Effects of Alloying Elements on Hydrogen Entry to Low Alloy Steels under a Cyclic Corrosion Condition

Tomohiko OMURA,1)* Hitoshi MATSUMOTO,2) Tatsuya HASEGAWA2) and Yusuke MIYAKOSHI2)

1) Steel Research Laboratory, Nippon Steel & Sumitomo Metal Corporation, 1-8 Fuso-cho, Amagasaki, 660-0891 Japan.
2) Yawata Works, Nippon Steel & Sumitomo Metal Corporation, 1, Konomi-machi, Kokurakita-ku, Kitakyushu, 803-0803 Japan.

(Received on June 30, 2015; accepted on July 31, 2015; J-STAGE Advance published date: February 4, 2016)

Hydrogen entry in low alloy steels and effects of alloying elements were investigated using a hydrogen permeation technique under a simulated atmospheric corrosion condition and an acidic solution. In the base steel, the hydrogen permeation coefficient sensitively varied depending upon the wetting and drying processes in the cyclic corrosion condition. Additions of Mo, Cu and Ni to the base steel were effective for suppressing hydrogen entry under the cyclic corrosion condition. These elements were also effective in the acidic solution with an initial pH of 3.5. The mechanism of the beneficial effects of these elements was considered to be a change in hydrogen overpotential, which leads to a decrease in hydrogen surface coverage.

S was also effective for suppressing hydrogen entry under the cyclic corrosion condition, although it drastically promoted hydrogen entry in the acidic solution. The detrimental effect in the acidic solution was considered to relate the production of H₂S, a catalytic promoter of hydrogen entry, accompanying with the chemical dissolution of soluble sulfide inclusions such as MnS. On the contrary, under the cyclic corrosion condition, dissolution of MnS inclusions would lead to an increase in pH because of the consumption of H⁺ ions in the thin water layer on the steel surface, resulting in the suppression of hydrogen entry.

KEY WORDS: alloying element; hydrogen permeation; cyclic corrosion.

1. Introduction

Hydrogen causes hydrogen embrittlement in high strength steels. 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 hydrogen embrittlement under atmospheric exposure.1) Therefore, hydrogen entry into steels has been widely studied to clarify the mechanism of hydrogen embrittlement in atmospheric environments. Kushida investigated absorbed hydrogen concentration in low alloy steels that were exposed at various sites in Japan.2) He revealed the site and time dependence of hydrogen absorption. Tsuru measured hydrogen entry from the thin water layer on the steel surface by hydrogen permeation techniques.3) He showed that hydrogen entry during a drying period after wetting closely relates change in pH and the potential. The authors of this paper previously investigated hydrogen entry into low alloy steels using hydrogen permeation techniques under atmospheric exposure, and reported that hydrogen entry strongly depended upon the time of the day, the season, and exposure locations.4,5) In addition, the authors clarified several environmental factors such as temperature, humidity and an amount of Cl⁻ on the steel surface strongly affected hydrogen entry using hydrogen permeation tests in a temperature–humidity controlled chamber, and compared preferential environmental conditions for hydrogen entry with those for a corrosion reaction.6)

In atmospheric environments, several alloying elements, such as Cu or Ni have been recognized to retard corrosion reaction in weathering steels.7) However, effects of such types of alloying elements on hydrogen entry in atmospheric environments have not been clarified yet. If a decrease in hydrogen entry by alloy design or surface modification is successfully achieved, hydrogen embrittlement can be suppressed in service environments. Therefore, in this study, effects of alloying elements on hydrogen entry into low alloy steels were investigated using a hydrogen permeation technique under a cyclic corrosion condition simulating atmospheric exposure. The results of the hydrogen permeation tests were compared with those of corrosion weight loss tests in the same cyclic corrosion condition to discuss the mechanism of hydrogen entry from the viewpoint of corrosion reaction. In addition, hydrogen permeation and weight loss tests in an acidic solution were conducted to compare the results with those in the cyclic corrosion condition.

