Effects of Cu Addition on Hydrogen Absorption and Diffusion Properties of 1470 MPa Grade Thin-walled Steel Tube under Atmospheric Corrosion

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Hydrogen embrittlement is caused by the introduction of hydrogen into steel and is critical for high strength steels. To clarify the effects of Cu addition on hydrogen absorption and diffusion properties of steel under atmospheric condition, corrosion test was conducted on a 1470 MPa grade thin-walled low carbon martensite steel tube. To this end, a martensite steel tube bearing 0.18% C, 0.4% Si, 1.5% Mn, 0.15% Cu, 0.01% Nb was prepared and compared with Cu free steel tube. As a result of EPMA mapping for the rust layer, Cu accumulated discretely on the rust/steel interface, especially in the bottom of pits of 0.15% Cu bearing steel tubes after the atmospheric corrosion test over 12 years. According to x-ray absorption near-edge structure (XANES) spectra, the valence of Cu in the rust layer was mainly +2 as Cu-(O, OH, SO4). The average and maximum diffusible hydrogen content level of 0.15% Cu bearing steel was lower than that of Cu free steel tube after the atmospheric corrosion test. The quantity of non-diffusible hydrogen was much higher than that of diffusible hydrogen. According to diffusion calculation results, hydrogen diffusion was so rapid that the long-term corrosion hysteresis seemed to have little influence on the diffusible hydrogen content. Furthermore, the short-term corrosion hysteresis may be the main determinant of diffusible hydrogen concentration. Having regard to the fact that the valance of Cu could also be 0 as reported by Shimizu et al., an inhibition mechanism from accumulated Cu on hydrogen-induced cracking was proposed. Eluted Cu⁺ ions in the rust layer may precipitate as metallic Cu at the microscopic cathode during the corrosion test. As a result, the microscopic cathode becomes inactivated as an electrochemical reaction site for hydrogen. The Cu alternates between precipitates and Cu ions depending on the relative humidity, and the condensation and pH of the water in the rust layer.

KEY WORDS: steel; martensite; hydrogen embrittlement; hydrogen absorption; hydrogen diffusion; delayed fracture; corrosion; copper; atmospheric corrosion.

1. Introduction

The effects of Cu addition on steel corrosion resistance under various environments have been intensively investigated.1–9) Shiotani et al.10) analyzed the rust layer that formed on a Cu bearing steel in bridge in a coastal and industrial area. Cu was found lying in the corrosion pit with sulfur in the lower part of the rust layer. Kimura et al.8,9) examined the electronic state of Cu in the rust layer using synchrotron radiation. It was reported that Cu did not substitute for Fe in goethite but existed as nanometer-sized Cu–O bond among the FeOOH octahedral linkage. It was proposed that Cu addition makes the goethite microstructure fine and reduces the corrosion rate. However, the phenomenon has not been explained from an electrochemical viewpoint.

In the case of high strength steels, not only the corrosion but also hydrogen embrittlement caused by the hydrogen absorbed into steel is critical.10–19) Omura et al.12) showed that hydrogen absorption into steel under atmospheric corrosion conditions depends on the time in day. Kushida et al.11) reported that Cu bearing steel showed a smaller corrosion rate and contained smaller amounts of diffusible hydrogen than the steel without Cu. However, the mechanism of the suppressive effects of Cu has not been clarified yet.

An immersion test in HCl solution and a cathodic hydrogen charge test are commonly used as accelerating evaluation methods of hydrogen embrittlement properties of high strength steels.20–26) Furthermore, it was reported that even under atmospheric circumstances, the pH of condensed water in the rust layer could decrease to 3 or less.27) Toyoda et al.24) reported substantial effects of Cu addition on the delayed fracture resistance of low carbon martensitic 1470 MPa grade steel immersed in HCl solution. They also reported that the results of delayed fracture resistance in
an immersion test using 0.1N-hydrochloric acid, (b) a cyclic corrosion test with 5% NaCl water spray, and (c) an atmospheric corrosion test had good correlation with each other. In a recent paper, they conducted hydrogen permeation tests and dynamic polarization measurements in HCl solution and clarified that the drastic suppression of hydrogen permeation current, $J_H$ of martensite steel by Cu addition was achieved with the reduction of cathodic current, $i_C$ and the hydrogen permeation ratio, $J_H/i_C$.

