Development of Weld Metal with High Toughness and Low Hardenability

High toughness and low hardenability in a submerged arc weld can be assured by reducing nitrogen and oxygen and microalloying with boron

BY K. SHINADA, Y. HORII AND N. YURIOKA

ABSTRACT. Submerged arc longitudinal welds on line pipes for sour gas service are required to have low hardenability because high hardness in the circumferential welds that contact the longitudinal is not desired. The longitudinal weld is also required to be very tough. However, raising toughness and reducing hardenability are, normally, opposing metallurgical effects.

In order to develop submerged arc weld metal with high toughness and low hardenability, a study was made concerning the effects of C, Mn, Si, Ti, Al, N, O and B on the nucleation of intragranular acicular ferrite and grain boundary ferrite. It was found that improved toughness and low hardenability are attained by designing a weld metal composition that retains an appropriate amount of Ti after the oxidation of Al while keeping a low level of oxygen and nitrogen, and dissipates grain boundary ferrite by adding a few ppm of boron in the presence of a low level of carbon equivalent.

The weld metal with low nitrogen and low oxygen also exhibited preferable resistance to sulfide stress corrosion cracking in sour gas environments.

Introduction

Large diameter, high-strength steel line pipes are produced by longitudinally joining them with a submerged arc (SA) welding process. For the structural integrity of pipelines, high toughness is desired not only in the heat-affected zone (HAZ) of the base metal, but also in the weld metal. High toughness in the weld metal can be obtained by providing a fine acicular ferrite microstructure through the effective use of Mn, Ti and B (Refs. 1–3).

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For line pipes used to transport H_2S-rich gas or sour gas, most concern is about the occurrence of sulfide stress corrosion cracking (SSCC) in service. To avoid SSCC, hardness is required to be not higher than 22 RC on the Rockwell C scale, or 248 HV on the Vickers scale with a 10-kg (22-lb) load. However, circumferential (girth) welding of line pipes on site is conducted generally with very low heat input. The low heat input welding causes a hardness increase not only in the pipe steel HAZ but also in the HAZ of the longitudinal weld metal, as indicated in Fig. 1.

Modern high-strength pipe steel is often manufactured by a thermomechanically controlled process (TMCP), which makes it possible to reduce the use of hardenable elements. On the other hand, high strength must be produced in the longitudinal weld metal without any thermomechanical treatment after welding. Thus, the addition of some hardenable elements is essential to provide a weld metal with high strength and high toughness. Therefore, it is more difficult to meet the HAZ hardness limitation in the longitudinal weld HAZ than in the pipe steel HAZ. Nevertheless, there has been an increasing demand for SA-welded line pipes with high toughness and low hardenability in the longitudinal weld metal.

KEY WORDS

SAW
SA Weld Metal
Line Pipe
Sour Gas Service
Corrosion Cracking
Toughness
Hardenability
Boron Content
Oxygen Content
Nitrogen Content

Experiment

Test Conditions

The weld metal in the present study was made by the SA welding process, in which the types of welding flux and compositions of welding wires were varied. Table 1 shows the composition and basicity of three different welding fluxes of a fused type, which were used to change the content of N and O in the SA weld metal. A varying amount of boron oxide was contained in the flux to control the boron content in the weld metal. Table 2 shows the chemical composition of the low-carbon types of welding wires with varying Mn, Ti and Al contents. These SA welding materials had been developed for the production of sour gas service line pipes. The plate used for the tests was of an API 5L X65 grade for sour gas service, and its chemical composition is shown in Table 3.

The welding was conducted by a conventional SA pipe welding method, using the groove shape shown in Fig. 2 and the welding conditions shown in Table 4. The welding length was 150 cm (60 in.) and test coupons were removed from the welds, except for the run-on and run-off portions of approximately 150 mm (6 in.). Figure 3 shows the location of removal of the coupons for Charpy tests, tensile tests and chemical analyses. All samples were taken from the second pass welds. The Charpy test pieces were taken from both the upper portion and the lower portion of the second pass weld. The microstructure was examined at the center and the lower portion of the second pass weld.

The girth weld was simulated by bead-on-plate welding with a gas metal arc (GMA) CO_2 welding process in a manner shown in Fig. 4. The composition of the GMA welding wire was 0.10C-0.60Si-1.50Mn, and the welding heat input was varied at two levels: 0.5 kJ/mm (12.7 kJ/in.) and 1.0 kJ/mm (25.4 kJ/in.), as shown in the GMA welding conditions in Table 5. Hardness of the weld metal HAZ was measured along

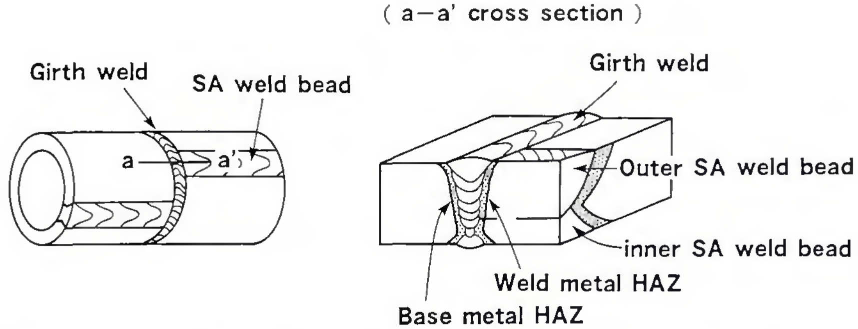

Fig. 1 — Longitudinal (seam) weld and girth weld in submerged arc welded line pipe.

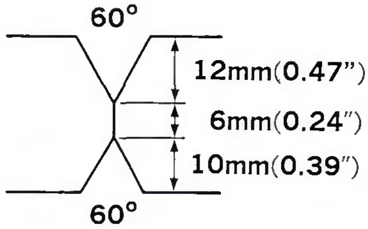

Fig. 2 — Groove shape for submerged arc longitudinal weld.

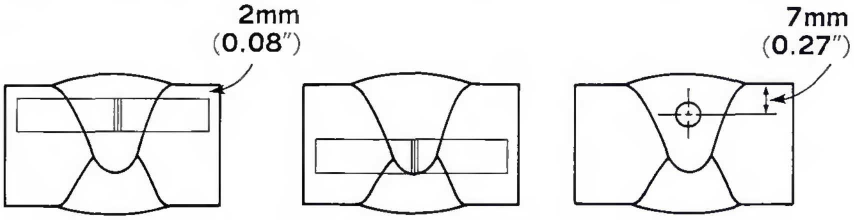

Fig. 3 — Removal locations for test coupons. A — Upper portion for Charpy test; B — lower portion for Charpy test; C — tensile test and chemical analysis.

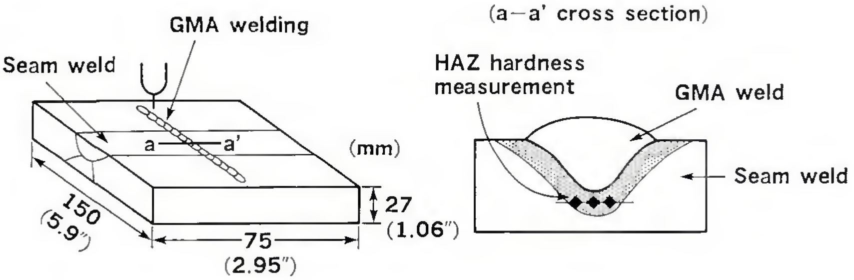

Fig. 4 — Test procedure for weld metal HAZ hardness measurement.