2. Experimental Procedure

Chemical compositions of steels used are shown in Table 1. The base material was a low alloy steel containing C, Mn,
Cr and B. An increase or addition of Cr, Mo, Cu, Ni and S were investigated. All the steels were melted in a vacuum induction furnace and cast into ingots that were forged at 1250°C and hot-rolled into 15 mm thick plates at 1250°C. These plates were quenched from 890°C and tempered at 420°C to adjust strength levels at a 1000 MPa grade.

Membrane specimens for hydrogen permeation tests with a 70 mm diameter and 0.5 mm thickness were cut from the steel plates. Hydrogen permeation tests were conducted under a cyclic corrosion condition using a test cell shown in Fig. 1. Both sides of the membrane specimen were polished using a No. 600 emery paper, and then one side was electroplated with Ni. The thickness of the Ni layer was 0.6 μm. After fixing the electroplated side to the test cell, the cell was filled with a 1M NaOH solution. The electroplated side was polarized at 0 V versus an Ag/AgCl reference electrode. The internal solution in the reference electrode was saturated KCl solution. The polished side was exposed to an external environment. The exposure and internal surface areas of the membrane were 23.7 cm². Synthetic sea water specified in ASTM-D-1141 was dropped on the exposed surface and then perfectly dried to be sea salt. The amount of sea salt on the membrane was 0.63 mg/cm² (0.3 mg/cm² of Cl⁻). The test cell was put into a temperature–humidity controlled chamber. Through the experiment, hydrogen atoms that permeate the membrane from the external surface were oxidized to hydrogen ions on the inner surface. Hydrogen oxidizing current density $J$ (A/cm²) measured by a potentiostat gives hydrogen permeation coefficient $J_L$ (A/cm), where $L$ is the thickness of the membrane (=0.05 cm). The tests were run for 336 h. Using the same membrane specimens, corrosion rate was measured by weight loss for 336 h.

Among the investigated materials, hydrogen diffusion coefficients $D$ can be different because adding alloying elements affects hydrogen trapping capacity. Change in $D$ can affect hydrogen permeation coefficient $J_L$ and surface hydrogen concentration $C_JL$ according to the following Eq. (1).

$$C_JL = \frac{J_L}{D}$$ (1)

However, it was confirmed that $J_L$ were identical among several steels which had different $D$ under atmospheric exposure. This means $J_L$ was determined by the environmental severity, and was not affected by hydrogen trapping capacity. Therefore, in this study, $J_L$ of each material was evaluated as a parameter which reflects velocity of hydrogen entry.

