Hydrogen Effects on Ultrafine-Grained Steels Processed by High-Pressure Torsion

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This article reviews the interactions between hydrogen and lattice defects produced by high-pressure torsion (HPT) process in ferritic iron and austenitic steels, and it shows the direction of development of hydrogen-resistant high-strength steels. In ferritic iron, grain boundaries as well as dislocations participate in hydrogen trapping. For austenitic steels, the contribution of grain boundaries to hydrogen trapping is negligible, while short-circuit diffusion occurs through them. Hydrogen trapping on precipitates caused by annealing after HPT processing depends on the affinity of hydrogen with constituting elements. In metastable austenitic steels, the presence of hydrogen suppresses deformation-induced martensitic transformation through enhanced slip planarity. If hydrogen-containing austenite transforms to martensite, excess hydrogen corresponding to a difference in the solubility between both phases is generated and diffuses out of the martensite, resulting in hydrogen concentration at the interphase. Deformation-induced martensite generated from ultrafine-grained austenite is used to simultaneously enhance strength and ductility without suffering from hydrogen embrittlement.

Keywords: hydrogen embrittlement, ultrafine-grained structures, high-pressure torsion, austenitic stainless steels, grain boundaries, deformation-induced martensitic transformation

1. Introduction

To date, superior high-strength steels have been produced through controlling the microstructures by alloying, mechanical processing, and heat treatment. Unfortunately, it is usual that the high-strength steels having a tensile strength higher than ~1200 MPa are susceptible to hydrogen embrittlement (HE). An important question arises whether the high strength is an unambiguously dominant factor in the mechanism of HE. Originally, the strengthening is often attained by a combination of several mechanisms, e.g., mutual interaction of dislocations, solid solution effect, grain refinement, and fine dispersion of precipitates. The presence of such various strengthening effects complicates understanding the mechanism of HE. The HE is closely related to the interaction between hydrogen and lattice defects such as vacancies, dislocations, grain boundaries, and precipitates. For this reason, the hydrogen/lattice defects interaction has been investigated by several approaches to elucidate the HE mechanism.

The authors have focused on severe plastic deformation (SPD) processes that not only refine the grain sizes but also produce a high density of lattice defects. Among SPD processes, high-pressure torsion (HPT) process is capable of imparting extremely high strain in quantitatively controlled manner. This article provides a new perspective for development of hydrogen-resistant high-strength steels based on the analyses of hydrogen influences on the ultrafine-grained steels processed by HPT.

2. Hydrogen Trapping in Ultrafine-Grained Ferritic Iron and Austenitic Steel

Figure 1 schematically illustrates the process of HPT, of which facility consists of a pair of tool-steel anvils having a shallow circular hole at the centre. A disk-shaped specimen is mounted on the hole and shear strain is imposed on the specimen by rotating the lower anvil with respect to the upper anvil under application of a high pressure. The equivalent strain, \( \varepsilon_{eq} \), introduced by the HPT process is estimated by the following equation:

\[
\varepsilon_{eq} = \frac{2\pi r N}{\sqrt{3}h},
\]

where \( r \) is the distance from the disk centre, \( N \) is the number of rotations, and \( h \) is the thickness of the disk.

Figures 2(a) and 2(b) show Vickers hardness, \( HV \), plotted as a function of the distance from the disk centre, \( r \), after HPT-processing of an Fe–0.01C (in mass%) ferritic iron with a body-centred cubic (bcc) structure and of an Fe–25Ni–20Cr austenitic steel (type 310S stainless steel) with a face-centred cubic (fcc) structure, respectively. The chemical compositions of the iron and steels included in the present article are summarized in Table 1. The HPT processing was conducted using 19 mm diameter disks with ~0.8 mm thickness under a pressure of 1.5 GPa at a rotation speed of 1 rpm for different numbers of turn. Each \( HV \) value represents an average of three measurements at equal distances along the radial direction.
direction spaced at 30° intervals in one quarter of a disk. The data points in Fig. 2 are replotted in Fig. 3 against equivalent strain using eq. (1). The HV values after different numbers of rotations are represented by a unique relation with equivalent strain for both Fe$_{0.01}$C and type 310S. The hardness is saturated to levels at HV $= 400$ for the Fe$_{0.01}$C and HV $= 500$ for the type 310S, which are more than four and three times greater than those of the corresponding unstrained specimens.

