Corrosion and Stress Corrosion Behavior of 13 Cr Martensitic Stainless Steels in CO2-H2-S-Cl Environment

Hayao Kurahashi, Yuji Sone, Kayoko Wada, Yoichi Nakai

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Corrosion and stress corrosion behavior of two types of 13 Cr martensitic stainless steels, C-Cr type (0.2%-13% Cr) and Cr-Ni type (0.02% C-13% Cr-3% Ni), were investigated in CO2 and CO2+H2S environments. The 13 Cr steels were resistant to CO2 corrosion at low partial pressure of CO2. High partial pressure of CO2 (30 atm), however, increases the corrosion rate of 13 Cr steels at above 150°C. When a small amount of H2S is mixed into CO2 environment, crevice corrosion resistance is greatly decreased. Susceptibility to cracking was measured by the slow strain rate technique in CO2+H2S environment and changes in the corrosion potential were measured during the test. The C-Cr type steel reveals an active state in all these environments and its resistance to cracking is inferior to the low alloy steel used. The Cr-Ni type steel reveals a passive state, but is translated into an active state by straining and resistant to cracking.

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1 Introduction
The uniform corrosion rates of low alloy steels are significantly increased in sweet environments where solution pH is lowered by CO₂ and non-protective corrosion product films form. On the other hand, sulfide stress cracking (SSC) is a more serious problem than uniform corrosion in sour environments because low alloy steels absorb a large amount of hydrogen due to the action of H₂S and become brittle. The most effective countermeasure against SSC has been considered to be the lowering of the hardness of steels. NACE recommends that the hardness of tubular goods for use in sour environments is lower than a Rockwell C hardness of 22.

A number of new developed gas and oil wells contain CO₂ and/or H₂S. Therefore, 13 Cr martensitic stainless steels and duplex stainless steels are often used for tubular goods instead of the low alloy steels used until recently. In recent years, even the use of Ni-based alloys has been considered. Of all such corrosion resistant alloys, 13 Cr steels have been used most widely because they are the least expensive and their strength can be modified easily by adjusting the carbon content and/or tempering temperature.

A minimum level of 13% chromium is required if steel is to exhibit passivity in a wide range of corrosive environments. The corrosion and SSC behavior of 13 Cr steel are more significantly affected by the content of CO₂ and H₂S in environments than those of other stainless steels containing more than 13% Cr and those of Ni-based alloys. The authors previously reported the

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following experimental results on the stress corrosion cracking of 13 Cr steels in environments containing CO₃ and/or H₂S.

(1) 13 Cr steels tempered at above 600°C are immune to stress corrosion cracking in CO₂ environments.

(2) In CO₂ environments containing various amounts of H₂S, the SSC susceptibility of 13 Cr steels increases with partial pressure of H₂S (P₃H₂). Some 13 Cr steels are subject to SSC even at 0.07 atm P₃H₂.

(3) When the yield strength of 13 Cr steels exceeds 60 kgf/mm², failure quickly occurs in the NACE condition. This critical strength (60 kgf/mm²) is lower than that of low alloy steels by 10 kgf/mm².

(4) The higher susceptibility of 13 Cr steels is caused by the fact that such steels absorb hydrogen more easily than do low alloy steels.

In the present work, the effect of temperature and P₃H₂ on the corrosion rate of 13 Cr steels was investigated in CO₂ and/or H₂S environments. SSC susceptibility was also examined from the view point of corrosion.

2 Experiments

2.1 Materials

Chemical compositions of the materials tested are shown in Table 1. There are many kinds of 13 Cr martensitic stainless steels, which can be divided into two main types:

(1) High carbon 13 Cr type (C-Cr type), which does not contain alloy elements other than Cr (such as SUS 420 J1 and J2).

(2) Low C-Ni-13 Cr type (Cr-Ni type), which is strengthened by Ni addition (such as CA6NM).

