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Fundamental Investigation on Electro-slag Welding†

—Flux Chemistry—

Nobuya IWAMOTO*, Jiro NOSE, Yutaka NAGANAWA**, Yoshiaki TSUNAWAKI*** and Yukio MAKINO******

Abstract

The effect of the constitutional change in the CaO-MnO-SiO_2 ternary system and the role of CaF_2 addition on the characteristics of welding fluxes were investigated. Fluxes were tested using the electro-slag welding process. Oxygen, nitrogen and chemical components in weld metal were studied, and also weld metal toughness was examined. It was concluded that absorbed energy of charpy was related not to oxygen only, but to the product of impurities' content of oxygen, nitrogen, sulphur, etc. in weld metal.

1. Introduction

In submerged-arc welding (SAW) and electro-slag welding (ESW) processes, flux serve a number of essential functions such as metal refinement, atmospheric protection, controlling arc stability and the improvement of the morphology of weld bead.

The production of industrial welding fluxes is based on raw materials of geological origin. Accordingly, these fluxes contain many constitutions which do not serve to improve the mechanical properties of weld joint, and residuals of the raw materials will influence on the physical and chemical behaviors of the flux. With these fluxes being used, the phenomenon of the slag/metal interaction is complicated, and the understanding of the influence of each chemical additives on the flux behavior becomes difficult.

Inclusive of these matters, the purpose of this paper is to investigate the recovery of metallic manganese or silicon, and the content and distribution of oxygen, nitrogen and other chemical components in weld metal with using the fluxes of the CaO-MnO-SiO_2 ternary system. This ternary system is commonly used with other commercial fluxes of the MnO-SiO_2, CaO-MgO-SiO_2 and CaO-MgO-SiO_2-Al_2O_3 systems. Besides, charpy V-notch test was carried out at several temperatures.

CaF_2 is usually contained in conventional fluxes, because it gives good mechanical properties of weld metal. It is well known that CaF_2 in flux performs lowering of oxygen content in weld metal. Therefore, the effect of CaF_2 addition in the experimental fluxes was also examined.

2. Experimental Procedures

2.1 Materials

The experimental fluxes were produced from melting of purified chemical components. The solidified flux was crushed and sized. The experimental fluxes used were classified into four series. No. 1 was the flux of the MnO-SiO_2 system and the mole ratio was 1/1. Series No. 2—No. 4 were the fluxes of the CaO-MnO-SiO_2 system and the mole ratios of each series were 1/2/3, 1/1/2 and 2/1/3. These series are indicated as line AB in the CaO-MnO-SiO_2 phase diagram. This is shown in **Fig. 1**. For comparison, the commercial fluxes of No. 5 and No. 6 which have nearly same basic components were also tested.

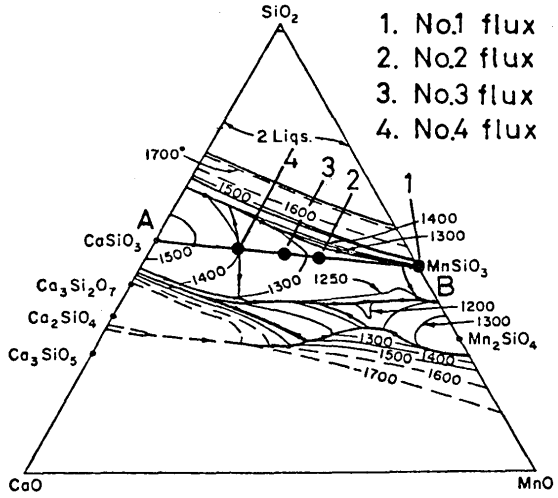

Fig. 1 Phase diagram of CaO-MnO-SiO_2 system

† Received on March 31, 1977

* Professor
** NIPPON KOKAN K.K. Technical Research Center
*** Research Instructor
**** Research Associate

Table 1 Chemical compositions of fluxes

Systems	No.	Chemical compositions of Fluxes (mole %)						
		SiO_2	MnO	CaO	MgO	TiO_2	Al_2O_3	CaF_2
CaO-MnO-SiO_2 flux system	1	50.38	49.62	-	-	-	-	-
	2	52.20	31.68	16.12	-	-	-	-
	3	52.14	22.29	25.57	-	-	-	-
	4	52.15	14.63	33.22	-	-	-	-
Commercial flux	5	44.08	19.86	16.88	5.94	2.62	1.60	9.02
	6	42.63	17.77	21.94	6.80	2.37	1.80	6.68
MnO-SiO_2-CaF_2 flux system	7	46.33	45.34	-	-	-	-	8.33
	8	40.83	39.71	-	-	-	-	19.46
	9	34.50	34.48	-	-	-	-	31.02
CaO-MnO-SiO_2-CaF_2 flux system	10	46.95	19.70	20.33	-	-	-	13.02
	11	41.50	17.25	24.93	-	-	-	16.32
	12	35.52	16.86	16.76	-	-	-	30.86

The addition of CaF_2 to the experimental fluxes of No. 1 and No. 3 was done to be about 30 mole per cent respectively. These series were designated as No. 7—No. 9 and No. 10—No. 12. CaF_2 of analytical grade reagent was mixed sufficiently to the experimental fluxes. Conventional fluxes of No. 5 and No. 6 also contain about 10 mole per cent CaF_2.The summary of chemical analyses of these fluxes is shown in **Table 1.**

