Environmental Factors Affecting Hydrogen Entry into High Strength Steel due to Atmospheric Corrosion

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Hydrogen entry into high strength steel has been investigated by hydrogen permeation measurements under wet-dry cyclic environments. Dominant environmental factors that control hydrogen entry were temperature, relative humidity, and the amount of sea salt on the steel surface. Corrosion rate increased with an increase in temperature, resulting in enhanced hydrogen permeation. Hydrogen entry was promoted at lower relative humidity (40–60%), by the hydrolysis of Fe³⁺ accelerated by condensed Cl⁻ ions in the water layer. A maximum hydrogen permeation coefficient was observed at the Cl⁻ amount of 0.03 kg/m² on the steel surface, corresponding to a maximum corrosion rate determined by an appropriate water layer thickness. Crack susceptibility of the steel has also been investigated by stress fracture tests under wet-dry cyclic environments. Steels with tensile strengths beyond 1400 MPa suffered from cracking at higher temperatures and the Cl⁻ of 0.03 kg/m². The fracture test results mean that crack susceptibility strongly depended upon the environmental severities which promoted hydrogen entry.

Keywords: low alloy steel, hydrogen permeation, atmospheric corrosion, hydrogen embrittlement, rust

1. Introduction

High strength steels are demanded in many fields. However, it is well-known that high strength steels with tensile strengths more than 125 kg/mm² (1225 MPa) suffer from delayed fracture, which is recognized as one type of mechanical degradation caused by hydrogen absorption.

Hydrogen entry into steels has been studied to evaluate the frequency of delayed fracture in atmospheric environments. Kushida investigated absorbed hydrogen contents in steels that were exposed to various sites in Japan.¹ He revealed the site and time dependence of hydrogen absorption. Tsuru et al. measured the hydrogen entry from a thin water layer on a steel surface by hydrogen permeation techniques.² He revealed that hydrogen entry during a drying period after wetting closely relates change in pH and the potential. The authors of this paper previously investigated the hydrogen entry into low alloy steels using hydrogen permeation techniques under atmospheric exposure, and reported that hydrogen entry strongly depended upon the time in day, the season, and exposure locations.³,⁴ However, the mechanism of hydrogen entry and its correlation with corrosion reactions in atmospheric environments have not been sufficiently clarified yet. Therefore, in this study, hydrogen permeation tests under cyclic environmental conditions simulating the atmospheric corrosion were carried out to discuss environmental factors affecting hydrogen entry. Simultaneously, stress fracture tests under the wet-dry cyclic environments were also conducted to clarify the relationship between hydrogen absorption and delayed fracture susceptibility.

2. Experimental Procedure

A low alloy steel, JIS (Japanese Industries Specification)-SCM435, was used for this study. Chemical compositions of this steel are shown in Table 1. The steel was melted in a vacuum induction furnace and cast into an ingot. The ingot was forged into 15 mm thick plates, and then quenched and tempered to adjust strength levels ranging from 1100 to 1600 MPa.

Membrane specimens for hydrogen permeation tests with a 70 mm diameter and 0.5 mm thick were cut from these steel plates. Hydrogen permeation tests were carried out under wet-dry cyclic environments using a test cell shown in Fig. 1. Both sides of the membrane were polished using No. 600 emery paper, and then one side was electroplated with nickel. After fixing the electroplated side to the test cell, the cell was filled with a 1 N NaOH solution. The electroplated side was polarized at 0 V versus potassium-saturated Ag/AgCl reference electrode using a potentiostat (Potentiostat-Galvanostat HA-151, made by Hokuto Denko). The polished side was not polarized. The cell was then mounted in a chamber. The chamber was divided into two parts by the specimen. One part was filled with 1 N NaOH solution and the other with water. The temperature and relative humidity in the chamber were controlled using a humidifier and a temperature and humidity controller. The concentration of sea salt was controlled with a salt dilution system.

