UDC669.15'26-194-462

Development of High Chromium Stainless Line Pipe

Hitoshi Asahi[*1]
Hiroshige Inoue[*1]
Koichi Nose[*1]
Naoshi Ayukawa[*2]
Taro Muraki[*1]
Hiroshi Tamehiro[*1]
Masaharu Oka[*1]

Abstract:

There is an active demand for corrosion resistant line pipes which have intermediate properties and price between a low alloy steel and a duplex stainless steel. To cope with this, a material based on 9 to 13% Cr steel for the corrosion resistant line pipe which has a good field weldability, has been developed. The basis of designing this material is that carbon content is made lower than 0.02% and the nitrogen lower than 0.01%, an amount of chromium and molybdenum is added to satisfy both CO_2*-corrosion resistance and SSC resistance, and some austenite forming elements are added to obtain the complete martensite structure. Further, it is indispensable to increase in the adding amount of nickel to obtain a higher toughness at the heat affected zone, and to add a certain amount of molybdenum to avoid embrittlement by PWHT. On the basis of the guideline above mentioned, materials can be successfully designed which are applicable corresponding to the environmental conditions in which these materials are to be used. They can be welded without preheating, and their mechanical properties at the portion of welded joints are good.*

1. Introduction

In OCTG, 13% Cr steels are widely used due to their excellent CO_2-corrosion resistance and low price. Not only API (American Petroleum Institute) standard 13% Cr steels (usually SUS 420 steel[1]), but also modified 12-13% Cr steels with improved corrosion resistance have been developed[1]. On the other hand, duplex stainless steels have been applied as corrosion-resistant linepipe[2]. Although the corrosion resistance of 13% Cr steels is sufficient in many cases, duplex stainless steels are used because the conventional 13% Cr steels represented by API-standard products have poor weldability. However, because the modified 13% Cr steels developed for use in steel OCTG have a decreased carbon content, they may meet the weldability requirements for linepipe. The development of these new materials and demand for lower-cost pipeline installation have promoted the development of high chromium stainless-steel pipeline represented by 13% Cr steels[3,4].

This paper describes the material factors affecting the properties of high chromium stainless steel linepipe and the properties of typical 9% - 13% Cr stainless linepipe.

2. Material Design

2.1 Properties of base metal

The advantage of corrosion-resistant linepipe is that it is not necessary to consider reductions in wall thickness by corrosion. **Fig. 1** and **Fig. 2** show the effects of chromium content on the corrosion rate in a moderately severe corrosive environment (CO_2

[*1] Technical Development Bureau
[*2] Head office

partial pressure: 0.4 MPa) and a severe corrosive environment (CO_2 partial pressure: 4.0 MPa), respectively. It is apparent that materials from approx. 9% - 13% Cr steels can be selected depending on the conditions of the service environments. Furthermore, higher corrosion resistance can be obtained by the combined addition of copper and nickel to lower-chromium-content steel. In general, lowering the carbon content is an effective means of improving weldability. However, an increase in the chromium content of low carbon steel also promotes ferrite phase and low-temperature toughness decreases, as shown in **Fig. 3**. Because the low-temperature toughness of the heat-affected zone (HAZ) is lower than that of the base metal, it is necessary to obtain a single martensitic phase by preventing the formation of a ferrite phase in order to ensure good HAZ toughness. The suppression of the formation of ferrite phase is also important to ensure good hot-workability during the pipe manufacturing process. The formation of ferrite can be suppressed by controlling the phase stability index I_{PS} to -9.4 or greater[5].

$I_{PS}=Ni+0.3Cu+0.2Mn+40C+34N-1.1Cr-1.8Mo$

Sulfide stress cracking (SSC) may occur in a "sour environment," i.e. one that contains H_2S. Molybdenum addition is effective in suppressing the occurrence of SSC. However, because SSC sensitivity increases when a ferrite phase is formed[6], a single martensitic phase is indispensable. **Fig. 4** shows the effects of molybdenum content and pH on the occurrence of SSC. The molybdenum content needed to suppress SSC varies depending on the environmental conditions (e.g., the partial pressure of H_2S and Cl^--concentration) and on whether the material is a base metal or HAZ.

