

Effect of Surface Hydrogen Concentration on Hydrogen Embrittlement Properties of Stainless Steels and Ni Based Alloys

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Hydrogen embrittlement properties of several stainless steels and Ni based alloys under cathodic charge (CHE) were investigated. Hydrogen concentration in the materials was varied by controlling hydrogen charging conditions. Slow strain rate test (SSRT) under cathodic charge in aqueous solution was carried out to evaluate CHE susceptibility. Mechanical degradation by hydrogen was evaluated by relative fracture elongation (relative fracture El.) against that in air. Critical surface hydrogen concentration (H_C), the maximum hydrogen at which El. was hard to be decreased, was derived from SSRT results under various hydrogen charging levels. H_C strongly depended on Ni equivalent (Ni_{eq}), which is a parameter consisting of alloy chemical compositions, reflecting stability of austenitic phase.

CHE test results were compared to susceptibilities to hydrogen gas embrittlement (HGE) and internal reversible hydrogen embrittlement (IRHE), which are caused by highly pressurized gaseous hydrogen. Materials accepting higher H_C generally showed higher resistance to HGE and IRHE. Comparing H_C to H_E , concentration of hydrogen absorbing from highly pressurized gaseous hydrogen, enables the risk assessment of hydrogen embrittlement in actual service conditions.

KEY WORDS: hydrogen embrittlement; hydrogen gas embrittlement; stainless steel; highly pressurized hydrogen.

1. Introduction

Hydrogen is a clean energy source, and has the potential to be widely used in various energy systems in the near future. Fuel cell vehicles equipped with cylinders containing hydrogen gas with high pressure up to 70 MPa are now being commercialized. Many hydrogen stations to supply fuel cell vehicles with gaseous hydrogen are under construction. For the safety and public acceptance of using hydrogen gas, it is important to investigate effects of hydrogen on reliability of structural materials used for the hydrogen systems. It is widely recognized that gaseous hydrogen decreases mechanical properties of steels and other kinds of metals. The environmental degradation caused by gaseous hydrogen is classified to following two types. One is hydrogen environment embrittlement (HEE) or hydrogen gas embrittlement (HGE), which occurs when a hydrogen-free material is mechanically tested in gaseous hydrogen near room temperatures.^{1–3)} HGE susceptibility is evaluated by tensile tests^{4,5)} or fatigue tests⁶⁾ in highly pressurized gaseous hydrogen. The other is internal reversible hydrogen embrittlement (IRHE), which occurs when a hydrogen pre-

charged material is mechanically tested in air. For IRHE evaluation, tensile tests in air were conducted after hydrogen is thermally pre-charged to the material in high temperature-high pressure gaseous hydrogen.^{7,8)} Researches on HGE and IRHE are now accelerated to establish standards and regulations for hydrogen storage materials in Japan. Various types of mechanical testing machines have been introduced in national research projects supported by New Energy and Industrial Technology Development Organization (NEDO). Many kinds of candidate materials including low alloy steels and austenitic stainless steels are now being evaluated, and appropriate materials have been developed for the high pressure hydrogen systems.⁹⁾ However, the assessment of HGE and IRHE needs special testing equipments capable to control extremely high pressure gaseous hydrogen. The limited availability of such testing equipments is a serious obstacle to collection of a large amount of important test data.

Cathodic hydrogen charging in an aqueous solution is widely used to assess hydrogen embrittlement. The technique can be a convenient alternative to those of HGE and IRHE. The comparison between the cathodic charging in the aqueous solution and the thermal charging in gaseous hydrogen was performed in terms of the hydrogen absorption¹⁰⁾ and the degrees of mechanical degradation¹¹⁾ in commercial type 316L and 304(L) austenitic stainless steels. However,

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relationship between hydrogen embrittlement caused by cathodic charge (CHE) and those by HGE or IRHE has not been clarified yet in a wide range of steel materials.

In this study, hydrogen absorption under cathodic charge to stainless steels and austenitic Ni based alloys was investigated. Effects of alloy chemical compositions and metallurgical features on CHE were evaluated by slow strain rate test (SSRT) under various cathodic charging conditions. An embrittlement index, critical surface hydrogen concentration against hydrogen embrittlement (H_C), was derived from the SSRT results to assess the CHE susceptibility quantitatively. The CHE susceptibility was compared to susceptibilities to HGE and IRHE evaluated in highly pressurized gaseous hydrogen. The similarity and the difference among CHE, HGE and IRHE were discussed from the viewpoints of hydrogen absorption and microstructural characteristics.

2. Experimental Procedure

Several kinds of austenitic stainless steels, duplex stainless steel and austenitic Ni based alloys were used in this study as listed in **Table 1**. Type 304L, 316L and high-nitrogen containing stainless steel (high N SS) are austenitic stainless steels. Type 304L and 316L were sheets on the market, which were solution heat treated. Laboratory melt sheets of high N SS with various amounts of nitrogen (N) from 0.19% to 0.34% were prepared to investigate the effect of N. The high N SS were solution heat treated at 1 060°C for 1 h. Duplex stainless steel (duplex SS) was a tube on the market, which was solution heat treated. Alloy 286 (A286), alloy 718 (A718) and alloy 725 (A725) are aging-strengthened types after solution heat treatment to obtain higher strength level than solution heat treated stainless steels. Laboratory melt A286 sheets with various amounts of Ni from 25% to 55% were prepared to investigate the effect of Ni. The A286 series were solution heat treated at 900°C for 1 h, followed by aging heat treatment at 720°C for 16 h to investigate the effect of the aging heat treatment. The A718 and A725 were bars on the market. Ni equivalent