Fig. 1 Hydrogen permeation test cell.
exposed to the external environment. The exposure and internal surface areas of the membrane were 23.7 cm$^2$. Synthetic sea water according to ASTM-D-1141 was dropped on the exposed surface and then dried to be sea salt. Next, the test cell was put into a temperature–humidity controlled chamber. Through experiments, hydrogen atoms that permeate the membrane from the external surface were oxidized to hydrogen ions on the nickel electroplated surface. Hydrogen oxidizing current density $J$ (A/cm$^2$) measured by potentiostat gives hydrogen permeation coefficient $JL$ (A/cm), where $L$ is the thickness of the membrane ($= 0.05$ cm). The tests were run for 336 hours.

Electrochemical impedance spectroscopy was carried out to estimate the corrosion rate of the steel. A two electrode cell system was used that consisted of a pair of disk and ring electrodes embedded in an epoxy resin, as shown in Fig. 2. The disk and ring electrodes, made of the same SCM435 steel, were electrically isolated. The area of the disk and ring was identical, 177 mm$^2$. The gap between the two electrodes was 0.1 mm. The surface was polished using No. 600 emery paper. Synthetic sea water was dropped on the surface and then completely dried. After that, impedance measurements were carried out at frequencies of 10 kHz and 10 mHz using an electrochemical device (Electrochemical Measurement Unit, SI-1280B, made by Solartron) by the FRA (Frequency Response Analysis) method in the temperature–humidity controlled chamber. The modulation amplitude of the applied voltage was 10 mV. Solution resistance $R_s$ was estimated from the impedance at high frequency (10 kHz), while the sum of polarization resistance $R_p$ and solution resistance $R_s$ was estimated from the impedance at low frequency (10 mHz). The reciprocal of $R_p$ is proportional to the corrosion rate.

Stress fracture tests under wet-dry cyclic environments were carried out to investigate the relationship between hydrogen entry and delayed fracture susceptibility. Fig. 3 illustrates the constant displacement apparatus. The specimens with a 2 mm thickness, 10 mm width and 75 mm length were machined from the steel plates. The notch shape was a U type 0.5 mm deep, and the notch root had a 0.1 mm radius. The stress concentration factor was almost three, simulating a typical shape of actual construction bolts. All surfaces were polished using No. 600 emery paper. Synthetic sea water was applied on both sides of the specimen and then dried. Next, the specimen was attached to the jig. Crack susceptibilities of the steel with various strengths were investigated under applied stress of 90% of actual tensile strengths in the temperature–humidity controlled chamber. The test duration was 336 hours.

A typical wet-dry cyclic environmental condition is shown in Fig. 4. One cycle consists of four processes. In this figure, symbols A, B, C, and D indicate a low temperature process at 283 K, a drying process with low relative humidity, a wetting process with high relative humidity and a hydrogen entry process with middle relative humidity, respectively. Duration time for each alternate process was 3 hours. Temperatures in processes B, C and D were identical, and were varied from 298 to 333 K. These test conditions were decided based on hydrogen permeation data under actual atmospheric exposure, the authors’ previous work. The data were obtained using a similar test cell to that shown in Fig. 1. The exposure site was a seashore in Nago in Okinawa, an island located at the southern-most part of Japan. The data show hydrogen permeation revealed a cyclic variation in each day. The hydrogen entry is accelerated in a daytime with high temperature and low relative humidity, while the hydrogen entry is retarded in a nighttime with low temperature and high humidity.
3. Results

