1. Introduction

13 mass% chromium steels are known to be resistant to CO₂ corrosion and are manufactured at a relatively lower cost as corrosion resistant steels. AISI 420 13 mass% chromium steels, of which carbon content is 0.2 mass%, are mainly used for OCTG (Oil Country Tubular Goods) in the wet CO₂ environments (sweet environments). However, these steels are hardly used in the wet H₂S environments (sour environments) because they are highly susceptible to sulfide stress cracking (SSC).1,2) These steels are generally used in the range of L80 grade of API Specification 5CT.3) However, the critical H₂S partial pressure, at which these steels are available in sour environments, is as low as less than 5×10⁻⁴ MPa.4)

Recently, many types of the modified 13 mass% chromium steels have been developed to improve SSC resistance.5–7) It is extremely important for these steels to keep the passivation in order to improve SSC resistance. For example, the addition of molybdenum and chromium is effective to keep the passivation. However, when these elements are excessively added, δ-ferrite is formed. Therefore, the effect of δ-ferrite on SSC in the low carbon 13 mass% chromium steels was investigated. SSC occurred in the case that δ-ferrite is formed to some extent because the corrosion potential was lowered to that of the active state. The occurrence of SSC did not depend on the difference of shape of δ-ferrite. The reason for the difference in corrosion potential with and without δ-ferrite is attributed to the existence of a chromium depleted zone due to the precipitation of chromium carbides or nitrides near the δ-ferrite.

KEY WORDS: 13 mass% chromium steel; sulfide stress cracking (SSC); sour environment; microstructure; δ-ferrite; martensite.

2. Experimental Procedure

2.1. Materials

Table 1 shows three kinds of 0.02 mass% carbon 13 mass% chromium steels. Steel A was melted in a 10 ton vacuum induction furnace and steels B and C were melted in a 50 kg vacuum induction furnace in a laboratory. The ingot reheated at 1250°C for 60 min was hot-rolled to 15 mm thick plates. Then, the plates were heat-treated. Table 2 shows the heat treatment conditions and mechani-
Steel A was double tempered at 680°C for 40 min and 600°C for 60 min. Steels B-1 and B-2 were heat-treated so as to obtain the same level of yield strength and steels C-1 and C-2 were also heat-treated to the same level of yield strength to evaluate SSC resistance.

Steels D to L indicated in Table 3 were also melted in a 50 kg vacuum induction furnace in a laboratory. The ingots were hot-rolled to 15 mm thick plates. Then, the plates were tempered at 650°C for 60 min. These specimens were used to measure the depassivation pH (pHd).

2.2. Microstructure Observation

The microstructure was observed by optical microscopy. The steels were etched in a picric acid saturated with ethanol and 5 mass% hydrochloric acid. The cross section in the rolling direction was observed.

2.3. EPMA Measurement

EPMA (Electron Probe Micro Analysis) measurement was performed to investigate alloying element concentration in the phase. An electron beam of 1 μm in diameter was used and a line analysis was carried out in the length of 100 μm.

2.4. TEM Observation

The extraction replica was observed with a TEM (Transmission Electron Microscope) and analyzed with an EDX (Energy Dispersive X-ray) spectrometer to identify the precipitate using fractured SSC test specimens.

2.5. SSC Test Solution

SSC test solution was 1 mol/l acetic buffer solution containing 5 mass% sodium chloride (5 mass% NaCl). The solution pH was adjusted from 3.3 to 4.5 mixing 5 mass% NaCl+1N acetic acid (CH₃COOH) with 5 mass% NaCl+1 mol/l acetic sodium (CH₃COONa). H₂S partial pressure was 0.01 MPa (0.1 atm) and the balance gas was carbon dioxide (CO₂). The test temperature was kept at 24±3°C.

2.6. Constant Load SSC Test

A constant load SSC test following NACE TM0177-90 method A was done to evaluate SSC resistance of low carbon 13 mass% chromium steels. Figure 1 shows the dimensions of the test specimens. The test specimens were machined from the middle thickness of tested steels in the rolling direction. They were polished with No. 320 and No. 600 emery paper in the longitudinal direction and degreased in acetone, then subjected to SSC test. The applied stress was 60% or 90% of the actual yield strength.

After the specimen was set in the test cell, the test solution, which had been deaerated for more than 24 hr, was poured into it and deaerated with N₂ gas for more than an hour to expel dissolved oxygen before introducing the test gas. Then a load was applied after the test gas was bubbled in the test cell for at least 30 min until the test solution was saturated. The test was started when the load was applied. The corrosion potential was measured simultaneously in the constant load SSC test specimen. Figure 2 shows the test apparatus for an electrochemical measurement. A saturated calomel electrode (SCE) was used as a reference electrode. The test specimens after failure were pickled by immersing the specimens in a boiling 18 mass% sodium hydroxide (NaOH)+0.3 mass% potassium permanganate (KMnO₄) solution for 5 min and subsequently in a boiling 10 mass% ammonium citrate ((NH₄)₂H₂C₆H₅O₇) solution for 5 min.

