Hydrogen-enhanced dislocation activity and vacancy formation during nanoindentation of nickel

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The effect of hydrogen on dislocation activities during the nanoindentation of Ni(110) is studied by molecular-dynamics simulation at 300 K. The results reveal that the critical event for the first dislocation nucleation during nanoindentation is due to the thermally activated formation of a small cluster with an atom's relative displacement larger than half the magnitude of the Burgers vector of partial dislocations. Hydrogen only enhances homogenous dislocation nucleation slightly; however it promotes dislocation emission, induces slip planarity, and localizes dislocation activity significantly, leading to locally enhanced vacancy formation from dislocations. The present results, thus, prove hydrogen-enhanced localized dislocation activity and vacancy formation to be the main reason of hydrogen embrittlement in metals and alloys.

I. INTRODUCTION

Hydrogen energy, as an environmentally clean energy source and a way to reduce reliance on fossil fuel sources for our future, has been attracting public attention all the more in recent years and thereby H-powered fuel cell vehicles are going to be of practical use in the foreseeable future. A crucial issue that confronts the use of hydrogen energy is hydrogen embrittlement (HE), whereby H reduces ductility and fracture stress and thus degrades the mechanical properties of almost all metals and alloys. Despite extensive studies over one century, the fundamental aspects of the HE process have not been fully understood until now. In relation to this, three candidate mechanisms have been developed, including H-induced hydride formation, H-enhanced decohesion, and H-enhanced localized plasticity (HELP).[1] The first mechanism has been determined to be operative in systems in which hydrides can be formed with or without stress-field application. For a system in which hydride formation is impractical, HE occurs by the second or third mechanism. The second mechanism assumes that H in solid solution weakens the atomic bonding at the crack tip and thus materials fail at a low applied stress. The third mechanism suggests that solute H enhances the mobility of dislocations, which results in localized plasticity in places such as the vicinity of cracks where the H concentration is high, thus leading to macroscopic brittle fracture by locally ductile processes. A new mechanism, the hydrogen-enhanced strain-induced vacancy (HESIV), has been proposed recently.[2] The HESIV mechanism suggests that hydrogen enhances the creation and accumulation of vacancies through interactions between hydrogen and vacancies during plasticity deformation, thus promotes void formation and crack propagation.

We focus on the effects of H on dislocation activity in Ni, the key ingredient in the HELP mechanism in this study. The concept of HELP was originally proposed by Beachem;[3] now, there is a large body of evidence showing that H induces localized plasticity in metals, leading to enhanced fracture.[1,4] Lynch suggested that HELP is due to H adsorption at crack tips, which facilitates the injection of dislocations from crack tips,[5,6] but the current model of HELP shows that H shields the interaction between dislocations and obstacles, leading to enhanced dislocation mobility.[7] However, the base of the current HELP mechanism has only been examined theoretically through self-consistent elasticity calculations using finite-element methods.[7] No studies have been conducted to verify atomistically the H-affected dislocation motion leading to HELP until now, although H-enhanced void nucleation was found by molecular-dynamics (MD) and Monte Carlo (MC) simulations.[8] We thus perform MD simulation on the H-affected indentation process of Ni(110) in the present study to elucidate the atomistic processes of H altering dislocation mobility. We also examine the vacancies that are formed during nanoindentation in an effort to demonstrate how H-affected dislocation motion can lead to HE.

