Martensitic Stainless Steel Seamless Pipe for Linepipe†

MIYATA Yukio[*1] KIMURA Mitsuo[*2] KOSEKI Tomoya[*3]

Abstract:

A martensitic stainless steel seamless pipe for linepipe application, KL-HP12CR, has been developed with good weldability, mechanical properties and corrosion resistance. Weldability is improved by the reduction of both C and N content. C reduction is also effective to the improvement of CO_2 corrosion resistance achieving the corrosion rate less than 0.127 mm/y under the CO_2 environment at 160°C and 2.0 MPa. It can be applied under the H_2S environment at pH4.0 and 0.001 MPa, since the resistance to sulfide stress cracking (SSC) is improved by Mo addition. The pipe has X80-grade strength and sufficient low temperature toughness for the practical use as a linepipe. Post weld heat treatment (PWHT) in a few minutes, the reduction of C content and addition of Ti are effective to prevent intergranular stress corrosion cracking (IGSCC) at the heat affected zone. Further application of the pipe is expected for the transportation of product fluid with corrosive gas such as CO_2, as an economical material with low life cycle cost.

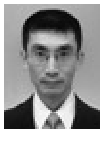
1. Introduction

Due to increasing concern about the depletion of oil resources, oil and gas wells are being operated at ever-higher temperatures and pressures, and the production fluid generally contains CO_2, making it more corrosive. As a result, it is important to prevent CO_2 corrosion for the pipelines called flowlines and gatheringlines which transport the fluid before eliminating corrosive substances and water. Furthermore, the fluid often contains trace amounts of H_2S, so measures to prevent sulfide stress cracking (SSC) are also needed. Under such corrosive environments, the conventional method of preventing corrosion is to use carbon steels as the linepipe material and to inject an inhibitor into the fluid[1]. Corrosion prevention by an inhibitor, however, increases the operating cost particularly in offshore pipelines, so inhibitors are being used less, particularly in view of the recent focus on life cycle cost. Another reason for not using inhibitors is concern about pollution caused by accidental leakage. Therefore, there is demand for an economical material for linepipes that does not require an inhibitor. Existing corrosion resistant alloys for linepipes include duplex stainless steels[2], but these have drawbacks of very high material cost, difficulty in controlling the welding heat input, and excess anticorrosion action in many cases, even though the steels have excellent corrosion resistance.

In comparison, martensitic stainless steels generally show poor weldability, and require preheating and long post welding heat treatment (PWHT). Consequently, martensitic stainless steels are rarely used for pipelines in view of pipe-laying efficiency. Nevertheless, martensitic stainless steels have an appropriate level of CO_2 corrosion resistance, and are inexpensive compared with duplex stainless steels.

With this background, JFE Steel has used its extensive steel-making technologies to improve the weldability of martensitic stainless steels by decreasing the C and N contents, and by controlling the added alloying elements, thus developing a martensitic stainless steel seamless pipe for linepipes offering excellent weldability and corrosion resistance. This paper describes the development and characteristics of the steel pipe.

† Originally published in *JFE GIHO* No. 9 (Aug 2005), p. 13–18



*1 Senior Researcher Manager,
Tubular Products & Casting Res. Dept.,
Steel Res. Lab.,
JFE Steel

*2 Dr. Eng.,
Senior Researcher Deputy General Manager,
Tubular Products & Casting Res. Dept.,
Steel Res. Lab.,
JFE Steel

*3 Staff Deputy General Manager,
Products Service & Development Sec,
Products Service & Development Dept.,
Chita Works,
JFE Steel

Table 1 Results of y-groove cracking tests for low C + N martensitic stainless steels

Material		Preheating temperature		
		30°C	70°C	100°C
0.03C-0.01N	11Cr-1.0Ni-0.5Cu	Crack	Crack	Crack
0.01C-0.03N	11Cr-1.0Ni-0.5Cu	Crack	Crack	Crack
0.01C-0.01N	12Cr-1.0Ni-0.5Cu	No crack	No crack	No crack
0.01C-0.01N	12Cr-1.0Ni-1.0Cu	No crack	No crack	No crack
0.01C-0.01N	12Cr-2.0Ni-0.5Cu	No crack	No crack	No crack

Plate thickness: 15 mm
Welding material: Type 410H SMAW, 4ϕ (Diffusible hydrogen; 4.28 cm^3/100 g)
Welding conditions: Current; 160 A, Voltage; 24–26 V, Speed; 150 mm/min
Test conditions: Room temperature; 30°C, Humidity; 60%RH

2. Progress of Development

2.1 Target Characteristics

The target characteristics for development were as listed below.