2.2 Properties of HAZ

The effects of material factors on the properties of HAZ were investigated by using materials subjected to a simulated welding heat-cycle treatment with a maximum heating temperature of 1400°C. In high chromium steels, the microstructure of HAZ becomes martensitic irrespective of the welding heat input (cooling rate). Therefore, the hardness of HAZ is almost a function of the carbon content, as shown in **Fig. 5**, and increases with carbon content. A higher carbon content in steel decreases the low-temperature toughness of HAZ, as shown in **Fig. 6**. The effect of nickel content on the low-temperature toughness of HAZ is summarized in **Fig. 7**. Although the microstructure is fully matensitic regardless of nickel content, low-temperature toughness improves with nickel content. It is also known that the addition of titanium results in the formation of TiN, thus improving low-temperature toughness. However, as shown in **Fig. 8**, the excessive addition of titanium decreases low-temperature toughness.

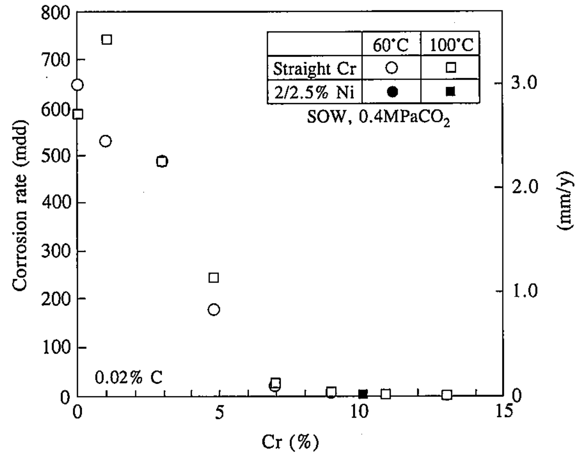


Fig. 1 Effect of chromium content on the corrosion rate (CO_2: 0.4MPa)

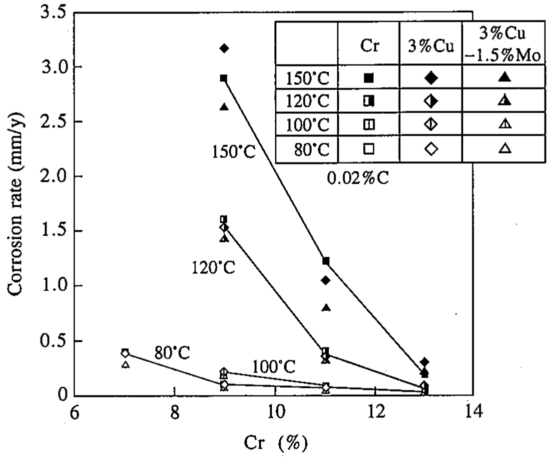


Fig. 2 Effect of chromium content on the corrosion rate (CO_2: 4.0MPa)

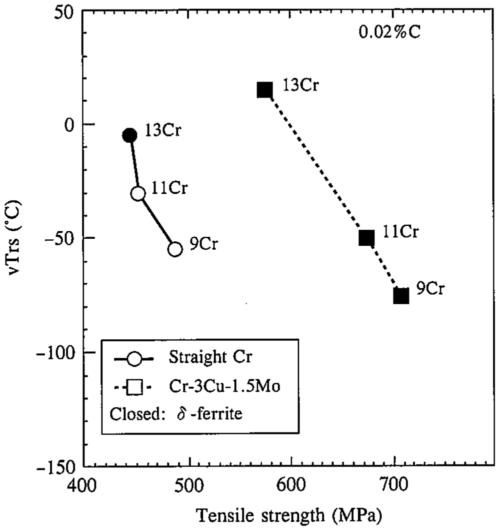


Fig. 3 Effect of chromium content and microstructure on the low-temperature toughness of base metal

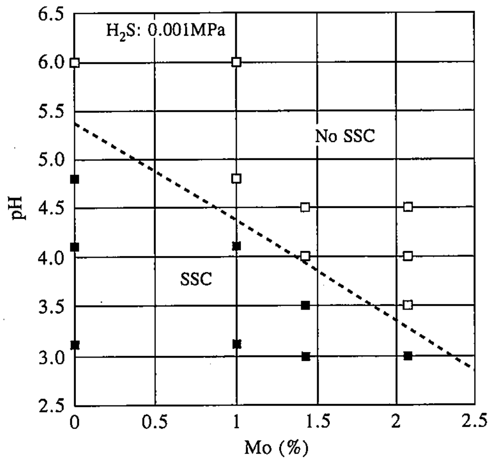


Fig. 4 Effects of molybdenum content on the occurrence of SSC

Higher nitrogen content also decreases low-temperature toughness greatly, especially when post-weld heat treatment (PWHT) is applied. When PWHT is conducted for steels without molybdenum addition, the toughness of HAZ decreases remarkably, as shown in **Fig. 9**. For steels without molybdenum addition, the fracture surface after PWHT are intergranular cracks, which indicates that temper embrittlement occurs. Temper embrittlement is suppressed by molybdenum addition.

