Electrochemical Nanoindentation Study on Influence of Hydrogen on Local Mechanical Properties of Fcc Metals at Slow Strain Rate

Kota TOMATSU,* Kaori MIYATA and Tomohiko OMURA


A nanoindentation apparatus with an electrochemical cell for cathodic hydrogen charging and a wide dynamic range of load duration time was developed, and influence of hydrogen on local mechanical properties of Type 316L stainless steel, pure Ni, and three kinds of Ni–Cr bialloy (56Ni-43Cr, 69Ni-30Cr, 79Ni-20Cr) was investigated. For Type 316L stainless steel and pure Ni, nanohardness was increased by about 10% and unchanged, respectively, by hydrogen charging at load duration time between 0.1 s and 10 800 s. On the other hand, for Ni–Cr bialloys, degree of nanohardness increase by hydrogen charging was reduced with increase in load duration time. As a result, for 69Ni-30Cr and 79Ni-20Cr, hydrogen caused softening at long load duration time of more than 600 s. Hydrogen embrittlement susceptibility of each sample was also evaluated by slow-strain rate tensile tests, and compared with the observed nanoindentation results. The tendency was found that, for samples with higher hydrogen embrittlement susceptibility, softening is caused by hydrogen charging at long load duration time.

KEY WORDS: nanoindentation; hydrogen embrittlement; stainless steel; nickel; Ni–Cr bialloy.

1. Introduction

Hydrogen embrittlement (HE) is a phenomenon where hydrogen degrades strength or toughness of high-strength steel, and remains a major problem in steel industry. Although HE has been extensively investigated for decades, there are still many uncertainties on its mechanism. One of difficulties in the HE problem arises from the complexity that hydrogen is trapped at various kinds of microstructure such as a grain boundary, a precipitate, and a micro void, and interaction between hydrogen and the individual microstructure is not clear.1) Meanwhile, information on influence of hydrogen on mechanical properties such as hardness and plasticity is important because HE is a kind of fracture phenomenon. Therefore, in order to elucidate the HE mechanism, characterization of influence of hydrogen on mechanical properties of small volume by means of local analytical tools is expected. Historically, nanoindentation (NI) has been employed to measure hardness, elastic modulus, and elastic limit of thin-film materials4,5) or miniature structures,4,5) and is considered promising for this purpose.

At room temperature, hydrogen diffuses in metals and finally desorbs from the metal surface. This means that, even if hydrogen is fully charged into a sample, hydrogen concentration at the subsurface region immediately drops in the air.6) On the other hand, NI is known to be a surface sensitive method, and a typical indentation depth is less than 1 μm. Thus, for the application of NI to the HE problem, in-situ measurements in hydrogen are required. The first in-situ measurements have been conducted by A. Barnoush et al. with an electrochemical nanoindentation (EC-NI), where indentation was performed in electrolyte during cathodic hydrogen charging.7–9) In load-displacement curves of NI measurements, a discrete jump of the displacement with respect to the load, referred to as a “pop-in”, is often observed at elasticity limit. A. Barnoush et al. have found that pop-in load is lowered during hydrogen charging for many metals (e.g., Al, Cu, Ni,7) FeAl,8) and Fe-3%Si(9)), and proposed that hydrogen lowers critical shear stress for homogeneous dislocation nucleation.

However, it is expected that strain rates widely used in the previous NI studies are too fast to cause HE. It is well known that HE becomes pronounced at slower strain rates, where solute hydrogen atoms can follow mobile dislocations. For instance, in slow strain-rate tensile tests (SSRT) of pure iron, hydrogen changes neither fracture elongation, elastic modulus, and elastic limit of thin-film materials2,3) or miniature structures,4,5) and is considered promising for this purpose. However, it is expected that strain rates widely used in the previous NI studies are too fast to cause HE. It is well known that HE becomes pronounced at slower strain rates, where solute hydrogen atoms can follow mobile dislocations. For instance, in slow strain-rate tensile tests (SSRT) of pure iron, hydrogen changes neither fracture elongation, elastic modulus, and elastic limit of thin-film materials2,3) or miniature structures,4,5) and is considered promising for this purpose.

