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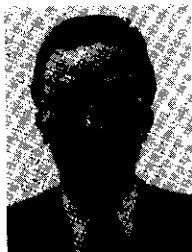
Hayao Kurahashi, Yuji Sone, Kayoko Wada, Yoichi Nakai

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The body can be viewed from the next page.

Corrosion and Stress Corrosion Behavior of 13 Cr Martensitic Stainless Steels in CO_2-H_2S-Cl^- Environment[*]

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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 CO_2 and non-protective corrosion product films form[1]. 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 H_2S and become brittle[2]. 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[3].

A number of new developed gas and oil wells contain CO_2 and/or H_2S[4]. 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[4]. 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 CO_2 and H_2S in environments than those of other stainless steels containing more than 13% Cr and those of Ni-based alloys. The authors previously reported the

following experimental results on the stress corrosion cracking of 13 Cr steels in environments containing CO_2 and/or H_2S[5].

(1) 13 Cr steels tempered at above 600°C are immune to stress corrosion cracking in CO_2 environments.

(2) In CO_2 environments containing various amounts of H_2S, the SSC susceptibility of 13 Cr steels increases with partial pressure of H_2S (P_{H_2S}). Some 13 Cr steels are subject to SSC even at 0.07 atm P_{H_2S}.

(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 P_{H_2S} on the corrosion rate of 13 Cr steels was investigated in CO_2 and/or H_2S 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 strengthen 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 prag mill. Steel B was a laboratory heat. It was melted in a vacuum induction furnace and hot rolled into 13-mm thick sheet. Tempering temperature and mechanical properties are shown in **Table 2**. Specimens of steel A

Table 2 Tempering temperature and mechanical properties of steels used

Steel	Heat No.	Tempering temp. (°C)	Yield strength (kgf/mm²)	Tensile strength (kgf/mm²)	Elongation (%)
A	A1	710	63.6	78.4	24.1
A	A2	600	77.1	96.2	18.8
B	B1	710	81.1	94.2	17.9
B	B2	600	76.4	84.7	21.7
C		650	70.4	76.4	25.0

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 CO_2 environment without H_2S were conducted in a 5-l Hastelloy-Alloy-C-lined autoclave in order to examine the effects of CO_2 pressure (P_{CO_2}) and temperature (25–250°C in these tests). Specimens ($3t \times 25W \times 50L$ mm) were polished with 360# wet silicon carbide paper and degreased with acetone. The autoclave was purged, pressurized to 1 or 30 atm with CO_2 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 CO_2 and/or H_2S environments were performed in NaCl solutions saturated with gases containing various amount of CO_2 and H_2S at a pressure of 1 atm balanced with N_2 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 CO_2 and H_2S, and pH value are tabulated in **Table 3**. The condition I test was conducted in an aerated NaCl solution without CO_2 or H_2S 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

Table 1 Chemical composition of steels used (wt%)

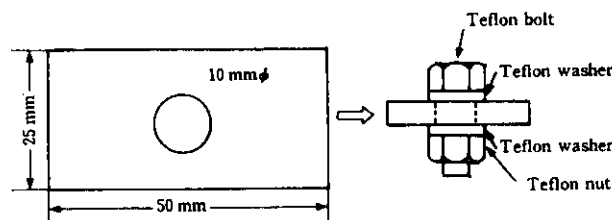|	C	Si	Mn	P	S	Cr	Ni	Mo	Nb
A	0.20	0.75	0.76	0.010	0.004	13.2	—	—	—
B	0.02	0.47	0.50	0.020	0.005	12.8	2.95	—	—
C	0.23	0.29	0.51	0.012	0.004	1.06	—	0.60	0.034