Table 1—Chemical Composition of Fluxes Tested

Flux No.	CaO + MgO + BaO	MnO	Al_2O_3	$TiO_2 + SiO_2$	F	Other	Basicity
	Chemical Composition (wt-%)						
FA	45.0	—	23.0	7	25	$CaCO_3$ 1% mix	6.43
FB	35.0	—	43.0	17	5		2.06
FC	22.0	4.0	32.0	34	7		0.65

Basicity = $(CaO + MgO + BaO)/(TiO_2 + SiO_2)$

Table 2—Chemical Composition of Welding Wires Tested

No.	C	Si	Mn	Ni	Ti	Al	N	O
	Chemical Composition (wt-%)							
1	0.03	0.06	3.97	0.46	0.06	—	0.0016	0.0014
2	0.03	0.06	4.44	0.46	0.06	—	0.0017	0.0014
3	0.03	0.02	2.03	—	—	—	0.0020	0.0020
4	0.01	0.06	1.97	—	—	0.032	0.0017	0.0035
5	0.01	0.07	1.95	—	0.12	0.021	0.0017	0.0025
6	0.10	0.60	1.50	—	—	0.050	0.0040	0.0035

No. 1 to No. 5 wires are employed for SA welding.
No. 6 wire is employed for GMA welding (CO_2).

the line tangent to the bottom of a GMA weld, as shown in Fig. 4. The highest value among measured hardness is the maximum hardness of weld metal HAZ. The load of the Vickers hardness testing was 10 kg (22 lb).

Stress corrosion cracking tests were conducted on simulated HAZs of SA weld metals. The test coupons for the SCC tests were removed from the upper portion of the SA welds. Then they were subjected to induction heating to 1400°C (2550°F) followed by quenching into a coolant with varying cooling capability. As a result, HAZs of SA welds with varying hardness were simulated. Fluxes FA and FC were used to make test welds for the SCC tests. The boron content was increased in some welds to a level exceeding the appropriate level for weld metal toughness, to obtain a higher HAZ hardness in the weld metal. This enabled us to find the critical minimum hardness for SCC.

The constant strain method was used as shown in Fig. 5, and test pieces were immersed for 21 days at 25°C (77°F) in an NACE solution of 25%NaCl, 0.5% CH_3COOH and saturated H_2S.

Test Results

Sound weld metal without discontinuities, as shown in the macrophotograph in Fig. 6, was obtained in all cases using the welding materials of Tables 1 and 2. The weld metal with low N and low O was obtained when using Flux FA, while high N and low O were obtained with Flux FB, and low N and high O were obtained with Flux FC. The boron content ranged from 1 to 9 ppm in Flux FA and from 13 to 20 ppm in Flux FC, while its content was kept at 9 ppm in Flux FB. The IIW carbon equivalent (CE_{IIW}) ranged between 0.343 and 0.418% mainly because of the difference in Mn content. Weld metals W1 to W8, in Table 6, were used to examine toughness, tensile strength and HAZ hardness. Weld metals W9 and W10 were used for the SSC tests.

Figures 7 and 8 show the Charpy test results at the upper portion and the lower portion of the SA weld, respectively. The experimental data denoted

Table 3—Chemical Composition of Base Metal Used for the Test

Chemical Composition (wt-%)													
C	Si	Mn	P	S	Nb	Ni	Mo	Ti	Al	B	N	O	CE %
0.06	0.27	1.08	0.005	0.0005	0.04	0.30	0.21	0.013	0.028	0.0001	0.0019	0.0020	0.31

CE = C + Mn/6 + Ni/15 + Cu/15 + Mo/5 + V/5 (IIW formula %)

Table 4—Welding Condition for Submerged Arc (SA) Longitudinal Welding

Weld Pass	Current A	Voltage V	Speed mm/min (in./min)	Heat input kJ/mm (kJ/in.)
1st	1300/1000/800	36/37/39	1200 (47.2)	5.75 (146)
2nd	1350/1010/850/730	33/38/38/38	1400 (55.1)	6.13 (156)

in the figures are the minimum of three Charpy test results. Toughness in terms of Charpy impact energy was higher, as a whole, at the upper than at the lower portion of the SA welds. The toughness of the SA welds was found to be influenced by N and O content. The highest toughness was obtained in the welds made with Flux AF, with low N and low O. The second highest was in those using Flux FC, with low N and high O, and the lowest was in those using Flux FB, with high N and low O.

In the weld metal made with Flux FA, a higher toughness was obtained even with as little as 1 ppm B, but even higher toughness is obtained in the 4 and 6 ppm B alloys. Also, toughness decreased to a slight extent with an increase in CE_{IIW} or an increase in Mn content. The effect of boron was more significant in the lower portion of the weld rather than in the upper part. It was found that more than 4 ppm boron is necessary to assure high toughness in the lower part of the weld on steel of 0.35% CE_{IIW} welded with Flux FA.

Figures 9–11 show SA weld metal microstructures at the weld centers and weld roots. Intragranular microstructures in all the welds were a mixture of acicular ferrite (AF) and upper bainite (UB). Microstructures at grain boundaries consisted of grain boundary ferrite (GBF) and/or ferrite side plate (FSP). The development of these microstructures is influenced by the content of Mn, B, N and O. Both GBF and FSP were observed in the lower portion of the weld made with Flux FA in the steel of 0.36% CE_{IIW}, as shown in Fig. 9, while both microstructures tended to decrease with an

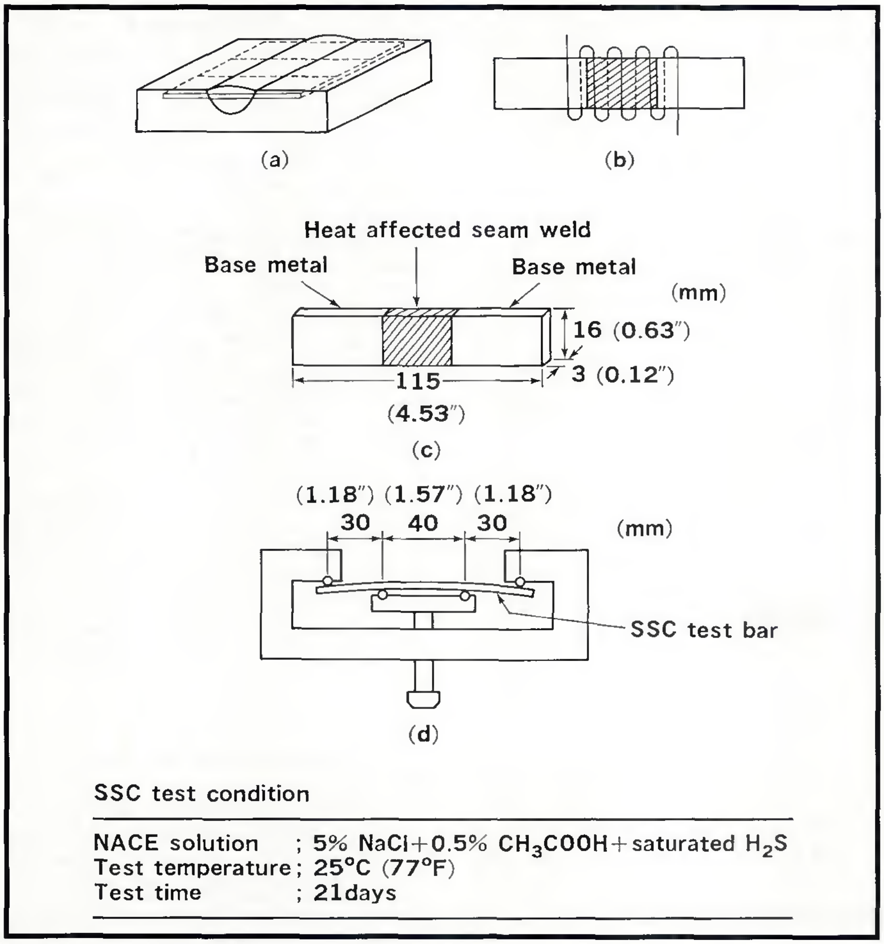

Fig. 5 — Test procedure for sulfide stress corrosion evaluation of the weld metal.