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However, it is expected that strain rates widely used in the previous NI studies are too fast to cause HE. It is well known that HE becomes pronounced at slower strain rates, where solute hydrogen atoms can follow mobile dislocations. For instance, in slow strain-rate tensile tests (SSRT) of pure iron, hydrogen changes neither fracture elongation nor morphology of fracture surface at strain rates of more than 10−5/s.10) Equivalent strain ε around an imprint formed by a spherical indenter with a curvature radius of R is given by the following equation:

$$\varepsilon \approx \frac{1}{5} \frac{\sqrt{R^2 - (R - h_c)^2}}{R}$$

where $h_c$ is a depth of the imprint.11) Substituting typical numerical values ($R=1$ μm, and $h_c=200$ nm) into Eq. (1), ε=0.1 is obtained. Load duration time $\Delta t$ of NI apparatus is typically a few seconds, and therefore, a strain rate (\(\varepsilon/\Delta t\)) is estimated to be about $10^{-2}$/s, which is much faster than
The function $A(x)$ in Eqs. (3) and (4) is a projected area of an imprint with a depth of $x$, and its form is obtained from indentions into a standard specimen (e.g., fused silica). The distance between the sample and the indenter is gradually changed by time because of TD of the indenter and the sample. As a result, when $\Delta t$ is long, the $P-h$ curves are distorted, causing inaccuracy both in $E_r$ and $H_n$.

In the present study, in order to compensate TD and to realize NI measurements at longer $\Delta t$, $P-S$ curves were recorded. Additionally, $E_r$ was separately measured by the O-P method at short $\Delta t$, where influence of TD is negligible. The change in $S$ can be recorded in real time by modulating $P$ and by detecting the synchronized signals in $h$ with a lock-in amplifier. By substituting the measured $S$ and $E_r$ into the Sneddon’s equation in Eq. (3), $h$ at given load $P$ was obtained. Subsequently, $P-h$ and $P$-$H_n$ curves were calculated by substituting, $S$, $P$ and the obtained $h$ into Eqs. (2) and (4), respectively. In principle, $S$ measured instantaneously with the lock-in technique is hardly affected by TD. Hence, the $P-h$ and $P$-$H_n$ curves calculated with the above procedures are also not affected by TD.

### 2.2. Procedure

Type 316L stainless steel (Type316L), pure Ni, and three kinds of Ni–Cr bialloy (56Ni-43Cr, 69Ni-30Cr, and 79Ni-20Cr) with chemical composition in Table 1 were used as samples for the EC-NI measurements. In order to remove residual strain, commercial cold-rolled sheets of Type316L and pure Ni were annealed in an infrared vacuum furnace at 1 270 K for 1 800 s and 900 s, respectively, followed by furnace cooling. On the other hand, as-forged samples were used for Ni–Cr bialloys. The forging temperature was set to about 1 270 K. The sample surfaces, where an indenter is pressed, were mechanically polished with abrasive papers and alumina compounds, and finished by electrochemical polishing. It was identified with atomic force and optical microscopes that all the samples have equiaxed grains, and approximate grain size is 20 $\mu$m for Type316L, 200 $\mu$m for pure Ni, and commonly 50 $\mu$m for the Ni–Cr bialloys. It was also confirmed by X-ray diffraction and transmission electron microscopy (TEM) that all the Ni–Cr bialloys are fully composed of fcc phase and no bcc phase exists.

The EC-NI measurements were performed with a commercial nanoindentation apparatus (Hysitron TriboIndenter 950) with a custom-build electrochemical cell as illustrated in Fig. 2. Volume of electrolyte in the electrochemical cell is about 1 cm$^3$. Hydrogen was charged into the sample at room temperature using borate buffer solution (pH. 8.6) and a platinum counter electrode under current control. Cathodic current density was commonly set to 2.5 A/m$^2$ for all the samples. For the indenter, a spherical diamond indenter

