Effects of Cu Addition on Hydrogen Absorption and Diffusion Properties of 1 470 MPa Grade Thin-walled Steel in a Solution of HCl

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(Received on August 19, 2010; accepted on November 30, 2010)

Hydrogen embrittlement is caused by the introduction of hydrogen into steel and is critical for high strength steels. To clarify the effects of the addition of Cu on the suppression of hydrogen embrittlement in a solution of HCl, hydrogen permeation tests and dynamic polarization measurements were conducted on TS 1 470 MPa grade, low-carbon martensite steels. To this end, steels containing 0.19% C, 0.2% Si, 1.3% Mn, Cr, Ti, Nb and B were prepared with and without 0.16% Cu. For comparison, ferrite and pearlite steels were also examined. The results of hydrogen permeation tests indicated that the steady-state hydrogen permeation current (JH) of steel containing 0.16% Cu was considerably lower than that of basic steel in 0.1 N HCl at the corrosion potential. Moreover, the JH of martensite steel was suppressed by the addition of Cu, and the cathode current, (iC) and the JH/iC were reduced. The results obtained in this study corroborated the hypothesis that the 1 or 2 μm metallic Cu particles precipitated on the surface of the steel in a solution of HCl suppressed the cathodic reaction and the introduction of hydrogen. The hydrogen diffusion constant (Deff) was obtained from hydrogen permeation tests under a potential gradient. Cu addition has only small effect on Deff regardless of microstructure. The occupancy of trap site (nX) was estimated to be greater than 99% independent of Cu content and microstructure.

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

1. Introduction

The effects of Cu on the corrosion resistance of steel have been intensively investigated under a variety of different conditions.1–9) Shiotani et al.6) analyzed a layer of rust on a weathering steel bridge located in a coastal industrial zone and found that Cu and sulfur were present in corrosion pits in the lower region of the rust layer. Kimura et al.8,9) examined the electronic state of Cu in the rust layer using synchrotron radiation and found that Cu existed as CuO and did not displace the Fe in goethite. Thus, the authors proposed that the addition of Cu altered the microstructure of goethite and reduced the corrosion rate. However, an electrochemical mechanism for the aforementioned effect has not been provided.

In high strength steels, corrosion and hydrogen embrittlement caused by the introduction of hydrogen into steel is critical.10–19) Omura et al.12) demonstrated that hydrogen absorption into steel under atmospheric conditions depends on the time of day. Kushida et al.11) reported that Cu-based steel displays a lower corrosion rate and contains smaller amounts of diffusible hydrogen than steel without Cu. However, the mechanism of the suppressive effects of Cu has not been clarified.

Immersion tests in solutions of HCl and hydrogen cathode charge tests are commonly used to evaluate the hydrogen embrittlement properties of high strength steels.20–26) Even under atmospheric conditions, the pH of the water film in the rust layer can decrease to 3 or less.27) Toyoda et al.24) reported that the addition of Cu had a significant effect on the delayed fracture resistance of low-carbon martensitic 1 470 MPa grade steel immersed in a solution of HCl. And they also reported that the results of delayed fracture resistance in (a) an immersion test using 0.1 N-hydrochloric acid, (b) a cyclic corrosion test with 5% NaCl water spray, and (c) an atmospheric corrosion test had good correlation with each other. However, a quantitative evaluation of the electrochemical effects of Cu has not yet been conducted.

On the other hand, Inagaki et al.28) systematically investigated the effects of Cu on hydrogen-induced cracking of pipe line steels. The addition of Cu enhanced the formation of a protective and impermeable FeS surface film in hydrogen sulfide-saturated synthetic seawater. Accordingly, Cu-
based steels displayed excellent resistance to hydrogen-induced cracking. Although the mechanism of this effect was determined, the results cannot be applied to steel in a solution of HCl because FeS film cannot exist at a pH < 4.

Thus, in the present study, hydrogen permeation tests and dynamic polarization measurements were conducted to determine the effects of Cu on steel immersed in a solution of HCl.