3.1 Hydrogen entry under simulated atmospheric corrosion

Figure 5 shows a typical result of the hydrogen permeation tests under a wet-dry cyclic environment. The amount of sea salt on the membrane was 0.063 kg/m$^2$ (0.03 kg/m$^2$ of Cl$^-\text{)}$. The result shows that hydrogen permeation coefficient varied sensitively depending upon temperature and humidity. At 333 K, hydrogen permeation coefficient revealed high values at relative humidity of 40% (process B) and 60% (process D), while hydrogen permeation coefficient decreased during the period of 90% (process C). Hydrogen permeation coefficient at 283 K (process A) was lower than that at 333 K. In this figure, reciprocals of polarization resistance, $1/R_p$, measured by impedance, are also plotted (right side axis), as an indication of corrosion rate. At 333 K, the corrosion rate showed a maximum during the process C (relative humidity of 90%). Thus, an opposite relationship with relative humidity was observed between hydrogen permeation and corrosion rate. The result implies that environmental factors accelerating atmospheric corrosion, that are humidity and temperature, do not necessarily promote hydrogen entry. The corrosion rate in the process A (283 K) was lower than that in the processes B, C and D, showing the same tendency as hydrogen permeation.

Figure 6 summarizes the results of long period wet-dry cycle tests with various amounts of sea salt on the membrane. The temperature and humidity were controlled as same as that shown in Fig. 5. Note that the amount of Cl$^-$ on the steel surface greatly affected hydrogen entry. Hydrogen permeation coefficient showed a maximum with the Cl$^-$ of 0.03 kg/m$^2$, as shown in Fig. 6(b). Hydrogen permeation coefficient increased with time just after starting the test and gradually decayed after showing a maximum at about 200 hours. In addition, the dependence of hydrogen permeation on relative humidity changed slightly during the test. Just after starting the test, hydrogen permeation coefficient increased in the processes B and D, then decreased in the processes A and C, showing double spikes in each cycle as shown in Fig. 5. After 150 hours, hydrogen permeation coefficient showed the highest in the process D. At around 300 hours, hydrogen permeation coefficients in the processes B, C and D were almost identical.

Hydrogen permeation coefficients observed for the tests with the Cl$^-$ of 0.3 and 0.003 kg/m$^2$ were less than that with the Cl$^-$ of 0.03 kg/m$^2$, as shown in Figs. 6(a) and (c). Corrosion rates (reciprocals of polarization resistance, $1/R_p$) in the process C in Fig. 4 (333 K, 90% relative humidity) are also shown in Fig. 6. The corrosion rate revealed a maximum for the test with the Cl$^-$ of 0.03 kg/m$^2$, showing the same tendency as hydrogen permeation.

Figure 7 shows the effect of testing temperature on hydrogen permeation with the Cl$^-$ of 0.03 kg/m$^2$. The temperatures which were identical in the processes B, C and D, were varied from 298 to 333 K. The test results show that hydrogen permeation coefficient drastically increased with an increase in the maintenance temperature. Corrosion rates in the process C measured by impedance are also shown in these figures. The results of impedance experiments indicate that corrosion rate increased with an increase in the maintenance temperature, showing the same tendency as hydrogen permeation.
3.2 Crack susceptibility under simulated atmospheric corrosion

Figure 8 shows the results of stress fracture tests conducted with various steel’s tensile strengths and the amounts of Cl⁻ on the specimen surface. The temperature in the process B, C and D was 333 K. With the Cl⁻ of 0.3 kg/m² on specimens as sea salt, no cracks occurred in the tensile strength range investigated. With the Cl⁻ of 0.03 kg/m², specimens with tensile strengths of 1554 and 1673 MPa fractured. With the Cl⁻ of 0.003 kg/m², a specimen with tensile strength of 1673 MPa fractured. The test results indicate that the 0.03 kg/m² Cl⁻ was the most severe condition in terms of crack susceptibility.

Figure 9 shows the effect of the temperature on the crack susceptibility with the Cl⁻ of 0.03 kg/m². The test results indicate that hydrogen permeation increased with an increase in temperature as shown in Fig. 7. This tendency corresponds to an increasing corrosion rate, also shown in Fig. 7 [reaction [a] above].