Fig. 1 Specimen for crevice corrosion test

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Table 3 Test conditions for immersion test in $CO_2 + H_2S$ environment

| | Temp. (°C) | NaCl (wt%) | Gas composition (atm) | | | Solubility of gas (calculated) | | pH[*3] | Testing Period |
			P_{CO_2}	P_{H_2S}	P_{N_2}	CO_2 (ppm)	H_2S (ppm)		
I	80	3.5	0	0	1.0 air	0.4	0	6.0	
II	25	3.5	1.0	0	0	550	0	5.0	
III	25	3.5	0.7	0.007	Bal.	880	21	5.2	
IV	25	3.5	0.7	0.07	Bal.	880	210	4.9	720 h (30 day)
V	25	3.5	0.7	0.3	0	880	904	4.7	
VI	25	3.5	0	1.0	0	0	3 000[*2]	5.0	
VII[*1]	25	5.0	0	1.0	0	0	3 000[*2]	3.9	

[*1] NACE condition (0.5% Acetic acid addition, initial pH 3.0)
[*2] Measured value at the end of test was about 2 900 ppm
[*3] 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 CO_2 and/or H_2S

SSC behavior of 13 Cr steels was examined with SSRT (slow strain rate technique) in environments containing CO_2 and/or H_2S. While a specimen as illustrated in **Fig. 2** was being strained, the change in corrosion potential (E_{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^{-5}/s under conditions IV, V, VI and VII as shown in Table 3.
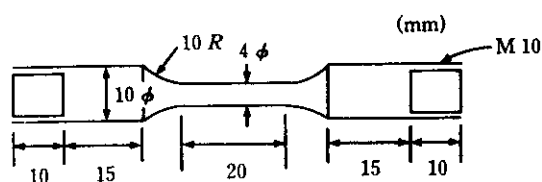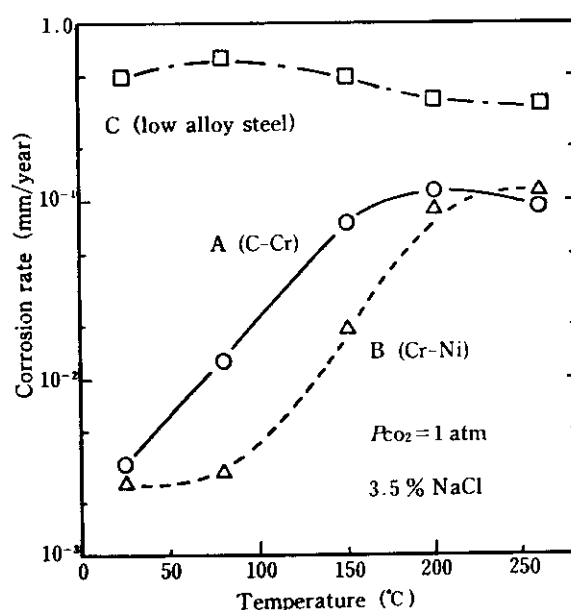

Fig. 2 Specimen for SSRT test

3 Results

3.1 Corrosion Behavior in CO_2 Environments

Figures 3 and 4 show the effect of temperature on corrosion rate at P_{CO_2} of 1 and 30 atm, respectively. At 1 atm P_{CO_2}, the corrosion rate of steel C (low alloy steel) was

Fig. 3 Effect of temperature on corrosion rate for low alloy steel and 13 Cr steels in sweet environment ($P_{CO_2} = 1$ atm)

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_{CO_2} of 1 atm.

At 30 atm P_{CO_2}, 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
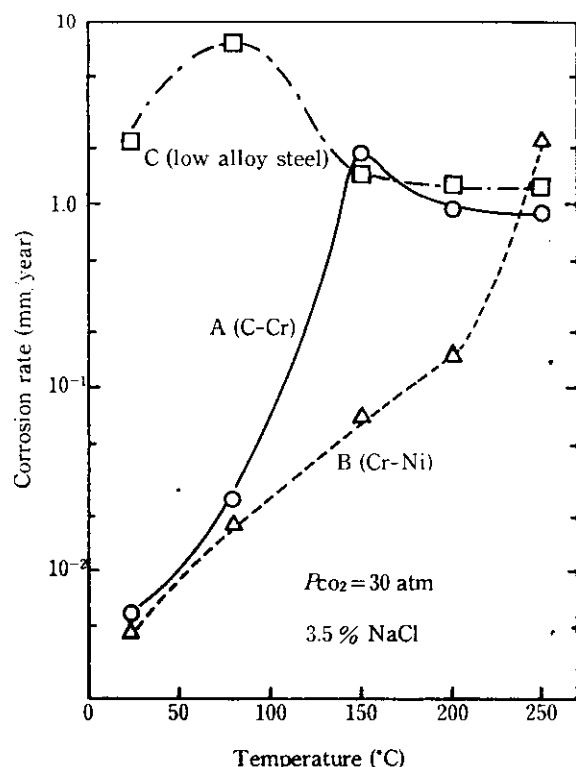
Fig. 4 Effect of temperature on corrosion rate for low alloy steel and 13 Cr steels in sweet environment (P_{CO_2} = 30 atm)