Steel A is SUS 420 J1 (C-Cr type), while steel B belongs to the Cr-Ni type. Steel C is a low alloy steel KO90SS produced by Kawasaki Steel for oil tubular goods. Steel C was used for comparison with the 13 Cr steels. The specimens of steel A and C were cut from mill-finished seamless pipes produced by the nag mill.

Steel B was a laboratory heat. It was melted in a vacuum induction furnace and hot rolled into 13-mm thick sheets. Tempering temperature and mechanical properties are shown in Table 2. Specimens of steel A and B were tempered at both 600 and 710°C. The corrosion tests, however, were performed with specimens tempered at 710°C.

2.2 Corrosion Test

Corrosion tests in a CO₂ environment without H₂S were conducted in a 5-1 Hastelloy-Alloy-C-lined autoclave in order to examine the effects of CO₂ pressure (P₃CO₂) and temperature (25-250°C in these tests). Specimens (3 × 25 W × 50 L mm) were polished with 360# wet silicon carbide paper and degreased with acetone.

The autoclave was purged, pressurized to 1 or 30 atm with CO₂ gas as required, and heated to a predetermined temperature. 3.5% NaCl solution was used as the corrosive agent. Under some of the conditions, crevice corrosion tests were conducted with the type of specimen shown in Fig. 1. The test duration was 100 h for corrosion tests and 72 h for the crevice corrosion tests.

Corrosion and crevice corrosion tests in CO₂ and/or H₂S environments were performed in NaCl solutions saturated with gases containing various amounts of CO₂ and H₂S at a pressure of 1 atm balanced with N₂ gas for 30 days. The gas was bubbled in the test cell for the duration of the test period. The gas composition, NaCl concentration, testing temperature, calculated solubility of CO₂ and H₂S, and pH value are tabulated in Table 3. The condition I test was conducted in an aerated NaCl solution without CO₂ or H₂S at 80°C in order to examine the effect of oxygen on corrosion. Condition VII is the NACE condition which is widely used to observe the

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Table 1 Chemical composition of steel used

<table>
<thead>
<tr>
<th>Steel</th>
<th>C (wt%)</th>
<th>Si (wt%)</th>
<th>Mn (wt%)</th>
<th>P (wt%)</th>
<th>S (wt%)</th>
<th>Cr (wt%)</th>
<th>Ni (wt%)</th>
<th>Mo (wt%)</th>
<th>Nb (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.20</td>
<td>0.75</td>
<td>0.76</td>
<td>0.010</td>
<td>0.004</td>
<td>13.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>0.02</td>
<td>0.47</td>
<td>0.30</td>
<td>0.020</td>
<td>0.005</td>
<td>12.8</td>
<td>2.95</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C</td>
<td>0.23</td>
<td>0.29</td>
<td>0.51</td>
<td>0.012</td>
<td>0.004</td>
<td>1.06</td>
<td>—</td>
<td>0.60</td>
<td>0.034</td>
</tr>
</tbody>
</table>

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Table 2 Tempering temperature and mechanical properties of steels used

<table>
<thead>
<tr>
<th>Steel</th>
<th>Heat No.</th>
<th>Tempering Temp (°C)</th>
<th>Yield Strength (kgf/mm²)</th>
<th>Tensile Strength (kgf/mm²)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A1</td>
<td>710</td>
<td>63.6</td>
<td>78.4</td>
<td>24.1</td>
</tr>
<tr>
<td>A</td>
<td>A2</td>
<td>600</td>
<td>77.1</td>
<td>96.2</td>
<td>18.8</td>
</tr>
<tr>
<td>B</td>
<td>B1</td>
<td>710</td>
<td>81.1</td>
<td>94.2</td>
<td>17.9</td>
</tr>
<tr>
<td>B</td>
<td>B2</td>
<td>600</td>
<td>76.4</td>
<td>84.7</td>
<td>21.7</td>
</tr>
<tr>
<td>C</td>
<td>C</td>
<td>650</td>
<td>70.4</td>
<td>76.4</td>
<td>25.0</td>
</tr>
</tbody>
</table>