(1) Weldability: Welding without preheating
(2) HAZ maximum hardness: HV350 or smaller
(3) CO_2 corrosion resistance: Resistance to a corrosive environment of 5% NaCl, CO_2 partial pressure of 3.0 MPa, 150°C
(4) SSC resistance: Resistance to an environment of 5% NaCl, 0.001 MPa H_2S, pH4.0
(5) Strength: X80 grade (550 MPa or higher yield strength (YS))
(6) Low temperature toughness: 100 J or larger Charpy absorbed energy at −40°C

2.2 Composition Design Concept

The composition of the steel pipe was designed considering the effects of alloying elements in the martensitic stainless steel on the weldability, corrosion resistance, hot-workability, and other characteristics. Specifically, the improvement of weldability was studied based on a composition of KO-13Cr (0.20C-13Cr-0.03N) for OCTG for a CO_2 environment, while maintaining equivalent corrosion resistance in the base material. From the results of the study concerning the effect of chemical composition on the hot-workability and other characteristics mentioned below, the composition of the steel was ultimately determined to be 12Cr-5Ni-2Mo-0.01N with 0.015% or less C.

2.2.1 Weldability

Since welding of martensitic stainless steels tends to cause weld cracking, preheating is applied to prevent cracking in practice. Weld cracking is thought to be caused by hydrogen which is dissolved in the weld metal and the heat affected zone (HAZ) of the weld, and by the hardening and residual stress induced by the martensitic transformation at the HAZ[3]. Accordingly, an effective means to prevent weld cracking, from the material side, is to decrease the C and N contents and hence suppress the hardening induced by the martensitic transformation. **Table 1** shows the result of the y-groove weld cracking test on low C + N martensitic stainless steels[4]. Steels containing 0.03% of C or N suffered weld cracking, while steels in which both the C and N contents were reduced to 0.01% did not suffer weld cracking even at the preheating temperature of 30°C. This result suggests that welding without preheating is possible only if the C and N contents are decreased to 0.01%. JFE Steel has the steel making technology to produce steels with such low C and N level.

2.2.2 CO_2 corrosion resistance

Reduction in the C content also improves the CO_2 corrosion resistance. **Figure 1** shows the result of CO_2 corrosion tests for martensitic stainless steels having various chemical compositions[4]. The corrosion rates given in the figure show good correlation with the CO_2 corrosion indexes defined by Cr − 10C + 2Ni. The figure shows that increasing the Cr or Ni content and decreasing the C content improve the CO_2 corrosion resistance. This improvement is presumably because the reduction in the C content decreases the amount of Cr carbide, thereby increasing the amount of dissolved Cr which effectively prevents corrosion.

