Hydrogen Embrittlement Susceptibility of High Strength Corrosion Resistant Alloy

Masayuki SAGARA¹, Yusaku TOMIO¹, Masaki UEYAMA², Tomohiko OMURA¹, Masanari KIMOTO¹, Hisashi AMAYA³

¹Nippon Steel & Sumitomo Metal Corporation, Steel Research Laboratories, Japan
² Nippon Steel & Sumitomo Metal Corporation, Amagasaki Steel Works, Japan
³ Nippon Steel & Sumitomo Metal Corporation, Wakayama Steel Works, Japan

1. Abstract

The ultra-high strength corrosion resistant alloy (CRA) OCTG with 140ksi grade meant for extreme High-Pressure High-Temperature (x-HPHT) gas well applications has been developed. The strength of the alloy is enhanced by alloying nitrogen and cold working. The developed alloy has exhibited equivalent stress corrosion cracking resistance in severe sour condition to UNS N08535 with conventional 110ksi grade, despite its higher strength (140ksi grade). Also, it is important to evaluate the resistance to Hydrogen Embrittlement (HE) to demonstrate the robustness of the material with high strength. In this study, the susceptibility to HE of the developed CRA was investigated under simulating Cu plating processes to the thread of coupling with varied conditions in laboratory. Cu plating processes are one of the countermeasures against galling trouble. Absorbed hydrogen concentration was measured under each Cu plating and pretreatment processes. Threshold hydrogen concentration which may cause HE for the alloy was measured by Slow Strain Rate Tests (SSRT) under cathodic hydrogen charging condition, to compare the actual absorbed hydrogen in the alloy through Cu plating processes. It was confirmed that the developed alloy was immune to HE by the absorbed hydrogen through the Cu plating processes, even its high strength.

Key words: CRA, Hydrogen Embrittlement, High Strength, Cold Work, Nickel

2. Introduction

As explorations and developments for extreme High-Pressure High-Temperature (x-HPHT) hydrocarbon reservoirs with corrosive environments have been increasing, the demand for higher strength materials is increasing for x-HPHT corrosive deeper well applications. Corrosion resistant alloys (CRAs) have been used for exploration and production wells in high pressure and high temperature with significant amount of hydrogen sulfide, carbon dioxide and chloride ion.¹,²,³ Oil country tubular goods (OCTG) for HPHT wells containing hydrogen sulfide requires the high strength of material (or wall thickness) and good corrosion resistance.⁴,⁵,⁶ Hence development of high strength CRAs with good corrosion resistance are critical to the development of these HPHT wells.

When tightening threads of OCTG, galling of metals at the thread should be taken into account. Cu plating on the thread is one of the countermeasures against galling trouble. Under a copper plating operation on the threads, a cathodic polarization treatment generates hydrogen atoms and gases. Electrodegreasing, electropolishing and nickel strike processes also can be hydrogen sources. The presence of hydrogen raises the hydrogen embrittlement (HE) susceptibility of high strength grades, even in the case of CRAs.
An ultra-high strength CRA OCTG with 140ksi grade meant for x-HPHT well applications has been developed. The strength of the material is enhanced by alloying nitrogen and cold working. The strengthening methods of solid solution strengthening and work hardening were adopted for the developed material of 140 ksi grade.

In this study, the susceptibility to HE of the developed CRA was investigated. Firstly, hydrogen charging tests were carried out under laboratory Cu plating and pretreatment processes to quantify absorbed hydrogen concentration. Then, the evaluation method using SSRT under cathodic charging condition was employed to determine the HE susceptibilities of some variation of alloys. Threshold hydrogen concentration determined by SSRT under cathodic hydrogen charging condition was compared with the actual absorbed hydrogen in the alloy through simulating Cu plating processes.

