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High Cr Stainless Steel OCTG with High Strength and Superior Corrosion Resistance†

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Abstract:

New martensitic stainless steel pipes (HP13Cr, UHP15Cr) which improve the CO_2 corrosion resistance and sulfide stress corrosion (SSC) resistance of API-13Cr were developed and their application limits were clarified. The composition of the products features low C and addition of Ni and Mo. CO_2 corrosion resistance was greatly improved by adopting a high Cr, low C composition design, while SSC resistance was substantially improved by Mo addition. The critical temperature for HP13Cr in high CO_2 environments is 160°C. UHP15Cr has high strength, with Yield strength (YS) exceeding 861 MPa, and can be used in high CO_2 environments at temperatures up to 200°C. These new martensitic steel pipes show excellent properties in sweet, high temperature, high CO_2 environments and slightly sour environments containing small amounts of H_2S where conventional 13Cr pipes could not be used.

1. Introduction

The martensitic stainless steel pipe API-13Cr, which has been standardized by the American Petroleum Institute (API), is representative of oil country tubular goods (OCTG) for use in wet carbon dioxide (CO_2) environments. Because 13%Cr steel pipes possess excellent CO_2 corrosion resistance, demand for this product has increased annually[1,2)].

Nevertheless, there were problems with API-13Cr, in that its corrosion resistance deteriorates at well temperatures exceeding 100°C and it cannot withstand use in some cases, depending on the partial pressure of CO_2[3)]. With more active development of deep wells in recent years, oil wells are increasingly characterized by severe corrosion conditions, which include high temperatures, high partial pressures of CO_2, and high Cl^- concentrations, and the CO_2 corrosion resistance of 13%Cr is frequently inadequate. Moreover, with the increasing number of cases where hydrogen sulfide (H_2S) is generated by water injection, even when a CO_2 environment existed in the initial period, and increasing development of wells containing H_2S from the beginning, corrosion cracking caused by H_2S (sulfide stress cracking: SSC) has become a problem. API-13Cr does not have enough SSC resistance for these conditions[4,5)]. In oil and gas wells with these types of environments, 22Cr duplex stainless steel pipes or higher alloy steel pipes have come to be used[6)]. However, as problems with 22Cr stainless and similar products, these pipes have unnecessarily high corrosion resistance in many cases, and the strength necessary in OCTG must be obtained by cold drawing, resulting in substantially higher costs. Therefore, there was strong demand for the development of new OCTG which possess high corrosion resistance superior to that of API-13Cr while also offering a reasonable cost in comparison with duplex stainless steel.

To meet these requirements, JFE Steel developed two new martensitic stainless steel pipes, HP13Cr and UHP15Cr, with new compositions which improve CO_2 corrosion resistance and SSC resistance.

This paper clarifies the effects of environmental factors and alloying elements on the corrosion resistance of martensitic stainless steel, and describes the history of development of HP13Cr and UHP15Cr with improved CO_2 corrosion resistance and SSC resistance, as well as their application limits in oil and gas environments.

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2. Development of HP13Cr

2.1 Development Concept

13Cr steel pipes show excellent CO_2 corrosion resistance in environments with temperatures of 100°C or less. However, these pipes show general corrosion in environments exceeding 100°C, and they cannot withstand use in environments with high partial pressures of CO_2[4]. Furthermore, pitting occurs in high Cl^- environments. Therefore, JFE Steel developed HP13Cr-1 as an OCTG for use in severe high temperature CO_2 environments where 13Cr is not suitable for use and HP13Cr-2 for increased sour resistance in addition to CO_2 corrosion resistance. The development targets are presented below.

(1) CO_2 corrosion resistance: Applicable at 150°C
(2) SSC resistance: No occurrence of SSC under conditions of H_2S: 0.01 MPa, pH4.5
(3) Good hot workability in Mannesmann process

Addition of alloying element is effective for improving CO_2 corrosion resistance. Reduced C or increased Cr and Ni is effective for improving general corrosion resistance in wet CO_2 environments[7], and Mo addition is effective for increasing pitting resistance. Therefore, as the concept of the new composition, the C content was reduced and Ni was increased to improve general corrosion, and Mo was added to improve pitting resistance.