(Ni_{eq}) in Table 1, a parameter consisting of chemical compositions of alloys, expresses relative effects of alloying elements to Ni on the stability of austenitic phase.¹²⁾ Higher Ni_{eq} value means the higher stability of austenitic phase. It is reported that susceptibility to HGE strongly depends on Ni_{eq} in the case of 300 series stainless steels.¹³⁾

Cathodic hydrogen charging tests were conducted for the measurement of concentration of hydrogen absorbing in the investigated materials. 0.5 mm thick plate specimens were taken from the materials. The surfaces of the specimens were polished with No. 600 emery paper before charging with hydrogen. The test solutions were three types - 3% NaCl solution, 3% NaCl solution containing 3 g/L NH_4SCN and 1 N H_2SO_4 solution containing 1.4 g/L $(NH_2)_2SC$. NH_4SCN and $(NH_2)_2SC$ are the catalysts which promote hydrogen entry into metallic materials. Details of hydrogen charging conditions are as follows. For type 304L and 316L, 1 N H_2SO_4 solution containing 1.4 g/L $(NH_2)_2SC$ was used under the cathodic current densities of 0.01, 0.1, 1 and 10 mA/cm². For the high N SS, hydrogen charge was conducted under the following conditions; -0.9 V (vs. Ag/AgCl) in 3% NaCl solution, -1.2 V (vs. Ag/AgCl) in 3% NaCl solution containing 3 g/L NH_4SCN , 1 mA/cm² and 10 mA/cm² in 1 N H_2SO_4 solution containing 1.4 g/L $(NH_2)_2SC$. For the duplex SS, 3% NaCl solution was used under the potentials at -0.8, -0.85, -0.9 -1.0 and -1.2 V (vs. Ag/AgCl). For the A286, hydrogen charge was conducted under the following conditions; -0.9 V and -1.2 V (vs. Ag/AgCl) in 3% NaCl solution, and 0.1 mA/cm² and 10 mA/cm² in 1 N H_2SO_4 solution containing 1.4 g/L $(NH_2)_2SC$. For the A718 and A725, 3% NaCl solution was used under the potentials at -0.8, -0.9 -1.0 and -1.2 V (vs. Ag/AgCl). All samples were charged for 48 h at constant potentials or constant cathodic current densities at ambient temperature. Absorbed hydrogen concentration in the samples was measured using thermal desorption analysis (TDA) with a quadrupole mass spectrometer at a heating rate of 10°C/min from ambient temperature to 600°C. All TDA profiles showed a single peak, and the degassing of

Table 1. Chemical compositions of alloys used (mass%).

Material	C	Si	Mn	Ni	Cr	Mo	N	Others	Ni_{eq}
304L	0.02	0.35	1.36	9.08	18.15	0.23	0.050	–	22.9
316L	0.02	0.53	0.88	12.04	17.82	2.09	0.041	–	27.0
High nitrogen stainless steel	0.19N	0.03	0.41	4.47	13.73	22.15	2.08	0.19	35.4
	0.30N	0.04	0.44	4.44	12.24	22.22	2.08	0.30	Nb, V 34.0
	0.34N	0.03	0.41	4.41	12.31	22.18	2.11	0.34	33.9
Duplex stainless steel	0.014	0.30	0.50	6.67	24.88	3.09	0.30	2%W	26.7
A286	25Ni	0.05	0.38	1.01	25.16	14.75	1.28	0.005	37.8
	35Ni	0.05	0.40	1.02	34.56	15.00	1.29	0.006	2%Ti 47.4
	45Ni	0.05	0.39	1.02	44.43	15.03	1.29	0.006	57.3
	55Ni	0.05	0.39	1.02	53.71	15.89	1.29	0.005	67.1
A718	0.018	0.04	0.01	53.81	18.09	2.90	0.004	1%Ti, 5%Nb	68.7
A725	0.008	0.03	0.07	58.25	21.05	8.07	0.008	2%Ti, 3.5%Nb	80.0

$$Ni_{eq} \text{ (mass\%)} = Ni + 0.65Cr + 0.98Mo + 1.05Mn + 0.35Si + 12.6C$$

hydrogen completely finished up to 600°C.

SSRT under cathodic charge was carried out to evaluate the resistance to hydrogen embrittlement (cathodic hydrogen embrittlement–CHE). Round bar smooth tensile specimens were taken with the axis in the rolling direction from the materials. The tensile specimen had a 2.54 mm gauge diameter with a 25.4 mm gauge length. The gauge lengths were polished with No. 600 emery paper before the tests. SSRT was carried out at ambient temperature in the same solutions as the hydrogen charging tests. A strain rate was $4.2 \times 10^{-6} \text{ s}^{-1}$ at the cross head speed referred to the original gauge length. Fracture elongation (El.) and reduction of area (R.A.) under cathodic charge were measured and compared to the values in air. The fracture surfaces of the specimens were observed using a Scanning Electron Microscope (SEM) after SSRT.

Highly pressurized hydrogen gas tests were conducted using a SSRT apparatus in highly pressurized gaseous hydrogen. For HGE evaluation, SSRT was carried out in an autoclave pressurized with gaseous hydrogen from 45 MPa to 90 MPa at ambient temperature. The purity of the testing hydrogen gas was 99.99999%. The autoclave was evacuated and replaced with the hydrogen gas several times to remove air completely, then filled with the hydrogen and pressurized.