Figure 4 shows maps taken by orientation imaging microscopy (OIM) and bright-field images with selected-area electron diffraction (SAED) patterns taken by transmission electron microscopy (TEM) in the Fe$_{0.01}$C after processing by HPT for $N = 1$ and 8.$^{11}$ The former maps were obtained from electron backscatter diffraction (EBSD) analysis at $r = 6.5$ mm where the hardness level was approximately uniform [Fig. 2(a)]. The average grain size, $d_{15}$, separated by high-angle grain boundaries with misorientation angles greater than 15° was $125$ nm after 1 turn [Fig. 4(a)]. The average grain size slightly increased with rotation: $d_{15} = 134$ nm after 4 turns and 141 nm after 8 turns [Fig. 4(b)]. The grain boundary fraction of the misorientation angle in the range of 2 to 5° decreased with increasing number of rotations, and the misorientation angle distribution for $N = 8$ was found to be close to a random distribution. It was also found from Figs. 4(c) and 4(d) that, for the

Table 1 Chemical compositions of steels used for HPT processing.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>H*</th>
<th>Others</th>
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<tbody>
<tr>
<td>Fe$_{0.01}$C</td>
<td>0.01</td>
<td>0.01</td>
<td>0.23</td>
<td>0.012</td>
<td>0.015</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.07</td>
<td>—</td>
</tr>
<tr>
<td>JIS-SUS304</td>
<td>0.05</td>
<td>0.58</td>
<td>1.24</td>
<td>0.025</td>
<td>0.003</td>
<td>8.09</td>
<td>18.54</td>
<td>—</td>
<td>2.2</td>
<td>—</td>
</tr>
<tr>
<td>JIS-SUS316L</td>
<td>0.010</td>
<td>0.53</td>
<td>0.77</td>
<td>0.023</td>
<td>0.001</td>
<td>12.13</td>
<td>17.16</td>
<td>2.86</td>
<td>1.5</td>
<td>—</td>
</tr>
<tr>
<td>JIS-SUS310S</td>
<td>0.04</td>
<td>0.42</td>
<td>0.38</td>
<td>0.019</td>
<td>$&lt;0.001$</td>
<td>20.31</td>
<td>24.69</td>
<td>—</td>
<td>4.7</td>
<td>—</td>
</tr>
<tr>
<td>JIS-SUH660</td>
<td>0.04</td>
<td>0.05</td>
<td>0.42</td>
<td>0.016</td>
<td>0.001</td>
<td>24.30</td>
<td>13.59</td>
<td>1.09</td>
<td>1.2</td>
<td>0.26V, 0.17Al, 2.22Ti, 0.003B</td>
</tr>
</tbody>
</table>

*The hydrogen content was measured by thermal desorption spectrometry.
specimen after $N = 8$, the grain boundaries were well-defined when compared to the specimen after $N = 1$. X-ray diffraction (XRD) measurements confirmed that the dislocation density was decreased with increasing number of rotations.

Figure 5 shows the OIM maps and TEM micrographs of the type 310S after processing by HPT for $N = 1$ and 10. The average grain size after 1 turn was reduced to $\sim 85 \text{ nm}$ [Fig. 5(a)]. There was no marked increase in the average grain size ($d_{15} = \sim 83 \text{ nm}$) for $N = 10$ [Fig. 5(b)].
fraction of low-angle grain boundaries with the misorientation angle in the range of 2°–5° was found to be higher in the type 310S than in the Fe–0.01C, and the rate of decrease in this fraction with increasing number of rotations was lower in the type 310S than in the Fe–0.01C. These differences should be reasonable because the type 310S contains many alloying elements and has a low stacking fault energy, both of which suppress the recovery of dislocations and a subsequent change in microstructure. This is supported by the TEM observation for the HPT-processed type 310S, where there is no significant difference in the dislocation microstructure between \( N = 1 \) and 10 [Figs. 5(c) and 5(d)].