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_{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_{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 4 Effect of crevice on corrosion rate for 13 Cr steels in a immersion test under a pressure of 30 atm CO₂ gas at 150°C for 72 h

(mm/year)

A (C—Cr)		B (Cr—Ni)	
Creviced	Crevice free	Creviced	Crevice free
1.36	1.47	0.04	0.05

atm P_{CO_2} are shown in **Table 4**. Neither steel A nor B suffered from crevice corrosion.

Consequently, when 13 Cr steels are used in CO₂ environments not containing H₂S, only general corrosion needs to be taken into account at high temperatures and high P_{CO_2}.

3.2 Corrosion Behavior in CO₂ + H₂S Environments

Figure 5 shows the effect of P_{H_2S} on corrosion rate in CO₂ + H₂S environments at 25°C. This figure also contains data obtained in an environment free of CO₂ or H₂S (open air conditions) at 80°C. Both C-Cr and Cr-Ni 13 Cr steels exhibited similar changes in corrosion rate with P_{H_2S}. When the CO₂ environment was contaminated with 0.007 to 0.3 atm P_{H_2S}, their corrosion rates increased slightly, but were only 0.02 mm/year even at 0.3 atm P_{H_2S}. 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_{H_2S}, and similar pits were found for Cr-Ni steel at 0.3 atm P_{H_2S}.

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
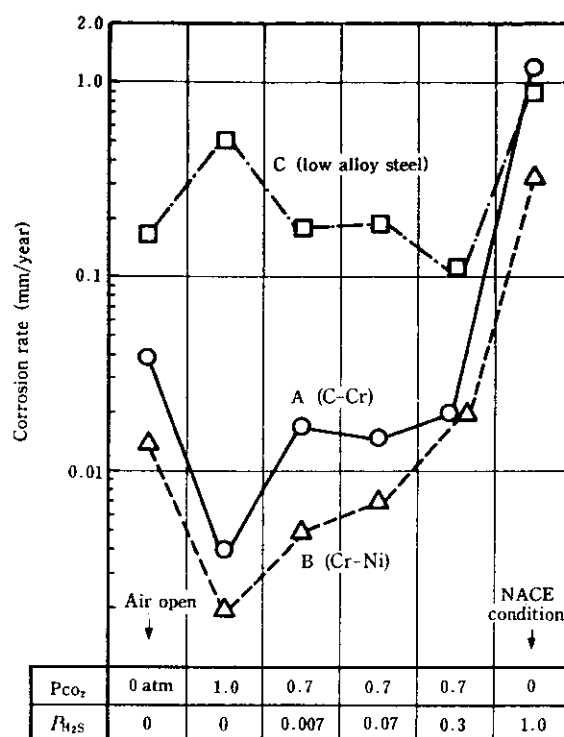