For IRHE evaluation, thermal hydrogen pre-charge was conducted to specimens. 0.5 mm thick plate specimens and plate tensile specimens with 2 mm thick were exposed to gaseous hydrogen of 80 to 98 MPa at the temperature range from 85 to 250°C for 48 to 1 000 h. The test temperatures and times were chosen to result in a uniform hydrogen distribution through the thickness of the samples. After the exposure tests, absorbed hydrogen concentration was measured by TDA. SSRT was also carried out in air at ambient temperature using the hydrogen pre-charged tensile specimens.

3. Results

3.1. Hydrogen Absorption under Cathodic Charge

Hydrogen charging tests were carried out to obtain concentrations of hydrogen absorbing in the materials. **Figure 1** shows the test results for high N SS under various charging conditions for 48 h. The measured value shown in Fig. 1 was an average concentration of hydrogen in the material. The results indicate hydrogen concentration can be controlled by charging conditions. There was no significant effect of N concentration on hydrogen absorption. Absorbed hydrogen concentration in other materials showed the similar tendency to the high N SS.

However, there must be a distribution of hydrogen in the plate specimen because of low diffusivities of hydrogen in austenitic alloys. The concentration profile of hydrogen through the thickness of the specimen can be calculated in accordance with the diffusion equation consisting of several parameters—thickness of the plate, hydrogen diffusion coefficient D of each material and the hydrogen charging time.^{11,14} **Figure 2** is an example of calculated results of hydrogen distribution in a 0.5 mm thick plate specimen of the high N SS charged with hydrogen for 48 h. The average concentration of hydrogen was 22 ppm. In

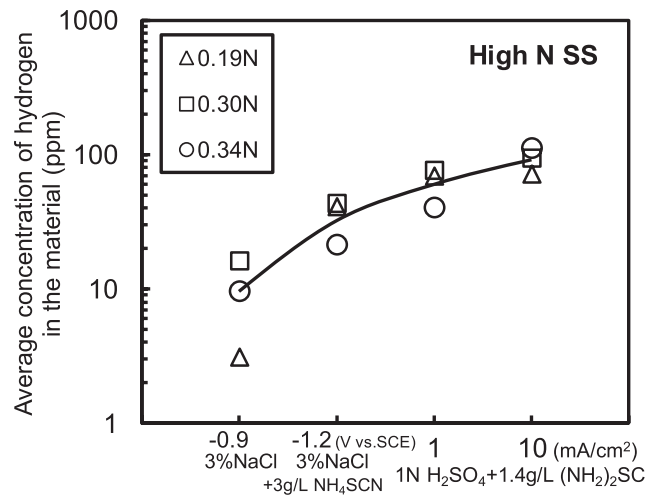


Fig. 1. Average concentration of hydrogen absorbing in high nitrogen stainless steel (high N SS) under cathodic charge.

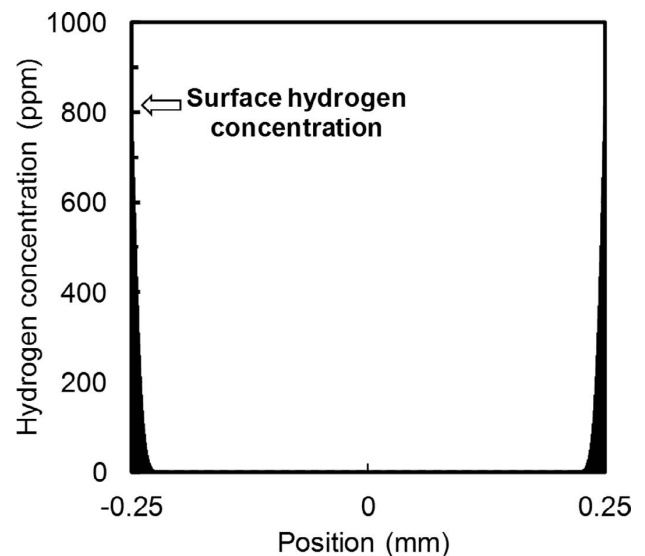


Fig. 2. Distribution of hydrogen in a plate specimen.

this calculation, hydrogen diffusion coefficient D of each material is $1.8 \times 10^{-12} \text{ cm}^2/\text{s}$ for 304L, 316L and high N SS,¹⁵ $3.0 \times 10^{-9} \text{ cm}^2/\text{s}$ for duplex SS,¹⁶ $9.4 \times 10^{-12} \text{ cm}^2/\text{s}$ for A286,¹⁷ and $2.0 \times 10^{-11} \text{ cm}^2/\text{s}$ for A718 and A725.¹⁷ Surface hydrogen concentration was obtained from the measured values of hydrogen concentration (in Fig. 1) and the calculated hydrogen distribution profiles (in Fig. 2) in each material. The surface hydrogen concentrations were 38 times for 304L, 316L and high N SS, 17 times for A286, 12 times for A718 and A725 to the measured hydrogen concentrations. The surface hydrogen concentration in duplex SS was equivalent to the measured value due to the higher D than that for the other austenitic alloys.

Cracks caused by hydrogen nucleate at the specimen surface under the cathodic charge. When the crack propagates, hydrogen is charged successively to the crack tip from the aqueous solution. Therefore, susceptibility to hydrogen embrittlement was discussed based on the surface hydrogen concentration as follows.