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Fig. 1 Specimen for crevice corrosion test

KAWASAKI STEEL TECHNICAL REPORT
Table 3  Test conditions for immersion test in CO₂ + H₂S environment

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>NaCl (wt%)</th>
<th>Gas composition (atm)</th>
<th>Solubility of gas (calculated)</th>
<th>pH</th>
<th>Testing Period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P\textsubscript{CO₂}</td>
<td>P\textsubscript{H₂S}</td>
<td>P\textsubscript{O₂}</td>
<td>CO₂ (ppm)</td>
</tr>
<tr>
<td>I</td>
<td>80</td>
<td>3.8</td>
<td>0</td>
<td>0</td>
<td>1.0 air</td>
</tr>
<tr>
<td>II</td>
<td>25</td>
<td>3.5</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>III</td>
<td>25</td>
<td>3.5</td>
<td>0.7</td>
<td>0.007</td>
<td>Bal.</td>
</tr>
<tr>
<td>IV</td>
<td>25</td>
<td>3.5</td>
<td>0.7</td>
<td>0.07</td>
<td>Bal.</td>
</tr>
<tr>
<td>V</td>
<td>25</td>
<td>3.5</td>
<td>0.7</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>VI</td>
<td>25</td>
<td>3.5</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>VII</td>
<td>25</td>
<td>5.0</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
</tr>
</tbody>
</table>

* NACE condition (0.5% Acetic acid addition, initial pH 3.0)  
* Measured value at the end of test was about 2,900 ppm  
* pH was measured at the end of test

SSC susceptibility of steels and the HIC (hydrogen-induced cracking) susceptibility of line pipe steels. Condition VI was used only for the SSC test mentioned below. The specimen is the same as for the autoclave test mentioned above.

2.3 SSC Test in Environments Containing CO₂ and/or H₂S

SSC behavior of 13 Cr steels was examined with SSRT (slow strain rate technique) in environments containing CO₂ and/or H₂S. While a specimen as illustrated in Fig. 2 was being strained, the change in corrosion potential (E\textsubscript{corr}) was measured with a saturated calomel electrode (SCE). After a specimen and a capillary were set in a test cell, a solution saturated with a given gas was circulated through the cell for 24 h prior to the SSRT test. SSRT tests were conducted at a strain rate of 8.3 × 10⁻³/s under conditions IV, V, VI and VII as shown in Table 3.

![Fig. 2 Specimen for SSRT test](image)

3 Results

3.1 Corrosion Behavior in CO₂ Environments

Figures 3 and 4 show the effect of temperature on corrosion rate at P\textsubscript{CO₂} of 1 and 30 atm, respectively. At 1 atm P\textsubscript{CO₂}, the corrosion rate of steel C (low alloy steel) was 0.6 mm/year at 80°C and 0.4 mm/year at 250°C. On the other hand, the corrosion rate of C-Cr type 13 Cr steel (steel A) increased with temperature and reached a maximum (0.1 mm/year) at 200°C. The corrosion rate of Cr-Ni type 13 Cr steel (steel B) also increased with temperature up to 250°C, but was only 0.1 mm/year even at 250°C. These results show that both types of 13 Cr steels can be used at temperatures of up to 250°C at P\textsubscript{CO₂} of 1 atm.

At 30 atm P\textsubscript{CO₂}, steel A was extremely resistant to corrosion up to 80°C but revealed a maximum corrosion rate of 1.4 mm/year at 150°C and corroded at a rate of...
atm $P_{\text{CO}_2}$ are shown in Table 4. Neither steel A nor B suffered from crevice corrosion.

Consequently, when 13 Cr steels are used in CO$_2$ environments not containing H$_2$S, only general corrosion needs to be taken into account at high temperatures and high $P_{\text{CO}_2}$.