Table 5—Welding Condition for Gas Metal Arc (GMA) (CO_2) Girth Welding

Method	GMAW (CO_2)
Wire	No. 6 1.2 mm (0.047 in.)
Heat input	0.5 kJ/mm (12.7 kJ/in.); 200 A 22 V 530 mm/min (20.9 in./min)
	1.0 kJ/mm (25.4 kJ/in.); 250 A 25 V 370 mm/min (14.6 in./min)

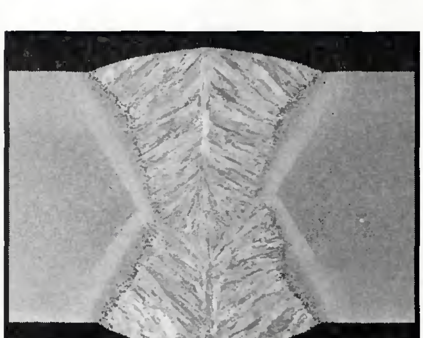

Fig. 6 —Macrophotograph of submerged arc weld section.

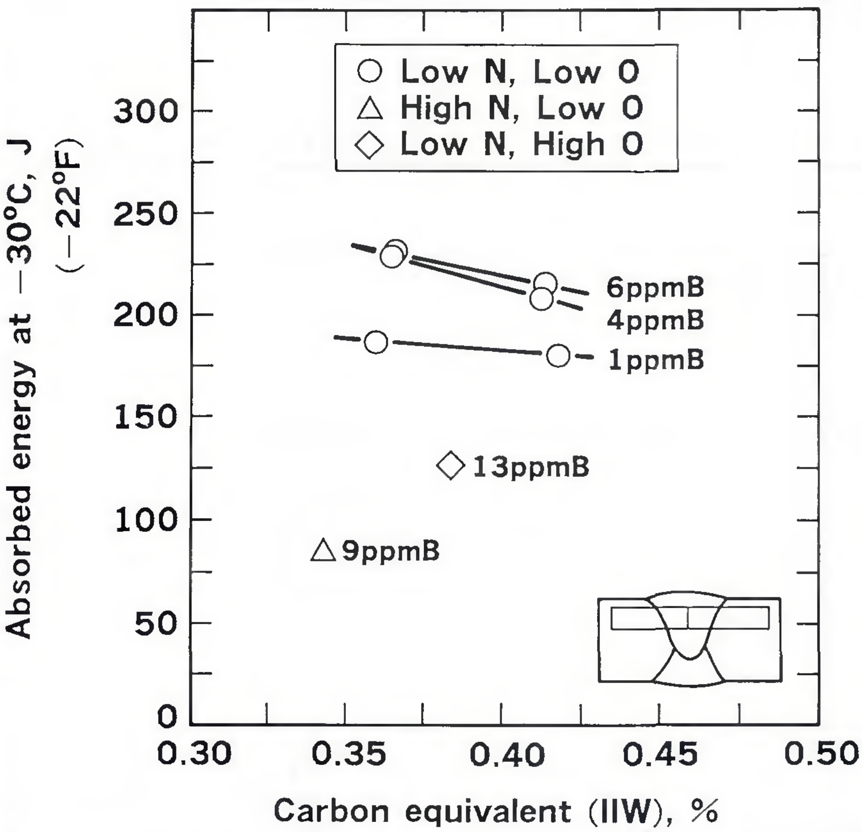

Fig. 7 — Relationship between carbon equivalent (CE_{IIW}) and toughness of submerged arc weld metal in the upper portion of the weld.

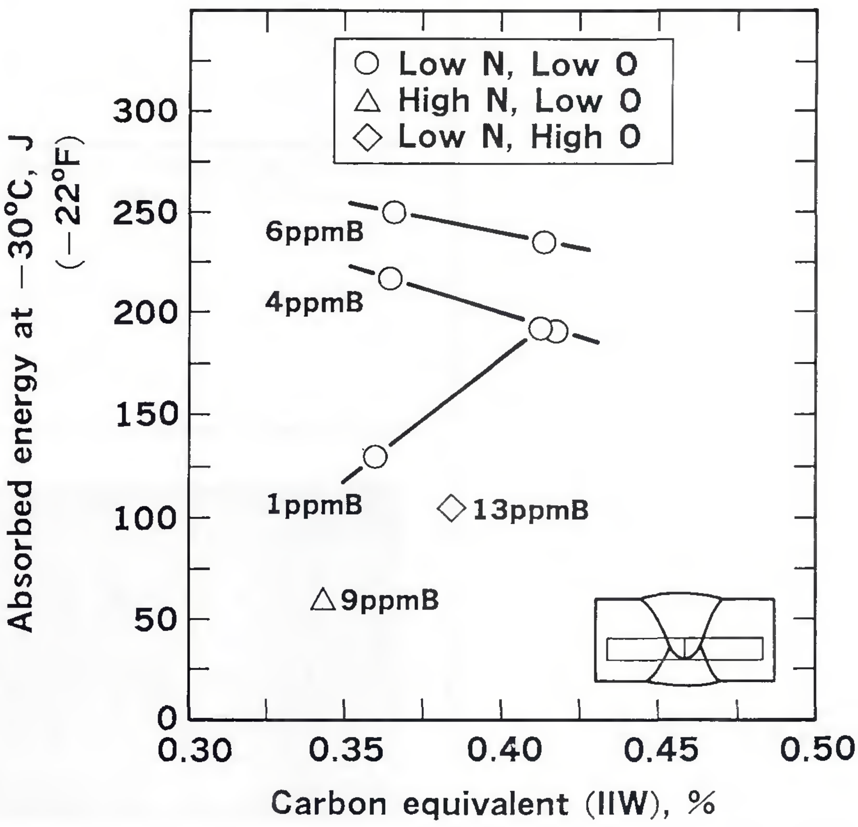

Fig. 8 — Relationship between carbon equivalent (CE_{IIW}) and toughness of submerged arc weld metal in the lower portion of the weld.

increase of boron content from 1 to 4 or 6 ppm. At the weld center, GBF and FSP disappeared when boron was 4 and 6 ppm. When the CE_{IIW} of the steel was 0.41%, GBF and FSP were not formed even in the lower part of the weld with 4 ppm boron and using Flux FA, as seen in Fig.10. However, GBF was clearly observed in welds W7 and W8, as seen in Fig. 11, both of which are of either high-N or high-O types and characterized by low toughness.

The results of hardness tests of weld metal HAZs are shown in Fig. 12. Maximum HAZ hardness increased with a decrease in welding heat input. When heat input was as low as 0.5 kJ/mm (12.7 kJ/in.), the hardness of the weld metal HAZ exceeded 248 HV 10, which is considered to be the maximum permissible value for sour gas service pipes. However, this limitation was not exceeded when heat input was increased to 1.0 kJ/mm (25.4 kJ/in.) and the Mn content in the weld metal was less than 1.7%. As seen in the weld metal with low N and low O using Flux FA, the weld metal HAZ hardness increased with an increase of boron content. The high N-low O weld metal and low N-high O weld exhibited lower HAZ hardness than the weld metal made with Flux FA, in spite of their higher boron contents.

The tensile strength of the weld metal increased with an increase of Mn content or CE_{IIW}, as shown in the tensile test results in Fig. 13. Tensile strength also increased with an increase of boron content in the weld metal made with Flux FA, because boron prevents the nucleation of grain boundary ferrite, which is softer than the lower temperature transformation products such as acicular ferrite and upper bainite.

The test results on SSC of the weld metal are shown in Figs. 14 and 15. The critical hardness, which is the maximum permissible hardness for avoiding the occurrence of SSC, was for the low N-low O weld metal, while it was 250 HV 10 for the low N-high O weld metal. In other words, the weld metal with low N and low O is more resistant to SSC than that with low N and high O. The SSC characteristics of weld metal were influenced not only by hardness, but also by the composition of the weld metal.

