Hydrogen Entry and its Effect on Delayed Fracture Susceptibility of High Strength Steel Bolts under Atmospheric Corrosion

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Research on hydrogen embrittlement (delayed fracture) susceptibility of high strength steel bolts was reviewed from the viewpoint of metallurgical factors enhancing the resistance to delayed fracture, assessment of delayed fracture susceptibility based on the hydrogen absorption from atmospheric environments, and the mechanism of hydrogen entry into steel under atmospheric exposure.

Resistance to delayed fracture was quantified based on the threshold hydrogen concentration \( C_{th} \) by means of laboratory constant load tests under cathodic hydrogen charging. Vanadium containing anti-delayed fracture steel bolts had higher \( C_{th} \) values than conventional steel bolts, and showed good resistance to delayed fracture at tensile strength levels of 1 400 MPa under actual atmospheric exposure.

Susceptibility to delayed fracture was evaluated by comparing \( C_{th} \) to absorbed hydrogen concentration \( C_0 \) into steel bolts under atmospheric exposure. The good resistance to delayed fracture of Vanadium steel high strength bolts was attributable to sufficiently higher \( C_{th} \) than \( C_0 \). Hydrogen permeation experiments under atmospheric exposure enabled more exact measurements of sub-surface hydrogen concentration into steel. Hydrogen permeability under atmospheric exposure showed a strong dependence on the time of the day, seasons and exposure locations.

Mechanism of hydrogen entry was investigated by hydrogen permeation measurements under laboratory wet-dry cyclic conditions. Dominant factors that control hydrogen entry were temperature, relative humidity, and the amount of sea salt on the steel surface. Dependence of hydrogen permeability under actual atmospheric environments on daily temperature-humidity cycle, season and locations were explainable based on the effect of temperature, humidity and sea salts.

KEY WORDS: hydrogen entry; delayed fracture; high strength steel bolts; hydrogen permeation; atmospheric exposure.

1. Introduction

High strength steels are demanded in many fields to reduce the total weight of construction materials or automobiles. However, it is well-known that high strength steels, especially high strength steel bolts with tensile strengths more than 125 kg/mm² (1 225 MPa), suffer from delayed fracture under atmospheric exposure. It is recognized that delayed fracture is one type of mechanical degradation caused by hydrogen absorption from external environments. It is important to clarify the optimum material design and appropriate evaluation methods for preventing delayed fracture of high strength steel bolts.

Kushida et al. suggested that constant load tests and Slow Strain Rate Test (SSRT) under cathodic hydrogen charging conditions, which simulate pitting bottoms or crevices with pH around 3.5\(^2\), to evaluate delayed fracture susceptibility. Yamasaki et al. compared threshold hydrogen concentration of several high strength steels to absorbed hydrogen concentration under laboratory cyclic corrosion tests to rate delayed fracture susceptibility.\(^3\) From the viewpoint of material design for preventing delayed fracture, several high strength steel bolts, which contain Titanium, Vanadium and Molybdenum, were reported.\(^2\)–\(^6\) Recently, Vanadium containing steels were widely used as ultra high strength bolts with good resistance to delayed fracture.\(^2\)–\(^4\)

Hydrogen entry into steels has been studied to evaluate the frequency of delayed fracture under actual atmospheric environments.\(^6\)–\(^11\) Site and time dependence of hydrogen absorption\(^7\) and difference in absorbed hydrogen concentrations at various portions in actual bolts exposed at a seashore\(^8\) were reported. Akiyama et al. suggested SSRT under a wet condition using specimens with corrosion products formed under actual atmospheric environments or cyclic corrosion tests, to reproduce enhanced hydrogen entry influenced by the rust layer and to homogenize the hydrogen distribution in a specimen.\(^6\)–\(^9\)–\(^11\)

It is also important to understand the mechanism of hydrogen entry according to atmospheric corrosion to assess the environmental risk of delayed fracture. Tsuru et al. measured the hydrogen entry from a water droplet on a steel surface by laboratory hydrogen permeation techniques.\(^12\) They revealed that hydrogen entry during a drying period after wetting closely related change in pH and the potential. Sundararajan et al. investigated effects of artificial crevices on hydrogen entry by similar techniques.\(^13\)–\(^15\)
The authors of this paper have been also investigated delayed fracture susceptibility of high strength steel bolts in view of its correlation to hydrogen entry under atmospheric exposure, and the mechanism of hydrogen entry under atmospheric corrosion conditions. In this paper, research activities on delayed fracture evaluation of high strength steel bolts were reviewed from the following viewpoint – metallurgical factors enhancing the resistance to delayed fracture, assessment of delayed fracture susceptibility based on the hydrogen absorption from atmospheric environments, and environmental factors affecting hydrogen entry.