3. Experimental

3.1 Materials
In order to investigate the susceptibility of hydrogen embrittlement, specimens from seamless pipes, various grade of austenitic CRA, duplex stainless steel, martensitic stainless steel and low alloy steel OCTGs were used in this study. For austenitic alloy and duplex stainless steel, the strengths were adjusted by cold drawing after solution heat treatment. In case of martensitic stainless steel and low alloy steel, their strengths were adjusted by quenching and tempering heat treatments. The chemical compositions and the mechanical properties are listed in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>N</th>
<th>W</th>
<th>YS(ksi)</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2535-140</td>
<td>0.017</td>
<td>0.30</td>
<td>0.60</td>
<td>32.6</td>
<td>24.6</td>
<td>3.1</td>
<td>0.20</td>
<td>-</td>
<td>162.0</td>
<td>Austenitic alloy</td>
</tr>
<tr>
<td>25CRW</td>
<td>0.014</td>
<td>0.30</td>
<td>0.50</td>
<td>6.7</td>
<td>24.9</td>
<td>3.1</td>
<td>0.30</td>
<td>2.0</td>
<td>125.2</td>
<td>Duplex stainless steel</td>
</tr>
<tr>
<td>13Cr</td>
<td>0.19</td>
<td>0.22</td>
<td>0.49</td>
<td>0.1</td>
<td>12.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>80.1</td>
<td>Martensitic stainless steel</td>
</tr>
<tr>
<td>P110</td>
<td>0.27</td>
<td>0.35</td>
<td>1.3</td>
<td>-</td>
<td>0.5</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>121.0</td>
<td>Low alloy steel</td>
</tr>
</tbody>
</table>

3.2 Measurement of absorbed hydrogen concentration \( (C_0) \)
Hydrogen charging tests using coupon specimens were carried out under laboratory Cu plating and pretreatment processes to quantify absorbed hydrogen concentration \( (C_0) \). Effects of electrodegreasing, electropickling, Ni strike and Cu plating processes on hydrogen absorption were investigated. The test conditions simulated immersion type plating and brush plating processes. Absorbed hydrogen concentration was measured by Thermal Desorption Analysis (TDA) to detect diffusible hydrogen concentration which affects hydrogen embrittlement. Detailed test conditions are summarized in Tables 2 and 3. Specimen sizes are shown in Fig.1.

<table>
<thead>
<tr>
<th>Plating</th>
<th>Degreasing</th>
<th>Electropickling</th>
<th>Ni strike</th>
<th>Cu plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immersion</td>
<td>NaOH=25g/L</td>
<td>NiCl₂·6H₂O=250g/L HCl=80mL/L</td>
<td>NiCl₂·6H₂O=250g/L HCl=80mL/L</td>
<td>CuSO₄·5H₂O=250g/L H₂SO₄=60mL/L</td>
</tr>
<tr>
<td>Brush</td>
<td>NaOH=25g/L</td>
<td>H₂SO₄=50mL/L</td>
<td>NiCl₂·6H₂O=250g/L HCl=80mL/L</td>
<td>CuSO₄·5H₂O=250g/L H₂SO₄=60mL/L</td>
</tr>
</tbody>
</table>
3.3 Measurement of threshold (Critical) hydrogen concentration ($C_{th}$)

Slow Strain Rate Tests (SSRT) were carried out under cathodic hydrogen charging. Tensile stress (TS), fracture elongation (El) and reduction of area (RA) under several cathodic charging conditions were compared to those in air to evaluate the resistance to hydrogen embrittlement. Relative TS, relative El and relative RA, which are the ratio of TS, fracture El and RA between in air and under cathodic charging, were evaluated.

Hydrogen charging tests using coupon specimens were carried out to correlate SSRT properties and absorbed hydrogen concentration under the same cathodic charging conditions. Absorbed hydrogen concentration was measured by Thermal Desorption Analysis (TDA) to detect diffusible hydrogen concentration which affects hydrogen embrittlement. Relative TS,
relative El and relative RA were correlated to diffusible absorbed hydrogen concentration. Threshold hydrogen concentration ($C_{th}$) to hydrogen embrittlement was defined as the critical hydrogen concentration where relative TS, relative El and relative RA are more than 90%. Detailed test conditions are summarized in previous papers.[7,8,9]

4. Results and discussion

4.1 Measurement of absorbed hydrogen concentration ($C_0$)

For each material, hydrogen charging tests were carried out under the condition of simulating Cu plating and pretreatment processes to quantify absorbed hydrogen concentration ($C_0$). The results of TDA profiles for 2535-140 pretreated and Cu-plated are shown in Fig.2. Figure 2(a) and (b) show TDA profiles of SM2535-140 under immersion plating and under blush plating, respectively. Hydrogen peaks at around 120°C in each figure were increased by pretreatment processes. TDA profiles of 25CRW pretreated and Cu-plated are shown in Fig.3. Hydrogen peaks between 100°C and 150°C were increased by pretreatment processes. On the other hand, hydrogen peaks higher than 200°C is considered to be bulk hydrogen in austenitic phase as well as SM2535-140 in Fig.2. TDA profiles of 13Cr are shown in Fig.4. Hydrogen peaks at around 200°C were increased by pretreatment processes. TDA profiles of P110 are shown in Fig.5. Hydrogen peaks at around 200°C were increased by pretreatment processes. Hydrogen peaks at 450°C were considered to be non-diffusible hydrogen.