![Fig. 1. Dimensions of constant load test specimen.](image1)

![Fig. 2. Schematic drawing of constant load tester.](image2)
2.7. Polarization Measurement

An anodic polarization measurement of low carbon 13 mass% chromium steels before loading was done in sour environments. The test specimens were degreased in acetone, polished with No. 320 and No. 600 emery paper and coated with silicon resin leaving 3 cm² for measurement. The potentiodynamic measurements were started at a scan rate of 10 mV/min in the anodic direction from the corrosion potential after the test solution was saturated with H₂S gas.

2.8. Depassivation pH (pH₄) Measurement

The effect of alloying element (chromium, nickel, copper and molybdenum) on depassivation pH (pH₄) was investigated using low carbon 11 to 15 mass% chromium steels shown in Table 3. The specimens were degreased in acetone, polished with No. 320 emery paper and coated with silicon resin leaving 1 cm² for measurement. Just before the test specimen was immersed in the sufficiently deaerated acetic buffer solution containing 5 mass% NaCl saturated with H₂S partial pressure of 0.01 MPa and a different pH at 25°C, it was pickled in 50 mass% sulfuric acid at 60°C to remove the air formed film until hydrogen gas bubbled from the specimen surface. This means that the initial condition of the specimen was active. Then, the specimen was immersed in the test solution as soon as possible after washing it in water. The corrosion potential of the specimen was monitored during 96 hr. pH₄ was determined as pH at which the corrosion potential rose drastically.

3. Results

3.1. SSC Test of Steels A, B and C

Table 4 shows the SSC test results of steel A in the pH of 3.5 and H₂S partial pressure of 0.01 MPa. Applied stress was 90% of actual yield strength. No SSC occurred for four test specimens and SSC occurred in a few hours for three test specimens. The four specimens that did not fail were shiny and no pitting occurred after SSC test. On the other hand, the three failed specimens were black and underwent general corrosion.

The SSC test results of steel B in the pH of 3.5 to 4.5 and H₂S partial pressure of 0.01 MPa are indicated in Table 5. The applied stress was 90% of the actual yield strength. In test specimens of steel B-1, no SSC occurred in the pH of 3.5 and test specimens were shiny and no pitting occurred after SSC test. SSC occurred in the pH of 3.5 in a few hours in two test specimens of steel B-2, which were black and showed general corrosion. In the pH of 4.0, SSC occurred and no SSC occurred in the pH of 4.5 in steel B-2.

Table 6 shows the SSC test results of steel C in the pH of 3.3 and H₂S partial pressure of 0.01 MPa. The applied stress was 60% of the actual yield strength. In steel C-1, SSC occurred in a few hours and SSC occurred in 60 hr in steel C-2. All test specimens of steel C after SSC test were black and underwent general corrosion.

3.2. Microstructure of Steels A, B and C

The optical micrographs of cross section of test specimens of steel A after SSC test are shown in Fig. 3. No δ-ferrite was formed in test specimens in which no SSC occurred (Fig. 3(a)). On the other hand, δ-ferrite was formed in three test specimens in which SSC occurred (Fig. 3(b)). These results suggest that SSC occurs when δ-ferrite exists.

Figure 4 shows the microstructure of as-rolled and that after heat treatment of steel B. Some δ-ferrite was observed parallel to the rolling direction in the as-rolled specimen. In the microstructure of steel B-1, no δ-ferrite is observed. This is caused by the homogenizing heat treatment for six hours in the austenite region. However, δ-ferrite is formed along the prior-austenite grain in steel B-2. This is because heat treatment at 1350°C was performed. The fraction of δ-ferrite phase in steel B-2 was 10.0%.

The microstructure of as-rolled and that after heat treatment of steel C is shown in Fig. 5. Some δ-ferrite appears parallel to the rolling direction in the as-rolled specimen. Some δ-ferrite was observed in steel C-1. The fraction of δ-ferrite phase in steel C-1 is 8.6%. However, no δ-ferrite is formed in the microstructure of steel C-2 because this steel was heat-treated in the austenite region for three hours.

3.3. EPMA Measurement

EPMA was performed to measure chromium and molyb-
denum concentration in the martensite phase and the δ-ferrite phase. Figure 6 indicates EPMA results of steel B-2. The molybdenum concentration in the δ-ferrite was twice as high as that in the martensite and the chromium concentration in the δ-ferrite was 1.2 times as high as that in the martensite.