Discussion

Weld Metal Hardness and Boron

On-site girth welding of line pipes is conducted with speed and thus with very low heat input, generally not more than 1.0 kJ/mm (25.4 kJ/in.). A reduction of carbon is most effective in decreasing the HAZ hardness, especially for low heat input welding. Therefore, the car-

Table 6—Chemical Composition of Submerged Arc (SA) Weld Metals

WM No.	Flux No.	Chemical composition (wt-%) C	Si	Mn	P	S	Ni	Cu	Mo	V	Al	Ti	Nb	B	N	O	CE %
W1	FA	0.06	0.17	1.54	0.006	0.002	0.27	0.04	0.12	0.003	0.017	0.010	0.026	0.0001	0.0027	0.0219	0.360
W2	FA	0.06	0.17	1.58	0.007	0.002	0.27	0.04	0.11	0.003	0.015	0.010	0.025	0.0004	0.0029	0.0197	0.365
W3	FA	0.06	0.17	1.58	0.007	0.002	0.27	0.04	0.11	0.003	0.016	0.011	0.025	0.0006	0.0027	0.0147	0.366
W4	FA	0.06	0.18	1.87	0.006	0.002	0.34	0.04	0.11	0.003	0.017	0.014	0.026	0.0001	0.0023	0.0158	0.418
W5	FA	0.06	0.18	1.83	0.007	0.002	0.33	0.04	0.11	0.003	0.016	0.013	0.026	0.0004	0.0028	0.0190	0.413
W6	FA	0.06	0.18	1.85	0.007	0.002	0.34	0.04	0.11	0.003	0.017	0.014	0.026	0.0006	0.0027	0.0222	0.414
W7	FB	0.06	0.34	1.44	0.008	0.002	0.28	0.03	0.13	0.004	0.018	0.008	0.030	0.0009	0.0074	0.0259	0.343
W8	FC	0.05	0.28	1.70	0.007	0.004	0.34	0.03	0.12	0.008	0.017	0.029	0.030	0.0013	0.0033	0.0491	0.384
W9(1)	FA	0.04	0.18	1.54	0.008	0.004	0.32	0.04	0.14	0.003	0.020	0.009	0.026	0.0009	0.0025	0.0190	0.352
W10(1)	FC	0.04	0.21	1.68	0.011	0.004	0.44	0.02	0.18	0.006	0.020	0.025	0.005	0.0020	0.0038	0.0360	0.385

CE = C + Mn/6 + Ni/15 + Cu/15 + Mo/5 + V/5 (IIW formula %)
(1) The W9 to W10 weld metals are used for sulfide stress corrosion cracking tests.

Table 7—Calculated Boron Content Necessary to Combine Remaining Oxygen and Nitrogen

No.	Chemical Composition (ppm) Si	Al	Ti	B	N	O	Calculated results (ppm) $\Delta[O]_1$	O as TiO	$\Delta[O]_2$	O as SiO_2	$\Delta[O]_3$	B as B_2O_3	N as TiN	ΔN	B as BN	Free B
W1	1700	160	103	1	28	188	67	23	44	58	−14	0	9	19	15 (1)	0
W2	1700	160	103	4	28	188	67	23	44	58	−14	0	9	19	15 (4)	
W3	1700	160	103	6	28	188	67	23	44	58	−14	0	9	19	15 (6)	
W4	1800	167	137	1	26	190	62	33	29	62	−33	0	12	14	11 (1)	0
W5	1800	167	137	4	26	190	62	33	29	62	−33	0	12	14	11 (4)	
W6	1800	167	137	6	26	190	62	33	29	62	−33	0	12	14	11 (6)	
W7	3400	180	80	9	74	259	123	19	104	116	−12	0	7	67	52 (9)	0
W8	2800	170	290	13	33	491	363	68	295	96	199	106 (13)	25	8	0 (0)	0

(1) ( ) Denotes boron actually combined with oxygen or nitrogen.

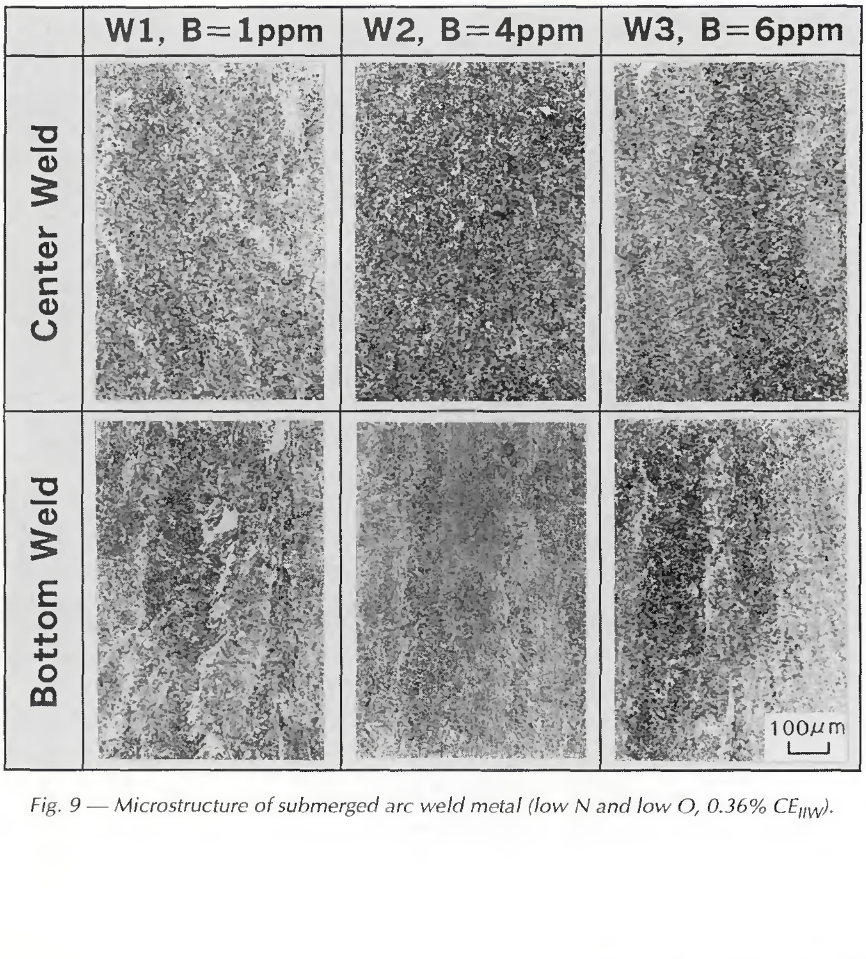

Fig. 9 — Microstructure of submerged arc weld metal (low N and low O, 0.36% CE_{IIW}).

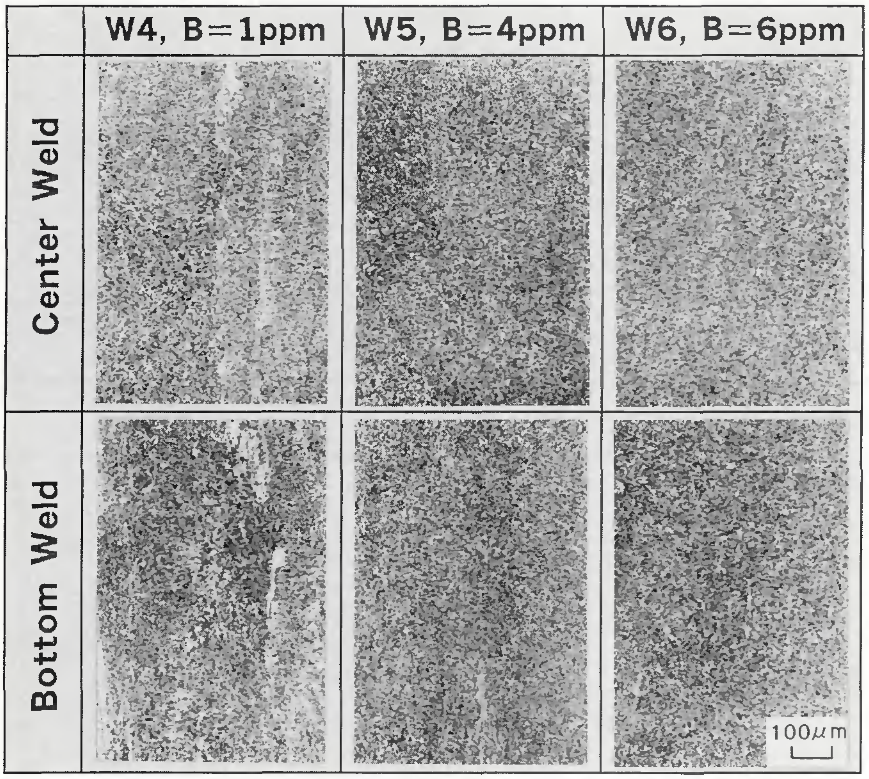

Fig. 10 — Microstructure of submerged arc weld metal (low N and low O, 0.41% CE_{IIW}).