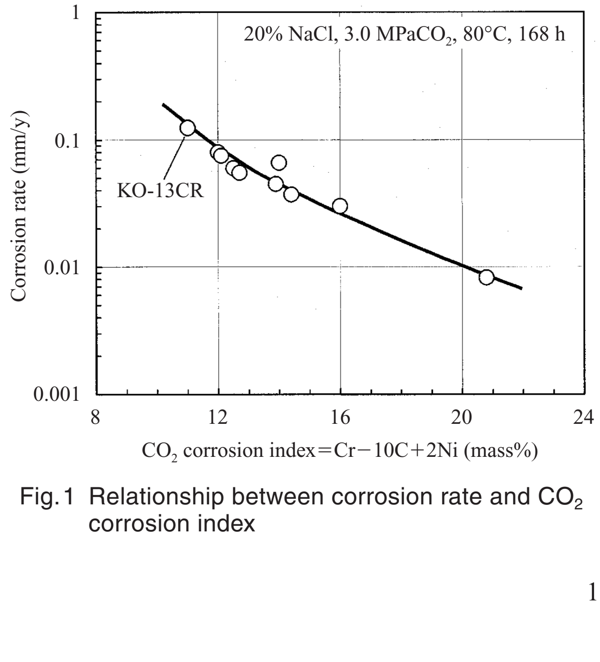


Fig. 1 Relationship between corrosion rate and CO_2 corrosion index

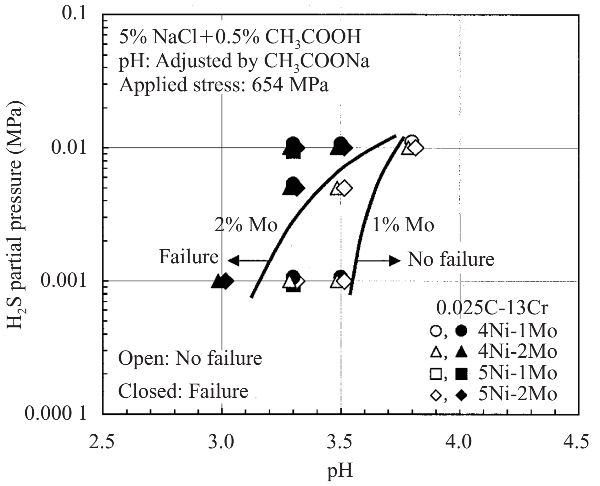


Fig. 2 Effects of Ni and Mo on SSC resistance of 0.025C-13Cr steels

2.2.3 SSC resistance

Since SSC in martensitic stainless steels begins from pitting, improving the resistance to pitting improves the SSC resistance. The alloying element molybdenum is known to improve resistance to pitting. **Figure 2** shows the effects of Ni and Mo on the SSC resistance[5]. As can be seen, an increase in the Ni content from 4% to 5% makes no difference to the test results, while increasing the Mo content from 1% to 2% moves the boundary of SSC occurrence toward low pH and high H_2S partial pressure, or to severer environments. This phenomenon suggests that adding 1% Mo is sufficient to ensure SSC resistance under the environment of 5% NaCl, 0.001 MPa H_2S, pH4.0, which is the development target. Since, however, the resistance to pitting at the HAZ may become lower than that of the base material[6], 2% Mo was added to the developed material to secure stable resistance to pitting.

Table 2 Chemical compositions of base metal and welding wires for girth welding

(mass%)

Material	C	Cr	Ni	Mo	N
Base metal	<0.015	12.0	5.1	2.0	0.01
GTAW wire	0.01	25.3	9.5	4.0	0.27
GMAW wire	0.02	25.1	9.6	4.0	0.27

3. Characteristics of Developed Steel Pipe

This capter describes the characteristics of the developed steel, focusing on the results of tests on a seamless steel pipe of 273 mm in outer diameter and 12.7 mm in wall thickness. A seamless steel pipe was manufactured with the steel having the chemical composition shown in **Table 2**, which was then treated by quenching and tempering to obtain an X80 grade product. With this product, and using 25Cr duplex stainless steel as welding material, a girth welded joint was prepared by applying GTAW to the first pass, and GMAW to the second pass. The chemical compositions of the respective welding materials are given in Table 2, and the welding conditions are given in **Table 3**. No preheating or PWHT was given.

3.1 Mechanical Properties

Table 4 shows the results of tensile tests. The strength of X80 grade was assured, and the welded joint fractured in the base metal, thus showing favorable characteristics. **Figure 3** shows the hardness distribution of a cross section of the welded joint. As shown, the

Table 4 Result of tensile tests for the welded joint and base metal

Material	YS (MPa)	TS (MPa)	El (%)	Fracture position
Welded joint	–	856	30	Base metal
Base metal	634	827	34	–

YS: Yield strength, TS: Tensile strength, El: Elongation

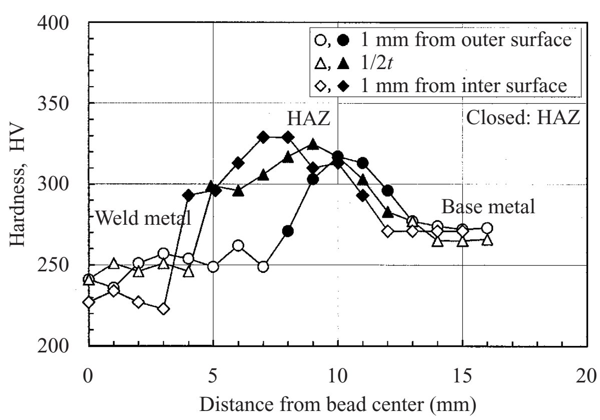


Fig. 3 Hardness distribution in the welding joint

Table 3 Girth welding conditions

Pass	Welding method	Welding material	Welding position	Shielding gas	Interpass temperature (°C)	Current (A)	Voltage (V)	Speed (mm/min)	Heat input (kJ/mm)
1	GTAW	2.0 mmϕ	5G	100% Ar	<25	148	13.5	44	2.7
2	GMAW	1.2 mmϕ	5G	100% Ar	25	145	15.0	75	1.7