2.3 Concept of material design

The chromium and molybdenum contents necessary to obtain

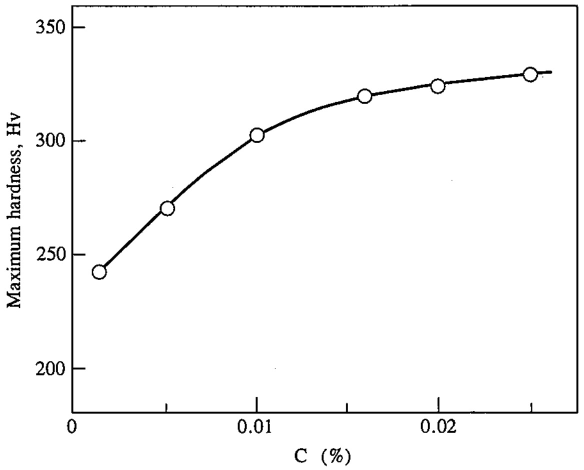


Fig. 5 Effect of carbon content on the maximum hardness of HAZ

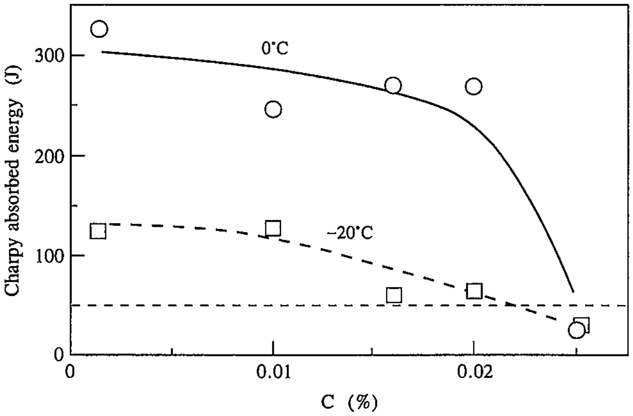


Fig. 6 Effect of carbon content on the toughness of HAZ

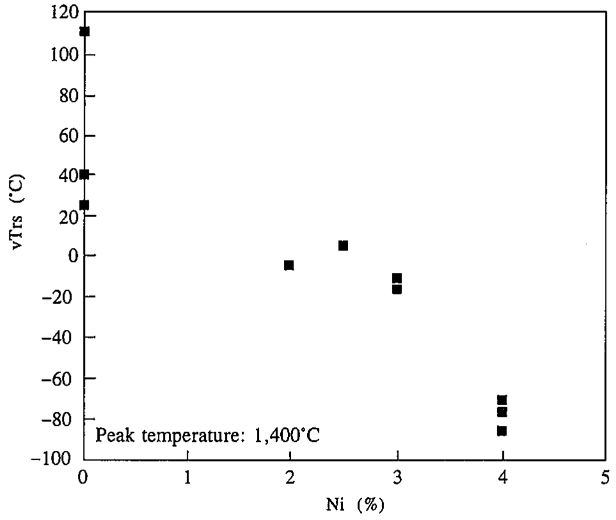


Fig. 7 Effect of nitrogen content on the toughness of HAZ

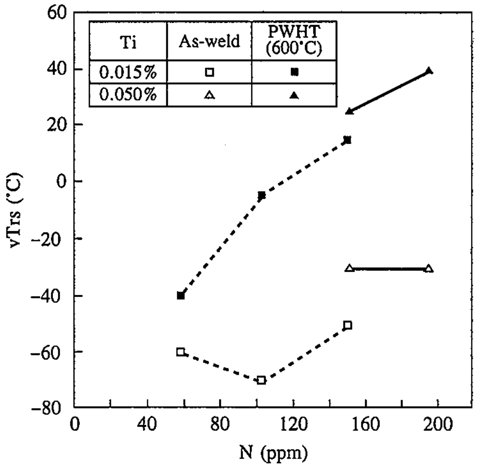


Fig. 8 Effect of nitrogen content and titanium content on the toughness of HAZ

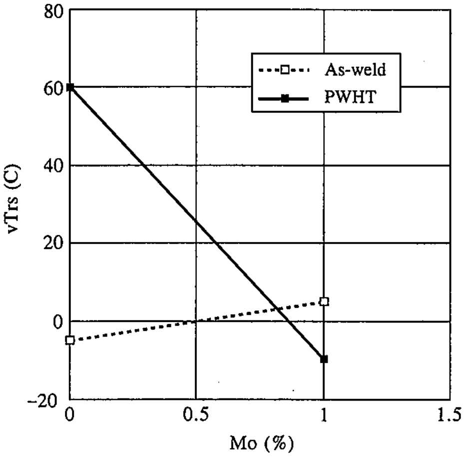


Fig. 9 Effect of molybdenum addition and PWHT on the toughness of HAZ