3.2. Hydrogen Embrittlement Susceptibility under Cathodic Charge

Hydrogen embrittlement under cathodic charge (CHE) was evaluated by SSRT. **Figure 3** shows relative fracture elongation (relative fracture El.) of the representative materials. “Relative” means the ratio of fracture elongation under cathodic charge to that in air. The horizontal axis is the surface hydrogen concentration estimated previously. Various materials had their own “H-relative fracture El. curves”. The H-relative fracture El. curve of high N SS was located at the highest position in Fig. 3. This means that the high N SS had the highest resistance to CHE. Even in the high N SS, however, excessive hydrogen beyond 2 000 ppm decreased relative fracture El. On the contrary, Ni based alloy A725 was degraded by a small amount of hydrogen around 10 ppm.

Figure 4 shows examples of fracture surfaces of the high N SS after SSRT. Reduction of area (R.A.) was decreased

by the cathodic hydrogen charging as shown in Figs. 4(b)–4(d) compared to that in air in Fig. 4(a). The R.A. decreased according to an increase in surface hydrogen concentration. There was no remarkable difference in morphology of the fracture surfaces between Figs. 4(a) and 4(b). As shown in Figs. 4(c) and 4(d), smooth fracture surfaces were observed along the external surface of the specimens under the severe hydrogen charging conditions. **Figure 5** shows side views of the specimens shown in Fig. 4. Many sub-cracks were observed on the specimens under severe hydrogen charging conditions as shown in Figs. 5(c) and 5(d). The sub-cracks corresponded to the smooth fracture surfaces around the specimen shown in Figs. 4(c) to 4(d). The number and size of the sub-cracks increased depending on the surface hydrogen concentration.

Figure 6 shows fracture surfaces of A718 and A725 after SSRT. In these materials, the values of R.A. were extremely low even in air. In A725, remarkable intergranular cracks

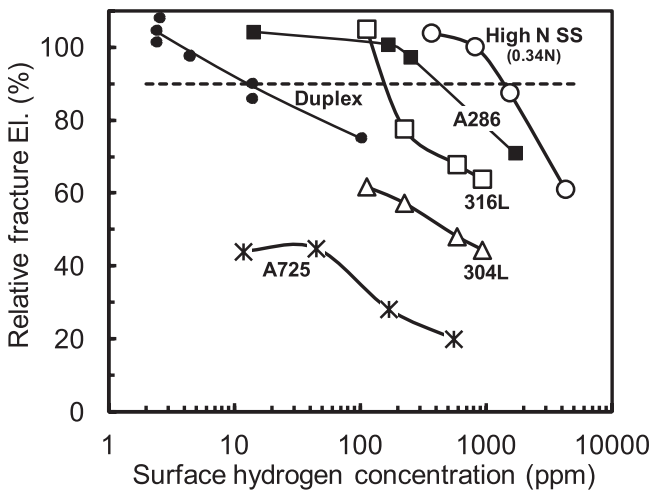


Fig. 3. Effect of surface hydrogen concentration on relative fracture elongation.

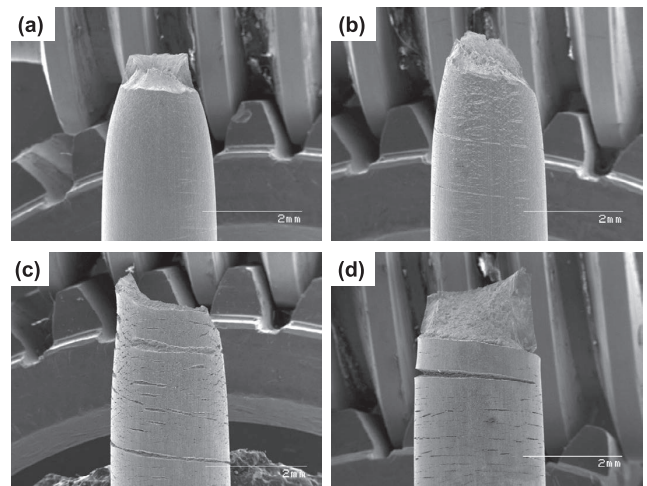


Fig. 5. Side views of high nitrogen stainless steel after SSRT. (a) In air, (b) surface H concentration of 815 ppm, (c) 1 540 ppm, (d) 4 271 ppm.

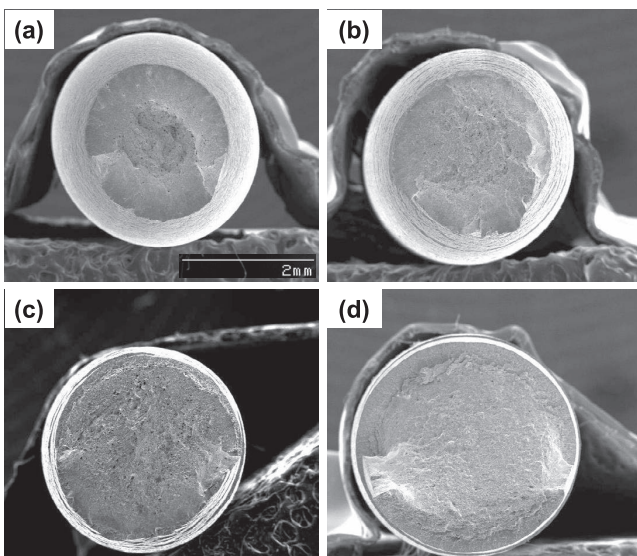


Fig. 4. Fracture surfaces of high nitrogen stainless steel after SSRT. (a) In air, (b) surface H concentration of 815 ppm, (c) 1 540 ppm, (d) 4 271 ppm.