On the other hand, where sour resistance is concerned, the mechanism of SSC in 13Cr is basically hydrogen embrittlement, but these cracks initiate and propagate from the bottom of pits. Therefore, two points are important for improving SSC resistance: reduction of the amount of hydrogen which permeates into the steel and improvement of pitting resistance. In particular, when pitting occurs, the pH in the pit decreases, accelerating hydrogen permeation. This means that a further increase in the amount of Mo addition is effective for improving sour resistance.

It may also be noted that, in 13Cr pipes, a δ-ferrite phase precipitates in the austenite phase in the high temperature region if the amount of ferrite-forming elements is increased. It is known that the precipitation of this δ-ferrite phase is linked to reduced hot workability and deterioration of corrosion resistance. C and Ni are austenite formers, and Mo is a ferrite former. Thus, because a low C, Mo-added composition would promote formation of the δ-ferrite phase, the amount of Ni addition was decided in consideration of the phase balance. The concept described above is shown in **Fig. 1**.

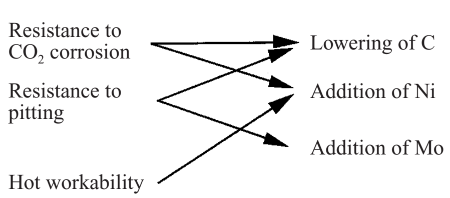

Fig. 1 Concepts of alloy design

2.2 Experimental Procedure

The materials used in this research were small ingots of a base 13Cr steel with reduced C contents and added Ni and Mo. The chemical composition of the steels tested are shown in **Table 1** (HP13Cr-1) and **Table 2** (HP13Cr-2). The ingots were rolled to a thickness of 12 mm, held at 1 000°C for 40 min, and given quenching treatment by air cooling, followed by tempering to obtain the specified strength.

CO_2 corrosion resistance was evaluated by a crevice corrosion test and U-bend SCC test. The crevice corrosion test was performed, using specimens 3 mm$t$ × 25 mm$w$ × 50 mm$l$ taken from the center of thickness of the sample materials, by creating a crevice with a polytetrafluoroethylene jig, followed by immersion in an autoclave. CO_2 corrosion resistance was evaluated by the general corrosion rate (mm/y) converted from weight loss. The U-bend SCC test was performed by taking specimens 2 mm$t$ × 10 mm$w$ × 75 mm$l$ from the center of thickness of the sample materials and performing U-bend, followed by immersion in the autoclave. As test conditions, in both tests, a 20%NaCl aqueous solution was used and the partial pressure of CO_2 was adjusted to 3.0 MPa. The test temperature and time were 150°C and 168 h, respectively. The tests were also performed with

Table 1 Chemical composition of steels tested for HP13Cr-1

(mass%)

Steel	C	Si	Mn	Cr	Ni	Mo
A	0.015	0.45	0.45	12.9	2.9	0.97
B	0.010	0.44	0.46	12.9	3.9	0.94
C	0.020	0.46	0.45	13.3	4.0	0.99
D	0.030	0.46	0.45	13.0	4.0	1.00
E	0.015	0.47	0.45	12.8	3.9	–
F	0.025	0.46	0.46	13.3	4.1	0.74
API-13Cr	0.20	0.56	0.6	13.1	–	–

Table 2 Chemical composition of steel tested for HP13Cr-2

(mass%)

Steel	C	Si	Mn	Cr	Ni	Mo
G	0.027	0.25	0.46	13.3	4.0	0.99
H	0.027	0.25	0.45	13.1	4.0	2.04
I	0.026	0.25	0.46	13.0	5.0	1.06
J	0.026	0.25	0.45	13.1	5.0	2.07

API-13Cr steel pipes as a comparison material.