Table 1 Typical environmental conditions under which the high chromium stainless steel linepipe is applied

Type	Temperature (°C)	P_{CO_2} (MPa)	H_2S	Weldability	Low temperature toughness, vE_{-20}
A	120	4.0	Little	No cold cracking	>501
B	100 80	0.4 4.0	None	No cold cracking	>50J
C	100 80	0.4 4.0	Very little	No cold cracking	>50J

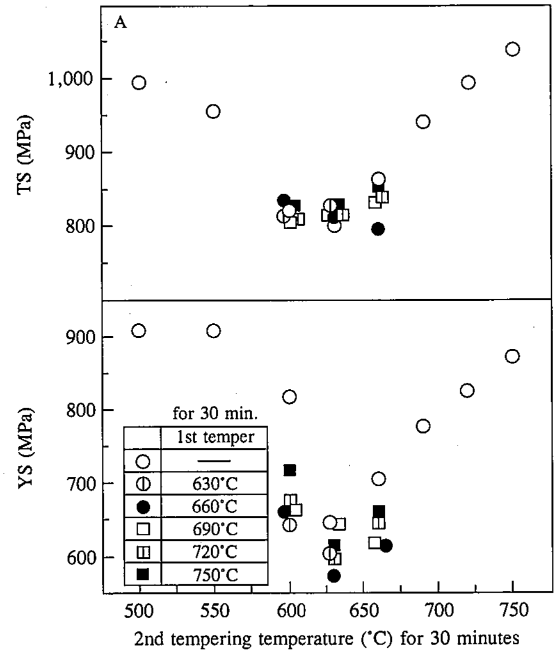
Table 2 Examples of the chemical composition of materials to suit environmental conditions

Type	C	Si	Mn	P	S	Cr	Ni	Cu	Mo	Ti	Al	N
A	0.009	0.31	0.49	0.015	0.001	10.9	5.1	0.49	2.0	0.010	0.028	0.003
B	0.011	0.30	0.50	0.011	0.001	10.1	2.0	–	–	0.011	0.030	0.004
C	0.010	0.30	0.50	0.012	0.001	8.9	2.5	–	1.0	0.010	0.031	0.003

