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The body can be viewed from the next page.

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1 Introduction

A representative example of oil country tubular goods (OCTG) for use in wet CO₂ gas environments is 13%Cr martensitic stainless steel pipe, which is included in the standards of American Petroleum Institute (API) as API-13Cr. The use of 13%Cr OCTG in the oil field has increased over the last several years, because of its superior CO₂ corrosion resistance.[1,2]

However, there have been problems with API-13Cr because its CO₂ corrosion resistance deteriorates when the oil well temperature exceeds 150°C, making it unable to withstand use.[3] Recent years have also seen an increase in the number of wells with severe corrosion environments characterized by high temperature, high partial pressure of CO₂, and high concentration of chloride ions. In many cases, the CO₂ corrosion resistance of 13%Cr pipes is inadequate for these conditions. Moreover, in an increasing number of cases, water injection generates H₂S, or H₂S is present in the well from the outset. Although H₂S causes the problem of sulfide stress cracking (SSC), API-13Cr does not provide adequate resistance to SSC.[4,5] In these environments 22Cr duplex stainless steel pipes or higher alloy pipes have been used.[6] However, 22Cr stainless steel pipes and

similar products frequently possess higher corrosion resistance than is necessary, and also incur higher costs. Because of these problems, a new OCTG has been required as an intermediate product between API-13Cr and 22Cr duplex stainless steel.

In response to this need, a new martensitic stainless steel pipe, HP-13Cr, was developed with a new composition that offers improved CO₂ corrosion resistance and SSC resistance.

This report clarifies the factors which affect the corrosion resistance of 13Cr steel pipes and the effect of alloying elements, discusses the development of the HP-13Cr steel pipe with improved CO₂ corrosion resistance and SSC resistance, and describes the possible range of application of the new product.

2 Development of Pipe with Excellent CO₂ Corrosion Resistance

2.1 Concept of Development

Higher partial pressures of CO₂ in the environment and elevated temperatures accelerate the general corrosion of 13Cr steel,[4] and higher concentrations of chloride ions accelerate pitting. **Figure 1** shows the effect of alloying elements on the rate of CO₂ corrosion. In a wet
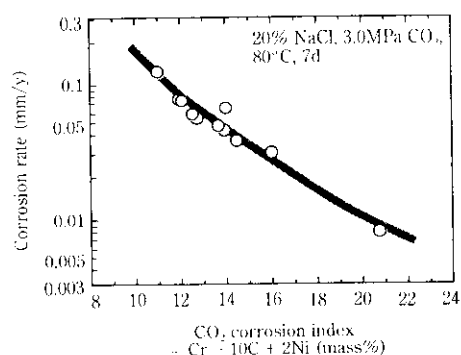
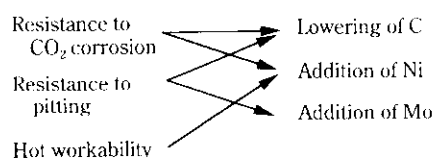Fig. 1 Relation between CO_2 corrosion index and corrosion rate

Fig. 2 Concepts of alloy design

CO_2 environment, adopting a low C composition or increasing the content of Cr and Ni is effective for improving general corrosion resistance, while the addition of Mo is effective for improving pitting resistance. Accordingly, the concept of the new composition was to reduce the C content and add Ni in order to improve general corrosion resistance, and to add Mo to improve pitting resistance.

Incidentally, with 13Cr pipes, if the content of ferrite former elements is increased, a δ-ferrite phase precipitates in the austenite phase in the high-temperature region. The precipitation of this δ-ferrite is thought to be related to reduced hot workability and deterioration of corrosion resistance. C and Ni are austenite-formers, and Mo is ferrite-former. Because the low-C, Mo-added composition of the new steel tends to promote the formation of the δ-ferrite phase, the amount of Ni addition was decided in consideration of the phase balance. The concept described above is illustrated in **Fig. 2**.

