Effects of Stress and Plastic Strain on Hydrogen Embrittlement Fracture of a U-bent Martensitic Steel Sheet

Yuki SHIBAYAMA,1,2) Tomohiko HOJO,1) Motomichi KOYAMA,1) Hiroyuki SAITO,3) Ayumi SHIRO,3) Ryo YASUDA,3) Takahisa SHOBU,4) Takashi MATSUMOTO5) and Eiji AKIYAMA1)

1) Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, 980-8577 Japan.
2) Graduate School of Engineering, Tohoku University, 6-6-01-2 Aramaki Aza Aoba, Aoba-ku, Sendai, 980-8579 Japan.
3) National Institute for Quantum and Radiological Science and Technology (QST), 1-1-1, Kouto, Sayo-cho, Hyogo, 679-5148 Japan.
4) Japan Atomic Energy Agency (JAEA), 1-1-1, Kouto, Sayo-cho, Hyogo, 679-5148 Japan.
5) Tottori University, 4-101 Koyama-cho-minami, Tottori, 680-8552 Japan.

* Corresponding author: E-mail: hojo@imr.tohoku.ac.jp

The effects of stress and plastic strain distributions on the hydrogen embrittlement fracture of the U-bent martensitic steel sheet specimen were investigated. The hydrogen embrittlement testing of the U-bent specimen was performed. Fracture morphology mainly consisting of intergranular fracture was found inside the hydrogen charged U-bent specimen, which indicated that the crack initiation took place in the interior, and shear lips were found near both surfaces of the U-bent sheet. The synchrotron X-ray diffraction measurement and the finite element simulation were utilized to analyze the stress and plastic strain distributions in the thickness direction of the U-bent specimen. The elastic strain distributions obtained by the measurement showed a good agreement with the simulation. The crack initiation site of the hydrogen-charged U-bent specimen was considered to be correspondent with the region where the tensile stress was the highest, suggesting that the maximum tensile stress predominantly determine the crack initiation.

KEY WORDS: martensitic steel; hydrogen embrittlement; X-ray diffraction; finite element simulation.

1. Introduction

High-strength steels have been applied for automobiles and structural materials to reduce the weight and size of the components. However, hydrogen embrittlement should be concerned for high-strength steels because hydrogen embrittlement susceptibility increases with increasing the tensile strength.1) Especially, the hydrogen embrittlement susceptibility of the press-formed advanced high-strength steels (AHSSs) of the tensile strength of 1 500 MPa grade applied for the automotive structural part is predicted to be high. To characterize hydrogen embrittlement susceptibility of the automotive parts of press-formed high-strength steel sheets, the hole-expanding,2) disk pressured,3) deep drawn,4–7) stretch-formed8) and U-bent9–16) specimens have been adopted. In general, in the evaluation method for hydrogen embrittlement properties using a U-bent specimen, a rectangular steel sheet is first bent in a U-shape to introduce a plastic strain, and then the feet of the U-bent steel sheet are tightened by a bolt and nut to apply elastic strain (i.e. stress). Subsequently, cathodic hydrogen charging or immersion in hydrochloric acid is conducted to introduce hydrogen into the samples, and the occurrence of cracking due to the introduced hydrogen is examined. In this method, the criterion of the occurrence of hydrogen embrittlement is identified with the three variables, namely applied plastic strain, applied stress and absorbed diffusible hydrogen content.

The previous paper of authors have proposed an evaluation method of hydrogen embrittlement property using a U-bent specimen.16) In the method, the bolt-tightened U-bent specimen was charged with hydrogen by galvanostatic polarization and the current density was increased in a stepwise manner until fracture takes place, and the critical hydrogen charging condition was obtained. In the previous study, the degree of tightening of the U-bent specimen was varied by measuring the stress using a strain gauge attached on the outer surface of the top of the specimen. However, the dependence of the critical hydrogen charging condition on the applied stress at the outer surface was not apparent.
for the martensitic steel sheet used.\textsuperscript{16} Since the fractography suggested that the crack initiation site in the U-bent specimen was located around the center in the thickness direction, estimation of the stress and plastic strain distributions in the thickness direction was thought to be required to improve the evaluation method.

