Electroslag Welding of Heavy Section 2¼ Cr - 1 Mo Steel

A high strength, tough 0.85 Mn-0.02 V type weld is deposited by a new filler metal, and control of Cu and Mn along with control of stress relief cooling rate are important for prevention of thermal embrittlement

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ABSTRACT. A new electroslag welding filler metal was developed for heavy section pressure vessels of 2¼ Cr-1 Mo steels. Welds made with the filler metal displayed strength and toughness after a long stress relief heat treatment, followed by quenching. It was achieved by increasing manganese content more than normal and by the small addition of vanadium. The quality of weld metal was maintained at a slow quenching rate of 9 C/min (16 F/min) and also with variations in penetration in base metals during welding.

Thermal embrittlement of weld metals during operation at about 450 C (850 F) was studied by means of an accelerated embrittling technique (G.E. Step Cooling treatments). There was an optimum content of manganese to reduce the embrittlement. Because of its detrimental effect, it was necessary to keep the copper content below 0.10% in weld metals. It was important, after stress relief heat treatment, to cool as rapidly as possible to prevent thermal embrittlement since loss of the toughness due to slow cooling still remained after step-cooling treatments.

A linear relation between tensile strength at room temperature and at 435 C (815 F) was confirmed, and an experimental formula was proposed for the estimation of tensile strength of electroslag weld metals with their chemical compositions.

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Introduction

Although electroslag welding has been developed as a high efficiency process for heavy section steel plates, there have been only a few instances where it has been successfully applied to the fabrication of high pressure vessels made of low-alloy steels. There are two reasons for this:

1. Despite the long hours of stress relief heat treatment always given to the welded joint after welding, no welding material so far developed has been capable of producing electroslag welded joints having sufficient high temperature strength and toughness for these vessels.

2. Without water quenching, heavy section low-alloy steel plates do not develop sufficient toughness, even when they are subsequently tempered and stress-relieved, but electroslag welded pressure vessel shells are liable to be deformed during the water quenching processes.

In Japan, where air pollution is a major issue, the concentration of SO_2 in the atmosphere is officially limited to below 0.05 ppm. As a result, heavy oil used as fuel in Japan must contain less than 1.0% of sulfur at present, and only around 0.55% in the future.

Direct desulfurization processes have been developed to obtain such a low sulfur heavy oil from a high sulfur crude oil. In the process, heavy oil and hydrogen gas are mixed at a temperature of 400 to 450 C (approximately 750 to 840 F) under a pressure of 100 to 170 Kg/cm² or 9.8 to 16.7 MPa (1422 to 2417 psi), and the sulfur is removed to a level of 0.3 to 0.5% as H_2S in the presence of a nickel base catalyzer.

Under these circumstances, in 1972, projects for building large scale heavy oil direct desulfurization plants were taken up by many oil refineries in Japan, and the development of suitable electroslag welding filler metals for 2¼ Cr-1 Mo heavy section pressure vessels of these plants was undertaken to promote the fabrication of the vessels.

Very little data on electroslag welding of 2¼ Cr-1 Mo steel (ASTM A 387Gr.22) plates are available (Refs. 1,2). It has been reported by Miyano *et al* (Ref. 1) that commmercial 2¼ Cr-1 Mo electroslag weld metals have tensile strength between 55 and 66 Kg/mm² or 539 and 647 MPa (78000 and 94000 psi) at room temperature and also absorbed energy at 0 C (32 F) in Charpy V-notch impact tests, vEo, between 7 and 15 kg-m (50 and 180 ft-lb) within stress relief (SR) conditions from 19.9 to 20.7 in Larson-Millers temper parameters (T.P.) which are expressed by the following formula:

$$T.P. = T\,(20 + \log t) \times 10^{-3}$$

where T is the stress relieving temperature in degrees Kelvin and t is the holding time in hours. However, as shown later in Fig. 7, in order to guarantee a tensile strength above 45 Kg/mm² or 44 MPa (64000 psi) at 435 C (815 F), the tensile strength must be over 56.2 Kg/mm² or 551 MPa (79,900 psi) at room temper-

Table 1 — Chemical Composition of Test Welding Wires, wt – %

No.	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	Nb	Ti
10	0.131	0.34	0.85	0.011	0.006	0.04	0.06	2.55	1.02	0.011	0.009	—
20	0.163	0.35	0.91	0.008	0.009	0.05	0.06	2.78	1.01	0.025	0.014	—
21	0.133	0.31	0.87	0.008	0.009	0.05	0.07	2.58	0.96	0.025	0.013	—
22	0.126	0.32	0.85	0.008	0.008	0.25	0.06	2.60	0.96	0.025	0.013	—
23	0.133	0.30	1.77	0.011	0.008	0.12	0.05	2.59	0.96	0.017	0.011	—
24	0.126	0.28	0.55	0.012	0.014	0.14	0.12	2.48	1.01	0.025	0.008	—
30	0.125	0.15	0.88	0.013	0.011	0.09	0.10	2.48	1.02	0.009	0.005	0.079
40	0.129	0.15	0.92	0.013	0.014	0.07	0.07	2.46	1.02	0.049	0.006	0.091
41	0.105	0.12	0.98	0.012	0.009	0.10	0.06	2.76	1.00	0.060	0.005	0.190
42	0.072	0.23	0.93	0.012	0.009	0.10	0.09	2.44	1.04	0.060	0.004	0.089
43	0.125	0.23	1.01	0.008	0.008	0.02	0.22	2.67	1.11	0.042	0.006	0.115
50	0.108	0.25	0.93	0.008	0.008	0.02	0.02	2.79	1.17	0.021	0.013	0.112
51	0.130	0.23	0.95	0.009	0.007	0.01	0.03	2.72	1.14	0.021	0.012	0.067
52	0.098	0.20	0.92	0.010	0.009	0.04	0.04	2.52	1.00	0.024	0.008	0.019
53	0.062	0.17	0.84	0.007	0.012	0.04	0.07	2.60	0.92	0.022	0.016	0.016
60	0.128	0.24	0.92	0.011	0.009	0.05	0.06	2.53	1.04	0.052	0.008	0.078
61	0.075	0.29	0.95	0.014	0.009	0.05	0.06	2.55	1.02	0.058	0.004	0.110
62	0.106	0.18	0.80	0.010	0.008	0.02	0.01	2.76	1.07	0.028	0.010	0.103
70	0.158	0.08	1.21	0.008	0.011	0.05	0.02	2.33	0.96	0.017	0.009	—
71	0.102	0.05	1.40	0.008	0.011	0.09	0.07	2.51	0.87	0.035	0.017	—
72	0.091	0.05	1.05	0.006	0.008	0.04	0.07	2.29	0.94	0.021	0.002	—
73	0.147	0.05	1.07	0.012	0.009	0.13	0.10	2.53	0.92	0.022	0.005	—
74	0.101	0.09	0.75	0.009	0.006	0.10	0.08	2.50	1.00	0.029	0.022	0.021
75	0.119	0.09	1.33	0.007	0.008	0.05	0.27	2.65	0.89	0.060	0.024	—
80	0.155	0.25	1.32	0.008	0.007	0.02	0.08	2.43	1.07	0.010	0.008	—
81	0.129	0.37	1.20	0.005	0.012	0.02	0.01	2.20	1.04	0.007	0.004	—
90	0.104	0.19	0.90	0.013	0.010	0.07	0.09	2.63	0.99	0.031	0.032	—
91	0.151	0.33	1.23	0.008	0.008	0.01	0.24	2.66	1.09	0.041	0.006	—
92	0.140	0.34	1.14	0.012	0.007	0.05	0.01	2.46	0.97	0.023	0.003	—
93	0.142	0.24	1.19	0.012	0.011	0.09	0.02	2.51	0.94	0.045	0.009	—
100	0.111	0.29	1.07	0.010	0.007	0.09	0.10	2.50	0.97	0.035	0.004	—

Table 2 — Chemical Composition of Test Flux, wt – %

Desig.	Grain size mesh	SiO_2	MnO	MgO	CaO	Al_2O_3	CaF_2
YF-15	20 x D	42	20	4	17	3	13

ature. Therefore, electroslag welded joints produced with conventional materials are not enough for heavy section uses. New welding materials capable of producing electroslag welded joints having a tensile strength 2 to 3 Kg/mm^2 or 0.02 to 0.03 MPa (3000 to 4000 psi) stronger than presently obtainable joints are needed.