In this study, to clarify the effects of Cu addition on hydrogen absorption and diffusion properties under atmospheric corrosion, an atmospheric corrosion test was conducted on a 1470 MPa grade thin-walled steel tube.

### 2. Experimental

Table 1 shows the chemical composition and tensile strength of the 1470 MPa grade steel tubes used for the atmospheric corrosion test, which are the same electric resistance welded tubes as previously reported. CuLC represents Cu bearing steel which contains 0.15 mass% Cu. LC represents Cu free steel. They have lower than 0.50% carbon equivalents. A small amount of Nb was added for the precipitation hardening. So, the Ti addition in CuLC was aimed to guarantee the hardenability of boron, not for structural refinement. A scantling of Ti addition in CuLC represents Cu free steel. They have lower than 0.50% carbon equivalents. A small amount of Nb was added for the precipitation hardening. So, the Ti addition in CuLC was aimed to guarantee the hardenability of boron, not for the structural refinement. A scantling of Ti addition in CuLC was thought to have little effect on the hydrogen absorption and diffusion properties in this study. As shown in Fig. 1, they have finely dispersed carbide in the martensite lath as a result of quenching and tempering before being formed into a tube under the condition that was previously reported. The tube size was 31.8 mm in diameter, 2.0 mm in thickness and 150 mm long. An electro-deposition coat was not applied.

An atmospheric corrosion test was also conducted under the same conditions previously described. Tube specimen were put in an insulated bar facing southward inclined 25 degrees to the horizontal direction in a coastal industrial zone in Kawasaki. The weld seam was situated in the upper side. The amount of air born NaCl was about 0.07 mg/dm²/day. The exposure test started in April. No cracks were induced over 12 years by the combination of corrosion and residual stress. The thickness of the tube decreased about 0.01 mm/y, including the rust layer, from atmospheric corrosion. The exposed sample was collected twice under the conditions shown in Table 2. The first collection was conducted in the afternoon on a sunny day in December after 12 years and 8 months of exposure. The second collection was done in the afternoon on a sunny day in August after 13 years and 4 months of exposure. Significant difference in macroscopic corrosion rate was not observed between with and without Cu samples.

The rust layers of the first samples were characterized with an Electron Probe Micro Analyzer (EPMA) and X-ray Absorption Fine Structure (XAFS) analysis. The sample for EPMA and compositional mapping of the rust layer was cut off about 10 mm from the tube edge without water. Flaking of the rust layer did not occur. The sample was embedded in epoxy resin and polished with diamond paste and ethanol in one direction. After carbon deposition, the sample was analyzed with EPMA. The accelerating voltage and the beam current of the incident electrons were set to 15 kV and 1.5 × 10⁻⁷ A, respectively. This experimental condition provided spatial resolution of about 1 μm. To evaluate the chemical states of Cu in the rust layer, Cu–K edge XAFS measurements were carried out for the rust powder scraped off from the tube surface of CuLC. The fluorescence – yield mode XAFS spectra were recorded using a 7-elements solid-state detector at the beam line BL-27B, Photon Factory, KEK (Tsukuba, Japan). XAFS spectra were also recorded for some reference materials Cu (foil), Cu2O, CuO, CuSO4, CuCl2, and CuS using transmission mode.

Diffusible hydrogen was evaluated by Thermal Desorption Spectroscopy (TDS) after the corrosion test. The sample was immediately put into liquid nitrogen after the collection. Ahead of the measurement, the sample was cut into a 2 × 10⁻⁶ × 50³ mm sized rectangular coupon from the specific circumferential position in the tube. The rust and pits were completely removed from all surfaces with grindstone and # 400 emery paper. After that, the sample was chilled with liquid nitrogen intermittently. The TDS analysis was conducted using a gas chromatograph at a constant heating rate of 200°C/h and a sampling interval of 5 min. To evaluate the variation of diffusible hydrogen during

