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Development for Material and Application Technique of Stainless Steel Line Pipes

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Abstract

The stainless steel line pipe materials of Nippon Steel & Sumitomo Metal Corporation were introduced especially for its chemical contents, physical properties and corrosion resistance. The conventional stainless steel line pipes can be categorized into martensitic grade and duplex grade. These materials show the corrosion resistance in the condition containing carbon dioxide, chloride ion and little amount of hydrogen sulfide. On the other hand, it had been reported that heat affected zone of super martensitic stainless steel welded joints had susceptibility of inter granular stress corrosion cracking (IGSCC) in CO_2 environment at elevated temperature. Based on the research for the mechanism, it was cleared that post weld heat treatment (PWHT) was effective to prevent the material from IGSCC. Then, the new duplex stainless steel DP25U was introduced as cost-effective material. The new material was characterized with both showing SSC and elevated temperature SCC resistance without PWHT.

1. Introduction

Oil and gas that come up to the wellhead from the bottom hole through the tubing are transported to the petroleum refinery system after the treatment at a separator and gas dehydrator. Some of the line pipes for transportation from the wellhead to the gathering station are called gathering lines or flowline, and the line pipes from the gathering station to the petroleum refinery system are called trunk lines. Furthermore, the pipe for transporting the production fluid from the seabed to a facility at the sea level is called a riser pipe (**Fig. 1**). As corrosion resistance is required to these pipes in addition to mechanical strength and weldability, countermeasures to corrosion such as lining, coating, electrochemical corrosion protection, inhibiters and so on are applied. However, considering environmental effects, maintenance problems, and the difficulty in using the abovementioned countermeasures, corrosion resistant alloy (CRA) line pipes are mainly used.

For a CO_2 free environment, line pipes of carbon steel and low alloy steel are used with attention paid to the susceptibilities of hydrogen induced cracking (HIC), sulfide stress cracking (SSC) and

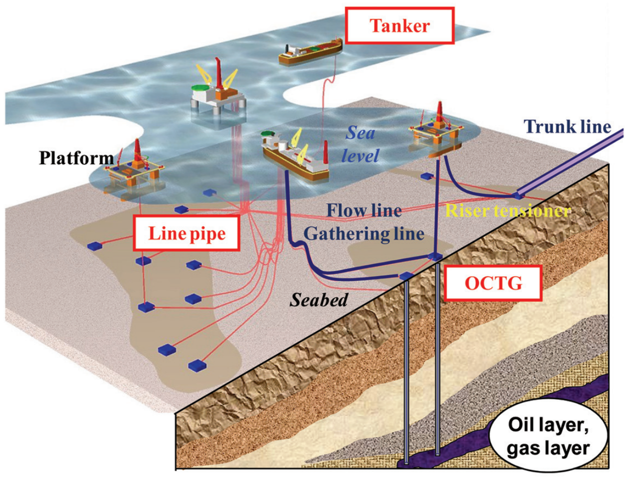

Fig. 1 Diagram of production and transportation for oil and natural gas

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stress oriented hydrogen induced cracking (SOHIC). On the other hand, where CO_2 corrosion is harsh, CRA line pipes are used. The stainless steel line pipes are categorized basically into two types: the first one is the so-called solid line pipe comprising a single material; the other is a clad or lined pipe comprising a two-layer structure having an internal pipe and external pipe. With regard to the clad and lined pipes, the corrosion resistance on the inner side is secured by using austenitic stainless steel such as type 316L or high nickel alloy such as Alloy625, while carbon steel is used for the external layer. The characteristic features of clad and lined pipes are that they are producible at lower cost compared with the solid CRA line pipe having equivalent performance; however, the solid CRA is superior for its shorter lead time in production.

Nippon Steel & Sumitomo Metal Corporation supplies solid seamless line pipes of CRA, which are usable in CO_2, Cl^- and H_2S environments. Its product lineup is introduced hereunder together with the problem and the countermeasure for stress corrosion cracking of Super 13Cr steel (13CrS) in a Cl^- environment. Regarding solid line pipes that need girth-welding process while being laid, it was reported that weldable super martensitic stainless steels were susceptible to stress corrosion cracking (SCC) at elevated temperatures. A new duplex stainless steel, which can be applicable even with as-welded, has been developed having sufficient resistance to SCC at elevated temperatures.

2. Product Lineup of Stainless Steel for Line Pipes

CRA line pipes of Nippon steel & Sumitomo Metal are practically used for flow line applications in CO_2, H_2S and Cl^- environments. The grades and characteristics of such products are shown hereunder.

