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Optimizing Welding Condition for Excellent Corrosion Resistance in Duplex Stainless Steel Linepipe*


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1 Introduction

With the development of corrosive oil and gas fields and further the application of the secondary recovery method to such fields, stainless steel, which offers excellent anti-corrosion properties, has been adopted as an essential material. Duplex stainless steel has been attracting attention, in particular, as a linepipe material for natural gas which contains large volumes of CO_2.

Duplex stainless steel consists of ferrite and austenite, with an optimum combination ratio of the phases (generally 40-60% austenite; the rest ferrite)[1]. Duplex stainless steel possesses both the excellent resistance to chloride SCC of ferritic stainless steels and the good notch toughness and the resistance to other types of corrosion of austenitic stainless steels.

However, caution must be paid to the deterioration of the corrosion resistance of the weld metal and HAZ of the girth weld joints which results from an unbalance of the austenite/ferrite fraction in the microstructure.

This paper discusses methods of improving the corrosion resistance of the girth weld joint, which is generally not solution annealed after welding.

2 Experimental Procedure

The materials used for tests were three kinds of API 5L X70 grade pipe, a double submerged arc welding (DSAW) UOE pipe (508 mm OD × 14.3 mm *t*, pitting index (PI)[2] = Cr + 3Mo + 16N = 34.1) and two seamless pipes (219.1 mm OD × 19.05 mm *t*, PI = 32.2 and 34.1), the nominal chemical compositions of which were 22Cr-5.5Ni-3Mo-0.15N (ASTM A790 S31803, DIN 1.4462).

The austenite fraction, toughness, and resistance to pitting corrosion of the HAZ were studied with simulated HAZ specimens (PI = 32.2, N = 0.13%).

The influence of welding heat input on pitting corrosion resistance was tested in a 10% $FeCl_3 \cdot 6H_2O$ solution at 30°C for 24 h. Two kinds of seamless pipes were examined, one with a high pitting index (PI = 34.1) and one with a low pitting index (PI = 32.2). Test specimens were taken from the melt-run gas tungsten arc weld (GTAW) beads. The welding heat input was varied

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from 3 to 42 kJ/cm by changing the welding speed while maintaining a constant current of 200A and voltage of 12V. Furthermore, welded specimens produced by submerged arc welding (SAW), gas metal arc welding (GMAW), and GTAW, with 9% nickel matching wires were prepared. The specimen sizes were 40 mm$W$ × 50 mm$L$ × 6 mm$t$ (W, transverse to welding direction; L, welding direction; and t, thickness) for the melt run GTAW beads and 40 mm$W$ × 50 mm$L$ × 2 mm$t$ for the others. Each specimen had the weld metal at the center of the specimen. To understand the influence of heat input more precisely, the simulated HAZ specimens were examined.

For girth welding, the shielded metal arc welding (SMAW) method was employed. Test specimens were taken from the location of 1 mm inside the root pass. All specimens were polished with #240 abrasive paper.

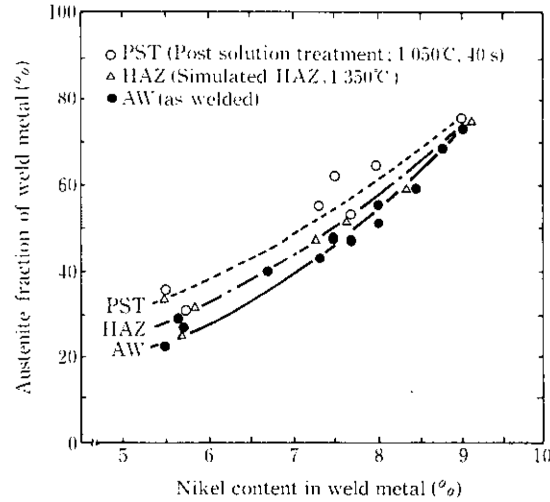


Fig. 1 Relationship between Ni content and changes in austenite fraction of the weld metals due to weld reheat thermal cycle, and short-time solution treatment

3 Results and Discussion

3.1 Metallurgical Characteristics of the Girth Weld HAZ

A weld metal of chemical composition similar to the base metal shows a ferrite-rich microstructure in the as-welded condition and thus requires the addition of austenite formers if an appropriate austenite fraction is to be maintained.