The SSC test was performed in accordance with the constant load test specified in NACE-TM0177-90 method A[8]. The test solution used was a 5%NaCl + 0.5%CH_3COOH solution, which was adjusted to pH2.8–4.5 by adding CH_3COONa. Specimens subjected to stress loading were immersed in the test solution for 30 days at 24°C while passing a mixed gas consisting of 1–25%H_2S + CO_2 balance at 0.1 MPa through the solution. The applied stress was set at 100% specified minimum yield strength (SMYS).

A hydrogen permeation test was performed to investigate the effects of environmental factors and alloying elements on hydrogen permeation. Specimens were placed between a cell containing a test solution simulating a corrosive environment and a cell for use in measuring the hydrogen permeation rate, and hydrogen permeating from the environment side was measured as the anode current.

As in the SSC test, a 5%NaCl + 0.5%CH_3COOH solution adjusted to pH2.8–4.5 by CH_3COONa addition was used as the environment side solution, and the hydrogen permeation rate was measured while passing a mixed gas consisting of 1–10%H_2S + CO_2 balance at 0.1 MPa. The thickness of the specimens was 1 mm, and the area of the part where hydrogen permeation was measured was 7 cm^2.

2.3 Improvement of CO_2 Corrosion Resistance

The crevice corrosion test results and SCC test results are shown in **Table 3**. The corrosion rate of the API-13Cr steel pipe was more than 1 mm/y. In contrast, the corrosion rates of the sample steels were 0.05 mm/y or less in all cases, showing excellent CO_2 corrosion resistance. CO_2 corrosion resistance was not affected when the C content was varied between 0.01% and 0.03%. The corrosion rate of the steel without Mo addition was 0.05 mm/y, which was a large value in comparison with 1% Mo steel. However, because this value is sufficiently low in comparison with that of API-13Cr steel, a combination of C reduction and Ni addition is considered effective in improving CO_2 corrosion resistance.

In the SCC test, SCC was observed in the samples without Mo addition and with 0.75% Mo addition. On the other hand, SCC did not occur in the 1% Mo steel regardless of the C and Ni contents. Based on this fact, it can be understood that 1% addition of Mo is necessary for securing SCC resistance. Although SCC did not occur in the API-13Cr steel pipe, this is considered to be because API-13Cr shows a general corrosion mode.

In the sample steels with reduced C, the amount of carbides was small in comparison with API-13Cr, resulting in a higher content of Cr in the matrix, which is effective for corrosion resistance. It is thought that this suppressed the anode reaction in corrosion. Accordingly, reducing the C content is considered effective for improving CO_2 corrosion resistance.

Figure 2 shows the distribution of elements in the corrosion products which formed on the surfaces of steel A and the API-13Cr steel pipe in the CO_2 corrosion test, as determined by EPMA analysis. In both cases, these are specimens which were corroded under conditions of a partial pressure of CO_2 of 3.0 MPa and temperature of 150°C. With the API-13Cr steel, a corrosion product with a thickness of approximately 25 μm was observed, but in contrast, the corrosion product on steel A was extremely thin, at approximately 5 μm. Both corrosion products were Cr enriched and contained virtually no Fe. Furthermore, because it is known that Ni reduces the dissolution current in the active state in steels containing Cr, the possibility that Ni reduced corrosion is also conceivable in the present case.

In addition to the corrosion test results described above, the Ni balance was also considered from the viewpoint of hot workability. As a result, the HP13Cr-1 steel pipe (0.025C-13Cr-4Ni-1Mo) was developed as an OCTG with excellent CO_2 corrosion resistance.