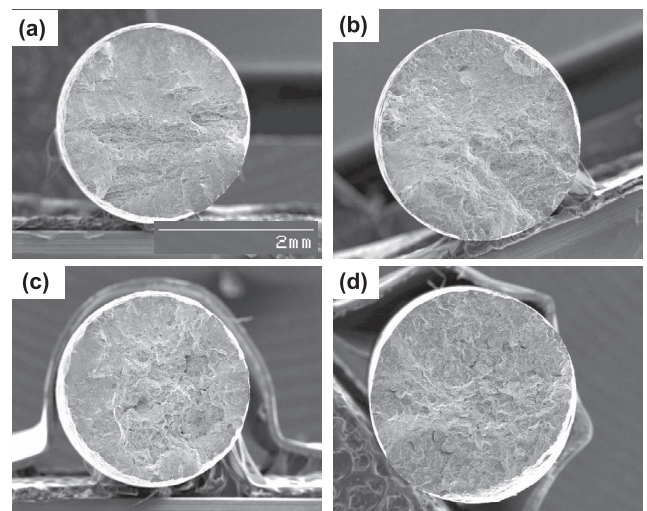


Fig. 6. Fracture surfaces of A718 and A725 after SSRT. (a) A718 in air, (b) A718 under the surface H concentration of 506 ppm, (c) A725 in air, (d) A725 under the surface H concentration of 553 ppm.

were observed under cathodic charge as shown in Fig. 6(c). **Figure 7** shows side views of the specimens shown in Fig. 6. Many sub-cracks along grain boundaries were observed under hydrogen charge as shown in Figs. 7(b) or 7(d).

Figure 8 shows the effect of nitrogen (N) concentration on relative fracture El. of the high N SS. It was observed that addition of N had no significant effect on CHE susceptibility.

Figure 9 shows the effects of Ni concentration and aging heat treatment on relative fracture El. of A286. An increase in Ni concentration decreased relative fracture El. of both the solution heat treated and the aged samples. Furthermore, it was confirmed that the aging heat treatment decreased relative fracture El.

In this study, critical surface hydrogen concentration (H_C) was defined as the highest surface hydrogen concentration at which relative fracture El. was more than 90%, in order to discuss the CHE susceptibility quantitatively. H_C is understood as the maximum surface hydrogen concentration which is hard to cause hydrogen embrittlement in each

material. H_C was obtained from the intersection of a dotted line (90% of relative fracture El.) and the H-relative fracture El. curve of each material in Figs. 3, 8 and 9. **Figure 10** shows the H_C of each material as a function of $Ni_{eq}^{12)}$ a parameter indicating the stability of austenitic phase. It was observed that there was the best Ni_{eq} range where the maximum H_C was obtained. High N SS and A286 were located in the best range. Materials with lower Ni_{eq} showed lower H_C while materials with excessive Ni_{eq} also showed lower H_C .

3.3. Comparison among Susceptibilities to CHE, HGE and IRHE

HGE susceptibility was evaluated by SSRT in highly pressurized gaseous hydrogen for the comparison with that to CHE. **Figure 11** shows relative reduction of area (relative R.A.) under highly pressurized gaseous hydrogen as a function of Ni_{eq} . The figure includes several reported data⁴⁾ as indicated by * marks. Relative R.A. in Fig. 11 shows similar dependence on Ni_{eq} to H_C in Fig. 10. There was the best range of Ni_{eq} to obtain the highest relative R.A. and H_C . This means materials with lower or excessive Ni_{eq} show lower resistance to both HGE and CHE. Secondly, aging heat treatment decreased both relative R.A. and H_C of labo-

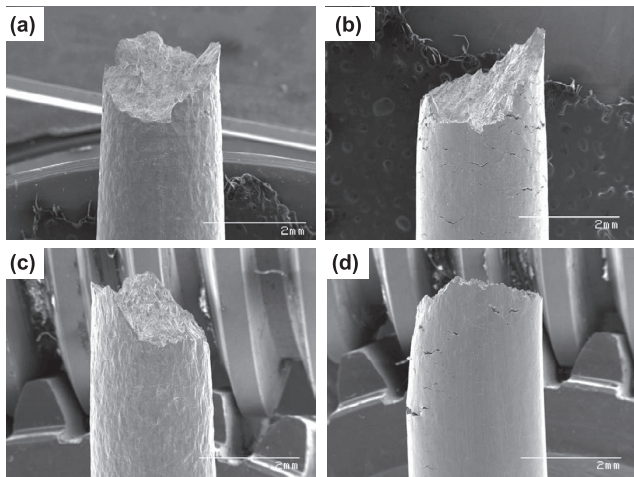


Fig. 7. Side views of A718 and A725 after SSRT. (a) A718 in air, (b) A718 under the surface H concentration of 506 ppm, (c) A725 in air, (d) A725 under the surface H concentration of 553 ppm.