Girth weld joints, which are field fabricated and generally used in the as-welded condition, needs the above-mentioned measure for chemical composition, while seam weld metals of welded pipes do not, because solution annealing after factory welding (short-time solution treatment) is expected to recover the amounts of austenite fraction in the seam weld metals. The design concepts of the chemical composition of the two weld metals differs in two cases accordingly. Basically, however, appropriate austenite fractions can be easily obtained by controlling the chemical composition of the welding materials.

Figure 1 shows that the austenite fraction increase in proportion to increases in nickel content. It appears that the nickel content needed to obtain a weld metal with a 40 to 60% austenite fraction should be controlled in the range of 6.0 to 7.5% for seam welds and in the range of 7.0 to 8.5% for girth welds, with a 0.13 to 0.14% nitrogen content.

Absorbed energy improved with short time solution treatment or weld reheating, contributing to low temperature toughness of the weld metal. The absorbed energy of a seam weld metal was 160 J at −40°C and that of a GTA girth weld metal was 170 J at −40°C in the as-welded condition.

On the other hand, the HAZ in the as-welded condition shows a low austenite fraction as shown in **Photo 1**, because the chemical compoisition of the HAZ is determined by that of the base metal.

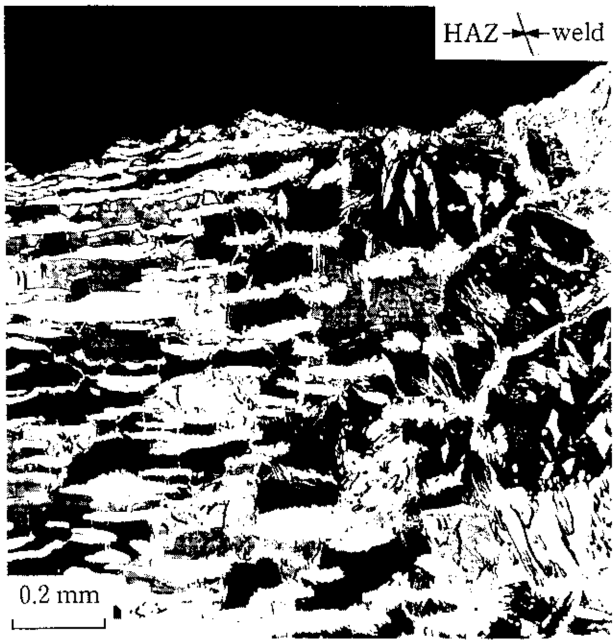


Photo 1 A microstructure of the shielded metal arc girth weld HAZ

In seam welds, the base metal adjacent to the longitudinal weld is subjected to heat cycles in the seam welding process itself as well as in the girth welding, as shown in **Fig. 2**. Furthermore, a short-time solution treatment is usually applied after seam welding. Effects of reheating through multi-pass girth welding or short-time solution treatment were examined with simulated heat cycles. **Figure 3** shows the austenite fraction and toughness of a simulated HAZ (PT = 1350°C, using a cooling time from 800°C to 500°C of 11 sec) in the cross welded area. As shown, both the austenite

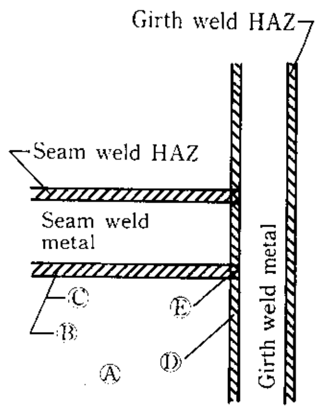


Fig. 2 Schematic showing of the cross welded area in a DSAW-UOE pipe resulting from a seam and a girth weldings