Fig. 5 Effect of H₂S partial pressure on corrosion rate of low alloy steel and 13 Cr steels in CO₂ + H₂S environment at 25°C except air open condition (80°C)
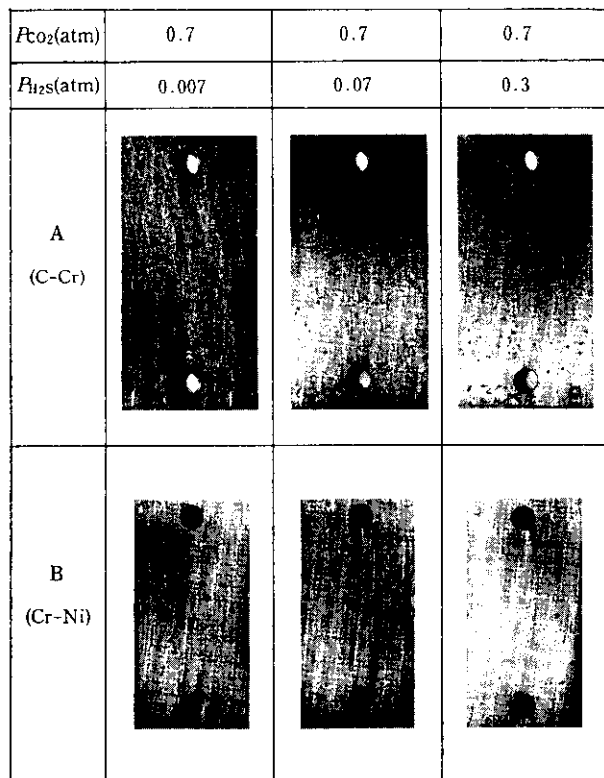
	Air open					NACE condition
P_{CO_2}	0 atm	1.0	0.7	0.7	0.7	0
P_{H_2S}	0	0	0.007	0.07	0.3	1.0

P_{CO_2}(atm)	0.7	0.7	0.7
P_{H_2S}(atm)	0.007	0.07	0.3
A (C-Cr)			
B (Cr-Ni)			

Photo 1　Overall appearance of flat specimens after 720 h exposure in CO_2-H_2S-Cl^- environments at 25°C

general corrosion.

In open air conditions without CO_2 or H_2S, both types of 13 Cr steel suffered from pitting corrosion, with corrosion rates higher than those in all CO_2 + H_2S 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 in the CO_2 environment without H_2S, with a corrosion rate of 0.5 mm/year . However, when a small amount of H_2S was added to the CO_2 environment, the corrosion resistance of low alloy steel increased with P_{H_2S}. The corrosion rate was 0.18 mm/year at 0.007 atm P_{H_2S} and 0.11 mm/year at 0.3 atm P_{H_2S}. Apparently, sulfide film formed, preventing further attack, as shown by H. Thomason.[6] However, the corrosion resistance of the low alloy steel in the NACE condition was inferior to that in the CO_2 environment without H_2S.

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 P_{H_2S}. This shows that H_2S is a significant factor in crevice corrosion. Steel B exhibited slight crevice corrosion

Table 5　Test results of crevice corrosion

Temperature (°C)	NaCl (%)	P_{CO_2}	P_{H_2S}	P_{N_2}	C—Cr		Cr—Ni	
80	3.5	0	0	1.0 air	×	×	△	△
80	3.5	1.0	0	0	○	○	○	○
25	3.5	0.7	0.007	Bal.	○	○	○	○
25	3.5	0.7	0.07	Bal.	×	×	○	○
25	3.5	0.7	0.3	0	×	×	△	△
25	5.0	0	1.0	0	—	—	—	—

(Header: Environmental test condition — Gas composition (atm); Test result)

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

P_{CO_2}(atm)	0.7	0.7	0.7
P_{H_2S}(atm)	0.007	0.07	0.3
A (C-Cr)			
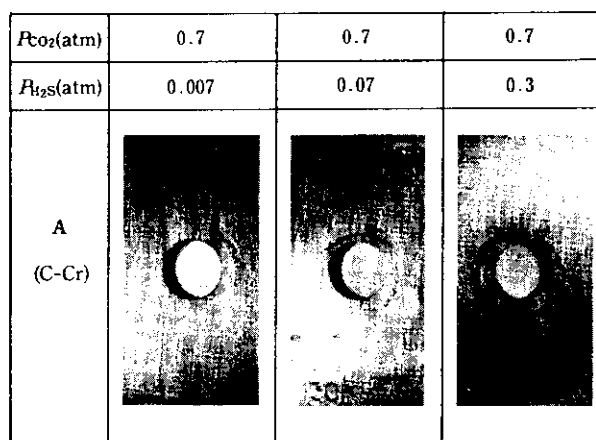
Photo 2　Overall appearance of creviced specimens after 720 h exposure in CO_2-H_2S-Cl^- environments at 25°C

at 0.3 atm P_{H_2S}. Under the NACE condition, 13 Cr steels suffered no crevice corrosion, but showed general corrosion.