Table 3 Corrosion and SCC test results

Steel	Corrosion rate (mm/y)	SCC
A	0.036	NC
B	0.024	NC
C	0.023	NC
D	0.028	NC
E	0.05	C
F	0.027	C
API-13Cr	1.152	NC

NC: No SCC, C: SCC

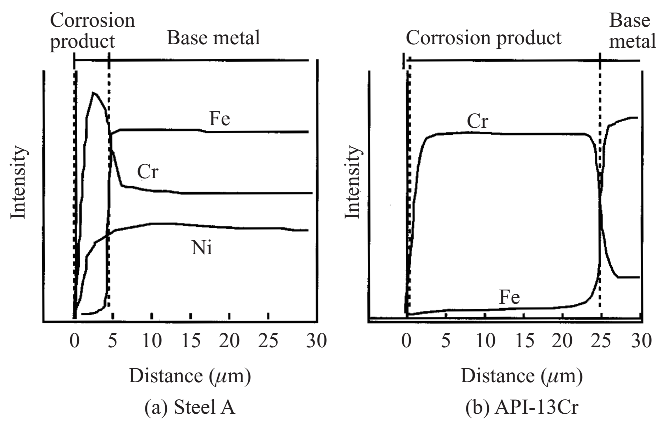

Fig.2 Distribution of Fe, Cr, and Ni on the cross section of corrosion product in CO_2 environment

2.4 Improvement of SSC Resistance

Sulfide stress cracking in martensitic stainless steel originates at pits and propagates by hydrogen embrittlement. Accordingly, improvement of pitting resistance and suppression of hydrogen permeation into the steel are effective means of improving SSC resistance. Mo addition is effective for improving pitting resistance. The effect of the Mo content on SSC is shown in **Fig. 3**. Resistance to SSC was improved by increasing the Mo content from 1% to 2%. Although virtually no effect in improving SSC resistance can be observed under a condition of pH3.0, at pH3.2 or higher, the effect of Mo addition became apparent.

Figure 4 shows the results of measurements of the hydrogen permeation rate under conditions of pH3.5 and H_2S: 0.01 MPa. With the 1% Mo steel, the hydrogen permeation rate showed a tendency to increase with time. It is thought that this shows a phenomenon in which the passivation film is destroyed. On the other hand, the hydrogen permeation rate of the 2% Mo steel increased to a maximum of approximately 18 μA and decreased thereafter. This is thought to show the effect of repassivation resulting from the increased Mo content.

Furthermore, as shown in **Fig. 5**, with pH4.0, the hydrogen permeation rate is greatly reduced in comparison with pH3.5, and at pH4.5, hydrogen permeation is no longer observed. This is considered to show that permeation of hydrogen from the steel surface has ceased because the passivation film has become stable, preventing further corrosion. In explaining the effects of Mo addition, it is thought that Mo enhances pitting resistance, thereby preventing pitting, which is the point of origin for SSC, and at the same time, Mo has the effect of reducing the amount of hydrogen permeating into the steel. In particular, because hydrogen permeation is accelerated by the reduced pH in pits, Mo addition is essential for improving sour resistance in cases where pitting occurs.

