Simulation of Hydrogen Embrittlement at Crack Tip in Nickel Single Crystal by Embedded Atom Method

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A molecular dynamics simulation by the embedded atom method was conducted to investigate hydrogen embrittlement of a nickel single crystal, which is composed of 163311 nickel atoms on the nanometer scale and has a [011]-oriented notch under uniaxial tension along the [100] direction at room temperature. The hydrogen-free specimen showed good ductility associated with pronounced blunting of the crack tip. Hydrogen influence was most serious in the specimen that had been hydrogen-charged in the notched (100) planes ahead of the crack tip. In the specimen that had been hydrogen-charged in the notched area, a hydrogen-assisted fracture occurred macroscopically on the (100) plane perpendicular to the tensile direction and the elongation at failure decreased with increasing hydrogen content. A low hydrogen content caused strain localization only, while a high hydrogen content caused microvoid formation in the notched area as well. The specimen containing a thin layer of hydride fractured and exhibited brittleness due to significant microvoid formation and subsequent microvoid growth and linkage at the early stage of deformation. The simulation results show good agreement with the published experimental observations.

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1. Introduction

Nickel and nickel-based superalloys have been used for high-temperature devices, e.g., gas turbines, nuclear power plants and aerospace engines. These materials are sensitive to substances in the operating atmosphere such as hydrogen, oxygen or water vapor, so that atmospheric degradation, particularly hydrogen embrittlement (HE), has been a serious problem for these materials. Extensive experimental studies of HE of nickel\(^1\) and nickel-based alloys\(^2\)\(^–\)\(^7\) have been conducted to clarify the process and to ensure the safety of nuclear power engineering and aerospace technology. Even though many experimental studies have been conducted, the effect of hydrogen on the material behavior is very complicated; thus, so far no definitive HE mechanisms of nickel have been established.\(^1\)\(^–\)\(^2\)

Recently, computer simulations using, for example, molecular dynamics (MD), have been applied to elucidate the HE mechanism of metals and alloys at the atomistic level. In particular, the embedded atom method (EAM), which was originally developed by Daw and Baskes based on the density-functional theory,\(^3\)\(^,\)\(^4\) involves the many-body effects and avoids the ambiguity of volume dependence. Thus, EAM has been widely applied to examine the mechanical behavior of materials.\(^5\)\(^,\)\(^6\)\(^,\)\(^7\) EAM was firstly applied to HE of nickel.\(^8\)\(^–\)\(^10\) Hydrogen-induced fracture,\(^1\)\(^1\)\(^,\)\(^12\)\(^,\)\(^13\)\(^,\)\(^16\)\(^,\)\(^17\) dislocation dynamics influenced by hydrogen,\(^1\)\(^8\) and the segregation of hydrogen in the lattice defects\(^1\)\(^9\)\(^,\)\(^20\) have been studied to clarify the HE process of nickel at the atomistic level. In the studies on fracture, Daw and Baskes\(^13\)\(^,\)\(^14\) investigated the influence of hydrogen on the fracture of nickel by the energy minimization method using a semi-infinite slab model consisting of 17 layers of (111) planes with a total of 136 nickel atoms in the simulated region. A small precrack was created inside the simulated region by removing four nickel atoms from the middle plane before simulation. External stresses were applied perpendicularly to the outer (111) planes so that the fracture was constrained to be brittle. It was observed that hydrogen reduced the fracture stress of nickel in the absence of plasticity. Daw and Baskes\(^16\) also studied the influence of hydrogen on the crack tip plasticity of nickel by MD at room temperature using a similar model. Hydrogen was observed to facilitate the formation of a dislocation at the crack tip. Hoagland and Heinisch\(^17\) studied the influence of a single hydrogen atom on the crack tip configuration of nickel by MD near 0 K using a cylindrical model with a radius of 5 nm and a periodical thickness of 0.352 nm along the cylinder axis. It was found that hydrogen facilitated crack propagation and assisted dislocation emission depending on the orientation of the model.

In these simulations, the effect of hydrogen on the fracture of nickel on the nanometer scale with a significant amount of plastic deformation has not been studied, even though experimental studies have shown that HE of nickel usually involves a considerable amount of plasticity.\(^6\)\(^–\)\(^7\)

In this study, an MD simulation with EAM was conducted to study the uniaxial tensile processes of nickel single crystals containing different numbers of hydrogen atoms at room temperature, where a large amount of plasticity was allowed to occur. In particular, attempts were made to investigate the effect of hydrogen distribution on the fracture, which is essential to understand the HE process but still remains uncertain following numerous investigations.\(^12\) The three-dimensional (3D) crack tip model on the nanometer scale, which was originally proposed by our group\(^11\) to study HE of iron, was used in the simulation to reveal the influence of hydrogen on the fracture. The simulation results are discussed in comparison with published experimental results.