Although the toughness of electroslag welded joints produced with conventional materials seems sufficient for practical purposes, decrease in notch toughness of the weld metal after extended operation around 450 C (842 F) should be considered. When the extensive use of 2¼ Cr-1 Mo steel (e.g., A 542C4 and A542C3) expected in the near future is taken into consideration, high toughness is also desirable for a T.P. value as low as 19.0 to 20.0, and improvements in welding materials are also needed for these reasons.

Experimental Procedure

With a view to establishing reliable electroslag welding technology for A387Gr.22 (2¼ Cr-1 Mo) heavy section steel plate thicknesses of 150 to 250 mm (5.9 to 9.8 in.), it was aimed to develop a welding material to satisfy all the requirements for the steel. Besides these requirements, hot tensile strength over 45 Kg/mm^2 or 44 MPa (64,000 psi) at 435 C (815 F) and vEo value over 10 kg-m (72 ft-lb) are also requested after quenched at a cooling rate [mean cooling rate from 900 C (1650 F) to 400 C (750 F)] over 15 C/min (27 F/min), and then stress-relieved under conditions corresponding to a temper parameter by Larson and Miller (T.P.) of 19.9 to 20.7 degrees Kelvin (35.8 to 37.3 degrees Rankin).

Experiments were conducted with experimentally produced wires having the compositions shown in Table 1 combined with a commercial neutral flux YF-15 (see Table 2 for composition) under the standard welding conditions commonly used in actual fabrication. Test welds were quenched and tempered after welding, and subjected to mechanical and metallurgical tests.

In addition, weld specimens were subjected to the G.E. step cooling treatment, a widely used accelerated embrittling treatment, and the chemical composition of the weld metal was studied in conjunction with postweld heat treatment conditions to find a way of reducing embrittlement during the use of these pressure vessels around 450 C (842 F) for extended periods.

Results and Discussion

Improvement of Weld Metal Strength

Because the weld metal of electroslag welded joints is primarily evaluated by its properties after quenching or normalizing and tempering or stress relieving treatments, its strength can be improved by an appropriate improvement of the hardenability of the weld metal and proper utilization of precipitation hardening through tempering or stress relieving treatments.

The hardenability of weld metal can be effectively improved by increasing its carbon and manganese contents. As shown in Fig. 1, the strength of the weld metal of 2¼ Cr-1 Mo steel was found to increase when its carbon content was increased. It was concluded that as long as toughness did not deteriorate excessively, the carbon content should be increased up to approximately 0.14%. Manganese was also found to contribute to improve strength up to 1.0%; however, a further increase was not only ineffective, but also caused a substantial reduction in toughness. A noteworthy aspect of the effect of the manganese content is that an increase in the content from 0.65% to 0.75% resulted in an improvement in toughness. This is considered to indicate that there is a certain optimum manganese content at which the weld metal becomes its toughest, so that in order to secure maximum toughness in such a weld metal, the addition of an optimum amount of manganese is necessary.

Carbide producing elements such as V, Nb and Ti are said to be effective in increasing the precipitation hardenability of the weld metal. According to Tanino (Ref. 3), NaCl type carbides such as V_4C_3 and NbC precipitate coherently within the ferrite matrix. However, coherent precipitation of titanium carbide has not yet been reported. These fine coherent precipitation carbides produced during the tempering process of quenched martensite are expected to contribute substantially to the improvement in strength, unless they do not grow into coarse carbide grains.

Figure 2 shows the relation between the tensile strength of electroslag weld metals and variations in V or Ti content. As can be seen, an increase of 3 to 4 Kg/mm² or 0.028 to 0.041 MPa (4000 to 6000 psi) in tensile strength was achieved by adding

Table 3 — Comparison of Toughness Among Weld Metals of Various Compositions (0.25Si - 0.8Mn type)

Stress relief condition in temper parameter, °K(°R)	Minor alloying content: Less than 0.01V (0.95Mn)	0.015V	0.03V	0.015Ti-0.010V	0.015Ti-0.020V-0.010Nb	0.02Ti-0.03V
	Average absorbed energy[(a)] in CVN tests, kg-m (ft-lb)					
19.0 (34.2)	—	16.5 (119.2)	—	3.8 (27.5)	4.3 (31.1)	1.7 (12.3)
19.8 (35.6)	18.3 (132.2)	—	19.2 (138.7)	—	—	—
20.7 (37.3)	—	16.5 (119.2)	20.3 (146.7)	4.8 (34.7)	—	6.1 (44.1)
20.9 (37.6)	16.5 (119.2)	21.7 (156.8)	—	—	6.4 (46.3)	—

(a) Average values of three test specimens.

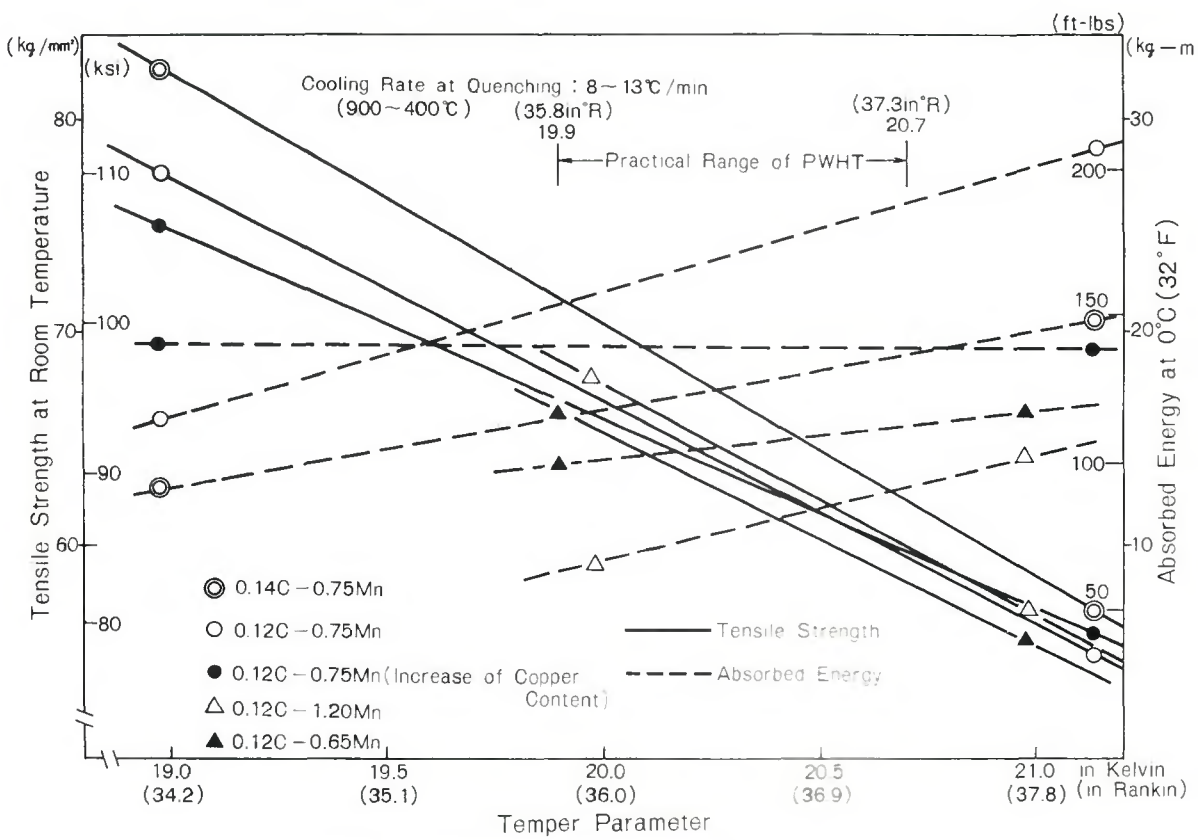

Fig. 1 — Effects of carbon and manganese contents on tensile strength and toughness of 2¼ Cr-1 Mo weld metals (0.25Si-0.015V-0.01Nb type by No. 20-24 filler metals)

