Hydrogen Embrittlement of Ultrafine-grained Austenitic Stainless Steels Processed by High-pressure Torsion at Moderate Temperature

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The effect of hydrogen on the plasticity of ultrafine-grained austenite was studied on type 304, 316L, and 310S stainless steels processed by high-pressure torsion at moderate temperature. Like austenitic steels with ordinary grain sizes, the hydrogen-induced ductility loss for the ultrafine grains became more pronounced with decreasing stability of the austenitic phase. For all the steels, the uniform elongation was limited by strengthening due to the ultra grain refinement; the ultrafine-grained 310S stable austenitic steel further exhibited a small local elongation due to a lack of martensitic transformation. The ductility loss due to hydrogenation for 316L steel with an intermediate austenite stability was retained to a moderate level. The ultrafine-grained 304 metastable austenitic steel exhibited a serious ductility loss induced by hydrogen showing localised shear deformation. This suggests that the dynamic martensite transformation plays a crucial role in the hydrogen embrittlement of ultrafine-grained metastable austenitic steel.

KEY WORDS: hydrogen embrittlement; ultrafine grains; austenitic stainless steels; martensitic transformation; high-pressure torsion; micro-tensile testing.

1. Introduction

Stable austenitic stainless steels such as type 316L have been used in the hydrogen industry because of their low susceptibility to hydrogen embrittlement (HE). While reducing the content of rare metals in these steels is important from an economic viewpoint, the reduction in nickel content decreases the stability of the austenitic phase below room temperature range.1) Metastable austenitic steels such as type 304 suffer from a severe HE that is presumably attributed to the martensitic transformations induced by deformation.2–7) In addition, improved strengthening without sacrificing their good ductility has been a major challenge for using austenitic stainless steels as structural materials. Unfortunately, in general, high strength of materials intensifies the susceptibility to HE. However, the HE mechanism involves interactions between hydrogen and various defects such as dislocations, grain boundaries, precipitates, and solution atoms. Therefore, the contribution of each defect to the HE of the austenitic steel may be quite different for the operative strengthening mechanisms.

It has been widely known8–10) that precipitation-hardened austenitic steels such as A286 suffer from severe HE because of the promotion of planar slip. In addition, some interstitial atoms such as nitrogen and carbon promote deformation localisation in austenitic steels.11,12) In contrast, it was reported13,14) that introducing dislocations into 316L steels without any martensitic transformation increased the hydrogen trapping, but led to a slight ductility loss due to hydrogen itself.

Our previous study using thermal desorption spectrometry revealed15) that the ultra grain refinement enhanced a short-circuit diffusion of hydrogen atoms in the 310S and 660 stable austenitic steels. While the ultrafine-grained 310S steel exhibited a minor ductility loss induced by hydrogen, the uniform deformation was significantly reduced by strengthening because of the ultra grain refinement.16) As for a 304 metastable austenitic steel, an ultrafine-grained two-phase microstructure was produced through reversion of the deformation-induced martensite, which resulted in mitigation of the ductility loss due to both hydrogenation and ultra grain refinement.17,18) This finding suggests that the presence of martensite prior to the hydrogenation may mitigate HE. Similar phenomena were observed in metastable austenitic steels with ordinary-sized grains.19–21) Meanwhile, Macadre
et al. have recently reported that the hydrogen-induced ductility loss of the Fe–16Cr–10Ni metastable austenitic steel decreased for grains over the size range of 1 to 6 μm produced by thermal reversion of deformation-induced martensite. However, the HE behaviour of a metastable austenitic steel with reduced grains down to the ultrafine region has not yet been clarified.

Recently, we have successfully obtained ultrafine grains of 304 metastable austenitic steel by processing through high-pressure torsion (HPT) at moderate temperatures. For ultrafine-grained materials, the deformation mechanism is quite different from that of materials with ordinary grain sizes. The present study was initiated to clarify the effect of hydrogen on the deformation behaviour of the ultrafine-grained austenitic steels with different stabilities of the austenitic phase, with a special focus on the role of martensite for the HE of the metastable austenitic steel with ultrafine grains.