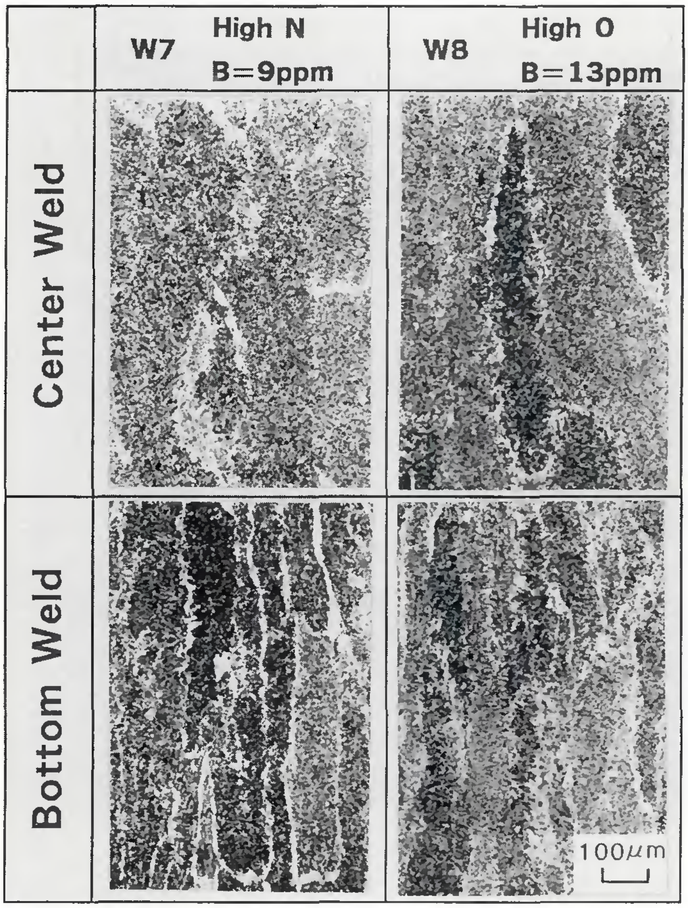

Fig. 11 — Microstructure of submerged arc weld metal (high N and high O).

bon content in the longitudinal weld of sour gas service line pipes has been decreased to a level of 0.05%, as seen in Table 6. It is well known that a few ppm of boron significantly increases HAZ hardness by the suppression of grain boundary ferrite formation. Modern structural steel, including line pipe steel, contains O and N at a very low level, and thus most of the boron remains free, *i.e.*, not fixed with O and N, resulting in a hardenability increase with even a very low boron content.

The HAZ hardenability is described by the critical cooling time for full martensite structures; steel and weld metals with higher hardenability have longer critical cooling times, *i.e.*, HAZ microstructures become martensitic with longer cooling times or slower welding cooling rates. The HAZ hardenability increase by boron can be equated to that due to carbon content (Ref. 4). Figure 16 relates the boron content to a comparable carbon equivalent that would yield the same increase in hardenablity (Ref. 5). The boron effect levels off and the maximum effect by a few ppm of boron is equivalent to that of 0.9% (900 ppm) carbon. It is seen that the maximum hardenability is attained at 4 ppm boron in steel with 20 ppm N and at 10 ppm boron in steel with 70 ppm N, while at a much higher critical boron content (B_x) in weld metal. It follows that boron in the weld metal influences the HAZ hardness less significantly than in steel. This is because weld metal contains O and N at a higher level than in steel and boron is more likely to be combined with O and N, thereby becoming less effective in the weld metal. With a decrease in the O and N content in the weld metal, B_x decreases and approaches that of steels, *i.e.*, a sharp effect of boron on weld metal HAZ results. The formula for predicting weld metal HAZ hardness is described in the Appendix. Figures 17 and 18 show the comparison of measured weld metal HAZ hardness and that predicted by the formula, using the chemical composition in Table 7. Good agreement between the experiment and prediction is found.

As seen in the presence of grain boundary ferrite in Fig. 11, boron was inactive at 9 ppm for the weld metal with high N and low O and at 13 ppm for the weld metal with low N and high O. However, Fig. 12 shows that hardness increased to some extent in the weld metal with high N when welded with 1.0 kJ/mm (25.4 kJ/in.) heat input, but not with 0.5 kJ/mm (12.7 kJ/in.). This is presumably because some boron nitride (BN) dissolved to make free boron only in higher heat input welding condition. It was reported that boron soluble in iodine methyl, which is considered to be free boron, increased when Ti-B containing weld metal was heated over 1050°C (1922°F) (Ref. 6). Therefore, nitrogen should be minimized to avoid an unexpected increase in weld metal HAZ hardness. Also, the effect of the decomposition of BN, as a function of welding heat input, must be taken into account in the formula for the weld metal HAZ hardness. At any rate, it is important to determine the appropriate total content of boron while also taking into account the Al, Ti, Si, N and O content, when the control of the weld metal HAZ hardness is necessary.

Weld Metal Composition and Toughness

In the series of weld metals examined in the present study, intragranular microstructures were satisfactorily refined through the formation of fine acicular ferrites (AF). Grain boundary ferrite (GBF) was distinctly observed in welds W7 (high N-low O) and W8 (low N-high O). Grain boundary ferrite was more likely to be formed in the lower part of the weld than in the weld surface because more boundaries are available in the lower portion, due to the finer austenitic grain size there. Horii, *et al.* (Ref. 7), found that the oxidization reaction of elements in the molten Ti-B containing weld metal occurs in the order of their affinity with oxygen. Aluminum is first oxidized followed by the oxidation of Ti, Si, B, and Mn, in that order. They also recognized that these elements are not completely oxidized, but rather 85% of Al, 70% of Ti and 3% of Si, as approximate values, are oxidized. Therefore, the amount of oxygen that combines with Al, Ti and Si is calculated as follows:

First, oxygen oxidizes Al,

$$\text{O as } Al_2O_3 = \frac{48}{54} \times 0.85 \times \text{Al} \quad (1)$$

$$\Delta[O]_1 = \text{total O} - \text{O as } Al_2O_3 \quad (2)$$

If effective oxygen remains after Al oxidization, *i.e.*, $\Delta[O]_1$ is positive, Ti is oxidized,

$$\text{O as TiO} = \frac{16}{48} \times 0.7 \times \text{Ti} \quad (3)$$

$$\Delta[O]_2 = \Delta[O]_1 - \text{O as TiO} \quad (4)$$

If effective oxygen remains after Ti oxidization, *i.e.*, $\Delta[O]_2$ is positive, Si is oxidized,