3.4. TEM Observation

The extraction replica prepared for the fractured SSC specimen of steel B-2 was observed with a TEM and analyzed with an EDX spectrometer to identify the precipitates. Figure 7(a) shows the transmission electron micrographs and Fig. 7(b) shows the EDX analysis of precipitates of extraction replica indicated in arrows. Many chromium carbides or nitrides precipitate along the δ-ferrite grain.
boundary. However, chromium carbides or nitrides did not precipitate in the δ-ferrite phase.

3.5. Polarization Measurement of Steels B and C

Figure 8 shows anodic polarization curves of steel B-1 without δ-ferrite and steel B-2 with δ-ferrite. The corrosion potential of steel B-1 was −500 mV (SCE). The critical current density of the active–passive region was 3 μA/cm². The passive current density was 1.2 μA/cm² and it showed a low value. The corrosion potential of steel B-2 was −600 mV (SCE) and the critical current density of the active–passive region was 500 μA/cm². The passive current density was 20 μA/cm². The critical current density of the active–passive region of steel B-2 was 200 times higher than that of steel B-1. The passive current density of steel B-2 was 17 times higher than that of steel B-1.

3.6. Electrochemical Measurement during SSC Test of Steels B and C

The effect of δ-ferrite on SSC resistance was investigated using the electrochemical method. The SSC test of steel B-1 without δ-ferrite and steel B-2 with δ-ferrite formed along the prior-austenite grains was performed as indicated in Fig. 9. The H₂S partial pressure was 0.01 MPa and pH was 3.5. The corrosion potential of steel B-1 before H₂S gas was introduced was −450 mV (SCE), which existed near the redox potential of hydrogen (E₉(ox/red)). This potential shifted to −520 mV (SCE) after H₂S gas was intro-

Fig. 6. EPMA analysis showing chromium and molybdenum concentration of martensite and δ-ferrite.
(a) Chromium and molybdenum concentration profile.
(b) Scanning electron micrograph showing scanning location.

Fig. 7. (a) Extraction replica and (b) EDX analysis of precipitates along the ferrite boundary.

Fig. 8. Polarization curves of 0.02mass%C–13mass%Cr steel with and without δ-ferrite.

Fig. 9. Corrosion potential versus test duration of constant load test followed by NACE TM0177-90A.
duced. This potential corresponded to the corrosion potential in the anodic polarization curve indicated in Fig. 8. No SSC occurred and the corrosion potential was kept at −520 mV (SCE) after the loading during 720 hr test. The test specimen after SSC test showed metallic color.

The corrosion potential of steel B-2 before H\textsubscript{2}S gas was introduced existed at near −520 mV (SCE). After H\textsubscript{2}S gas was introduced, the corrosion potential was lowered to the corrosion potential of the active state, SSC occurred in a few hours after the loading. The test specimen showed black color and underwent general corrosion.

Figure 10 shows the optical micrograph of SSC test specimen of steel B-2 after pickling. δ-ferrite and martensite phases were observed. Figure 11 shows the scanning electron micrographs of steel B-2 after SSC test. Intergranular fracture (Fig. 11(a)) and quasi-cleavage fracture (Fig. 11(b)) were observed in the fractured specimen.

The SSC test of steel C-1 with elongated δ-ferrite parallel to the rolling direction and steel C-2 without δ-ferrite were carried out at H\textsubscript{2}S partial pressure of 0.01 MPa and at pH of 3.3 (Fig. 12). The corrosion potential of steel C-2 was kept at −240 mV (SCE) near the redox potential of sulfur (E\textsubscript{S (ox/red)}). After H\textsubscript{2}S gas was introduced, the corrosion potential shifted to −500 mV, which was in the passive region, then, the corrosion potential did not change and no SSC occurred until 50 hr after the loading. However, the corrosion potential of steel C-2 was lowered to the corrosion potential of the active state. In this case SSC occurred in 60 hr. On the other hand, the corrosion potential of steel C-1 existed at near −500 mV (SCE) before H\textsubscript{2}S gas was introduced. After introducing H\textsubscript{2}S gas, the corrosion potential shifted to −600 mV (SCE) immediately which is the active state and SSC occurred in a few hours.

