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Development of Sour-Resistant 13%Cr Oil-Country Tubular Goods with Improved CO_2-Corrosion Resistance

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Abstract:

A material design concept for 13%Cr oil-country tubular goods (OCTG) was established and its properties were made clear, which has a sharply improved CO_2-corrosion resistance and a sour resistance compared with those of 13%Cr OCTG of API specifications being generally used. It has been made possible to improve the CO_2-corrosion resistance without generating any ferrite phase by adding copper and nickel in combination. The mechanism of improving in the CO_2-corrosion resistance by adding copper and nickel in combination is presumed to be because that the corrosion film is made amorphous and that a copper layer is formed under the corrosion film. Further, the sour resistance is improved by adding molybdenum, especially adding more than 1.5% of molybdenum in weight. The low carbon-13%Cr-Cu-Ni-Mo steel developed on the basis of these basic studies is a high strength steel with good low temperature toughness being superior in the CO_2-corrosion resistance and the sour resistance, which can be applied to many cases of such severe environments as the duplex stainless steel is to be applied.

1. Introduction

Oil-country tubular goods (OCTG) of martensitic 13%Cr stainless steel are corrosion-resistant OCTG, and meet American Petroleum Institute (API) specifications. SUS420 contains 0.2%C and 13%Cr, and is a commonly-used material in this category. This type of steel has good corrosion resistance in CO_2-containing environments, and is in increasing use because of its low price[1]. It has been clarified that the use of 13%Cr OCTG helps reduce the total cost of producing oil and gas[2]. Therefore, authors expect to find these goods in increasing use. Another of their major features is the ease with which their strength can be increased because of their martensitic properties. Duplex stainless steel containing 22% or 25%Cr is excellent in terms of corrosion resistance, but expensive, not only because of the high alloying cost, but also because of the inevitable process of cold working. Authors feel it is desirable to develop OCTG of martensitic high-chromium stainless steel that is more corrosion-resistant than 13%Cr OCTG of API specifications, but still less expensive than duplex stainless steel.

Table 1 shows typical environmental conditions under which such OCTG is expected to be in use. The major requirements for them are as follows: (1) corrosion resistance in extremely wet

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environments containing a high partial pressure of CO_2 and a large amount of Cl^- at high temperatures; (2) resistance to stress cracking in hydrogen-sulfide-containing environments; (3) high strength; and (4) good low-temperature toughness.

This report describes a material design concept for 13%Cr OCTG meeting these requirements and exceeding the corrosion resistance of conventional 13%Cr OCTG[3-6]. It also shows a comparison with API-specified 13%Cr steel.

2. Improvement of CO_2-Corrosion Resistance

2.1 Effects of alloying elements on CO_2-corrosion resistance

Figs. 1 and **2** show the effects of alloying elements on corrosion rate in synthetic ocean water (SOW), under a CO_2 partial pressure of 4 MPa at 120°C and 180°C. As seen in **Fig. 1**, a reduced carbon content in SUS420 steel results in a lower corrosion rate. As the carbon content decreased, so did the chromium carbide quantity, and hence the soluble chromium content increased. Because chromium carbide accelerates corrosion by acting as a cathode site, a decrease in the chromium carbide quantity results in the suppression of corrosion.

As shown in **Fig. 2**, chromium, molybdenum, and copper improve corrosion resistance. Among them, copper has the greatest effect, as is also apparent in **Fig. 3**. Generally, chromium also improves corrosion resistance, but forms ferrite, thereby limiting the addition of chromium to the martensite structure. In **Fig. 3**, the addition of copper to 14% (Cr + 1.6 Mo) allows martensitic transformation, but no addition of copper to 20% (Cr + 1.6 Mo) results in the formation of ferrite.Both show a similar corrosion rate.