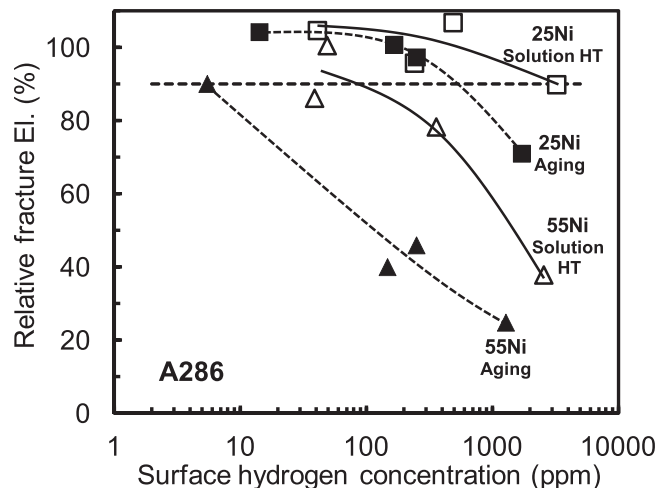


Fig. 9. Effects of Ni concentration and heat treatment on relative fracture elongation of A286.

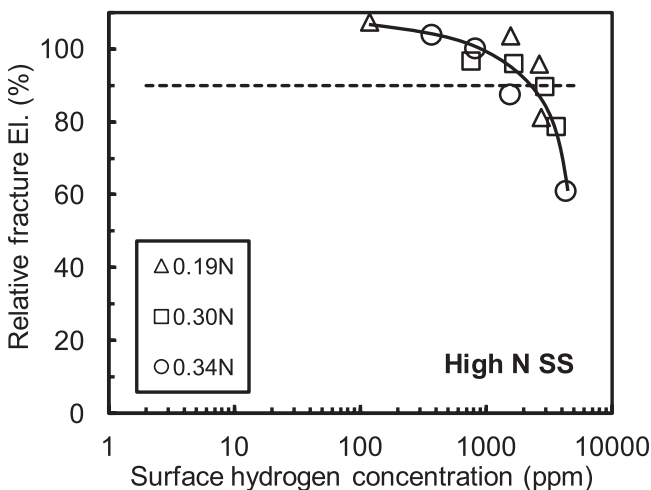


Fig. 8. Effect of N concentration on relative fracture elongation of high nitrogen stainless steel (high N SS).

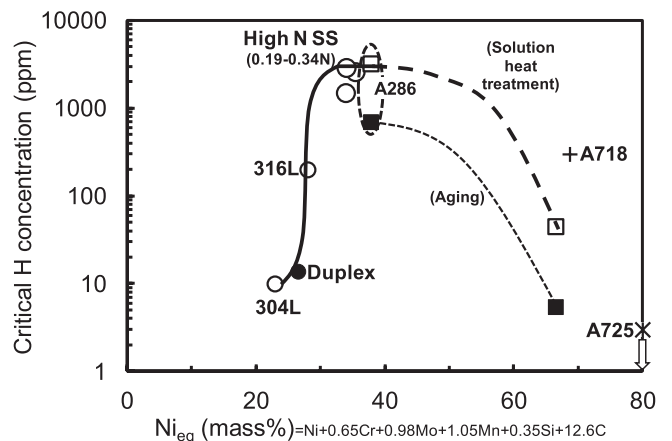


Fig. 10. Effect of Ni equivalent on critical surface hydrogen concentration.

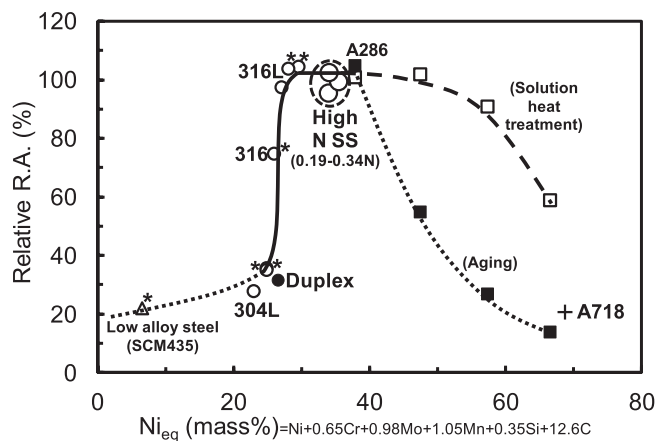


Fig. 11. Effect of Ni equivalent on susceptibility to hydrogen gas embrittlement (*: reported data⁴⁾).

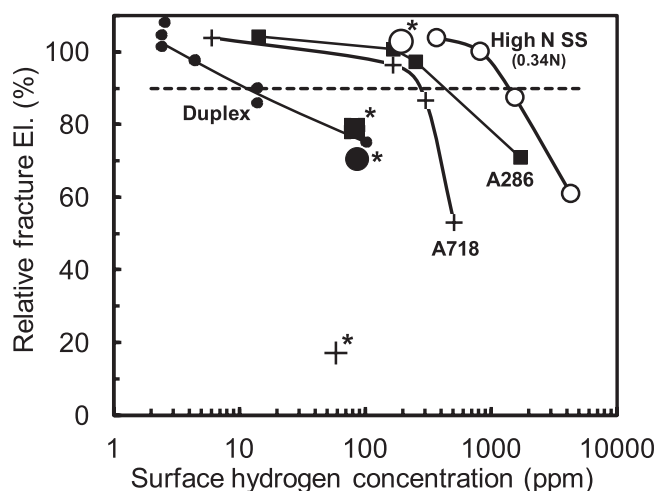


Fig. 12. Comparison between relative fracture El. in CHE and IRHE (*: IRHE test results).

ratory melt A286. On the contrary, the different point was that several materials (type 316L and aged A286) showed 100% of relative R.A. in Fig. 11 while these materials showed medium H_C in Fig. 10.