$$\text{O as } SiO_2 = \frac{32}{28} \times 0.03 \times \text{Si} \quad (5)$$

$$\Delta[O]_3 = \Delta[O]_2 - \text{O}SiO_2 \quad (6)$$

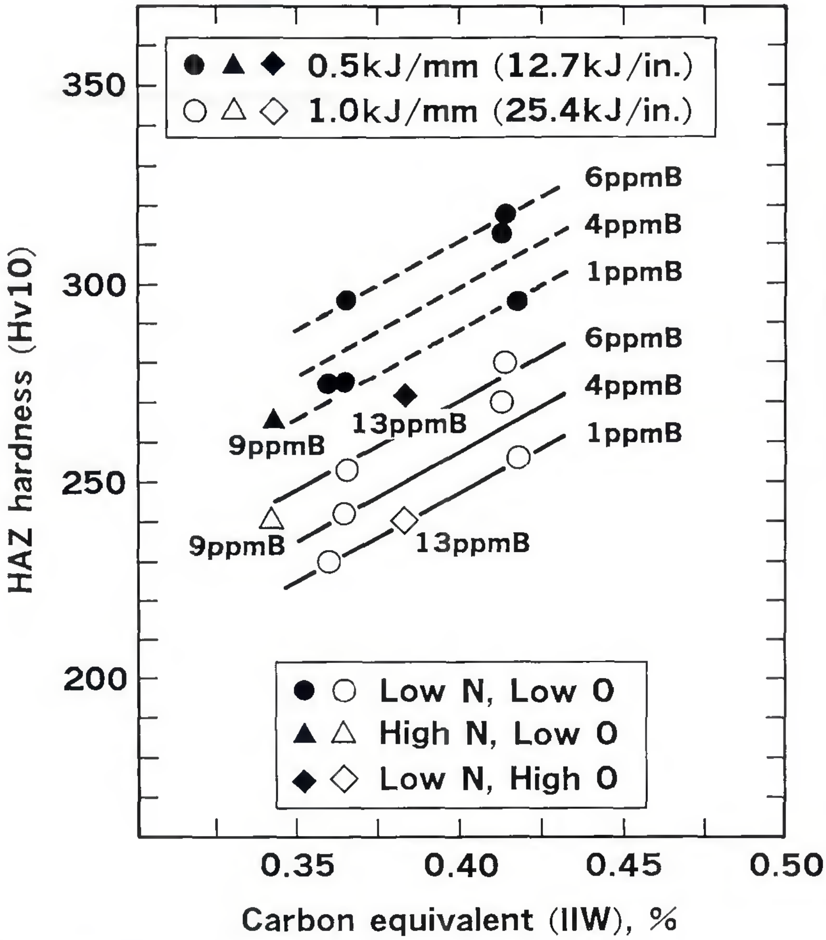

Fig. 12 — Results of HAZ hardness measurements.

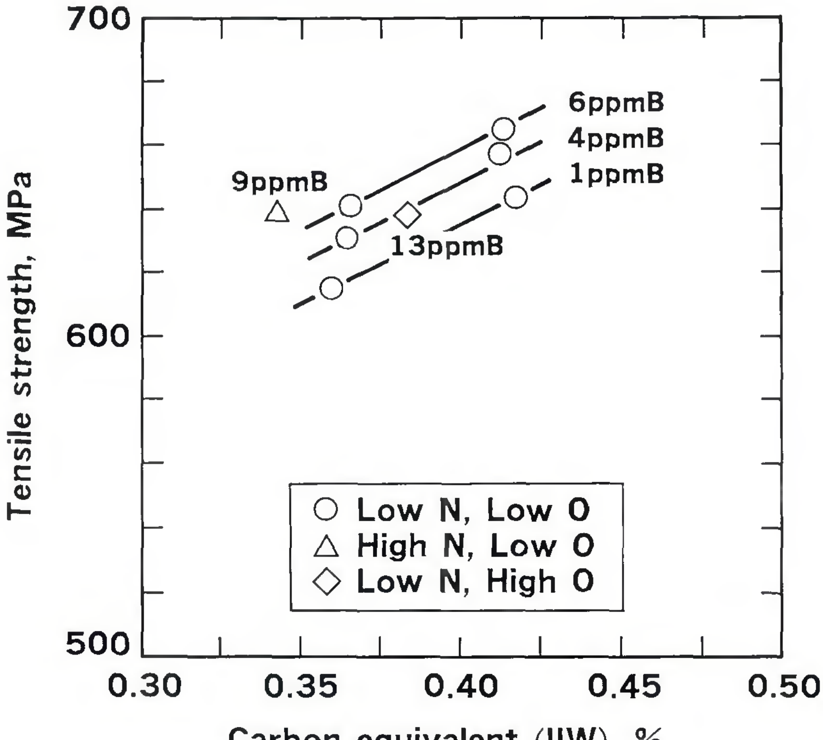

Fig. 13 — Relationship between carbon equivalent and tensile strength.

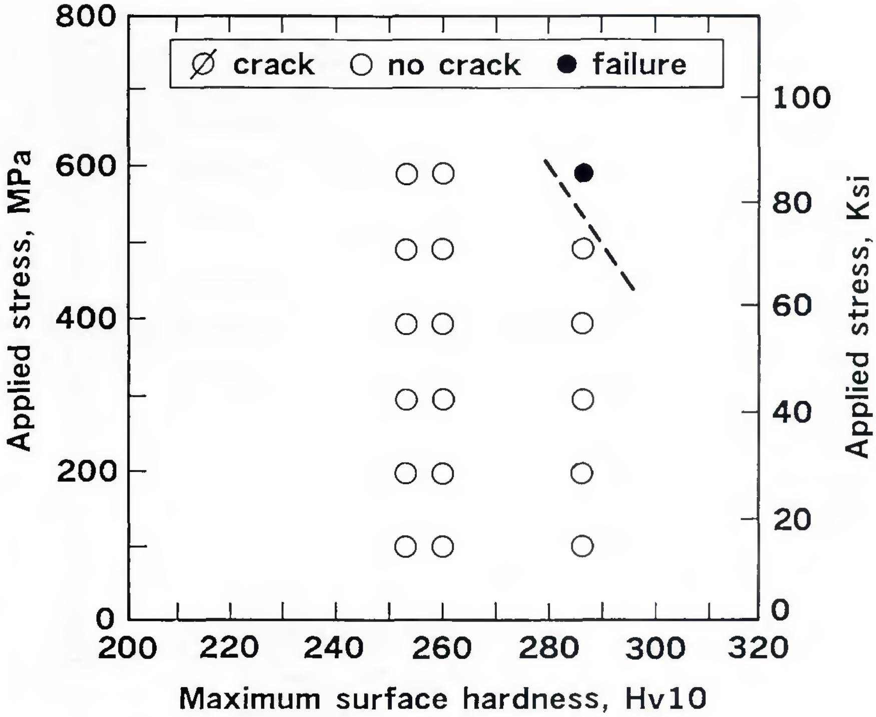

Fig. 14 — Results of sulfide stress corrosion test (low N and low O, 9 ppm B).

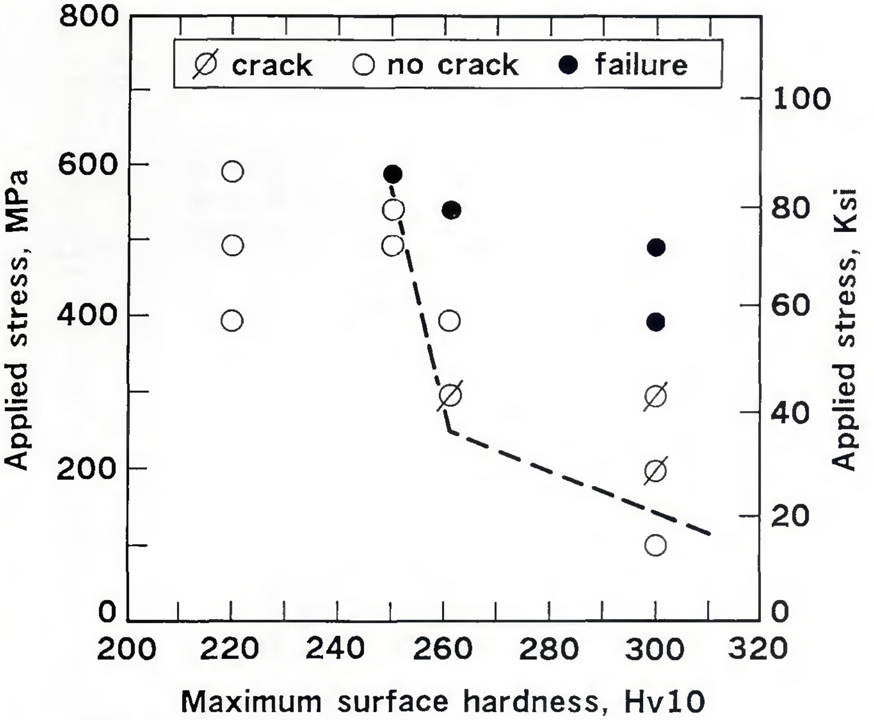

Fig. 15 — Results of sulfide stress corrosion test (low N and high O, 20 ppm B).