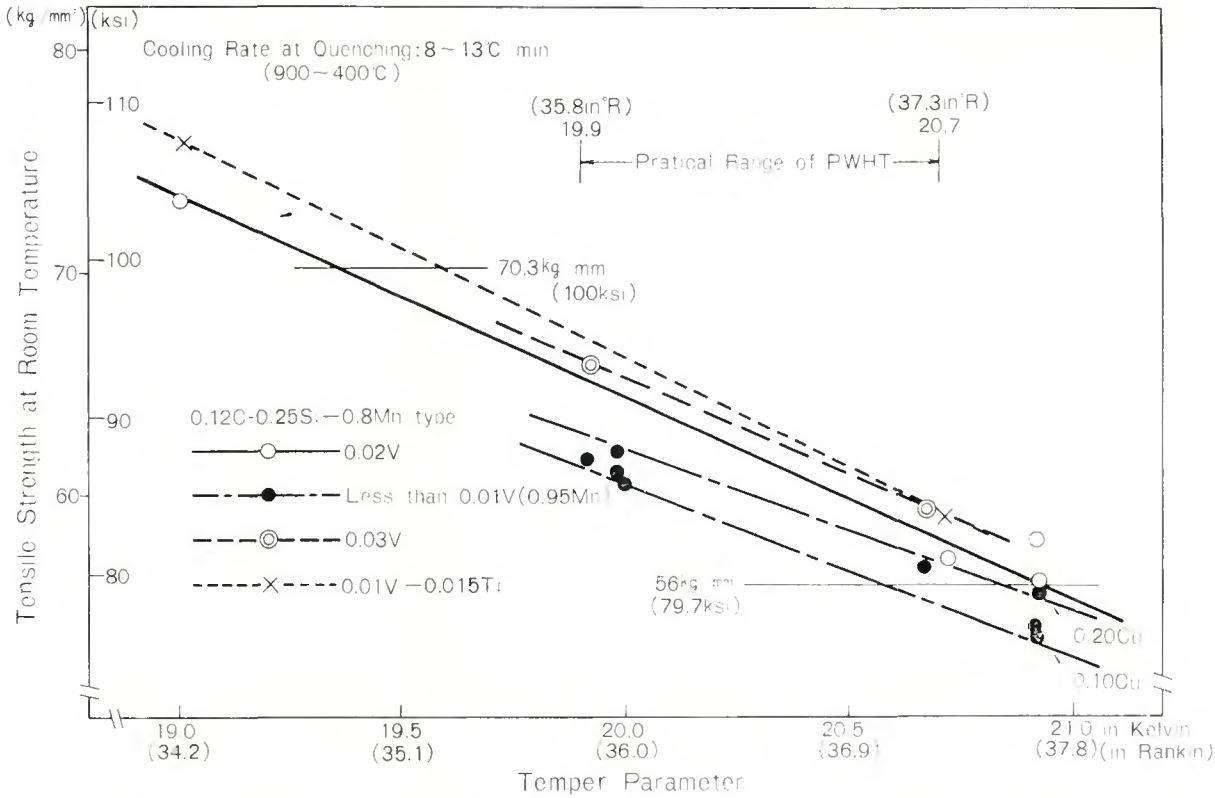

Fig. 2 — Influences of V and Ti on tensile strength of 2¼ Cr-1 Mo weld metals (0.12C-0.25Si-0.8Mn type by No. 10, 80, 81, 100 and 30 filler metals)

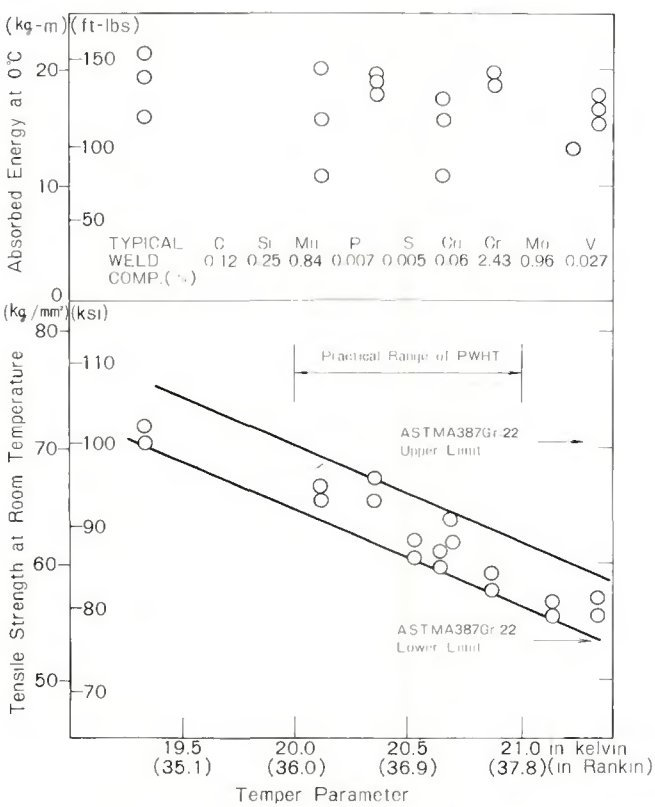

Fig. 3 — Tensile strength and toughness of the newly developed 0.85Mn-0.02V type weld metal, depending on the temper parameter (No. 100 filler metal)

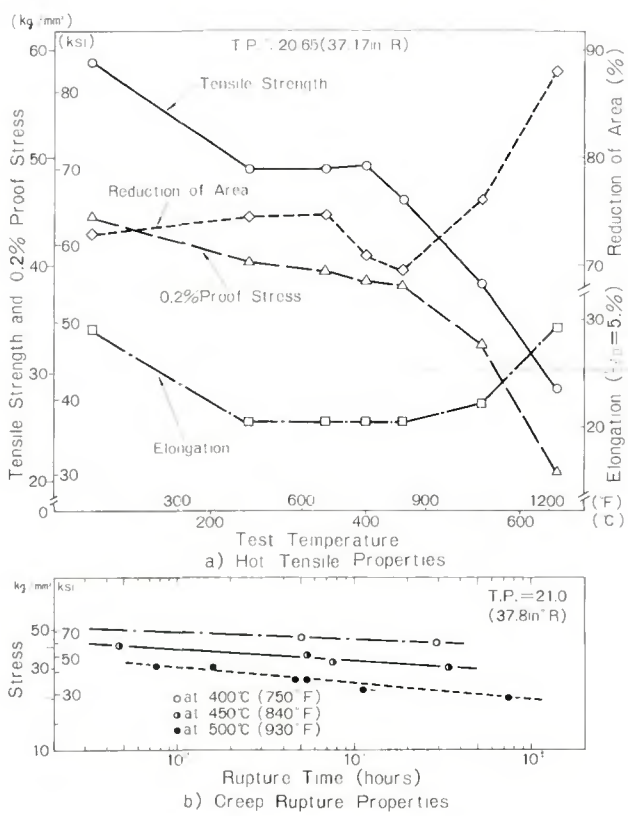

Fig. 4 — Hot tensile and creep rupture properties of the newly developed weld metal (No. 100 filler metal)

a small amount of these elements. The strength was substantially improved still further when V, Nb, and Ti were added together.

A noteworthy point in this regard was that the toughness of the weld metal differed substantially, depending on the added elements. Weld metals containing Ti with or without V and Nb were comparatively low in toughness as shown in Table 3. On the other hand, weld metal to which only vanadium was added exhibited favorable impact values vEo over 10 kg-m (72 ft-lb) for a wide range of T.P.

From the above results, it was concluded that when the heavy section weld metal contained as much carbon as the base metal (up to approx. 0.14%), as much as 0.85% Mn, and around 0.02% V, its strength and toughness could be satisfactorily improved.

Figure 3 shows the tensile strength at room temperature and the absorbed energy at 0 C in CVN tests of the weld metal obtained using the newly developed filler metal as plotted against T.P. With the practically employed heat treatment range shown somewhat extended towards high T.P. for safety, the weld metal is seen to satisfy ASTM specifications. The impact value is seen to lie above 10 kg-m (72 ft-lb) for a wide range of T.P.