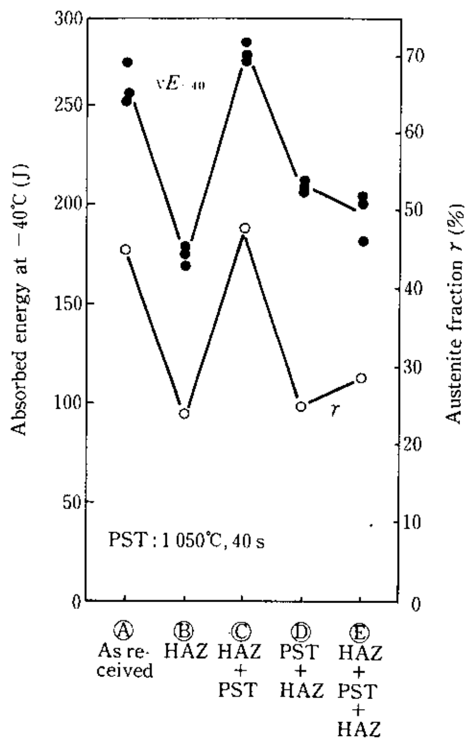


Fig. 3 Absorbed energy and austenite fraction of the simulated HAZ in a cross welded area

fraction and toughness were reduced by the welding thermal cycles (Ⓑ), but were improved by short-time solution treatment following welding (Ⓒ). The seam weld HAZ of a DSAW pipe is consequently expected to have almost the same corrosion resistance as the base metal. **Table 1** is an example of the results of a corrosion test of a DSAW pipe and its seam weld which was short-time solution treated. Both the HAZ and seam weld metal show performance equal to that of the base metal.

However, the austenite fraction and toughness again deteriorated as a result of girth welding thermal cycles after the short-time solution treatment (Ⓓ, Ⓔ), meaning these properties depend on the final thermal cycle.

Toughness should be no problem (absorbed energy at −40°C was about 180 J) even if the thermal history ends with a welding thermal cycle (girth welding HAZ). The austenite fraction, however, falls to the range of 20 to 30% in the as-welded heat affected condition. Although in multi-pass girth welding, the reheating effect of subsequent passes should improve the corrosion resistance of the HAZ, the root pass HAZ, which is in contact with the environment, is not always reheated by subsequent passes.

These results indicate that a decrease in the austenite fraction of the HAZ resulting from field girth welding is generally unavoidable. The girth HAZ is an area where much care should be taken from the standpoint of corrosion damage assessment.

3.2 Corrosion Properties of Girth Weld Joint

Pitting corrosion resistance of the girth weld HAZ was examined from the viewpoints of welding heat input, welding method, and the pitting index of the base metal. This section will describe methods of improving the pitting corrosion resistance of grith weld joints.

3.2.1 Influence of welding heat input on pitting corrosion

The results of pitting corrosion tests in a ferric chloride solution are given in **Fig. 4**. The corrosion rates can be regarded as the result of the corrosion behavior of the weld HAZ, because most pits were located in the HAZ adjacent to the weld fusion line. Pitting corrosion resistance markedly improved with an increase in the welding heat input in both the high and the low pitting index base metals. It also significantly improved with an increase in the pitting index of the base metal. How-

Table 1 Corrosion test results of DSAW pipe

Test	Solution	Condition	Results	
			Base metal	Seam weld
Intergranular corrosion	65% HNO_3	Boiling, 48 h, 5 times	0.175 g/m²·h	0.181 g/m²·h
Chloride SCC	90 g/l NaCl+1 bar CO_2	Boiling, 500 h	No cracking	No cracking
Pitting corrosion	10% $FeCl_3 \cdot 6H_2O$	30°C, 24 h	No pitting	No pitting