3.2 Corrosion Behavior in CO$_2$ + H$_2$S Environments

Figure 5 shows the effect of $P_{\text{H}_2\text{S}}$ on corrosion rate in CO$_2$ + H$_2$S environments at 25°C. This figure also contains data obtained in an environment free of CO$_2$ or H$_2$S (open air conditions) at 80°C. Both Cr-Cr and Cr-Ni 13 Cr steels exhibited similar changes in corrosion rate with $P_{\text{H}_2\text{S}}$. When the CO$_2$ environment was contaminated with 0.007 to 0.3 atm $P_{\text{H}_2\text{S}}$, their corrosion rates increased slightly, but were only 0.02 mm/year even at 0.3 atm $P_{\text{H}_2\text{S}}$. This figure was about one tenth of that of low alloy steel (steel C). The corrosion morphologies of 13 Cr steels are shown in Photo 1. Many small pits were detected in C-Cr steel even at 0.07 atm $P_{\text{H}_2\text{S}}$ and similar pits were found for Cr-Ni steel at 0.3 atm $P_{\text{H}_2\text{S}}$.

The corrosion resistance of 13 Cr steels was drastically reduced under the NACE condition. C-Cr steel had a corrosion rate of 1.3 mm/year. This value was larger than that of steel C (0.9 mm/year). Neither type of 13 Cr steel exhibited pitting corrosion, but both showed

1.0 mm/year at temperatures from 200 to 250°C. Steel C corroded rapidly at a rate of 7.5 mm/year at 80°C. Its corrosion rate, however, decreased drastically at above 150°C, where it became the same as that of steel A. On the other hand, steel B was free from corrosion up to 200°C, but corroded more rapidly than either steel A or C at 250°C. These results show that in higher $P_{\text{CO}_2}$ environments, the advantage of high corrosion resistance in 13 Cr steels disappears at above a critical temperature correlated with chemical composition. At $P_{\text{CO}_2}$ of 30 atm, this critical temperature is 150°C for C-Cr steel and 250°C for Cr-Ni steel.

Under these conditions, although steel A, B and C all exhibited general corrosion, pitting corrosion was not detected in spite of the use of a 3.5% NaCl solution.

The results of crevice corrosion tests at 150°C and 30

<table>
<thead>
<tr>
<th>steel</th>
<th>Corrosion rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (C-Cr)</td>
<td>1.36</td>
</tr>
<tr>
<td>B (Cr-Ni)</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Table 4: Effect of crevice on corrosion rate for 13 Cr steels in an immersion test under a pressure of 30 atm CO$_2$ gas at 150°C for 72 h (mm/year)
Table 5 Test results of crevice corrosion

<table>
<thead>
<tr>
<th>Environmental test condition</th>
<th>C—Cr</th>
<th>Cr—Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>NaCl (%)</td>
<td>CO₂</td>
</tr>
<tr>
<td>80</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>3.5</td>
<td>1.0</td>
</tr>
<tr>
<td>25</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>25</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>25</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>25</td>
<td>5.0</td>
<td>0</td>
</tr>
</tbody>
</table>

○: no crevice corrosion
△: slight crevice corrosion
×: heavy crevice corrosion
—: general corrosion

Photo 1 Overall appearance of flat specimens after 720 h exposure in CO₂-H₂S-Cl⁻ environments at 25°C

In open air conditions without CO₂ or H₂S, both types of 13 Cr steel suffered from pitting corrosion, with corrosion rates higher than those in all CO₂ + H₂S environments except the NACE condition. This indicates that the corrosion resistance of 13 Cr steels is strongly affected by the presence of oxygen.

On the other hand, the corrosion resistance of low alloy steel (steel C) was significantly inferior to the CO₂ environment without H₂S, with a corrosion rate of 0.5 mm/year. However, when a small amount of H₂S was added to the CO₂ environment, the corrosion resistance of low alloy steel increased with P₄H₂S. The corrosion rate was 0.18 mm/year at 0.007 atm P₄H₂S and 0.11 mm/year at 0.3 atm P₄H₂S. Apparently, sulfide film formed, preventing further attack, as shown by H. Thomason. However, the corrosion resistance of the low alloy steel in the NACE condition was inferior to that in the CO₂ environment without H₂S.