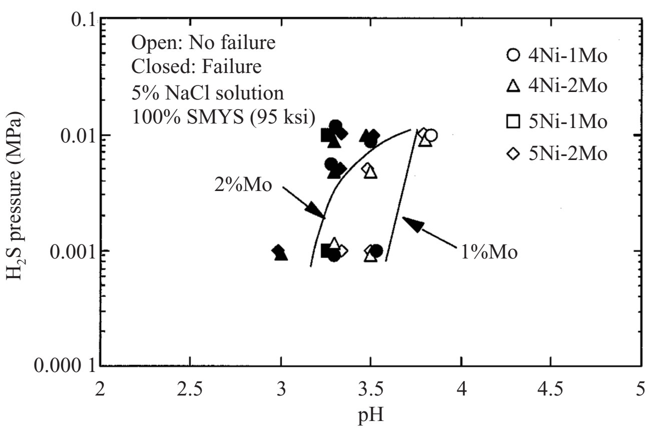

Fig. 3 Effect of Mo content on the resistance to SSC

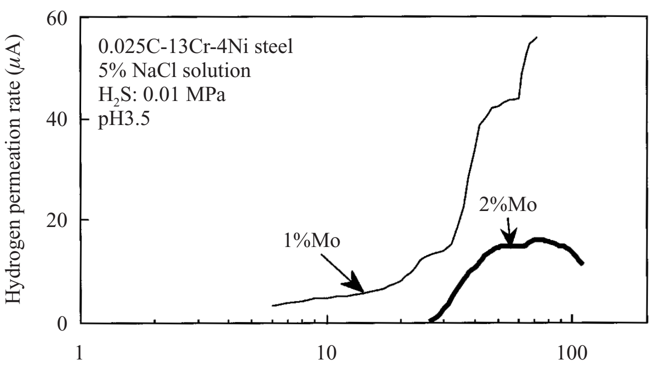

Fig. 4 Hydrogen permeation test result

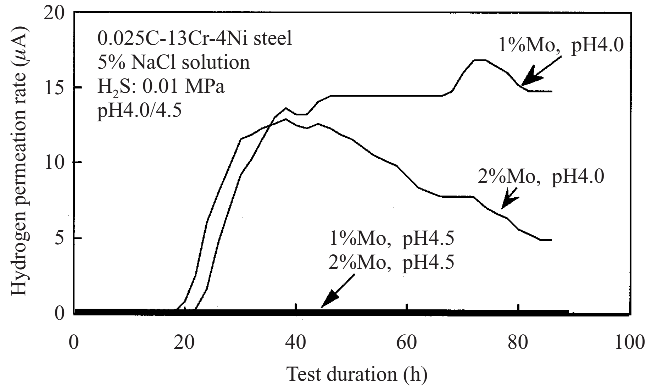

Fig. 5 Hydrogen permeation test result

Based on these results, the HP13Cr-2 steel pipe (0.025C-13Cr-5Ni-2Mo), which has excellent CO_2 corrosion resistance and sour resistance, was developed by setting the Mo content at 2% to improve sour resistance and increasing the Ni content to secure hot workability.

3. Development of UHP15Cr Steel Pipe

3.1 Development Concept

As also shown in Table 3, HP13Cr has excellent CO_2 corrosion resistance at higher temperatures than the conventional 13% Cr steel pipe, but its application limit is around 160°C. On the other hand, with increasing development of deeper wells in oil well environments, requirements for steel pipes with a combination of high strength and the ability to withstand high temperatures have also increased. JFE Steel therefore developed the UHP15Cr steel pipe as a high strength pipe which further improves the corrosion resistance of HP13Cr. The development targets are shown below.

(1) YS≧861 MPa (125 ksi)
(2) Applicable limit temperature: 200°C (CO_2: 10 MPa)
(3) Applicable limit partial pressure of H_2S: 0.01 MPa (pH4.5)
(4) Good hotworkablility in Mannesmann process

Table 4 Chemical composition of steel tested for UHP15Cr

(mass%)

C	Cr	Ni	Mo	Cu
0.02	14–20	3–9	1–4	0–2

Increasing the contents of alloying elements such as Cr, Ni, Mo, Cu is effective for improving corrosion resistance. In particular, Cr is the most effective element for improving CO_2 corrosion resistance[9]. However, Cr also promotes the formation of ferrite. Alloying element addition was therefore studied based on the concept of HP13Cr, controlling the Ni balance in consideration of hot workability while at the same time also considering sour resistance.

3.2 Experimental Procedure

As sample materials, small steel ingots with HP13Cr steel as the base composition and varied contents of Cr, Ni, Mo, and Cu were used. The range of chemical compositions of these samples is shown in **Table 4**.

CO_2 corrosion resistance was evaluated using plate-shaped immersion test specimens. The corrosion test was performed by immersion in an autoclave using specimens 3 mm*t* × 25 mm*w* × 50 mm*l* taken from the center of thickness of the sample materials. CO_2 corrosion resistance was evaluated by the general corrosion rate (mm/y) converted from weight loss.