If the hydrogen-trapping sites are lattice defects in the material, the total hydrogen content, \( C_{\text{H}} \), is the sum of the equilibrium hydrogen content within the lattice, \( C_L \), and the content of hydrogen trapped with lattice defects, and it can be simply expressed by: \(^{1)}\)

\[
C_{\text{H}} = C_L + \sum_j (\alpha n_T N_T),
\]

(2)

where \( n_T \) is the fraction of trap sites filled with hydrogen, \( N_T \) is the number of trap sites per unit volume, \( \alpha \) is the unit conversion and \( j \) denotes the type of trap site. Here, \( n_T \) can be expressed by: \(^{1)}\)

\[
\frac{n_T}{1 - n_T} = \frac{c_L}{1 - c_L} \exp \left( \frac{H_B}{RT} \right),
\]

(3)

where \( c_L \) is the atomic fraction of lattice sites filled with hydrogen, \( H_B \) is the binding energy of hydrogen with the trap site, \( R \) is the gas constant and \( T \) is the absolute temperature. Thus, hydrogen trapping is dependent on the binding energy of hydrogen with the trap site. Here, the \( N_T \) values are calculated using the following equations:

(for dislocation)

\[
N_T = \pi r_d^2 \rho N_L,
\]

(4)

(for grain boundary)

\[
N_T = L_{gb} w_{gb} N_L,
\]

(5)

where \( \rho \) is the dislocation density, \( r_d \) is the effective distance from the dislocation, \( L_{gb} \) is the total length of grain boundaries higher than 2° per unit area, \( w_{gb} \) is the width of grain boundary, and \( N_L \) is the number of lattice sites per unit volume. The calculations of \( N_T \) required below use \( r_d = b \), \( w_{gb} = b \), \( N_L = 5.2 \times 10^{29} \text{m}^{-3} \) for the tetragonal site in Fe–0.01C and \( N_L = 2.6 \times 10^{29} \text{m}^{-3} \) for the octahedral site in type 310S. The value of \( \rho \) was estimated from the EBSD measurements, using the following equations: \(^{20)\}

(for bcc metals)

\[
\rho = \frac{14.4 \xi^2}{b^2};
\]

(6)

(for fcc metals)

\[
\rho = \frac{16.1 \xi^2}{b^2},
\]

(7)

where \( b \) is Burgers vector and \( \xi \) is the lattice microstrain. By performing a least-squares fit to the plot of \( \beta \cos \theta \lambda^{-1} \) against \( \sin \theta \lambda^{-1} \) for the measured \( \alpha \) iron peaks (110), (211) and (220), or \( \gamma \) iron peaks (111), (200), (220) and (311), the \( \xi \) values were determined by the following equation: \(^{21)\}

\[
\frac{\beta \cos \theta}{\lambda} = \frac{0.9}{\delta} + \frac{2 \xi \sin \theta}{\lambda},
\]

(8)

where \( \lambda \) is the wavelength of the Co K\( _\alpha \) radiation, \( \beta \) is the line width of the measured XRD peaks, \( \theta \) is the diffraction angle, and \( \delta \) is the coherent domain size. The value of \( L_{gb} \) was used from the EBSD analysis carried out in this study.

Figures 6(a) and 6(b) show a comparison of the measured hydrogen contents, \( C_{\text{H,meas}} \), against the calculated hydrogen contents, \( C_{\text{H,calc}} \), according to eqs. (2) through (5) for the HPT-processed, 60% cold-rolled and unstrained (solution-treated) specimens subjected to hydrogen charging in the Fe–0.01C and type 310S, respectively. \(^{11)\} The hydrogen charging conditions, which are shown in the figure, produced a nearly uniform hydrogen distribution throughout the thin specimens. The specimens were stored in liquid nitrogen (77 K) for the Fe–0.01C and at 188 K for the type 310S immediately after removal from the autoclave. The value of \( C_{\text{H,meas}} \) was measured by thermal desorption spectrometry (TDS) using a quadrupole mass spectrometer at a heating rate of 0.5 K s\(^{-1} \) for
the Fe-0.01C and 0.33 K s⁻¹ for the type 310S from a 5 mm × 5 mm square platelet cut from the outer region beyond 4 mm from the centre of the HPT-processed disk. It is demonstrated that both the hydrogen contents agree well. For the Fe-0.01C, the values of \( C_{\text{H,calc}} \) were calculated by regarding dislocations and grain boundaries including low-angle grain boundaries as the trap sites. Considering the binding energies of hydrogen with the lattice defects in iron, \( H_B = 26.04 \text{ kJ mol}^{-1} \) for dislocations and 19.68 kJ mol⁻¹ for grain boundaries,³ it is well anticipated that grain boundaries as well as dislocations can be trapping sites for hydrogen atoms. In other words, in bcc iron, the grain boundaries not only increase the strength but also are a contributor in hydrogen trapping.