The results of crevice corrosion tests of 13 Cr steels are shown in Table 5. The overall appearance of steel A specimens after the immersion test is shown in Photo 2. Steel A suffered from crevice corrosion even at 0.07 atm P₄H₂S. This shows that H₂S is a significant factor in crevice corrosion. Steel B exhibited slight crevice corrosion at 0.3 atm P₄H₂S. Under the NACE condition, 13 Cr steels suffered no crevice corrosion, but showed general corrosion.

These results show that in a CO₂ environment containing a small amount of H₂S, crevice corrosion is the most serious problem for 13 Cr steels.

3.3 SSC Behavior in CO₂ + H₂S Environments

SSRT tests were conducted under condition IV, V, VI and VII as shown Table 3. The pH values of all conditions except VII were about 4.8, and were not affected by P₄H₂S. Typical curves of change in E₀ during the SSRT test and stress-strain curves are shown in Figs. 6 and 7. E₀ initially did not change during the tests in Fig. 6, but on the other hand, E₀ began to drop in Fig. 7 immediately after the specimen was strained, and fell continuously.
Fig. 6 Stress-strain curve and change of corrosion potential during SSRT test for low alloy steel in 3.5% NaCl solution saturated with 100% H$_2$S gas.

Fig. 7 Stress-strain curve and change of corrosion potential during SSRT test for Cr-Ni steel in 3.5% NaCl saturated with 100% H$_2$S gas.

The patterns of change in $E_{corr}$ were divided into the two types illustrated by Figs. 6 and 7. C-Cr 13 Cr steel and low alloy steel showed the former pattern under all conditions used in this work, with an $E_{corr}$ of $-670 \sim -710$ mV (vs. SCE). Cr-Ni 13 Cr steel also exhibited the former pattern under the NACE condition ($E_{corr} = -630$ mV), but showed the latter under all other conditions tested. In those cases except NACE condition, $E_{corr}$ dropped from $-470 \sim -590$ mV to $-650$ mV. $E_{corr}$ before straining was $-470 \sim 500$ mV for Cr-Ni 13 Cr steel tempered at 710°C (B1) and $-550 \sim -590$ mV for that tempered at 600°C (B2).

The effect of H$_2$S solubility on the degree of embrittlement is shown in Fig. 8. The degree of embrittlement was evaluated in terms of the ratio of elongation under each test condition ($E_{emb}$) to elongation in air ($E_{emb}$), and a low ratio indicates a relatively greater degree of embrittlement. Although H$_2$S solubility under condition VI is the same as that under condition VII (NACE condition), 13 Cr steels were significantly brittle under the NACE condition, with degrees of embrittlement larger than those of the low alloy steel (steel C). Under all conditions, steel A2 exhibited the same degree of embrittlement as that obtained under the NACE condition. Steel A1, B1, and B2 retained their ductilities when H$_2$S solubility was small. However, steel A1 was more susceptible to SSC than low alloy steel under all conditions used. On the other hand, although the degree of embrittlement of Cr-Ni steel tempered at 600°C was the same as that of the low alloy steel (steel C), that of Cr-Ni steel tempered at 710°C (B1) was smaller than that of steel C. Steel B1 did not show any embrittlement at 0.07 atm P$_{H_2S}$. Calculated solubility is 160 ppm under this condition.

From the results of SSRT tests in CO$_2$ + H$_2$S environments except the NACE condition, the SSC susceptibility of steels used in this work was ranked as follows.

$$A2 \ll A1 < C \ll B2 < B1$$

In these conditions, steel C, B2, and B1 failed under local elongation, while steel A1 and A2 failed in the brittle mode without local elongation.