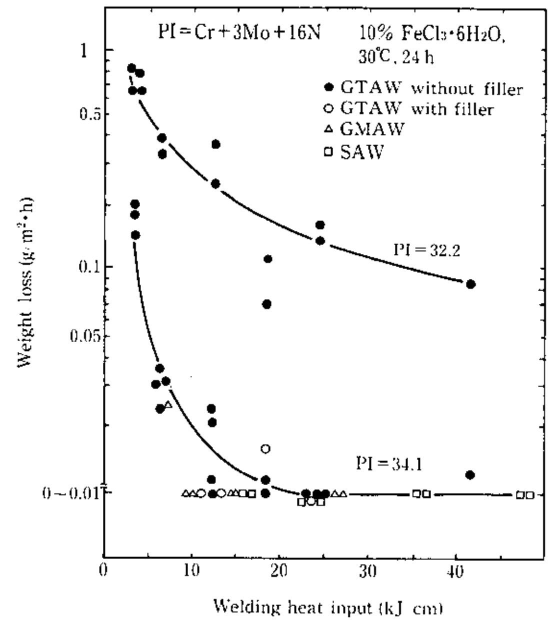


Fig. 4 Influence of welding heat input on the pitting corrosion resistance of the weld HAZ

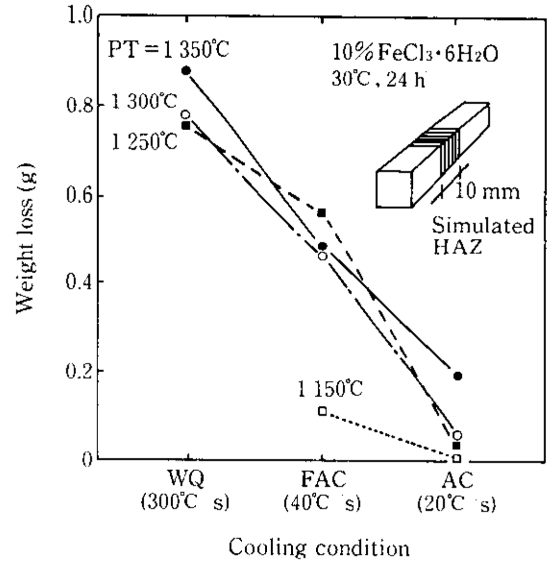


Fig. 5 Influence of cooling rate on the pitting corrosion resistance of the simulated HAZ

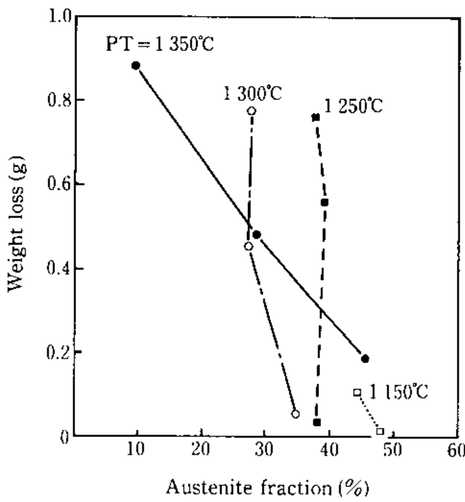


Fig. 6 Relationship between weight loss and the austenite fraction (An rearrangement of Fig. 5 by means of the austenite fraction)

ever, pitting corrosion performance appears to be independent of welding method.

Girth weld joints of high pitting index base metals (PI $\geqq$ 34.0) produced with a welding heat input greater than 10 kJ/cm are almost free of pitting corrosion problems.

Microstructures of the HAZ resulting from low heat input welding do not differ greatly from those with large heat input welding. To understand the influence of cooling rate on pitting corrosion resistance, simulated HAZ specimens were examined. Specimens (11 mm$W$ × 100 mm$L$ × 11 mm$t$) cut from the low pitting index base metal were heated to elevated temperatures and cooled at three different rates: 300°C/s (water quenching), 40°C/s (forced air cooling), and 20°C/s (air cooling). Holding time at the peak temperature was 3 sec for each specimen.