2. Experimental

2.1. Specimen Preparation

The chemical composition of the steels evaluated in this study is provided in Table 1. After quenching and tempering, the carbon content was adjusted to obtain steel with a grade of 1470 MPa, and Mn, Cr, Ti and B were added to improve the quench hardenability. To obtain Cu-based steel, 0.16% Cu was added to the base formulation. Figure 1 shows the hot-rolling and heat treatment conditions applied to the specimens. Laboratory vacuum-melted and hot-rolled 50 mm thick plates were hot-rolled into 4 mm thick sheets after reheating at 1250°C for 1 h, and the finishing temperature was controlled at 850°C. After storing the sheets at 600°C for 1 h, the materials were furnace-cooled to room temperature. Hot-rolled sheets were heat-treated at 950°C for 5 min in a salt bath and were immediately water quenched and tempered at 200°C for 5 min. The resulting Cu-based specimens were labeled as CuM, and specimens without Cu were labeled as BM. For comparison, hot-rolled specimens were also examined prior to quenching and tempering, and the resulting Cu-based materials were labeled as CuFP. Alternatively, specimens without Cu were labeled as BFP. The surface of the specimens was finished with #800 wet abrasive paper to obtain material with a thickness of 1.0 mm. After etching with 2% Nital, the microstructure of the specimens was observed with a scanning electron microscope (SEM). The hardness of the materials was measured with a micro Vickers hardness tester.

Figure 2 shows the size and geometry of the specimens used in the hydrogen permeation tests. For comparison, electroplated copper specimens were also prepared from the base alloy. The entire surface and one-half of the surface of the specimens were electroplated in a solution of 210 g/L copper sulfate and 52 g/L sulfuric acid after pickling in 10% hydrochloric acid for 5 s and were labeled as BM-hCu and BM-wCu, respectively. An electrolytic current of −10 mA/cm² was applied for 5 s, and 2 mm of the width of BM-hCu was stripped from the specimen. The materials evaluated in the hydrogen permeation tests are listed in Table 2.

2.2. Electrochemical Measurement

As shown in Fig. 3, hydrogen permeation tests were conducted in a solution of HCl at the corrosion potential. The environmental side of the cell was filled with deaerated 0.1 N HCl, and the hydrogen detection side was filled with deaerated 0.1 N NaOH. A Pt plate was used as the counter electrode, and a Luggin capillary was connected to the SCE reference electrode. Prior to the test, the surface of the hydrogen detection side was electroplated with 45 g/L of NiCl₂, 300 g/L of NiSO₄, and 35 g/L of H₃BO₃ at −10 mA/cm² for 120 s. The hydrogen detection side was polarized at a constant potential of +100 mV (vs. SCE) for prompt ionization of permeated hydrogen atoms.

To determine the hydrogen diffusion constant (D eff), hydrogen permeation tests were conducted under a potential gradient in the cell shown in Fig. 3. The environmental side

<table>
<thead>
<tr>
<th>Mark</th>
<th>Steel</th>
<th>Heat treatment</th>
<th>Microstructure</th>
<th>Surface treatment</th>
<th>Hv (0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>Base</td>
<td></td>
<td>Tempered martensite</td>
<td>None</td>
<td>437</td>
</tr>
<tr>
<td>CuM</td>
<td>Cu added</td>
<td>Quench and tempered</td>
<td>Half Cu electroplated</td>
<td>443</td>
<td></td>
</tr>
<tr>
<td>BM-hCu</td>
<td>Base</td>
<td></td>
<td>Whole Cu electroplated</td>
<td>437</td>
<td></td>
</tr>
<tr>
<td>BM-wCu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BFP</td>
<td>Base</td>
<td>As hot-rolled</td>
<td>Ferrite and pearlite</td>
<td>None</td>
<td>181</td>
</tr>
<tr>
<td>CuFP</td>
<td>Cu added</td>
<td></td>
<td></td>
<td>162</td>
<td></td>
</tr>
</tbody>
</table>