Regarding the type 310S, there was a linear relation between the hydrogen content and the dislocation density despite the fact that the grain sizes were largely different between the HPT-processed and solution-treated (or cold-rolled) specimens.¹¹ This concludes that the grain boundaries rarely contributed to the hydrogen trapping in the type 310S. In Fig. 6(b), the values of \( C_{\text{H,calc}} \) which were calculated by considering only dislocations as the trap sites in eq. (2), are in good agreement with the measured values as \( C_{\text{H,meas}}/C_{\text{H,calc}} = 0.94 \). This finding can be interpreted by the significantly low binding energy of hydrogen with grain boundaries, i.e., ~0 kJ mol⁻¹ compared to that with dislocations, i.e., 13.5 kJ mol⁻¹.²² In the type 310S specimens after processing by HPT, therefore, the contribution of grain boundaries to hydrogen trapping can be neglected. Consequently, an important conclusion arises that, in fcc austenitic steels, an appropriate post-HPT annealing decreases hydrogen trapping to be comparable to the solution-treated material through decreasing the dislocation density, while the strengthening owing to the grain refinement is retained.

3. Grain-Boundary Diffusion and Precipitation Trapping of Hydrogen in Austenitic Steels

Figures 7(a) through 7(c) plot the Vickers hardness, \( HV \), against the average grain size, \( d_{15} \), through annealing after HPT processing for Fe-0.01C,¹⁵ type 310S and Fe-25Ni-15Cr-Ti (type 660 austenitic steel),¹⁶ respectively. For each of the steels, it is apparent that the hardening is mainly controlled by the average grain size having high-angles of misorientations. Nevertheless, the \( HV \) values of the specimens annealed at the lower temperatures appear to be higher than those expected from the Hall-Petch relations, although in general, the \( HV \) rather decreases for grain sizes less than ~0.3 µm.²³ It was reported that hardening occurred by annealing the accumulative roll bonded pure aluminium at a temperature of 423 K.²⁴ However, for the type 310S and 660 steels that contain a large amount of alloying elements, the deviations from the Hall-Petch relations were large compared to that of the Fe-0.01C with little content of alloying elements. It is considered that these deviations can be due to precipitations during the post-HPT annealing, although softening should occur because of the grain growth and the recovery of dislocations. This section focuses on the precipitate trapping and grain-boundary diffusion of hydrogen in austenitic steels.

To examine the hydrogen diffusion including the hydrogen trapping effect, thermal hydrogen gas charging was conducted on the two types of the HPT-processed samples. The hydrogen charging conditions, which are shown in the figure, are sufficient to produce a nearly uniform hydrogen distribution in the thin specimens. This examination was further followed by observing the room-temperature hydrogen release behaviour. Figure 8 shows the residual hydrogen content, \( C_{\text{H,R}} \), plotted against room-temperature holding time, \( t \), after the removal of the charged specimens from the autoclave for both types of the steels.¹⁶ The measured hydrogen diffusivity, \( D_{\text{meas}} \), was derived by fitting the
equation of Demarez et al.\textsuperscript{25}) to the slope of the ln $C_{HR}$ vs. $t$ relation in Fig. 8:

\begin{equation}
C_{HR} = C_{H0} \exp\left[-\left(\frac{\pi^2 h^2}{a^2} + \frac{2\pi^2 \kappa}{a^2}\right) D_{\text{meas}} t\right].
\end{equation}

where $C_{H0}$ is the hydrogen content at $t = 0$ and $\beta$ is a constant. Equation (9) was modified to apply for the square-shaped specimen with a thickness, $h$, and a side length, $a$. In both steels, $D_{\text{meas}}$ was higher in the HPT-processed specimens than in the solution-treated specimens (Fig. 8), despite the fact that the former specimens contained high-density hydrogen trap sites such as dislocations. It is necessary to compare the hydrogen diffusivity after subtracting the dislocation trapping effect.