2. Metallurgical Factors Enhancing Resistance to Delayed Fracture

Optimum metallurgical design is important for preventing delayed fracture at high strength levels. Following is an example of anti-delayed fracture steel bolts and the evaluation of delayed fracture susceptibility. The materials used were conventional Boron containing steel bolts (B steel) and Vanadium containing high strength steel bolts (V steel). Figure 1 is a tensile test specimen with a circumferential notch, which simulates stress concentration factor on a thread on actual bolts. Constant load tests under cathodic charging conditions were conducted at a constant potential ranging from −0.8 to −1.5 V vs. potassium-saturated Ag/AgCl reference electrode using a potentiostat under 90% of Tensile Strength (TS) for 200 hours. Absorbed diffusible hydrogen concentration in a tested specimen was measured by Thermal Desorption Analysis (TDA) at a heating rate of 10°C/min with quadrupole mass spectrometer. Threshold hydrogen concentration \( C_{th} \) was defined as the maximum hydrogen concentration measured in the specimen which survived after a 200 hours test. In this technique, hydrogen was successively charged into the specimen. On the contrary, constant load tests in air using a plated specimen pre-charged with hydrogen were also often used. It is reported that \( C_{th} \) show equivalent values by both successive hydrogen charging methods and plating methods.

Figure 2 shows the \( C_{th} \) of the B steel and the V steel at various strength levels. \( C_{th} \) decreased with the increase in strength in both steels, indicating that higher strength steel tends to suffer from delayed fracture. The V steel showed higher \( C_{th} \) than conventional B steel. Additionally, the most severe cathodic charging condition under which specimen survived could be translated to the threshold hydrogen permeation coefficient \( J_{L_{th}} \). Hydrogen permeability could be measured by Devanathan type double cell methods using a membrane specimen. Figure 3 shows the \( J_{L_{th}} \) of the B steel and the V steel. Although the \( J_{L_{th}} \) showed similar tendency to \( C_{th} \), the deference in \( J_{L_{th}} \) between the conventional B steel and the V steel was smaller than that in \( C_{th} \). Furthermore, changes in the \( J_{L_{th}} \) depending upon strength levels are similar between the B steel and the V steel, although the \( C_{th} \) of the V steel showed stronger dependence upon strength than the B steel.

Figure 4 illustrates metallurgical features of conventional
steel and V steel affecting delayed fracture susceptibility. In conventional steel tempered at lower tempering temperatures, delayed fracture crack initiates and propagates along film-like carbides M₃C (M = Fe, Cr, Mo) at prior austenite grain boundaries. Conventional steel also contains much dislocation, which is harmful to hydrogen embrittlement by absorbing much diffusible hydrogen. V steel contains fine MC carbides (M = V, Mo), which enable higher temperature tempering due to precipitation hardening. In V steel, the higher temperature tempering spheroidizes M₃C and eliminates dislocation from the quenched matrix. Both spheroidization of M₃C and decrease in dislocation density must enhance resistance to delayed fracture in V steel, although it is difficult to separate each effect because high temperature tempering affects both M₃C morphology and dislocation density simultaneously. Additionally, the fine MC carbides trap and stabilize hydrogen. The higher Cₚ of V steel than conventional B steel in Fig. 2 is attributable to the above mentioned metallurgical features - M₃C spheroidization, decrease in dislocation density and hydrogen trapping effects by fine MC carbides. The strong dependence of Cₚ of the V steel on strength in Fig. 2 is also attributable to the change in the amount of fine MC carbides depending upon tempering temperatures. On the contrary, the deference in Jₚ between conventional B steel and V steel was smaller than that in Cₚ and showed the similar dependence on strength as shown in Fig. 3. That means hydrogen absorption and desorption occurred according to a change in seasonal environmental factors. Figure 6 also indicates the Cₚ near the surface was higher than the average value in a bolt. This result means that it is necessary to pay special attention when cutting the sample from a bolt to measure the exact absorbed hydrogen concentration.