The cyclic corrosion condition is shown in Fig. 2. One

---

### Table 1. Chemical compositions of steels used (mass%).

<table>
<thead>
<tr>
<th>Mark</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Ni</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>0.21</td>
<td>0.15</td>
<td>0.83</td>
<td>0.011</td>
<td>0.009</td>
<td>0.25</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0015</td>
</tr>
<tr>
<td>1Cr</td>
<td>0.19</td>
<td>0.15</td>
<td>0.80</td>
<td>0.010</td>
<td>0.010</td>
<td>1.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0018</td>
</tr>
<tr>
<td>3Cr</td>
<td>0.19</td>
<td>0.15</td>
<td>0.80</td>
<td>0.009</td>
<td>0.012</td>
<td>2.98</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0020</td>
</tr>
<tr>
<td>0.7Mo</td>
<td>0.20</td>
<td>0.15</td>
<td>0.83</td>
<td>0.009</td>
<td>0.009</td>
<td>0.25</td>
<td>0.74</td>
<td>–</td>
<td>–</td>
<td>0.0013</td>
</tr>
<tr>
<td>2Mo</td>
<td>0.22</td>
<td>0.15</td>
<td>0.89</td>
<td>0.007</td>
<td>0.009</td>
<td>0.26</td>
<td>1.94</td>
<td>–</td>
<td>–</td>
<td>0.0015</td>
</tr>
<tr>
<td>0.1Cu</td>
<td>0.21</td>
<td>0.15</td>
<td>0.82</td>
<td>0.010</td>
<td>0.010</td>
<td>0.25</td>
<td>–</td>
<td>0.10</td>
<td>–</td>
<td>0.0019</td>
</tr>
<tr>
<td>0.3Cu</td>
<td>0.20</td>
<td>0.15</td>
<td>0.81</td>
<td>0.009</td>
<td>0.010</td>
<td>0.25</td>
<td>–</td>
<td>0.30</td>
<td>–</td>
<td>0.0018</td>
</tr>
<tr>
<td>1Ni</td>
<td>0.20</td>
<td>0.15</td>
<td>0.80</td>
<td>0.010</td>
<td>0.011</td>
<td>0.25</td>
<td>–</td>
<td>–</td>
<td>1.00</td>
<td>0.0019</td>
</tr>
<tr>
<td>3Ni</td>
<td>0.19</td>
<td>0.15</td>
<td>0.81</td>
<td>0.009</td>
<td>0.010</td>
<td>0.25</td>
<td>–</td>
<td>–</td>
<td>2.96</td>
<td>0.0019</td>
</tr>
<tr>
<td>0.03S</td>
<td>0.23</td>
<td>0.14</td>
<td>0.82</td>
<td>0.008</td>
<td>0.031</td>
<td>0.25</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0013</td>
</tr>
<tr>
<td>0.3S</td>
<td>0.21</td>
<td>0.13</td>
<td>0.83</td>
<td>0.010</td>
<td>0.300</td>
<td>0.26</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

---

Fig. 1. Hydrogen permeation cell for cyclic corrosion tests.

Fig. 2. Cyclic corrosion test condition.
cycle consists of four processes. In this figure, symbols A, B, C, and D indicate a low temperature process at 10°C, a drying process with low relative humidity (RH), 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 h. The maintenance temperature in processes B, C and D was 60°C. The test condition was decided based on authors’ previous work.5)

For comparison, hydrogen permeation tests in an acidic solution were conducted using a Devanathan type double cell9) in Fig. 3. The solution was a buffered solution containing 0.2M CH₃COONa and 0.185M HCl at an initial pH of 3.5. The acidic solution is often used for evaluating susceptibility to hydrogen embrittlement of high strength steel bolts10) since the solution is considered to simulate local corroded areas with low pH such as pitting bottoms or crevices.11) Corrosion rate was measured in the same solution by weight loss. The temperature of hydrogen permeation and weight loss tests was 24°C. The test results were compared with those in the cyclic corrosion condition.

3. Results
3.1. Hydrogen Entry under a Cyclic Corrosion Condition

Figure 4 shows a typical result of a hydrogen permeation test for the base steel under the cyclic corrosion condition. The result shows that the hydrogen permeation coefficient sensitively varied depending upon the wetting and drying processes. Similar results were obtained in the previous work.6)

Figure 5 shows the test results of the base steel and the 3% Cr bearing steel in a short period. In the base steel, the hydrogen permeation coefficient exhibited high values at a relative humidity of 60% (process D), whereas the value decreased during the period of 40% (process B) and 90% (process C) at 60°C. In the 3% Cr steel, the hydrogen permeation coefficient exhibited high values at a relative humidity of 90% (process C), whereas the value decreased during the period of 40% (process B) and 60% (process D). In the both steels, little hydrogen permeation was monitored at 10°C (process A).

Figures 6 and 7 show the effects of Mo and Cu, respectively. It was observed that additions of Mo and Cu were effective for suppressing hydrogen entry. The shapes of the hydrogen permeation curves of the 2% Mo steel and the 0.3% Cu steel were similar to that of the base steel.

Figure 8 shows the effect of Ni. The addition of Ni drastically suppressed hydrogen entry, especially at relative humidity of 40% (process B) and 60% (process D) at 60°C.

