Influence of Hydrogen on Local Mechanical Properties of Pure Fe with Different Dislocation Densities Investigated by Electrochemical Nanoindentation

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In order to investigate influence of dislocation density on hydrogen embrittlement behavior, local mechanical properties of pure Fe with different dislocation densities were measured during hydrogen charging at various load duration times by electrochemical nanoindentation. For as-annealed samples and severely plastically deformed ones with low temperature annealing, hydrogen charging did not change nanohardness at any load duration times between 1 s and 10 800 s. On the other hand, for cold-rolled samples and severely plastically deformed ones without annealing, hydrogen charging caused softening, and the degree of the softening increased at longer load duration times. Consequently, it was found that hydrogen causes softening for samples with higher dislocation density at slower strain rates. The observed softening seems to be caused by increase in dislocation mobility or suppression of work-hardening due to hydrogen atoms trapped around dislocations.

KEY WORDS: nanoindentation; hydrogen embrittlement; dislocation density; iron.
sities were made, and influence of hydrogen on their local mechanical properties was measured by EC-NI.

2. Experimental

Following the steps shown in Fig. 1, pure Fe was subjected to cold rolling and severe plastic deformation, and samples with different dislocation densities were made: as-annealed (AA), cold-rolled (CR), and severely plastically deformed samples (SPD). The annealing was performed in vacuum at 1273 K for more than 1800 s. A reduction rate of the cold rolling was set to 80%. On the other hand, the severe plastic deformation was performed by HPT process,9) where disc samples with a diameter of 10 mm and a thickness \( t \) of 0.85 mm were torsionally deformed under compressive pressure of 5 GPa at room temperature. The number of turns \( N \) was set to five. After the HPT process, \( t \) was decreased to 0.60 mm. A sample with almost the same grain size as, but lower dislocation density than SPD, was also tried to be made by annealing SPD at 473 K for 3600 s (SPD+A) as in Ref. 4). Purity of Fe is shown in Table 1. Commercial pure Fe (Nilaco, 99.99%) with 6 ppm C was used for AA and CR, and pure Fe with 11 ppm C for SPD and SPD+A.

For measuring areas, where indenters are pressed by EC-NI, rolling planes were selected for CR, and areas near the disc center at \( r \approx 1 \text{ mm} \) (\( r \) is a distance from the disk center) for SPD and SPD+A. Equivalent strain of the measuring area of CR is 1.9, and that of SPD calculated from Refs. 10 and 11) \((N = 5, t = 0.60 \text{ mm}, \text{ and } r = 1 \text{ mm})\) is 4.57. Nanohardness of the measuring area in the air were 2.5 GPa, 3.2 GPa, 3.7 GPa, and 3.6 GPa for AA, CR, SPD, and SPD+A, respectively. For SPD, nanohardness was identical in the areas of \( r \geq 0.5 \text{ mm} \). The nanohardness in the air was obtained at load duration time \( t_{\text{uni}} \) of 5 s with the same experimental conditions as for the EC-NI measurements described below. In order to obtain flat and clean surfaces, the sample surface including the measuring area was mechanically polished and finished by electrochemical polishing.

A schematic of experimental setup of the EC-NI measurements is illustrated in Fig. 2. A diamond cube-corner indenter was pressed into the sample surfaces under load control in electrolyte with and without hydrogen charging at room temperature. In order to investigate strain rate dependence, \( \Delta t \) was changed between 0.1 s and 10 800 s at common maximum displacement of about 200 nm. For \( \Delta t < 5 \text{ s} \), nanohardness was obtained by analyzing recorded load-displacement curves by an Oliver-Pharr method. On the other hand, for \( \Delta t \) typically more than 600 s, TD of the indenter causes inaccuracy in the recorded load-displacement curves. Therefore, for \( \Delta t \geq 5 \text{ s} \), load-displacement curves and load-nanohardness ones were indirectly calculated from Young’s modulus and load-contact stiffness relations recorded by modulating the load. The details of the TD compensation method have been described elsewhere.8) Frequency and amplitude of the load modulation were set to 200 Hz and 1.25%–3% of the applied load, respectively. Young’s modulus, which is necessary for the TD compensation, was separately obtained from indentations at \( t_{\text{uni}} = 5 \text{ s} \), where TD is negligible.

