HYDROGEN RELATED BRITTLE CRACKING OF METASTABLE
TYPE-304 STAINLESS STEEL

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Abstract

Among stainless steels, Type-316 steel is stable and shows high resistance to hydrogen-induced brittle cracking, but the meta-stable Type-304 steel shows a high susceptibility to the hydrogen-induced embrittlement and cracking. Mechanism of hydrogen-induced brittle cracking of the Type-304 steel was studied by AE monitoring under various combination of static and dynamic elastic and plastic deformations in a charging solution at room temperature and 80ºC. Here, the hydrogen was supplied before and during tensile testing. We detected a number of AE signals from the Type-304 steel with hydrogen charging during dynamic plastic deformation at room temperature and observed hydrogen-induced cracks, while no AE for the Type-304 charged by hydrogen and deformed at 80ºC. Maximum load of the Type-304 steel with hydrogen charging decreased to 30% that of the steel without charging. Type-304 steel, hydrogen charged after being quenched in liquid nitrogen, produced few AE during tensile loading at room temperature. We detected no AE from Type-316 steel during plastic deformation in charging solution at both temperatures. Hydrogen-induced brittle fracture of Type-304 steel was confirmed to be induced by both gliding dislocations and deformation-induced lath martensite. Hydrogen is supposed to be transferred to the martensite by gliding dislocations accompanying protons.

Keywords: Meta-stable austenitic stainless steel, hydrogen induced brittle fracture, strain induced martensite, gliding dislocation

Introduction

Meta-stable austenitic stainless steels are known to be susceptible to hydrogen embrittlement. Many researchers reported that strain-induced martensite suffered hydrogen embrittlement [1, 2]. Fracture type was intergranular (IG). Carpenter et al. reported that AE signals from sensitized Type-304 steel, during tensile loading in a charging solution, were produced by the IG-cracks caused by the grain boundary separation. Here the IG-cracking occurred when hydrogen charging was continued till the maximum load. They proposed a transport model by moving dislocations [3, 4]. Direct demonstration of this model is impossible at present, even if we use any kind of advanced analysis equipments. Collection of reliable data, which can or cannot support this model, is needed.

In this report, we studied the hydrogen embrittlement of Type-304 and -316 steels by monitoring AE during quasi-static loading in a charging solution at 25ºC and 80ºC.

Experimental procedure

We used commercially available Type-304 and -316 stainless steels. Chemical composition
is shown in Table 1. Test specimens of Fig. 1 were prepared by an electro-discharge machine to produce identical specimens. Width in gage section was controlled to 15 mm. A notch with the tip radius of 0.2 mm was induced on one side. These samples were abraded by silicon carbide abrasive papers of 150, 300, 400, 600, 800, 1000 and 1500 mesh, and mirror polished by aluminum oxide powder. The specimen was sensitized at 650°C for 24 hours in low-pressure furnace after solution treatment at 1050°C for 1 hour, and quenched in water. The specimen was sealed by rubber-based coating material, except for the exposure area of 15 mm x 10 mm. Hydrogen was charged in an H₂SO₄ solution of pH:2, at cathodic current density of 1 mA/cm² using a potentiogalvanostat.

Table 1 Chemical composition of austenitic stainless steel used (mass %).

<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>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 304</td>
<td>0.05</td>
<td>0.61</td>
<td>1.56</td>
<td>0.04</td>
<td>0.024</td>
<td>8.55</td>
<td>18.2</td>
<td>balanced</td>
</tr>
<tr>
<td>Type 316</td>
<td>0.05</td>
<td>0.57</td>
<td>0.82</td>
<td>0.02</td>
<td>0.0006</td>
<td>11.3</td>
<td>17.5</td>
<td>balanced</td>
</tr>
</tbody>
</table>

We monitored AE using four small AE sensors (PAC, Type- PICO), which were mounted on the sample as they make a line. Outputs of two sensors (channels 2 and 3 in the gage section) were amplified by a pre-amplifier (Gain: 40 dB) and fed to a personal computer. Two more sensors (channels 1 and 4 on the shoulder) were used to discriminate the friction noise from the signals. We monitored the crack propagation by a CCD camera.