### Table 1. Chemical composition of the fcc metals used in the present study. The unit is mass%.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Fe</th>
<th>N</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>56Ni-43Cr</td>
<td>0.009</td>
<td>0.03</td>
<td>0.5</td>
<td>43</td>
<td>0.14</td>
<td>0.0037</td>
<td>56.11</td>
<td>–</td>
</tr>
<tr>
<td>69Ni-30Cr</td>
<td>0.004</td>
<td>0.01</td>
<td>0.5</td>
<td>30.27</td>
<td>0.12</td>
<td>0.0031</td>
<td>69.17</td>
<td>–</td>
</tr>
<tr>
<td>79Ni-20Cr</td>
<td>0.002</td>
<td>&lt;0.01</td>
<td>0.51</td>
<td>20.22</td>
<td>0.18</td>
<td>0.0027</td>
<td>79.41</td>
<td>–</td>
</tr>
<tr>
<td>pure Ni</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>99</td>
</tr>
<tr>
<td>Type316L</td>
<td>&lt;0.03</td>
<td>&lt;1</td>
<td>16–18</td>
<td>Bal.</td>
<td>–</td>
<td>10–14</td>
<td>2–3</td>
<td>–</td>
</tr>
</tbody>
</table>
with $R = 1 \, \mu m$ was used. In order to compensate TD, $P$ was modulated at 200 Hz with Hystron’s nanoDMA III option. The load amplitude was dynamically changed during indentation, and set to 1.25% or 3% of $P$. $E_r$ used for the TD compensation was separately obtained from indentations at $t = 5$ s. The indenter was pressed into grain interiors under load control, and influence of hydrogen was investigated for the same grain at the same $t$; different grains were pressed at different $t$. $P_{\max}$ was chosen so that $h_{\max}$ becomes around 200 nm, and strain rate was controlled by changing $\Delta t$ between 0.1 s and 10 800 s.

SSRT was performed to investigate HE susceptibility of each sample. For Ni–Cr bialloys, the samples with chemical composition in Table 2 was used, whereas, for the other fcc metals, the same samples as in Table 1 were used. For recrystallization, the Ni–Cr bialloys were annealed at temperatures given in Table 2, and a grain size of 100 $\mu m$ was commonly obtained. Tensile test specimens with 2.54 mm diameter and 25.4 mm gage length without a notch were strained at a strain rate of $3 \times 10^{-4}$ s$^{-1}$ at room temperature.

For the electrolyte, 1N-H$_2$SO$_4$ was used, and 1.4 kg/m$^3$ of CH$_3$N$_2$S was added as a poison. Before the tests, hydrogen was precharged for 10 800 s at cathodic current density of 300 A/m$^2$. During the tests, on the other hand, cathodic current density was decreased to 10 A/m$^2$. The specimens were strained until they are fractured. Morphology of the fracture surface was observed by scanning electron microscopy.

3. Results

3.1. EC-NI Results

3.1.1. Preliminary Experiment

First of all, it was examined if the TD compensation described in Section 2.1 is obtained using 56Ni-43Cr as a sample. $P$-$h$ curves with and without the TD compensation at $\Delta t = 3$ 600 s in the air are shown in Figs. 3(a) and 3(b), respectively. $P$-$h$ curves with the TD compensation in electrolyte without hydrogen charging are also shown in Fig. 3(c). In order to examine reproduducibility, three curves were obtained by pressing the indenter into the same grain in the same experimental conditions. Because $S$ is not obtained with a lock-in technique during unloading, only the loading segments of the $P$-$h$ curve were plotted in the figures. Some spikes were seen in the $P$-$h$ curves with the TD compensa-

![Fig. 2. Schematic of the electrochemical nanoindentation apparatus developed in the present study.](image)
tion at small loads. Generally, $A_r$ is inaccurate for very small $h_r$. As a result, $h_r$, numerically obtained from Eq. (3) using $E_r$ and $S$ is erroneously diverged at small loads, which results in the observed spikes. As expected, a large variation was seen for the $P$-$h$ curves without the TD compensation, whereas the variation was suppressed for the $P$-$h$ curves with the TD compensation both in the air and in electrolyte. It was confirmed that the TD compensation is successfully applied at $\Delta t$ up to 10 800 s.

3.1.2. Influence of Hydrogen

Influence of hydrogen on local mechanical properties at a fast strain rate ($\Delta t=5$ s) was investigated by comparing $P$-$h$ curves obtained with and without hydrogen charging. Changes in $H_n$ obtained by the O-P method are shown in Fig. 4(a). The value of $H_n$ in the figures is an average of about 15 data, and the error bar is their standard deviation. During hydrogen charging, $H_n$ was increased by about 30% for 56Ni-43Cr, and by about 10% for Type316L. In contrast, hydrogen charging did not affect $H_n$ of pure Ni, 69Ni-43Cr, and 79Ni-20Cr. It was found that the degree of $H_n$ increase observed for 56Ni-43Cr was different among different grains. However, large increase by more than 20% was always observed for this sample. When hydrogen charging was stopped, $H_n$ returned to the original value before the hydrogen charging. The observed change in $H_n$ is therefore caused by diffusive hydrogen charged into the samples. Changes in $E_r$ and those in pop-in load by hydrogen charging are also shown in Figs. 4(b) and 4(c), respectively. For all the samples, hydrogen charging changed neither $E_r$ nor pop-in load.