Wang et al.\textsuperscript{17,19} performed slow strain rate tensile test of circumferentially notched round bar specimens of a martensitic steel pre-charged with hydrogen. They carried out the finite element (FE) simulation to analyze the stress and the plastic strain distributions in the specimen and estimated the accumulated hydrogen concentration considering the stress-induced hydrogen accumulation. They have reported that the relationship between the peak value of the maximum principal stress for fracture and the estimated local diffusible hydrogen concentration followed the power law and that localization of the stress and hydrogen slightly inside of the notch root of the specimen strongly affected the degradation of mechanical properties of the martensitic steel.

For the U-bent specimen, it must be also important to know the stress distribution and their effects on hydrogen embrittlement fracture. For the mechanism of hydrogen embrittlement of the dual-phase (DP) steel,\textsuperscript{12,15} transformation-induced plasticity (TRIP)-aided steel and partitioning (Q&P) steel of the U-bent specimen,\textsuperscript{15} it has been reported that the initiation of the fracture due to the hydrogen embrittlement was the coalescence of microvoids and micro-fractures, which were introduced by the relatively high plastic deformation of the U-bent specimen, and that these defects accelerated the crack propagation. Therefore, it is required to consider the effect of plastic deformation on hydrogen embrittlement of the U-bent specimen as well as the stress and hydrogen distributions.

In this study, the hydrogen embrittlement testing of the U-bent specimen of a martensitic steel sheet was performed. Aiming at clarifying the effect of the stress distribution inside of the U-bent specimen on the occurrence of hydrogen embrittlement, the synchrotron X-ray radiation in SPring-8 was utilized because hard X-rays can penetrate the steel sheet specimen, which enables us to obtain X-ray diffraction data inside of the specimen. In addition, finite element analysis was carried out to obtain the stress and plastic strain distributions. The stress distributions experimentally obtained by means of the energy-dispersive X-ray diffraction using the hard X-rays and that calculated from the FE simulation were compared, and the effects of stress and plastic strain distributions on the hydrogen embrittlement fracture of the U-bent specimen were examined.

2. Experimental Procedure

2.1. Preparation of the U-bent Specimen

A commercial JIS-SCM435 steel sheet was normalized at 800°C for 1 800 s, quenched from 900°C for 900 s and subsequently tempered at 400°C for 1 800 s. After the heat treatment, the steel sheet was ground to a thickness of 1.6 mm. The resultant microstructure of the heat-treated steel sheet was tempered martensite as shown in Fig. 1. The tensile strength was 1 492 MPa. Rectangular specimens of 100 mm length × 30 mm width × 1.6 mm thickness with two holes for bolt tightening were machined from the heat-treated steel sheet as shown in Fig. 2(a). The rectangular sample was deformed into a U-bent specimen using a U-bending jig with an upper roll with a radius of 10 mm (Fig. 2(b)) so that the bending radius of the specimen was 10 mm. Then, the stress was applied to the U-bent specimen by tightening a bolt and nut (Fig. 2(d)). The applied stress (elastic strain) was measured by using a strain gauge attached on the outer surface of the top of the U-bent specimen and the elastic strain was set to a level of 4 854×10−6, which is correspondent to 1 000 MPa.

2.2. Hydrogen Embrittlement Test

The hydrogen embrittlement test of the bolt-tightened U-bent specimen followed the method described in the previous paper.\textsuperscript{16} Hydrogen charging to the specimen was carried out using galvanostatic polarization in a 3 wt% NaCl aqueous solution containing 0.3 g/L or 3.0 g/L of NH₄SCN at 25°C. The absolute value of the applied hydrogen charging current density was increased in a stepwise manner and each step was kept for about 12 h in order to obtain a homogeneous distribution of hydrogen concentration throughout the specimens. The specimen surface was interval-filmed with a digital camera to record the crack initiation and propagation. The hydrogen charging current density was increased step-wisely until hydrogen embrittlement occurred. After the test, the fracture surface was cut out from the specimen and was observed by using a scanning electron microscope.