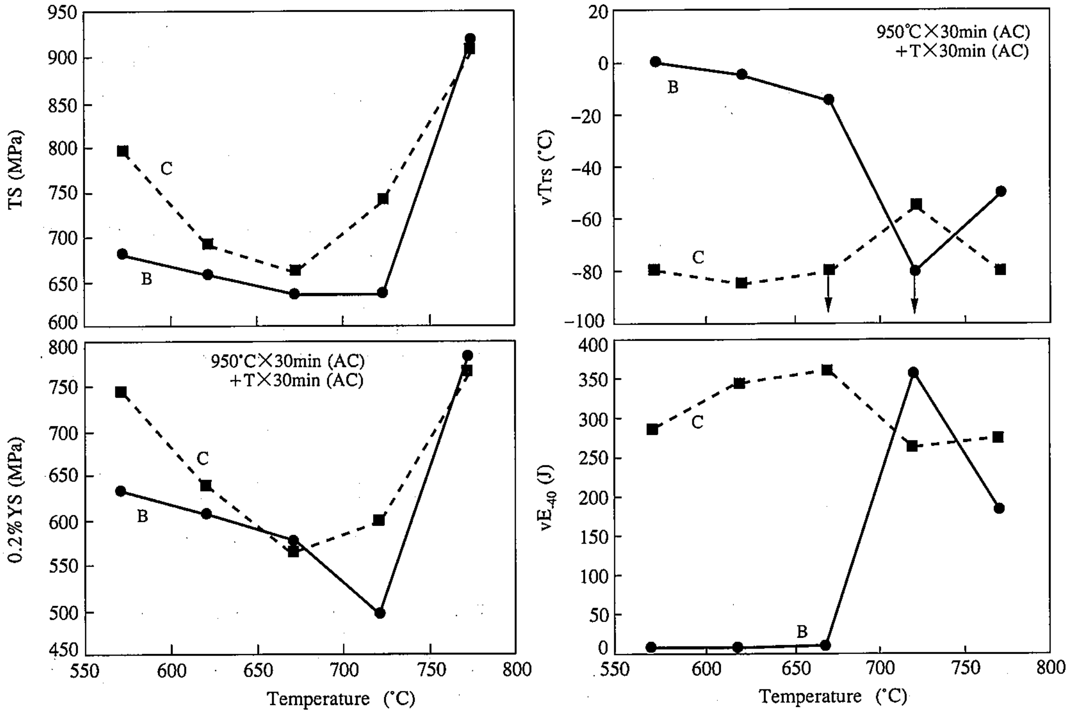
corrosion resistance and SSC resistance are primarily determined by the temperature, Cl- concentration, pH, and CO_2 and H_2S partial pressures of the service environment. Secondly, the contents of nickel and copper, which form austenite, are controlled to meet the condition of I_{PS} so that a single martensitic phase can be obtained by suppressing the formation of ferrite. Because increases in carbon and nitrogen content result in poor weldability and other properties, they should be not more than 0.02% and 0.01%, respectively. Increased toughness in HAZ requires an

Table 3 Mechanical properties of materials used in welding test

Type	YS(MPa)	TS(MPa)	EL(%)	vE_{-40}(J)	vE_{-20}(J)
A	580	814	28.0	260	–
B	577	637	23.1	–	>300
C	566	663	24.9	–	>300



(a) Steel A



(b) Steel B and C

Fig. 10 Strength change due to tempering temperature

Table 4 Welding conditions employed in the field welding test

Material	A		B and C	
Welding method	GMAW	GTAW	GMAW	SMAW
Welding method	Duplex, 329N 0.02%C - 7.3%Ni - 24.5Cr - 3.1%Mo - 0.19%N			Duplex lab. prod. 0.03%C - 8.0%Ni - 26.5%Cr - 3.3%Mo -0.2%N
Groove material	V shape, 60°	U shape	V shape, 90°	V shape, 90°
Pre-heat	None	None	None	None
Heat-input	1.5kJ/mm	1.3kJ/mm	1.4kJ/mm	1.5kJ/mm
Inter pass temperature	Lower than 150°C			

increased nickel content. PWHT is usually unnecessary, but to avoid risk, the addition of approx. 0.5% molybdenum is recommended, as the toughness of HAZ is decreased significantly by PWHT.

3. Properties of Typical Materials

Table 1 shows the environmental conditions under which 9-13%Cr stainless steel linepipe is typically employed. **Table 2** shows the chemical compositions of materials that are used under the conditions described in **Table 1**.

3.1 Heat-treatment characteristics and strength

Because the microstructure of as-rolled materials and as-normalized materials is martensitic, these materials are tempered to obtain the target strength as well as the appropriate elongation and toughness. The tempering curves of individual steels are shown in **Fig. 10**. Because it is difficult to lower strength in Steel A due to the higher alloy content, double tempering is necessary to attain X80 and X90 grades. For Steels B and C, X70 and X80 can be obtained by ordinary tempering. **Table 3** shows the mechanical properties of materials used in the evaluation process described in the subsequent sections.

3.2 Mechanical properties and weldability of weld joint

This section describes the weld joint properties of Steels A, B and C welded under the field welding conditions shown in **Table 4**. All the welding materials were 25% Cr duplex stainless steels. Cold cracking did not occur without preheating, and sound weld joints were obtained. From the results of y-groove weld cracking tests conducted in accordance with JIS Z3158 shown in **Table 5**, it is also apparent that cold cracking did not occur without preheating. **Photo 1** and **Fig. 11**, respectively, show the macrostructure and hardness distribution of the typical welds. In Steel C, the hardness is decreased significantly by PWHT. **Table 6** shows the mechanical properties of the weld joints. The absorbed energy in the V-notch Charpy test at -20°C is 50J or more and meets the required property for the environmental conditions of most pipelines. Steel B should not be subjected to PWHT because no molybdenum has been added to it.