3. Hydrogen Entry and Delayed Fracture Susceptibility under Atmospheric Environments

Exposure tests and measurement of hydrogen absorption using high strength steel bolts are important to evaluate the actual risk of delayed fracture. Exposure tests using the V steel bolts with several strength levels are reviewed as follows. The exposure site was a seashore in Nago in Okinawa, an island located at the southernmost part of Japan. The initial number of each strength level was 938. The applied stress was 85% of Yield Strength (YS). Exposed bolts were checked periodically and collected to measure the absorbed hydrogen concentration in them. It was confirmed that bolts with strength levels less than 1 500 MPa survived, while bolts at 1 521 MPa suffered from delayed fracture.

Figure 5 is an example of Thermal Desorption Analysis (TDA) profiles on exposed bolts for 135 days. Diffusible hydrogen evolved at lower temperatures (1st peak), and non-diffusible hydrogen evolved at higher temperatures (2nd peak). Summation of the 1st peak in Fig. 5 was defined as diffusible absorbed hydrogen concentration C₀, which affects delayed fracture. It was confirmed that C₀ varied according to the exposure duration as shown in Fig. 6. That means hydrogen absorption and desorption occurred according to a change in seasonal environmental factors. Figure 6 also indicates the C₀ near the surface was higher than the average value in a bolt. This result means that it is necessary to pay special attention when cutting the sample from a bolt to measure the exact absorbed hydrogen concentration.

Hydrogen permeation tests under atmospheric exposure were also conducted to detect exact time-dependent subsurface hydrogen concentration as follows. Membrane
specimens with a 70 mm diameter and 0.5 mm thickness were used. 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 (Fig. 7), the cell was filled with a 0.1N NaOH solution. The electroplated side was polarized at 0 V versus potassium-saturated Ag/AgCl reference electrode using a potentiostat. The polished side was exposed to the external environment at the same place along the seashore to bolts at Nago City in Okinawa. Through experiments, hydrogen atoms that permeate the membrane from the external surface were oxidized to hydrogen ions on the electroplated surface. Hydrogen oxidizing current density \( J \) (A/cm²) gives hydrogen permeation coefficient \( J_L \) (A/cm), where \( L \) is the thickness of the membrane (= 0.05 cm). Several tests were started on different seasons. Figure 8 shows hydrogen permeation coefficient in actual environments \( J_{L_{\text{env}}} \) as a function of the test duration. The profile in May showed higher values than that in October. The \( J_{L_{\text{env}}} \) in May revealed a cyclic variation each day. The hydrogen entry is accelerated during daytime with high temperature and low relative humidity, while the hydrogen entry is retarded during nighttime with low temperature and high relative humidity. It was observed that the \( J_{L_{\text{env}}} \) was also affected by the exposure sites, depending upon the amount of sea salt on the steel surface.\(^{16-18} \) That means \( J_{L_{\text{env}}} \) had no dependence on the chemical compositions or strengths of the materials because the \( J_{L_{\text{env}}} \) reflects the environmental severity from the viewpoint of hydrogen entry.

Figure 9 shows the seasonal alteration of the number of fractured bolts at 1 521 MPa of TS and the maximum values of \( J_{L_{\text{env}}} \). Fractures of bolts tended to occur in the hot season from April to September. In the same hot season, the \( J_{L_{\text{env}}} \) also showed higher values than those in other seasons. That indicates hydrogen entry has a large effect on delayed fracture susceptibility. The \( C_0 \) and \( J_{L_{\text{th}}} \) at 1 521 MPa were extremely small as shown in Figs. 2 and 3. However, delayed fracture susceptibility of 1 521 MPa steel bolts was not clearly explained based on the balance between \( C_0 \) and \( J_{L_{\text{th}}} \) in Fig. 6. Hydrogen permeation measurements showed that delayed fracture occurred when the \( J_{L_{\text{env}}} \) in Fig. 8 exceeded the threshold values \( J_{L_{\text{th}}} \) in Fig. 3, indicating the sub-surface hydrogen measured by permeation techniques strongly affect delayed fracture susceptibility. Below 1 500 MPa, the \( C_0 \) and \( J_{L_{\text{th}}} \) were sufficiently larger than \( C_0 \) and \( J_{L_{\text{env}}} \), showing good resistance to delayed fracture.

Fig. 6. Absorbed diffusible hydrogen concentration into exposed bolts.