2.3. Analysis of Elastic Strain by Synchrotron X-ray Diffraction Method

The beam line BL14B1 of QST (National Institutes for Quantum and Radiological Science and Technology) at SPring-8 was used for the energy-dispersive X-ray diffraction measurements\textsuperscript{19,20} to analyze the stress distributions in the as-U-bent and bolt-tightened U-bent specimens. The specimen preparation procedures are the same as those mentioned above.

In this study, the white X-rays and a Ge semiconductor detector were used. Figure 3(a) shows the pass way of the white X-rays of incident and diffraction sides, and the gauge volume viewed from the X-axis direction. The height of both incident and receiving slits were 50 μm, and
the widths of the incident and receiving slits were 300 and 500 μm, respectively. The penetrated X-rays were limited by the collimator of 50–200 μm, and the detector was set at a diffraction angle, $2\theta$, of 10°. Since the hydrogen embrittlement crack formed on the U-bent specimen parallel to the width direction (perpendicular to the circumferential direction), the elastic strain in the circumferential direction has the predominant role on cracking. Therefore, the elastic strain in the circumferential direction was measured in this study. As shown in Fig. 3(b), the X-ray measurements were carried out at 20 points in the top of the U-bent part with an interval of 100 μm within the range of $y = \pm 1$ mm from the center of the thickness ($y = 0$). Note that the measured profile of each point included the diffraction characteristics in the gauge volume whose cross-sectional size was roughly 50 μm in height × 600 μm in depth, and the resolution of the analysis was limited by the gauge volume. When the measurement point was near the edge of the specimen, the diffraction peak was low because the gauge volume partially covered the outside of the specimen. The data points near the edge of the specimen were omitted. The diffraction peak of $\alpha$-Fe321 was approximated by the Gaussian function to obtain the peak-center energy. The elastic strain in the circumferential direction was simulated from Eq. (1) using the lattice spacings, $d$ and $d_0$. Here, $d$ is the lattice spacing of the measured point and $d_0$ is the lattice spacing of the undeformed part without stress. The lattice spacings of $d$ and $d_0$ were obtained from the correspondent peak-center energies of the $\alpha$-Fe321 diffraction peaks obtained from the strained part, $E_{in}$, and the undeformed part, $E_{in0}$, respectively.

$$\varepsilon = \frac{d - d_0}{d_0} = \frac{E_{in} - E_{in0}}{E_{in0}} \quad \text{(1)}$$

2.4. FE Simulation of U-bent Specimens

In this study, the finite element (FE) simulation was conducted to estimate the stress distributions in the U-bent specimen introduced during the U-bending, the as-U-bent specimen after the spring-back following the U-bending and the bolt-tightened U-bent specimen. The FE model of the U-bent specimen was assumed as an isotropic elasto-plastic model. The strain hardening was assumed to be isotropic as well, following a Swift law (Eq. (2))

$$\sigma = a(b + \varepsilon)^N \quad \text{(2)}$$

in which $a$, $b$ and $N$ are material-dependent parameters, which have been identified using the least square method on the true stress-strain data obtained from a tensile test of the tempered martensitic steel sheet. Mechanical parameters used in this FE analysis are listed in Table 1, and the comparison between the true stress-strain curve experimentally measured and that approximated using the Swift law are

---

**Fig. 2.** Preparation procedure of U-bent specimen; (a) rectangular specimen; (b) stage 1, three-point bending; (c) stage 2, tools removal; (d) stage 3, tightening U-bent specimen with a bolt and nut.

**Fig. 3.** Geometry of specimen and beam alignment; (a) schematic of gauge volume using transmitted diffraction X-ray; (b) measurement positions and mounted positions of strain gauges.
shown in Fig. 4.