Figure 4 is a plot of the hot tensile and creep rupture properties. High pressure vessels for the heavy oil direct desulfurization process are normally designed based on hot tensile strength, and minimum limit values are specified in ASME Standards. However, values somewhat lower than these have been adopted because these values are difficult to guarantee in practice. The value of 45 Kg/mm² or 44 MPa (64,000 psi) is generally accepted as the design hot tensile strength at 435 C (815 F), and the newly developed welding filler metal is seen to amply satisfy this requirement.

Influence of Welding Procedure On Mechanical Properties

As is well known, in electroslag welding the fusion of base metal becomes excessive when welding voltage is raised above an optimum level. To clarify the influence of the welding conditions on the mechanical properties of the weld metal, specimens were welded under the two sets of welding conditions shown in Table 4, and two weld metals with 38 and 64% base metal dilution ratios were obtained. The cross sections of weld metals are shown in Fig. 5 and their chemical compositions are shown in Table 5.

The weld metal under condition B had higher silicon content and lower chromium content than the weld metal under condition A. This can be explained as resulting from increased transfer of silicon from the flux and increased loss of chromium in the welding wire both caused by the increased slag pool size. It should be noted that, in weld metal B, the oxygen content was significantly higher than in weld metal A. This may be interpreted as an oxygen enrichment phenomenon caused by an increase of weld heat input, such as that of the SES welding process (Ref. 4).

The results of tensile tests at room

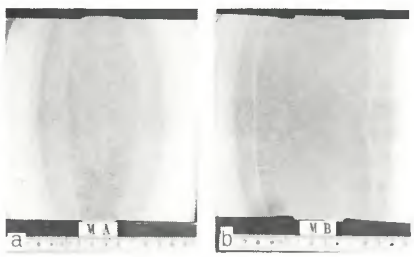

Fig. 5 — Cross sections of weld metals with different penetrations: a — 38% dilution ratio; b — 64% dilution ratio

Table 4 — Welding Conditions[a]

Symbol	Base metal thickness, mm	No. of electrodes	Current, A	Voltage, V	Upward welding speed, mm/min	Distance between electrodes, mm	Weaving width, mm	Dilution ratio, %
A	150	2	480 ~500	42 ~43	11.5	55	45	38
B		3	550 ~560	54 ~56	17.5	55	10	64

(a) 1 in. = 25.4 mm

Table 5 — Chemical Compositions of Weld Metals and Test Materials, wt – %

Symbol	Sampling position	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	V	Nb	N	O
A	Plate surface	0.140	0.22	0.88	0.009	0.008	0.03	0.03	2.42	1.02	0.031	<0.005	0.0087	0.0083
	Mid. thickness	0.138	0.22	0.88	0.009	0.008	0.04	0.04	2.43	1.02	0.033	<0.005	0.0089	0.0085
B	Plate surface	0.136	0.29	0.86	0.010	0.012	0.02	0.04	2.29	1.01	0.025	<0.005	0.0088	0.0145
	Mid. thickness	0.139	0.28	0.83	0.010	0.012	0.02	0.04	2.32	1.01	0.029	<0.005	0.0087	0.0133
Base metal[a] (150 mm thick.)		0.121	0.25	0.56	0.010	0.006	0.02	0.04	2.45	1.01	0.010	<0.005	—	—
Welding wire[a] (3.2 mm diam.)		0.155	0.25	1.30	0.007	0.009	—	—	2.43	1.07	0.042	—	—	—

(a) 1 in. = 25.4 mm

temperature and elevated temperature given in Table 6 show that the tensile strength at room temperature and high temperature was not appreciably influenced by the dilution ratio nor by the original position of the specimens in the thickness direction of the plates. On the other hand, as shown in Fig. 6, while the impact value varied little at a dilution ratio of 38%, toughness deteriorated considerably and the impact value also changed greatly for a dilution ratio of 64%. This marked decrease in toughness accompanying an increase in the dilution ratio was thought to be primarily caused by an increase in the oxygen content.

From the above, it was evident that the impact value remained within the range normally considered satisfactory for heavy section pressure vessels (vE_{10} or $vE_{20} \geq 4.8$ kg-m) when the dilution ratio was maintained within a deviation of ±10 to 20% from the value (40 to 50%) corresponding to the standard welding conditions. On the other hand, to secure a high toughness value and to prevent acceleration of thermal embrittlement caused by increased silicon content during operation as described later, dilution by the base metal had to be kept at the lowest possible level. The macrostructure and microstructure of the weld metal under standard welding conditions are shown in Fig. 7.

Influence of Postweld Heat Treatment Conditions

In fabricating pressure vessels from heavy section steel plates, the plates are quenched (normalized) and tempered either after the hot bending process of the steel plates or after their electroslag welding. Quench cooling rate has a considerable effect on the toughness of the plates, and toughness is substantially reduced in 2¼ Cr-1 Mo plates, when the cooling rate between 900 C (1650 F) and 400 C (750 F) is lower than 10 C/min (18 F/min).

Although no report has been published on this subject for electroslag weld metals, quenching experiments have been performed with weld metal specimens made with the newly developed welding material at various cooling rates. Results showed that, while the vEo value remained relatively unchanged, the fracture appearance transition temperature (FATT or vTrs) gradually increased as the cooling rate of quenching was decreased as shown in Table 7. However, toughness was still in the satisfactory range for practical purposes

Tables 6 — Influence of Dilution Ratio on Tensile Strength of Weld Metals

Dilution ratio	Heat treatment	Temper parameter	Original location of specimens (depth from surface)	Normal tensile test: 0.2% Y.S.[b] σ_{02}, kg/mm² (ksi)	Normal tensile test: U.T.S.[b] σ_B, kg/mm² (ksi)	Normal tensile test: σ_{02}/σ_B	Normal tensile test: Elong. (%)	Normal tensile test: R.A. (%)	Hot tensile test[a]: 0.2% Y.S.[b] σ_{02}, kg/mm² (ksi)	Hot tensile test[a]: U.T.S.[b] σ_B, kg/mm² (ksi)	Hot tensile test[a]: Elong. (%)	Hot tensile test[a]: R.A.[b] (%)
38%	930 CX4h (A.C.) (5.5 C/min) 1 665 CX7h (A.C.) 685 CX6h (50 C/H)	19.98	10 m/m	55.5 (78.9)	68.2 (97.0)	0.81	25	72	46.1 (65.6)	54.9 (78.1)	17	68
			32	55.9 (79.5)	68.3 (97.1)	0.82	25	65	47.5 (67.6)	55.9 (79.5)	16	68
			53	56.2 (79.9)	68.5 (97.4)	0.82	25	71	46.4 (66.0)	55.2 (78.5)	17	68
			75						46.7 (66.4)	54.9 (78.1)	16	68
	930 CX4h (A.C.) (5.5 C/min) 2 665 CX7h (A.C.) 720 CX19h (50/H)	21.13	10	42.0 (59.7)	57.9 (82.4)	0.73	30	74	35.0 (49.8)	46.4 (66.0)	19	69
			32	42.8 (60.9)	58.2 (82.8)	0.74	29	73	35.7 (50.8)	46.6 (66.3)	18	69
			53	42.9 (61.0)	58.2 (82.8)	0.74	29	73	35.2 (50.1)	46.4 (66.0)	20	66
			75						35.7 (50.8)	47.1 (67.0)	19	60
64%	Same as 1	19.98	10	56.6 (80.5)	68.6 (97.6)	0.83	24	70	45.8 (65.1)	54.2 (77.1)	16	66
			32	56.6 (80.5)	68.6 (97.6)	0.83	23	70	46.3 (65.9)	54.6 (77.7)	15	68
			53	56.3 (80.1)	68.2 (97.0)	0.83	24	71	46.2 (65.7)	54.0 (76.8)	16	69
			75						46.3 (65.9)	54.4 (77.4)	16	67
	Same as 2	21.13	10	42.6 (60.6)	57.6 (81.9)	0.74	29	73	34.7 (49.4)	45.3 (64.4)	21	70
			32	42.4 (60.3)	57.5 (81.8)	0.74	29	70	35.0 (49.8)	46.0 (65.4)	19	70
			53	42.0 (59.7)	57.2 (81.4)	0.73	30	74	34.7 (49.4)	45.5 (64.7)	19	70
			75						35.1 (49.9)	45.4 (64.6)	19	71
	Typical requirements			≥31.5 (≥44.8)	52.7 ~70.3 (75.0~100.0)	≤0.83	≥18	≥45	≥29.0 (≥41.2)	≥45 (≥64.0)	≥15	≥50

(a) Test temperature: 435 C, diam of specimen; 10 mm , G.L. = 50mm
(b) Y.S. — yield strength; U.T.S. — ultimate tensile strength; R.A. — reduction in area; ksi x 1000 = psi

when the cooling rate was reduced to around 9 C/min (16 F/min). The strength of the weld metal was also satisfactory, showing stable values for cooling rates above 9 C/min (16 F/min).