Fig. 4 shows how the a combined addition of copper and nickel improves corrosion resistance. If the substrate steel con-

Table 1 Typical environments for 13%Cr OCTG with high corrosion and sour resistance

Well type	Water type	Cl^- (ppm)	CO_2 (MPa)	H_2S (MPa)	pH	Bottom hole tempereture (°C)
Oil	Formation	70,000	2	0.002	4.5	160
Gas	Condensed	0	2	0.002	3.3	160

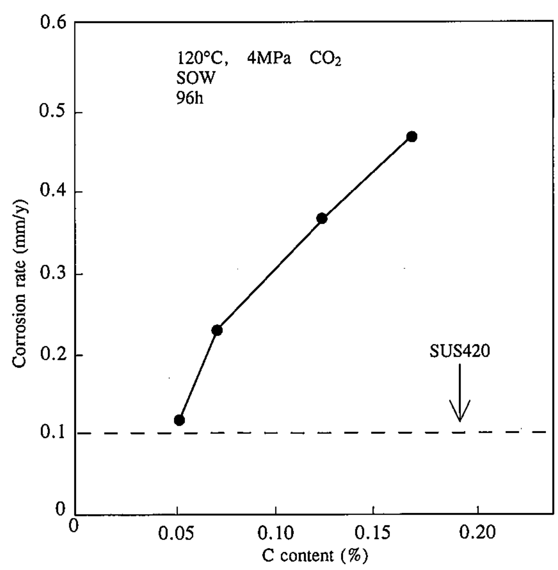


Fig. 1 Effect of carbon content on corrosion rate (13%Cr-0.12%N, SOW, 4MPa CO_2, 120°C, 96h)

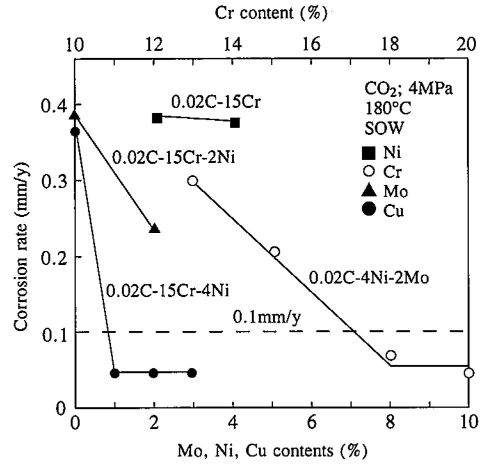


Fig. 2 Effect of chromium, molybdenum, nickel, and copper content on corrosion rate (SOW, 4MPa CO_2, 180°C, 96h)

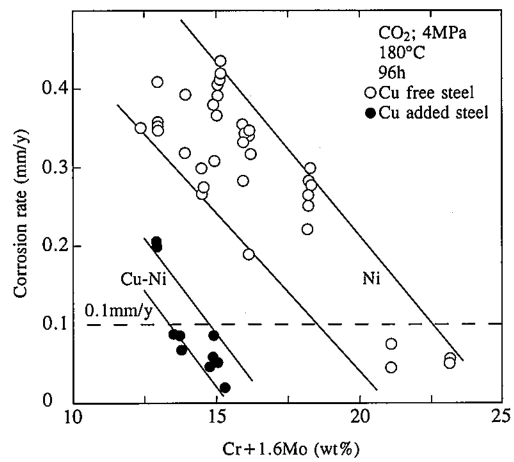


Fig. 3 Effect of the combined addition of copper and nickel on corrosion rate (SOW, 4Mpa CO_2, 180°C, 96h)

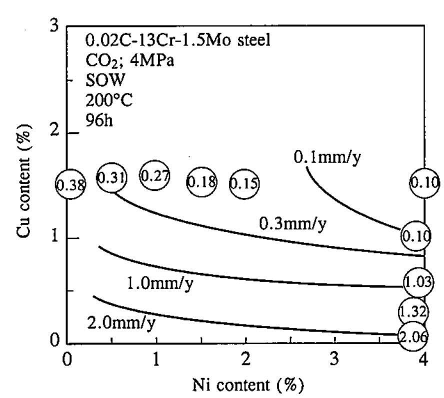


Fig. 4 Effect of the combined addition of copper and nickel on corrosion-rate (SOW, 4MPa CO_2, 180°C, 96h)