5G: Horizontal fixed position

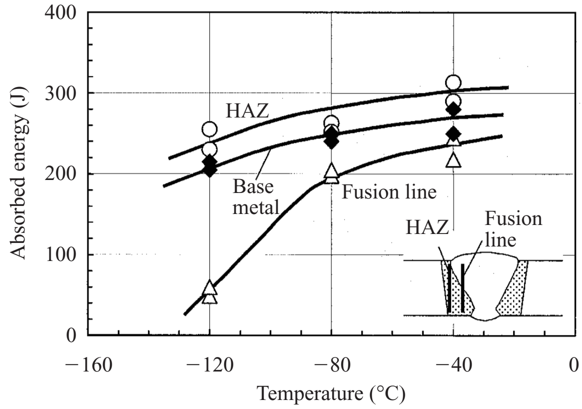


Fig. 4 Relationship between Charpy absorbed energy and temperature

maximum hardness at the HAZ is about HV330, which satisfies the target value of HV350 or smaller. **Figure 4** shows the result of Charpy tests for the welded joint. The attained absorbed energy is about 200 J even at −80°C as well as at −40°C, which proves the excellent low temperature toughness of the developed steel.

3.2 CO_2 Corrosion Resistance

The CO_2 corrosion resistance was evaluated by measuring weight loss in an immersion test under an environment of high temperature and high CO_2 partial pressure. **Figure 5** shows the test results plotted against the test temperature and CO_2 partial pressure. The numeral given to every plot is the corrosion rate. Assuming that a corrosion rate of 0.127 mm/y (5 mpy) is generally acceptable as a standard, the developed material is judged to be suitable under an environment of 160°C and 2.0 MPa CO_2.

3.3 SSC Resistance

The SSC resistance at the welded joint was evaluated by a constant load tensile SSC test. The solution was an aqueous mixture of 5% or 10% NaCl with 0.5% CH_3COOH, and the pH was adjusted in the range from 3.5 to 5.0 using CH_3COONa. The test gas was a mixture of H_2S at partial pressures from 0.001 to 0.007 MPa with the balance of CO_2 to make the total pressure 0.1 MPa. The applied stress was 567 MPa, which is equivalent to 90% of the YS of the base material. **Figure 6** shows the test results plotted against the pH and H_2S partial pressure. As can be seen, although SSC occurred at the HAZ at pH3.5, no SSC occurred under the target environment of pH4.0 and H_2S partial pressure of 0.001 MPa.