Another important factor in post-weld heat treatment is the cooling rate in the stress relieving process. Because this was found to have a significant relation to thermal embrittlement characteristics during the operation of pressure vessels made of 2¼ Cr-1 Mo steel, a description is given later in relation to embrittlement.

Influence of Alloying Elements On Weld Metal Strength

To enable electroslag welding processes to be applied to 2¼ Cr-1 Mo steels with strength higher than that of A387Gr.22, such as A542 C4, C3 or C1, the contribution rate of each alloying element to the strength of the weld metal must be known so that a proper composition may be designed for a given strength requirement. Weld metal specimens were made from the 18 types of welding wires experimentally produced except for Ti-bearing wires in Table 1. These were heat treated under constant conditions (T.P. = 20.9 in degrees Kelvin), and the tensile strength was expressed in a formula in which the contribution of each element was added using the multiregression analysis method. The results are shown in Fig. 8 where the deviation ranges of alloying elements were as follows: C — 0.10 to 0.16%; Si — 0.11 to 0.28%; Mn — 0.63 to 1.15%; Cr — 2.25 to 2.46%; V — 0.005 to 0.034%; Nb — 0.002 to 0.015%.

Although the influences of such elements as molybdenum were also obviously important and required clarification, the extent of their contribution on the properties of the weld metal was not clarified since their deviations were small in the specimens employed in the experiments.

The strength evaluation formula given in Fig. 8 does not have a satisfactorily high multiple correlation coefficient, and it requires further refinement through the incorporation of more data.

High temperature strength is a major criterion in the design of pressure vessels and is guaranteed by testing actual weld metal specimens. With 2¼ Cr-1 Mo steels, a high degree of correlation is observed between tensile strength at 435 C (815 F) and tensile strength at room temperature. A similar correlation experimentally obtained for electroslag weld metals of the steel is plotted in Fig. 9. According to the diagram, to secure a tensile strength above 45 Kg/mm² or 44 MPa at 435 C (64,000 psi at 815 F), the composition of the weld must be such that a tensile strength of 56 Kg/mm² or 55 MPa (80,000 psi) or greater is obtained at room temperature.

The required strength for 2¼ Cr-1 Mo steel plates to keep the hot tensile strength is around 54 Kg/mm² or

Table 7 — Effects of Quench Cooling Rate on Toughness of 2¼Cr-1Mo Weld Metals (0.8Mn-0.01V type)

Mean cooling rate (900 ~ 400 C or 1650 ~ 750 F)		vEo (vE at 32 F)		vTrs	
9 C/min	(16 F/min)	18.0 kg-m	(130 ft-lb)	−25 C	(−13 F)
14	(25)	17.5	(127)	−30	(−22)
17	(31)	18.5	(134)	−35	(−31)

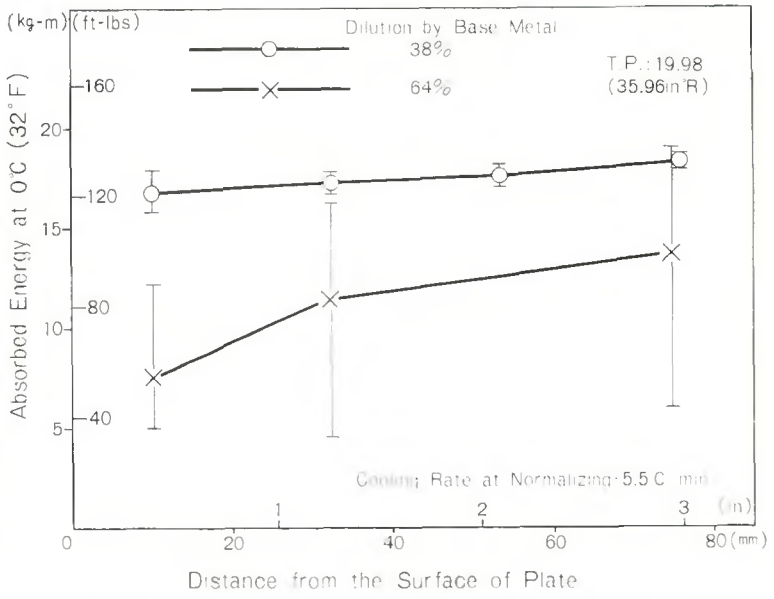

Fig. 6 — Change of the absorbed energy of weld metal in CVN tests by original location of specimens. (Notched at the middle of weld by No. 80 filler metal)

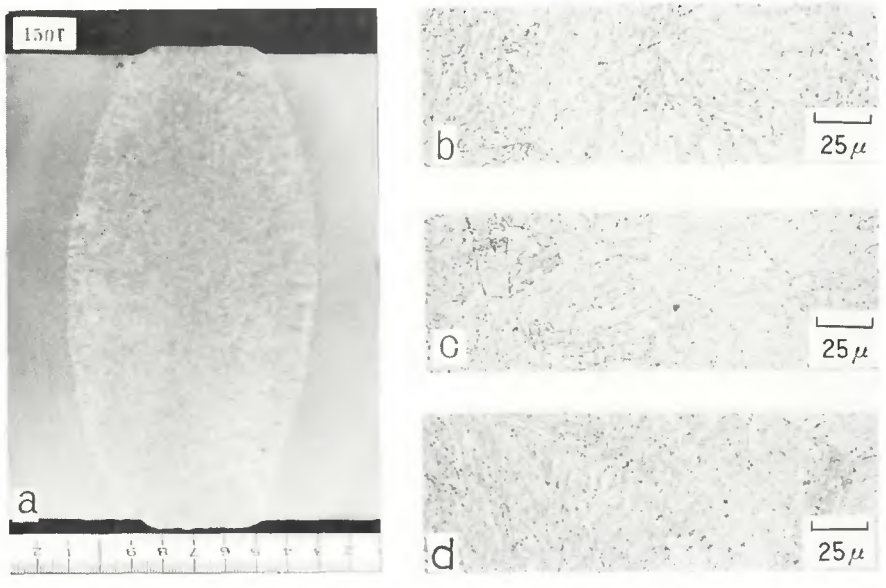

Fig. 7 — Macro- and microstructures of weld metal deposited under standard welding conditions: a — macrostructure; b — near surface; c — one-quarter of thickness from surface; d — at one-half the thickness

530 MPa (77,000 psi) at room temperature, a value slightly lower than that for weld metal. This would serve to show the difficulty of guaranteeing high temperature strength for weld metals.

Thermal Embrittlement of Weld Metal

Changes in toughness of various high temperature pressure vessels after extended operation has been investigated, and a deterioration of toughness — especially in weld metals — has been attracting attention (Ref. 5).

With 2¼ Cr-1 Mo steels, this type of loss of toughness has also been observed at a temperature range between 400 and 450 C (750 and 840 F) corresponding to the operating temperature range of the heavy oil direct desulfurization process. Although the embrittlement phenomenon is generally regarded as a type of temper embrittlement by most researchers, there are some features that made it difficult to be regarded simply as temper embrittlement. It is, therefore, referred to as embrittlement during high temperature operation (or simply, thermal embrittlement) in this paper.

An accelerated embrittling technique (Ref. 6) proposed by A. E. Powers of the General Electric (popularly referred to as the G.E. Step Cooling treatment) is generally employed as a method of experimentally producing the embrittlement in a comparatively short time. A step cooling cycle comprising 593 C (1100 F) for 1 h, 538 C (1000 F) for 15 h, 524 C (975 F) for 24 h, 496 C (925 F) for 60 h, 468 C (875 F) for 125 h, and 316 C (600 F) air cooling, was adopted in the present series of experiments.