II. METHODS

MD simulation with the embedded-atom method (EAM) potential for the Ni-H system[9,10] is applied to the simulation of nanoindentation on the Ni(110) surface. We use the velocity form of the Verlet algorithm to evolve the system, and the Nosé-Hoover thermostat[11,12] to maintain the temperature at 300 K. The time increment for each MD step is chosen to be 1 fs. The rectangular computational cell is $27.877 \times 28.160 \times 14.436$ nm^3 and contains 1 048 320 Ni atoms. The effect of H is studied by precharging 10 000 H atoms, a concentration of ~1 at. % H, which is larger than the concentration obtained by thermal charging but less than the concentration obtained by cathodic charging of H in Ni experimentally, homogeneously in the model before simulation. Free boundary conditions are applied on the top and bottom surfaces, and periodic boundary conditions are applied on the side surfaces. The purpose of the free boundary for the bottom surface is to let dislocation loops emitted from the region under the indenter tip to slip through the bottom surface and not to bounce back during nanoindentation. This prevents contaminating the very behavior of dislocations underneath the indenter tip by the bounced dislocations if fixed boundary conditions are applied to the bottom surface. The momentum of the cell along the indentation direction is removed during
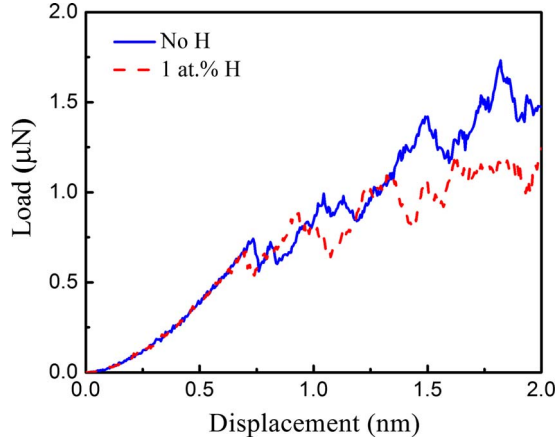
FIG. 1. (Color online) Load-displacement curve of Ni(110) during nanoindentation.

the simulation of indentation to prevent the whole cell from downward translational motion due to the force applied by the indenter. An equilibrium configuration for indentation simulation is obtained by relaxing the initial configuration using the limited-memory Broyden-Fletcher-Goldfarb-Shanno (BFGS) method. The whole relaxed configuration is then expanded following the lattice constant at 300 K obtained by Dupuy *et al.*[13] to account for thermal expansion for the MD simulation of nanoindentation at 300 K. Nanoindentation simulation is then performed on this final configuration using a strongly repulsive potential by Kelchner *et al.*[14] to model a spherical rigid indenter with a tip radius of 10 nm. Indentation simulation is conducted by moving the tip downward at a constant speed of 10 m/s.

We developed a method that can be applied to quantitatively visualize lattice defects such as dislocations and stacking faults during twin or slip deformation in atomistic simulations.[15] The method, however, also visualizes the region where a full dislocation is passed through, which is not what we want in this study. We therefore modify the method by defining the deformation index (DI) of Ni atom i as the maximum relative displacement of atom i with respect to its nearest neighbors j: $DI_i = \max(|\vec{r}_{ij} - \vec{r}_{ij}^0|)/a_0$, where $\vec{r}_{ij}^0$ is the

relative position vector of atoms i and j in the reference lattice, $\vec{r}_{ij}$ is the closest vector to $\vec{r}_{ij}^0$ in the deformed state, and a_0 is the lattice constant. The modified DI is 0.4 for partial dislocations and 0.7 for full dislocations, respectively. Dislocations can thus be visualized quantitatively by coloring atoms with the DI. Any lattice imperfections, torsion, and structure changes can also be displayed clearly by this method.

III. RESULTS AND DISCUSSION

A. Dislocations and H effects

Atomistic load-displacement curves are shown in Fig. 1, where the first abrupt drops in load or pop in indicate homogeneous dislocation nucleation. The first pop in occurs at an indentation depth of 0.735 nm in the H-free specimen while it occurs at a depth of 0.700 nm in the 1 at. % H specimen. The results demonstrate that H enhances dislocation nucleation, as the pop-in event of the 1 at. % H specimen occurs somewhat earlier than that of the H-free specimen. It is also shown that H enhances dislocation mobility significantly because the load of the 1 at. % H specimen is lower than that of the H-free specimen at the same displacement.