The FE simulation was conducted under the two-dimensional plane strain assumption. The specimen was meshed using 4 nodes reduce integration elements with a size of 0.05 mm. The total number of elements and nodes were 64000 and 66033, respectively. Non-interpenetration and friction coefficient of 0.1 at a contact condition between the bending rolls in Fig. 2(b), which were assumed to be rigid bodies, and the U-bent specimen were imposed in this simulation. The FE simulation of U-bending and the elastic strain applied by bolt tightening was carried out in three steps. In the 1st step (Fig. 2(b)), the upper roll pushed down the rectangular specimen to bend the specimen until the displacement reached the value used in the experiment. Then, the upper roll returned to the initial position to complete the U-bent forming in the 2nd step (Fig. 2(c)). Finally, in the 3rd step, the feet of the U-bent specimen were tightened by the bolt and nut (Fig. 2(d)). To compare with the elastic strain in the circumferential direction measured by means of the synchrotron X-ray diffraction, the elastic strain in the circumferential direction was calculated by the FE simulation. In addition, the distributions of the maximum principal stress and equivalent plastic strain in the bolt-tightened U-bent specimen were calculated.

3. Results and Discussion

3.1. Hydrogen Embrittlement Test and Fractography

The hydrogen embrittlement test was conducted on the 1500 MPa grade tempered martensitic steel U-bent specimen of $R = 10$ mm with the applied stress of 1000 MPa on the outer surface of the top of the specimen. Since the specimen charged with hydrogen in a 3 wt% NaCl + 0.3 g/L NH$_4$SCN aqueous solution was not fractured even at high hydrogen charging current density, the hydrogen charging solution was replaced to a 3 wt% NaCl + 3 g/L NH$_4$SCN aqueous solution to enhance hydrogen entry. The hydrogen embrittlement fracture occurred 9 h after the current density was increased to 0.6 A/m$^2$.

Figure 5 shows the fracture surfaces of the hydrogen-charged U-bent specimen. The U-bent specimen exhibited an intergranular fracture appearance mixed with quasi-cleavage morphology in the interior in the thickness direction (Figs. 5(a) and 5(c)). The observed region was around the center in the width direction of the specimen. A shear lip region could also be observed in the vicinity of the outer surface of the U-bent specimen (Figs. 5(a) and 5(b)). The intergranular fracture evidenced brittle fracture mechanism, and hydrogen in the steel presumably decreased the cohesive interatomic forces, leading to brittle crack initiation and propagation through the grain boundaries. On the other hand, because of the difference in the plastic constraints between the surface and the interior of the specimen the brittle crack was arrested and shear lips were formed by shear failure with plastic deformation near the surface of the specimen. An obvious step was observed around the center in the thickness direction. This step might be formed when the crack propagated toward the inner surface of the specimen. Thus, the fractography suggested that the crack was initiated in the region below the shear lip and above the large step in the image of Fig. 5(a) and that the crack propagated toward the outer and inner surfaces of the specimen. Figure 5(d) shows the magnified view of a region located at a distance in the width direction from the region shown in Fig. 5(a), and at the position in the thickness direction slightly close to the outer surface compared with that in Fig. 5(c). The fracture surface consisted of dimples and quasi-cleavage patterns mixed with a small amount of intergranular fracture surface showing less brittle features than the region shown in Fig. 5(c). The region shown in Fig. 5(d) is probably correspondent to the region where the crack, initiated around the center of the width direction, propagated.

3.2. Analysis of Stress Distribution

Figure 6 shows energy-dispersive X-ray diffraction patterns of the undeformed specimen obtained with the data acquisition time of 180 s. Numbers of peaks of diffraction planes appeared in the range from 50 to 150 keV, and the $\alpha$-Fe$_{321}$ diffraction peak was sufficiently high for the elastic strain measurement. Figure 7 shows the $\alpha$-Fe$_{321}$ diffraction peak of the undeformed specimen measured at the center of the thickness direction, $y = 0$, and the positions ±0.4 mm away from the center. Here, the position means the location of the center of the gauge volume shown by the hatched rhombus in Fig. 3(a). These three profiles were almost the same, and the peak energy corresponding to no elastic strain, $E_{\text{as}}$, was determined to be 92.79 keV.