The propensity to embrittle is usually measured in terms of the shift in the FATT observed in CVN tests, ΔFATT or ΔvTrs. The value is thought to have little physical meaning because the fracture mechanism is different between the metal before and after the embrittling treatment. Simple cleavage brittle fracture prevails before the treatment, but grain boundary brittleness is also involved after the treatment. Therefore, the absolute values of toughness after embrittling treatment were considered to be more important theoretically, as well as for practical purposes.

The FATT (vTrs) after the embrittling treatment (as well as the value given by the following formula that may be called thermal embrittlement parameter (TEP) proposed by the Gulf) was employed in addition to ΔFATT (ΔvTrs) for evaluating embrittlement:

$$vTr_{40}\,(SR) + 1.5\,(vTr_{40}\,(GESC) - vTr_{40}\,(SR))$$

where vTr_{40} (SR) is transition temperature for 40 ft-lb (5.5 kg-m) before

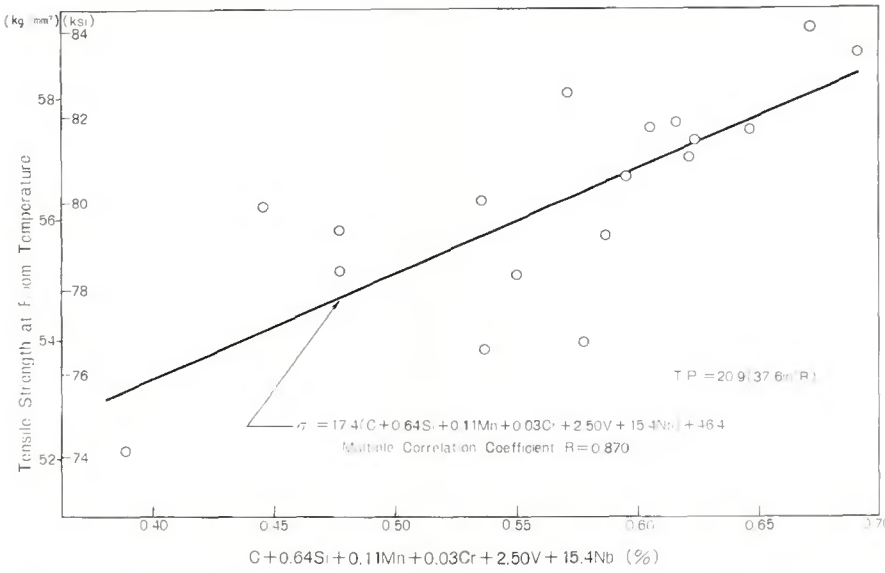

Fig. 8 — Influences of alloying elements on tensile strength of weld metal

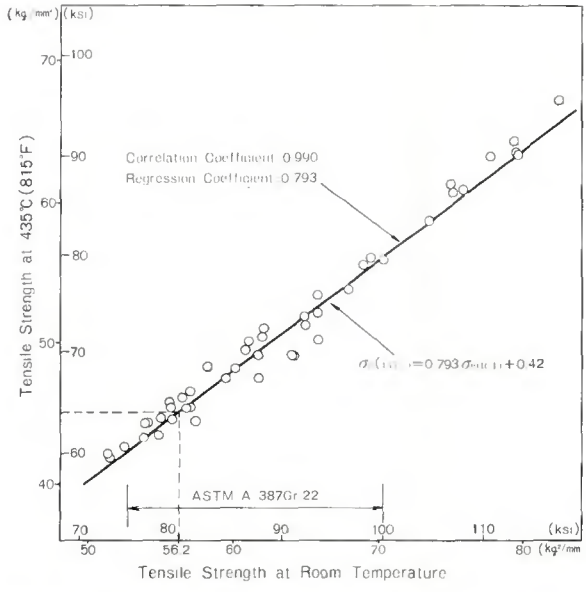

Fig. 9 — Correlation between tensile strength of weld metals at room temperature and at 435 C (815 F)

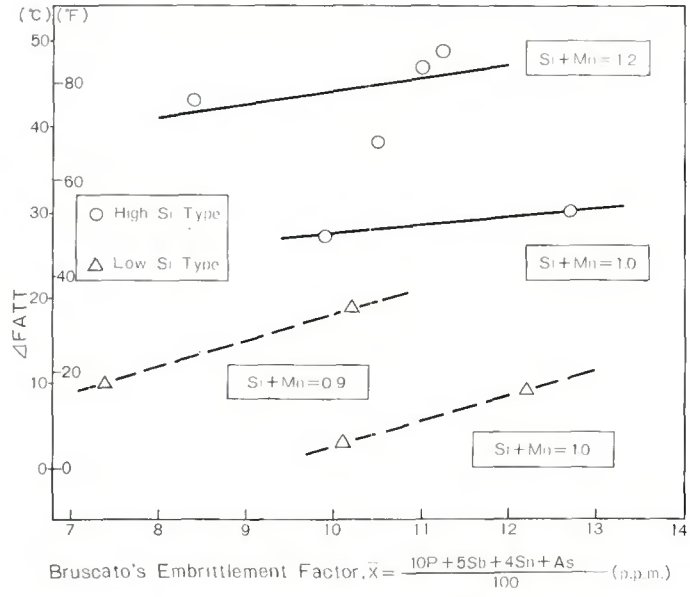

Fig. 10 — Influences of impurity elements on thermal embrittlement

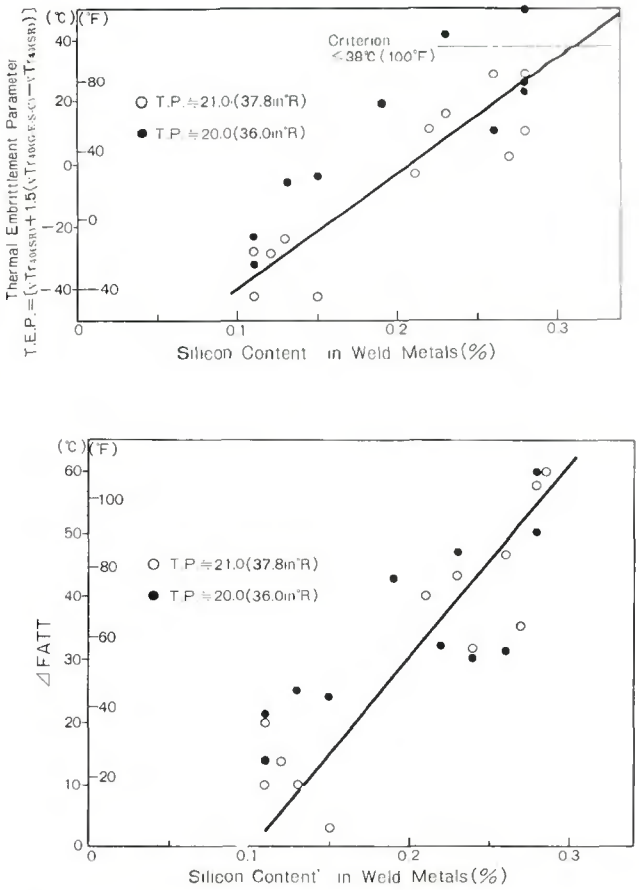

Fig. 11 — Effects of silicon on thermal embrittlement. The upper is rating by the TEP; the lower is rating by ΔFATT

