane and the slip plane in Cu[2] and Ni[3] are less than 16°, the crack extends in a brittle fashion instead of dislocation emission. *In situ* observation in a transmission election microscope (TEM) showed that for both ductile and brittle materials dislocation emission and motion occurred firstly during loading and after the dislocation emission and motion developed to a certain extent microcrack initiated or main crack propagated[7,8]. In the quasi 3-D simulation, a periodic boundary condition is applied along the thickness, and the periodic boundary condition may preclude dislocation emission for some orientations of the crack plane relative to the slip plane. The first objective of this work is to prove, using 3-D molecular dynamics simulation, that cracks will emit dislocation prior to extending no matter what orientation of the crack is.

The mechanism of hydrogen embrittlement has been extensively investigated[8]. Many experiments show that hydrogen-enhanced dislocation emission and motion are the key of hydrogen-induced cracking[8]. A quasi 3-D MDS using pair potentials showed that the hydrogen enhanced dislocation emission in Al during mode II loading[9]. A 3-D MDS by the embedded atom method (EAM) showed that hydrogen in iron promoted the processes of cavity nucleation, cavity linkage and, finally fracture[6]. The second objective of this work is to study the effect of hydrogen on dislocation emission and crack propagation in nickel using 3-D MDS with the EAM potentials.

1 Calculation procedure

The EAM potentials for Ni and Ni + H systems proposed by Baskes et al.[10,11] are used in this simulation. The x axis of a single edge-cracked crystal is along the crack propagation direction, the y along the normal of the crack plane, and the z along the [110] direction. The length of the crystal along the x axis is 12.32 nm. The width along the y axis is also 12.32 nm, and the thickness along the z axis is 3.52 nm. The length of the edge crack, which is through the thickness, is 5.52 nm, and the width is 0.53 nm. The inclination angles θ between the crack plane and the $(1\bar{1}1)$ slip plane are 0°, 45° and 90°, respectively. If $\theta = 0$, the x and y axes are along the

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$[\bar{1}12]$ and $[1\bar{1}1]$ directions, respectively. If $\theta = 90°$, the x and y axes are along the $[\bar{1}1\bar{1}]$ and $[\bar{1}12]$, respectively. If $\theta = 45°$, the inclination angle between the x axis and the $[\bar{1}12]$ direction or the y and the $[1\bar{1}1]$ is 45°. The number of atoms used here is 122000. There are 1123 hydrogen atoms randomly distributed in the interstitial sites of the Ni crystal. Hydrogen concentration is about one atom fraction in percent.

The loading rate under mode I loading is $dK_I/dt = 0.01$ MPam$^{1/2}$/ps. The displacement boundary condition is to be used. The displacements of the atoms at the boundary corresponding to each K_I are determined according to the plane strain linear elastic displacement field for a cracked solid[2]. The inner atoms move following the second law of Newton, and the leapfrog algorithm[2,3] is used to calculate the positions and velocities of the inner atoms. The temperature is kept at 40°K.

In the 3-D mode the question is how to define the positions of dislocations emitted from a loaded crack tip. The energy of atoms around dislocation line is higher than that of the other atoms. Therefore, the energy of the inner atoms is calculated during loading, when the energy of several neighboring atoms is higher than that of the other atoms by 0.2 to 0.3 eV, the atomic configuration in the xoy plane is checked to define the position of dislocation. For an edge crack through the thickness, a straight dislocation through the thickness is emitted.

2 Simulation results

For pure nickel, when the crack plane is along the $(1\bar{1}1)$ slip plane, i.e., $\theta = 0°$, the first Shockely dislocation is emitted from the crack tip at the stress intensity factor $K_I = 0.42$ MPam$^{1/2}$, as shown in Fig.1. Fig.1(a) is the 3-D mode and Fig.1(b) is the atomic configuration in the xoy plane containing a dislocation. The slip plane of the Shockely dislocation is along the $(1\bar{1}\bar{1})$ plane, Burgers vector is along the $[1\bar{1}2]$ direction, and the half atomic rank is along the $[1\bar{1}\bar{2}]$ direction. Fig.1 shows that the critical stress intensity factor for partial dislocation emission in Ni is $K_{Ie}(\theta = 0°) = 0.42$ MPam$^{1/2}$. If one atom fraction in percent of hydrogen atoms are randomly distributed in the interstitial sites of Ni, the first Shockely dislocation will be emitted when $K_I^*(\theta = 0) = 0.38$ MPam$^{1/2}$, as shown in Fig.2. In the Ni + H, the slip plane of the dislocation is along the $(1\bar{1}\bar{1})$ plane, Burgers vector is along the $[1\bar{1}2]$ direction, and the half atomic rank is along the $[1\bar{1}\bar{2}]$ direction. Fig.2 indicates that hydrogen decreases the critical stress intensity for dislocation emission from $K_{Ie}(\theta = 0) = 0.42$ MPam$^{1/2}$ to $K_{Ie}^*(\theta = 0) = 0.38$ MPam$^{1/2}$, and thus enhances dislocation emission.

