1. Introduction

Duplex Stainless steels (DSSs) have become very common structural materials in many applications, particularly pressure vessel, oil, gas and underwater pipelines due to their high level of corrosion resistance and good mechanical properties.1–3) On the other hand, the main concern in the durability of DSSs, is their interplay with hydrogen especially in the presence of stress.4–6) These combination lead to a degradation of mechanical properties and delayed fracture, known as hydrogen embrittlement (HE).7–9) According to the authors, previous research,6,7) the main cause of the fracture in the case of HE in DSS is closely related to the microstructure composed of the co-existing two phases (ferrite and austenite), combined with the local stress state in the material. Hydrogen diffusion in the ferrite proceeds much faster than in the austenite, despite the lower solubility than in the austenite.10–12)

Several researches and experiments have been devoted to characterizing and determining the factors affecting HE,13–17) while the process is not fully understood yet. However, for realizing this mechanism, accurate knowledge on hydrogen solubility, diffusivity and distribution within their microstructure is needed.18–20)

The hydrogen atoms in steels have been roughly divided into two categories: one is non-diffusive hydrogen atom strongly trapped by stable trapping sites such as precipitates and inclusions, and the other is diffusive hydrogen atom that are in the interstitial site of the matrix or lightly trapped by less stable sites such as dislocations and grain boundaries.21–25)

The most important issue is the behaviour of diffusive hydrogen in the microstructure that affects the failure: whether it is in the interstitial lattice site or lightly trapped by some lattice defects, and where the diffusion path is. Acquiring such information is extremely difficult by common analysing technique such as scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDXS), since hydrogen is small in quantity and its X-ray cannot be detected. Thermal desorption spectroscopy (TDS) is a useful method for analysing hydrogen state in a specimen,26) but this method can determine average hydrogen concentration in a specimen and is unable to find the local
distribution of hydrogen.\textsuperscript{27}) Acquiring such kind of data about local distribution of hydrogen has become possible by applying hydrogen visualization method like hydrogen microprint technique (HMPT).\textsuperscript{25,28)}

The HMPT is a technique for visualizing the hydrogen that released from the surface of samples. The basic principle of HMPT\textsuperscript{25,28)} is to apply a high-resolution liquid nuclear emulsion to the surface or cross section of a previously hydrogen-charged sample (Fig. 1). When hydrogen atoms are emitted from the specimen, they react with silver bromide in a gelatine film, leaving silver particles on the specimen surface. After fixing, for removing remaining silver bromide, we can observe the emission points of hydrogen atoms as silver particles.

Regarding to the previous research on the distribution of hydrogen in DSS by HMPT, García observed the specimen surface opposite to hydrogen-charged side where charging was made after emulsion was covered, and claimed that hydrogen desorption occurs preferentially at the interphase boundary between austenite and ferrite phases, which acts as a diffusion path of hydrogen.\textsuperscript{29)} However, it is not certain if this path is continuous from one side to the other, since he did not show the microstructure of his sample. On the other hand, Luu \textit{et al.}\textsuperscript{29)} applied HMPT on DSS specimens nearly in the same condition as García’s, and found hydrogen permeation rate and diffusivity in ferrite is higher than in austenitic phase of duplex stainless steel, and more hydrogen distribution on ferritic phase can be detected by hydrogen microprint technique. They did not mention on the phase boundary as the diffusion path.

Overviewing briefly the previous reports, a discrepancy has remained on the diffusion path. Also, no quantitative discussion has been made. In this paper, hydrogen diffusion path and distribution inside the microstructure of a DSS specimen, immediately after electrolytically hydrogen charging and after keeping for a long time, have been investigated by HMPT. The results obtained have been discussed more quantitatively than in the previous reports.

2. Experimental Procedure

2.1. Material and Hydrogen Charging Method

The material used in this study is an SUS329J4L sheet with 1 mm thickness and annealed at 1055°C for 18 min and then water-cooled, containing 51 Vol% ferrite and 49 Vol% austenite phases both elongated in the rolling direction. Example of the microstructure of the etched specimen is shown in Fig. 2. By using the EDX-equipped SEM (Hitachi 3400 with Horiba 51-XMX0001), the concentration of Cr and Ni elements was quantitatively measured inside the two phases by assuming the material as a purely ternary alloy, to confirm the relationship between the phase and contrast in the etched specimen in the SEM image. The average chemical composition of the material in mass\% is listed in Table 1. The result of the quantitative analysis previously reported\textsuperscript{7)} is again shown in Table 2 for reference. From this
result, it is concluded that the light area with larger amount of Cr looking like matrix is ferrite, while the dark area with larger amount of Ni looking like island-shaped precipitate phase is austenite. Test pieces, with a gage portion of 12 mm in length and 5 mm in width, were cut from the sheet in the longitudinal direction by electric discharge machining (EDM), ground with waterproof abrasive paper up to 3000 grit, mirror-finished by buffing with diamond paste up to 0.25 μm, and finally etched with aqua regia. The surfaces were rinsed with distilled water, cleaned ultrasonically in acetone, and then dried quickly by warm air. The charging was performed at room temperature (RT) onto the one side of the gage portion of the test pieces (the other sides were insulation-coated) for 1.5 and 24 h with platinum anode in a sulfuric acid aqueous solution with pH = 2.5 containing 0.1 mass% of NH₄SCN as a hydrogen recombination inhibitor with a current density of 100 A·m⁻² and voltage of 10 V.