These results shows that in a CO_2 environment containing a small amount of H_2S, crevice corrosion is the most serious problem for 13 Cr steels.

3.3 SSC Behavior in CO_2 + H_2S 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 P_{H_2S}. Typical curves of change in E_{corr} during the SSRT test and stress-strain curves are shown in **Figs. 6** and **7**. E_{corr} did not change during the tests in Fig. 6, but on the other hand, E_{corr} began to drop in Fig. 7 immediately after the specimen was strained, and fell continuously
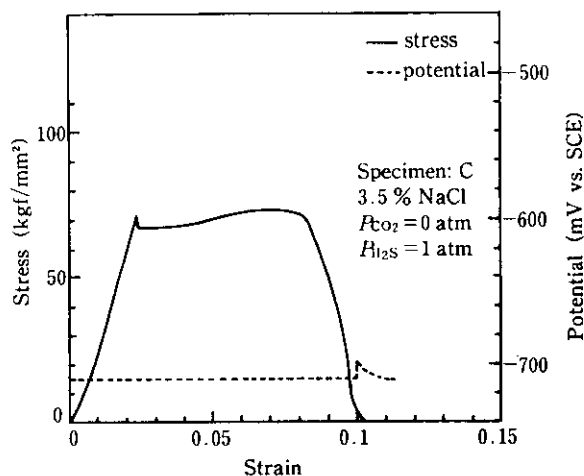
Fig. 6 Stress-strain curve and change of corrosion potential during SSRT test for low alloy steel in 3.5% NaCl solution saturated with 100% H_2S gas
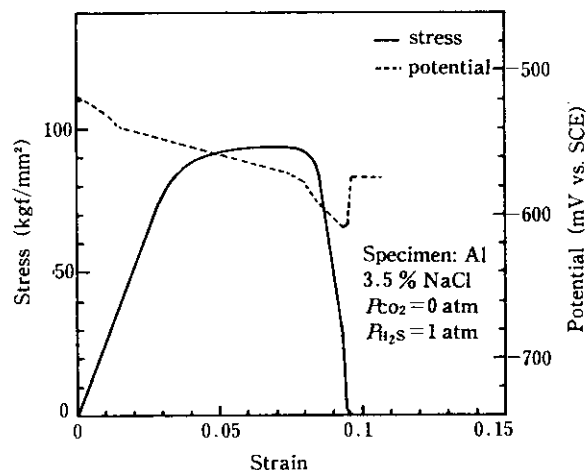

Fig. 7 Stress-strain curve and change of corrosion potential during SSRT test for Cr-Ni steel in 3.5% NaCl saturated with 100% H_2S gas

Fig. 8 Effect of H_2S solubility on the degree of embrittlement measured by SSRT test in $CO_2 + H_2S$ environment

until the specimen failed. 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 $(E_{corr} \approx -630$ 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_2S solubility on the degree of embrittle-