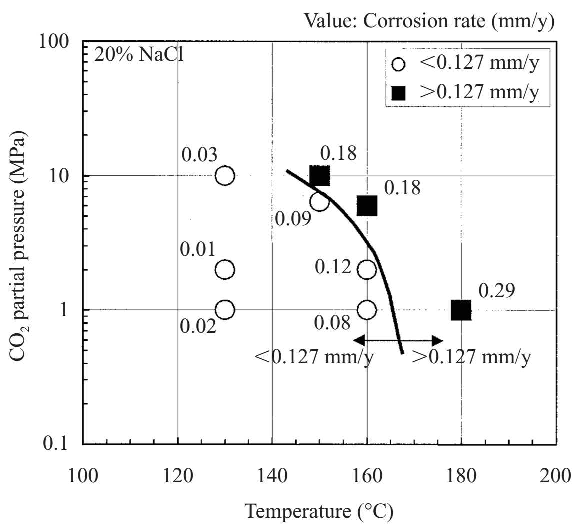


Fig. 5 CO_2 corrosion test results of the base metal

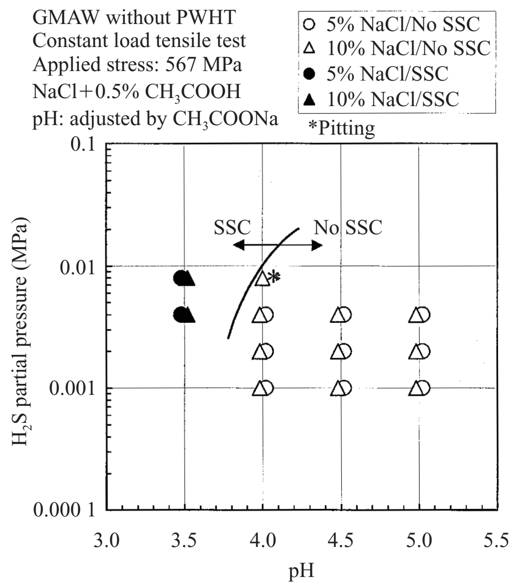


Fig. 6 SSC test results of the welded joint

4. Intergranular Stress Corrosion Cracking at Girth Weld

According to a recent paper[7)], a laboratory study found that intergranular stress corrosion cracking (IGSCC) occurred at the girth weld of a sample having the similar compositions to the developed steel, under a high temperature CO_2 environment. In addition, another paper reported that gas leakage occurred due to IGSCC in an actual pipeline using a material, free from Mo, having the similar compositions to the developed steel[8)].

Some results of our investigations on the mechanism of this phenomenon and on preventive measures[9)] are described below.

4.1 Mechanism of IGSCC Generation

To identify the effect of welding conditions on the sensitization behavior, SCC tests were conducted using samples which were subjected to two passes of simulated welding thermal cycles. For conducting the tests under severer conditions, the corrosive environment was brought to pH2.0, and the U-bend test method, which

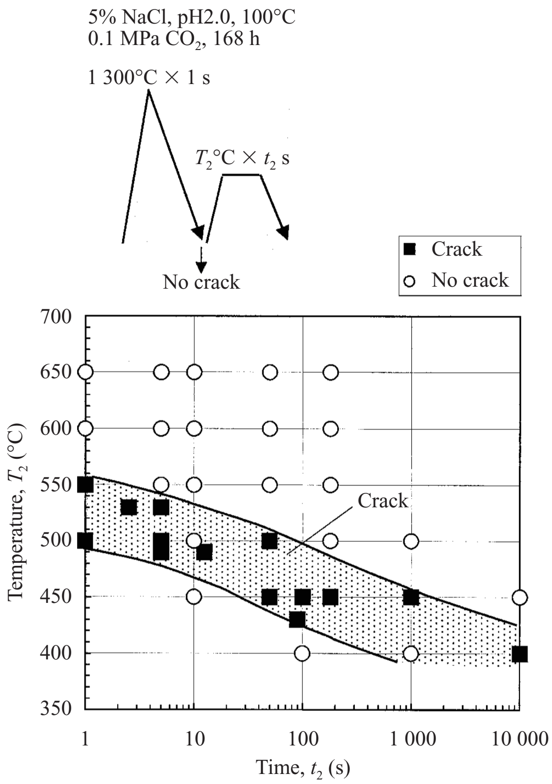


Fig.7 Results of U-bend SCC tests for simulated HAZ

can apply larger strains, was used. **Figure 7** gives plots of SCC test results under the second pass condition. The figure shows that some of samples with the second pass thermal cycle suffered cracks. The samples which were subjected only to the first pass did not suffer cracks.

These results suggest that the cause of IGSCC is as follows. When carbon, which is dissolved under high temperature heat cycles, precipitates during the subsequent heat cycle as carbide at the grain boundary of prior-austenite, a Cr-depleted zone forms in the vicinity of the carbide at the grain boundary, thereby sensitizing the material.

4.2 Method to Prevent IGSCC

Since IGSCC is presumably caused by the Cr-depletion zone, potential methods to prevent IGSCC include performing PWHT to diffuse Cr for recovering from Cr depletion, and establishing very low C content and to add Ti for suppressing the precipitation of Cr carbide.

To confirm the effect of PWHT, a material containing 100 ppm of C was sensitized by two passes of heat cycles, followed by a third pass of heat cycles under various conditions. Thus prepared samples were evaluated by the U-bend SCC test similar to that described above. The results are shown in **Fig. 8**. As shown, the sensitized samples did not suffer cracks after heating to a temperature range from 550°C to 700°C for several minutes. This effect was probably because the heat treatment satisfactorily enhances Cr diffusion, thus diminishing the Cr-depleted zone. IGSCC will be prevented by applying PWHT for a short time, within several minutes, which does not significantly hinder the efficiency of practical pipe-laying.