2.2. HMPT

The surface of the test pieces was etched to reveal the microstructure, and then hydrogen-charged for 1.5 and 24 h, and then covered with nuclear emulsion (Ilford L4 diluted with distilled water by 4 times) containing AgBr in a darkroom with wire loop method, as quickly as possible (30 min) after the charging. For some of the test pieces, the charged surface was covered with the emulsion after holding the test pieces for 300 h at room temperature. Furthermore, to investigate the hydrogen distribution and diffusion path in the middle-thickness portion, the 24 h charged test pieces were cut, and their cross section was etched and covered with the emulsion.

Subsequently, after holding all the above samples at RT for 24 h from the emulsion covering, the specimen was placed into the fixing solution (Super Fuji Fix) for totally 15 min (2 min in the darkroom and 13 min in the lab environment), and then rinsed with running water for 15 min, dried naturally and observed with an SEM (Hitachi S3400) equipped with an EDX device to confirm the detected particle to be silver. The procedures of hydrogen charging, holding, emulsion covering, etc. are illustrated schematically in Fig. 3.

3. Results and Discussion

To observe trapping sites, diffusion path and distribution of hydrogen in the microstructure, immediately after charging and after keeping time, HMPT has been applied on the same side of hydrogen-charged surface and cross section of specimens. Figures 4(a) and 4(b) show HMPT/SEM images of the test pieces immediately after 1.5 h and 24 h hydrogen-charged. The small white spots observed are fine silver grains, confirmed by SEM-EDX. It is revealed that most of hydrogen atoms are detected in the interphase boundary as reported by García,28) while some are in the ferrite matrix as reported by Luu et al. 29) According to the finite element simulation results on hydrogen diffusion in DSS at 20°C,30) the hydrogen concentration is decreased to about 10% of the surface concentration at a point of about 40
μm from the surface for the diffusion time of 0.33 h. Since diffusion distance is roughly proportional to the square root of time, 10% of the surface concentration will be attained at distances of 85 μm and 340 μm from the surface for the charging time of 1.5 h and 24 h, respectively. In the present study, hydrogen was detected on the charged side, i.e., the detected hydrogen atoms once diffused inward during charging and then migrated backward during keeping time of 24 h for HMPT. In the case of the backward diffusion, concentration gradient is completely different, but it can be deduced that the detected hydrogen atoms were from distances roughly the same magnitude as the above values.

The silver grains were classified according to the location in the microstructure into those on phase boundaries, inside ferrite and austenite grains. The area fraction of silver grains in the viewing area is illustrated in Fig. 5 with the result of the relative area fraction in microstructure in Fig. 6 for better understanding. Figure 5 shows that the amount of desorbed hydrogen (total area fraction of silver grains) is naturally increased from 5.6% to 11.3% as the charging time increases from 1.5 h to 24 h. An important feature in Fig. 6 is that the silver grains have been detected mostly on the phase boundary of the specimen with the shortest charging time, while in the 24 h charged sample, silver particles visualized in the matrix increases in relative comparison with those in the interphase region. This effect of charging time is probably caused by the diffusion of hydrogen from the ferrite matrix to the boundary, like the diffusion during keeping for HMPT (24 h). Although the fraction of ferrite phase changed slightly as shown in the caption of Fig. 4, we judged this change to be negligibly small compared to the change of the area fraction affected by the charging time. The same judgment was made on the effect of holding time, which will be mentioned in the next paragraph.

Figures 7(a) and 7(b) show the HMPT/SEM images of the hydrogen-charged specimens with the same charging condition of the above specimens and kept for 300 h at the ambient air prior to emulsion covering. The area percentage and relative fraction of silver grains in the viewing area is illustrated in Figs. 8 and 9, respectively. It is noticed from Fig. 8 that the total fraction of silver grains is naturally increased by increasing the charging time, as is the same in Fig. 5. By comparing Fig. 8 with Fig. 5, it is also noticed that the total fraction of silver grains decreased by increasing the keeping time from charging to emulsion covering in each charging time compared to the unkept specimen (inevitable keeping time, i.e., time for handling: 0.5 h). This means that the amount of remaining hydrogen atoms was naturally decreased by the keeping at RT for 300 h. From Fig. 9, it is found that the relative fraction of the silver particles in the ferrite matrix is increased by increasing the charging time from 1.5 h to 24 h. By comparing Fig. 9 with
Fig. 6, the relative fraction of silver particles on the boundary is increased by increasing keeping time from unkept to 300 h both in the cases of 1.5 and 24 h charging. The hydrogen atoms in unstable site will be diffused out during the keeping of 300 h or move to more stable trapping sites, while those in stable trapping site will remain. Thus, the feature in the specimens after 300 h keeping reflects the distribution of stable site for hydrogen, and hence the phase boundary can be regarded as the preferential stable site for hydrogen in the DSS compared to the ferrite matrix. In other words, it is concluded that the boundary has higher binding energy with hydrogen than some trapping site within the ferrite matrix. The effect of keeping time is in accord with the diffusion of hydrogen from the ferrite matrix toward the outside of the specimen as well as to the boundary, like the diffusion during keeping for HMPT (24 h).