Regarding the grade of steel, product line up comprises conventional steels having three chemical compositions. Moreover, a new stainless steel DP25U for line pipe use has been developed. The progress of the development and steel characteristics will be described in section 4. The three chemical compositions of conventional steels are introduced hereunder. **Table 1** shows the chemical compositions of stainless steels for line pipes. First of all materials, DP8 (UNS S31803) was put into practical use in 1980s as weldable duplex stainless steel line pipes; following this in 1990s, super duplex stainless steel DP3W (UNS S39274) having improved seawater corrosion resistance was developed and put into practical use.

On the other hand, the conventional 13Cr martensitic stainless steel OCTG grade (AISI420) have been practically used for CO_2 environment. It is known, however, that the 13Cr stainless steels are susceptible to SSC in slightly sour conditions. Therefore, Super 13Cr steel that has SSC resistance, as a consequence of alloying molybdenum, with protective surface film was developed.[1] Furthermore, in 1990s, weldable super 13Cr martensitic stainless steels, which were improved for weldability by decreasing carbon content, have been used for slightly sour conditions at elevated temperatures.[2, 3] Mechanical properties of the CRA line pipes are shown in **Table 2**. 13CrS has a yield strength of 80ksi grade, DP8 has a yield strength of 65ksi grade, and DP3W has a yield strength of 80ksi grade.

Regarding corrosion resistance, the limit of the corrosion resistance of CRA line pipes is shown in **Fig. 2** related to the parameters of temperature and H_2S partial pressure, enabling selection of optimum material for the environment.

3. Stress Corrosion Cracking of Super 13Cr Steel for Line Pipe Use and Measures for Stress Corrosion Cracking Mitigation

3.1 Stress corrosion cracking at welds of Super 13Cr steel for line pipe use in a high temperature environment.

Owing to its corrosion resistance, workability in construction, and significant savings in the life cycle cost, demand for Super 13Cr steel for line pipe use had increased. However, during early 2000s, susceptibility to stress corrosion cracking at the heat affected zone (HAZ) of welds in high temperature CO_2 environments was reported.[4-6] Following phenomena have been clarified.

- Stress corrosion cracking occurs in HAZ of GMAW (gas metal arc welded) girth welds of a pipe.
- The cracking is classified as intergranular stress corrosion cracking (IGSCC) that propagates along the former austenite

Table 1 Chemical compositions of CRA line pipes

Material	Chemical composition (mass%)								
	C	Cr	Ni	Mo	W	Cu	Ti	N	PREW *
13CrS (UNS S41525)	Max. 0.03	11.5-13.5	4.5-7.0	2.0-3.0	-	-	0.01-0.50	-	
DP8 (UNS S31803)	Max. 0.03	21.0-23.0	4.5-6.5	2.5-3.5	-	-	-	0.08-0.20	Min. 34
DP3W (UNS S39274)	Max. 0.03	24.0-26.0	6.0-8.0	2.5-3.5	1.5-2.5	0.20-0.80	-	0.24-0.32	Min. 40

* Cr + 3.3 (Mo + 0.5W) + 16N

Table 2 Mechanical properties of CRA line pipes

	Temperature (˚C)	Yield strength (MPa)	Tensile strength (MPa)	Hardness (HV)
13CrS (UNS S41525)	25	Min. 550	Min. 750	Max. 310HV
	100	Min. 540	Min. 690	-
DP8 (UNS S31803)	25	Min. 450	Min. 640	Max. 28HRC
	100	Min. 380	Min. 575	-
DP3W (UNS S39274)	25	Min. 550	Min. 800	Max. 32HRC
	100	Min. 480	Min. 725	-

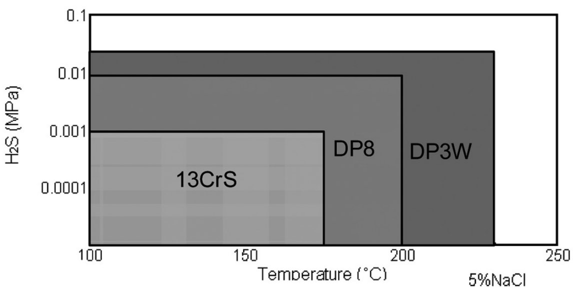


Fig. 2 Material selection guidelines for environments

Table 3 SCC test results of S13CrS
(4 point bend tests: 25%NaCl, 10 bar CO_2, 110°C, 720 h)

No.	Welding	Wire	PWHT	Applied stress (%) AYS	SCC
1	GMAW (Cu backing)	Super duplex	No	100	3/3
2			No	90	3/3
3			650°C × 5 min.	100	0/3

grain boundaries. The crack does not penetrate through the duplex stainless steel weld metal.