### Table 1. Composition of the steels.

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.19</td>
<td>0.22</td>
<td>1.35</td>
<td>0.01</td>
<td>0.003</td>
<td>0.18</td>
<td>0.00</td>
<td>0.015</td>
<td>0.011</td>
<td>0.0012</td>
</tr>
<tr>
<td>Cu added</td>
<td>0.19</td>
<td>0.21</td>
<td>1.31</td>
<td>0.01</td>
<td>0.003</td>
<td>0.17</td>
<td>0.06</td>
<td>0.015</td>
<td>0.010</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

![Fig. 1. Hot-rolling and heat treatment conditions of the specimens.](image)

![Fig. 2. Size and geometry of a specimen subjected to the hydrogen permeation test.](image)

![Fig. 3. Schematic illustration of the cell used in the hydrogen permeation test.](image)

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was filled with 0.5 vol% $\text{H}_2\text{SO}_4$ and 1.4 g/L of $(\text{NH}_2)_2\text{CS}$, and a Pt plate was used as the counter electrode. $\text{H}_2\text{SO}_4$ provides higher steady-state hydrogen permeation current ($J_h$) than $\text{HCl}$\textsuperscript{29}); therefore $\text{H}_2\text{SO}_4$ was adopted as cathode electrolyte. The current density was controlled at $-10$ mA/cm$^2$ for the quench and tempered specimen. It was controlled at $-5$ mA/cm$^2$ for the as-hot-rolled specimen. The condition of the hydrogen detection side was the same as the hydrogen permeation test in $\text{HCl}$ solution at the corrosion potential.

Dynamic polarization measurements were conducted in deaerated 0.1 N $\text{HCl}$ with a 1 cm$^2$ working electrode. A Luggin capillary was connected to the SCE reference electrode, and a Pt ribbon separated by a semi-permeable membrane was used as the counter electrode. After maintaining the corrosion potential for 1 min, a potential was applied to the cell. The potential was applied at a rate of $+20$ mV/min to $+500$ mV (vs. SCE), and the resulting anode polarization current ($i_a$), was recorded. Subsequently, after maintaining the corrosion potential again, a potential was applied at a rate of $-20$ mV/min to $-1500$ mV (vs. SCE) to obtain the cathode polarization current, ($i_c$).

All of the electrochemical measurements were conducted at 25°C.

3. Results

3.1. Effects of Cu Addition on Hydrogen Absorption Properties

Figure 4 shows the SEM microstructures of the specimens. Quenched and tempered specimens displayed a lath martensite structure, and finely dispersed cementite was observed in the martensite lath. Alternatively, hot-rolled specimens possessed a ferrite and pearlite structure. Table 2 shows the hardness of investigated materials. The hardness level of the martensite and the ferrite and pearlite steel are corresponding to about TS 1460 MPa and TS 550 MPa, according to the hardness conversion table of JIS handbook, respectively. The thickness of the electroplated Cu layer was approximately 1 µm, which was determined by cross-sectional SEM observation.

Figure 5 shows the time dependence of the hydrogen permeation current ($J_h$) of martensite steel in a solution of $\text{HCl}$ at the corrosion potential. The results indicated that the $J_h$ of base steel increased over time and reached a constant value. On the other hand, the $J_h$ of Cu-based steel reached a maximum value and decreased gradually until a steady-state was achieved. The steady-state $J_h$ of Cu-based steel was considerably lower than that of the base steel. Figure 6 shows the time dependence of the $J_h$ of ferrite and pearlite steels. Similar to martensite steels, the $J_h$ of Cu-based steel was considerably lower than that of the base steel. As shown in Fig. 7, the $J_h$ of electroplated specimens was also lower than that of the base steel. The steady-state $J_h$ values of the specimens are provided in Table 3.