3.3 Corrosion Resistance

The effect of alloying elements on CO_2 corrosion resistance under a condition of 200°C is shown in **Fig. 6**. In a CO_2 environment at 200°C, increasing Cr, Ni, Mo, and Cu is effective for improving corrosion resistance, and particularly in high CO_2 environments, an increased content of Cr is most effective for enhancing CO_2 resistance. To reduce the corrosion rate in a 200°C environment with a partial pressure of CO_2 of 10 MPa to 0.127 mm/y or less, it is necessary to secure a CO_2 corrosion index (CCI: Cr + 0.65 Ni + 0.6 Mo + 0.55 Cu) of 20.5 or higher.

Because Cr is a strong ferrite-forming element, it is necessary to increase the Ni content so as to prevent precipitation of the δ-ferrite phase. It is also necessary to add 2% Mo in order to secure pitting resistance and

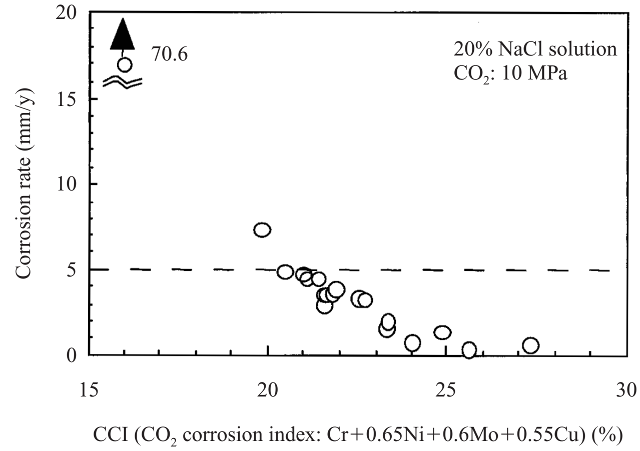

Fig. 6 Effect of alloying elements on CO_2 corrosion rate

SSC resistance. Therefore, 0.03C-15Cr-6Ni-2Mo-1Cu was adopted as the composition system for UHP15Cr in consideration of satisfying both corrosion resistance and hot workability while also securing strength.

4. Actual Pipe Production Results

HP13Cr-1 with excellent CO_2 resistance, HP13Cr-2 with improved sour resistance, and UHP15Cr with high strength combined with improved corrosion resistance at high temperatures were produced by seamless rolling, and their properties were evaluated. The dimensions of the pipes were outer diameter: 88.9 mm (3½”), thickness: 6.45 mm and outer diameter: 114.3 mm (4½”), thickness: 6.88 mm. The comparison material used was 13Cr steel pipe adjusted to the same grade at the same thickness and outer diameter as HP13Cr. The chemical compositions of the sample pipes are shown in **Table 5**. The strengths of the HP13Cr and UHP15Cr steel pipes was adjusted to YS: 650 MPa (95 ksi) grade and 861 MPa (125 ksi) grade, respectively.

The results of a high temperature tensile test of the UHP15Cr steel pipe are shown in **Fig. 7**, together with the test results for a 25Cr duplex stainless steel pipe. At 200°C, the YS of the 25Cr duplex stainless steel decreased by approximately 150 MPa in comparison with its YS at room temperature. In contrast, the decrease in UHP15Cr was limited to approximately 50 MPa, and the difference between the two expanded to 100 MPa. Because high strength is secured in duplex

Table 5 Chemical composition of pipes

(mass%)

	C	Si	Mn	Cr	Ni	Mo	Cu
HP13Cr-1	0.025	0.25	0.46	13.1	4.0	1.0	–
HP13Cr-2	0.025	0.25	0.40	13.0	5.1	2.0	–
UHP15Cr	0.03	0.22	0.28	14.7	6.3	2.0	1.0
13Cr	0.20	0.23	0.44	13.0	–	–	–