Based on the trap model by Oriani,\textsuperscript{26}) Hagi and Hayashi evaluated\textsuperscript{27}) the measured hydrogen diffusion coefficient, $D_{\text{meas}}$, including trapping effect using

\begin{equation}
D_{\text{meas}} = \frac{D_{\text{net}}}{1 - \kappa + \kappa \exp\left(\frac{H_B}{RT}\right)}.
\end{equation}

where $D_{\text{net}}$ is the net hydrogen diffusion coefficient, $H_B$ is the binding energy of hydrogen with the trap site where $H_B = 13.5$ kJ mol$^{-1}$ for dislocations,\textsuperscript{22}) $\kappa$ is the ratio of the number of trap sites to that of total lattice sites and is given by eq. (4) for dislocations.

\begin{equation}
\frac{N_T}{N_L} = \frac{\pi}{4} a^2 \rho.
\end{equation}

The dislocation density was determined by XRD measurement. Figure 9 shows plots of $D_{\text{net}}$ against the reciprocal $d_1^{-1}$ of both steels increases with increasing population of grain boundaries. For the type 310S (Fig. 9(a)), the plot of $D_{\text{net}}$ vs. $d_1^{-1}$ exhibits a nearly linear relation independent of the precipitation. This indicates that, excluding the dislocation trapping effect, the hydrogen diffusion was controlled by the grain boundary diffusion, namely, the short-circuit diffusion, but not affected by the precipitation of $\alpha$-FeCr. The short-circuit diffusion through the grain boundaries has been well established in austenitic metals with high activation energies for the hydrogen lattice diffusion.\textsuperscript{28-30)}

As for the type 660 (Fig. 9(b)), the trend in the hydrogen diffusion of the annealed specimens containing the precipitates lies below that of the specimens without the precipitates.
(not annealed). This was attributed to the hydrogen trapping on the γ'-Ni₃(Al,Ti) and η-Ni₅Ti precipitates. Titanium is a hydride forming element, while Ni, Fe and Cr have a weak affinity to hydrogen. Nakatsuka et al. also reported ³⁵) that not only hydride forming elements, e.g., Ti, but also hydride non-forming elements, e.g., Ni, makes a strong chemical bond with hydrogen, when both of these form compounds. In the type 660, therefore, the hydrogen absorption capacity in the matrix is decreased through consumption of Ni and Ti by the precipitation of γ'-Ni₃(Al,Ti) or η-Ni₅Ti, while these precipitates contribute to hydrogen trapping. As for the type 310S, it is suggested that hydrogen trapping on the σ-FeCr precipitates is significantly small compared to the effect of Cr consumption on the hydrogen absorption capacity in the matrix. Hence, a comparison between the results of the type 660 and 310S concludes that the contribution of the precipitates to the hydrogen trapping is dependent on the affinity of hydrogen with the alloying elements and their complexes.

4. Deformation-Induced Martensitic Transformation and Hydrogen Behaviour in Metastable Austenitic Steels

Austenitic stainless steels of interest are well established as structural materials in various industrial sectors owing to their superior corrosion resistance. Among them, metastable austenitic stainless steels possess high strain-hardening ability, which leads to prolonged uniform elongation. These characteristics have been attributed to deformation-induced martensitic transformation. The martensitic transformation characteristics, which are widely known as transformation-induced plasticity (TRIP), are used to simultaneously enhance strength and ductility.³²,³³ However, it has been pointed out³⁴-³⁶ that martensite may deteriorate the resistance to HE, and this observation has often prevented the application of metastable austenitic stainless steels as structural materials in the field of hydrogen industries. This section addresses the role of the deformation-induced martensitic transformation in the mechanism of HE of metastable austenitic stainless steels.