3.2. Effects of Cu on Hydrogen Diffusion Constant

According to the following equation, the $D_{\text{eff}}$ of the specimens was calculated from the results of the hydrogen permeation tests, and the $D_{\text{eff}}$ values are shown in Table 3:

$$J_h = 2.32 \times 10^{-10} \times \frac{D_{\text{eff}}}{x} \times \frac{10^{15}}{T} \times \frac{1}{\mu_0}$$

$$D_{\text{eff}} = \frac{2.32 \times 10^{-10} \times J_h \times \mu_0 \times x}{10^{15} \times T}$$

Table 3. Electrochemical properties in 0.1 N hydrochloric acid.

<table>
<thead>
<tr>
<th>Mark</th>
<th>Steel</th>
<th>Microstructure</th>
<th>Hydrogen permeation current, $J_h$ (µA/cm$^2$)</th>
<th>Hydrogen diffusion constant, $D_{\text{eff}}$ (cm$^2$/s)</th>
<th>Corrosion potential (mV vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>Base</td>
<td>Structure</td>
<td>$1.43$</td>
<td>$2.6 \times 10^4$</td>
<td>$-497$</td>
</tr>
<tr>
<td>CuM</td>
<td>Cu added</td>
<td>Tempered martensite</td>
<td>$0.65$</td>
<td>$2.6 \times 10^4$</td>
<td>$-490$</td>
</tr>
<tr>
<td>BM-Cu</td>
<td>Base</td>
<td>Structure</td>
<td>$0.51$</td>
<td>$1.8 \times 10^4$</td>
<td>$-526$</td>
</tr>
<tr>
<td>BM-wCu</td>
<td></td>
<td></td>
<td>$0.85$</td>
<td>$2.5 \times 10^4$</td>
<td>$-522$</td>
</tr>
<tr>
<td>BFP</td>
<td>Base</td>
<td>Ferrite and pearlite</td>
<td>$2.96$</td>
<td>$3.6 \times 10^4$</td>
<td>$-512$</td>
</tr>
<tr>
<td>CuFP</td>
<td>Cu added</td>
<td>Structure</td>
<td>$0.74$</td>
<td>$3.9 \times 10^4$</td>
<td>$-510$</td>
</tr>
</tbody>
</table>

*: At the corrosion potential
where $t_{0.63}$ is the required time to achieve a $J_{i,H}/J_{a}$ of 0.63, $L$ is the thickness of the specimen. Equation (1) is derived directly from Fick’s second law so that it is applicable independently of crystal structure. The $D_{\text{eff}}$ of martensite steels was significantly lower than that of ferrite and pearlite steels, and the addition of Cu had a minor effect on the $D_{\text{eff}}$. Moreover, electroplating the entire copper layer also had little effect on the $D_{\text{eff}}$.

3.3. The Effects of Cu on the Polarization Behavior

The corrosion potential of the specimens in 0.1 N hydrochloric acid is shown in Table 3. The corrosion potential of the materials ranged from $-490$ to $-526$ mV vs. SCE, and the following trend was observed: CuM $>$ BM $>$ CuFP $>$ BFP $>$ BM-wCu $>$ BM-hCu. Figure 8 shows the energy-dispersive X-ray (EDX) spectra and the X-ray diffraction pattern of the surface of BM-wCu. The penetration depth of X-ray was about 2 $\mu$m with the power of 40 kV and 50 mA. The results indicated that Fe was present in the surface of the specimen. Figure 9 shows the polarization behavior of martensite steels in 0.1 N hydrochloric acid. The results revealed that the cathodic and anodic polarization curves were affected by the addition of Cu. The polarization current neighborhood of the corrosion potential was decreased by Cu addition. Figure 10 shows the polarization behavior of ferrite and pearlite steels in 0.1 N hydrochloric acid. Similar to the martensite steels, the $i_c$ of ferrite and pearlite steels around the corrosion potential decreased due to the addition of Cu. Figure 11 shows the polarization curves of Cu electroplated specimens in 0.1 N hydrochloric acid. The results indicated that the $i_c$ around the corrosion potential was also lowered by electroplated Cu layer.