2. Materials and Methods

The materials used in this study were 304 (JIS–SUS304), 316L (JIS–SUS316L), and 310S (JIS–SUS310S) commercial austenitic stainless steels. Table 1 shows the chemical compositions and the stacking fault energy, εSF, values, which were calculated using the Schramm equation:

\[
\gamma_{SF} / \text{mJ} \cdot \text{m}^{-2} = -53 + 6.2(\%\text{Ni}) + 0.7(\%\text{Cr}) + 3.2(\%\text{Mn}) + 9.3(\%\text{Mo}) \quad \ldots \ldots \ldots (1)
\]

Solution treatment was performed at a temperature of 1323 K for 1 h. The Vickers hardness, HV, of the steels after the solution treatment was 177 ± 8 for 304, 168 ± 12 for 316L, and 158 ± 7 for 310S; the error range represents the 95% confidence interval. Disc-shaped samples with a diameter of 19 mm and an approximate thickness of 0.8 mm were subjected to HPT at a temperature of 473 K in atmospheric conditions. The displacement rate was chosen to be 0.1 mm·s⁻¹. The HPT-processed samples were finished with electro-chemical polishing. A set of specimens was cathodically charged with hydrogen for 336 h at a current density of 27 A·m⁻² in a H₂SO₄ aqueous solution (pH = 3.5) maintained at a temperature of 353 K. These charging conditions are expected to induce a negative gradient in the hydrogen content at a depth of ~300 μm from the specimen surface in the austenitic phase. The tensile test was performed at a crosshead speed of 0.2 mm·min⁻¹, corresponding to an initial strain rate of 2.2×10⁻³ s⁻¹, at room temperature in air. The gauge section of the tensile specimen was monitored during the tensile test using an optical microscope, in order to dynamically measure the strain as a function of time.

Micro-tensile tests and ex-situ TEM were performed using the 473K-HPT-processed samples of the 304 steel to examine the difference in the deformation microstructure between the samples with and without hydrogenation. Micro-tensile specimens with their gauge sections of 50 μm × 20 μm × 20 μm were fabricated using an FIB, so that the LD could be parallel to the circumferential direction of the HPT-processed disc. The hydrogen charging time was chosen as 7 h such that the 20 μm thick specimen was saturated with hydrogen, and the other charging conditions were the same as the millimetre-sized specimen. The micro-tensile tests were performed at room temperature under laboratory atmospheric conditions. The displacement rate was chosen to be 0.1 μm·s⁻¹ so as to obtain a similar initial strain rate (2×10⁻³ s⁻¹) in the tensile tests using the millimetre-sized specimen. The details of the micro-tensile test are described elsewhere. Samples for ex-situ TEM were fabricated from the fracture specimens using an FIB.

3. Results and Discussion

3.1. Deformation Behaviour of Ultrafine-grained Austenitic Steels with Different Austenite Stabilities

Figure 1 shows the TEM bright-field images with selected area electron diffraction (SAED) patterns of the 304, 316L, and 310S steels subjected to processing through HPT at a temperature of 473 K. The grains were elongated along the

| Table 1. Chemical compositions and the corresponding calculated stacking fault energy, εSF, of the austenitic stainless steels used in this study. |
|-----------------|---|---|---|---|---|---|---|---|---|---|
|                | C  | Si | Mn | P  | S  | Ni | Cr | Mo | εSF |
| 304             | 0.06 | 0.50 | 1.47 | 0.032 | 0.025 | 8.17 | 18.38 | –  | 15.2 |
| 316L            | 0.010 | 0.34 | 1.67 | 0.035 | 0.013 | 12.17 | 16.76 | 2.00 | 58.1 |
| 310S            | 0.04 | 0.42 | 0.38 | 0.019 | < 0.001 | 20.31 | 24.69 | –  | 91.4 |
The average grain size was determined to be ~90 nm for the 304, ~60 nm for 316L, and ~59 nm for 310S steel using the intercept method. In these samples, a close examination showed twinned structures inside some of the fine grains, as previously shown elsewhere. Although some spots of \( \alpha' \) martensite are evident in the 304 and 316L steels, the SAED pattern indicates that the microstructure was mainly composed of fine austenite grains (Figs. 1(a) and 1(b)).