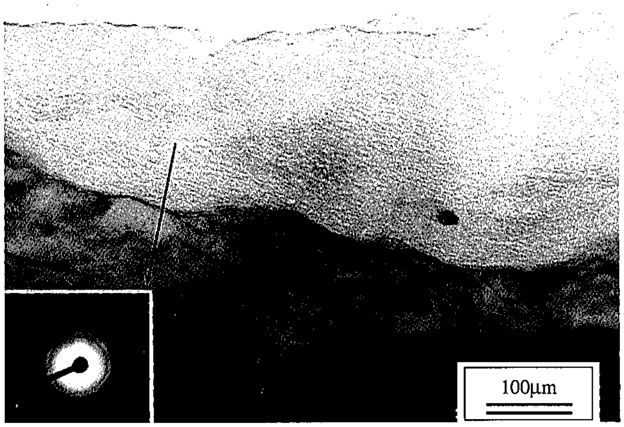


Photo 1 Bright-field image and diffraction pattern of a crosssection of a corrosion film with the combined addition of copper and nitrogen taken using a field emission-type transmission electron microscope

tains no copper, the corrosion film formed is polycrystalline, while with a combination of copper and nickel, it is amorphous[7]. **Photo 1** shows a bright-field image of a crosssection of a corrosion film taken using a field emission-type transmission electron microscope (FE-TEM). The electron diffraction pattern in this photo shows a halo, indicating that material is amorphous. An amorphous material has a homogeneous structure, known to have excellent corrosion resistance[8]. Accordingly, the good corrosion resistance of the copper- and nickel-containing steel may be due to the amorphous nature of the corrosion film.

Fig. 5 shows the distribution of elements in a crosssection of a corrosion film obtained by EDX analysis using the FE-TEM with an electron beam 1 nm in diameter. In this figure, it is clear that there is a copper-enriched layer immediately under the film[7]. This may indicate either that copper contributes to making corrosion products amorphous, or that copper itself improves the corrosion resistance of steel because it is stable in an acidic, oxygen-free environment.

2.2 Inhibition of the formation of cracking in sour environments

Fig. 6 shows effects of temperature and H_2S partial pressure on cracking of 13%Cr steel. This figure clarifies that this material has the highest cracking sensitivity near room temperature. Sulfide stress cracking (SSC), a type of hydrogen embrittlement,