Hydrogen charging was performed under current control, and cathodic current density was set to 2.5 A/m\(^2\). For electrolyte and a counter electrode, borate buffer solution (pH 8.62) and a Pt wire were used, respectively. It was confirmed that, in the present hydrogen charging conditions, no corrosion occurs at the sample surfaces during the measurements. Prior to the indentations during the hydrogen charging, precharge was performed for more than 1200 s at the same cathodic current density \((i.e., 2.5 \text{ A/m}^2)\) to saturate hydrogen concentration in the sample subsurface. It was confirmed by thermal desorption analysis that the present hydrogen charging condition is mild, and about 0.1 ppm of diffusive hydrogen is charged for AA.

![Fig. 1. Preparation steps for samples with different dislocation densities.](image)

![Fig. 2. Schematic of experimental setup of EC-NI measurements.](image)

<table>
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<th>Table 1. Chemical composition of pure Fe used in the present study. The unit is mass%.</th>
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<td><strong>Samples</strong></td>
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<td>AA</td>
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<td>CR</td>
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<tr>
<td>SPD</td>
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<td>SPD+A</td>
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NA: Not analyzed
Textures and degree of deformation of each sample were confirmed by measuring inverse pole figure (IPF) images and Kernel average misorientation (KAM) ones of electron back-scattering diffraction (EBSD). For SPD and SPD+A, the images were obtained at the positions of \( r \geq 0.5 \) mm. The dislocation density was also confirmed by analyzing (110), (211), and (220) reflections of X-ray diffraction (XRD) by a Williamson-Hall method.\(^{13}\) Analysis area of XRD is about 20 mm in diameter.

3. Results

3.1. Microstructure and Dislocation Density

The sample AA was composed of equiaxed grains, and an average grain size was about 300 \( \mu m \). IPF and KAM images of CR, SPD, and SPD+A are shown in Figs. 3 to 5, respectively. Frequency distribution of the KAM value is also shown for SPD and SPD+A. The blank (black) areas near the grain boundary in the KAM images correspond to the areas where Kikuchi bands of EBSD are ambiguous. The KAM data in these areas were excluded to obtain the frequency distribution. For CR, large non-equiaxed grains and ultrafine ones with a diameter of about 1 \( \mu m \) were formed (Fig. 3). High KAM areas appeared both in the non-equiaxed grains and the ultrafine ones. On the other hand, SPD and SPD+A were fully composed of ultrafine grains (Figs. 4 and 5). An average grain size was almost the same between SPD and SPD+A: 0.41 \( \mu m \) for SPD and 0.53 \( \mu m \) for SPD+A. High KAM areas were fewer for SPD+A than for SPD, indicating that dislocation density is decreased and strain is released by the annealing at 473 K.

In Table 2, dislocation density of each sample obtained by XRD is shown. The sample with the highest dislocation density was SPD, and the dislocation density was the order of \( 10^{15} \) m\(^{-2} \). In contrast, AA contained very few dislocations, and the dislocation density was the order of \( 10^{12} \) m\(^{-2} \). In accordance with the KAM images in Figs. 4 and 5, dislocation density of SPD+A was smaller than that of SPD. The dislocation densities of SPD+A was slightly smaller than that of CR, and the order of \( 10^{14} \) m\(^{-2} \).

3.2. Influence of Hydrogen on Local Mechanical Property

The indenter was pressed into interiors of large equiaxed grains for AA, and interiors of large non-equiaxed grains

![Fig. 3.](image3.png)  
(a) IPF and (b) KAM images of CR. The arrows represent the areas where ultrafine grains are formed. (Online version in color.)

