1. Introduction

Duplex stainless steel (DSS), which consists of two-phase microstructures of austenite and ferrite, exhibits better ductility and weldability than ferritic stainless steel, and higher strength and resistance to chloride stress corrosion cracking than austenitic stainless steel. On the other hand, their low resistance to hydrogen embrittlement (HE) is one of the main problems in maximizing the service life of DSSs in industry. It is believed that for duplex stainless steels, embrittlement involves a combination of mechanisms of mainly HEDE (Hydrogen Enhanced Decohesion) in ferrite and mainly HELP (Hydrogen Enhanced Local Plasticity) in the austenitic phase.

When the susceptibility of metallic materials to HE is phenomenologically studied, usually tensile tests are carried out for the specimens pre-charged with hydrogen and/or in the hydrogen charging environment, and the degree of degradation in ductility (tensile strength in very severe case) is investigated with fractographic analysis and/or crack path analysis.

Elhou et al. reported that electrolytic charging with hydrogen caused significant reduction in elongation to failure in DSS specimens with and without cold working. They attributed the results to the damage in the passive film caused by plastic deformation and deformation structure that form in the austenite and ferrite phases. They also claimed that cracks initiated and propagated in the ferrite phase and arrested in the austenite phase or at the phase boundary.

Recently, we preliminarily assessed tensile properties on an SUS329J4L DSS electrolytically charged with hydrogen at a strain rate of $1.38 \times 10^{-6}\text{s}^{-1}$, and found the increase in the sensitivity to HE with increasing charging time. This was closely coincided with the fractographic analysis, i.e., the increase in the area without dimples. However, tensile tests should be carried out over wider range of strain rates since HE is a phenomenon closely correlated to hydrogen diffusion. Also, more detailed fractographic analyses and the behavior of hydrogen correlated with the above phenomenon have remained uncertain. This paper will present some further analyses on the HE in the above DSS by means of tensile tests in wider range of strain rates and detailed fractography. In addition to the tensile tests associated with fractography, TDS (Thermal Desorption Spectroscopy) was conducted in this study to obtain information on hydrogen concentration. Although TDS is unable to measure the local concentration at the crack tip, it is frequently used to discuss the behavior of hydrogen since it can quantify the amount of hydrogen.

KEY WORDS: duplex stainless steel; hydrogen embrittlement; electrolytic hydrogen charging; tensile test; strain rate effect; fractography; thermal desorption spectroscopy.
2. Specimen and Experimental Procedures

2.1. Specimen and Hydrogen Charging

The material used in this study is a 2B-finished SUS329J4L sheet of 1 mm thickness, whose chemical composition is shown in Table 1. From this sheet, tensile test pieces with a gauge area of 12 mm in length and 5 mm in width were cut by electric discharge machining parallel to the rolling direction. Then each test piece was polished with waterproof abrasive paper up to 2 000 grit, and finally mirror-finished with buffing by alumina abrasive grains of 0.3 μm. The surfaces were rinsed with distilled water, cleaned ultrasonically in acetone, and dried quickly by warm air. Hydrogen charging was carried out onto both sides of gauge portion of the test piece in sulfuric acid solution with pH of 2.5 containing 0.1 mass% of NH₄SCN as a hydrogen recombination inhibitor at room temperature with the use of platinum anodes at a current density of 100 A/m² and voltage of 10 V. Test pieces charged for 1.5, 6 and 24 h were prepared.

2.2. Tensile Test

Tensile tests were carried out at room temperature on test pieces both without and with charging at different charging times and at various strain rates \(\dot{\varepsilon}\) ranging from \(1.38 \times 10^{-7}\) to \(1.38 \times 10^{-3}\) s\(^{-1}\) including what is called slow strain rate region. For each condition, three tests were performed, and average values of the results obtained will be reported. The relative error did not exceed 15%. The total duration of the longest tensile test (\(\dot{\varepsilon} = 1.38 \times 10^{-7}\) s\(^{-1}\)) was 935 h. In the case of electrolytically charged specimens, tests were performed immediately after hydrogen charging but without simultaneous charging, i.e., charging was not made during the tests. Fractography was conducted with a scanning electron microscope (SEM, Hitachi S-2150) using secondary electron image.

2.3. Microstructural Analysis

In order to examine the microstructure, the samples were polished and etched with an etchant (HCl: HNO₃ is 3:1 in volume) for 1 min. The microstructures were examined using an SEM (TM3030) with back scattered electron image. The microstructure of the specimen prior to the test is shown in Figs. 1(a), 1(b) and 1(c). The austenite grain cluster generally has light contrast, whereas the ferrite grains have relatively dark contrast. Both phases have elongated shape in L direction. The grain size and volume fraction of each phase are shown in Table 2.