Figure 9 shows the effect of S. The increase in S was effective for a decrease in hydrogen permeation coefficient especially at a relative humidity of 90% (process C).
Figure 10 is a summary of effects of alloying elements on hydrogen entry under the cyclic corrosion condition. The vertical axis represents the average value of the hydrogen permeation coefficients at 60°C. The average value means summation of JL during the process B, C and D divided by all duration time at 60°C. As mentioned previously, additions of Mo, Cu, Ni and S were effective for suppressing hydrogen entry. Apparently, addition of Cr slightly decreased the average hydrogen permeation coefficient as shown in Fig. 10. However, addition of Cr promoted hydrogen entry at a relative humidity of 90% as shown in Fig. 5, although addition of Mo, Cu, Ni and S suppressed hydrogen entry under all tested relative humidity. Therefore, in this study, it was judged that Cr does not have beneficial effect for suppressing hydrogen entry.

Results of weight loss tests in the cyclic corrosion condition are summarized in Fig. 11. Additions of Mo and Cu slightly decreased the corrosion rate, whereas additions of Cr, Ni and S increased the corrosion rate. The comparison between Figs. 10 and 11 implies that alloying elements accelerating atmospheric corrosion do not necessarily promote hydrogen entry.

3.2. Hydrogen Entry in an Acidic Solution

Figure 12 shows hydrogen permeation coefficients in the acidic solution with an initial pH of 3.5. The vertical axis represents the maximum hydrogen permeation coefficients during the immersion tests. It was observed that additions of Cr, Mo, Cu and Ni were effective for suppressing hydrogen entry, although an increase in S drastically promoted hydrogen entry.

Figure 13 shows results of weight loss tests in the acidic solution. Additions of Cu and S slightly decreased the corrosion rate, whereas additions of Cr, Mo and Ni slightly
increased the corrosion rate. The comparison between Figs. 12 and 13 implies hydrogen entry does not simply correlate with corrosion reaction.

4. Discussion

4.1. Mechanism of Hydrogen Entry into Low Alloy Steels under a Cyclic Corrosion Condition

In the cyclic corrosion condition, hydrogen permeation coefficients sensitively varied depending upon the wetting and drying processes as shown in Figs. 4 to 9. In the base steel, the hydrogen permeation coefficient exhibited high values at a relative humidity of 60% (process D), whereas the value decreased during the period of 40% (process B) and 90% (process C). The mechanism of the dependence of the hydrogen entry on relative humidity can be explained as follows:

In the cyclic corrosion condition, water layer forms on the steel surface. In usual cases, the pH in the water layer on the steel surface would be neutral. Therefore, cathodic reaction is supposed to be mainly oxygen reduction. However, a decrease in pH because of hydrolysis of Fe ions resulting in hydrogen evolution could be expected, following a series of reactions:[4,6]

\[ \text{[a] Anodic dissolution as } \text{Fe}^{2+} \text{ ion (Corrosion of the steel)} \]
\[ \text{[b] Oxidation of } \text{Fe}^{2+} \text{ into } \text{Fe}^{3+} \text{ ions} \]
\[ \text{[c] Hydrolysis of } \text{Fe}^{3+} \text{ accelerated by Cl}^{-} \text{ ions, followed by a pH drop} \]
\[ \text{[d] Hydrogen evolution resulting in hydrogen entry} \]

Figure 14 shows a thermodynamical prediction of the compositions of the water layer formed by salts as a function of relative humidity.[12] For simplicity, the surface salt was assumed to consist of 90% NaCl and 10% MgCl₂. The prediction shows that the compositions of the water layer are decided by relative humidity, regardless of the amount of Cl⁻ on the steel surface. The concentration of existing anion, Cl⁻, increases with a decrease in relative humidity. The condensed Cl⁻ ions in the water layer would cause hydrolysis of Fe³⁺ ions (reaction [c] above), resulting in a pH drop. In addition, it has been reported that an increase in Cl⁻ ions accelerates the oxidation from Fe²⁺ to Fe³⁺ ions (reaction [b] above).[13]