![Fig. 1 Schematic of specimen and sensor location.](image)

![Fig. 2 Load - time diagram for the sensitized Type-304 specimens with various crosshead speeds in a charging solution.](image)

**Experimental results**

*Tensile loading in charging solution*

Tensile load was applied to Type-304 specimen in a charging solution using crosshead control method, in the following sequence: (1) Increase the load at constant crosshead speed. (2) When a small load drop (~0.1 kN, probably from the start of cracking) was detected, crosshead
was stopped and held. (3) Then, monitor the load decrease for 3 hour.

In these tests, hydrogen charging was started with the loading. The crosshead speed was varied between 0.05 mm/min to 0.4 mm/min. Figure 2 shows the load-time diagram at crosshead speeds of 0.4, 0.2, 0.1 and 0.05 mm/min for the sensitized Type-304 specimen at 25°C. A fine smooth line indicates that of a non-charged specimen at crosshead speed of 0.1 mm/min. Five specimens show different behavior in the plastic range. The specimens hydrogen-charged during loading showed extensive load decay. Initial decay and the total load decay were larger at higher loading rates. The curve of the charged specimen at crosshead speed of 0.1 mm/min agrees fairly well that of the non-charged specimen, but deviates slightly at large loads. The maximum load reached was 5 to 6.5 kN. The maximum load increased with an increase of crosshead speeds.

Figure 3 shows changes of cumulative AE counts with time. Detected AE signals were classified by their frequency characteristics into two types (Type-A and -B) as shown in Fig. 4. Type-A was detected after the maximum load and showed broad frequency components. In contrast, Type-B was detected throughout loading. Frequency spectrum of the Type-B showed a limited frequency component and resembles the noise from hydrogen gas evolution in SCC [5]. We selected Type-A as the crack signal. We detected many signals during load increasing period, but few signals during the initial portion of the load decay. For two samples with crosshead speeds of 0.2 and 0.4 mm/min, we again detected signals during rapid load decay period after incubation times. However, we did not detect AE during load decay for two specimens with lower crosshead speeds of 0.05 and 0.1 mm/min. Detail mechanism of AE generation rate and its dependency on the crosshead speed is a future problem.

Figure 3 Cumulative AE counts for the sensitized Type-304 specimens with various crosshead speeds in a charging solution.

Figure 5 shows CDD images of crack progression. White spots in the image are hydrogen gas bubbles. Timing of crack progression from the notch bottom agreed roughly with the first AE timing at 1,100 s, as shown by the photo (a) at 1,800 s. We observed a crack with large opening at the maximum load (photo (c)), but after that, a fine crack during load decay (photo (d)).

Figure 6 shows post-test SEM of the sample with the crosshead speed of 0.1 mm/min. We observed a number of IG-cracks and falling-off of grains around the notch. Here the falling-off of grains was caused by the grain boundary separation. As these cracks were considered to be
Fig. 4 Two types of AE signals detected and their power spectra.

Fig. 5 CCD images of crack propagation of the sensitized Type-304 specimen with crosshead speed of 0.4 mm/min in charging solution. (a) 1800 s (after detection of first AE) (b) 2300 s (c) 2440 s (at max load) (d) 13200 s.
Fig. 6 SEM images of the sensitized type-304 specimen surface around the notch with crosshead speed of 0.1 mm/min at 25°C in charging solution.

Fig. 7 Fracture surface of the sensitized sample with crosshead speed of 0.1 mm/min at 25°C in charging solution. Both dimple and cleavage fracture surfaces are shown.

caued by strain-induced martensite, we measured ferrite amount near the main crack using a ferrite meter. It was measured as 7%. Figure 7 shows fracture surface of another sample loaded to final fracture in the same charging condition. We observed both dimple and cleavage fracture surfaces, and deep grooves along the elongated grains.

Effect of strain-induced martensite on hydrogen induced cracking

We studied effect of strain induced martensite on the hydrogen-induced cracking using Type-304 and -316 steels. Transition temperature (M_d) of austenite to martensite of the Type-304 steel is 30°C, so we then compared the crack susceptibilities of the Type-304 steel at 25 and 80°C. We deformed the sensitized Type-304 sample, with charging at 80°C (0.1 mm/min) and detected no AE. The maximum load was not reached in loading up to 6 kN, while we observed high AE activity and the maximum load of 5.3 kN for the loading at 25°C (Fig. 3). Martensite amount was measured as below 1.0%. This result implies that the martensite is a necessary factor to cause the hydrogen-induced cracking.