2.2 Experimental Procedure

The sample materials were laboratory heats with a basic 13Cr steel composition and reduced C content and added Ni and Mo. The chemical composition of the respective sample steels are shown in **Table 1**. The sample ingots were rolled to a thickness of 12 mm, soaked for 40 min at 1 000°C, and quenched by air cooling. The specified strength was then obtained by tempering.

CO_2 corrosion resistance was evaluated by the crevice corrosion test and U-bend stress corrosion cracking (SSC) test. The crevice corrosion test was performed using specimens 3 mmt × 25 mmw × 50 mml taken from the center of the plate thickness of the sample material. After creating a crevice with a teflon jig, the specimens were immersed in an autoclave. CO_2 corrosion resistance was evaluated by the general corrosion rate (mm/y), which was obtained by conversion from corrosion loss. In the U-bend SCC test, specimens 2 mmt × 10 mmw × 75 mml were taken from the center of the plate thickness of the sample material, and were immersed in an autoclave after U-bending. As test conditions, a 20% NaCl solution and CO_2 gas partial pressure of 3.0 MPa were used in both cases. The test temperature was 150°C, and period was 168 h. As a comparison material, an API-13Cr steel pipe was also tested.

2.3 CO_2 Corrosion Resistance

The results of the crevice corrosion test and SCC test are shown in **Table 2**. In contrast to the corrosion rate of the API-13Cr pipe, which was more than 1 mm/y, the corrosion rate of the newly-developed steel was 0.05 mm or under with all the compositions tested, showing excellent CO_2 corrosion resistance. Even when the C content was varied between 0.01% and 0.03%, there was no effect on CO_2 corrosion resistance. The corrosion rate of the Mo free steel was 0.05 mm/y, which is high in comparison with 1%Mo steel, although sufficiently low when compared with API-13Cr. From this fact, it is considered that C reduction and Ni addition are more effective than Mo addition for improving CO_2 corrosion resistance.

In the SCC test, SCC was observed in the Mo free

Table 1 Chemical composition of steels tested (mass %)

Steel		C	Si	Mn	Cr	Ni	Mo
HP13Cr	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	0.00
	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	0.60	13.1	–	–

steel and the 0.75% Mo steel. On the other hand, no SCC was observed in 1% Mo steel, regardless of the contents of C and Ni. This indicates that a 1% addition of Mo is necessary to secure SCC resistance. No SCC was observed in the API-13Cr steel tube, but this result was attributed to the general corrosion morphology of the material.

Corrosion in a high temperature CO_2 environment proceeds with Cr carbides as the cathodic site of the corrosion reaction. Accordingly, it is considered that the cathodic reaction involved in corrosion was suppressed in the newly-developed steel, because the carbide content of the new steel, which has a reduced C content, was small in comparison with that of API-13Cr. In addition, decreasing the Cr carbide content results in a proportional increase in the content of Cr, which is effective in preventing corrosion, and it can therefore be thought that the anodic reaction in corrosion is also suppressed. Thus, reducing the C content is considered to be effective in improving CO_2 corrosion resistance.

Figure 3 shows the distribution of elements obtained by an EPMA analysis of the corrosion product which formed on the surface of steel A and the API-13Cr pipe in the CO_2 corrosion test. In both cases, the test pieces were corroded under conditions of a CO_2 partial pressure of 3.0 MPa and temperature of 150°C. A corrosion

Table 2   Crevice corrosion test and SCC test results

Steel	Crevice corrosion (mm/y)	SSC U-bend
A	0.036	NC
B	0.024	NC
C	0.023	NC
D	0.028	NC
E	0.050	C
F	0.027	C
API-13Cr	1.152	NC

NC: No crack, C: Crack

(a) Steel A	(b) API-13Cr

Fig. 3   Distribution of Fe, Cr and Ni on the cross section of corrosion product in CO_2 environment

product having a thickness of approximately 25 μm was observed on the API-13Cr steel. In contrast, the thickness of the corrosion product on steel A was extremely thin, at approximately 5 μm. Both corrosion products contained virtually no Fe and were Cr enriched. Ni enrichment was not detected in the corrosion product on steel A.