- Mechanical removal of the surface scale formed during the welding process and application of post welding heat treatment (PWHT) are effective in improving crack susceptibility.
- The material in which the crack occurred at actual field was the lean grade 13Cr steel (Mo free). However, according to the result of the laboratory test conducted later, as shown in **Table 3**, even the grade containing Mo was susceptible to IGSCC in GMAW with cupper backing.[7, 8]

Thereafter, up to the latter half of 2000s, the oil and gas industry continued to conduct detailed research on the mechanism of SCC and its countermeasures.

3.2 Mechanism of stress corrosion cracking and its mitigation

The crack originated in the Cr-depletion zone at the grain boundaries in the vicinity of the surface oxidation in HAZ. The Cr-depletion zone has been considered to be a result of selective oxidization of Cr and the diffusion of Cr at the grain boundaries. While surface scale is formed in welding process, Cr is taken into the scale and dechromium layer is formed at the vicinity of the surface. Particularly, rate of diffusion of Cr is high at the former austenite grain boundaries, therefore, a Cr concentration profile is obtained as shown in **Fig. 3**. This Cr-depletion zone could be the cause of SCC.[8, 9] On the other hand, when PWHT is applied, Cr is supplied to the Cr-depletion zone which is recovered as shown in **Fig. 4**.[8, 9] Thus, PWHT eliminates initiation of the crack. In consistency with this mechanism, IGSCC was not observed at the four-point bend test specimens whose scale of the root pass was mechanically removed.[6]

Thereafter, regarding the crack propagation path, the mechanisms of two basic phenomena in high temperature HAZ have been proposed. These phenomena are explained in terms of Ti addition to the material.

For Ti free-Super 13Cr stainless steels, it is presumed that Cr-depletion zone is formed at the former austenite grain boundaries. This Cr-depletion zone in the vicinity of the carbide is considered to increase the IGSCC susceptibility. The carbide can precipitate at the former austenite grain boundary, in the subsequent welding heat cycle, next to the carbon solution in primary heat cycle at a high temperature. This understanding is supported by the fact that the lowering of C content of material and addition of Ti to improve the susceptibility of IGSCC.[10]

On the other hand, such significant carbides are not thought to precipitate in Super 13Cr steel containing Ti. Concerning that cause of cracking is different from that in the Ti-free type Super 13Cr steel, it was considered that free P that segregated at grain boundaries lowers the resistance to IGSCC. Namely, PWHT promotes diffusion of Mo to former austenite grain boundaries and forms P-containing Laves phase or another Mo-rich phase. Increase in Mo at former austenitic grain boundaries enhances corrosion resistance, while free P is taken into the Laves phase. Thus Super 13Cr steel

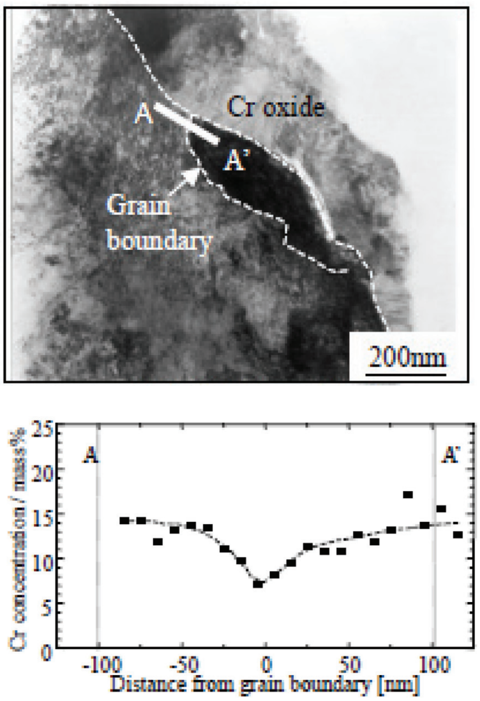


Fig. 3 TEM (transmission electron microscope) micrograph at the vicinity of surface oxide layer and results of line analysis around the grain boundary by EDS (energy dispersive spectroscopy) for as welded material