The M_d temperature of the Type-316 steel is -28°C, and this steel produces no strain-induced martensite at 25°C. In order to confirm this, the sensitized Type-316 steel was tensile tested in
the charging solution at 25°C, by the same method as in the previous section. This steel produced three AE during the loading to 6 kN, indicating no susceptibility to hydrogen-induced cracking, as shown in Fig. 8.

Effect of Hydrogen charging and thermal martensite

Experimental data of previous sections suggested an importance of both the martensite and gliding dislocations during plastic deformation. The test in this section intends to confirm these. We attempted AE monitoring from the sensitized, and then nitrogen quenched and pre-charged Type-304 steel during tensile loading in air. Hydrogen was charged for 144 hr at current density of 10 mA/cm² (charge amount of 5184 C/cm²) prior to the loading. This specimen possesses thermally-induced martensite of approximately 15% near the notch bottom.

Figure 9 shows load-time curves of the quenched and pre-charged specimens in air. We detected no AE and no crack. Thermally-induced martensite increased the yield load by approximately 14% over that of the sensitized Type-304 steel without hydrogen charge, but is immune from the hydrogen-induced cracking. This implies that simultaneous supply of protons and generation of dislocation are needed for hydrogen-assisted cracking.

Fig. 8 Load-time diagram and cumulative AE count for sensitized 316 specimens with charging at 25°C.

Fig. 9 Load–time diagram for the pre-charged sample quenched in liquid nitrogen in air. For comparison, sensitized sample without charging was shown.

Discussion

The martensite is a necessary condition for hydrogen-induced cracking but not the sufficient condition, as demonstrated by the last section’s experiment using quenched samples. Figures 2 and 3 imply that both the gliding dislocation by dynamic plastic deformation and the strain-induced martensite, and of course the diffusible protons, are necessary for hydrogen embrittlement. The grain boundary separation occurs when these three condition were simultaneously satisfied. These results agree with the results by Carpenter et al. [4]. We, however, could not explain the complicated AE behavior during load decay in Fig. 3. These must be explained based on the rate process of proton diffusion and martensite formation. Unsolved problems are
1) How the protons are transferred to the martensite at the tip of notch and growing crack, and
2) How the martensite distributes in the austenitic grains.

Diffusion coefficient of proton in the austenitic phase is as low as $10^{-12}$ cm$^2$/s, million times
smaller than $(10^{-6}$ cm$^2$/s) in the ferritic phase. Thus the proton can not quickly diffuse through the
austenitic grains. Fast and sufficient supplement of protons to the martensite will be possible
by gliding dislocation accompanying the protons or self-diffusion through the martensite. No
advanced analysis equipment at present can differentiate them, but we can compare the crack
velocity and proton diffusion rate under controlled stress intensity. The second problem in-
cludes a contentious martensite path for proton diffusion and the grain boundary separation.
The grain boundary separation can be explained by the martensite formation along the chromium
depleted zone. Distribution of the martensite, and possibly the initiation of crack, will be re-
vealed by the advance analysis equipment.

We recently observed frequent grain boundary separations in polythionic APC-SCC of sensi-
tized Type-304 steel [5]. AE were detected when the steel suffered the grain boundary separa-
tion. Detailed mechanism is not well understood. There is a possibility of hydrogen-induced
 grain boundary separation in the APC-SCC.

Conclusion

In order to study the mechanism of hydrogen embrittlement of austenitic stainless steel, we
monitored AE. Results are summarized below:
1) We detected AE and crack for the sensitized type 304 when it is exposed to both the dynamic
plastic deformation and hydrogen charging simultaneously. Much AE were continuously
emitted during plastic loading at higher cross head speeds.
2) Experiment suggests that hydrogen assisted cracking occurs when sufficient protons were
 transferred to the strain induced martensite. Diffusion path and trap site of protons have to
be studied in future.

References