To confirm the effect of reduction in C content and addition of Ti, materials with various C and Ti contents were evaluated. With the samples treated by a heat cycle of 450°C for 1 000 s, a condition that easily induces sensitization, a U-bend SCC test similar to that applied before was performed. As a severer test condition, samples which had a notch of stress concentration factor 4 at the U-bend section were separately tested. **Figure 9**

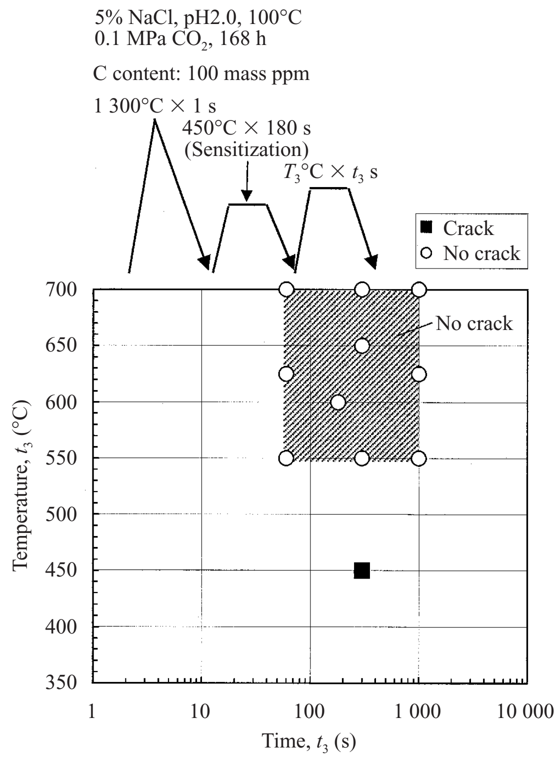


Fig.8 Effects of thermal cycle conditions after sensitization on SCC behavior

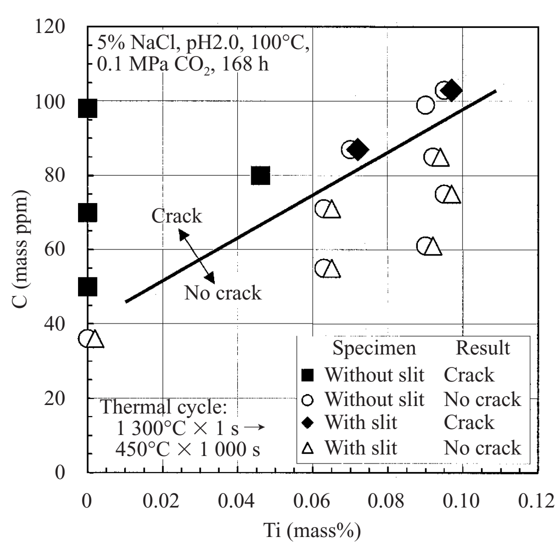


Fig.9 Effects of C and Ti on SCC test results

shows the SCC test results arranged by the C and Ti contents. The figure shows that reduction in C content and addition of Ti suppress the cracks. This is presumably because the suppression of dissolved C during welding and the conversion to Ti carbide suppress the precipitation of Cr carbide which causes Cr depletion. Therefore, reduction in C content and addition of Ti are effective ways of improving the resistance of the material to IGSCC.

5. Conclusion

This paper described the development and characteristics of a seamless steel pipe made of martensitic stainless steel for linepipes, having improved weldability. The weldability of the steel pipe has been improved by decreasing the C and N contents, and the excellent mechanical properties and corrosion resistance have been achieved by the optimization of other alloying elements.

The major characteristics of the steel are given below.

(1) The steel has excellent weldability free from weld cracking even without preheating.

(2) The steel has X80 grade strength, and low temperature toughness of 200 J or larger Charpy absorbed energy at −40°C.

(3) The steel has excellent CO_2 corrosion resistance, giving 0.127 mm/y or smaller corrosion rate under an environment of 160°C and 2.0 MPa CO_2.

(4) The steel has excellent SSC resistance under an environment of pH4.0 and H_2S partial pressure of 0.001 MPa.

(5) Intergranular stress corrosion cracking is prevented by a short period (several minutes) of PWHT. Reduction in C content and addition of Ti are effective to improve the IGSCC resistance of the material.

Since the material has excellent weldability, mechanical properties, and corrosion resistance, its application to pipelines transporting production fluid containing corrosive gases such as CO_2 is expected to be expanded as an economical material with a low life cycle cost.

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