Fig. 7. Schematic illustration of hydrogen permeation test cell.

Fig. 8. Hydrogen permeation coefficient under atmospheric exposure.

Fig. 9. Seasonal dependence of the maximum hydrogen permeation coefficient and the frequency of delayed fracture.
4. Mechanism of Hydrogen Entry under Atmospheric Corrosion

Hydrogen entry under atmospheric environments strongly depended upon time in the day, season and exposure site as shown in Fig. 8. Understanding the mechanism of hydrogen entry into steel under atmospheric exposure is important to evaluate the environmental risk on delayed fracture. The following is the laboratory hydrogen permeation experiment results under cyclic corrosion environments. The material used was conventional Cr–Mo bearing steel, JIS (Japanese Industrial Standards) SCM435 at strength level of 1 100 MPa.

A similar test cell to the exposure type in Fig. 7 was used, except for that the membrane was set horizontally to place sea salt on it. Synthetic sea water according to ASTM-D-1141 was dropped on the exposed surface and then dried, which became sea salt. The test cell was put into a temperature–humidity controlled chamber to apply wet-dry cycle to accelerate corrosion. Hydrogen permeation current was measured successively.

Electrochemical impedance spectroscopy was also 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. The disk and ring electrodes, made of the same SCM435 steel, were electrically isolated. The surface was polished using No.600 emery paper. Synthetic sea water was dropped on the surface and then completely dried. Impedance measurements were carried out at frequencies of 10 kHz and 10 mHz 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.

Figure 10 shows a typical result of the hydrogen permeation tests under a wet-dry cyclic environment. The amount of sea salt on the membrane was 6.3 mg/cm2 (3 mg/cm2 of Cl–). A typical wet-dry cyclic environmental condition is also indicated in Fig. 10. One cycle consists of a low temperature process at 10°C, a drying process with low relative humidity, a wetting process with high relative humidity and a hydrogen entry process with middle relative humidity. Duration time for each alternate process was 3 hours. The result shows that hydrogen permeation coefficient varied sensitively depending upon temperature and humidity. At 60°C, hydrogen permeation coefficient revealed high values at relative humidity of 40% and 60%, while hydrogen permeation coefficient decreased during the period of 90%. Hydrogen permeation coefficient at 10°C was lower than those at 60°C. Reciprocals of polarization resistance, $1/R_p$, measured by impedance, are also plotted (right side axis), as an indication of corrosion rate. At 60°C, the corrosion rate showed a maximum at relative humidity of 90%. That means an opposite relationship with relative humidity was observed between hydrogen permeation and corrosion rate. The corrosion rate at 10°C was lower than that at 60°C, showing the same tendency as hydrogen permeation.

Figure 11 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 the same as that shown in Fig. 10. Note that the amount of Cl– on the steel surface greatly affected hydrogen entry. Hydrogen permeation coefficient showed a maximum with the Cl– of 3 mg/cm2, as shown in Fig. 11(b). Hydrogen permeation coefficients observed for the tests with the Cl– of 30 mg/cm2 and 0.3 mg/cm2 were less than that with the Cl– of 3 mg/cm2, as shown in Figs. 11(a) and 11(c). Corrosion rates (reciprocals of polarization resistance, $1/R_p$) in the process at 60°C at 90% of RH are also shown in Fig. 11. The corrosion rate revealed a maximum for the test with the Cl– of 3 mg/cm2, showing the same tendency as hydrogen permeation.

Figure 12 shows the effect of testing temperature on hydrogen permeation with the Cl– of 3 mg/cm2. The maintenance temperatures at low RH, high RH and middle RH were altered from 10°C to 60°C. The test results show that hydrogen permeation coefficient drastically increased with an increase in the maintenance temperature. The results of impedance experiments indicate that corrosion rate increased...
with an increase in the maintenance temperature, showing the same tendency as hydrogen permeation.

The effects of environmental factors such as temperature, relative humidity and the amount of sea salt 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 Fe^{2+} ion (Corrosion of the steel)
[b] Oxidation of Fe^{2+} into Fe^{3+} ions
[c] Hydrolysis of Fe^{3+} accelerated by Cl– ions, followed by a pH drop
[d] Hydrogen evolution resulting in hydrogen entry

Hydrogen permeation increased with an increase in temperature as shown in Fig. 12, corresponding to an increasing corrosion rate [reaction [a] above].