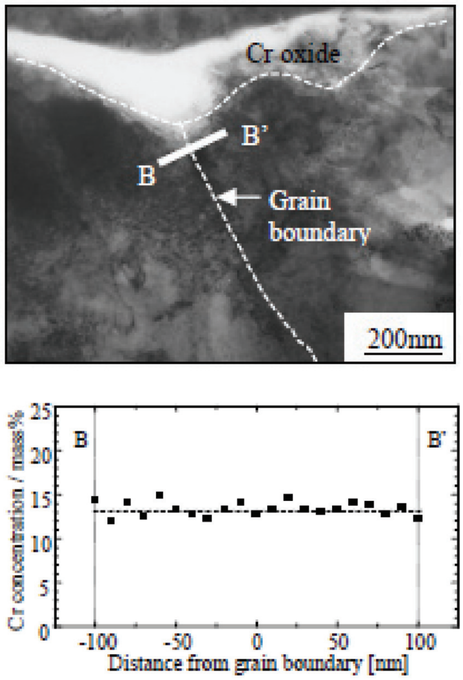


Fig. 4 TEM micrograph at the vicinity of surface oxide layer and results of line analysis around the grain boundary by EDS for PWHT material

containing Ti shows the sufficient IGSCC resistance. The following two facts support the above reasoning.

- As the result of the observation by a transmission electron microscope (TEM), enriched Mo enhanced by PWHT enriches at

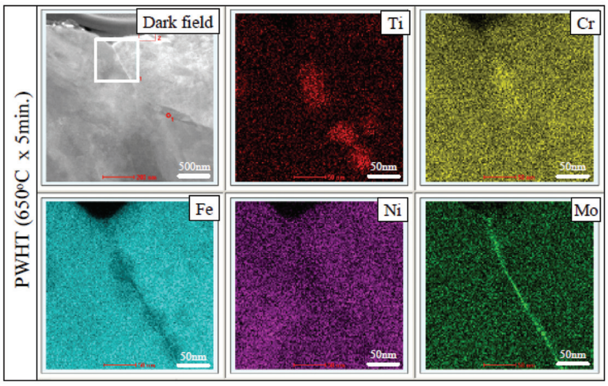


Fig. 5 Elemental distribution in the vicinity of surface at HAZ of PWHT material by STEM/EDS mapping

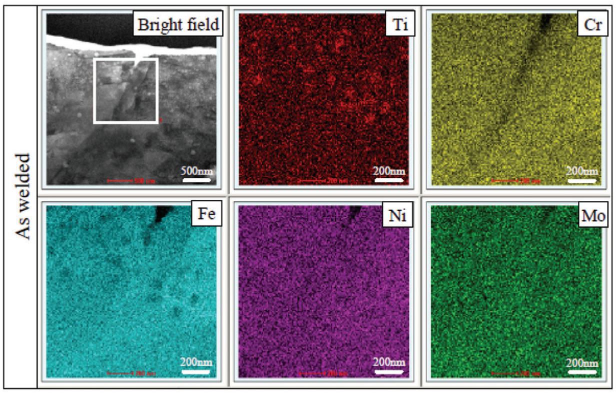


Fig. 6 Elemental distribution in the vicinity of surface at HAZ of as welded material by STEM (scanning transmission electron microscopy)/EDS mapping

former austenite grain boundaries, as shown in **Fig. 5**, while this is not observable in as-welded material, as shown in **Fig. 6**.[11)]

- Precipitation of the Laves phase where P is concentrated at grain boundaries after long time PWHT was identified.[12)]

From these results, it has been clarified that the appropriate post weld heat treatment (PWHT) is able to eliminate susceptibility by reducing crack initiation and propagation paths. Elucidation of the abovementioned mechanism and the establishment of application technologies have been jointly conducted with a user for CRA line pipes. As the result, the user released the report of IGSCC mechanism and countermeasures.[13)]

4. Development of New Type Duplex Stainless Steel DP25U

4.1 Objective of development and composition designing

For Super 13Cr steel line pipes, as mentioned in section 3, PWHT is effective in preventing stress corrosion cracking in welds. On the other hand, PWHT might be a negative factor in the efficiency of laying operations and the cost efficiency in some cases. Duplex stainless steels can be applicable in as-welded condition although that might have the problem of high capital expenditure.

To overcome these problems, the new duplex stainless steel DP25U was developed, which is applicable without PWHT and categorized to be of an intermediate grade between conventional duplex stainless steel and Super 13Cr steel.