4. Discussion

4.1. Effects of Cu on the Hydrogen Absorption Properties of Steel

As shown in Table 3, the corrosion potential of martensite steel was slightly higher than that of ferrite and pearlite steel, which may be attributed to the difference of the corrosion potential of the constituents of each microstructure. The potential of Cu-based steel was higher than that of base steel, which may be due to the effect of Cu in the steel matrix. Alternatively, the corrosion potential of Cu electroplated BM-wCu and BM-hCu was lower than that of base steel, which may be due to the decrease of the corro-
Table 4. The hydrogen permeation ratio.

<table>
<thead>
<tr>
<th>Mark</th>
<th>At the corrosion potential in 0.1N HCl solution</th>
<th>With cathodic potential gradient in H2SO4 and (NH2)2CS solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( J_i / i_c (\text{mA/cm}^2) )</td>
<td>( J_i / i_c (\text{mA/cm}^2) )</td>
</tr>
<tr>
<td>BM</td>
<td>1.43</td>
<td>4.35 72</td>
</tr>
<tr>
<td>CuM</td>
<td>0.65</td>
<td>29 69</td>
</tr>
<tr>
<td>BM+Cu</td>
<td>0.51</td>
<td>4 46</td>
</tr>
<tr>
<td>BM-wCu</td>
<td>0.85</td>
<td>5 55</td>
</tr>
<tr>
<td>BFP</td>
<td>2.96</td>
<td>17 61</td>
</tr>
<tr>
<td>CuFP</td>
<td>0.74</td>
<td>11 6.7</td>
</tr>
</tbody>
</table>

Table 5. Parameters of hydrogen permeation tests under a potential gradient in a solution of H2SO4 and (NH2)2CS

<table>
<thead>
<tr>
<th>Mark</th>
<th>( D_i (\text{cm}^2/\text{s}) )</th>
<th>( J_i (\text{mA/cm}^2) )</th>
<th>Hydrogen concentration, ( C_i (\text{ppm}) )</th>
<th>( D_i/D_L )</th>
<th>( C_i/C_X (1-n_X) )</th>
<th>( n_X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>2.6 \times 10^4</td>
<td>72</td>
<td>3.72</td>
<td>0.028</td>
<td>7440</td>
<td>202</td>
</tr>
<tr>
<td>CuM</td>
<td>2.6 \times 10^4</td>
<td>69</td>
<td>3.44</td>
<td>0.028</td>
<td>6880</td>
<td>194</td>
</tr>
<tr>
<td>BM+Cu</td>
<td>1.8 \times 10^4</td>
<td>46</td>
<td>3.26</td>
<td>0.019</td>
<td>6520</td>
<td>129</td>
</tr>
<tr>
<td>BM-wCu</td>
<td>2.5 \times 10^4</td>
<td>55</td>
<td>3.00</td>
<td>0.027</td>
<td>6000</td>
<td>153</td>
</tr>
<tr>
<td>BFP</td>
<td>3.6 \times 10^4</td>
<td>61</td>
<td>0.22</td>
<td>0.38</td>
<td>440</td>
<td>171</td>
</tr>
<tr>
<td>CuFP</td>
<td>3.9 \times 10^4</td>
<td>60</td>
<td>0.21</td>
<td>0.41</td>
<td>420</td>
<td>168</td>
</tr>
</tbody>
</table>

The cathode current \( (i_c) \) decreased due to the addition of Cu as shown in Fig. 9, which is corresponding to following reaction:

\[
\text{H}^+ + e \rightarrow \text{H}_{\text{ads}} \tag{2}
\]

where \( \text{H}_{\text{ads}} \) represents hydrogen adsorbed on the cathode surface. A part of adsorbed hydrogen dissolved into steel and the remaining hydrogen was gasified as following reaction:

\[
\text{H}_{\text{ads}} \rightarrow \text{H}_{\text{diss}} + \frac{1}{2} \text{H}_2 \tag{3}
\]

where \( \text{H}_{\text{diss}} \) represents hydrogen dissolved in steel.