It has been reported in the EC-NI study by A. Barnoush et al. that pop-in load of pure Ni is decreased by hydrogen charging, which is different from the present results. Pop-in load is known to be strongly affected by dislocation density, surface roughness, and also an apex condition of the indenter. It seems that the discrepancy in the influence of hydrogen on the pop-in load arises from difference in these experimental conditions.

Next, $\Delta t$ dependence of influence of hydrogen was investigated using TD compensation. $P$-$h$ curves of 69Ni-30Cr at $\Delta t$ of 5 s, 600 s, and 10 800 s are shown in Figs. 5(a) to 5(c), respectively. The $P$-$h$ curves at $\Delta t \leq 600$ s are an average of five curves, and those at $\Delta t > 600$ s are an average of three curves. At $\Delta t = 5$ s, traces of the $P$-$h$ curves with and without hydrogen charging were identical, indicating that $H_n$ was not changed by hydrogen charging. On the other hand, at longer $\Delta t$, a maximum displacement of the $P$-$h$ curves was increased during hydrogen charging, indicating that $H_n$ was decreased.

In Fig. 6, the relation between $\Delta t$ and the change in $H_n$ corresponding to the data in Fig. 5 is plotted. In the figure, results of the other samples were also given. For different $\Delta t$, $H_n$ of different grains was measured. Therefore, in order to eliminate crystalline orientation dependence, the change in $H_n$ was represented by the rate $\Delta H_n$ calculated from the following equation:

$$\Delta H_n = \left( \frac{H_n^{\text{with}}}{H_n^{\text{without}}} - 1 \right) \times 100, \quad (\text{5})$$

where $H_n^{\text{with}}$ and $H_n^{\text{without}}$ are $H_n$ with and without hydrogen charging at the same $P$, respectively. Error bars of $\Delta H_n$ were shown for 56Ni-43Cr as a representative. A degree of error was almost the same for the other samples. For Ni–Cr bialloys, $\Delta H_n$ was decreased with increase in $\Delta t$. As a result, for 69Ni-30Cr and 79Ni-20Cr, hydrogen-induced softening was seen at $\Delta t \geq 600$ s. On the other hand, for Type316L and pure Ni, $\Delta H_n$ were about 10% and around zero, respectively, irrespective of $\Delta t$.

3.2. Slow Strain-rate Tensile Test

Reduction in fracture elongation by hydrogen charging and morphology of fracture surface of the hydrogen-charged specimen are summarized in Table 3. For Type316L, fracture elongation was not significantly reduced by hydrogen
Table 3. Reduction in fracture elongation by hydrogen charging, and morphology of fracture surface in SSRT.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reduction in fracture elongation (%)</th>
<th>Morphology of fracture surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>60Ni-39Cr</td>
<td>25</td>
<td>Intergranular</td>
</tr>
<tr>
<td>70Ni-29Cr</td>
<td>66</td>
<td>Intergranular</td>
</tr>
<tr>
<td>80Ni-19Cr</td>
<td>89</td>
<td>Intergranular</td>
</tr>
<tr>
<td>pure Ni</td>
<td>18</td>
<td>Quasi-cleavage &amp; dimple</td>
</tr>
<tr>
<td>Type316L</td>
<td>3</td>
<td>Dimple</td>
</tr>
</tbody>
</table>

4. Discussion

It is recognized from the $\Delta H_n - \Delta t$ relation in Fig. 6 that hydrogen charging tends to increase $H_n$ at fast strain rates, and to decrease $H_n$ at slow strain rates. It is also recognized from comparison between the $\Delta H_n - \Delta t$ relation in Fig. 6 and the HE susceptibility in Table 3 that hydrogen charging causes softening at slow strain rates for samples with higher HE susceptibility. In Fig. 7, relation between $\Delta H_n$ at $\Delta t = 3600$ s and reduction in fracture elongation in SSRT is plotted to clarify this relationship. Because the data in Fig. 6 are somewhat dispersed and have a large error, $\Delta H_n$ at $\Delta t = 3600$ s was determined by fitting the data in Fig. 6 to a straight line in logarithmic scale,

$$\Delta H_n = A \log \Delta t + B,$$

where $A$ and $B$ are fitting parameters. It can be confirmed from Fig. 7 that larger softening is caused for the samples with higher HE susceptibility such as 79Ni-20Cr, whereas softening is not caused for the samples with lower HE susceptibility such as Type316L.