Figure 2 shows the nominal stress–strain curves of the ultrafine-grained specimens. The yield and ultimate tensile strengths are higher for 316L and 310S than for 304. This is because the microstructures of the 316L and 310S steels were composed of austenite grains with average sizes of ~60 nm, which were smaller than the ~90 nm for 304 steel (Fig. 1). For all the specimens, the nominal stress reached the ultimate tensile strength of 1.6–1.8 GPa at a nominal strain of approximately 3%. Therefore, the uniform elongation was restricted by the ultra grain refinement in these austenitic steels. Notably, the 304 steel exhibits a prominent stress drop in the nominal stress–strain curves just after the onset of necking, while showing a larger elongation-to-failure compared to the 316L and 310S steels (Fig. 2). To determine the cause of this stress drop, the microstructural evolution at the necked part during the deformation process was examined using EBSD analysis by interrupting the tensile tests at predetermined strains. Figure 3 shows the true stress–strain curves for the ultrafine-grained specimens of the 304 steel and the corresponding phase maps, obtained from the mid-thick section at the necked region of the specimens, and the (110) pole figures of martensite. The true stress was determined using the narrowest width of the specimen at the moment. The stress drop in the nominal stress–strain curves (Fig. 2) corresponds to a plateau region up to a true strain of 0.08 in the true stress–strain curve (circles in Fig. 3(a)). While martensite was almost invisible just after the onset of necking (Fig. 3(b)), the fraction of martensite increased to 82% at a true strain of 0.12 after the end of the plateau region (Fig. 3(c)). In the strain-hardening region, the (110) fibre texture of martensite intensified (Fig. 3(d)). These findings suggest that the plateau region in the true stress–strain curve could be attributed to the formation of martensite, and that the deformation of the formed martensite led to subsequent strain hardening, resulting in the large elongation-to-failure.

Fig. 1. TEM bright-field images with SAED patterns of the ultrafine-grained samples of 304, 316L, and 310S steels produced through HPT processing at a temperature of 473 K. Green and red indicate austenitic and martensitic phases, respectively. The beam axis is nearly parallel to the radial direction of the HPT-processed discs. The arrows indicate the twinned fine grains. (Online version in color.)

Fig. 2. Nominal stress–strain curves for the ultrafine-grained specimens of the 304, 316L, and 310S steels.
3.2. Effect of the Austenite Stability on the HE Susceptibility of Ultrafine-grained Austenitic Steels

Figure 4 shows comparisons of the true stress–strain curves between the uncharged and hydrogen-charged specimens. There is no significant difference in the level of the flow stress between the uncharged and hydrogen-charged specimens. The ductility loss induced by hydrogenation becomes less pronounced with increasing austenite stability. The hydrogen-charged specimen of 304 steel is fractured in the plateau region. In the 316L steel, the uncharged specimen exhibits a two-step work hardening, whereas the hydrogen-charged specimen is fractured at the end of stage I. As for the 310S steel, the uncharged and hydrogen-charged specimens exhibit almost the same stress–strain curves, which have a low strain-hardening rate when compared to the other steels.

Figure 5 shows the fracture surfaces of the ultrafine-grained specimens. It was confirmed from matching of frac-
ture surfaces that the uncharged 304 and 316L specimens exhibit cup-and-cone fractures (Figs. 5(a) and 5(c)), while shear fractures were prevalent in the hydrogen-charged specimens (Figs. 5(b) and 5(d)). Therefore, the loss in ductility due to hydrogenation can be attributed to hydrogen-induced shear localisation. The ultrafine-grained specimen of the 310S steel was fractured by shear localisation, even in the absence of hydrogen (Fig. 5(e)).

Figure 6 shows plots of the reduction-of-area against the ultimate tensile strength for the ordinary-grained (ST) and ultrafine-grained (473K-HPT) specimens with and without hydrogen pre-charging. Like the ordinary-grained specimens, the hydrogen-induced ductility loss for the ultrafine-grained steels was more pronounced with a lower stability of the austenitic phase. In the 310S steel, the reduction-of-area was less owing to the ultra grain refinement, while the hydrogen-induced ductility loss was minor. This is attributed to a low strain-hardening rate in the ultrafine-grained specimens of the 310S steel regardless of the hydrogenation (Fig. 4(c)) for lack of martensitic transformations. As a result, the reduction-of-area of the hydrogen-charged ultrafine-grained specimens for 310S is almost equivalent to that for 316L, despite the fact that the 310S steel is insensitive to HE compared to the 316L steel.
As for the 304 steel, the hydrogen-charged specimen was fractured in the plateau regime (Fig. 4(a)). This implies that the dynamically formed martensite may be responsible for severe hydrogen-induced ductility loss. In the following section, the microstructural evolution at the necked region of the hydrogen-charged ultrafine-grained 304 steel is discussed using the results of micro-tensile testing and subsequent ex-situ TEM examination.