Results of the pitting corrosion tests in a 10% $FeCl_3 \cdot 6H_2O$ solution at 30°C for 24 h are plotted in **Fig. 5**. Weight loss declined in proportion to reduction of the cooling rate. Slow cooling from an elevated temperature can give a higher austenite fraction than rapid cooling because of the acceleration of austenite precipitation. A rearrangement of Fig. 5 for the austenite fraction is shown in **Fig. 6**, which clearly demonstrates that the same austenite fraction specimen does not necessarily result in the same corrosion weight loss, and further, that the corrosion resistance of the simulated HAZ is greatly influenced by the cooling rate. A distinctively microstructural aspect of the pitted specimens was the preferential attack of the ferrite phase and the ferrite/ferrite boundary when cooled rapidly. The initiation site of the pitting corrosion of the HAZ of an actual GTAW joint was identified as the ferrite/ferrite grain boundary, as shown in **Photo 2**. The reason for the difference in the pitting corrosion resistance of the HAZs with low and high welding heat input will presumably be the difference in the pitting corrosion resistance of their respective ferrite phases.

3.2.2 Mechanism of improvement in pitting corrosion resistance due to slow cooling

The ferrite phase in the simulated HAZ of the low pitting index base metal was examined in detail to elucidate the mechanism of pitting corrosion behavior as influenced by the cooling rate during welding.

Photo 3 shows microstructures etched electrically with

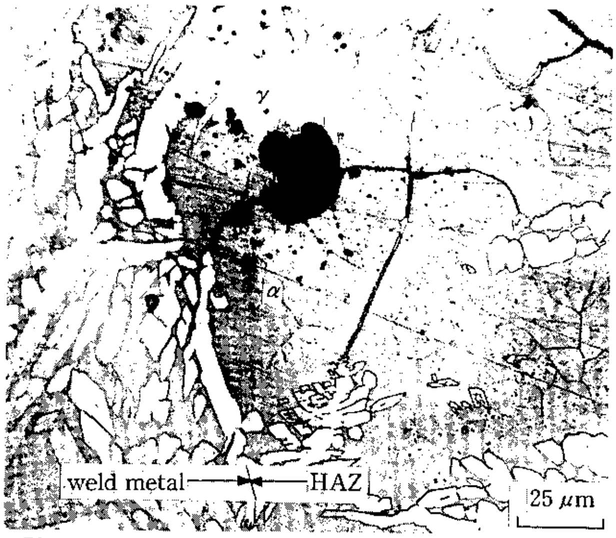


Photo 2 Initiation sites of the pitting corrosion in HAZ (22°C, 10% $FeCl_3 \cdot 6H_2O$)

a 10% oxalic acid solution. Simulated HAZs were heated to 1250°C and cooled (rapid, 300°C/s; slow, 20°C/s). The ferrite/ferrite grain boundaries and ferrite matrix in the rapidly cooled HAZ were attacked severely and deeply. **Photo 4** shows an electron micrograph of precipitates found on the extraction replicas. Precipitates were found in both the rapidly and the slowly cooled HAZs. These precipitates were identified as chromium nitride (Cr_2N, CrN) by electron diffraction analysis, EDX (Energy dispersive X-ray) analysis, and EELS (Electron energy loss spectroscopy) analysis.

These results suggest that the solute nitrogen, formed in the ferrite phase as a result of the decrease in the austenite phase during the weld heating process, is precipitated as chromium nitride regardless of the cooling rate. However, during rapid cooling, chromium near the nitride precipitates is depleted because the time available for diffusion is insufficient for chromium to heal the chromium depletion. During slow cooling, chromium diffusion heals the depleted area.