If effective oxygen still remains after Si oxidization, *i.e.*, $\Delta[O]_3$ is positive, B is oxidized,

$$B \text{ as } B_2O_3 = \frac{21.6}{48} \times \Delta[O]_3 \qquad (7)$$

The amount of nitrogen to fix free boron is calculated in the same manner as the above. Nitrogen first fixes Ti as TiN,

$$\Delta N = N - \frac{14}{48} \times 0.3 \times Ti \qquad (8)$$

When ΔN is positive,

$$B \text{ as } BN = \frac{10.8}{14} \times \Delta N \qquad (9)$$

The amount of boron given in Equation 9 is used to fix free nitrogen in weld metal.

The results of oxidization and nitrification in the weld metal of Table 6 using Equations 1 through 9 are listed in Table 7. For all the weld metals examined, $\Delta[O]_1$ was positive, and thus the formation of Ti-oxides, which act as nucleation sites for acicular ferrite (AF) (Refs. 1, 2), is expected. Intragranular acicular ferrite (AF) was observed in all the tested weld metals. Boron oxides are not formed in all cases except for weld metal W8 as expected, since $\Delta[O]_3$ is negative. In weld metal W8, boron is completely oxidized and no free boron remains so that the formation of GBF is not suppressed, as shown in Fig. 11.

The boron necessary to combine with the remaining free nitrogen was calculated. Table 6 shows that the necessary boron for weld metals W1 to W6 is between 11 and 15 ppm. This amount is slightly higher than the total boron measured by chemical analysis. This implies that no free boron exists, but free boron does remain because GBF disappeared in the weld metal with 4 and 6 ppm boron, as seen in Figs. 9 and 10. On the other hand, boron is considered to be completely nitrified and no free boron remains in weld metal W7, because of a high nitrogen content. In fact, GBF is found to a greater extent in the weld metal W7, as shown in Fig. 11.

Compatibility of High Toughness and Lower Hardenability

The toughness of the weld metal with low N-low O was higher for a CE_{IIW} of 0.36% and 4 ppm B than for a CE_{IIW} of 0.41% and 1 ppm B, as seen in Fig. 8. The weld metal HAZ hardness was lower for 0.36%CE_{IIW} and 6 ppm B than for 0.41%CE_{IIW} and 1 ppm B, as seen in Fig. 12. As for microstructures, GBF disappeared in the weld metal of 0.36% CE_{IIW} when B was over 4 ppm. It is thus determined that high toughness in weld metal and low hardness in weld metal

HAZ can be concurrently assured by reducing the CE_{IIW} and effectively using a small amount of boron. Substantial amounts of boron must be added to the weld metal with high N to combine free nitrogen, which is very detrimental to toughness. However, the existence of excessive BN is not desirable because of the HAZ hardness increase as mentioned previously. The toughness of the weld metal W8 with high oxygen can be improved through the addition of a sufficient amount of Al and Ti, both of which have stronger affinities with oxygen than B, so that $\Delta[O]_3$ becomes negative.

Manufacturing of Weld Metal with Low N and Low O

The oxygen content in weld metal decreases in the order of Flux FC, FB and FA as seen in Table 6. It is well known that the oxygen content in weld metal decreases with an increase in flux basicity, which is expressed as $(CaO + MgO + BaO)/(TiO_2 + SiO_2)$. Basicity was highest in Flux FA and lowest in Flux FC, as seen in Table 1. The nitrogen content was highest in weld metal W7 made with Flux FB, as seen in Table 6. When the oxygen content is very low, the partial pressures of CO_2 and CO gas adjacent to the welding arc are considered to be low. Therefore, the purge of air caught up between the flux powder is not facilitated and nitrogen gas pressure from the air increases around the welding arc, resulting in high N in the weld metal. This is the presumed reason why high nitrogen content rose in weld metal W7 with low O and not in W8 with high O.

However, the nitrogen content was not high in the weld metal made with Flux FA, which is also characterized by low O, like the weld W7. Flux FA contains calcite ($CaCO_3$) which decomposes during welding to generate CO_2 gas. The increase of CO_2 gas pressure results in lower partial pressure of air around the welding arc and accordingly, low N in the weld metal results. It is essential to add $CaCO_3$ into the flux of a low-O type to produce weld metal with low O as well as low N.

Conclusions

A metallurgical study has been conducted to develop longitudinal submerged arc welds on line pipes for sour gas service possessing high toughness as well as low hardenability when welded on in the field. Findings in this study are as follows:

1) The hardness of the weld metal HAZ caused by subsequent welding, such as girth welding, is influenced by the heat input of the subsequent weld-

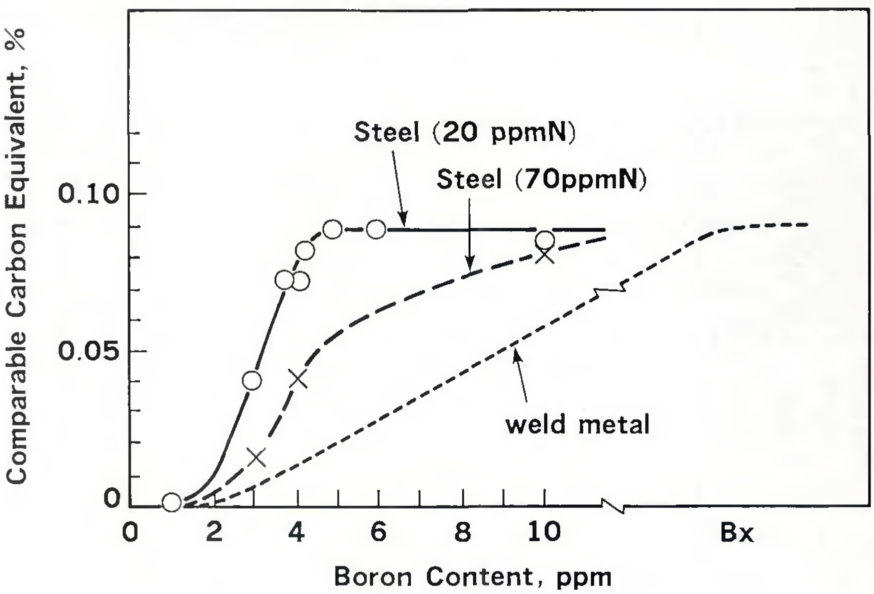

Fig. 16 — Relationship between HAZ hardenability increment and total B.