As described in the introduction, García claimed that the boundary acts as diffusion path of hydrogen in the DSS, which is roughly the same conclusion as Yalçın and Edmonds, while Luu et al. claimed only the faster permeation rate in the ferrite than the austenite. To discuss the diffusion path, the cross section of the specimen, 24 h hydrogen-charged and 0.5 h held at room temperature prior to emulsion covering, was subjected to HMPT. Figures shows the resultant HMPT/SEM image. It is revealed that most of hydrogen atoms are detected in the interphase boundary, while some are in the ferrite matrix, qualitatively the same as seen on the charged surface (Fig. 4 (b)). The area percentage and relative fraction of silver grains in the viewing area are illustrated in Figs. (a) and (b), respectively. It is noticed from Fig. (a) that the total fraction of silver grains is 1.7%. Hydrogen was detected most inside the phase boundary and next in the ferrite phase. From Fig. (b), it is found that the relative fraction of the silver particles on the boundary is 70.6% and the relative fraction on the matrix is 23.5%. By comparing these values with those in Fig. 6, it is revealed that the fraction of hydrogen atoms at the boundary against inside the ferrite matrix is smaller in the middle of the specimen than on the surface. This phenomenon can be explained in terms of the binding energy of hydrogen with the boundary and with some trapping site inside the ferrite matrix, and in terms of the microstructure (isolated gamma phase), which is illustrated in Fig. 12 together with expected hydrogen diffusion path. At the surface, all the boundaries are connected to the surface and hence the difference in the fraction of the hydrogen atoms in terms of the site can follow majorly the difference in the binding energy of hydrogen with the boundary and with some trapping site inside the ferrite matrix. Although we do not have any quantitative data of binding energy in DSS, it should be larger in the boundary than in the ferrite matrix, as we discussed in relation to Fig. 9 compared to Fig. 6. Thus,
Fig. 9. Relative area fraction of the silver grains in the HMPT images of the test pieces after 1.5 h (a) and 24 h (b) hydrogen charging corresponding to the conditions in Fig. 8.

Fig. 10. SEM images of HMPT from the cross section of specimens after 24 h hydrogen charging (regional volume fraction is 52% alpha and 48% gamma). The specimens were emulsion-covered as soon as possible after charging (holding time, 0.5 h).

Fig. 11. Area fraction (a) and relative area fraction (b) of the silver grains in the HMPT images for the cross section of test pieces after 24 h hydrogen charging. Viewing area: 1 337 μm².

Fig. 12. Schematic image of expected hydrogen diffusion path within the microstructure of cross section.

the ratio of hydrogen detected at the boundaries is relatively high in the observation on the surface. On the other hand, some of hydrogen should diffuse toward the other side of the specimen according to the concentration gradient of hydrogen, during which hydrogen atoms must leave the boundary and be inside the ferrite matrix for a certain period. This is presumed to be the reason why the ratio of relative fraction of hydrogen at the boundary is smaller in the cross section (in the middle thickness region, Figs. 10 and 11(a)) than on the surface (Figs. 4 to 6). In other words, some of the hydrogen
atoms on their way from one boundary to another were detected as the hydrogen inside the ferrite matrix.

4. Conclusion

Hydrogen concentration, diffusion and distribution inside the microstructure of specimens immediately after electrolytic hydrogen charging and after keeping for 300 h have been investigated by means of HMPT as a function of charging time, and quantitative analysis has been made in terms of the sites where hydrogen atoms were desorbed.

HMPT carried out on the charged side of the specimens revealed that the percentage of silver particles was largest at phase boundary, next inside ferritic phase, and the lowest inside the austenite phase. Hence, the phase boundary in DSS is the most stable trapping site. During the keeping, hydrogen atoms inside the ferrite matrix were presumed to be preferentially diffused out to the charged surface compared to those at the interphase boundary. HMPT results on the cross section confirmed that some of the charged hydrogen atoms diffuse according to the hydrogen concentration gradient toward the other side, leaving the interphase boundary to the ferrite matrix because of the microstructural aspect (isolated gamma phase).

REFERENCES