### Table 1. Chemical composition and tensile strength of 1470 MPa grade thin-walled low carbon martensite steel tubes.

<table>
<thead>
<tr>
<th>Steel Type</th>
<th>Chemical composition (mass%)</th>
<th>TS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuLC</td>
<td>C: 0.18, Si: 0.4, Mn: 1.5, P: 0.01, S: 0.01, Cu: 0.15, Nb: 0.01, Ti: 0.001, B: 0.45</td>
<td>1490–1560</td>
</tr>
<tr>
<td>LC</td>
<td>C: 0.17, Si: 0.4, Mn: 1.8, P: 0.01, S: 0.01, Cu: 0.001, Nb: 0.01, Ti: 0.001, B: 0.49</td>
<td>1520–1560</td>
</tr>
</tbody>
</table>

* Ceq. = C + Si/24 + Mn/6

### Table 2. Collection conditions of atmospheric corrosion samples.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Timing</th>
<th>1st Collection</th>
<th>2nd Collection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration</td>
<td>12 years and 8 months</td>
<td>13 years and 4 months</td>
<td></td>
</tr>
<tr>
<td>Weather</td>
<td>Shine</td>
<td>Shine</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>13:30</td>
<td>13:30</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>15°C</td>
<td>27°C</td>
<td></td>
</tr>
<tr>
<td>Humidity</td>
<td>38%</td>
<td>49%</td>
<td></td>
</tr>
</tbody>
</table>

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atmospheric corrosion, a diffusion calculation was conducted based on the Fick’s second law:

\[
\frac{\partial C_h}{\partial t} = D_{eff} \frac{\partial^2 C_h}{\partial x^2} \tag{1}
\]

where \( C_h \) is the hydrogen concentration in the steel, \( t \) is the time, \( D_{eff} \) is the effective hydrogen diffusion coefficient, and \( x \) is the position in the wall thickness direction. \( C_h \) was calculated by the finite element method code ANSYS. The value of \( D_{eff} \) was extracted from the actual measurement of low carbon martensite steel.\(^{24}\)

Fig. 2. Compositional mapping of the cross-section of the first CuLC specimen (upper surface; base material).

Fig. 3. Compositional mapping of the cross-section of the first CuLC specimen (side surface).

Fig. 4. Compositional mapping of the cross-section of the first LC specimen (side surface).
3. Results

3.1. Compositional Mapping of the Rust Layer

Figure 2 shows the result of x-ray intensity mapping of the first CuLC specimen from the cross-section of the tube’s upper side surface. As was observed in the cyclic corrosion test with saltwater spray, Cu accumulated discretely on the rust/steel interface, especially in the bottom of pits. As discussed in detail later, this may be a precipitated metallic Cu from the eluted Cu$^{2+}$ ion in a condensed water layer that was emerged during the atmospheric corrosion on the tube surface. This accumulation is expected from inhabitation of the pitting growth and hydrogen entry at the points where Cu exists. X-ray signals of Cu are also detected at the lower part of scale layer with broader distribution and weaker intensity compared with the Cu detected on the rust-steel interface.

As compared with Fig. 2, it was not necessarily the case that Cu accumulation existed at the rust-steel interface, which was because the water condensation rarely emerged on the side surface, as it was parallel to the gravitational force direction. Cu concentration in the rust layer was 3 mass% at the place indicated by an arrow, as determined by Scanning Electron Microscope - Energy Dispersive X-ray (SEM-EDX) analysis. The Cu distribution coincided with a surfer distribution to some extent, although often not completely. These results obtained from EPMA analysis suggest that there are two types of Cu enrichment in the rust layer on CuLC surface; one is on the rust-steel interface with sharp distribution and the other is in the lower rust layer with rather broad distribution. Figure 4 shows the EPMA mapping of the LC specimen for comparison. As might be expected, Cu accumulation was not observed.

Figure 5 shows Cu–K edge XANES spectrum recorded for rust powder scraped off from CuLC surface exposed for 12 years and 8 month with spectra for polished CuLC surface. The spectra measured for some reference materials are also indicated in the figure. Extended x-ray absorption fine structure (EXAFS) analysis for Cu on polished CuLC surface revealed that Cu atom in the bulk CuLC dissolved mainly in the state of substitutional solid solution in bcc-Fe structure. The edge position of the spectrum for the rust was higher than that for the polished surface and Cu foil (metal), which showed that the Cu in the rust layer was oxidized. By comparing the edge position of the XANES spectra, it would appear that the valence of Cu in the rust was mainly +2. However, the XANES spectrum differs from those of the reference materials with divalent Cu. The spectrum is somewhat close to those of CuO and CuSO$_4$ rather than those of CuS and CuCl$_2$. The EXAFS analysis showed that oxygen is the nearest neighbor atom of Cu in the rust. We considered that the dominant chemical state of Cu atom was Cu-(O, OH, SO$_4$) in the rust layer.