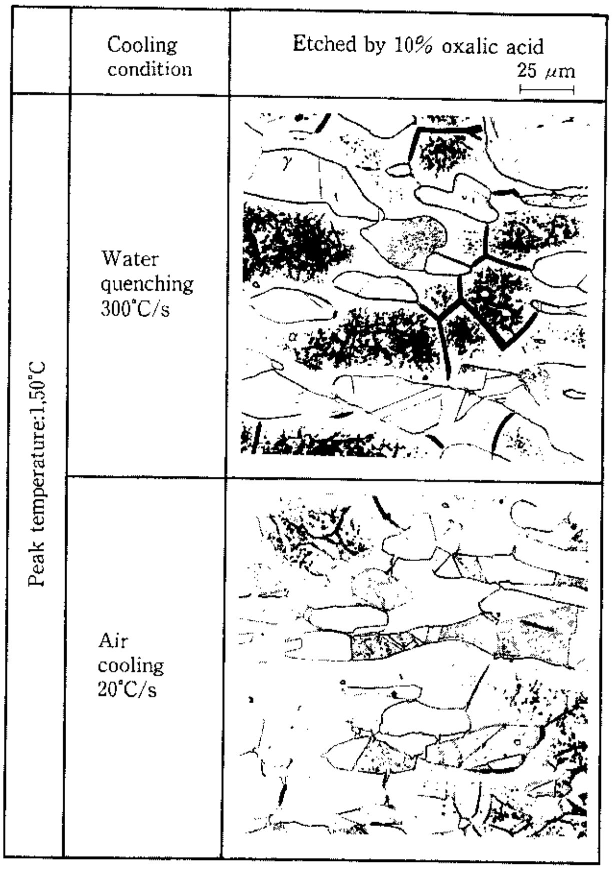


Photo 3 Comparison of sensitization between the simulated HAZs cooled rapidly and slowly

Furthermore, less nitride could be precipitated during slow cooling because more nitrogen could diffuse to the austenite phase. Supporting this conjecture is the result that even in rapid cooling the ferrite phase adjacent to the austenite phase was not sensitized, as shown in **Photo 5**.

The influence of the welding heat input on the corrosion resistance was obtained in 65% nitric acid test (ASTM A262 Practice C) as shown in **Photo 6** as well as

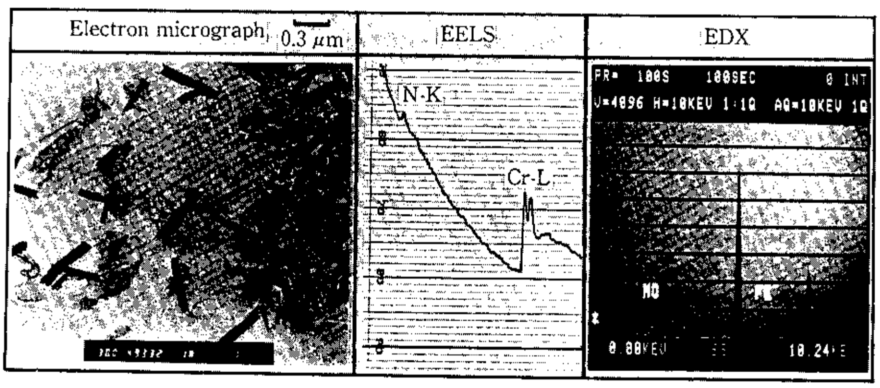
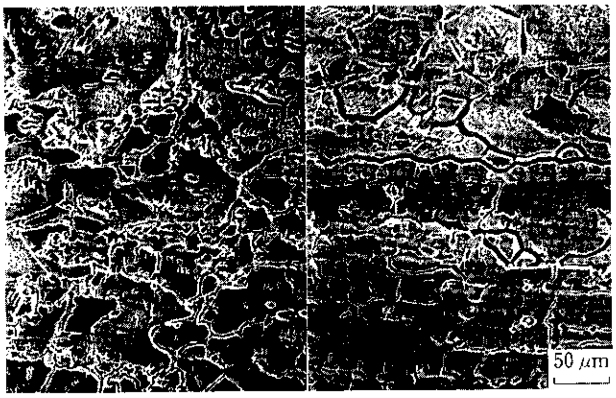


Photo 4 An example of electron micrograph and EELS analyses of precipitates found in the both simulated HAZs cooled rapidly and slowly

Photo 5 A SEM observation of an oxalic acid etched specimen (PT = 1350°C, water quenched)



200 A
12 V
6 cm/min

200 A
12 V
24 cm/min

Photo 6 SEM observations of the gas tungsten arc girth weld HAZs after ASTM A262 prac. C test (The rapidly cooled specimen–low heat input specimen–shows ditch structure.)

in the ferric chroride pitting test.