Regarding the state of the respective elements in this environment, it can be estimated that Fe exists in ion form, Cr exists in oxide form, and the metallic state of Ni is thermodynamically stable. This agrees with the results of the analysis by EPMA, which showed Cr enrichment but detected virtually no Fe. Because Ni shows little tendency to ionization and the metallic state is stable, it was not possible to confirm the existence of Ni in the EPMA analysis of the corrosion film. Because it is known that Ni reduces the dissolution current in the active region in steels which contain Cr, it is considered possible that Ni suppressed corrosion in this case.

However, it is thought that the transfer of ions, etc. was facilitated by the comparatively rough corrosion film which formed here, and the corrosion film on steel A was thin. These and other points suggest a high possibility that the difference in the corrosion rates of steel A and the API-13Cr was not due to the corrosion-preventive effect of the corrosion film, but rather was due to a difference in the rate of the corrosion reaction. Accordingly, it can be thought that the most important reasons for the excellent corrosion resistance of the newly-developed steel are the increase in the effective Cr content and the reduction in the number of cathodic reaction sites, which were due to the decrease in C.

2.4 Pipe Manufacturing Results and Corrosion Resistance

In addition to the results of the study of corrosion resistance described above, the contents of C, Ni, Mo, and other elements were also decided in consideration of the hot workability of the steel. Pipes with an outer diameter of 88.9 mm (3-1/2″) and a wall thickness of 6.45 mm were then manufactured by seamless rolling, and their features were investigated. Strength was adjusted to a 95 ksi (650 MPa) grade yield strength. The comparison material was a 13Cr steel pipe with the same wall thickness and outer diameter, adjusted to the same grade. The chemical composition of the sample pipes is shown in **Table 3**.

The CO_2 corrosion test was performed with specimens 3 mmt × 25 mmw × 50 mml, which were taken from the plate thickness center of the sample steel pipes

Table 3   Chemical composition of pipes $_{(mass\%)}$

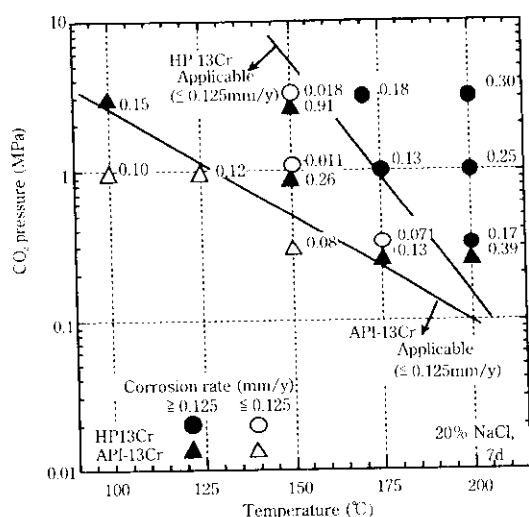| Pipe	C	Si	Mn	Cr	Ni	Mo
HP13Cr	0.025	0.25	0.46	13.1	4.0	1.0
API-13Cr	0.20	0.23	0.44	13.0	–	–

Fig. 4 CO₂ corrosion test results of HP13Cr and API-13Cr pipes

and immersed in an autoclave. Test solution was a 20%NaCl solution. After saturation with CO₂ at 0.3–3.0 MPa, the solution was heated to 100–200°C and held at this temperature for 7 d. The corrosion rate (mm/y) was calculated based on a measurement of the weight of the specimens before and after the test, and was used to evaluate CO₂ corrosion resistance.

The results of the CO₂ corrosion resistant test are shown in Fig. 4. The corrosion rate (mm/y) at each temperature is expressed by the figures appended to the symbols. The standard for judging whether the material could be used or not was a corrosion rate of 0.125 mm/y. The HP-13Cr pipes showed a lower corrosion rate than the API-13Cr pipe and can be used at higher temperatures and higher CO₂ partial pressures, and were therefore judged superior to API-13Cr in CO₂ corrosion resistance.