A detailed dislocation nucleation during the nanoindentation of Ni(110) is shown in Fig. 2, where snapshots of the H-free specimen at indentation depths of (a) 0.738 nm and (b) 0.742 nm, and of the 1 at. % H specimen at indentation depths of (c) 0.701 nm and (d) 0.706 nm are shown. Only atoms with a DI larger than 0.2, i.e., half the magnitude of the Burgers vector of partial dislocations are displayed. It is clearly observed that a partial dislocation loop bounding a stacking fault has developed, as shown in Fig. 2(a). The loop expands and the second partial dislocation loop nucleates rapidly upon continuing loading, as shown in Fig. 2(b). A comparison of Figs. 2(a) and 2(b) with Figs. 2(c) and 2(d) clearly indicate that the dislocation loop in the 1 at. % H specimen is formed slightly earlier than that in the H-free specimen. We repeat the MD simulation with the same initial configuration and different starting velocities of atoms and find that in most cases dislocation nucleation occurs earlier
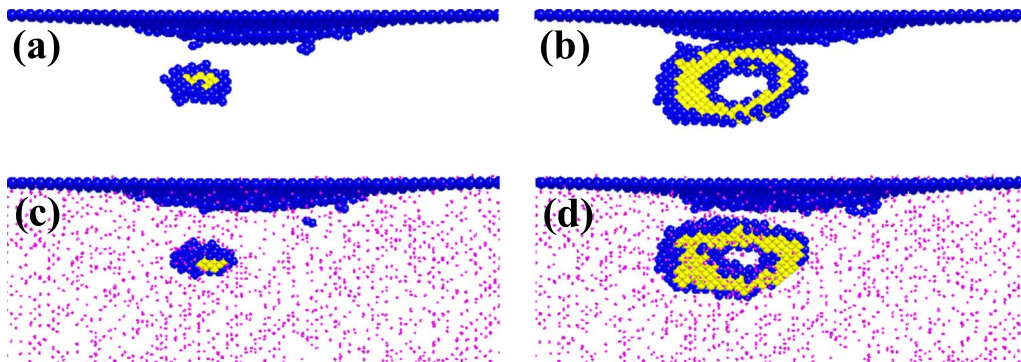

FIG. 2. (Color online) Dislocation nucleation during nanoindentation on Ni(110). Snapshots of the H-free specimen at indentation depths of (a) 0.738 nm and (b) 0.742 nm, and of the 1 at. % H specimen at indentation depths of (c) 0.701 nm and (d) 0.706 nm. Only Ni atoms with DI larger than 0.2 (half of the magnitude of the Burgers vector of partial dislocations $1/6\langle 112 \rangle$) are shown to demonstrate the configurations three dimensionally. Ni atoms are colored according to DI with blue (dark gray) corresponding to surfaces and partial dislocations and yellow (light gray) to stacking faults. H atoms are shown by small pink (dark gray) spheres.

in the 1 at. % H specimen than that in the H-free specimen, as is also indicated in Fig. 1. Our results are thus in agreement with the recent experimental investigations for stainless steel[16] and Ni,[17,18] which showed that H enhances the dislocation nucleation.

We analyze dislocation nucleation carefully to clarify how the dislocation loop is evolved. It is found that the dislocation nucleation begins with the formation of a small cluster in which the DIs of the atoms are larger than 0.2, as shown in Fig. 2(a). A cluster with more than two atoms will certainly evolve to form an embryo of dislocation loop and clusters with only two atoms will disappear in a very short time. This finding is in agreement with the experimental results of the extremely small activation energy and activation volume,[19] which indicates that the critical event for the first dislocation nucleation during nanoindentation is on the atomic scale. Note here that according to our definition of DI, if atom i has a $DI_i = |\vec{r}_{ik} - \vec{r}_{ik}^0|/a_0$, where k is one of its neighbors, the atom k will have a relative displacement with respect to atom i that equals to DI_i and the DI of atom k will then be equal to or larger than DI_i. If one atom has a DI larger than 0.2, at least one of its neighbors will also have a DI larger than 0.2, and the minimum size of the cluster is 2. Zuo *et al.*[20] suggested that the critical event of the first dislocation nucleation occurs by having one individual atom achieving a critical relative displacement with respect to its neighbors. Their analysis, however, is similar to ours and the critical event should also occur with the cluster whose size is at least 2.