3.2. Absorbed Hydrogen in the Steel

Figure 6 shows the hydrogen evolution profiles of CuLC and LC after the atmospheric corrosion test. There was an evolution peak around 170°C, which may correspond to hydrogen trapped in dislocations that was introduced by the martensite transformation or the rolling of the tube. Two TDS specimens were taken from the first tube. Six were taken from the second one. The concentration of desorbed hydrogen from each specimen is shown in Table 3. The hydrogen detected up to 300°C is considered diffusible hydrogen. The hydrogen detected up to 220°C was also counted, corresponding to the first TDS peak. The diffusible
hydrogen content varied widely among the specimens. The diffusible hydrogen content level of CuLC and LC overlapped. The diffusible hydrogen content level of first CuLC is considerably lower than first LC. However, difference of the diffusible hydrogen content level was not observed between second ones. Combined, the average and maximum value of CuLC was lower than that of LC, as shown in Fig. 7. This result may be due to a mild inhibition effect of Cu addition on the corrosion reaction and hydrogen permeation, as described previously. Comparing the diffusible hydrogen content in terms of circumferential position, the upper position contained more than the lower and the side position. This difference may be due to the different thickness and duration of the water film that formed in the rust layer.

4. Discussion

4.1. Hydrogen Absorption and Diffusion

To consider the wide variation of diffusible hydrogen content among the specimens, a parametric diffusion calculation was conducted. Table 4 shows the calculation conditions. It was assumed that hydrogen permeated into an infinite steel sheet, 2-mm thick at both surfaces. In absorption cycle, the hydrogen concentration at the surface \( C_{hs} \) was fixed at 0.048 ppm. This value is corresponding to twice the maximum absorbed hydrogen up to 300°C in Table 3. In desorption cycle, it was fixed at 0 ppm. The similarity rule is applicable to the hydrogen concentration profile. Therefore, \( C_{hs} \) does not affect the shape of the \( C_h \) profile as long as the temperature range is considered.
as $D_{\text{eff}}$ is constant. $D_{\text{eff}} = 2.6 \times 10^{-6}$ cm$^2$/s is the reported value for a low carbon martensite steel at 25°C.\textsuperscript{28)} $D_{\text{eff}} = 3.6 \times 10^{-5}$ cm$^2$/s is the reported value for a low carbon ferrite and pearlite steel at 25°C.\textsuperscript{28)} $D_{\text{eff}} = 1.2 \times 10^{-6}$ cm$^2$/s is an estimated value for the low carbon martensite steel at 15°C, assuming the dependency of $D_{\text{eff}}$ on the temperature is the same as the dependency of the hydrogen diffusion constant in a regular interstitial lattice, $D_L$.\textsuperscript{30)} $D_{\text{eff}} = 2.6 \times 10^{-7}$ cm$^2$/s is the formally configured value as a tenth of the base value. Diffusion retardation caused by trapping in the dislocations that were generated by plastic deformation was taken into account. The standard absorption and desorption cycle duration were set to 6 h and 18 h, respectively, which represented the daily range of temperature and relative humidity. The absorption cycle time was prolonged in Case 5.

Figure 9 shows the time dependency of the $C_h$ profiles. In Case 1, $C_h$ traversed almost the same thickness as $C_{hs}$ by the end of the absorption cycle. When 1 cycle passed, $C_h$ returned to the first level at 0 ppm. In Case 2, some retardation was recognized as compared to Case 1. However, the general tendency was the same as in Case 1. In Case 3, $C_h$ reached the same level as $C_{hs}$ immediately. In Case 4 and 5, $C_h$ did not reach homogeneously to the level of $C_{hs}$ by the end of the absorption desorption cycle. However, an accumulative effect was not observed after many cycles. Figure 10 shows the time dependency of $C_h$ at the 1/2 and 1/4 of thickness points. In each case, $C_h$ changed periodically between the maximum and minimum $C_{hs}$ values.