Figure 8 shows the $\alpha$-Fe$_{321}$ diffraction profile of the as-U-bent specimen. Figure 8(a) shows the diffraction patterns obtained at $y = \pm 0.3$ mm, and the $\alpha$-Fe$_{321}$ diffraction energy peak shifted from $E_{\text{as}}$ to the low energy direction at $y = -0.3$ mm and to the high energy direction at $y = +0.3$ mm. The peak energy shifts to the low and high energy directions indicate the increase and decrease in the

**Table 1.** Mechanical parameters of the steel sheet.

<table>
<thead>
<tr>
<th>$E$/MPa</th>
<th>$v$</th>
<th>$a$</th>
<th>$b$</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>206 000</td>
<td>0.3</td>
<td>1.8419</td>
<td>0.0001</td>
<td>0.0485</td>
</tr>
</tbody>
</table>

$E$: Young’s modulus, $v$: Poisson’s ratio, $a$, $b$, $N$: material-dependent parameters.

![Fig. 4](image-url)  
**Fig. 4.** True stress-strain behaviors of experimental and identification data of tempered martensitic steel sheet.
lattice spacing, $d$, respectively. In other words, the tensile and compressive stresses were applied at the measured portions of $y = -0.3$ and $+0.3$ mm, respectively. On the other hand, the $\alpha$-Fe321 diffraction energy peak obtained at $y = +0.1$ mm of the as-U-bent specimen shown in Fig. 8(b) was broad, suggesting superposition of peaks. The diffraction peak could be deconvoluted to two Gaussian peaks with negative and positive shifts from $E_{0\theta}$. This indicates that portions with tensile and compressive stresses coexisted in the gauge volume.

By using the synchrotron X-ray radiation, the elastic strains inside of the U-bent specimens were successfully measured. Figure 9 indicates the comparison of the in-depth distributions of the elastic strain in the circumferential direction measured by using synchrotron X-ray diffraction with that obtained by FE simulation. Figures 9(a) and 9(b) show the result for the as-U-bent specimen and the bolt-tightened specimen with the applied tensile stress of 1 000 MPa at the outer surface of the top, respectively. There was a good agreement between the elastic strain distributions obtained by means of synchrotron X-ray diffraction measurement and FE simulation both for the as-U-bent and bolt-tightened specimens. Near the center in the thickness direction, the $\alpha$-Fe321 diffraction energy peaks measured were broad.
and they could be deconvoluted to two peaks at low and high energy compared to $E_{n0}$, which were correspondent to the tensile and compressive elastic strains, respectively, as representatively shown in Fig. 8(b). This indicates that the stress state changed from tensile to compressive sharply in the gauge volume when the gauge volume was around the center. Correspondingly, the FE simulation showed the sharp change of the elastic strain from tensile to compressive around the center in the thickness direction. As shown in Fig. 10, the similar trend of the elastic strain distributions was observed when the average elastic strain in the circumferential direction measured by synchrotron X-ray diffraction and that calculated using FE simulation as a function of the position in the thickness direction. As shown in Fig. 10, the similar trend of the elastic strain distributions was observed when the average elastic strain in the circumferential direction measured by synchrotron X-ray diffraction and that calculated using FE simulation as a function of the position in the thickness direction. As shown in Fig. 9(a), in the as-U-bent specimen, the compressive residual strain in the circumferential direction existed near the outer surface, whereas the tensile residual strain existed near the inner surface because of the large degree of spring-back after U-shape bending. The maximum tensile and compressive strains existed inside of the specimen and the residual stress gradient along the thickness direction near the center was steep. From the outer surface to the maximum tensile elastic strain region, the elastic strain was linearly increased whereas the opposite tendency was observed from the inner surface to the maximum compressive elastic strain region in the as-U-bent specimen, and the elastic strain distribution was nearly symmetric with the center of the thickness direction as the axis of symmetry. As shown in Fig. 9(b), the outer surface of the bolt-tightened U-bent specimen exhibited tensile elastic strain due to the applied tensile stress of 1 000 MPa to the outer surface of the top of the U-bent specimen, and the elastic strain gradient was less steep than that of the as-U-bent specimen. The maximum tensile and compressive elastic strains appearing near the center in the thickness direction were almost the same as that of the as-U-bent specimen.