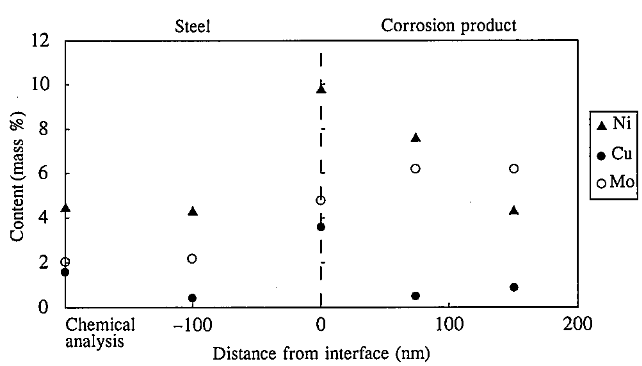


Fig. 5 Distribution of alloying elements in a crosssection by TEM-EDX

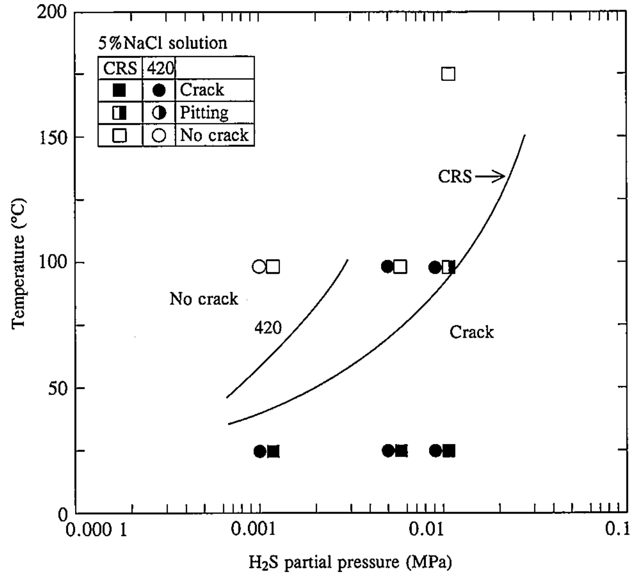
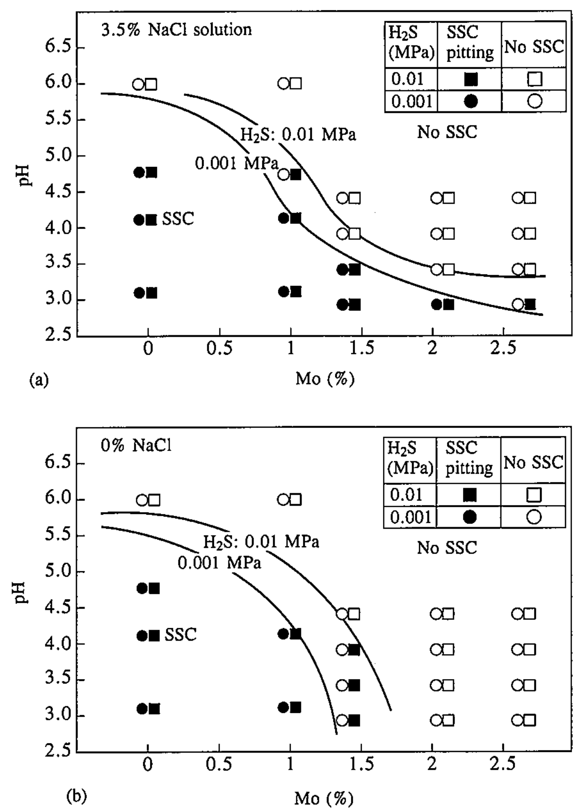


Fig. 6 Effects of H_2S partial pressure and temperature on cracking in sour environments (four-point V-notch bending under 100% yield stress in a 5% NaCl solution under 4 MPa of CO_2 for 336 hours)



(a) In "formation" water containing 3.5% NaCl; (b) In "condensed" water containing no NaCl (four-point V-notch bending under 100% yield stress and 4 MPa of CO_2 for 336 hours)

Fig. 7 Effect of molybdenum on resistance to sulfide stress corrosion is the cause of cracking near room temperature. **Fig. 7** shows the effects of molybdenum on sulfide stress cracking in water containing Cl^- (equivalent to formation water), and in water containing no Cl^- (equivalent to condensed water). From this figure, it is clear that as the molybdenum content increases, no sulfide stress cracking tends to occur in a wider range of environmental conditions. In particular, 1.5% or more of molybdenum is effective in preventing this type of cracking. However, too much added molybdenum will cause ferrite to form, degrading the resistance to sulfide stress cracking[9]. Therefore, it will be necessary to add other alloying elements to compensate for this unfavorable behavior.

2.3 Material design for highly corrosion- and sour-resistant 13%Cr steel

The addition of copper and nickel to 12%Cr steel may yield high CO_2-corrosion resistance. The addition of molybdenum is necessary, depending on the partial pressure of hydrogen sulfide in the actual environment. In this case, as mentioned above, an adequate amount of molybdenum is important in controlling the formation of ferrite. The seamless steel pipe rolling process generally used for the production of OCTG requires high hot workability ; in order to realize this, the formation of ferrite must be suppressed at the reheating temperature of the material before rolling. **Fig. 8** shows the relationship between the formation of ferrite and the modified amount of alloying elements, which is known as the phase stability index (I_{ps}). For coefficient values of -9.4 or larger, ferrite does not form. Based on this relationship, **Table 2** gives the chemical composition of the major components of some types of highly corrosion- and sour-resistant 13%Cr steel.