Table 1. Chemical composition of the SUS329J4L specimen in mass%.

| C  | Si  | Mn  | Cr   | Mo  | N  | Ni  | Fe  |
|----|-----|-----|------|-----|----|-----|-----|
| 0.013 | 0.53 | 0.83 | 25.04 | 3.07 | 0.14 | 7.01 | Bal |

Fig. 1. Microstructure of the specimen. (a) L-LT section, (b) L-ST section around middle thickness and (c) L-ST section including the surface at low magnification.

![Microstructure](image1)

![Microstructure](image2)

![Microstructure](image3)

Table 2. Grain size in 3 directions (\(d_L\), \(d_{LT}\), \(d_{ST}\)) and volume fraction (\(V_F\)) of ferrite and austenite phases.

\[
\begin{array}{cccc}
\delta & 5.91 & 3.14 & 2.12 & 0.51 \\
\gamma & 4.95 & 3.39 & 2.21 & 0.49 \\
\end{array}
\]

Fig. 2. Stress-Strain curves for samples uncharged and charged for the indicated times at a strain rate of \(1.38 \times 10^{-5}\) s\(^{-1}\).
2.4. TDS
The characteristics of hydrogen desorption were investigated by means of TDS with a machine EMD-WA1000S/W where hydrogen desorption is measured under ultra-high vacuum. After charging, the samples were cut into a size with 5 mm × 5 mm and set in the chamber of TDS device.14–18) After the pressure in the main chamber reaches 3 × 10⁻⁷ Pa and below, the specimen is (i) kept at 100°C for 30 min in order to remove the moisture adhering to the surface of the specimen and existing in the hydrated oxide film of the specimen, (ii) heated from 100°C to 600°C at a constant heating rate of 100°C/h and cooled in the chamber to room temperature, and (iii) re-heated under the same condition as (ii) in order to measure the background hydrogen pressure depending on the temperature. During the test, H₂⁺ ion current is electrically measured by the quadrupole mass spectrometer with a sampling rate of 2 s⁻¹. The heating is indirectly made through the stage baked by infrared radiation.

3. Results and Discussion

3.1. Tensile Test and Fractography
Figures 2, 3(a) and 3(b) show the results of tensile tests as a function of charging time at a strain rate of \( \varepsilon = 1.38 \times 10^{-6} \text{s}^{-1} \), stress-strain curves, plots of ultimate tensile strength (UTS) and elongation against charging time, respectively. Both UTS and elongation decrease with increasing charging time, but the tendency is more marked in the elongation. Tensile properties of specimens with and without hydrogen charging are shown in Figs. 4(a) and 4(b) as a function of strain rate for the charging time of 24 h. As in Figs. 3 (a) and 3(b), hydrogen charging does not influence so much on the UTS irrespective of strain rate. The detrimental effect of hydrogen is distinctly observed in the case of elongation particularly at strain rates around 10⁻⁴ s⁻¹. Here, to assess the extent of degradation more explicitly, the HE index defined as Eq. (1) was calculated based on difference in the elongation to failure between samples with and without hydrogen charging,

\[
I(\delta) (\%) = \left( \frac{\delta_{\text{uncharged}} - \delta_{\text{charged}}}{\delta_{\text{uncharged}}} \right) \times 100 \quad (...) (1)
\]

where \( \delta_{\text{uncharged}} \) and \( \delta_{\text{charged}} \) are the elongations to failure of uncharged and charged samples, respectively. The \( I(\delta) \) values are plotted in Fig. 4(c). As can be seen from the results, whereas the extent of degradation is relatively small at strain rates around 10⁻⁷ s⁻¹, it increases with increasing strain rate and reach a maximum at the strain rate of 1.38 × 10⁻⁴ s⁻¹. Beyond this strain rate, it again decreases slightly.

The phenomenon that the extent of degradation took maximum at an intermediate strain rate of about 10⁻⁴ s⁻¹ can be correlated with two facts: (i) hydrogen is released during the tensile test and the amount of released hydrogen will be smaller with increasing strain rate; (ii) HE is based on the diffusion of hydrogen.

In Figs. 5 and 6, fracture surfaces are shown for the test pieces uncharged and charged for 24 h, respectively, tested at the strain rate of 1.38 × 10⁻⁴ s⁻¹. Figure 7 shows the fracture surface of the 24 h-charged samples as a func-
tion strain rates. Qualitative analysis revealed the existence of two fracture types: areas with and without dimples, as shown in Figs. 5 and 6. According to this classification, the fraction of area without dimples \( F_{\text{wod}} \) was derived with respect to the total fracture surface area, and again plotted as a function of strain rate in Fig. 8. It is to be noted that tendency of \( l(\delta) \) is in good agreement with that of \( F_{\text{wod}} \). In the case of the uncharged specimen, the small but not negligible value of \( F_{\text{wod}} \) about 10% was considered to be affected by shear lip region adjacent to the original surface. The shear lip is classified as a typical ductile fracture surface as well as the area with dimples. Thus, in spite of the small value of \( F_{\text{wod}} \), the uncharged specimen was concluded to be fractured in almost completely ductile manner.