Table 4 shows the hydrogen permeation ratio \( (J_i/i_c) \) in 0.1 N HCl at the corrosion potential. \( J_i/i_c \) is the ratio of hydrogen dissolved into steel, \( \text{H}_{\text{diss}} \) to the total amount of reduced hydrogen, \( \text{H}_{\text{ads}} \) at the cathode surface via reaction (3). As the \( i_c \) value at the corrosion potential, the initial cathodic polarization current, before the intentional polarization, was adopted. The precise initial \( J_i \) cannot be obtained because of the incubation time of hydrogen diffusion in the hydrogen permeation test, therefore the value of \( J_i \) was approximated by \( J_c \) in this calculation on the presumption that \( J_i \) reaches the same value as \( J_c \) in a short period of the time.

Along with the drastic suppression of the \( J_i \) of martensite steel due to the addition of Cu, a reduction in the \( i_c \) and \( J_i/i_c \) was also observed. The \( J_i \), \( i_c \) and \( J_i/i_c \) of pearlite and ferrite steel were also decreased by Cu addition. The \( i_c \), of Cu electroplated BM-wCu and BM-hCu at the corrosion potential was significantly smaller than that of non-electroplated specimens. This result dovetails with the fact that the exchange current density of Cu was smaller than that of Fe by one order of magnitude, which was reported by Uhlig and Revie.32)

Toyoda et al.34) proposed a mechanism for the effect of the addition of Cu on the delayed fracture resistance of 1470 MPa grade steel immersed in a solution of HCl. Specifically, Toyoda et al. suggested that the 1 or 2-µm metallic Cu particles precipitated on the steel surface suppressed the cathodic reaction and the introduction of hydrogen. In the present study, the \( J_i \) of ferrite and pearlite steel at the corrosion potential was suppressed, and the \( i_c \) and \( J_i/i_c \) were reduced due to the addition of Cu. Thus, the results obtained in the present study corroborate the hypothesis of Toyoda et al. electrochemically.

\( J_i \) data obtained under a cathodic potential gradient in a solution of H2SO4 and (NH2)2CS are provided in Table 4. In this experiment, the value of the \( i_c \) was intentionally controlled. The value of \( J_i \) was extracted from the \( D_{i eff} \) which was obtained from the hydrogen permeation tests. Compared to the results obtained at the corrosion potential in 0.1 N HCl, the value of \( J_i \) increased significantly. Thus, the effect of Cu on the suppression of \( J_i/i_c \) was reduced.

4.2. Cu addition and Trapping Effects on Hydrogen Diffusion

Along with hydrogen absorption, hydrogen diffusion properties are also important for dealing with hydrogen embrittlement. Table 5 shows the parameters extracted from hydrogen permeation tests under a potential gradient. Cu addition has only small effect on \( D_{i eff} \) regardless of microstructure, which may be due to small interaction between solute Cu and diffusible hydrogen.

The \( D_{i eff} \) of steel varies significantly and is dependent on the presence of precipitates and dislocations which cause trapping effects, as well as the chemical composition and microstructure of the steel.33) Consequently, the occupancy of the trap site \( (n_X) \) of each specimen was calculated by using the obtained parameters of hydrogen permeation tests.

The concentration of hydrogen at the cathode side \( (C_0) \) was obtained from the following equation:

\[
C_0 = \frac{J_c \times L}{D_{i eff} \times F \times \Delta \rho} \tag{4}
\]

where \( F (=96 500 \text{C/mol}) \) is the Faraday constant and \( \Delta \rho (=7.86 \text{g/cm}^3) \) is the specific gravity of steel.34)