Diffusible absorbed hydrogen concentrations are summarized in Figs.6 to 9. Diffusible hydrogen was calculated by the summation of the TDA profiles in Figs.2 and 4 from room temperature to 600°C in the case of 2535-140, 25CRW and 13Cr. On the other hand, diffusible hydrogen was calculated in Figs.5 and 6 from room temperature to 300°C in the case of P110. The difference between immersion plating and brush plating was small in the case of 2535-140 and 25CRW, while the absorbed hydrogen concentration through brush plating was slightly higher than that through immersion plating in the case of P110 and 13Cr due to the higher cathodic current density in each pretreatment process.
Fig. 2(a) TDA profiles of SM2535-140 under immersion plating.

Fig. 2(b) TDA profiles of SM2535-140 under brush plating.
Fig. 3 (a) TDA profiles of SM25CRW-125 under immersion plating.

Fig. 3 (b) TDA profiles of SM25CRW-125 under brush plating.
Fig. 4(a) TDA profiles of 13Cr under immersion plating.

Fig. 4(b) TDA profiles of 13Cr under brush plating.
Fig. 5(a) **TDA profiles of P110 under immersion plating.**

Fig. 5(b) **TDA profiles of P110 under brush plating.**
**Fig. 6** Absorbed hydrogen concentration into 2535-140.

**Fig. 7** Absorbed hydrogen concentration into 25CRW.
Fig. 8 Absorbed hydrogen concentration into 13Cr.

Fig. 9 Absorbed hydrogen concentration into P110.
4.2 Assessment of the Hydrogen embrittlement susceptibility under Cu plating processes, evaluated with SSRT in cathodic charging condition

Hydrogen charging tests were carried out to obtain concentrations of hydrogen absorbing in each material. Previous papers show the estimated result of surface hydrogen concentration for each alloy under various charging conditions for 48 hours.\cite{7,8} Alloys are 2535-140 (Austenitic alloy of 140ksi grade) and 25CRW (super duplex stainless steels). In this calculation, hydrogen diffusion coefficient D of each material is $1.0 \times 10^{-15}$ (m$^2$/s) for 2535-140 and $3.0 \times 10^{-13}$ (m$^2$/s) for 25CRW. Surface hydrogen concentration was obtained from the measured values of hydrogen concentration by TDA and the calculated hydrogen distribution profiles in each material. The results indicate the hydrogen concentration can be affected by charging conditions, i.e., the surface hydrogen concentration increases with cathodic current density.

Susceptibility to hydrogen embrittlement under cathodic charge (CHE) was evaluated by SSRT. As well as the results of surface hydrogen concentration, relationship between relative fracture elongation of 2535-140 (Austenitic alloy of 140ksi grade) and 25CRW (super duplex stainless steels), and surface hydrogen concentration in previous paper.\cite{7,8} Each material had their own “surface hydrogen concentration (H) vs - relative fracture El.” relationships.

In this study, critical surface hydrogen concentration ($C_{th}$) was defined as the highest surface hydrogen concentration at which relative fracture El. was more than 90%, in order to discuss the CHE susceptibility quantitatively. $C_{th}$ is understood as the maximum surface hydrogen concentration beyond which material could be susceptible to HE. Figure 10 shows the critical hydrogen concentration of each material as a function of Ni$_{eq}$, a parameter indicating the stability of austenitic phase in the formula below,

$$\text{Ni}_{eq} \text{ (mass%)} = \%\text{Ni} + 0.65\%\text{Cr} + 0.98\%\text{Mo} + 1.05\%\text{Mn} + 0.35\%\text{Si} + 12.6\%\text{C}.$$ 

It was observed that there was an appropriate Ni$_{eq}$ range where the $C_{th}$ was higher and hence lower susceptibility to HE. 2535-140 as well as A286 (aging) were located in the appropriate range. Materials with lower Ni$_{eq}$ showed lower $C_{th}$ while materials with excessive Ni$_{eq}$ also showed lower $C_{th}$.