Therefore, higher values of hydrogen permeation coefficients at relative humidity of 60% than those at 90% are considered to be caused by the condensed Cl⁻ ions resulting in the pH drop. At a lower relative humidity of approximately 40%, the hydrogen permeation coefficient was slightly lower than that at 60%. This would be due to the decrease in corrosion rate at lower relative humidity caused by the reduction in dissolved oxygen in the condensed Cl⁻ ions in the water layer.[4,6]

4.2. Effects of Mo, Cu and Ni on Hydrogen Entry

Additions of Mo, Cu and Ni were effective for suppressing hydrogen entry as shown in Fig. 10 in the cyclic corrosion condition. The beneficial effects of these elements depended upon the wetting and drying periods as shown in Figs. 6 to 8. As shown in Fig. 15, the degree of the suppression of hydrogen entry caused by adding these alloying elements was estimated. The ratios of hydrogen permeation coefficients between alloyed steels and the base steel, JL/M/JL_Base, were calculated under the processes B (40%), C (90%) and D (60%), respectively. All JL/M and JL_Base are the final values at each process as shown in Fig. 15. For example, in the 3% Ni bearing steel in Fig. 15, the ratios JL/M/JL_Base at relative humidity of 40% and 60% revealed
lower values than that at 90%. The ratios reflect preferential conditions for suppressing hydrogen entry for each alloying element.

Figure 16 shows the $J_{LM}/J_{LBase}$ ratios as a function of relative humidity. In this figure, plots between relative humidity of 90% and 60% (approximately at 75%) correspond to peaks of hydrogen permeation at the border lines between 90% and 60% of relative humidity in Figs. 6 to 8. It was confirmed that the ratios of Mo, Cu and Ni bearing steels decreased with a decrease in relative humidity. This means these elements were effective for suppressing hydrogen entry especially at lower relative humidity conditions. As discussed previously, pH in the water layer formed during cyclic corrosion tests is considered to drop at lower relative humidity because of the condensed Cl$^-$ ions as shown in Fig. 14. The efficiency of Mo, Cu and Ni at lower relative humidity implies that these elements work especially in lower pH conditions. In Fig. 16, the $J_{LM}/J_{LBase}$ ratios in the acidic solution with the initial pH of 3.5 were also plotted. The low $J_{LM}/J_{LBase}$ ratios of Mo, Cu and Ni in the acidic solution support the above mentioned mechanism.

The mechanisms of the beneficial effects of Mo, Cu and Ni for suppressing hydrogen entry in the acidic conditions are estimated as follows. One possible mechanism is that these elements are enriched at the metal-electrolyte interface, and slow down the corrosion process. Actually, it was observed that Mo and Cu slightly decreased the corrosion rate as shown in Fig. 11 in the cyclic corrosion condition. However, Ni showed no beneficial effect for suppressing corrosion in this study. On the contrary, Shiraga et al. have already reported that Ni is effective for preventing hydrogen entry and suggested that the mechanism would be an enhancement of the protectiveness because of Ni enrichment at the metal-electrolyte interface. Another mechanism is a change in hydrogen overpotential. Table 2 shows free corrosion potentials of the base steel and alloyed steels. It was observed that Mo, Cu and Ni bearing steels showed higher free corrosion potentials than the base steel, reflecting a lower hydrogen overpotentials. It is generally recognized that hydrogen fugacity increases with an increase in hydrogen overpotential. The increase in hydrogen fugacity leads to an increase in hydrogen surface coverage, resulting in the promotion of hydrogen entry into the steel. Therefore, higher free corrosion potentials by adding Mo, Cu and Ni would have the beneficial effect on a decrease in the amount of adsorbed atomic hydrogen on the steel surface.