From the above test results, the improvement of the corrosion resistance in girth weld HAZ due to the slow cooling rate is not attributed to the recovery of austenite fraction, but to the disappearance of the chromium depleted area. The girth weld is applied in the as-welded condition and the root pass which is in contact with the environment is not always reheated by subsequent passes. Therefore a welding procedure with slow cooling rate is recommendable from the view point of the pitting corrosion resistance of the HAZ.

3.3 Corrosion Test Results of Two Kinds of Girth Weld Joints

The materials used were an API 5L X 70 grade seamless pipe (PI = 34.1) and a DSAW pipe of the same grade, and their shielded metal arc girth weld joints in the as-welded condition. Root pass welding was carried out with a heat input of 10 to 15 kJ/cm.

The results are summarized in **Table 2**. The corrosion performance of the root pass weld metal and HAZs with a slow cooling rate was found to be identical to that of the base metal.

3.4 H_2S SCC Tests in Autoclave

Although duplex stainless steels have the excellent resistance to SCC in CO_2-Cl^- environments, even a small quantity of H_2S can affect the SCC resistance of duplex stainless steels. A seamless pipe (PI = 34.1) and its shielded metal arc girth weld joint were used for tests. **Figure 7** shows the influence of temperature and partial pressure of H_2S on SCC susceptibility. Duplex stainless steel is very susceptible to crack at around 100°C. All the cracks started at the bottom of pits and passed through the ferrite phase, as shown in **Photo 7**. The H_2S SCC of the weld joint occurred mainly in the HAZ.[3)] Increased chloride concentration reduces the critical partial pressure of H_2S. An example is shown in **Fig. 8**. The critical partial pressure of H_2S for SCC is estimated at 10^{-2}MPa in a 5% NaCl solution and at 10^{-3}MPa in a 20%NaCl solution.

4 Conclusions

The metallurgical characteristics and corrosion performance of girth weld joints of the duplex stainless

Table 2 Results of corrosion tests under the atmospheric pressure

		Seamless pipe		UOE pipe girth joint
		Pipe body	Girth joint	
Intergranular corrosion test	ASTM A262 Prac. E ($CuSO_4$-H_2SO_4)	No IGC*	No IGC	No IGC
	ASTM A262 Prac. C (Boiling 65%HNO_3)	No IGC (0.151)**	No IGC (0.171)	No IGC (0.182)
Pitting corrosion test	10%$FeCl_3 \cdot 6H_2O$, 30°C, 24 h	No pitting	No pitting	No pitting
	150 g/l NaCl-0.1 MPa CO_2, 80°C, 28 d	No pitting	No pitting	No pitting
Cl^--SCC U-bend test	$CaCl_2$ (pH=6.5), 100°C, 500 h	No cracking	No cracking	No cracking
CO_2-SCC U-bend test	90 g/l NaCl-0.1 MPa CO_2, Boiling, 28 d	No cracking	No cracking	No cracking

* Intergranular corrosion, ** weight loss(g/m²·h)

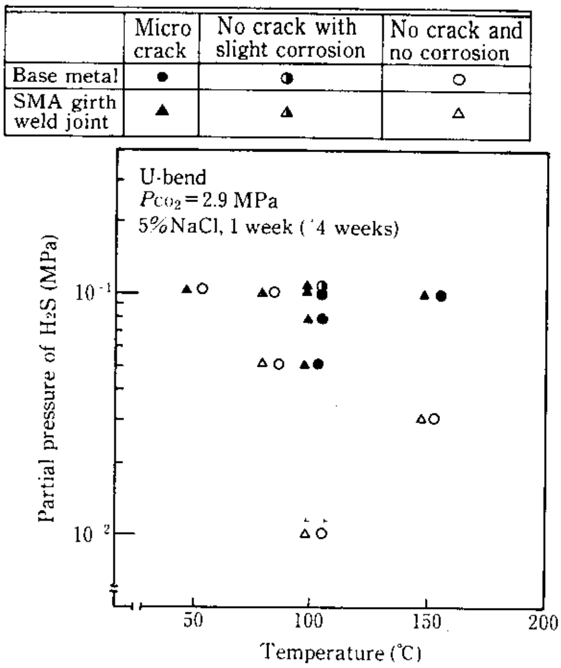


Fig. 7 Influence of temperature and partial pressure of H_2S on the SCC susceptibility