3. Properties of Highly Corrosion- and Sour-Resistant 13%Cr Steel

After rolling to form a seamless pipe of highly corrosion- and sour-resistant 13%Cr steel for OCTG, it is necessary to temper the pipe to obtain the required strength. The developed OCTG steels are highly hot-workable and provide satisfactory surface

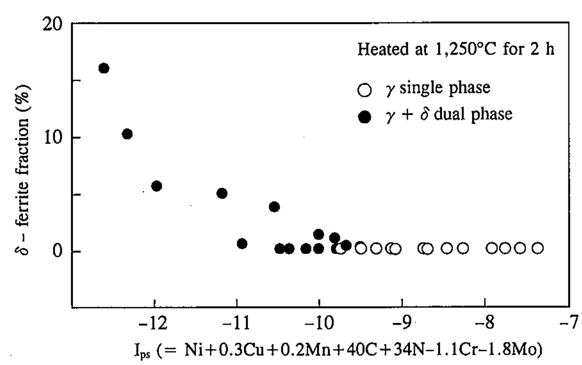


Fig. 8 Effect of the phase stability index on the formation of ferrite at 1,250°C

Table 2 Major chemical compositions of 13%Cr steel (mass %)

	C	Cr	Mo	Ni	Cu	N
NT-CRS	0.03	12.7	1.43	4.54	1.51	0.041
NT-CRSS	0.02	12.3	2.03	5.80	1.48	0.015
API (420)	0.20	12.7	—	0.13	—	0.030

Table 3 Strength of 13%Cr steel (in MPa (ksi))

	Specification			Measured	
	Grade	YS	TS	YS	TS
NT-CRS-95	C95	655-758(95-110)	>723(105)	709(103)	875(127)
NT-CRSS-110	C110	758-861(110-125)	>827(120)	821(119)	929(135)
API	L80	551-655(80-95)	>655(95)	590(86)	774(112)

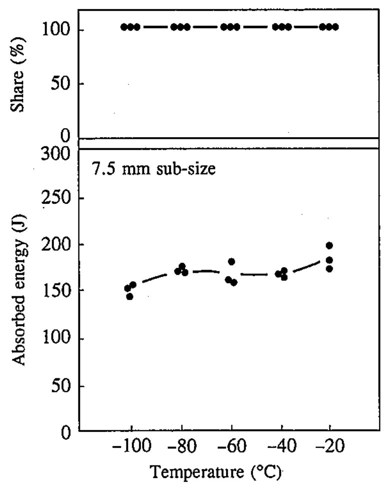


Fig. 9 Results of a V-notch Charpy test for NT-CRS with a sub-size of 7.5 mm in the L-direction

smoothness. 13%Cr OCTG of API specifications are L80 in grade, while the developed steels are C95 and C110 (where the number designates the specified minimum yield strength in ksi; 1 ksi = 6.89 MPa). **Table 3** shows the specified and typical strengths of each type of steel. From the results of the V-notch Charpy impact test shown in **Fig. 9**, it can be seen that one of our materials is excellent in terms of low-temperature toughness. As seen in **Fig. 10**, its yield strength is slightly dependent on temperature. The strength decreases by no more than 10% from room temperature to that in an oil well.

Fig. 11 shows the dependence of the corrosion rate on temperature and salt concentration for NT-CRS. For a CO_2 partial pressure as high as 4 MPa, the corrosion rate is satisfactorily low, 0.1 mm/year or less, even in an aggressive environment containing 20% NaCl below 150°C. In condensed water with no NaCl, this material is sufficiently corrosion-resistant up to 200°C. NT-CRSS behaves similarly. In comparison with these materials of our own development, 13%Cr steel with API specifications has inferior resistance to CO_2 corrosion: 0.1 mm/year or less below 100°C.