3 Development of Pipe with Excellent SSC Resistance

3.1 Concept of Development

Although the mechanism of SSC in 13Cr steel pipes is basically hydrogen embrittlement, the cracks in SSC develop from the bottom of pits in many cases. Thus,

two points are important for improving SSC resistance; these are reducing the amount of hydrogen which permeates the steel and improving pitting resistance. The influence of alloying elements and environmental factors on SSC resistance and hydrogen permeation behavior was therefore investigated with the purpose of improving the SSC resistance of HP-13Cr steel pipes.

3.2 Experimental Procedure

The sample material was based on the composition of the HP-13Cr steel pipe. Laboratory ingots with varying contents of Mo and Ni were used. The chemical composition of the respective samples is shown in Table 4. The ingots were rolled to a thickness of 12 mm, heated to 1 000°C for 40 min quenched by air cooling, and tempered to obtain the specified strength.

The SSC test was performed in accordance with the constant load test specified in NACE-TM0177-96, method A[7]. The test solution was a 5%NaCl + 0.5%CH₃COOH solution adjusted to a pH of 2.8–4.5 by adding CH₃COONa. This solution was allowed to permeate the test pieces, which were under stress loading, for 30 d at 24°C, while a balanced mixed gas of 1–25% H₂S + CO₂ at 0.1 MPa was passed through the solution. The applied stress was 100% SMYS (specified minimum yield strength).

A hydrogen permeation test was conducted to investigate the effect of alloying elements on the diffusion coefficient of hydrogen and the effect of environmental factors and alloying elements on hydrogen permeation. A test piece was inserted between a cell containing a test solution which simulated a corrosion environment and a cell which was used to measurement of the hydrogen permeation rare, and the hydrogen permeating from the environment side was measured as the anode current.

The hydrogen diffusion coefficient was measured by passing a -100 mA/cm² cathodic current with a galvanostat, using a 0.5%H₂SO₄ + 0.1%SC(NH₂)₂ solution on the environment side.

The hydrogen permeation rate was measured using the same solution as in the SSC test on the environment side (5%NaCl + 0.5%CH₃COOH solution, adjusted to a pH of 2.8–4.5 by adding CH₃COONa) while passing a balanced mixed gas of 1–10%H₂S + CO₂ at 0.1 MPa. The thickness of the specimens was 1 mm, and the surface area where hydrogen permeation was measured was 7 cm².

Table 4 Chemical composition of steels tested
(mass %)

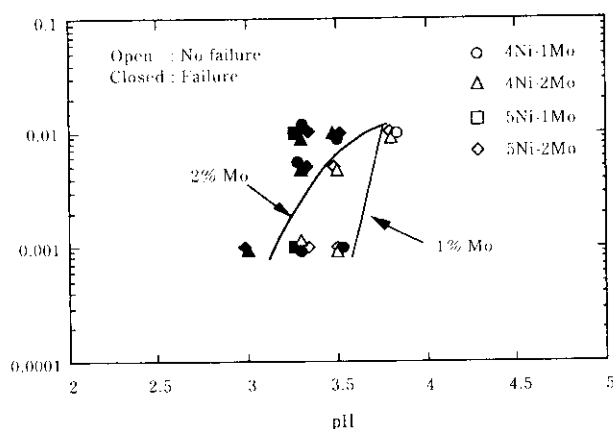| Steel		C	Si	Mn	Cr	Ni	Mo
HP13Cr	G	0.027	0.25	0.46	13.3	4.0	0.99
	H	0.027	0.25	0.45	13.1	4.0	2.04
	I	0.026	0.25	0.46	13.0	5.0	1.06
	J	0.026	0.25	0.45	13.1	5.0	2.07

Fig. 5 Effects of Mo content on the resistance to SSC

3.3 SSC Resistance

The effect of Ni and Mo on SSC is shown in **Fig. 5**. Although increasing the content of Ni from 4% to 5% had no effect on SSC resistance, increasing the Mo content from 1% to 2% improved SSC resistance. Under conditions of pH 3.0 or pH 3.8, Mo showed virtually no effect in improving SSC resistance, but in the pH range of 3.2 to 3.5, an Mo addition effect appeared. Because Mo is an element which is effective in improving pitting resistance, it was particularly effective on the high pH side, where pits tend to serve as points of origin for SSC.