Figure 10 shows OIM observations of Fe–18Cr–8Ni (type 304 stainless steel) specimens processed by HPT (N = 1) with and without hydrogen pre-charge.¹⁰) The hydrogen precharging was conducted by exposure to 10 MPa pressure hydrogen gas at a temperature of 508 K for 200 h. Martensitic transformation occurred in both the specimens and the disk plane of HPT-processed specimens tended to be parallel to \{111\}_γ // (1120) or \{110\}_γ // (0001). [Figs. 10(a) and 10(b)]. High resolution imaging showed that ε martensite was formed more frequently in the hydrogen-precharged specimen than in the uncharged specimen. This is visible as areas of bright yellow in Fig. 10(d). The fraction of ε martensite was 0.3–4.0% for the uncharged specimen and 0.3–15.6% for the hydrogen-precharged specimen, although the fraction range is rather large. HPT processing produced less transformed α' martensite in the hydrogen-precharged specimen than in the uncharged specimen [Figs. 10(c) and 10(d)]. This is clearly observed in Fig. 11(a) which shows the variation of the volume fraction of α' martensite phase with strain in type 304.¹⁰) It can be seen that, for the range of approximately 12 < \(\varepsilon_{\text{eq}}\) < 35, martensitic transformation induced by HPT processing was decreased due to hydrogen precharge. In Fe–16Cr–12Ni–2Mo-low C (type 316L stainless steel) specimen with higher austenite stability, the fraction of martensite induced by HPT was also reduced in the presence of hydrogen as compared to that without pre-charge [Fig. 11(b)]. These findings are consistent with the observation that less deformation-induced martensite was formed at a fatigue crack tip in a hydrogen-charged fatigue specimen than in an uncharged fatigue specimen of type 304.³⁷) Abraham and Altstetter³⁸) showed by slip line observation that the presence of hydrogen enhances slip localization in tensile-tested type 310S stainless steel. Nano-indentation studies on a 21-6-9 austenitic stainless steel by Nibur et al.³⁹) and on type 304 and 316L by Mine et al.⁴⁰) also revealed that hydrogen promotes planar dislocation gliding. It is possible that hydrogen restricted the number of
activated slip systems resulting in enhanced slip planarity. Thus, it is concluded that hydrogen causes a decrease in the intersection of slip systems which can be nucleation sites for α' martensite.\textsuperscript{41,42)}

Using thermal desorption analysis,\textsuperscript{43)} hydrogen content in a specimen can be calculated by integrating the hydrogen desorption profile. In materials with high hydrogen diffusion rates, e.g., bcc iron, the temperature associated with maximum hydrogen desorption during TDS generally indicates the binding energy of hydrogen with trap sites. On the other hand, in the fcc austenitic steels, hydrogen desorption is controlled by hydrogen diffusion and the peak temperature indicates hydrogen diffusivity. In other words, higher diffusivity results in a lower peak temperature of a hydrogen desorption profile.

Figures 12(a) and 12(b) show hydrogen desorption profiles of the solution-treated specimen, cold-rolled specimen and HPT-processed specimen for the type 304 and type 316L, respectively.\textsuperscript{10)} For these measurements, hydrogen charging was conducted by exposure to 94 MPa pressure hydrogen gas at 553 K for 200 h. For the type 304 material hydrogen-charged in the solution-treated state, the peak of hydrogen desorption profile appeared at 606 K and the integrated hydrogen desorption profile, i.e., the hydrogen content, \( C_H \), was 89.4 ppm (in mass). The hydrogen content was much less for the HPT-processed specimen than for the cold-rolled specimen and the peak temperature was shifted to a lower temperature. The HPT-processed type 304 specimen contained approximately 90\% martensite in contrast to 22\% martensite for the cold-rolled specimen. Therefore, the increase in deformation-induced martensite lowered the hydrogen saturation level but enhanced the average hydrogen diffusion rate. It is considered that the difference in hydrogen content between the HPT-processed specimen and the unstrained specimen is due to excess hydrogen that is generated owing to martensitic transformation.