2. Molecular Dynamics Simulation

MD with EAM was applied for the simulation. Details of the MD method are described elsewhere.\(^2\)\(^1\) We used the velocity form of the Verlet algorithm to develop the system, and
the ad hoc velocity scaling method to keep the temperature fixed. The EAM potentials for the nickel-hydrogen system proposed by Baskes and coworkers\(^{19,23,24}\) were used in the simulation. This set of potentials was obtained by fitting to a wide range of properties of the nickel-hydrogen system; in particular, the stacking fault energy of nickel was well represented.\(^{19}\)

Experiments revealed that the notched shape enhanced hydrogen-assisted crack nucleation.\(^{25}\) Thus, a 3D model of a nickel single crystal with a crack tip was designed for the simulation, as shown in Fig. 1. The X-, Y- and Z-axes of the model were along the [100], [011] and [011] directions, respectively, while the crack front was parallel to the Z-axis. This geometry has designed to position two primary slip planes, \(i.e.,\) (111) and (111), parallel to the crack front so that the dislocation behavior could be easily observed. The thickness of the crack was designed to be twice as much as the lattice constant of face-centered cubic nickel \((a = 0.352\) nm) to simulate an ultimately sharp crack tip. The geometric size of the model was \(40a \times 20\sqrt{2}a \times 20\sqrt{2}a\) in the X-Y-Z direction, with a total number of 163311 nickel atoms.

The influence of hydrogen was studied by precharging different numbers of hydrogen atoms into the model with various distributions before simulation. Four types of hydrogen distribution specimens, namely, the notched area type specimen, the slip plane type one, the near crack tip type one and the homogeneous type one, were used to examine the effect of hydrogen distribution on HE, as shown in Fig. 2. The cross section of the model along (011) plane is shown in the figure. The number of hydrogen atoms was selected to be of five levels: 100, 500, 1000, 2000 and 4122. The hydrogen atoms were assumed to occupy the octahedral interstitial sites of nickel \((a)\) in the notched \((100)\) planes ahead of the crack tip in the notched area type specimen, \((b)\) along the \((111)\) and \((111)\) slip planes in the slip plane type one, \((c)\) near the crack tip in the near crack tip type one and \((d)\) in the upper part of the model in the homogeneous type one. In the case of 4122 hydrogen atoms, the hydrogen-charged region was equivalent to a thin layer of nickel hydride \((\text{NiH})\) in the notched area type specimen. Lower hydrogen content was then obtained to a thin layer of nickel hydride in the notched area type specimen. Higher hydrogen content was then obtained by randomly choosing a specified number of interstitial sites.

A displacement-boundary condition was applied along the X-axis and free boundary conditions were applied along the Y- and Z-axes to simulate the tensile behavior of the nanometer-scale specimen. Before the uniaxial tension, a certain number of time steps were applied for sufficient relaxation, where the specimens were not subjected to any boundary constraint. The uniaxial tensile displacement perpendic-ular to the \((100)\) crack plane was then enforced on the two ends of the model in the X-axis. The displacement-boundary conditions for these two ends with \(S_X\) preset using a kind of smooth loading method\(^{21}\) to avoid the influence of sudden tensile loading after sufficient relaxation are shown in Fig. 3. At the \(n\)th time step, when \(n_c = n \leq n_r + n_t + n_c\), the magnitude of the displacement \(S_X\) was calculated using the following equation

\[
S_X(n) = -S_0 \left( \frac{n - n_r}{n_t} \right)^4 + 2S_0 \left( \frac{n - n_r}{n_t} \right)^3 ,
\]

and when \(n_r + n_t < n \leq n_r + n_t + n_c\),

\[
S_X(n) = S_0 + \frac{n - n_r - n_t}{n_c} (S_1 - S_0) ,
\]

where \(n_r = 1, 000, n_t = 20, 000\) and \(n_c = 185, 000\) are the time steps for relaxation, transition and constant-strain-rate tension, respectively. \(S_1 = 6.336\) nm is the total amount of displacement for 100% elongation and \(S_0 = S_1 n_t / (n_t + 2 n_c)\). The time increment for each MD step was chosen to be \(1.0 \times 10^{-15}\) s. The simulation was conducted at room temperature \((293.15\) K\) and calculations were continued until fracture occurred.