These results showed that increasing the amount of Mo addition is effective in improving SSC resistance.

3.4 Effect of Alloying Elements on Hydrogen Diffusion Coefficient

In order to evaluate quantitatively the hydrogen content in the steel, the hydrogen diffusion rate was measured electrochemically. When the number of hydrogen trap sites is large, the apparent hydrogen diffusion coefficient becomes small. **Figure 6** shows the hydrogen diffusion coefficients of API-13Cr steel pipe and steels G
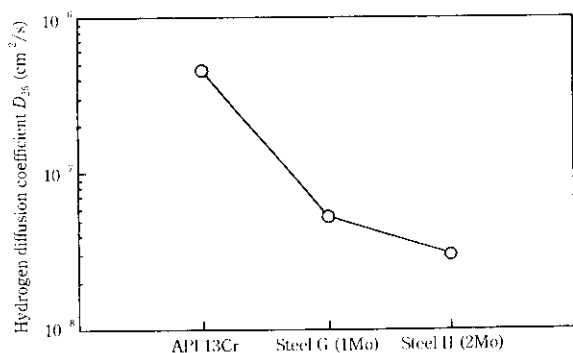
and H. Increasing the amount of Mo and Ni has the effect of decreasing the hydrogen diffusion coefficient. In other words, by increasing the content of Ni and Mo, the content of hydrogen is also increased. A reduction in the hydrogen diffusion coefficient accompanying the addition of alloying elements has been reported previously.[8] It is thought that the diffusion of elements is obstructed when substitutive-type alloying elements permeate the Fe lattice. In comparison with ordinary 13Cr steel, HP-13Cr steel, which has a high content of Mo and Ni, has a low hydrogen diffusion coefficient, and its content of hydrogen is large. In other words, HP-13Cr steel has higher hydrogen embrittlement sensitivity than API-13Cr steel pipe.

3.5 Effect of Mo and Environmental Conditions on Hydrogen Permeation of Steel

As mentioned above, the hydrogen embrittlement sensitivity of HP-13Cr steel is high in comparison with that of low-alloy steels and API-13Cr steel pipes. Accordingly, the excellent SSC resistance of HP-13Cr steel is considered to result from suppression of hydrogen permeation into the steel. Hydrogen permeation of the steel was therefore evaluated quantitatively using 1% Mo steel (steel G) and 2% Mo steel (steel H) to clarify the effect of environment conditions and the Mo content.

Figure 7 shows the results of measurements of the hydrogen permeation rate under conditions of pH: 3.5, H_2S: 0.01 MPa. With 1%Mo steel, the hydrogen permeation rate showed a tendency to increase with time. This considered to show a phenomenon in which the passivation film is destroyed. On the other hand, the hydrogen permeation rate of 2%Mo steel reached its maximum at approximately 18 μA and decreased thereafter, which is considered to show the effect of the increased Mo content in promoting repassivation.

Figure 8 shows the results of measurements of the hydrogen permeation rate under conditions of pH: 3.0, H_2S: 0.001 MPa. Under these conditions, after hydrogen permeation reached its maximum value with both 1%Mo steel and 2%Mo steel, hydrogen continued to permeate the steel at a substantially constant rate. This
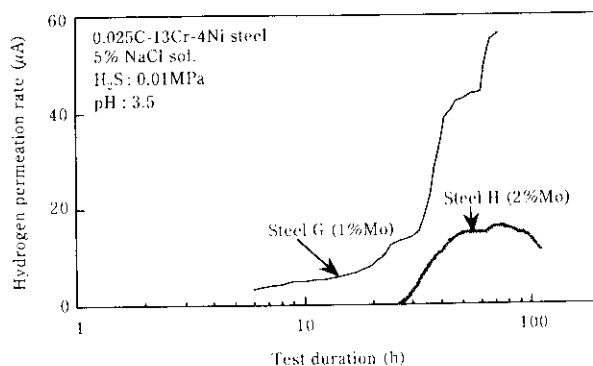