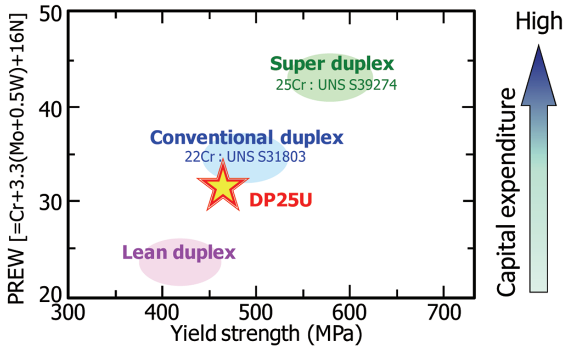


Fig. 7 Category of developed duplex stainless steel

For the designing material composition, at first, Cr content was increased from the level of Super 13Cr steel to skip the PWHT process and to stabilize the passivation film. Next, the existing duplex stainless steels of DP8 and DP3W contain Mo of more than 3 mass% to secure excellent corrosion resistance in an H_2S environment, as shown in Fig. 2. Reduction of the alloying cost, by decreasing the Mo content, was aimed at by limiting the application environment of DP25U to slightly sour environments. Furthermore, by adding Cu instead of Mo, securing corrosion resistance in an H_2S environment has also been achieved. On the basis of this designing concept, a laboratory test was conducted and the major composition of DP25U was determined as 25Cr–5Ni–1Mo–2.5Cu–0.18N.[14, 15)] Regarding the categorization in the whole duplex stainless steels, DP25U is, as shown in **Fig. 7**, categorized as the modified grade of the conventional duplex stainless steel rather than as a lean duplex steel with the composition of lowered Cr, Ni, and Mo contents and the increased Mn content.

4.2 Evaluating performance and determining applicability

Trial production of DP25U has already been conducted and its properties are introduced.

In the production process, final heat treatment for solution is applied after the pipe formation process. The mechanical properties and low temperature toughness are shown in **Figs. 8, 9**. DP25U has the yield strength of higher than 65ksi. Furthermore, DP25U has excellent toughness as it shows a high absorbed energy value at low temperatures. The corrosion resistance of the welded joint was investigated under the welding conditions shown in **Table 4** and assessed in comparison with the result of Super 13Cr steel.

At first, the result of evaluation for SCC susceptibility at high temperatures is shown in **Table 5**. This investigation was conducted by four-point bend test under the high Cl^- environment. The occurrence of SCC was not recognized for DP25U. Therefore, it has been made clear that DP25U shows SCC resistance at high temperatures without PWHT under the GMAW condition with copper backing.

Thereafter, regarding the assessment of SCC susceptibility in an H_2S environment, test conditions are shown in **Table 6**. The test was conducted in an H_2S environment at a temperature of 90 °C, where the duplex steel becomes most susceptible. The test conditions were set for the representative gas and oil environments as shown in Table 6.

The result of the test is shown in **Fig. 10** in the form of a map indicating recommendable environment with respect to pH and H_2S partial pressure. In the figure, the result of the test of the welded joints of Super 13Cr steel with PWHT applied is shown together with. SSC was not recognized in the welded joints of DP25U both in the oil condition and the gas condition even in the environmental