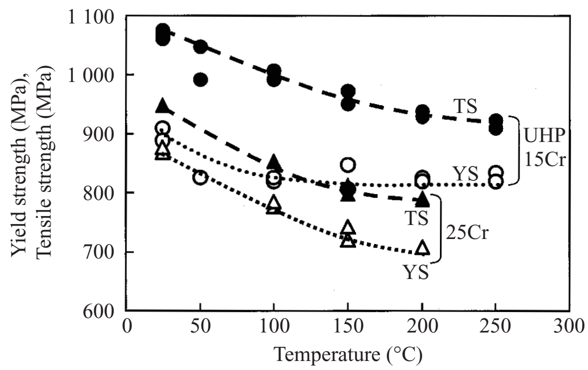

Fig. 7 Effect of temperature on tensile properties

stainless steel pipes by cold drawing, it is considered that the strength of this type of steel decreases when dislocations are released at high temperature. On the other hand, because strength is secured in UHP15Cr by microstructure and precipitation control, this steel has the distinctive feature of a small decrease in strength even at high temperatures.

The CO_2 corrosion test results of HP13Cr-1, HP13Cr-2, and UHP15Cr steel pipes are shown in **Fig. 8**. The limit in judging the applicability of the steels was a corrosion rate of 0.125 mm/y. The application limit is affected by the partial pressure of CO_2 gas and temperature. For example, the limit temperature for application of API-13Cr steel pipes under a condition of CO_2: 3 MPa is 100°C. In contrast, the limit temperatures for HP13Cr and UHP15Cr are 160°C and 200°C, respectively.

The SSC test results for the HP13Cr-2 and UHP15Cr steel pipes are shown in **Figs. 9** and **10**. The critical concentration of H_2S becomes high with the increase of pH. With HP13Cr, under a condition of pH3.0, SSC occurred even with a partial pressure of H_2S of 0.001 MPa, but at pH4.0, the critical partial pressure of H_2S at which SSC does not occur is 0.01 MPa. UHP15Cr displayed excellent resistance to SSC, in spite of its high strength of 125 ksi grade, and its critical partial pressure of H_2S at pH4.5 was 0.01 MPa.

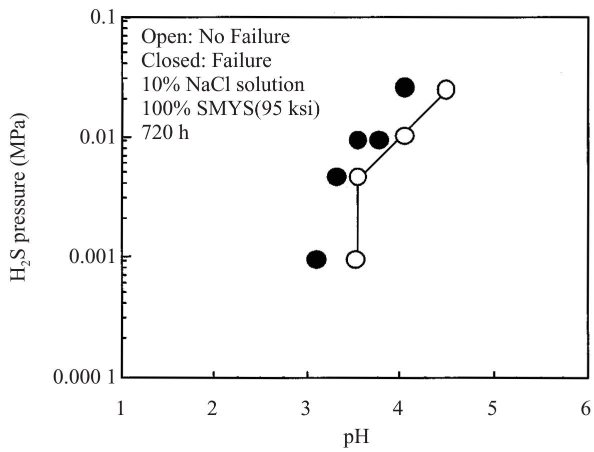

Fig. 9 SSC test results for HP13Cr-2

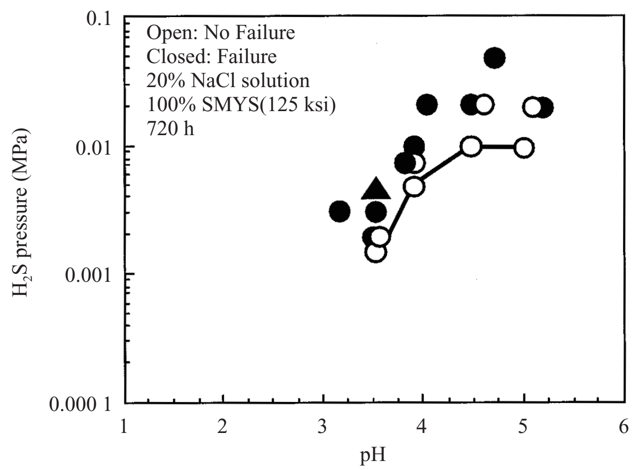

Fig. 10 SSC test results for UHP15Cr

The fracture surface of a test specimen of a UHP15Cr steel pipe after the SSC test is shown in **Photo 1**. Sulfide stress corrosion has originated at a pit and propagated by hydrogen embrittement. The excellent SSC resistance of UHP15Cr is attributed to improved pitting resistance resulting from its increased Cr content.