3. Results

The effect of hydrogen distribution on the deformation of the four types of hydrogen distribution specimens is shown in Fig. 4. General views of the atomic distribution of the specimens precharged with 100, 1000 and 2000 hydrogen atoms at the MD step of 80000 are shown in the figure. In the case of hydrogen-free specimen, good ductility associated with significant blunting of the crack tip and extensive slip deformation was observed to occur along the \((111)\), \((111)\) and \((111)\) planes intersecting around the crack tip, as shown in Fig. 4(a). In the case of hydrogen-charged specimen with 2000 hydrogen atoms, fracture occurred in the notched area type specimen, as shown in Fig. 4(b). Slip deformation was highly localized along the \((111)\) and \((111)\) slip planes, where hydrogen atoms were located, while slip deformation along the \((111)\) and \((111)\) planes was almost completely suppressed in the slip plane type specimen; thus, almost no deformation occurred in the triangular prism shown by \(T\), as shown in Fig. 4(d), while many cross slip deformations were observed in both near crack tip type and homogeneous type specimens, as shown in Fig. 4(f) and (h). In the case of 1000 hydrogen atoms, the deformation behaviors of both near crack tip type and homogeneous type specimens were similar to those with 2000 hydrogen atoms, as shown in Figs. 4(g) and (i). Both notched area type and slip plane type specimens still showed significant hydrogen effect in the case of 500 hydrogen atoms; however, the figures are not shown here. In the case of 100 hydrogen atoms, both notched area type and slip plane type specimens showed little hydrogen effect, as shown in Figs. 4(c) and (e). It is evident from the figure that hydrogen exerted the most serious effect on the notched area type specimen among the four types of specimens with the same number of hydrogen atoms, and a serious effect on the slip plane type specimen, while it had a minor effect on both near crack tip type and homogeneous type specimens. Based on these results, further simulations were primarily made on the notched area type specimen.

General views of the atomic distribution of the hydrogen-free specimen and the specimens of the notched area type at the MD step of 80000 are shown in Fig. 5. The hydrogen-free specimen showed good ductility in Fig. 5(a), as described in Fig. 4(a). Further calculations showed that fracture occurred via shearing along the \((111)\) slip plane at step 136000. In the hydrogen-charged specimens, the deformation behavior apparently depended on the hydrogen content. Fracture had already occurred macroscopically in the specimen with 4122
Fig. 1 3D crack tip model of a nickel single crystal for uniaxial tension.

Fig. 2 Hydrogen distribution in the cross section of the (011) plane of the crack tip model. (a): notched area type specimen, (b): slip plane type specimen, (c): near crack tip type specimen, (d): homogeneous type specimen. Nickel atoms: large blue spheres, hydrogen atoms: small red spheres.

Fig. 3 Smooth loading method for the simulation with displacement, velocity, acceleration and MD steps during uniaxial tension after relaxation. (A transition stage of $n_t$ time steps was designed for smooth loading.).


Fig. 5 General views of the atomic distribution of the hydrogen-free specimen in (a) and the specimens precharged with (b) 100, (c) 500, (d) 1000, (e) 2000 and (f) 4122 hydrogen atoms in the notched (100) planes ahead of the crack tip at the MD step of 80000. (Nickel atoms: large blue spheres, hydrogen atoms: small red spheres.)
hydrogen atoms on the (100) plane perpendicular to the tensile axis with a dominant feature of brittleness, as shown in Fig. 5(f). Although plastic deformation remained considerable and fracture had not occurred in specimens with less than 4122 hydrogen atoms, the crack front had extended into the notched area and the cross section of the notched area of these specimens was much smaller than that of the hydrogen-free specimen, as shown in Figs. 5(b), (c), (d) and (e). The total amount of deformation at fracture decreased with increasing hydrogen content.

The formation and movement of a mixed dislocation occurring in the hydrogen-free specimen during tension are shown in Fig. 6. The atoms on three adjoining layers are shown, as indicated by the legend in (a).

![Fig. 6](image)

Fig. 6 Emission and movement of a mixed dislocation in the hydrogen-free specimen. ((a): before simulation, (b): at MD step 36000, (c): at MD step 39000 and (d): at MD step 42000. Atoms on three adjoining (111) slip planes are shown, as indicated by the legend in (a).)