Upon continuing loading after the first dislocation nucleation, the full dislocation loop expands rapidly into the crystal, emerges at the surface, and interacts with other dislocations formed to produce complex dislocation structures under the indenter tip. These complex dislocation structures are rather stable and a continuous loading is needed to emit dislocation loops from them.

H not only alters dislocation nucleation during nanoindentation but also affects succeeding dislocation mobility in our MD simulations. The dislocation structure under the indenter tip, as is shown in Fig. 3, emits a dislocation loop at an indentation depth of 1.17 nm for the H-free specimen, and at an indentation depth of 0.97 nm for the 1 at. % H specimen. The present results, thus, provide us with the first atomistic evidence that H increases dislocation mobility by enhancing dislocation emission from complex dislocations structures. This is in contrast with the results of Hoagland and Baskes[21] who performed atomistic simulations by MD and MC to study the behavior of a Lomer-Cottrell Lock (LCL) in Ni under tension and found that H severely limited the motion of partial dislocations in the lock. In their work, the initial H distribution around the LCL was obtained by MC simulations at 295 K but dislocation motion was then simulated at 0 K. H, thus, does not move in response to dislocation motion, which will certainly impede dislocation and result in a strengthening effect by hydrogen due to the pinning effects of H atmosphere.[22]

A significant effect of H on dislocation mobility at an indentation depth of 2 nm is shown in Figs. 4(a)–4(d), where dislocation configurations and slip traces of the H-free specimen are shown in Figs. 4(a) and 4(c), and of the 1 at. % H specimen are shown in Figs. 4(b) and 4(d), respectively. It is
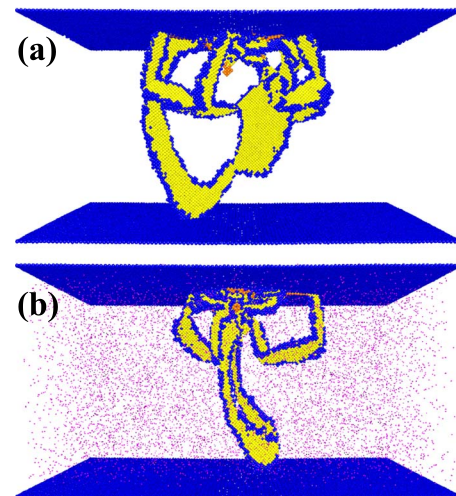

FIG. 3. (Color online) Dislocation loop emission during nanoindentation on Ni(110). Snapshots of the H-free specimen at an indentation depth of (a) 1.17 nm and of the 1 at. % H specimen at an indentation depth of (b) 0.97 nm. Ni atoms are colored according to DI with blue (dark gray) corresponding to surfaces and partial dislocations, yellow (light gray) to stacking faults, and orange (gray) to vacancies. H atoms are shown by small pink (dark gray) spheres.

easy to find by comparing Fig. 4(a) with Fig. 4(b) that the number of dislocations in the H-free specimen is larger than that in the 1 at. % H specimen and that the dislocation structure in the H-free specimen is much more tangled and distributed in a much larger region. Much more dislocations emitted from the dislocation structures disappear in the 1 at. % H specimen by slipping through the bottom surface, thereby leaving steps in a Burgers vector on the bottom surface. These two pictures, together with Fig. 1, thus provide us with further evidence that H enhances the emission of dislocations significantly and restricts the dislocation activity to a narrow area, leading to HELP. The results suggest that HELP is the result of enhanced dislocation emission from dislocation sources by H. Another pronounced effect of H is on slip planarity. As is shown in Figs. 4(c) and 4(d) of the top surfaces, the slip steps of the 1 at. % H specimen are denser and more closely packed than that of the H-free specimen, indicating H-enhanced slip planarity. This finding is in agreement with the experimental observations of the surface of stainless steel that H charging increases slip step height and spacing, as well as the number of slip steps.[16]