### Table 2. Free corrosion potentials in the acid solution (V, vs. Ag/AgCl).

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>2Mo</th>
<th>0.3Cu</th>
<th>3Ni</th>
<th>0.3S</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-0.576</td>
<td>-0.530</td>
<td>-0.537</td>
<td>-0.525</td>
<td>-0.691</td>
</tr>
</tbody>
</table>

4.3. Effect of S on Hydrogen Entry

S showed a completely different tendency to Mo, Cu and Ni. S slightly suppressed hydrogen entry as shown in Fig. 10 in the cyclic corrosion condition. However, the $J_{LM}/J_{LBase}$ ratio showed an opposite dependence on relative humidity to those of Mo, Cu and Ni as shown in Fig. 16. In addition, S drastically promoted hydrogen entry in the acidic solution as shown in Fig. 12. The mechanism was estimated as follows. S in steel mainly exists as a metallic sulfide such as MnS. MnS is known to be a typical soluble metallic inclusion in an aqueous solution. Therefore, MnS chemically dissolves in an acidic solution according to the following Eq. (2), resulting in the production of H$_2$S.

$$\text{MnS} + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2\text{S} \quad \text{(2)}$$

H$_2$S is a strong catalyst which promotes hydrogen entry into steels. The mechanism of the catalytic effect of H$_2$S is considered to be an increase in hydrogen overvoltage (corresponding to a decrease in the free corrosion potential). In this study, it was observed that S containing steels exhibited extremely lower free corrosion potentials than that of the base steel as shown in Table 2. This implies the production of H$_2$S according to the Eq. (2). Sato et al. have reported similar test results. They directly observed the promotion of hydrogen entry near MnS inclusions exposed to an aqueous solution using a micro hydrogen permeation cell. Under the cyclic corrosion condition, the addition of S slightly promoted hydrogen entry at lower relative humidity as shown in Fig. 16. The mechanism would be identical to that in an acidic solution. On the contrary, S had a beneficial effect on the suppression of hydrogen entry at higher
relative humidity. At higher relative humidity, pH must be sufficiently high because the condensation of $\text{Cl}^-$ ions is hard to occur. At higher pH, the solubility of MnS decreases according to the Eq. (2). In addition, the alkalinization of the electrolyte would be further accelerated because of the consumption of $\text{H}^+$ ions in the thin water layer by the dissolution of MnS according to the Eq. (2).

5. Summary

Effects of alloying elements on hydrogen entry under a cyclic corrosion condition and in an acidic solution were investigated. The following results were obtained.

1) In the base steel, the hydrogen permeation coefficient sensitively varied depending upon the wetting and drying processes in the cyclic corrosion condition. The hydrogen permeation coefficient exhibited high values at a relative humidity of 60%, whereas the value decreased during the period of 40% and 90%.

2) Additions of Mo, Cu and Ni to the base steel were effective for suppressing hydrogen entry under the cyclic corrosion condition. The efficiency of these elements was larger at lower relative humidity. These elements were also effective in the acidic solution. The mechanism is considered to be a change in hydrogen overpotentials, which leads to a decrease in hydrogen surface coverage.

3) S was also effective for suppressing hydrogen entry under the cyclic corrosion condition, although it drastically promoted hydrogen entry in the acidic solution. The detrimental effect is considered to relate the production of $\text{H}_2\text{S}$ caused by the chemical dissolution of MnS inclusions in the acidic solution. On the contrary, under the cyclic corrosion condition, it was considered that the dissolution of MnS inclusions lead to an increase in pH because of the consumption of $\text{H}^+$ ions in the thin water layer, resulting in the suppression of hydrogen entry.

Acknowledgement

The authors wish to thank Nippon Steel & Sumitomo Metal Corporation for allowing publication of this study. The assistances of co-workers in Nippon Steel & Sumitomo Metal Corporation are gratefully acknowledged.

REFERENCES