In the previous study of some of the authors of this paper, critical hydrogen content for hydrogen embrittlement fracture of the U-bent specimen, which is the same as that in the present study, was not clearly dependent on the stress applied by the bolt tightening. This result was presumably attributed to the less significant change in the maximum
tensile stress in the circumferential direction located near the center in the thickness direction of the U-bent specimen due to the bolt tightening.

3.3. Stress and Strain Distributions

Figure 11 shows the FE simulation results of the distributions of the stress in the circumferential direction, the maximum principal stress, hydrostatic stress and equivalent plastic strain for the bolt-tightened U-bent specimen with applied stress of 1 000 MPa on the outer surface of the top of the specimen. The maximum principal stress, the maximum tensile stress in the circumferential direction and the hydrostatic stress were located on the slightly outer surface side from the center of thickness direction, whereas the maximum compressive stress in the circumferential direction was seen at 0.15 mm from the center of thickness direction (Fig. 11(a)). In contrast, the maximum equivalent plastic strain appeared on both sides of the specimen surfaces (Fig. 11(b)). Comparing the distributions of the maximum principal stress and the stress in the circumferential direction and the fracture surface shown before, it was suggested that the stress in the circumferential direction has the dominant role in determining the occurrence of hydrogen embrittlement cracking. Though the location of the crack initiation site could not be pinpointed from the fracture surface observation, the crack was presumably initiated where the tensile stress was the maximum. It is noted that hydrogen accumulated due to the hydrostatic stress might affect the hydrogen embrittlement cracking in addition to the high stress in the circumferential direction in the position slightly close to the outer surface from the center in the thickness direction.

For the evaluation of hydrogen embrittlement property using U-bent specimens, stress is applied to the specimen commonly by tightening a bolt and nut with monitoring the applied stress on the outer surface of the top of the specimen as it was adopted in this study. However, the most important factor determining hydrogen embrittlement cracking is considered to be the maximum tensile stress in the interior, and it is required to estimate the stress distribution. In the present study, a good agreement between the stress distributions obtained by means of synchrotron X-ray diffraction and FE simulation has been shown, suggesting that the stress distribution obtained by using FE simulation is reasonable. Therefore, for the conventional evaluation method for hydrogen embrittlement property of U-bent specimens, FE simulation can be an effective tool.
4. Conclusions

The effects of the elastic and plastic strain distributions inside the U-bent specimen on the hydrogen embrittlement of the 1 500 MPa grade quenched and tempered martensitic high strength steel sheets were investigated. The synchrotron X-ray diffraction measurement and the finite element (FE) simulation were carried out to analyze the stress and plastic strain distributions in the thickness direction of the U-bent specimen. To compare the distributions with the initiation of the hydrogen embrittlement cracking of the U-bent specimen, fracture morphology was evaluated. The following conclusions can be drawn.

(1) Intergranular fracture was found inside the hydrogen charged U-bent specimen and shear lips were found near the outer and inner surfaces of the specimen. The crack initiation site was located in the interior of the specimen.

(2) There was a good agreement between the elastic strain distributions in the thickness direction obtained by means of synchrotron X-ray diffraction measurement and FE simulation. The peaks of tensile and compressive stresses coexisted near the center in the thickness direction of both the as-U-bent specimen and the bolt-tightened specimen. On the other hand, the peak value of the plastic strain of the specimen existed in the vicinity of both the outer and the inner surfaces of the specimen.

(3) The location of the crack initiation site was considered to be correspondent with the region where the tensile stress was the highest. The maximum tensile stress was predominant to determine the crack initiation over the plastic strain.

Acknowledgments

This article is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO). In addition, the part of this work was supported by JSPS KAKENHI Grant-in-Aid for Scientific Research on Innovative Areas “Hydrogenomics”, No. JP18H05513 and JP18H05514. Moreover, the stress analysis using synchrotron X-ray radiation at SPring-8 were supported by the QST Advanced Characterization Nanotechnology Platform under the remit of “Nanotechnology Platform” of the Ministry of Educa-