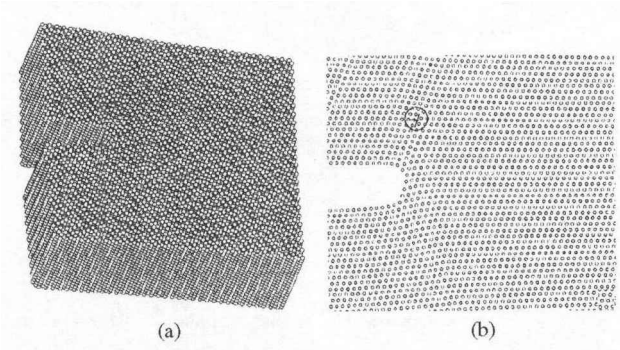

Fig.1. The first Shockely dislocation emitted from the crack tip at $K_I = 0.42$ MPam$^{1/2}$ for pure nickel when the crack plane along the $(1\bar{1}1)$ slip plane. i.e., $\theta = 0°$. (a) the 3-D mode; (b) the atomic configuration in the xoy plane containing the dislocation.

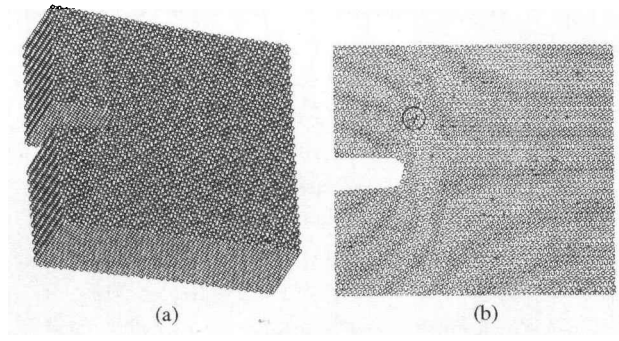

Fig.2. The first Shockely dislocation emitted from the crack tip at $K_I = 0.38$ MPam$^{1/2}$ for nickel containing one atom fraction in percent hydrogen when the crack plane along the $(1\bar{1}1)$ slip plane. i.e. $\theta = 0°$. (a) the 3-D mode; (b) the atomic configuration in the xoy plane containing the dislocation. The big circle for Ni and the small for H.

When the crack plane is along the $(\bar{1}12)$ plane, i.e. $\theta = 90°$, the first Shockely dislocation in Ni is emitted from the crack tip at $K_I(\theta = 45°) = 0.54$ MPam$^{1/2}$, as shown in Fig.3(a). The slip plane and Burgers vector of the dislocation are along the $(\bar{1}11)$ plane and the $[\bar{1}1\bar{2}]$ direction, respectively, and the half atomic rank is along the $[1\bar{1}2]$ direction. For the Ni + H, two Shockely dislocations are emitted from the crack tip at $K_I^*(\theta = 90°) = 0.42$ MPam$^{1/2}$, as shown in Fig.3(b). One of the dislocations is located at the notch tip and has the same slip plane and Burgers vector with Ni, i.e., $(\bar{1}11)$ $[\bar{1}1\bar{2}]$. The

other is located below the notch and has the slip plane of $(\bar{1}1\bar{1})$ and Burgers vector of $[\bar{1}12]/6$. The half atomic rank of the second dislocation is along the $[1\bar{1}2]$ direction. Fig. 3 indicates that hydrogen decreases the $K_{Ie}(\theta = 90°)$ from 0.54 $MPam^{1/2}$ to 0.42 $MPam^{1/2}$.