Relative humidity also greatly affected hydrogen entry, as shown in Fig. 10. The hydrogen permeation coefficient was larger at 40% and 60% of RH than that at 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 13 shows a thermodynamical prediction of the compositions of the water layer formed by salts as a function of relative humidity at 25°C. Although actual sea water contains various kinds of ions, the calculation was conducted under the assumption that the surface salts consisted of 90% NaCl and 10% MgCl₂ for simplicity. The prediction reveals that the compositions of the water layer are decided by relative humidity. Even at lower relative humidity around 40%, sea salt can form a water layer on the steel surface because sea salt usually contains MgCl₂, which acts as a greater moisture absorbent than NaCl. The content of existing anion, Cl–, increases with a decrease in relative humidity. 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. 11. Hydrogen permeation revealed a maximum with the Cl– of 3 mg/cm². The appropriate Cl– amount for hydrogen entry can be explained based on the thickness of the surface’s water layer. Figure 14 shows predicted water layer thicknesses based on the same thermodynamical calculation to Fig. 13. Figure 14 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 is the rate-controlling process for corrosion. It has been reported that corrosion rate shows a maximum at around 100 μm of water layer thickness. In this work, the corrosion rate revealed a maximum with the Cl– of 3 mg/cm², as shown in Fig. 14. The maximum hydrogen permeation coefficient at the Cl– of 3 mg/cm² in Fig. 11(b), relates a maximum corrosion rate at the critical water layer thickness (reaction [a] above). The excess Cl– (30 mg/cm²) on the steel retarded hydrogen entry, as shown in Fig. 11(a), corresponding to a decrease in the corrosion rate, due to an increase in the water layer thickness.

Fig. 12. Effect of temperature on hydrogen permeation.

Fig. 13. Calculated results of compositions of water layer.

Fig. 14. Calculated results of thickness of water layer.
5. Summary

Research activities on delayed fracture of high strength steel bolts were reviewed from the viewpoint of metallurgical factors affecting delayed fracture susceptibility, evaluation methods of delayed fracture and the mechanism of hydrogen entry into steel under atmospheric exposure. Optimum metallurgical design, the exact measurement of absorbed hydrogen concentration, and understanding environmental factors affecting hydrogen entry, were very important in preventing delayed fracture.

(1) Vanadium containing steel high strength bolts showed higher threshold hydrogen concentration $C_{th}$ than conventional steel bolts. The higher $C_{th}$ is attributable to the metallurgical features of the V steel – spheroidization of M3C ($M = \text{Fe, Cr, Mo}$) and decrease in dislocation density at lower relative humidity (40–60%) because Cl– ions corrosion rate. Hydrogen permeation coefficients were higher hydrogen permeability corresponding to an increase in steel surface. An increase in testing temperature increased relative humidity, and the amount of sea salt on the surface $C_{th}$, showing a strong dependence on temperature, humidity, and the amount of sea salt on the steel surface. Frequency of delayed fracture was explained based on the comparison of the maximum $JL_{env}$ to threshold hydrogen concentration $JL_{th}$.

(2) Hydrogen entry and delayed fracture susceptibility were correlated by exposure tests. Hydrogen permeation tests under atmospheric exposure enabled precise subsurface hydrogen concentration measurements. Hydrogen permeation coefficient $JL_{env}$ showed strong dependence on daily temperature-humidity cycle, seasons and exposure locations. Frequency of delayed fracture was explained based on the comparison of the maximum $JL_{env}$ to threshold hydrogen concentration $JL_{th}$.

(3) Mechanism of hydrogen entry under atmospheric corrosion was investigated by hydrogen permeation tests in laboratory cyclic corrosion conditions. Hydrogen permeation coefficients showed a strong dependence on temperature, relative humidity, and the amount of sea salt on the steel surface. An increase in testing temperature increased hydrogen permeability corresponding to an increase in corrosion rate. Hydrogen permeation coefficients were higher at lower relative humidity (40–60%) because Cl– ions concentrate in the water layer, resulting in the acceleration of hydrolysis of $\text{Fe}^{3+}$, followed by a pH drop. A maximum hydrogen permeation coefficient was observed at the Cl– amount of 3 mg/cm$^2$ on the steel surface, corresponding to a maximum corrosion rate determined by the maximum water layer thickness.

REFERENCES