Figure 13 shows hydrogen content vs. room-temperature holding time after the hydrogen-precharged specimens of the type 304 and 316L were processed by HPT, in order to
elucidate the transport of excess hydrogen produced by martensitic transformation. There was no pronounced increase in the residual hydrogen content vs. room-temperature holding time [Fig. 13].

Regarding the HPT processing of the hydrogen-precharged specimens, the martensite formation was localized and the formation of martensite was denser at the necking part. On the other hand, in the hydrogen-charged specimens, the plastic deformation was restricted: the uniform elongation was restricted despite the reduction in the plastic instability of the HPT-processed specimens. The annealing at 873 K after the HPT processing reduced the fraction of the martensite to ~31% [Fig. 15(d)]. This is attributed to a reverse transformation to austenite by the subsequent annealing. The average grain size, $d_{15}$, of ~0.43 µm was obtained for the austenite formed by reverse transformation after annealing at 873 K [Fig. 15(d)]. The XRD analysis revealed the dislocation density was $\sim 1.2 \times 10^{15}$ m$^{-2}$ for the HPT+873 K annealed specimens.

Figures 16(a) and 16(b) show true stress, $\sigma$, curves for the solution-treated and HPT+873 K annealed specimens, respectively. Here, $\sigma$ and $\varepsilon$ were calculated from engineering stress, $\sigma_{e}$, and engineering strain, $\varepsilon_{e}$, obtained by the miniature tensile tests (gage section: $0.5 \times 0.5 \times 1$ mm$^3$), using the following equations:

$$\sigma = \sigma_{e}(1 + \varepsilon_{e}) \quad \text{and} \quad \varepsilon = \ln(1 + \varepsilon_{e}).$$

The arrows in the figure indicate the onset of plastic instability, where necking occurs in the tensile test. A comparison of the uncharged specimens shows that the strain at the onset of plastic instability, i.e., the uniform elongation, of the HPT+873 K annealed specimens was much smaller than that of the solution-treated specimen. It is apparent that the flow stress was drastically increased by the HPT processing. The Ludwick equation interprets that, when the grain size is very small, the plastic instability condition was satisfied in the early stage of the deformation and accordingly the uniform elongation was restricted:

$$\sigma \geq \frac{d\sigma}{d\varepsilon}.$$  

Regarding the HPT+873 K annealed specimen for the type 304, dimple-like ductile fracture feature appeared on the fracture surface and the reduction of area (RA) remained high, as shown in Fig. 17, despite the reduction in the uniform elongation. Thus, an important conclusion emerges that the HPT+873 K annealed type 304 stainless steel did not lose the ductility in a broad sense, although the plastic deformation was localized at the necking part.

The ductility including the uniform elongation [Fig. 16(a)] and the RA [Figs. 14(b) and 14(f)] of the solution-treated specimen was reduced to half by hydrogen charging. There was no difference in the uniform elongation for the HPT+873 K annealed specimens by hydrogen charging [Fig. 16(b)]. For the specimen annealed at 873 K after processing by HPT, the RA is as large as ~60% despite the

5. Mitigation of HE by Grain Refinement in Metastable Austenitic Stainless Steel

Figure 14 shows the hydrogen effect on the fracture morphology of the solution-treated specimens for the type 304. The solution-treated specimen without hydrogen charge had a cup-and-cone type failure with typical dimples on the fracture surface [Fig. 14(a)], and the area reduction was large not only at the necking part but also at a part remote from the fracture surface [Fig. 14(b)]. Figure 14(c) indicates that the grains were substantially elongated in the direction parallel to the tensile axis and that the $\alpha'$ martensite was densely formed in the vicinity of fracture surface at a cross section of the tensile specimen. On the other hand, in the hydrogen-charged specimen at a content of ~25 ppm [Fig. 14(d)], the plastic deformation was localized and the formation of $\alpha'$ martensite was less than that in the uncharged specimen. The hydrogen-charged specimen ruptured on the plane macroscopically normal to the tensile direction and had many microcracks on the specimen surface after the tensile testing [Fig. 14(f)]. The fracture surface was composed of the features of quasi-cleavages and dimples [Fig. 14(e)].