Figure 12 is the comparison between susceptibilities to CHE and IRHE. The Ni based alloys, A286 and A718, were aged materials after solution heat treatment. For IRHE evaluation, thermal hydrogen pre-charge was conducted in high pressure–high temperature gaseous hydrogen up to 98 MPa at 250°C. The exposure conditions simulate the gaseous environments in the container of fuel cell vehicle and hydrogen station. TDA results indicated that all specimens absorbed hydrogen ranging from 80 ppm to 200 ppm. This means the concentration of hydrogen absorbing from the actual service environments, H_E , is in the range for the investigated materials. IRHE susceptibility of the thermal pre-charged tensile specimens was evaluated by SSRT in air. In Fig. 12, the horizontal axis is the “measured values of hydrogen concentration” in IRHE evaluation, while that is the “calculated surface concentration” in CHE evaluation. The IRHE test results are indicated by * marks in Fig. 12. IRHE susceptibilities of high N SS and duplex SS showed a good agreement with the CHE susceptibilities. The same

tendency had been already reported in type 304L and 316L.¹¹⁾ On the contrary, relative fracture El. of A286 and A718 were lower values in the IRHE condition than that in the CHE condition.

4. Discussion

4.1. Effects of Metallurgical Features on CHE Susceptibility

As previously described, the critical surface hydrogen concentration H_C , derived from SSRT under various cathodic charging conditions, is a quantitative index for evaluating the resistance to hydrogen embrittlement. Effects of metallurgical features on H_C were discussed as follows.

4.1.1. Nitrogen (N)

It was confirmed that N concentration had no significant effect on H_C as shown in Fig. 8 in the case of high N SS.

For stabilizing austenitic phase, N is expected to have a beneficial effect. While Hirayama's Ni_{eq} ¹²⁾ used in this study does not include a term of N, Itoga proposed another Ni_{eq} ⁵⁾ including a term of N for the evaluation of high N stainless steels.

On the contrary, a detrimental effect of N was also recognized. It was reported that N decreases the resistance to HGE¹⁸⁾ and CHE¹⁹⁾ of high Mn containing austenitic stainless steel such as type 205. The main mechanism is supposed to be a planer dislocation formation due to a decrease in stacking fault energy (SFE) by N.²⁰⁾ To increase SFE for the prevention of the planer dislocation formation, increasing alloying elements such as Ni or Cr is beneficial.^{21,22)} In the case of the high N SS, it is assumed that Ni and Cr compensate the detrimental effect of N.

4.1.2. Ni_{eq}

H_C showed a strong dependence on Ni_{eq} as shown in Fig. 10. There was the best Ni_{eq} range to obtain the maximum H_C . The high N SS and the A286 were located in the best Ni_{eq} range. The maximum H_C of these materials is attributable to the stability of austenitic phase.

Materials with lower Ni_{eq} showed lower H_C . It is attributable to martensitic transformation during deformation (304L) or containing ferrite phase (duplex SS), since the bcc crystal structure generally shows high susceptibility to hydrogen embrittlement. In the case of type 316L, martensitic transformation was not observed after SSRT under cathodic charge.¹¹⁾ However, there is a possibility that hydrogen-induced martensite phase which formed during hydrogen charging, decomposed and diminished after the test.

Materials with excessive Ni_{eq} showed also lower H_C . As these materials have high stability of austenitic structure, the mechanism is not martensitic transformation. Miyata observed a change in dislocation morphologies by hydrogen in Ni based alloys by a transmission electron microscope, and reported that hydrogen enhances a cross-slip and screw components of dislocations.²³⁾ The change in the dislocation motion by hydrogen could correlate with the hydrogen embrittlement of Ni based alloys. The other possible mechanism is Ni hydride formation.²⁴⁾ However, detailed mechanisms of hydrogen embrittlement have not been established

yet in Ni based alloys.

In Figs. 10 and 11, H_C was plotted as a function of Ni_{eq} suggested by Hirayama.¹²⁾ However, there may be another appropriate parameter reflecting hydrogen embrittlement susceptibility. One is the Ni_{eq} including wide range of alloying elements such as N or Cu⁵⁾ as discussed previously. The other is an index reflecting SFE.²²⁾ It was reported that IRHE susceptibility of type 304 strongly depended on not only martensitic transformation, but also SFE.²⁵⁾

4.1.3. Precipitation during Aging Heat Treatment

H_C of the A286 and the series with various Ni levels was decreased by aging heat treatment. In the A286, fine γ' phase precipitates during the aging. The γ' phase precipitates have a beneficial effect on strengthening, while it is reported that a planer dislocation formation is accelerated by γ' precipitates as follows.²⁶⁾ The nano-sized γ' phase is easy to be cut by dislocations during plastic deformation. Subsequent dislocations tend to follow the leading dislocation to slip on the same plane, resulting in the promotion of planar slip. The planer dislocation motion helps the transportation of dislocations and hydrogen to the initiation sites of hydrogen embrittlement such as grain boundaries.