B. Vacancies and H effects

We also find that vacancies, which are the product of dislocation interaction and motion, are formed during nanoindentation in the present simulation. These vacancies, as shown in Fig. 5, are characterized by their 12 neighboring atoms that are colored with DIs from 0.55 to 0.7.[23] H enhances the formation of vacancies significantly and the formation is highly localized owing to the H-induced localized activity of dislocations. This is in agreement with the experimental results of hydrogen thermal desorption analysis that
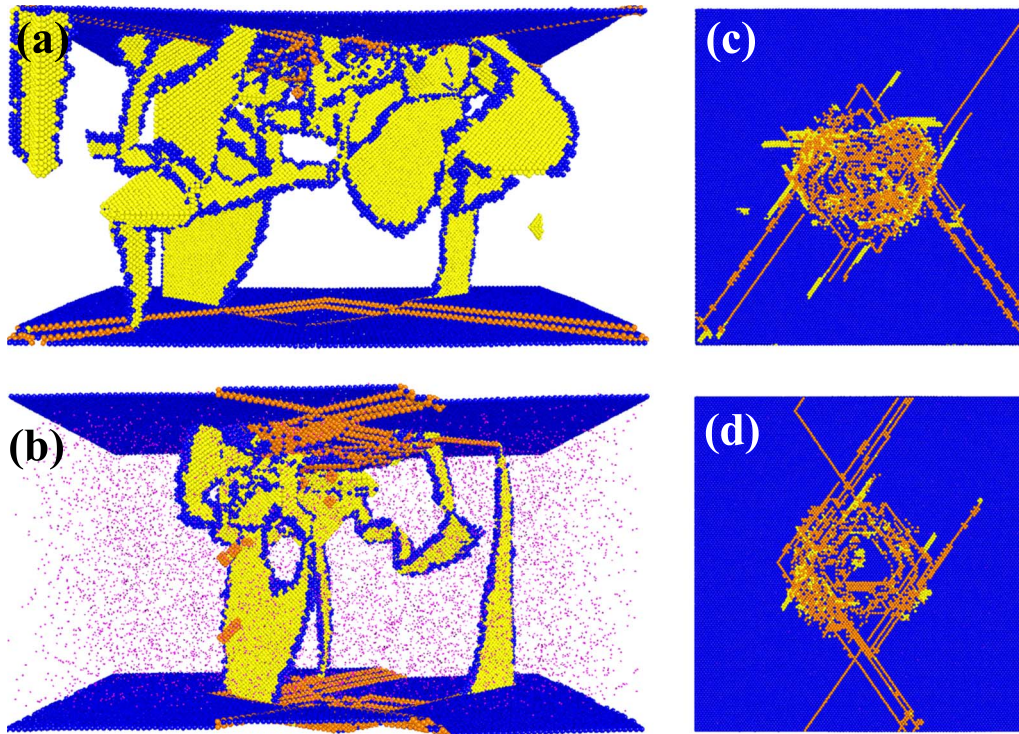
FIG. 4. (Color online) Dislocations and slip traces at the indentation depth of 2 nm. H-free specimen: three-dimensional view of dislocation configurations in (a) and slip traces in (c). 1 at. % H specimen: three-dimensional view of dislocation configurations in (b) and slip traces (d). Ni atoms are colored according to DI with blue (dark gray) corresponding to surfaces and partial dislocations, yellow (light gray) to stacking faults, and orange (gray) to vacancies and slip lines on the surface. H atoms are shown by small pink (dark gray) spheres.