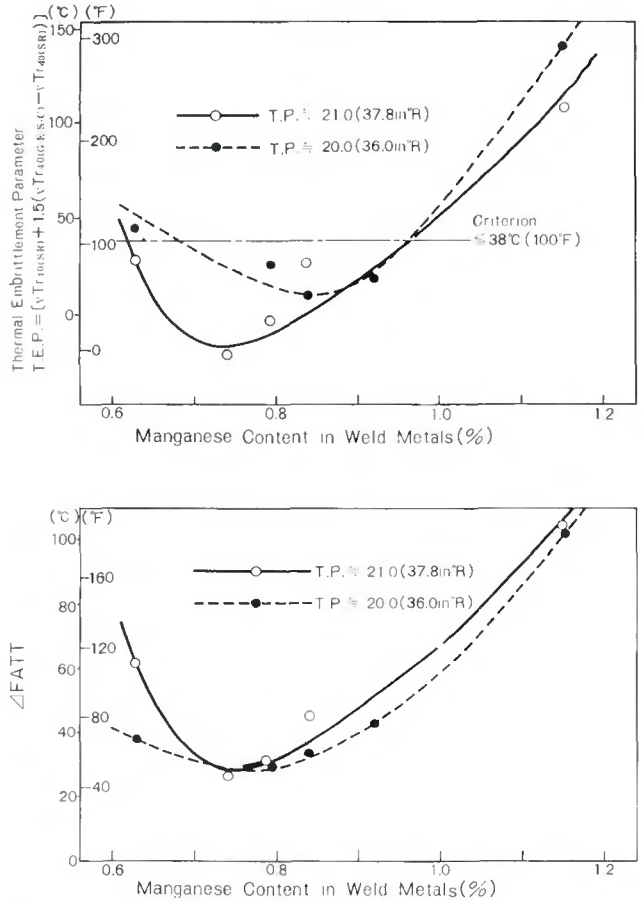

Fig. 12 — Effects of manganese on thermal embrittlement. The upper is rating by the TEP; the lower is rating by ΔFATT

the embrittling treatment (SR condition) in CVN tests. vTr_{40} (GESC) is transition temperature for 40 ft-lb after the G.E. Step Cooling treatment.

According to Bruscato (Ref. 7), the thermal embrittlement of 2¼ Cr-1 Mo weld metal produced by covered electrodes was influenced not only by the total amount of silicon and manganese in the weld metal, but also by the total content of the four elements as expressed by $\overline{X}$ = (10P + 5Sb + 4Sn + As)/100 (ppm). The relationships between the $\overline{X}$ values and the thermal embrittlement ratings of electroslag weld metals are shown in Fig. 10. The increment of FATT after GESC is seen to increase somewhat with an increase of $\overline{X}$ value in the figure but the degree is not much. Welding materials industrially produced today have $\overline{X}$ values around 10, so that making an effort to reduce impurities such as P, Sb, Sn, and As further for the purpose of reducing the embrittlement may be said to be of little practical significance.

As to the effects of silicon and manganese on the embrittlement of weld metal, there is agreement that a smaller amount of these elements results in smaller embrittlement. Experiments in this regard conducted with electroslag weld metal showed that both the ΔFATT and the TEP increased nearly in proportion to the silicon content as in Fig. 11.

As to manganese, as shown in Fig. 12, it was discovered for the first time that there was a certain optimum value at which thermal embrittlement was most reduced. Although the cause for this has not been clarified, similar optimum contents are also confirmed in weld metals produced by other processes (such as shielded metal arc welding). The optimum manganese content (0.7 to 0.85%) that resulted in the smallest thermal embrittlement nearly coincided with the optimum content for keeping the high tensile strength.

Among other alloying elements and impurity elements having an effect on thermal embrittlement of weld metals, copper is particularly important. Although the element has not been noticed for its influence so far, it was discovered that, as shown in Fig. 13, a reduction in the copper content resulted in a substantial reduction in thermal embrittlement. Up to now, general opinion has been that reducing the copper content was not advantageous in guaranteeing hot tensile strength. However, when its negative effect on thermal embrittlement is taken into consideration, copper should be reduced and other elements such as C and V should be util-

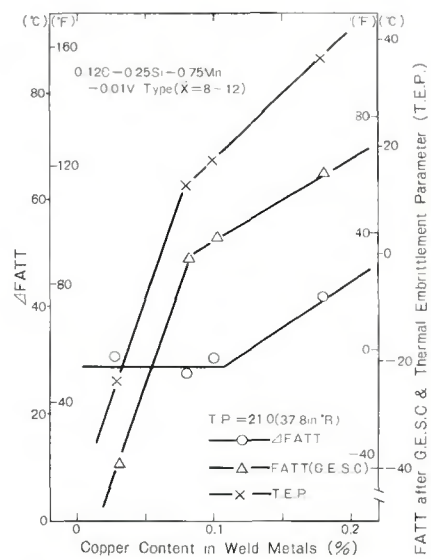

Fig. 13 — Influence of copper content on thermal embrittlement susceptibility

ized to achieve a guaranteeable high temperature strength.

Studies on the influence of C, Cr, Mo, and V on the thermal embrittlement of weld metal revealed that these elements had no appreciable effect within the content ranges of 0.08 to 0.16% for C, 2.25 to 2.55% for Cr, 0.93 to 1.07% for Mo, and 0.005 to 0.037% for V.

Various embrittlement mechanisms, such as equilibrium segregation (Ref. 8), nonequilibrium segregation (Ref. 9), and carbide rejection theories (Ref. 10), have been offered to explain the phenomenon involved, but at present, none are able to comprehensively explain the observed phenomena. Apart from embrittlement mechanism considerations, the fracture surfaces were observed and segregation of elements around the fracture surfaces was studied.

Some intergranular fractures were observed in high manganese type weld metals (1.15% Mn) in SR conditions as shown in Fig. 14. After the GESC treatment, however, the intergranular fracture extended over the entire surface. The concentration distribution of the major elements on the fracture surface was studied in the surface layer of 50 to 100 Å thickness by means of an ion microanalyzer (IMA). Typical results are shown in Fig. 15. The bombarding time is nearly proportional to the distance from the surface in the depth direction in the IMA measurement, but no exact depth can be obtained. While elements such as Si, V, Cr, and Mn were found to decrease towards the surface, copper alone was found to increase through this measurement.

This observation was thought to have some relation with the accelerating effect of copper in thermal embrittlement as shown in Fig. 13. However, further study is needed for a more exact clarification.

The fractured surfaces of the newly developed Mn-V type weld metal are shown in Fig. 16. The surface in SR conditions exhibits a quasi-cleavage and after the GESC treatment it changes into a mixture of quasi-cleavage and intergranular fractures. In a weld metal in which silicon content was reduced to an extreme degree with a sacrifice in strength, the fractured surface was mostly quasi-cleavage even after the GESC treatment as shown in Fig. 17, and thermal embrittlement was reduced to a great extent.

Discussion here has centered on the influences of alloying elements and impurity elements on thermal embrittlement. It was, however, further observed in the experiments that when the cooling rate in SR treatment was increased, not only the toughness of as-stress-relieved weld metal, but also its toughness after the GESC treatment was improved, as shown in Fig. 18. The improvement in toughness after SR treatment can be explained by the shorter time during which the metal goes through the embrittling temperature range resulting from quicker cooling. However, the fact that toughness is improved even after GESC treatment is impossible to explain at the present level of knowledge. This observation is very important for practical purposes. In order to improve the thermal embrittlement tendency of pressure vessels, manufacturers of pressure vessels

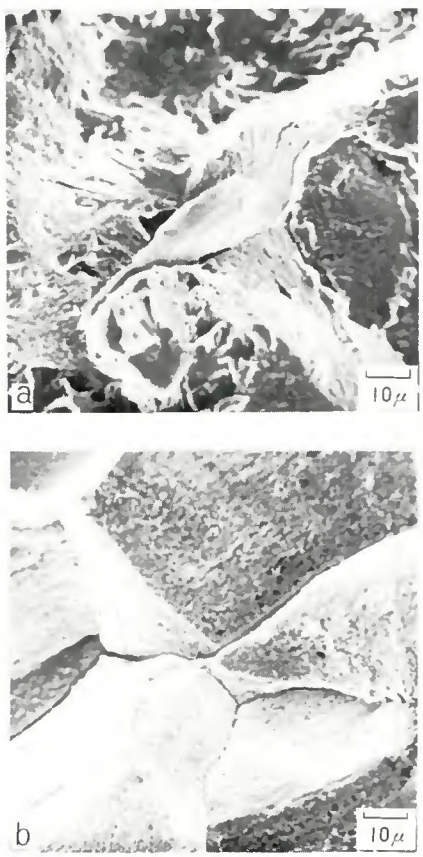

Fig. 14 — Scanning electron micrographs of fractures in high Mn type weld metal: a — as SR conditions; b — after SR and GESC treatment

