Hydrogen Environment Embrittlement on Austenitic Stainless Steels from Room Temperature to Low Temperatures

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Abstract. Hydrogen environment embrittlement (HEE) on austenitic stainless steels SUS304, 304L, and 316L in the high pressure hydrogen gas was evaluated from ambient temperature to 20 K using a very simple mechanical properties testing procedure. In the method, the high-pressure hydrogen environment is produced just inside the hole in the specimen and the specimen is cooled in a cooled-alcohol dewar and a cryostat with a GM refrigerator. The effect of HEE was observed in tensile properties, especially at lower temperatures, and fatigue properties at higher stress level but almost no effect around the stress level of yield strength where almost no strain-induced martensite was produced. So, no effect of HEE on austenitic stainless steels unless the amount of the ferrite phase is small.

1. Introduction
Stainless steels are also used in fuel-cell vehicle applications for storage tanks, mobile containers, and pipes due to their ductility at low temperatures and in hydrogen environments. Recently, it was also discussed that at a hydrogen gas station for the vehicle, high pressure hydrogen gas will be produced by evaporating liquid hydrogen quickly. The hydrogen embrittlement in meta-stable stainless steels has been evaluated so far [1-3] using thermally or electochemically hydrogen-charged materials. It has been shown that HEE in the temperature range from 200 K to 250 K is caused by strain induced martensite, while little or no HEE occurs at 77 K.

A hydrogen environment causes embrittlement at ambient temperature [4] and low temperatures [5-7] down to 80 K under 1.1 MPa gaseous hydrogen. However, no tensile or fatigue data was available neither for the higher pressure hydrogen and low temperature environments nor fatigue properties. A simple testing method for mechanical properties evaluation under high pressure hydrogen gas was developed [8] without using a high pressure gas chamber and was easily applied to low temperatures [9, 10]. The effects of HEE on fatigue properties of SUS304L at 10 MPa and 70 MPa and cryogenic temperatures were evaluated using the simple method [11, 12]. Stainless steels with higher strength would be used in the instruments of high pressure hydrogen system and the HEE of those steels was a major concern.

In this work, the HEE on the tensile and fatigue properties of meta-stable austenitic stainless steels were examined with behaviour of strain-induced martensitic transformation to study an available limit in high pressure hydrogen environment.
2. Experimental detail

2.1. Material and Specimens, and Testing
The materials used in this study are the commercial austenitic stainless steels, SUS 304, 304L and SUS 316L, hot-rolled and solution-treated round bars. The diameter of the bars was 13 mm. The typical chemical compositions of the materials are listed in TABLE 1. Round tensile specimens were machined from the bars and their diameter in the gage length was 6.25 mm and the length of parallel part was 34 mm. Hour-glass type round fatigue specimens were also machined and their diameter was 6 mm. The hole in the specimen was machined by a wire-cut and its diameter was less than 2 mm.

FIGURE 1 shows an illustration of this method. High pressure gas was filled into a small hole in the specimen from a gas cylinder or a portable compressor for 70 MPa test. This system has no compressor up to the cylinder pressure of 10-15 MPa and requires no extra cost for the testing. The temperature of the specimen with the high pressure gas was controlled by surrounding environment temperatures.

2.2. Testing
Tensile tests were carried out at from 298 K (RT) to 25 K. In the test at 25 K and 77 K, the specimen was in the cryostat with refrigerator and in liquid nitrogen dewar, respectively. In the tests from 100 K to 170 K and from 190 K to 280 K, the specimen was cooled by temperature-controlled nitrogen gas and temperature-controlled alcohol, respectively. The specimen temperature was measured by a thermo-couple attached on the specimen surface at middle of gage length. The crosshead-speed during tensile test was 3.6 mm/h. The effect of HEE is evaluated by the ratio of reduction of area (relative reduction of area) obtained in tensile tests using the specimen filled in hydrogen gas to that obtained in helium gas environment [6-10]; the ratio of 1.0 means no effect of hydrogen and the ratio becomes smaller when the effect of hydrogen increases. The tests were started one hour later after the inside pressure was set.

Fatigue tests were carried out at a stress ratio of 0.01 (tensile-tensile) and a frequency of 10 Hz at 298 K and 190 K.

| TABLE 1. Chemical compositions of stainless steels used in this study (wt. %). |
|-------------------------------|-------------------|-------------|-------------|-------------|-------------|-------------|------------|
| C    | Si    | Mn    | P     | S     | Ni    | Cr    | Mo |
| SUS304 | 0.06  | 0.50  | 1.53  | 0.029 | 0.026 | 8.19  | 18.41    |
| SUS304L | 0.016 | 0.53  | 1.03  | 0.029 | 0.003 | 9.42  | 18.01    |
| SUS316L | 0.025 | 0.48  | 1.52  | 0.032 | 0.018 | 12.04 | 16.84  | 2.04     |

Figure 1. An illustration of simple testing method for high pressure gas environments.
**Figure 3.** Effect of temperature on the relative reduction of area of SUS304L and 316L in 10 and 70 MPa hydrogen environment [10].
3. Results and discussion

3.1. Tensile properties

Figure 2 shows Load-displacement curves during tensile tests for SUS304L and 316L in 13 MPa hydrogen gas and 12 MPa helium gas at various temperatures [9]. The hydrogen environment tests for SUS304L show premature failure compared to the helium environment tests, which results in lower ultimate tensile strength, elongation, and reduction of area. In SUS316L, almost no HEE and small effect at 190 K were observed. Large HEE was observed in SUS304 at RT and 190 K and in SUS304L at 190 K, but almost no HEE below 100 K for those steels.