3.7. pH\textsubscript{d} Measurement

The effect of chromium, nickel, copper and molybdenum on depassivation pH (pH\textsubscript{d}) was investigated for low carbon 11 to 15 mass% chromium steels as indicated in Table 3 (Steel D to L). pH\textsubscript{d} decreased with increasing molybdenum, chromium and nickel content. On the other hand, copper does not affect pH\textsubscript{d} in sour environments. Using these relations, pH\textsubscript{d} was replotted as functions of chromium, nickel and molybdenum using the first regression equation. Figure 13 shows the effect of alloying element on pH\textsubscript{d} in H\textsubscript{2}S partial pressure of 0.01 MPa and 25°C. Molybdenum was the most effective element, then nickel and chromium followed.

4. Discussion

4.1. Effect of δ-Ferrite on SSC in Low Carbon 13 mass% Chromium Steel

Low carbon 13 mass% chromium steels with and without δ-ferrite had different SSC resistance even if they were of the same chemical composition and the same yield strength. It is suggested that this is attributed to the difference of corrosion potential of the specimen with and without δ-ferrite during H\textsubscript{2}S gas bubbling before the loading. That is, the corrosion potential of the steel with δ-ferrite
The corrosion potential shifted from the passive state to the active state after introducing H$_2$S gas in the case that δ-ferrite was formed parallel to the rolling direction or δ-ferrite was formed to some extent. The reason for the difference of shape of δ-ferrite was also higher than that without δ-ferrite. Therefore, the corrosion potential, which is determined by the intersection between an internal anodic polarization curve and an internal cathodic polarization curve, existed in the passive region when no δ-ferrite was formed in these steels and in the active region when some δ-ferrite was formed.

The corrosion potential shifted from the passive state to the active state after introducing H$_2$S gas in the case that δ-ferrite was formed to some extent. The corrosion potential did not depend on the difference of shape of δ-ferrite even if δ-ferrite was formed parallel to the rolling direction or along the prior-austenite grains. The reason for the difference in corrosion potential with and without δ-ferrite is as follows.

First, the possibility that the steel with the δ-ferrite is not able to keep the passivation by the decrease in chromium and molybdenum contents in the martensite is supposed. Because the δ-ferrite fraction is 10% in steel B-2 and the chromium and molybdenum contents are 12.50 mass% and 2.50 mass%, respectively, in steel B, the chromium and molybdenum contents are 12.45 mass% and 2.27 mass%, respectively, in the martensite of steel B-2 using chromium and molybdenum concentration profile as shown in Fig. 6. Since nickel is not contained in the δ-ferrite phase, assuming that the contribution of nickel to pH$_d$ was negligibly small, pH$_d$ of steel B-2 is 0.17 lower than that of steel B-1 by the difference of chromium and molybdenum contents of steels B-1 and B-2 in the martensite by extrapolating the relation between pH$_d$ and Cr$+1.6Ni+3.9Mo$ obtained in Fig. 13. However, SSC occurred even at the pH of 4.0 in steel B-2. It is also difficult to explain that the reason for the difference in the corrosion potential with and without the δ-ferrite is attributed to the decrease in chromium and molybdenum contents in the martensite.

Second, it is assumed that the formation of micro-cell between δ-ferrite and martensite due to the difference in chemical composition in each phase accelerates corrosion. From Fig. 6, chromium and molybdenum content in the δ-ferrite was higher than that in the martensite. That is, the δ-ferrite became a noble site and the martensite became a less noble site. However, it is difficult to understand that the reason for the difference in corrosion potential with and without the δ-ferrite is caused by the formation of micro-cell due to the existence of the δ-ferrite and the martensite because the fraction of the martensite, which is on a less noble side, is 90% and it is much larger than that of the δ-ferrite.

Third, it is presumed that the existence of a chromium depleted zone due to the precipitation of chromium carbides or nitrogen near the δ-ferrite grain boundary accelerates corrosion. The δ-ferrite and the martensite were observed in the fractured specimen after pickling as indicated in Fig. 10. This is attributed to the existence of a chromium depleted zone near the δ-ferrite grain boundary. From Fig. 7, many chromium carbides or nitrides precipitated along the ferrite grain boundary were observed. It is reported that a chromium depleted zone by the precipitation of the chromium carbides and nitrides near the δ-ferrite grain boundary exists.

Therefore, it is supposed that the existence of a chromium depleted zone due to the precipitation of the chromium carbides or nitrides near the δ-ferrite accelerates corrosion and the corrosion potential is lowered to the active state.

5. Conclusions

The effect of microstructure, δ-ferrite, on SSC in low carbon 13 mass% chromium steels was investigated in mild sour environments. The main conclusions are as follows.

(1) SSC occurs in the case that δ-ferrite is formed to some extent. The initiation of SSC does not depend on the difference of shape of δ-ferrite.

(2) The reason for the difference in anodic current density at the active state with and without δ-ferrite is caused by the existence of a chromium depleted zone due to the precipitation of the chromium carbides or nitrides near the δ-ferrite.

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