The formation and movement of a mixed dislocation occurring in the hydrogen-free specimen during tension are shown in Fig. 6. The atoms on three adjoining layers are shown by different colors in the figure. A 1/6[112] partial dislocation had arisen at the lower right corner of the (111) plane at step 36000 in Fig. 6(b), which was followed by a 1/6[211] partial dislocation from the same corner at step 39000 in Fig. 6(c). Between these two partial dislocations, a stacking fault was clearly observed. The partial dislocations moved towards the upper left corner one by one, and finally annihilated after a slip of Burger’s vector 1/2[101]. A trace of dislocation movement on the (111) slip plane, which crossed the (111) primary slip plane, was observed at step 42000 in Fig. 6(d). Detailed observations revealed that slip deformation occurred in all specimens via such kinds of dislocation emission and
movement. The first dislocation usually arose at around step 28000 and was almost not affected by hydrogen.

Cross-sectional views of the middle (100) plane \((x = 0)\) of the specimens precharged with 2000 and 4122 hydrogen atoms in the notched (100) planes are shown in Fig. 7 with the potentials represented by color according to the color bar, where blue indicates lower potential and red, higher potential. Microvoid formation was observed in both specimens in association with the formation of hydrogen molecule, as identified by the potentials of the hydrogen atoms. The potential of molecular hydrogen shown by yellow in the figure was appreciably lower than those of hydrogen atoms in the bulk shown by red. In the specimen with 4122 hydrogen atoms, microvoid formation firstly occurred at the crack tip and then rapidly shifted to the notched area ahead of the crack tip. The first microvoid in the notched area initiated at approximately 25000, as indicated by the arrow in Fig. 7(a), and appreciably grew in size at step 28000 in Fig. 7(b). The specimen finally fractured with little plastic deformation due to significant microvoid formation and subsequent microvoid growth and linkage at the early stage of deformation. In the specimen with 2000 hydrogen atoms, microvoids were also formed in the notched area at step 57000, as indicated by the arrow in Fig. 7(c), and was then followed by the formation of new microvoids at step 60000, as shown in Fig. 7(d). The ductility of this specimen was also significantly reduced due to the microvoid formation.

Cross-sectional views of the middle (100) plane \((x = 0)\) of the hydrogen-free specimen and the specimens precharged with different numbers of hydrogen atoms in the notched (100) planes at the MD step of 80000 are shown in Fig. 8, where the potentials are represented by color according to the color bar. In the hydrogen-free specimen shown in Fig. 8(a) or the hydrogen-charged specimens with less than 2000 hydrogen atoms shown in Figs. 8(b), (c) and (d), no microvoid formation was found until fracture occurred. Large \{111\} facets were only observed around the crack tip on the crack surface of the hydrogen-charged specimens, indicating that the deformation process was still completely a slip process, as shown in Figs. 8(b), (c) and (d). Moreover, the higher the hydrogen content, the smaller the area of the cross section and the deeper the crack front extended into the notched area. The specimens with 2000 and 4122 hydrogen atoms showed rather brittle fractograph, which appeared as a mixture of (100) plat areas and \{111\} facets, as shown in Figs. 8(e) and (f). A comparison with Fig. 7 revealed that the plat areas well corresponded to the locations where microvoid formation occurred. The minimum area of the (100) cross section in the notched region always decreased rapidly with increasing hydrogen content, as shown in Fig. 9. It was thus clarified that low hydrogen content facilitated crack propagation by causing localized plastic deformation around the hydrogen-charged region.

Finally, the influence of hydrogen precharged in the notched (100) planes ahead of the crack tip on the fracture of the notched single crystal of nickel is summarized in Fig. 10. The fracture behavior was strongly influenced by hydrogen. The higher the hydrogen content, the smaller the number of MD steps for crack propagation and fracture. The number of MD steps rapidly decreased with increasing number of hydrogen atoms below 1000 atoms and then decreased linearly with further increase in the number of hydrogen atoms for both crack propagation and fracture.

### 4. Discussion

On the basis of the above simulation results, the fracture of the nickel single crystal was most strongly promoted when the same number of hydrogen atoms was precharged into the notched area ahead of the crack tip. In the HE mechanism by Troiano, it was proposed that HE occurs in notched area...
slightly ahead of the crack tip, where the most severe triaxial-stress state exists and a sufficiently high hydrogen content is obtained via stress-induced diffusion of hydrogen. Following the recent estimation by Vehoff\textsuperscript{12} based on the experimental data on nickel single crystals, hydrogen-assisted crack growth occurs in the fracture process zone about several nanometers ahead of the crack tip, where an extremely high hydrogen content can be obtained by diffusion. Therefore, our simulation results are consistent with the mechanism by Troiano\textsuperscript{25} and strongly support the recent estimation by Vehoff.\textsuperscript{12} By precharging a sufficient number of hydrogen atoms into such a notched area region ahead of the crack tip, we avoided simulating the long-distance hydrogen diffusion, thereby successfully simulating the brittle fracture by hydrogen without hydrogen diffusion.