Relative humidity also greatly affected hydrogen entry, as shown in Fig. 5. The hydrogen permeation coefficient was larger in the processes B (relative humidity of 40%) and D (60%) than that in the process C (90%), while the corrosion rate increased with an increase in relative humidity. The contradictory tendency of the hydrogen entry to the corrosion rate can be discussed from the viewpoint of the compositions of the water layer formed on the steel as follows. Figure 10 shows a thermodynamical prediction of the compositions of the water layer formed by salts as a function of relative humidity at 298 K. In this calculation, chemical compositions in simple NaCl and MgCl₂ solutions were estimated from activity coefficients of water as a function of relative humidity at first, then those were extended to a NaCl-MgCl₂ system. For simplicity, the surface salts were assumed to consist of 90% NaCl and 10% MgCl₂. The details were derived from the original paper. The prediction reveals that the compositions of the water layer are decided by relative humidity, regardless of the amount of Cl⁻ on the steel surface. Even at lower relative humidity around 40%, sea salt

4. Discussion

4.1 Environmental factors affecting hydrogen entry

The effects of environmental factors such as temperature, relative humidity, the amount of sea salt, and the wet-dry cycle on hydrogen permeation are discussed as follows.

In usual cases, the pH in the water layer on the steel surface would be neutral in atmospheric environments. Therefore, cathodic reaction is supposed to be mainly oxygen reduction. However, a decrease in pH due to hydrolysis of Fe ions could be expected resulting in hydrogen evolution, following a series of reactions:

[a] Anodic dissolution as Fe²⁺ ion (Corrosion of the steel)
[b] Oxidization of Fe²⁺ into Fe³⁺ ions
[c] Hydrolysis of Fe³⁺ accelerated by Cl⁻ ions, followed by a pH drop
[d] Hydrogen evolution resulting in hydrogen entry

The experimental results indicated that hydrogen permeation increased with an increase in temperature as shown in Fig. 7. This tendency corresponds to an increasing corrosion rate, also shown in Fig. 7 [reaction [a] above].

Relative humidity also greatly affected hydrogen entry, as shown in Fig. 5. The hydrogen permeation coefficient was larger in the processes B (relative humidity of 40%) and D (60%) than that in the process C (90%), while the corrosion rate increased with an increase in relative humidity. The contradictory tendency of the hydrogen entry to the corrosion rate can be discussed from the viewpoint of the compositions of the water layer formed on the steel as follows. Figure 10 shows a thermodynamical prediction of the compositions of the water layer formed by salts as a function of relative humidity at 298 K. In this calculation, chemical compositions in simple NaCl and MgCl₂ solutions were estimated from activity coefficients of water as a function of relative humidity at first, then those were extended to a NaCl-MgCl₂ system. For simplicity, the surface salts were assumed to consist of 90% NaCl and 10% MgCl₂. The details were derived from the original paper. The prediction reveals that the compositions of the water layer are decided by relative humidity, regardless of the amount of Cl⁻ on the steel surface. Even at lower relative humidity around 40%, sea salt
can form a water layer on the steel surface because sea salt usually contains MgCl$_2$, which acts as a greater moisture absorbent than NaCl. The content of existing anion, Cl$^-$, increases with a decrease in relative humidity. It is well-known that Cl$^-$ ions accelerate hydrolysis of Fe$^{3+}$ ions due to the formation of the chloro-complex, resulting in a pH drop than that expected from the equilibrium constant of Fe(OH)$_3$. Thus, the condensed Cl$^-$ in the water layer would cause hydrolysis of Fe$^{3+}$ (reaction [c] above). Additionally, it has been reported that an increase in Cl$^-$ ions accelerates the oxidation from Fe$^{2+}$ to Fe$^{3+}$ ions (reaction [b] above).