4 Discussion

Corrosion of low alloy steels caused by water with a high CO$_2$ content poses a serious problem and has frequently been studied. D.W. Shannon reported that
corrosion becomes smaller as temperature increases. On the other hand, K. Masamura, et al. showed that the corrosion rate reaches its maximum at a temperature lower than 100°C and decreases with temperature at higher temperatures. The results obtained in this work are similar to the latter. The maximum corrosion rate occurred at 80°C. As \( P_{\text{CO}_2} \) increases, the maximum rate also rises. D.W. Shannon reported that while an unprotective FeCO\(_3\) film formed at lower temperatures, Fe\(_2\)O\(_4\) film formed at higher temperatures. This Fe\(_2\)O\(_4\) film protects carbon steel from corrosion.

The temperature dependence of corrosion behavior of C-Cr 13 Cr steel shows a similar tendency to that of low alloys steel. The critical temperature at which the corrosion rate reaches its maximum is 200°C at 1 atm \( P_{\text{CO}_2} \) and 150°C at 30 atm \( P_{\text{CO}_2} \). C-Cr steel, however, has considerable resistance to CO\(_2\) corrosion at temperatures below 100°C. This shows that the passive film of C-Cr steel is stable in this temperature range. However, the passive film becomes unstable at above the critical temperature, and C-Cr steel does not show the special quality of a stainless steel. That is, C-Cr steel suffers from CO\(_2\) corrosion in the same manner as low alloy steel in this temperature range. Cr-Ni steel also exhibits similar corrosion behavior at 250°C and 30 atm \( P_{\text{CO}_2} \) but under all of other conditions it is resistant to CO\(_2\) corrosion. 13 Cr steels suffer little of the crevice or pitting corrosion which are serious problems in stainless steels. Furthermore, as the authors showed in early work, 13 Cr steels tempered at above 600°C were immune to stress corrosion cracking (SCC) in CO\(_2\) environments. From these results, it may be said that when 13 Cr steels are used at below a critical temperature correlated with \( P_{\text{CO}_2} \) and their chemical composition, they will be immune to pitting corrosion, crevice corrosion, and SCC, and their general corrosion resistances will be superior to that of low alloy steels.

In a CO\(_2\) environment contaminated with a small amount of H\(_2\)S, general corrosion of 13 Cr steels increases slightly. On the other hand, crevice corrosion accelerates drastically. S. Tsujikawa, et al. have studied the effect of \( P_{\text{H}_2\text{S}} \) on crevice corrosion of SUS 444 ferritic stainless steel in a 3.5% NaCl solution at 80°C. Crevice corrosion resistance is evaluated as the potential denoted \( E_R \) at which the growth of crevice corrosion stops. \( E_R \) is measured by active to noble polarization of a specimen with crevicing. A higher \( E_R \) indicates that crevice corrosion resistance is higher. These researchers reported that the effect of H\(_2\)S was not found at \( P_{\text{H}_2\text{S}} \) below 0.003 atm but was found at 0.01 atm \( P_{\text{H}_2\text{S}} \) and saturated at \( P_{\text{H}_2\text{S}} \) above 0.03 atm. The \( E_R \) of SUS 444 is \(-200 \sim -300 \text{ mV (vs. SCE)}\) in an H\(_2\)S-free environment and drops to \(-530 \text{ mV}\) in an environment containing 0.03 atm \( P_{\text{H}_2\text{S}} \). Since the corrosion resistance of 13 Cr steels is inferior to that of SUS 444, it is reasonable to expect that the crevice corrosion of 13 Cr steels will be strongly accelerated by small amounts of H\(_2\)S. Although the present investigation was conducted at a lower temperature (25°C) than that used in S. Tsujikawa's work and crevice corrosion is more difficult to occur, C-Cr 13 Cr steel was found to suffer from crevice corrosion at 0.07 atm \( P_{\text{H}_2\text{S}} \).