In the present simulation, HE was observed in all specimens precharged with hydrogen atoms in the notched (100) planes ahead of the crack tip. The hydrogen-assisted fracture occurred macroscopically on the (100) precrack plane perpendicular to the tensile direction and the elongation at failure decreased with increasing number of hydrogen atoms. The detailed HE process strongly depended on the hydrogen content. A low hydrogen content caused strain localization only, and a considerable amount of plastic deformation at failure was still observed. A high hydrogen content caused microvoid formation and a significant reduction in the ductility of the specimen was observed. In particular, the specimen containing a thin layer of hydride fractured and exhibited brittleness due to significant microvoid formation and subsequent microvoid growth and linkage at the early stage of deformation. In contrast, the hydrogen-free specimen showed good ductility associated with significant blunting of the crack tip, and finally fractured via shearing along the slip plane.

HE of notched single crystal of nickel occurred at room temperature with a considerable amount of highly localized plasticity, as has been shown in many experiments.\textsuperscript{2–7} Kamdar\textsuperscript{22} studied HE of nickel single crystal with a sharp crack by means of a tensile test. Significant plastic deformation was observed to occur during crack growth so that the elongation at failure was still considerable. Hydrogen reduced the elongation at failure by approximately 35\% of that of the hydrogen-free specimen in this simulation. Lynch\textsuperscript{3,4} studied HE of nickel single crystal with a notch by means of a bending test, and found that the total amount of plastic deformation was greatly reduced by hydrogen, although extensive slip still occurred on slip planes intersecting the crack tip during crack growth. Fracture occurred approximately on the (100) plane perpendicular to the specimen axis nearly along the (100) direction. Eastman\textit{al.}\textsuperscript{5} investigated HE of nickel single crystal by means of a slow tensile test, and found that the mode of fracture caused by hydrogen was not truly “brittle” but had many features characteristic of a high-degree localized plasticity. Microvoid formation was not found during the whole tension. Vehoff and coworkers\textsuperscript{6,7} investigated HE of nickel single crystal with a notch by means of a low cycle fatigue test under tension. The crystal geometry of the specimen was the same as that of the present model. It was observed that all slip activities were localized at the crack tip. Detailed fractographic examinations revealed that the crack propagated by a mixture of alternating slip along the (111) plane and local brittle fracture along the (100) plane, while the fracture occurred macroscopically on the (100) plane. No microvoid formation was observed until the fracture. Furthermore, experimental studies revealed that nickel hydride caused inherent brittle fracture.\textsuperscript{26} Boniszewski and Smith\textsuperscript{26} reported that cracking could occur along the nickel/nickel hydride interface. Hinotani\textsuperscript{et al.}\textsuperscript{9} found in HE of nickel-chromium-iron alloys that surface cracks were induced by volume expansion due to hydride formation. Although no report on the microvoid formation in nickel hydride was found, Koike and Suzuki\textsuperscript{27} did observe in the HE of vanadium that microvoids nucleated within the vanadium hydride in front of the main crack tip, propagated backwards and joined the main crack tip. Although the specimen size of our simulation is of the nanometer scale, our simulation results show good agreement with the experimental results.

5. Conclusions

An MD simulation with EAM was conducted on HE of a nickel single crystal, which is composed of 163311 nickel atoms on the nanometer scale and has a [011]-oriented notch under uniaxial tension along the [100] direction at room temperature. The influence of hydrogen was examined by precharging different numbers of hydrogen atoms into the model with various distributions. The results obtained were as follows.

1. Hydrogen exerted the most serious effect on the notched area type specimen among the four types of specimens with the same number of hydrogen atoms, and a serious effect on the slip plane type specimen, while it had a minor effect on both near crack tip type and homogeneous type specimens. In contrast, the hydrogen-free specimen showed good ductility associated with significant blunting of the crack tip and finally fractured via shearing along the slip plane.

2. In the notched area type specimen, the hydrogen-assisted fracture occurred macroscopically on the (100) precrack plane perpendicular to the tensile direction and the elongation at failure decreased with increasing hydrogen content. A low hydrogen content caused strain localization only, while a high hydrogen content caused microvoid formation as well. In particular, the specimen containing a thin layer of hydride fractured and exhibited brittleness due to significant microvoid formation and subsequent microvoid growth and linkage at the early stage of deformation.

3. The simulation results show good agreement with the published experimental observations.

REFERENCES