The precise mechanism of the observed tendency that hydrogen causes hardening at fast strain rates and softening at slow strain rates is still not clear. However, it is likely that change in dislocation mobility by hydrogen may contribute. S. Taketomi et al. have investigated competitive motion between hydrogen and an edge dislocation in $\alpha$-Fe.
by atomic simulations, and found that hydrogen increases dislocation mobility at slow strain rates and decreases at fast strain rates.\textsuperscript{13} The increase and decrease in dislocation mobility result in hardening and softening, respectively. Although the detailed calculations are necessary, the same phenomena as those in α-Fe are likely to occur also in fcc metals. According to the calculations by S. Taketomi \textit{et al.}, the degree of softening (or hardening) is dominated by hydrogen diffusion coefficient, energy barrier for dislocation motion, or hydrogen concentration. It is considered that the observed difference in ΔH\textsubscript{f}-Δt relation among the different samples in Fig. 6 arises from the difference in these material properties.

Regarding the mechanism of the observed softening at slow strain rates, decrease in degree of work-hardening by hydrogen is also possible. H. K. Birnbaum \textit{et al.} have investigated hydrogen-dislocation interaction by calculation and environmental TEM observation, and suggested that hydrogen weakens repulsive interaction among the dislocations because hydrogen shields elastic fields.\textsuperscript{10,17} Meanwhile, K. Miyata has conducted TEM observations for Ni–Cr bialloys, which exhibited hydrogen-induced softening at slow strain rates in the present study, and reported that hydrogen enhances a cross-slip and increases screw components of dislocations.\textsuperscript{10} When the cross-slip frequently occurs like this, dislocations can move around sessile dislocations, and work-hardening is suppressed. At slow strain rates, the hydrogen shield effect and the hydrogen-enhanced cross-slip become pronounced because there is enough duration time for hydrogen to accumulate around dislocations. Thus, it seems that the observed softening at slow strain rates is also attributed to decrease in degree of work-hardening due to the hydrogen shield effect or the hydrogen-enhanced cross-slip.

\( H_e \) measured in the present study are of grain interiors, whereas samples with higher HE susceptibility exhibited an intergranular fracture as shown in Table 3. In order to fully understand the correlation between HE susceptibility and degree of softening at slow strain rates in Fig. 7, further information on interaction among dislocations, grain boundaries, and hydrogen, are necessary. For instance, TEM observations or mechanical tests of a microstructure containing a single grain boundary (e.g., microprop\textsuperscript{10} and microbending beams\textsuperscript{20,21}) would be useful for this purpose.

5. Summary

A nanoindentation apparatus with an electrochemical cell for cathodic hydrogen charging and a wide dynamic range of Δt was developed, and influence of hydrogen on local mechanical properties of five kinds of fcc metals (Type316L, pure Ni, 56Ni-43Cr, 69Ni-30Cr, and 79Ni-20Cr) was investigated. Furthermore, these observed results were compared with HE susceptibility evaluated by SSRT. As a result, the following findings were obtained.

1. For Type316L and pure Ni, \( H_e \) was increased by about 10% and unchanged irrespective of Δt. On the other hand, for Ni–Cr bialloys, degree of \( H_e \) increase by hydrogen charging was reduced with increase in Δt. Consequently, for 69Ni-30Cr and 79Ni-20Cr, hydrogen charging caused softening at Δt>600 s.

2. There is the tendency that hydrogen charging increases \( H_e \) at slow strain rates, and decreases at slow strain rates. There is also the tendency that, for samples with higher HE susceptibility, softening is caused by hydrogen charging at slow strain rates.

3. The hydrogen-induced hardening at fast strain rates and the hydrogen-induced softening at slow strain rates are qualitatively explained by change in dislocation mobility or decrease in degree of work-hardening.

Acknowledgements

The authors wish to thank Dr. Y. Nishiyama, Dr. N. Sano, and Prof. S. Ogata for their valuable suggestions.

REFERENCES