Martensitic transformation causes the low solubility but the high diffusivity of hydrogen in the martensite compared to the counterparts in the austenite matrix, as shown in the previous section. Taking this into consideration, it is natural to presume that the hydrogen concentration inside the austenite rather than the hydrogen uptake into the martensite formed by straining leads to the HE. It is then hypothesized that, if the formation of martensite is refined, the hydrogen concentration is minor.

Figure 15 shows the OIM maps of the type 304 disks after processing by HPT and subsequent annealing at a temperature of 873 K. The HPT processing induced an $\alpha'$ martensitic transformation with a volume fraction of ~78% [Fig. 15(a)]. It can be seen from Fig. 15(b) that a lamellar microstructure was developed by severe plastic deformation through HPT. By the XRD analysis, the density of dislocations in the $\alpha'$ martensite of the HPT-processed specimen was $\sim 6.5 \times 10^{15}$ m$^{-2}$. The annealing at 873 K after the HPT processing reduced the fraction of $\alpha'$ martensite to ~31% [Fig. 15(c)]. This is attributed to a reverse transformation to austenite by the subsequent annealing.
hydrogen charge [Figs. 17(a) and 17(b)]. It is concluded that, in the duplex microstructure consisting of austenite and \(\alpha'\) martensite developed by the HPT process and subsequent annealing, hydrogen of \(\sim 20\) ppm decreased the ductility to a minor extent through localized plastic deformation, but led to no severe HE as for the solution-treated specimen subjected to the hydrogenation under the same condition.

Figures 18(a) and 18(b) plot the elongation to failure against the tensile strength for the type 304\(^{13}\) and 310S specimens\(^{14}\) respectively. These specimens include the solution-treated, HPT-processed, and HPT+annealed specimens. The ductility was greater restored by post-HPT annealing in the type 304 than in the type 310S. This may be due to martensitic transformation induced during straining. Figure 19 presents the OIM maps in the vicinity of the fracture surface at a mid-cross section of the uncharged and hydrogen-charged, HPT+873 K annealed type 304 specimens. In both specimens, plastic flow was well developed in
the necking parts, although the $\alpha'$ martensite was slightly less formed in the hydrogen-charged specimen than in the uncharged specimen. It is therefore concluded that the ductility is relatively insensitive to hydrogen but it is a consequence of limited ductility due to enhanced strength.

6. Concluding Remarks

This article addresses coupled metallographic examination with hydrogen desorption analysis of ultrafine-grained steels after exposure to thermal hydrogen gas, and, in particular, focuses on hydrogen and mechanical behaviours in ultrafine-grained metastable austenitic steels produced by the process of high-pressure torsion (HPT) and annealing. The conclusions can be summarized as follows:

1. In bcc iron, grain refinement not only enhances the strength but also participates in hydrogen trapping.
2. In ultrafine-grained austenitic steel with an fcc structure,
the contribution of grain boundaries to hydrogen trapping is negligible.

(3) Short-circuit diffusion of hydrogen occurs through increased grain boundaries in ultrafine-grained austenitic steels produced by HPT.

(4) Annealing the HPT-processed austenitic steels promotes the precipitation of alloying elements through the strain energy introduced by HPT processing. Hydrogen trapping is strongly dependent on the hydrogen affinity with the alloying elements composing the precipitates.

(5) In metastable austenitic steels, \( \alpha' \) martensitic transformation is suppressed in the presence of hydrogen. This is attributed to enhanced planarity of slip due to hydrogen.

(6) If hydrogen-containing austenite is transformed to \( \alpha' \) martensite, excess hydrogen corresponding to a differ-
ence in the solubility between both phases is generated and diffuses out of the martensite with the high hydrogen diffusivity.

(7) Hydrogen charge in type 304 stainless steel with an ultrafine-grained (γ + α′) duplex microstructure at the level of ~20 ppm leads to no severe hydrogen embrittlement.

It is expected that deformation-induced martensite generated from ultrafine-grained austenitic steels is used to simultaneously enhance the strength and ductility without suffering from hydrogen embrittlement.

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REFERENCES