Therefore, when 13 Cr steels are used in CO\(_2\) environments with a small amount of H\(_2\)S, care must be given to crevice corrosion as well as to SSC. Special attention should be given to sites where crevice corrosion is thought to occur, that is, at coupling portions and beneath sludge deposits in oil tubular goods.

Generally, the passive film of stainless steel does not exist at below a critical pH. This critical pH is denoted as \( \text{pH}_{a} \). The accelerating effect of H\(_2\)S on crevice corrosion indicates that H\(_2\)S raises the \( \text{pH}_{a} \) of stainless steel. M. Miyuki, et al. reported that the \( \text{pH}_{a} \) of a duplex stainless steel was under 2.0 in a 5% NaCl + 0.5% acetic acid solution at 200°C, but that the \( \text{pH}_{a} \) rose to 2.8 after gas containing 0.1 atm \( P_{\text{H}_2\text{S}} \) was bubbled into the solution. The mechanism of crevice corrosion is considered to be as follows: In a crevice, first the dissolution of a small amount of iron occurs, and the pH is then lowered by hydros of iron. When the \( \text{pH}_{a} \) in the crevice reaches the \( \text{pH}_{a} \) active dissolution of stainless steel in the crevice begins immediately. If the environment contains a small amount of H\(_2\)S, the \( \text{pH}_{a} \) in the crevice may rapidly reach \( \text{pH}_{a} \) and crevice corrosion is thus accelerated. It has not to date been made clear, however, why the \( \text{pH}_{a} \) of stainless steel is increased by H\(_2\)S.

The SSC susceptibilities of 13 Cr steels in CO\(_2\) + H\(_2\)S environments were evaluated by SSRT tests. In an environment where \( E_{\text{corr}} \) of 13 Cr steels remains unchanged during the SSRT test, both C-Cr and Cr-Ni steels are more susceptible to SSC than is low alloy steel. \( E_{\text{corr}} \) of C-Cr steels does not change during SSRT test under the conditions used in this work. \( E_{\text{corr}} \) of low alloy steel also does not change under these conditions. On the other hand, \( E_{\text{corr}} \) of Cr-Ni steel decreases with strain under all conditions except the NACE condition, and when \( E_{\text{corr}} \) reaches the value obtained under the NACE condition, specimens ruptured. The degree of embrittlement of Cr-Ni steel under such conditions is the same as or smaller than low alloy steel. Consequently, in environments where 13 Cr steels become active, the degrees of embrittlement are larger than that of low alloy steel in the same manner as under hydrogen charging. On the other hand, in environments where 13 Cr steels do not become active, they reach the rupture point following the destruction of their passive film. In such cases, susceptibility to SSC is suppressed.

It has been made clear that oxygen accelerates pitting and crevice corrosion in 13 Cr steels. D. Combes, et al. report that 13 Cr oil tubular goods have been used
without problems in actual well environments, in spite of the presence of CO₂ and small quantities of H₂S. They state that this is attributable to the absence of oxygen in typical drilling conditions. Their findings thus support the view that oxygen is a major cause of corrosion in 13 Cr steels.

5 Conclusions

The following conclusions have been drawn from this study of the corrosion and SSC behavior of 13 Cr steels in CO₂ + H₂S environments.

1. Both C-Cr and Cr-Ni 13 Cr steel exhibit good corrosion resistance at 1 atm P_CO₂ without H₂S at temperatures below 250°C and suffer little pitting or crevice corrosion. They cannot, however, be used practically at 30 atm P_CO₂ or above a critical temperature which is 150°C for C-Cr steel and 250°C for Cr-Ni.

2. 13 Cr steels exhibit only slight general corrosion but suffer significantly from crevice corrosion in CO₂ environments which contain a small amount of H₂S.

3. The SSC susceptibility of 13 Cr steels is related to the stability of their passive films in CO₂ environments contaminated with small amounts of H₂S. When the passive film is not stable, SSC susceptibility is higher than that of low alloy steel. On the other hand, when it is stable, the SSC resistance is the same as or superior to that of low alloy steel.

References

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