In contrast, major difference which can be recognized even at low magnification is that the charged specimen has step-like fracture surface as indicated as “S” in Fig. 6(b), associated with delaminations (cracks parallel to the sheet). Figure 9 shows surface feature of a fractured test piece near the fracture point. Clearly, the step-like fracture surface can be observed on the piece. This means that the crack initiate at the surface, followed by the delamination and ductile fracture occurring in the core portion. Since tensile stress in the tensile direction is much higher than that in the thickness direction, crack should initiate perpendicular to the tensile direction at ferrite grains\(^{(1)}\) and then delamination occurs when nominal stress reaches the maximum, resulting in triaxial stress condition. The fracture process will be further discussed in detail elsewhere.

3.2. TDS

The TDS spectra, the curves of hydrogen desorption rate versus temperature, are shown in Fig. 10(a) for the samples uncharged and charged for various times. In Fig. 10(b), the

![Fig. 5](image5.png)

**Fig. 5.** SEM images of fracture surface of the sample without charging tested at 1.38 \( \times 10^{-5} \) s\(^{-1} \). (a): Overall view, (b) and (c): magnified view of areas without and with dimples, respectively.

![Fig. 6](image6.png)

**Fig. 6.** SEM image of fracture surface of the sample charged for 24 h and tested at 1.38 \( \times 10^{-4} \) s\(^{-1} \). (a): Overall view, (b) and (c): magnified view of areas without and with dimples, respectively.

![Fig. 7](image7.png)

**Fig. 7.** SEM images of fracture surface (overall view) of the samples charged for 24 h and tested at different strain rates. (a): 1.38 \( \times 10^{-7} \) s\(^{-1} \), (b): 1.38 \( \times 10^{-6} \) s\(^{-1} \), (c): 1.38 \( \times 10^{-5} \) s\(^{-1} \), and (d): 1.38 \( \times 10^{-3} \) s\(^{-1} \).

![Fig. 8](image8.png)

**Fig. 8.** Fraction of area without dimples, \( F_{\text{wod}} \), as a function of strain rate.

![Fig. 9](image9.png)

**Fig. 9.** Surface feature of a fractured test piece near the fracture point.
The slight higher value of desorption rate of impurity hydrogen, is mostly trapped at relatively stable below about 100 °C. The hydrogen in the uncharged sample, which is at 150 µm distance from the fracture point.

Fig. 10. Thermal desorption spectra of the samples uncharged and charged with the indicated charging times. (a): overall spectra, (b): magnified view of uncharged and 24 h-charged samples.

The effect of charging only appears in the temperature range of HE took a maximum at 1.38 × 10⁻⁴ s⁻¹. According to fracture surface evaluation, smooth area (area without dimples) also took a maximum at the strain rate of 1.38 × 10⁻⁴ s⁻¹, being consistent to the strain rate dependency of the HE index. By TDS, the concentration of the diffusive hydrogen was confirmed to increase with increasing charging time. Hence, the extent of HE was deduced to be dependent on the concentration of the diffusive hydrogen. The phenomenon that the extent of HE took a maximum at 1.38 × 10⁻⁴ s⁻¹ is considered to be correlated to the balance between hydrogen diffusion and hydrogen desorption during the test.

4. Conclusions

Tensile tests were performed on DSS(SUS329J4L) samples with and without electrolytic hydrogen charging at various strain rates ranging from 1.38 × 10⁻⁷ to 1.38 × 10⁻³ s⁻¹. Elongation to failure was confirmed to decrease with increasing charging time for testing at 1.38 × 10⁻³ s⁻¹, while UTS was not affected markedly by hydrogen charging. The extent of HE assessed with HE indexes took a maximum at a strain rate of 1.38 × 10⁻³ s⁻¹. According to fracture surface evaluation, smooth area (area without dimples) also took a maximum at the strain rate of 1.38 × 10⁻³ s⁻¹, being consistent to the strain rate dependency of the HE index. By TDS, the concentration of the diffusive hydrogen was confirmed to increase with increasing charging time. Hence, the extent of HE was deduced to be dependent on the concentration of the diffusive hydrogen. The phenomenon that the extent of HE took a maximum at 1.38 × 10⁻³ s⁻¹ is considered to be correlated to the balance between hydrogen diffusion and hydrogen desorption during the test.

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