Table 5 Results of y-groove weld cracking test

Material	Welding mothod	Heat input (kj/mm)	Pre-heat	Results
B	GMAW	0.7	Free	No crack
	SMAW	1.0	Free	No crack
	SMAW	1.5	Free	No crack
C	GMAW	0.7	Free	No crack
	SMAW	1.0	Free	No crack
	SMAW	1.5	Free	No crack

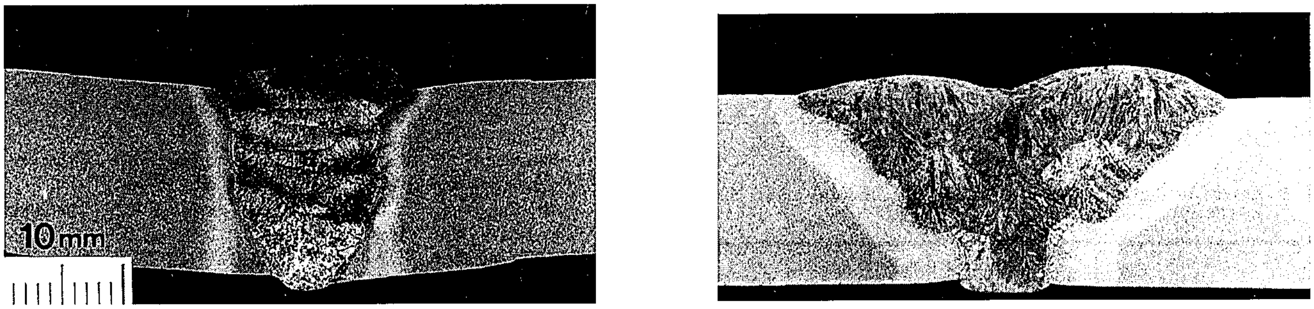
3.3 Corrosion resistance and SSC resistance of welds

Table 7 shows the CO_2-corrosion resistance of a base metal. In the corrosion tests conducted under conditions similar to those in which these steels are actually used, the corrosion rates of individual steels presumably do not exceed 0.1 mm/y, and all the steels have sufficient corrosion resistance. **Table 8** shows the results of the constant-load-type SSC test of weld joints of Steel A, which is a sour resistant steel. A crack occurred in HAZ. Steel A features SSC resistance in environments with a small concentration of H_2S and a partial pressure of 0.004 MPa.

4. Conclusions

Materials with good field weldability for corrosion-resistant pipeline were developed based on low-carbon 9% to 13%Cr steels. Major findings were as follows:

(1) The basic design concepts are to keep carbon and nitrogen content below 0.02% and 0.01%, respectively, to add chromium and molybdenum to meet CO_2 corrosion resistance and SSC resistance requirements, and to add austenite formers to obtain a fully martensitic structure.



(a) Steel A, GTAW

(b) Steel C, GMAW

Photo 1 Macrostructure of section of weld joints

(2) Nickel content can be increased in order to obtain higher HAZ toughness. Molybdenum can be added to avoid tempering embrittlement by PWHT.

(3) Steels produced based on these concepts can be welded without preheating, and the mechanical properties of weld joints are good.