The \( C_0 \) of martensite steel was significantly higher than the \( C_0 \) of ferrite and pearlite steel, and values between 3.72 to 3.00 ppm were obtained due to the presence of reversible trapping sites, such as the interface of fine cementite precipitates and matrix, and the dislocations introduced by quenching. According to the following equation, the \( D_{i eff} \) is related to the hydrogen diffusion constant in a regular interstitial lattice \( (D_L) \):

\[
D_{i eff} = \frac{C_L}{C_L + C_X (1-n_X)} D_L \tag{5}
\]

where \( C_L \) is the hydrogen concentration in the solid solution and \( C_X \) is the trapped hydrogen concentration.33) The value of \( D_L \) was calculated from the equation, \( D_L (\text{cm}^2/\text{s}) = 5.8 \times 10^{-4} \exp(4.5(kJ/mol)/RT) \), where \( T=278–318 \text{K} \) (=5–45°C) and \( C_0 = 0.0005 \text{ppm} \).35,36) At 25°C, the results indicated that \( D_L \) was equal to 9.4 \times 10^{-5} \text{cm}^2/\text{s} and the value of \( n_X \) was calculated as shown in Table 5. Regardless of the microstructure and Cu content of the specimen, \( n_X \)
was estimated to be greater than 99% under the experimental conditions.

The $D_{\text{eff}}$ of martensite steel decreased to approximately 3% of the $D_t$ due to the trapping effect. Moreover, the $D_{\text{eff}}$ of ferrite and pearlite steel was about 40% of the $D_t$. The observed dependence of $D_{\text{eff}}$ on the microstructure of the specimen may be one of the factors affecting hydrogen embrittlement properties under corrosive environments.

The ratio of the hydrogen concentration in trapping sites to the hydrogen concentration in the regular interstitial lattice of martensite steel ($C_{\text{H}}/C_{\text{t}}$) is approximately 7 000. Alternatively, the $C_{\text{H}}/C_{\text{t}}$ of ferrite and pearlite steel is about 400. The $J_{\text{H}}/J_{\text{t}}$ ratio indicates the contribution of trapped hydrogen to the total flux of hydrogen. By substituting $D_{\text{t}} = 9.4 \times 10^{-5}$ cm$^2$/s and $C_{\text{t}} = 0.0005$ ppm into Eq. (4), $J_{\text{t}}$ was estimated to be 0.36 $\mu$A/cm$^2$. Thus, the $D_{\text{eff}}$ of martensite steel decreased to 3% of the $D_t$. However, the concentration of hydrogen in trapped sites was 7 000 times greater than the concentration of hydrogen in the regular interstitial lattice. Consequently, the contribution of trapped hydrogen to the total hydrogen flux was about 200 times greater than that of hydrogen in the regular interstitial lattice independent of Cu content.

Meanwhile, the difference of $C_{\text{H}}$ between with and without Cu in Table 5 seems to be small compared to the significant inhibiting effect of Cu addition on hydrogen embrittlement in HCl solution. However, the value of $C_{\text{H}}$ in Table 5 was obtained under the condition that cathodic current was intentionally imposed, therefore, it does not mean a small difference around the corrosion potential.

Some of the aforementioned diffusion properties could be applied under different circumstances such as atmospheric corrosion; however, absorption properties are highly dependent on the specific conditions. Thus, further studies on corrosion and hydrogen entry under actual conditions must be conducted.

5. Conclusions

To clarify the effects of the addition of Cu to steel immersed in a solution of HCl, hydrogen permeation tests and dynamic polarization measurements were conducted on TS 1470 MPa grade low-carbon martensite steels. The conclusions of the study can be summarized as follows:

(1) In hydrogen permeation tests conducted in 0.1 N HCl at the corrosion potential, the steady-state $J_{\text{H}}$ of steel containing 0.16% Cu was considerably lower than that of base steel.

(2) The addition of Cu suppressed the $J_{\text{H}}$ of martensite steel, and the $J_{\text{t}}$ and $J_{\text{H}}/J_{\text{t}}$ were reduced.

(3) The results obtained in the present study corroborated the hypothesis that the 1 or 2-μm metallic Cu particles precipitated on the surface of steel suppressed the cathodic reaction and the introduction of hydrogen.

(4) Cu addition has only small effect on $D_{\text{eff}}$ regardless of microstructure. The occupancy of trap site ($n_{\text{tr}}$) was estimated to be greater than 99% independent of Cu content and microstructure.

Acknowledgements

The authors are deeply indebted to Dr. Mitsuhiro Kimura of the JFE Steel Corporation for helpful discussions.

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