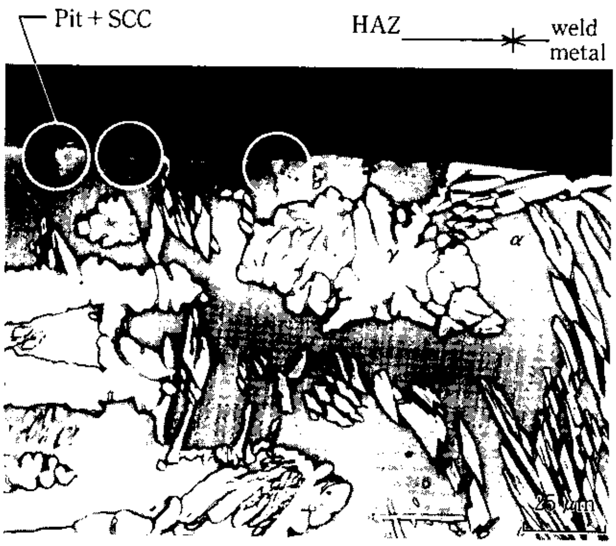


Photo 7 A cross sectional view of a shielded metal arc girth weld joint (White part, austenite; dark part, ferrite. Micro cracks initiated from the related pit bottom were located in the HAZ)

steel specified by ASTM A790 S31803 and DIN 1.4462 were examined in connection with the application of these materials to CO_2-Cl^- environment pipe.

The main results of this study are as follows:

(1) Poor corrosion resistance of HAZ is attributed not to the reduction of the austenite fraction but mainly to the chromium depleted area adjacent to chromium nitrides precipitated during the cooling.

(2) Short time solution annealing after seam welding will eliminate the chromium depleted areas and thus restore the corrosion resistance of the seam weld HAZ.

(3) The girth weld HAZ is applied in the as-welded condition and the root pass HAZ which is in contact with the environments is not always reheated by subsequent passes. Therefore the girth weld joint is an area where much care must be taken from the aspect of corrosion damage assessment.

(4) Improvement of the pitting corrosion resistance of the girth weld joints in the as-welded condition required the use of a high pitting index base metal (Cr + 3Mo + 16N = 34.0) and slow cooling rate welding procedures, independently of the welding method.

(5) Duplex stainless steel pipe can be applied with satisfactory results at a H_2S partial pressure up to 10^{-2}MPa in a 5% NaCl solution and 10^{-3}MPa in a 20% NaCl solution.

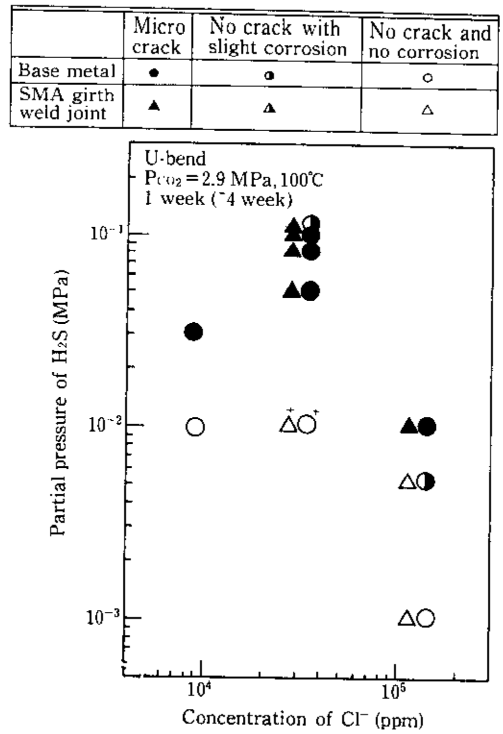


Fig. 8 Influence of chloride concentration on SCC susceptibility

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