FIGURE 3 shows HEE as a relative reduction of area for SUS304L and 316L from RT to 25 K [10]. At room temperature, 298 K, SUS304L showed small HEE, however, with decreasing temperature, the HEE increased and showed maximum around 200 K but the HEE decreased below 200 K and almost disappeared below 120 K.

Meta-stable austenitic stainless steel, such as SUS304 and 304L, showed remarkable HEE at low temperature, which is due to the increase of strain-induced martensitic phase at the temperatures. The author reported the amount of the martensitic phase during tensile tests at each strain level for SUS304L and 316L [13, 14]. The increase of the amount of the martensitic phase behaviour clearly explains the HEE of those steels from room temperature to 200 K. The diffusion of hydrogen in fcc materials is very slow below room temperature and almost no diffusion occurs at low temperature. So, the amount of the strain-induced martensitic transformation and the bcc martensitic phase are essential to the embrittlement in meta-stable austenitic stainless steels and diffusion of hydrogen play an important role in the embrittlement, which means that the effect of HEE increases in work-hardened meta-stable stainless steels, that is, there is no HEE until the materials deformed at a certain strain.

FIGURE 4 shows change of amount of strain-induced martensite during tensile tests at low temperatures in hydrogen and helium environment. The amount of strain-induced martensite during tensile tests was measured by Ferrite Scope and its probe was pointed on the specimen during tensile tests. The measured value was converted to the amount of martensite using the value obtained in the
previous works [13, 14].

First, no effect of hydrogen on the amount of martensite was observed. In hydrogen environment, specimens fractured over 30% of martensite phase, which might be a critical amount of martensite for HEE in static tests. So, if hydrogen gas was removed before the critical point, there is no HEE until specimen fracture.

Figure 5 shows the results of experiments that hydrogen gas was changed to helium gas during tensile test for commercial SUS630. The temperature dependency of HEE on SUS630 was reported in previous work [12]. At 300K in 10 MPa hydrogen, this steel failed at 1236 MPa, then the change gas at 1200 MPa was tried, but specimen failed in several seconds during stop loading for exchange gas. The specimen changed gas at 1100 MPa was deformed as if no hydrogen from the beginning.

At 260K and in 10 MPa hydrogen, this steel failed at 832 to 1006 MPa, the specimen changed gas at 752 MPa, 90% of 832 MPa, was deformed as if no hydrogen from the beginning.

These tests proved that no HEE until at a certain stress level or amount of bcc phase.

3.2. Fatigue properties
Stress vs. Number of cycles to failure curves for SUS304, 304L, and SUS316L obtained in hydrogen and helium environment at RT and 190K were shown in FIGURE 6a), b), and c) [11,12]. In SUS304 and 304L, fatigue lives in hydrogen environment decreased at higher stress level, 200 MPa or 250 MPa, at RT and 190 K. But no clear influence at a stress level of 150 MPa. This stress level is corresponding to the yield strength at RT. In SUS316L, influence of hydrogen is small even at a stress level of 250 MPa.

FIGURE 7 shows relation between amount of strain-induced martensite and stress-strain curves at the early-stage of tensile tests for SUS304L at RT and 190K. At RT and/or below 0.2 % proof stress, almost no martensite was produced even at low temperatures. At 190 K, the amount of martensite was about 8% at 5 % strain. The HEE on fatigue properties can be discussed as follows:

Meta-stable austenitic stainless steel, SUS304 and 304L, showed remarkable HEE in relative reduction of area at low temperature around 190 K [5-7, 9], which is due to the increase of strain-induced martensitic phase during plastic deformation at the temperatures. A remarkable HEE can be seen in the evaluation of relative reduction of area at low temperature around 190 K, however, fatigue properties at 190 K were better than those of at RT, which is mainly because that the strength at 190 K is higher than at RT. The amount of martensite might increase during testing above the stress level of 0.2 % proof stress, but below the proof stress almost no strain-induced martensitic transformation might occur, so no effect of HEE can be seen.
In SUS316L, the austenitic phase is much more stable than that of SUS304L and the effect of HEE is less also in S-N curves.

4. Conclusions
- No effect of hydrogen on the amount of martensite was observed during tensile tests.
- In the meta-stable stainless steels, there is no HEE until the certain amount of deformation in tensile tests.
- No HEE until at a certain stress level or amount of bcc phase.
- Fatigue life of SUS 304 and 304L in hydrogen environment decreased at higher stress level, 200 MPa or 250 MPa, at RT and 190K. No influence at a stress level of 150 MPa. In SUS316L, influence of hydrogen is small even at a stress level of 250 MPa.

FIGURE 6 Effects of hydrogen and specimen temperature on fatigue properties of SUS304, 304L, and SUS316L at RT and 190K [11,12].

In SUS316L, the austenitic phase is much more stable than that of SUS304L and the effect of HEE is less also in S-N curves.
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