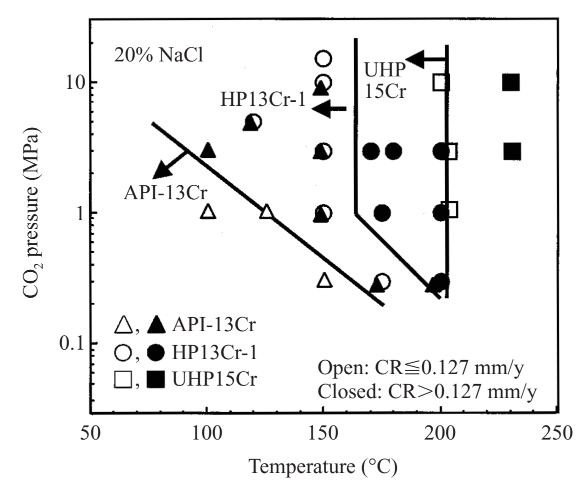

Fig. 8 CO_2 corrosion test results

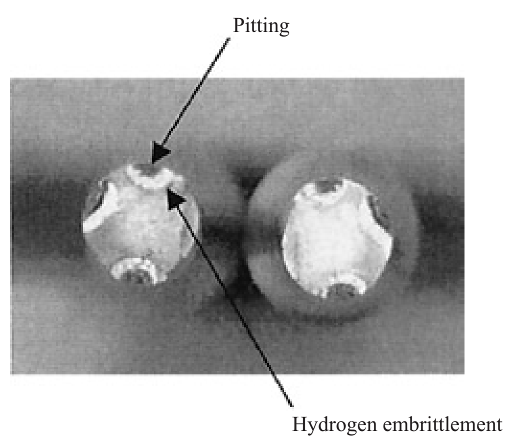

Photo 1 Fracture surface of SSC test specimen

5. Conclusion

(1) A new steel pipe with excellent CO_2 corrosion resistance, HP13Cr-1, was developed. HP13Cr steel has high CO_2 corrosion resistance in comparison with API-13Cr and can be used at high temperatures up to 160°C even under high partial pressures of CO_2. The excellent CO_2 corrosion resistance of HP13Cr is considered to be the result of (a) reducing the amount of Cr carbides, which form cathode sites in the corrosion reaction, by reducing the content of C, (b) increasing the content of Cr, which is effective for improving corrosion resistance, by reducing the amount of Cr carbides, and (c) suppressing the corrosion reaction by addition of Ni, which has only a slight tendency to ionize under high temperature, high partial pressure of CO_2 condition.

(2) A steel pipe which possesses excellent sour resistance in addition to CO_2 corrosion resistance, HP13Cr-2, was also developed. HP13Cr-2 has high sour resistance in comparison with HP13Cr-1, which was achieved by increasing the Mo content to 2%. It is considered that improved pitting resistance together with reduced permeation of hydrogen into the steel, which result from the increased Mo content, contribute to improved sour resistance.

(3) A steel pipe with high strength and excellent CO_2 corrosion resistance at temperatures up to 200°C, UHP15Cr, was developed. The UHP15Cr steel pipe possesses not only CO_2 corrosion resistance, but also excellent properties in sour environments. In comparison with duplex stainless steels, UHP15Cr shows only a small drop in yield strength (YS) at high temperatures and possesses high strength even in 200°C high temperature environments.

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