The above diffusion calculation results revealed that hydrogen diffusion was so rapid that the long-term corrosion hysteresis seemed to have little influence on the diffusible hydrogen content. Furthermore, the short-term corrosion hysteresis may be the main determinant of $C_h$. In terms of prevention of hydrogen-induced cracking, the tidemark $C_h$ level is important. If the Cu accumulated in the rust-steel interface has some effect on inhibition of the corrosion reaction and hydrogen permeation, then it may be very effective in the prevention of hydrogen-induced cracking. The bottom of a pit is a potential crack initiation site because of the stress concentration at this site. Consequently, even with the Cu distributed discreetly, accumulated Cu can be an inhibitor, as long as it is located at the bottom of a pit.

### 4.2. Effects of Cu Addition under Atmospheric Corrosion

Figure 11 shows a schematic illustration of the inhibition mechanism of accumulated Cu on hydrogen-induced cracking when a water condensation occurs after years of atmospheric corrosion. This mechanism explains well the inhibiting effect of Cu addition on delayed fracture resistance previously reported.\textsuperscript{24)} X-mark indicates the inhibited reaction and cracking by Cu precipitation on the microscopic
In general, hydrogen generation and entry occur at the microscopic cathode in a concave macroscopic anode. In this place, a water condensation may occur, and the pH may decrease during atmospheric corrosion. Eluted Cu\textsuperscript{+} ions in the rust layer may precipitate as metallic Cu at the microscopic cathode, in accordance with the ionization tendency during the corrosion test. As a result, the microscopic cathode becomes deactivated as an electrochemical reaction site for hydrogen. In fact, Shimizu et al. reported that the valence of Cu compounds was about 0 in the rust layer after a 10 cycle wet-dry cyclic corrosion test with 0.5% salt water spray.\textsuperscript{4}

In contrast, considering the results of XAFS spectra and EPMA mapping from this study, a large number of Cu presumably existed as Cu–(O, OH, SO\textsubscript{4}) in the rust layer. However, this result does not contradict the above-mentioned mechanism. One possibility is that the information of chemical state of Cu obtained by XAFS was mainly from Cu atom enriched in the rust. The information from Cu atom sharply enriched on the rust/steel interface might not be fully detected due to the difficulty of sample correction from rust/steel interface. To clarify this pinpoint chemical state of Cu, local analysis technique such as micro-beam XAFS is needed.\textsuperscript{31}

Questions still remain about quantitatively evaluating hydrogen-induced cracking. Consideration of localized hydrogen distribution that is induced by elastic stress concentration and the enhancement mechanism of concentrated hydrogen on cracking are still unclear.

5. Conclusions
To clarify the effects of Cu addition on hydrogen absorption and diffusion properties under atmospheric corrosion, an atmospheric corrosion test was conducted on a 1470 MPa grade thin-walled low carbon martensite steel tube. The conclusions are summarized as follows.

(1) Cu was accumulated discretely at the rust/steel interface, especially in the bottom of pits of a 0.15% Cu bearing steel tube after the atmospheric corrosion test.

(2) According to the XAFS spectra, the valence of Cu in the rust layer was mainly +2 as Cu–(O, OH, SO\textsubscript{4}).

(3) The average and maximum diffusible hydrogen content of 0.15% Cu bearing steel was lower than that of Cu-free steel after atmospheric corrosion tests.

(4) The quantity of non-diffusible hydrogen was much higher than that of diffusible hydrogen.

(5) According to diffusion calculation results, it was revealed that hydrogen diffusion was so rapid that the long-term corrosion hysteresis seemed to have little influence on the diffusible hydrogen content. Furthermore, the short-term corrosion hysteresis may be the main determinant of diffusible hydrogen concentration.

(6) Having regard to the fact that the valence of Cu could also be 0 as reported by Shimizu et al., an inhibition mechanism of accumulated Cu on hydrogen-induced cracking was proposed. Eluted Cu\textsuperscript{+} ions in the rust layer may precipitate as metallic Cu at the microscopic cathode during the corrosion test. As a result, the microscopic cathode becomes deactivated as an electrochemical reaction site for hydrogen. The Cu may alternates between precipitates and Cu ions depending on relative humidity, and the condensation level and pH of the water in the rust layer.
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