![Fig. 4.](image4.png)  
(a) IPF image, (b) KAM image, and (c) frequency distribution of KAM value of SPD. (Online version in color.)
and therefore nanohardness with and without hydrogen charging were obtained from the identical grain to eliminate influence of crystalline orientation. The change in nanohardness at different $\Delta t$ was represented by the rate $\Delta H_n$ given by the following equation:

$$\Delta H_n = \left( \frac{H_n^{\text{with H}}}{H_n^{\text{w/o H}}} - 1 \right) \times 100\%,$$  \hspace{1cm} \text{(1)}

where $H_n^{\text{with H}}$ and $H_n^{\text{w/o H}}$ are nanohardness with and without hydrogen charging at the same load, respectively. For AA and SPD+A, $\Delta H_n$ was around zero at any $\Delta t$ between 0.1 s and 10 800 s. On the other hand, for CR and SPD, $\Delta H_n$ was decreased with increase in $\Delta t$, and the tendency was found that larger softening is caused at longer $\Delta t$. Degree of the softening was larger for SPD than CR, and $\Delta H_n$ at $\Delta t = 3\,600$ s was about $-20\%$ and $-10\%$ for SPD and CR, respectively.

4. Discussion

It was revealed by the EC-NI measurements that hydrogen charging does not affect nanohardness for AA and SPD+A, but causes softening for CR and SPD at longer $\Delta t$ (Fig. 7). On the other hand, primary difference between SPD and SPD+A is dislocation density, and the grain size is the almost same between these two samples. This means that grain boundaries, which are likely to interact with hydrogen, do not contribute to the softening so much. Thus, the present EC-NI results indicate that softening is caused by hydrogen for samples with higher dislocation density at slower strain rates. In order to clarify this point, relation between $\Delta H_n$ at $\Delta t = 3\,600$ s and the dislocation density obtained by XRD (Table 2) is plotted in Fig. 8. $\Delta H_n$ at $\Delta t = 3\,600$ s was obtained by fitting the data in Fig. 7 to a straight line in logarithmic scale,

$$\Delta H_n = A \log \Delta t + B,$$  \hspace{1cm} \text{(2)}

where $A$ and $B$ are fitting parameters. It is confirmed from Fig. 8 that hydrogen decreases nanohardness for samples with dislocation density more than about $5 \times 10^{13}$ m$^{-2}$. The present EC-NI results are also qualitatively consistent...
Fig. 6. Load-displacement curves with and without hydrogen charging at different $\Delta t$ of (a) AA, (b) CR, (c) SPD, and (d) SPD+A.

Fig. 7. Relation between $\Delta t$ and $\Delta H_n$. Error bars are shown for SPD as a representative.

Fig. 8. Relation between dislocation densities obtained by XRD and $\Delta H_n$ at $\Delta t = 3600$ s.
with the nanoindentation results by D.-H. Lee et al., where softening is caused by hydrogen for sharper indenters generating more dislocations.\textsuperscript{51}

Regarding the mechanism of the hydrogen-induced softening at slow strain rates in the EC-NI measurements of fcc metals, the authors have proposed two models: (i) increase in dislocation mobility (e.g., decrease in energy barrier for kink-pair nucleation or kink migration in screw dislocations) and (ii) suppression of work-hardening.\textsuperscript{50} The latter is caused, for example, by hydrogen-enhanced cross-slip\textsuperscript{44} or reduction in repulsive interaction among dislocations due to shielding of elastic field by hydrogen.\textsuperscript{15,16} In both models, hydrogen atoms trapped around the dislocations play a roll. Therefore, softening is pronounced at slower strain rates, where the dislocations move slowly and more hydrogen atoms can accumulate around the dislocations.\textsuperscript{17}

One might think that contribution of dislocation mobility change to $H_0$ is trivial because dislocation intersections frequently occur in highly strained volume under the indenter, which likely dominates the deformation resistance of the sample.\textsuperscript{18} On the other hand, it is worth noting that interstitial solute atoms (e.g., carbon) diffusing in a lattice at elevated temperatures can decrease dislocation mobility, and increases deformation resistance in tensile tests even in high strain region (dynamic strain aging).\textsuperscript{19} This suggests that the increase in dislocation mobility by hydrogen can decrease the deformation resistance in high strain region and hence $H_0$.

Y. Koizumi et al. suggested by internal friction measurements and transmission electron microscopy that ultrafine dislocations and transmission electron microscopy that ultrafine dislocations and hence $H_0$ decrease the deformation resistance in high strain region (dynamic strain aging).\textsuperscript{19} This suggests that the increase in dislocation mobility by hydrogen can decrease the deformation resistance in high strain region and hence $H_0$.

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REFERENCES