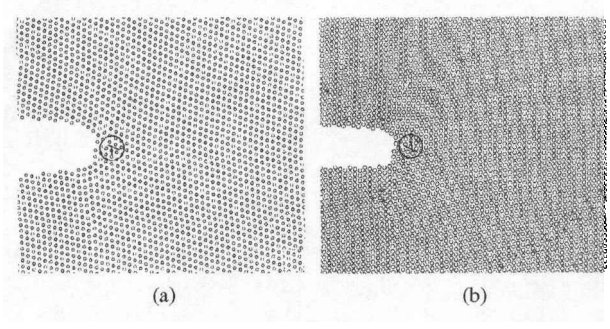

Fig. 3. The first Shockely dislocation emitted from the crack tip when the crack plane along the $(\bar{1}12)$ slip plane, i.e. $\theta = 90°$, at $K_I = 0.54$ $MPam^{1/2}$ for pure nickel (a), and at $K_I = 0.42$ $MPam^{1/2}$ for nickel containing one atom fraction in percent hydrogen, the big circle for Ni and small for H, (b).

If $\theta = 45°$, the calculation shows that one fraction in percent of hydrogen decreases the $K_{Ie}(\theta = 45°)$ from 0.40 $MPam^{1/2}$ to 0.36 $MPam^{1/2}$. The results simulated are listed in Table 1. Figs. 1~3 indicate that for both Ni and Ni + H, dislocations are firstly emitted during mode I loading no matter what orientation of the crack plane is, and hydrogen can enhance dislocation emission.

Table 1. The critical stress intensities for dislocation emission for Ni and Ni + H($MPam^{1/2}$)

Inclination angle θ	0°	45°	90°
Ni, K_{Ie}	0.42	0.40	0.54
Ni + H, K_{Ie}^*	0.38	0.36	0.42

If the load is continuously increased after the first dislocation is emitted, more dislocations are emitted from the crack tip. For Ni, when K_I increases to equal $K_I(\theta = 0) = 0.8$ $MPam^{1/2}$, many Schockely dislocations are emitted from the crack tip and a twin along the $[1\bar{1}2]$ (i.e. CD) direction is formed, and then the crack tip propagates from A to B, as shown in Fig. 4 (a). For Ni + H, many Schockely dislocations are emitted from the crack tip and a twin along the $[1\bar{1}2]$ direction is formed, and then the crack tip is propagated from A to B at $K_I^*(\theta = 0) = 0.76$ $MPam^{1/2}$, as shown in Fig. 4 (b). Fig. 4 shows that one atom fraction in percent of hydrogen decreases the critical stress intensity for crack propagation from $K_{Ip}(\theta = 0) = 0.80$ $MPam^{1/2}$ to $K_{Ip}^*(\theta = 0) = 0.76$ $MPam^{1/2}$. Because the simulated crystal is too small ($3.5 \times 12.3 \times 12.3$ nm^3), the two half crystals above and below the crack plane well rotate and bend, resulting in crack propagation after many dislocations are emitted. The critical stress intensity for crack propagation is much smaller than the fracture toughness of the material. Therefore, for a small crystal we cannot obtain the real fracture toughness of the material using 3-D MDS.

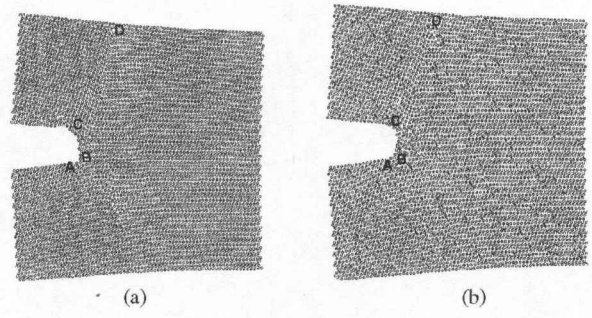

Fig. 4. The crack propagates from A to B after many Shockely dislocations emitted from the crack tip form a twin along the $[1\bar{1}2]$ direction (i.e. CD direction) at $K_I = 0.8$ $MPam^{1/2}$ for pure nickel (a), and at $K_I = 0.76$ $MPam^{1/2}$ for nickel containing one atom fraction in percent hydrogen, the big circle for Ni and small for H, (b).

3 Discussion

3-D MDS shows that for both systems of Ni and Ni + H, dislocations are firstly emitted during loading no matter what orientation of the crack plane is and crack will propagate after enough dislocations are emitted. Therefore, even for hydrogen embrittlement the local plastic deformation is a precondition of crack initiation and propagation. This result is consistent with the *in situ* TEM observations[7,8].