Maximum concentrations of hydrogen of 2535-140 and 25CRW absorbing through Cu plating and pretreatment processes shown in fig.s 7 and 8 were shown in fig.11. Critical hydrogen concentration ($C_{th}$) of each materials was higher than that of maximum absorbed concentration (Max. $C_0$ in fig.10), which indicated that these materials would not suffer from hydrogen embrittlement through Cu plating process.

The critical surface hydrogen concentration ($C_{th}$), derived from SSRT under various cathodic charging conditions, is a quantitative index for evaluating the resistance to hydrogen embrittlement. $C_{th}$ showed a strong dependence on Ni$_{eq}$ as shown in fig.10. The material 2535-140 was located in the appropriate Ni$_{eq}$ range to obtain the maximum $C_{th}$.\cite{7,8} The maximum $C_{th}$ of these materials is attributable to the stability of austenitic phase. Materials with lower Ni$_{eq}$ showed lower $C_{th}$. It is attributable to martensitic transformation during deformation (type 304L) since the bcc crystal structure generally shows high susceptibility to hydrogen embrittlement. On the other hand, materials with excessive Ni$_{eq}$ showed also lower $C_{th}$. As these materials have high stability of austenitic structure, the mechanism is not martensitic transformation. Miyata observed a change in dislocation morphologies by hydrogen in Ni based alloys by a transmission electron microscope, and reported that hydrogen enhances a cross-slip and screw components of dislocations.\cite{11} The change in the dislocation motion by hydrogen could correlate with the hydrogen embrittlement of Ni based
alloys. The other possible mechanism is nickel hydride formation. However, detailed mechanisms of hydrogen embrittlement have not been established yet in Ni based alloys.

Fig. 10 Effect of nickel equivalent on critical hydrogen concentration.

In this study, thinner coupon specimens than actual pipes were used as shown in Fig. 1, to detect little amount of absorbed hydrogen. However, in the case of an actual pipe, hydrogen is absorbed only near the surface because of the short time of pretreatment process as illustrated in Fig. 11. This means absorbed hydrogen concentration into an actual pipe will be extremely smaller than into a thin specimen.

Fig. 11 Hydrogen distribution in a specimen (a), and in an actual pipe (b)

Threshold stress as a function of absorbed diffusible hydrogen concentration of low alloy and martensitic stainless steels is shown in Fig. 12. It was confirmed that absorbed hydrogen levels through pre-plating processes in Figs. 8 and 9 are sufficiently lower than the hydrogen levels that cause hydrogen embrittlement. If the applied stresses for the materials are around...
110ksi (758MPa) and 80ksi (551MPa), the threshold stresses are assumed to be around 2ppm and 6ppm respectively, which is adequately higher than hydrogen absorption level by pre-plating.

![Graph showing Threshold stress as a function of absorbed hydrogen concentration of low alloy and martensitic stainless steels](image)

**Fig. 12** Threshold stress as a function of absorbed hydrogen concentration of low alloy and martensitic stainless steels

### 5. Summary

The susceptibility to hydrogen embrittlement of the high strength CRA was investigated under Cu plating processes with varied conditions in laboratory. Absorbed hydrogen concentration was measured under each Cu plating and pretreatment processes. Threshold hydrogen concentration which may cause hydrogen embrittlement for the alloy was measured by Slow Strain Rate Tests (SSRT) under cathodic hydrogen charging condition, to compare the actual absorbed hydrogen in the alloy through Cu plating processes.

(a) The absorbed hydrogen concentration through brush plating was slightly higher than that though immersion plating in the case of low alloy steel and martensitic stainless steel due to the higher current density. The absorbed hydrogen concentration through brush plating, however, was equivalent level of that of immersion plating in the case of austenitic alloy and duplex stainless steel.

(b) The developed austenitic alloy with 140ksi grade did not show any hydrogen embrittlement susceptibility even at the condition of high surface hydrogen concentration. It was confirmed that the developed alloy was immune to hydrogen embrittlement by the absorbed hydrogen through the Cu plating processes, even its high strength.

(c) Other referenced materials such as duplex stainless steels, martensitic stainless steel and low alloy were also investigated considering the comparison critical hydrogen concentration with absorbed hydrogen through Cu plating processes simulated in laboratory. It assumed that hydrogen absorption by pre-plating is adequately lower than the threshold level of hydrogen concentration.
References