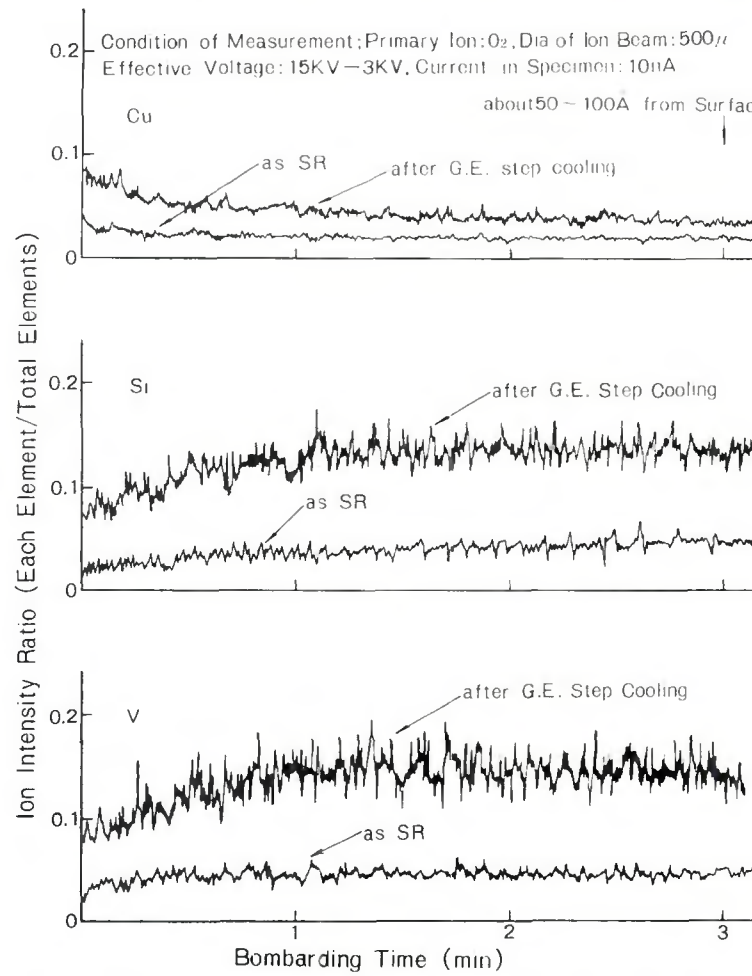

Fig. 15 — Results of IMA measurement of fractures of weld metal before and after GESC treatment. (No. 23 filler metal)

must give careful consideration to the cooling speed of the pressure vessels in the furnace during stress relief treatment.

Conclusions

A new electroslag welding filler metal was developed for heavy section pressure vessels of 2¼ Cr-1 Mo steels and reliable electroslag welding technology was established. The main conclusions are as follows:

1. Weld metal compositions of 0.85% Mn - 0.02% V type showed hot tensile strength over 45 Kg/mm^2 or 44 MPa (64,000 psi) at 435 C (815 F) and absorbed energy over 10 kg-m (72 ft-lb) at 0 C (32 F) in Charpy V-notch impact tests, together with satisfaction of requirements for A387 Gr. 22, after quenched and stress relieved conditions corresponding to a temper parameter by Larson and Miller of 19.9 to 20.7 in degrees Kelvin (35.8 to 37.3 in degrees Rankin).

The weld metal was obtained with a 1.20% Mn - 0.035% V type filler metal and a neutral flux of SiO_2-CaO-MnO-CaF_2 type.

2. The quality of weld metal was maintained even at a slow quenching rate of 9 C/min (16 F/min) and also at variation in penetration in base metals during welding.

3. Copper was a detrimental element to the thermal embrittlement of weld metals, confirmed by means of the G.E. Step Cooling treatment. The content should be kept less than 0.10% in weld metals. There was an optimum content of manganese to reduce the embrittlement, and the amount of 0.7 to 0.85% nearly coincided with the optimum content for keeping the high tensile strength without loss of the toughness.

4. It was important to make cooling after holding at stress relief heat treatments as fast as possible for the prevention of thermal embrittlement since loss of the toughness to slow cooling still remained after the step cooling treatment.

5. It was possible to estimate a hot tensile strength at 435 C (815 F) fairly accurately with a linear relation to tensile strength at room temperature (Fig. 9).

6. An experimental formula was proposed to estimate a tensile strength of weld metal with its chemical compositions (Fig. 8).

This technology has been actually employed with considerable success in the fabrication of reactor vessels of heavy oil direct desulfurization plants in Japan. Further application to other types of Cr-Mo steels is being considered.

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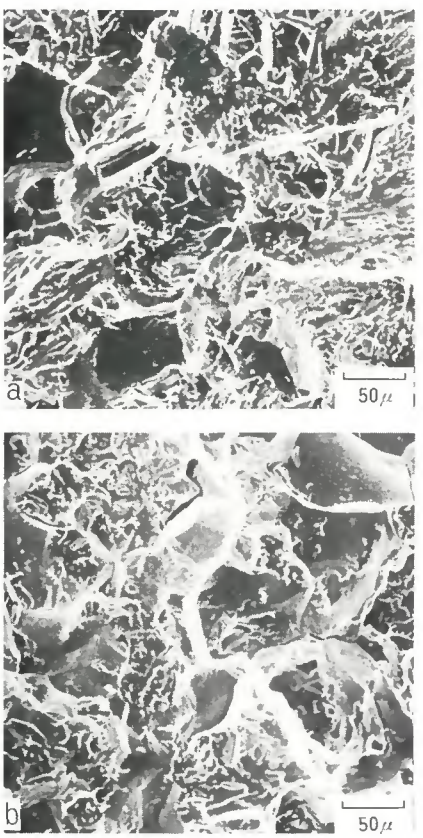

Fig. 16 — Scanning electron micrographs of fractures in newly developed Mn-V type weld metal: a — as SR conditions; b — after SR and GESC treatment

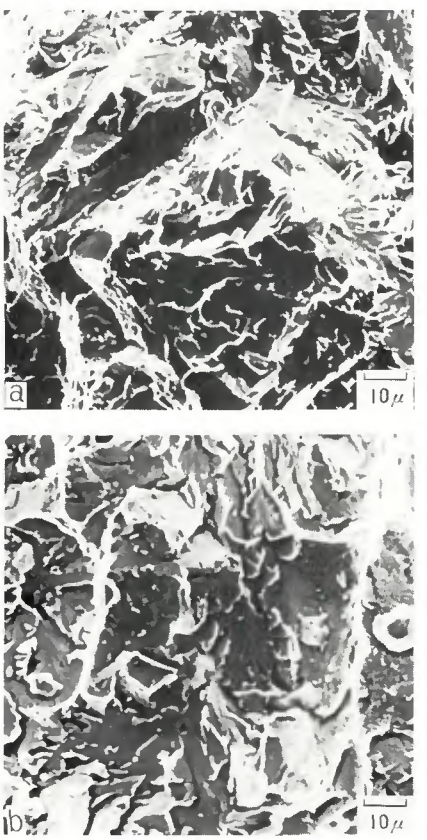

Fig. 17 — Scanning electron micrographs of fractures in extra low Si type weld metal: a — as SR conditions; b — after SR and GESC treatment

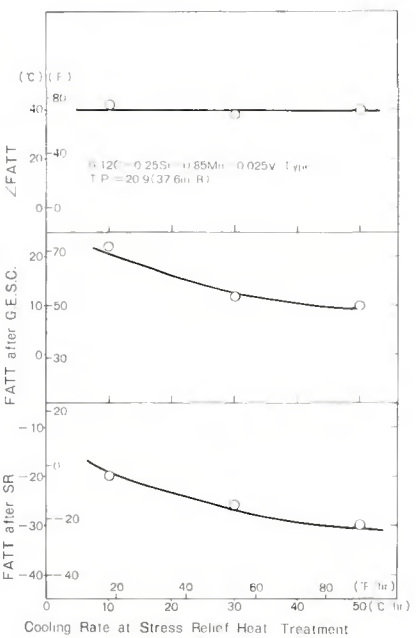

Fig. 18 — Influence of the SR cooling rate on the toughness of weld metal in SR conditions and after SR and GESC treatment. (No. 100 filler metal)