### 3.3. Microstructural Evolution during Micro-tensile Loading of Ultrafine-grained 304 Steel

**Figure 7** shows the SEM images of the fracture morphology for the micro-tensile specimens with and without hydrogen pre-charging of the ultrafine-grained 304 steel. While the uncharged specimen failed after strong necking (Fig. 7(a)), shear fracture was induced by the hydrogenation (Fig. 7(b)). The reduction-of-area for the hydrogen-charged specimen was 56%, which is lower than 76% for the uncharged specimen. These values are somewhat higher than the corresponding millimetre-sized specimens. **Figures 8 and 9** show the FIB images and the corresponding TEM images obtained from the longitudinal sections of the uncharged and

![Fig. 7](image)

**Fig. 7.** SEM images showing the fracture morphology of the uncharged (a) and hydrogen-charged (b) micro-tensile specimens of the ultrafine-grained 304 steel. LD and TD represent the loading and transverse directions, respectively.

![Fig. 8](image)

**Fig. 8.** (a) FIB image and (b–d) TEM bright-field images with SAED patterns obtained in the longitudinal cross-section of the uncharged micro-tensile specimen of the ultrafine-grained 304 steel after fracture. Green and red indicates austenitic and martensitic phases, respectively. (Online version in color.)
hydrogen-charged specimens, respectively. The SAED patterns show that martensite was mostly formed at the necked part of the uncharged specimen, as shown in the insets in Figs. 8(b)–8(d). The grains in the centre and periphery of the specimen were elongated along the loading direction and in the 45°-direction with respect to it, respectively (Figs. 8(b) and 8(d)). It was also found that the (110) fibre texture of martensite was well developed in the elongated directions, suggesting that the transformed martensite was severely deformed. In contrast, the grains in the hydrogen-charged specimen contain some amount of austenite, and the intensity of the texture is weak when compared to the uncharged specimen. This finding indicates that hydrogen caused the shear localisation to fracture before the completion of martensitic transformation. The hydrogen solubility is approximately an order of magnitude lower in martensite than in austenite. Therefore, excess hydrogen corresponding to the difference in solubility between the two phases can be generated owing to the martensitic transformation. Since the diffusion rate of hydrogen in martensite is significantly higher than that in austenite, it is plausible that the excess hydrogen can diffuse out of the formed martensite into the austenite retained between it. Although the hydrogen effect was not discussed, a finite-element method simulation study by Maresca et al. revealed that strain concentrates in the austenite retained between the martensite laths in a carbon steel. Considering this, it is anticipated that the excess hydrogen results in the promotion of shear deformation in the retained austenite.

In the 316L steel, the martensite formed during tensile loading in the presence of hydrogen is presumed to be in a low fraction like the ordinary-grained specimen. Thus, the excess hydrogen due to martensitic transformation could be limited, and therefore, a higher strain was needed to generate enough hydrogen for fracture.

4. Conclusions

The effect of austenite stability on the hydrogen embrittlement of ultrafine-grained austenitic steels was studied using the 304, 316L, and 310S steels subjected to processing by high-pressure torsion at a temperature of 473 K. The main findings can be summarised as follows:

(1) The ultimate tensile strengths of all the ultrafine-grained specimens were 1.6–1.8 GPa at a nominal strain of approximately 3%. The uniform elongation was limited owing to the ultra grain refinement, regardless of the hydrogenation.

(2) The ductility loss induced by hydrogen in the ultrafine-grained austenitic steels became less pronounced with increasing stability of the austenitic phase.

(3) Although the ultrafine-grained specimen of 310S was most insensitive to hydrogen, the ductility loss owing to ultra grain refinement was significantly large. For 310S, the reduction-of-area in the hydrogen-charged specimen was almost equivalent to that for 316L.

(4) After the onset of necking, a plateau regime in the true stress–strain curves appeared for the ultrafine-grained 304 steel. EBSD analysis at the necked part showed that the appearance of the plateau could be attributed to the martensitic transformation. In addition, hydrogen induced a premature failure in the plateau regime. These findings
suggest that excess hydrogen generated by martensitic transformation concentrates into the retained austenite, resulting in the promotion of shear localisation to fracture.

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