Fig. 12 shows the results of a constant-load sulfide stress cracking test for NT-CRSS-110 under different conditions of pH and H_2S partial pressure. In Cl^- containing water with a pH of 3.5 or lower, corrosion films of 13%Cr steel are unstable, resulting in severe corrosion. More hydrogen will then penetrate and cause hydrogen embrittlement cracking. At higher H_2S partial pressures, pitting corrosion occurs, lowering the pH at the bottom of the pit and producing cracking due to hydrogen embrittlement. At H_2S partial pressures below 0.01 MPa in high-temperature sour environments, no pitting occurs.

In condensed water with a pH of 3.0, no sulfide stress corrosion occurs at an H_2S partial pressure as high as 0.01 MPa. Condensed water does not contain components that have the

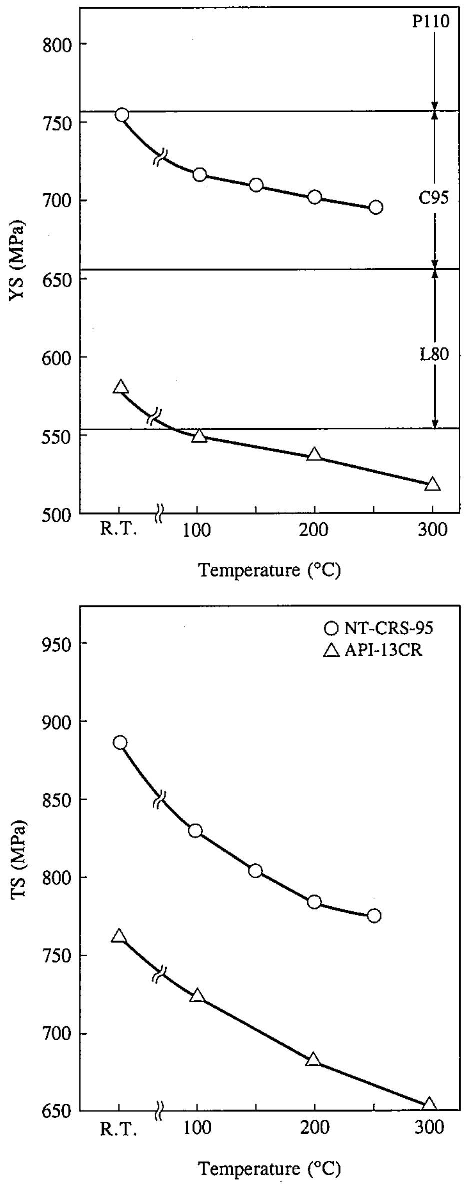


Fig. 10 Effect of temperature on strength for NT-CRS-95

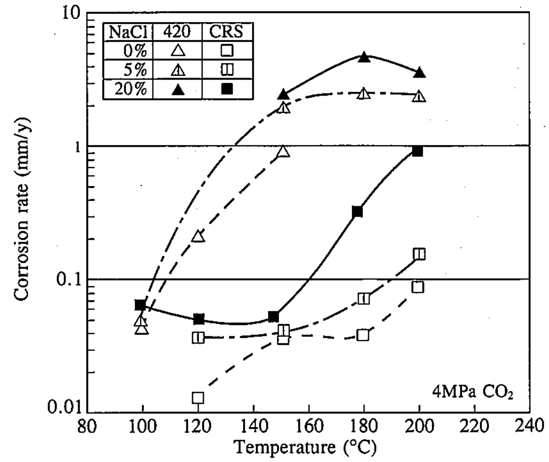


Fig. 11 Effect of temperature and NaCl concentration on corrosion rate under 4MPa CO_2 for 96 hours