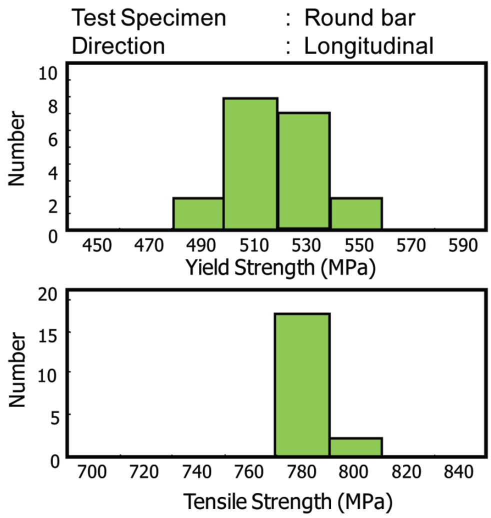


Fig. 8 Distribution for mechanical properties of developed material

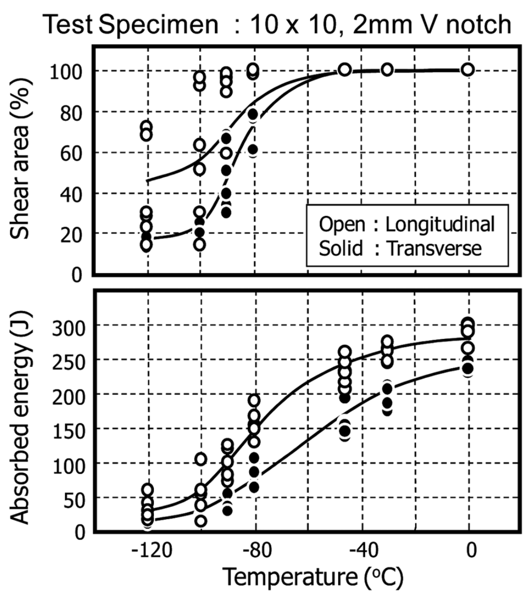


Fig. 9 Toughness of developed material

Table 4 Welding conditions for joints of DP25U

Welding process		Welding consumables	PWHT
GMAW (Cu backing)	1G	25%Cr duplex	No

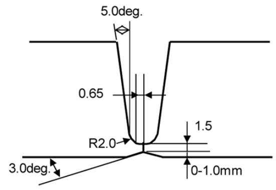
Process	PGMAW	Position: ASME 1G	
Joint design			
Preheat	None	Interpass temp.	150°C max.
PWHT	Not applied		

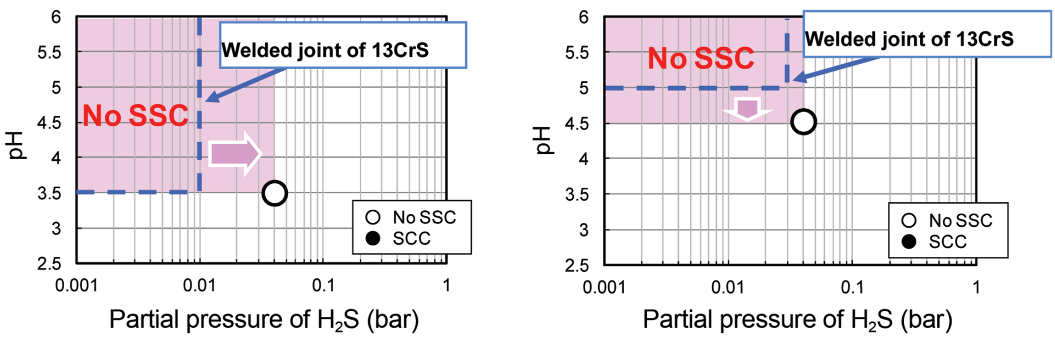
Table 5 SCC test results for welded joints of DP25U

Material	PWHT	Test conditions			Results
		Cl^- (mg/L)	CO_2 (bar)	Temp. (°C)	
DP25U	No	180,000	10	175	No SCC (0/2)
13CrS	No	180,000	10	110	SCC (2/2)
	650°C × 5 min				No SCC (0/2)

Note : No SCC / No tested samples

Table 6 SSC test results for welded joints of DP25U

Simulated condition	Solution	pH	Gas	Temp. (°C)
Gas	0.17 wt%NaCl (Cl^-: 1,000 mg/L)	3.5	0.04 barH_2S (CO_2 bal.)	90
Oil	25 wt%NaCl (Cl^-: 180,000 mg/L)	4.5		



(a) Gas condition (b) Oil condition

Fig. 10 Recommendable environments of new duplex stainless steel

condition where welded joints of Super 13Cr steel is difficult to apply. From these observations, it is clear that DP25U has superior corrosion resistance compared with that of Super 13Cr steel from the view point of SSC resistance as well.

5. Conclusion

The performance and the characteristics for a product line up of stainless steel for solid line pipes usable in corrosive environment containing CO_2, Cl^-, and H_2S have been summarized. Thereafter, the mechanism of stress corrosion cracking at elevated temperatures for as-welded (no PWHT) Super 13Cr stainless steel as CRA line pipes and its countermeasures for practical use have been described. This stress corrosion cracking is the intergranular stress corrosion cracking at the high temperature HAZ of welds, and by considering the mechanism, it has been made clear that such stress corrosion cracking is eliminated by applying appropriate post weld heat treatment. Finally, the concept of the development, composition, mechanical properties, and corrosion resistance of the welds of DP25U, a new duplex stainless steel for solid line pipe with as-welded, have been summarized.

It is expected that with the product line up of CRA line pipes and their application technologies, the range of applicability in laying line pipes and the cost minimization for users will be further expanded.

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