Sea salt on the steel surface had a complex effect on hydrogen entry, as shown in Fig. 6. Hydrogen permeation revealed a maximum with the Cl$^-$ of 0.03 kg/m$^2$. The appropriate Cl$^-$ amount for hydrogen entry can be explained based on the thickness of the surface’s water layer. Figure 11 shows predicted water layer thicknesses based on the same thermodynamical calculation as Fig. 10. Figure 11 indicates that the amount of Cl$^-$ on the steel surface proportionally increases the water layer thickness. It is well-known that the atmospheric corrosion rate shows a maximum at a certain water layer thickness, because the diffusion process of dissolved oxygen through the water layer becomes the rate-controlling process for corrosion. It has been reported that corrosion rate shows a maximum at around 100$\mu$m of water layer thickness.$^5$ In this work, the corrosion rate revealed a maximum with the Cl$^-$ of 0.03 kg/m$^2$, at which the calculated water layer thickness is around 100$\mu$m, as shown in Fig. 11. Thus, the maximum hydrogen permeation coefficient observed for the test with the Cl$^-$ of 0.03 kg/m$^2$ in Fig. 6(b), relates a maximum corrosion rate at the critical water layer thickness (reaction [a] above). The excess Cl$^-$ slightly decreased the corrosion rate, due to an increase in the water layer thickness as shown in Fig. 11. Furthermore, an increase in the water layer thickness results in a decreasing concentration of Fe$^{3+}$ ions in the solution, retarding the hydrolysis (reaction [c] above). Strictly, condensed Fe$^{3+}$ ions formed by rust accumulation could influence chemical compositions in the water layer. However, the thermodynamical calculation in this study ignores effects of Fe$^{3+}$ ions and rust formation for simplicity.

The hydrogen permeation coefficient increased with the wet-dry cycle, then gradually decreased after showing a maximum, as typically shown in Fig. 6(b). The time dependence of the hydrogen permeation is attributed to rust formation on the steel surface. In early cycles, it is assumed that rust formation would decrease the pH under the rust layer. Tsuru et al. reported that hydrogen evolution reaction was accelerated by a decrease in pH at the metal/corrosion products interface.$^2$ After a long period, accumulation of rust prevented hydrogen entry because of the low permeability of hydrogen through the rust layer. However, the mechanisms to prevent hydrogen entry by rust layer have not been clarified yet.

Figure 12 illustrates the mechanism of hydrogen entry. Hydrogen entry preferentially occurred at higher temperature and at a lower relative humidity with an appropriate Cl$^-$ amount (0.3 kg/m$^2$). Corrosion rate increased with an increase in temperature, resulting in enhanced hydrogen permeation. Hydrogen entry was promoted at lower relative humidity (40–60%) by the hydrolysis of Fe$^{3+}$ accelerated by condensed Cl$^-$ ions in the water layer. A maximum hydrogen permeation coefficient was observed with the Cl$^-$ amount of 0.03 kg/m$^2$ on the steel surface, corresponding to a maximum corrosion rate determined by an appropriate water layer.
The delayed fracture of high-strength steels preferentially occurs at the surface of sea salt on the specimen and testing temperatures as shown in the study. The variations of hydrogen entry in atmospheric environments strongly depend upon the environmental severity which promotes hydrogen embrittlement. The authors of this study assume uniformity of the water layer. However, thickness and chemical compositions of the water layer could be not uniform actually, and the an-uniformity could affect corrosion reactions and the hydrogen entry.

Experimental results in this study suggest the importance to monitor environmental factors, including temperature, relative humidity, and the amount of sea salt in order to evaluate the risk of delayed fracture. The authors of this paper previously reported that hydrogen entry into steels from atmospheric environments strongly depended upon the time in day, the season, and exposure locations. The variations of hydrogen entry in atmospheric environments could be explained by the experimental results in this study.

4.2 Crack Susceptibility in Wet-Dry Cyclic Environments

Crack susceptibility strongly depended upon the amount of sea salt on the specimen and testing temperatures as shown in Figs. 8 and 9, respectively. It has been reported that the delayed fracture of high-strength steels preferentially occurs in hot seasons and at seashores. The laboratory stress fracture tests in this study show good agreement with these tendencies of actual delayed fracture. Furthermore, the crack susceptibilities in wet-dry cyclic environments correlate to hydrogen permeation coefficients as discussed in the following.