H enhances the formation of strain-induced vacancies in the body-centered cubic (bcc) and face-centered cubic (fcc) metals and alloys.[24,25] First-principles calculations showed that the presence of H decreases the vacancy formation energy in bcc Fe (Ref. [26]) and fcc Al,[27,28] which leads to H-enhanced vacancy formation. The theoretical calculations also demonstrates that H facilitates vacancy clusterization in the form of line-shaped and tabulated vacancy clusters in Fe (Ref. [26]) and of planar vacancy clusters on the slip plane of Al,[28] leading to easier void formation and crack nucleation. The fundamental process of HE, thus, is clarified as H in metals

and alloys enhances dislocation activity locally, which results in the local high concentration of vacancies. Void formation and crack nucleation will consequently occur in the early stage of deformation of metals and alloys, leading to HE in the form of ductile rupture.

IV. CONCLUSION

In conclusion, MD simulation of the nanoindentation of Ni(110) is conducted at 300 K using the EAM potential. We find that the critical event for the first dislocation nucleation
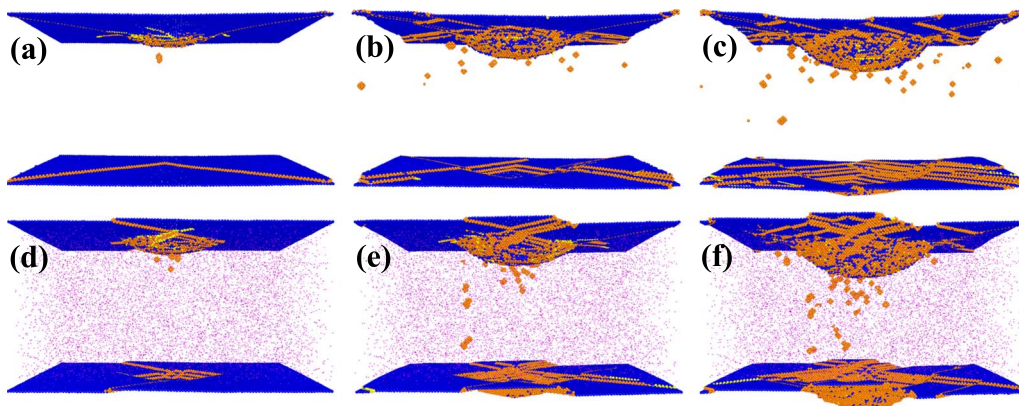

FIG. 5. (Color online) Vacancies during nanoindentation. Snapshots of the H-free specimen at indentation depths of (a) 1.5, (b) 2.5, and (c) 3.5 nm, and of the 1 at. % H specimen at indentation depths of (d) 1.5, (e) 2.5, and (f) 3.5 nm. Only Ni atoms with DI larger than 0.55 are shown to demonstrate vacancies three dimensionally. Ni atoms are colored according to DI with blue (dark gray) corresponding to surfaces and orange (gray) to vacancies and slip lines on the surface. H atoms are shown by small pink (dark gray) spheres.

during nanoindentation is due to the thermally activated formation of a small cluster in which the maximum relative displacement of the atoms are larger than half the magnitude of the Burgers vector of partial dislocations. H only enhances dislocation nucleation slightly; however it promotes dislocation emission, induces slip planarity and enhances localized dislocation activity significantly. The present results, thus, rather than support either the H adsorption model[5,6] or the H shielding model[7] for the HELP mechanism, suggest that HELP is due to the significantly enhanced dislocation mobility induced by eased dislocation emission from dislocation sources by H. HE is the result of earlier void formation and crack nucleation caused by the H-enhanced localized vacancy formation from dislocations. The results provide full insight into the complex process of HE, which helps us in understanding HE in more detail.

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