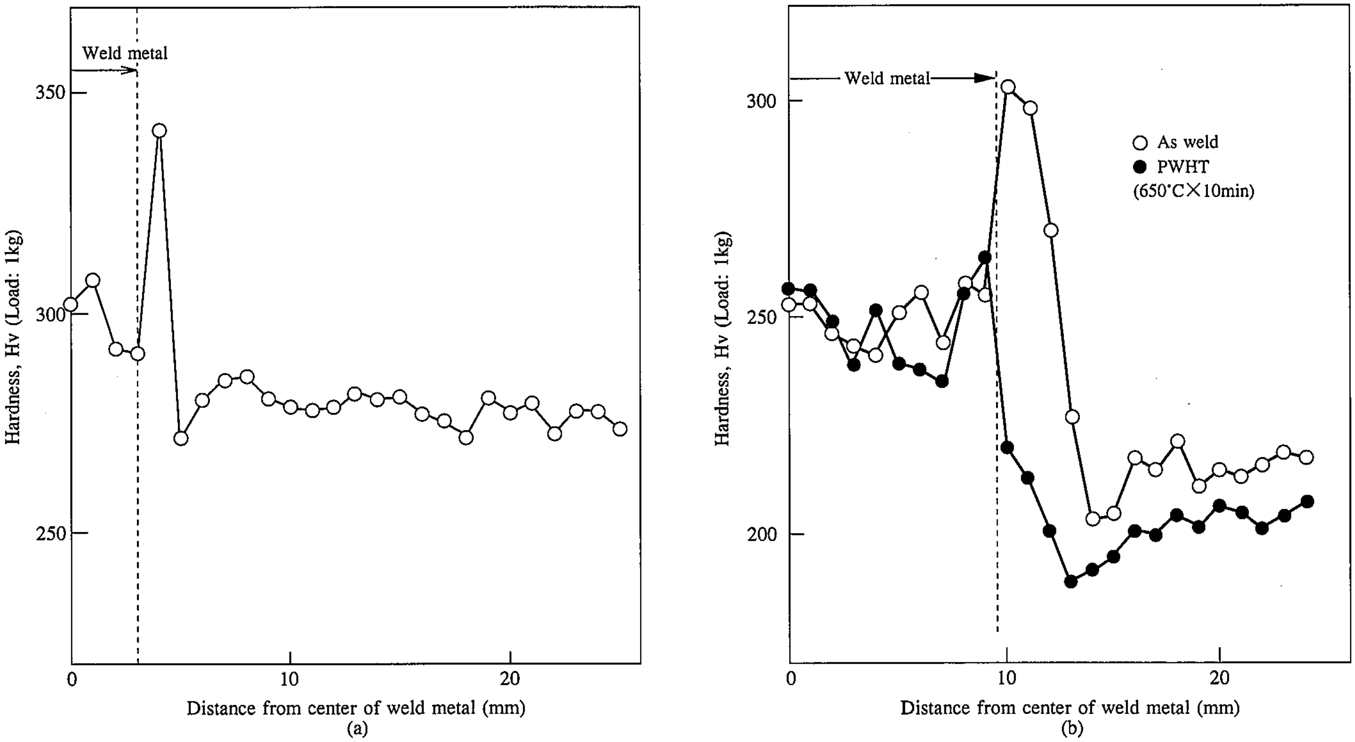


Fig. 11 Hardness distribution of weld joints

Table 6 Mechanical properties of weld joints

Weld joint			Weld tensile test		Charpy test, vE_{-20}(j)		
Type	Welding material	Welding method	YS (MPa)	TS (MPa)	Failure location	Fusion line	HAZ 1mm
A	Duplex	GMAW					
	Duplex	GTAW					259*
B	Duplex	GMAW	535	710	Base metal	83	
	Duplex	SMAW	547	644	Base metal	88	
C	Duplex	GAMW	545	699	Base meta;	111	
	Duplex	SMAW	582	680	Base metal	163	

* –30°C

Table 7 CO_2 corrosion resistance of base metal

Temperature	60°C	100°C	100°C	120°C
CO_2 pressure	0.4MPa	0.4MPa	4.0MPa	4.0MPa
A steel				0.080
B steel	0.007	0.011	0.107	
C steel	0.009	0.018	0.198	

Table 8 Results of the constant-load-type SSC test of weld joints (Steel A, GTAW)

	Cl^- (ppm)	pH	P_{H_2S} (MPa)	Balance gas	Stress (MPa)	Result
Formation water	68,000	4.5	0.004	CO_2	565	No SSC
Condensed water	1,000	3.5	0.004	CO_2	565	No SSC

References

1) Asahi, H. et al.: Shinnittetsu Giho. (362), 6 (1996)
2) Ume, K., Seki, N., Naganawa, Y., Hyodo, T., Satoh, K., Kuriki, Y. : Corrosion 86. Paper No.155, NACE, 1986
3) Moe, P., Rabben, K. and Andersen, T. : Corrosion 95. Paper No.97, NACE International, 1995.
4) Hoffmeister,H., Dietrich,S., Tystad,M., Knagenhjelm,O., Andersen,T. : Corrosion 95, Paper No.98, NACE Interantional. 1995.
5) Asahi, H., Hara, T., Kawakami, A., Takahashi, A. : Corrosion95. Paper No.79, NACE International, 1995.
6) Hara, T. and Asahi, H.: CAMP-ISIJ.9, 1392 (1996)