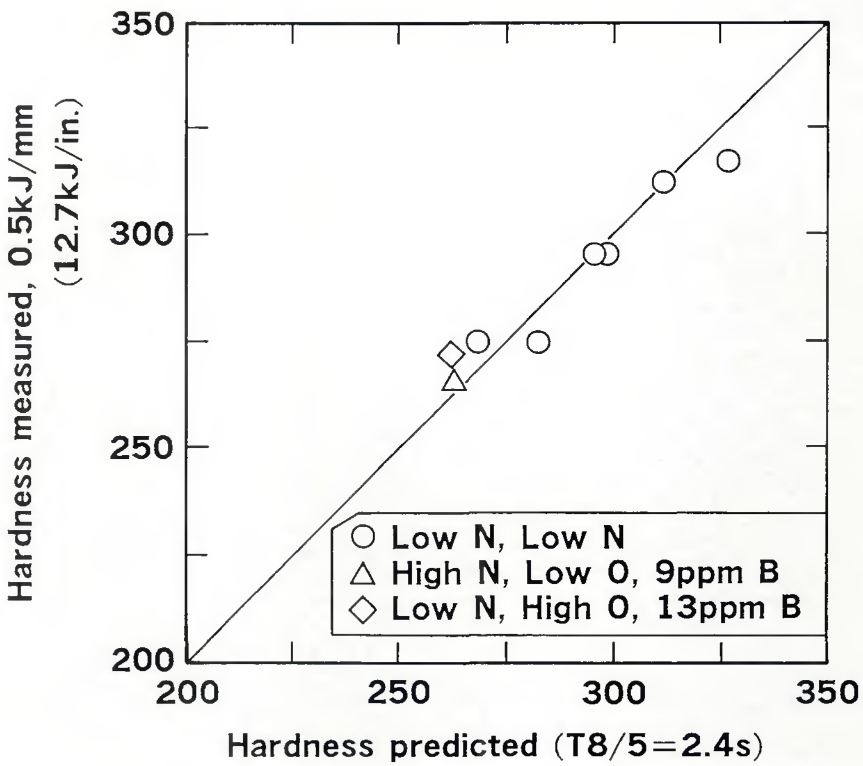

Fig. 17 — Relationship between predicted and measured hardness (0.5 kJ/mm, $T_{8/5}$ = 2.4 s).

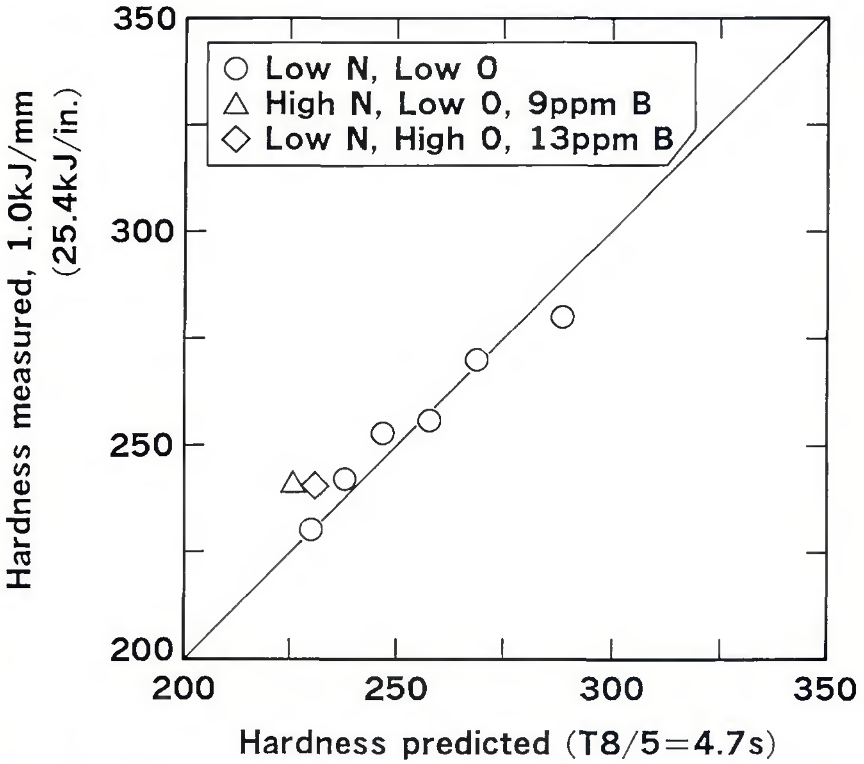

Fig. 18 — Relationship between predicted and measured hardness (1.0 kJ/mm, $T_{8/5}$ = 4.7 s).

ing, the carbon equivalent and the boron content of the weld metal. The effect of boron on the weld metal HAZ hardness is governed by the content of Al, Ti, Si, N and O. It is, thus, important to design appropriately the composition of the elements influencing the boron effect when controlling the weld metal HAZ hardness.

2) The toughness of the Ti-B containing weld metal is improved by the formation of acicular ferrite and by reducing the formation of grain boundary ferrite. The formation of Ti-oxide, which acts as a nucleation site for acicular ferrite, is predicted by the calculation based on the chemical composition of the weld metals. As expected, fine acicular ferrite was observed in the intragranular microstructures of all the tested weld metals. In the weld metal with low N and low O, grain boundary ferrite is not formed when the B content is 1 ppm and the CE_{IIW} is 0.41%, or when B is 4 ppm and CE_{IIW} is 0.36%. However, in the weld metal with either higher N or higher O, lower weld metal HAZ hardness is assured, but desirable toughness is not obtained because of the formation of grain boundary ferrite. In the weld metal with either high N or high O, an appropriate amount of free boron can remain if excessive nitrification and oxidization of boron are avoided.

3) High toughness in the weld metal and lower hardenability of the weld metal HAZ can be concurrently assured by designing low N and low O with an appropriate carbon equivalent and a boron content of approximately 5 ppm.

4) It is important to reduce the total amount of B because boron nitrides may decompose to form excessive free boron during subsequent welding. From this viewpoint, weld metal with low N and low O is desirable because the total boron can be designed to be at a low level.

5) High resistance to sulfide stress corrosion cracking in the NACE solution is found in the weld metal with low N and low O.

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Appendix

Prediction of Weld Metal HAZ Hardness (Ref. 4)

The hardness of weld metal HAZ may be predicted by substituting a welding cooling time from 800° to 500°C (1472°F to 932°F), $T_{8/5}$(s) into Equation A1. $T_{8/5}$ is given from welding conditions.

$$H_v = 206 + 442C + 98.5CEII + (80.5 + 402C - 89.5CEII)\arctan(x)$$

$$x(\text{radian}) = \frac{\log(T_{8/5}) - 2.30CEI - 1.35CEIII + 0.76}{1.15CEI - 0.673CEIII - 0.548} \quad (A1)$$

where, CEI is related with cooling time for full martensite:

$$CEI = C + \frac{Si}{24} + \frac{Mn}{8} + \frac{Cu}{15} + \frac{Ni}{12} + \frac{Cr}{8} + \frac{Mo}{4} + \Delta H$$

ΔH: additional increase in hardenability

$$\Delta H = \frac{-0.14(O[ppm] - 20)}{600} + \Delta BH$$

ΔBH: additional increase in hardenability caused by boron (Fig. 16)

$$B \le 2ppm, \quad \Delta BH(\%) = 0$$

$$2ppm < B \le B_x, \quad \Delta BH(\%) = \frac{0.09(B[ppm] - 2)}{(B_x[ppm] - 2)}$$

$$B > B_x, \quad \Delta BH(\%) = 0.09$$

$$B_x = 4 + \frac{45}{300}O^{(1)} + \frac{45}{50}N^{(2)} \quad \text{in ppm}$$

$$O^{(1)} = O - \frac{48}{54}(0.85Al) - \frac{16}{48}(0.70Ti) - 20 \quad \text{in ppm}$$

$$N^{(2)} = N - \frac{14}{48}(0.30Ti) - 20 \quad \text{in ppm}$$

CEII is related to bainite hardness:

$$CEII = C + \frac{Si}{24} + \frac{Mn}{7} + \frac{Cu}{7} + \frac{Ni}{9} + \frac{Cr}{5} + \frac{Mo}{2.5} + \frac{V}{5} + \frac{Nb}{3}$$

CEII is related to cooling time for full bainite:

$$CEIII = C + \frac{Mn}{6} + \frac{Cu}{20} + \frac{Ni}{9} + \frac{Cr}{5} + \frac{Mo}{4}$$

1. If O content of weld metal is negative, use 0 and if O content exceeds 300 ppm, use 300 in the hardness formula.

2. If N content of weld metal is negative, use 0 and if N content exceeds 50 ppm, use 50 in the hardness formula.