Fig. 6 Effects of alloying elements on hydrogen diffusion coefficient

Fig. 7 Hydrogen permeation rate test result
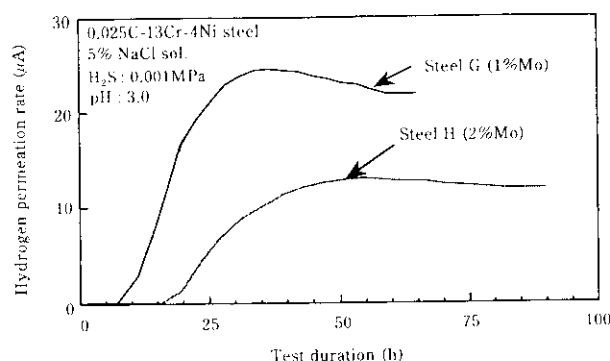
Fig. 8 Hydrogen permeation rate test result

Fig. 9 Hydrogen permeation rate test result

behavior agrees with the hydrogen permeability of low-alloy steel under conditions in which a protective film does not form. This shows that a passivation film does not exist on HP-13Cr steel under the condition of pH: 3.0 regardless of the Mo content, and corrosion therefore progresses at a constant rate. In other words, HP-13Cr steel shows extremely high SSC sensitivity under the condition of pH: 3.0, which indicates that it would be difficult to use this material under conditions where H_2S is present.

At a pH of 4.0, as shown in **Fig. 9**, the hydrogen permeation rate decreases greatly compared with the case when pH: 3.5. When the pH increases to 4.5, hydrogen permeation is no longer observed. This is considered to show that hydrogen permeation from the steel surface has stopped because the passivation film becomes stable at pH: 4.5, and corrosion no longer occurs.

From the foregoing, it is clear that HP-13Cr steel can be used even in sour environments, provided consideration is given to the limit H_2S concentration relative to the pH of the environment when conditions exceed pH: 3.

4 Conclusion

(1) In comparison with API-13Cr steel, HP-13Cr steel is superior in CO_2 corrosion resistance and can be used at higher CO_2 partial pressures and higher temperatures. The excellent CO_2 corrosion resistance of HP-13Cr steel is considered to be attributable to (a) a reduction in the Cr carbides that form cathode sites for the corrosion reaction, which is achieved by reducing the C content, (b) an increase in the effective Cr content available for preventing corrosion, which results from the reduction in Cr carbides, and (c) sup-
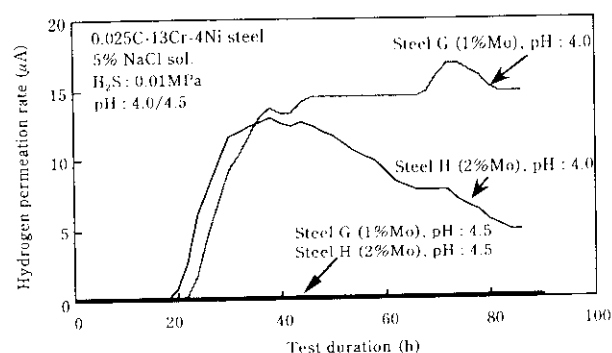
pression of the corrosion reaction by adding Ni, which shows only a slight tendency to ionize under high-temperature and high CO_2 partial pressure conditions.

(2) The most effective means of improving the SSC resistance of 13Cr steel is increasing the Mo content. Increasing the Ni content have no effect on SSC resistance. The effect of Mo in improving SSC resistance is due to improvement of hydrogen permeation.

Based on the knowledge described above; HP-13Cr steel pipes were developed using a low-C-13Cr-Ni-Mo composition design which provides excellent CO_2 corrosion resistance and SSC resistance.

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