The quasi 3-D MDS for Cu[2] and Ni[3] indicated that when the inclination angle between the crack plane and the (111) slip plane was less than 16°, the crack propagated first, while dislocation emission did not take place. This result is different with that of 3-D MDS and is a false appearance because of use of periodic boundary condition, so we cannot say that the ductile or brittle behavior of fcc metals depends upon the orientations of the crack relative to the crystal.

MDS showed the presence of hydrogen could facilitate dislocation emission. The reason that hydrogen enhances dislocation emission can be explained as follows. The critical stress intensity for the dislocation emission from a mode I crack tip is given by[12]

$$K_{Ie} = \frac{2}{\sin\varphi\cos(\varphi/2)}\left[\frac{\mu b}{(1-\nu)\sqrt{8\pi r_C}} + \sqrt{2\pi r_C}\left(\tau_f + \frac{4\gamma e^{2/3}\sin\varphi}{\pi r_C(4+e^3)}\right)\right] \quad (1)$$

where φ is the inclination angle between the crack plane and the active slip plane, μ the shear modulus, τ_f the lattice resistance, γ the surface energy, b the Burgers vector of the Shockely dislocation, r_C the dislocation core radius. The second term containing τ_f is much smaller than the other terms and can be ignored. The shear modulus μ is relative to the surface energy, e.g.[13]

$$\gamma = 2\mu(1+\nu)a^2/\pi^2 d, \quad (2)$$

where a is the diameter of the atom and the d the plane distance. Assume that hydrogen of low concentration does not affect a, d and r_C. Based on Eq.(1) and Eq.(2),

$$K_{Ie}^*/K_{Ie} = \gamma^*/\gamma. \quad (3)$$

The quasi 3-D MDS indicated that hydrogen decreased the critical stress intensity for cleavage of a Griffith crack along the only slip plane from $K_{IG} = \sqrt{2\gamma/A} = 1.03$ MPam$^{1/2}$ to $K_{IG}^* = \sqrt{2\gamma^*/A} = 0.93$ MPam$^{1/2}$[3]. Therefore, hydrogen decreases the surface energy from γ to γ^*, i.e. $\gamma^*/\gamma = 0.82$[3]. Substituting $\gamma^*/\gamma = 0.82$ into Eq.(3), $K_{Ie}^*/K_{Ie} = 0.82$. Simulation results shown in Table 1 indicate $K_{Ie}^*/K_{Ie} = 0.78 \sim 0.90$. Therefore hydrogen decreasing the surface energy causes the critical stress intensity for dislocation emission to decrease and enhances dislocation emission.

On the other hand, Li supposed[14] that n hydrogen atoms per unit length of dislocation could lower their fugacity from f_0 to f by residing in the emitted dislocation, and the energy barrier for the emission process was lowered by $\Delta E = nkT\ln(f_0/f)$ per unit length of dislocation. Hence the critical stress intensity for dislocation emission was lowered from K_{Ie} to K_{Ie}^*, i.e.

$$\ln(K_{Ie}^*/K_{Ie}) = -2\pi(1-\nu)nkT\ln(f_0/f)/\mu b^2. \quad (4)$$

For Ni, $\mu = 4.78\times10^4$ MPa, $\nu = 0.276$, $b = 1.44\times10^{-10}$ m and suppose that $n = 10^{10}$/m, $f_0/f = 100$, $T = 40$ K, we can obtain $K_{Ie}^* = 0.89\ K_{Ie}$.

4 Conclusions

(i) Three dimension molecular dynamics simulation shows that for both Ni and Ni + H dislocation is firstly emitted during loading no matter what the orientation of the crack plane is, and the crack propagates after many dislocations are emitted.

(ii) Molecular dynamics simulation indicates that hydrogen enhances dislocation emission and decreases the critical stress intensity for dislocation emission from $K_{Ie}(\theta = 0) = 0.42$ MPam$^{1/2}$ to $K_{Ie}^*(\theta = 0) = 0.38$ MPam$^{1/2}$.

(iii) Hydrogen decreases the critical stress intensity for crack progagation from $K_{IP}(\theta = 0) = 0.80$ MPam$^{1/2}$ to $K_{IP}^*(\theta = 0) = 0.76$ MPam$^{1/2}$, i.e., hydrogen promotes crack propagation.

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