4.2. Comparison of H_C to H_E

H_C is a quantitative index reflecting the resistance to hydrogen embrittlement as previously discussed. Additionally, comparison of H_C to absorbed hydrogen concentration from service environments (H_E), enables the risk assessment of hydrogen embrittlement. For example, H_C of the high N SS was 2 000 ppm as shown in Fig. 3. H_E was 200 ppm when the material was exposed to highly pressurized gaseous hydrogen (98 MPa) as shown in Fig. 12. Therefore, H_C is 10 times larger than H_E . This means the material has sufficiently high resistance to HGE or IRHE in highly pressurized hydrogen environments because of the high H_C .

Concentration of hydrogen absorbing from gaseous hydrogen is in a proportional to square root of hydrogen pressure according to Sievert's law under ideal conditions. Based on the theory, to charge hydrogen up to H_C (2 000 ppm) to the high N SS, extremely high hydrogen pressure (9 800 MPa) must be needed. This means the material has low possibility of hydrogen embrittlement in actual service conditions.

A ratio of H_C to H_E , the margin against hydrogen embrittlement, of each material is as follow. H_C/H_E is 8.5 for aged A286 (H_C : 700 ppm, H_E : 82 ppm), 2.5 for type 316L (H_C : 200 ppm, H_E : 81 ppm), 0.16 for duplex SS (H_C : 14 ppm, H_E : 81 ppm), 0.14 for type 304L (H_C : 10 ppm, H_E : 69 ppm), 0.08 for aged A286 with 55% Ni (H_C : 5.5 ppm, H_E : 69 ppm) and 5 for A718 (H_C : 300 ppm, H_E : 58 ppm). H_C of A725 could not be measured because this material showed a significant decrease in relative fracture El. under a small amount of hydrogen. H_E was ranged from 80 to 200 ppm in the investigated materials as previously described. On the contrary, H_C was varied widely depending on the materials. The wider range of H_C than H_E means that the level of H_C mainly decides the resistance to hydrogen embrittlement.

4.3. Comparison among Susceptibilities to CHE, HGE and IRHE

The following discussion was done to determine whether CHE, HGE and IRHE are similar phenomena or distinct types of hydrogen embrittlement.

H_C evaluated by SSRT under cathodic charge in Fig. 10 showed similar dependence on Ni_{eq} to relative R.A. evaluated by SSRT in highly pressurized gaseous hydrogen in Fig. 11. This means the relative susceptibility of the investigated materials to both CHE and HGE is similar. The estimated reason of the similarity between CHE and HGE is the successive hydrogen supply to the metal surface and crack tip from external environments during SSRT. Strictly, there is a following difference in hydrogen entry mechanism between CHE and HGE. In the CHE process, hydrogen entry occurs in accordance with reduction of H^+ ions resulting in adsorption of atomic H on the metal surface. In the HGE process, it is generally agreed that molecular hydrogen dissociates to atomic H on the fresh metal surface due to plastic deformation during SSRT.

In IRHE evaluation, successive hydrogen entry does not occur. However, the relation of relative R.A. to H_C in IRHE tests showed a good agreement in the high N SS and duplex stainless SS as shown in Fig. 12. The same tendency was observed in type 304L and 316L.¹¹⁾ On the contrary, in the case of the A286 and the A718, susceptibilities to CHE and IRHE were different. The difference in sensitivity must be related to metallurgical features of the Ni based alloys. One possibility is the effect of fine precipitates such as γ' in the A286 or γ'' in the A718 since both alloys are strengthened by the fine precipitations. It is reported that aged A286 showed higher susceptibility to IRHE, while solution heat treated A286 showed no susceptibility to IRHE.⁷⁾ It is considered that the coherent interface between the precipitates and the substrate of the Ni based alloys tends to accelerate non-uniform plastic deformation resulting in an increase in susceptibility to hydrogen embrittlement. Additionally, it is reported that A718 showed higher susceptibility to HGE at elevated temperatures up to 500°C.²⁷⁾ This implies hydrogen trapping situation can be different between cathodic charging at ambient temperature and exposure gaseous hydrogen at elevated temperatures in the case of A286 and A718.

5. Summary

Susceptibility to hydrogen embrittlement under cathodic charge (CHE) of stainless steels and Ni based alloys was evaluated using slow strain rate test. The CHE susceptibility was compared to that of hydrogen embrittlement caused by highly pressurized gaseous hydrogen (HGE and IRHE). The following results were obtained.

1) Critical hydrogen concentration H_C , the maximum hydrogen concentration at which fracture elongation is hard to be degraded, was derived from SSRT under various cathodic charging conditions. H_C strongly depended on Ni_{eq} , which is a parameter indicating the stability of austenitic phase. There was the best Ni_{eq} range where the maximum H_C was obtained. High nitrogen stainless steel and alloy 286, which were located in the best range, showed the maximum H_C .

2) Comparison of H_C to H_E , concentration of hydrogen

absorbing from service environments, enables the risk assessment of hydrogen embrittlement. In the case of the high nitrogen stainless steel, H_C (2 000 ppm) was 10 times larger than H_E (200 ppm). This indicates the material has low possibility of hydrogen embrittlement in actual service conditions.

3) Susceptibility to CHE showed similar dependence on Ni_{eq} to those to HGE and IRHE in the investigated materials. Exceptionally, in the case of Alloy 286 and 718, IRHE evaluation gave more severe results than CHE. It was assumed that precipitation during aging heat treatment in these Ni based alloys has a detrimental effect on IRHE.

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