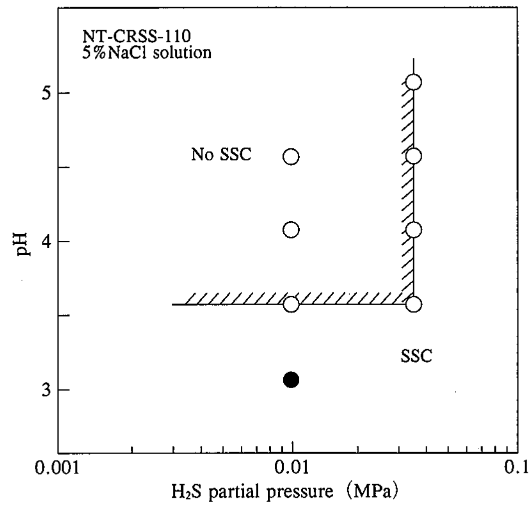


Fig. 12 Results of a constant-load sulfide stress cracking test for NT-CRSS-110 in environments in which pH values and H_2S partial pressure vary

buffering ability, and its pH value drops to approximately 3.0 through the dissolution of CO_2. Formation water contains mineral components, such as bicarbonates, that act as a buffer, and its pH is between 4 and 5. Accordingly, NT-CRSS-110 may be usable at oil and gas wells in environments in which use of duplex stainless steel has been considered suitable[10].

4. Advantages of using highly corrosion- and sour-resistant 13%Cr steel for OCTG

Oil-country tubular goods made of highly corrosion- and sour-resistant 13%Cr steel are excellent in terms of low-temperature toughness and sour resistance, and have high strength as well. The advantages of application of NT-CRSS-110 are briefly considered below. Tubing for OCTG is not supposed to be exposed to a high external pressure that causes collapse. Therefore, its wall may be thinner if it is made of a higher-strength material. Since the strength ratio of API-13%Cr OCTG to NT-CRSS-110 is 80/110 (=0.727), a wall approximately 30% thinner is feasible. The cost reduction due to the decrease in weight will make up for the increase in the material's cost. Furthermore, the lower corrosion rate will extend the life and contribute to the overall cost reduction. The most notable advantage of using NT-CRSS is that it is applicable in highly corrosive environments in which cold-drawn, duplex stainless steel has been considered the only candidate for use. Note that the latter type of stainless steel is extremely expensive.

5. Conclusions

Highly corrosion- and sour-resistant 13%Cr steel for OCTG has been developed. The characteristics of this material are as follows:

(1) The combined addition of copper and nickel not only helps maintain the martensitic structure, but is greatly effective in increasing CO_2-corrosion resistance.

(2) Increased CO_2-corrosion resistance through the combined

addition of copper and nickel may be due to an amorphous corrosion film and to the formation of a copper-enriched layer immediately under the film.

(3) The addition of molybdenum by 1.5% or more improves resistance to sulfide stress cracking.

(4) The developed 13%Cr steel , which is alloyed with copper, nickel, and molybdenum, is a high-strength and high-toughness steel with high CO_2-corrosion- and sour-resistance. This steel is applicable in environments in which duplex stainless steel is considered usable.

References

1) NACE International Publication 1F196 : "Survey of CRA Tubular Usage". NACE International, 1996.
2) Kermani, M. B., Weighill, G., Penslington, T., Elliot, G. : Corrosion 95. Paper No. 96, NACE International, 1995.
3) Tamaki, A. : Corrosion 89. Paper No. 469, NACE, 1989
4) Miyasaka, A., Ogawa, H. : Corrosion 90. Paper No. 67, NACE, 1990.
5) Hashizume, S. Takaoka, T., Minami, Y., Ishizawa, Y. : Corrosion 92. Paper No. 54, NACE, 1992.
6) Ueda, M., Kushida, T., Kondo, K., Kudo, T. : Corrosion 92. Paper No. 55, NACE, 1992.
7) Sugiyama, M., Hara, T., Asahi, H. : to be published in Transactions of the Japan Institute of Metals
8) Hashimoto, K., Masumoto, T. : Materials Science and Engineering. 23, p285, 1976.
9) Hara, T., Asahi, H.: CAMP-ISIJ. 9, 1392 (1996)
10) Denpo, K., Miyasaka, A., Ogawa, H. : The Second NACE International Symposium. 1989