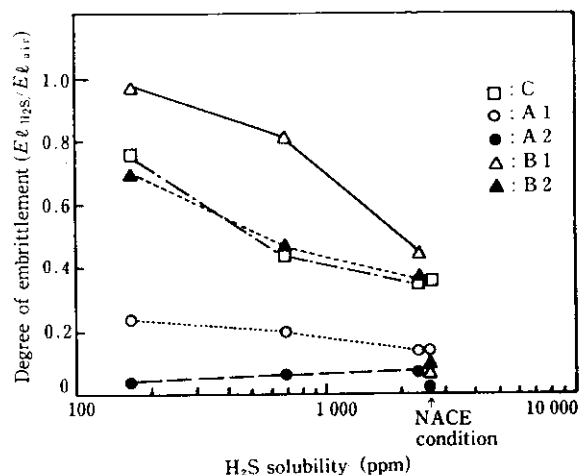ment is shown in **Fig. 8**. The degree of embrittlement was evaluated in terms of the ratio of elongation under each test condition (El_{H_2S}) to elongation in air (El_{air}), and a low ratio indicates a relatively greater degree of embrittlement. Although H_2S solubility under condition VI is the 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_2S 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 $CO_2 + H_2S$ environments except the NACE condition, the SSC susceptibility of steels used in this work was ranked as follows.

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

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[1] reported that

corrosion becomes smaller as temperature increases. On the other hand, K. Masamura, et al.[7] 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_{CO_2} increases, the maximum rate also rises. D.W. Shannon[6] reported that while an unprotective $FeCO_3$ film formed at lower temperatures, Fe_3O_4 film formed at higher temperatures. This Fe_3O_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_{CO_2} and 150°C at 30 atm P_{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_{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[5] 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_{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_2S, general corrosion of 13 Cr steels increases slightly. On the other hand, crevice corrosion accelerates drastically. S. Tsujikawa, et al.[8] have studied the effect of P_{H_2S} 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_2S was not found at P_{H_2S} below 0.003 atm but was found at 0.01 atm P_{H_2S} and saturated at P_{H_2S} above 0.03 atm. The E_R of SUS 444 is $-200 \sim -300$ mV (vs. SCE) in an H_2S-free environment and drops to -530 mV in an environment containing 0.03 atm P_{H_2S}. 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_2S. Although the present investigation was conducted at a lower temperature (25°C) than that used in S. Tsujikawa's work[8] and crevice corrosion is more difficult to occure, C-Cr 13 Cr steel was found to suffer from crevice corrosion at 0.07 atm P_{H_2S}.

Therefore, when 13 Cr steels are used in CO_2 environments with a small amount of H_2S, 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 pH_d. The accelerating effect of H_2S on crevice corrosion indicates that H_2S raises the pH_d of stainless steel. M. Miyuki, et al.[9] reported that the pH_d of a duplex stainless steel was under 2.0 in a 5% NaCl + 0.5% acetic acid solution at 200°C, but that the pH_d rose to 2.8 after gas containing 0.1 atm P_{H_2S} was bubbled into the solution. The mechanism of crevice corrosion is considered to be as follows[10]. In a crevice, first the dissolution of a small amount of iron occurs, and the pH is then lowered by hydrosis of iron. When the pH in the crevice reaches the pH_d, active dissolution of stainless steel in the crevice begins immediately. If the environment contains a small amount of H_2S, the pH in the crevice may rapidly reach pH_d and crevice corrosion is thus accelerated. It has not to date been made clear, however, why the pH_d of stainless steel is increased by H_2S.

The SSC susceptibilities of 13 Cr steels in $CO_2 + H_2S$ environments were evaluated by SSRT tests. In an environment where E_{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_{corr} of C-Cr steels does not change during SSRT test under the conditions used in this work. E_{corr} of low alloy steel also does not change under these conditions. On the other hand, E_{corr} of Cr-Ni steel decreases with strain under all conditions except the NACE condition, and when E_{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.[11] report that 13 Cr oil tubular goods have been used

without problems in actual well environments, in spite of the presence of CO_2 and small quantities of H_2S. 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 $CO_2 + H_2S$ environments.

(1) Both C-Cr and Cr-Ni 13 Cr steel exhibit good corrosion resistance at 1 atm P_{CO_2} without H_2S at temperatures below 250°C and suffer little pitting or crevice corrosion. They cannot, however, be used practically at 30 atm P_{CO_2} 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 CO_2 environments which contain a small amount of H_2S.

(3) The SSC susceptibility of 13 Cr steels is related to the stability of their passive films in CO_2 environments contaminated with small amounts of H_2S. 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.

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