Figure 13 summarizes crack susceptibilities as a function of the tensile strength of the steel and the observed maximum hydrogen permeation coefficient in wet-dry cyclic environments with various Cl\textsuperscript{-} amounts on the steel at 333 K. The result indicates that the crack susceptibility corresponds to the environmental severity which promotes hydrogen entry. However, the effects of cyclic variations of hydrogen entry shown in Figs. 6 and 7 have not been clarified yet. It is not obvious which is more essential for cracking, an instantaneous maximum hydrogen permeation or an average rate of hydrogen permeation.

To clarify the above question, stress fracture tests under cathodic charging were carried out at 298 K. Cathodic charging enables hydrogen entry into the specimens at a constant rate. Figure 14 shows the time-to-fracture curves of the steel with tensile strengths of 1673, 1554, and 1370 MPa. Hydrogen permeation coefficients in the vertical axis were controlled by cathodic current densities. As shown in this figure, time to fracture depended upon hydrogen permeation coefficients and strength levels. At each strength level, time to fracture was smaller at higher hydrogen permeation coefficients than that at lower hydrogen permeation coefficients. The tendency implies the following hydrogen embrittlement mechanism. At lower hydrogen permeation coefficients, hydrogen atoms have to migrate in the specimen and accumulate at a notch root (an area of triaxial stress), resulting in the fracture. This means a fracture requires a latent time for hydrogen diffusion and accumulation. Below a critical hydrogen permeation coefficient, embrittlement does not occur. The value is understood as the threshold hydrogen permeation coefficient. On the contrary, at higher hydrogen permeation coefficients, fracture occurred in short periods. These results mean that the amount of the hydrogen derived from external environments easily exceed the steel’s threshold value.

Hydrogen embrittlement should be discussed based on hydrogen content in the steel. Surface hydrogen content $C_s$ (mass ppm) can be estimated from the following equation:

$$C_s = 1.318 JL/D,$$

where $JL$ is a hydrogen permeation coefficient (A/cm$^2$/s) and $D$ a hydrogen diffusion coefficient (cm$^2$/s). In this study, $D$ was measured by hydrogen permeation transients under cathodic charging at various temperatures, using a Devanathan type double cell. When permeation flux reaches 50% of its steady state value, the following equation relates thickness $L$ (1.5 mm), the measured time to reach 50% of steady state value, $t_{1/2}$ (s), and diffusion coefficient $D$ (cm$^2$/s):

$$D = L^2/(7.14t_{1/2}).$$

$D$ of the SCM435 steel with tensile strength of 1554 MPa was $1.9 \times 10^{-6}$ and $6.95 \times 10^{-7}$ (cm$^2$/s) at 333 and 298 K, respectively. Thus, the ratio between $D_{308K}$ and $D_{333K}$ was approximately 1/3.

Figure 14 shows the relationship between maximum hydrogen permeation coefficients $JL_{\text{max}}$ observed in wet-
5. Conclusion

Environmental factors affecting hydrogen entry into high strength steel were investigated by hydrogen permeation tests under wet-dry cyclic conditions. Additionally, cracking behaviors were evaluated by stress fracture tests under the wet-dry cyclic environments. The following conclusions were drawn:

1. Temperature, relative humidity, and the amount of sea salt on the steel surface strongly affected hydrogen entry. Corrosion rate increased with an increase in temperature, resulting in enhanced hydrogen permeation.

2. Hydrogen permeation coefficients were higher at lower relative humidity (40–60%), because Cl⁻ ions concentrate in the water layer at lower relative humidity, resulting in the acceleration of hydrolysis of Fe⁺⁺⁺, followed by a pH drop.

3. A maximum hydrogen permeation coefficient was observed at the Cl⁻ amount of 0.03 kg/m² on the steel surface, corresponding to a maximum corrosion rate determined by the maximum water layer thickness that does not retarded by O₂ diffusion process.

4. Steels with tensile strengths beyond 1400 MPa suffered from cracking at higher temperatures and the Cl⁻ of 0.03 kg/m² on the steel surface. The fracture test results mean that crack susceptibility strongly depended upon the environmental severities which promoted hydrogen entry.

REFERENCES