The electrode used is the commercial wire of 3.2 mm dia. which contains low-Si and high-Mn. Mild steel plate of 50 mm thickness was used. Chemical analyses of the electrode wire and plate material are shown in **Table 2.**

Table 2 Chemical composition of base metal and filler metal

		Plate Thickness	Elements (wt %)				
			C	Si	Mn	P	S
Base metal	SM41	50 mm	0.14	0.19	0.71	0.014	0.018
Filler metal	LowSi,HighMn		0.12	0.02	1.91	0.011	0.012

2.2 Welding procedure

ESW process was performed with single electrode in air. Prior to welding, the plate and groove surface were ground and cleaned to remove mill scale and rust. Almost all weldings were accomplished with the standard welding conditions of 500 amp., 45 v. and 1.75 cpm. as travel speed, but in some cases current, voltage and travel speed were mutually varied in order to accomplish good welding. Because some fluxes showed spattering and generation of arc between wire and molten slag.

All the weldings were carried out with a constant voltage power supply of alternating current. Before the use, every flux was baked at 350°C for 2 hr.

2.3 Sampling location and analytical methods

The dimension of weld joint and the sampling location for the analyses of oxygen, nitrogen and other chemical components are shown in **Fig. 2.** Oxygen and

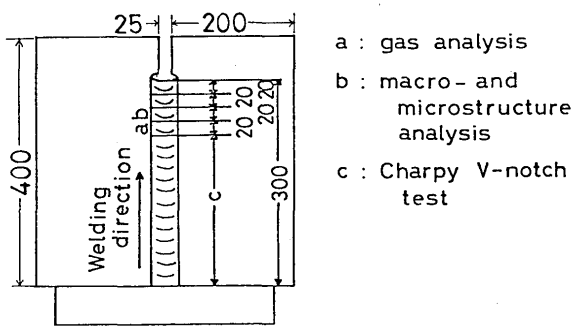

Fig. 2 Dimension of weld joint and sampling location

nitrogen contents were determined with TC-30 Nitrogen/Oxygen Determinator (Leco Co. Ltd.). The sample for the analyses of oxygen and nitrogen contents in weld metal were sectioned to a small block of 3 mm square and 15 mm length and polished with using emery paper and washed with a supersonic waves. Analyses of chemical components such as C, Si, Mn, P and S in weld metal were performed with using emission spectrochemical analysis. Analyses of slag and flux were carried out by X-ray fluorescence analysis and wet chemical quantitative method. The slag was sampled from the top of weld bead after welding operation.

3. Experimental Results and Discussion

The constitutional changes of the MnO and SiO_2 contents between flux and slag are shown in **Fig. 3.**

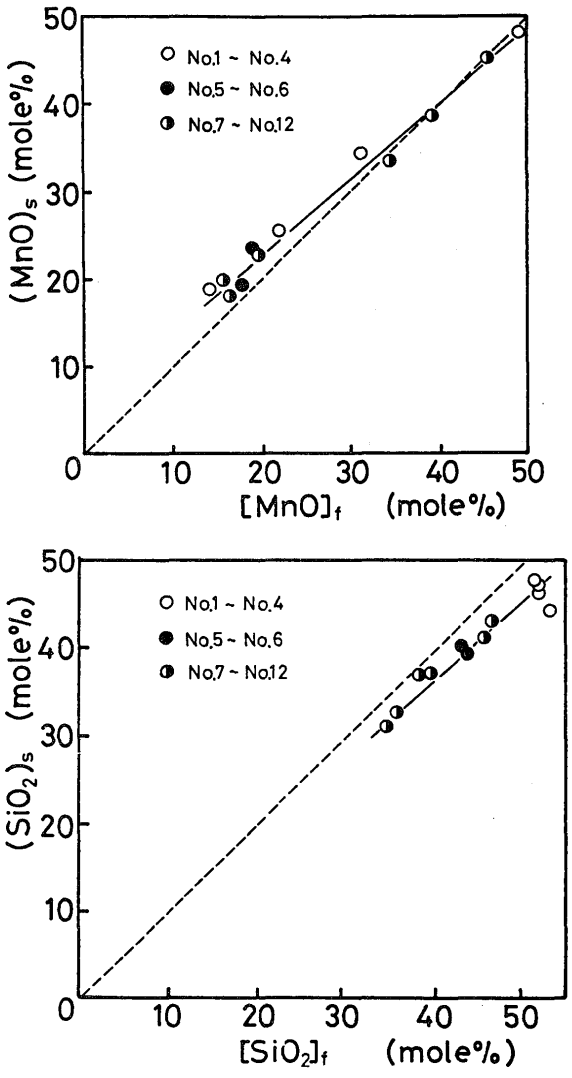

Fig. 3 Relation of MnO and SiO_2 contents between flux and slag

This figure shows an increase of the MnO content of slag, and the degree of increment is found to be large with reducing the MnO content of flux. On the other hand, a decrease of SiO_2 content of slag is indicated. These tendencies are recognized for all fluxes. This may be considered as general trend when the electrode wire of low-Si and high-Mn contents is used.

The average contents of oxygen and nitrogen in weld metal are shown in **Fig. 4.** The decrease of oxygen

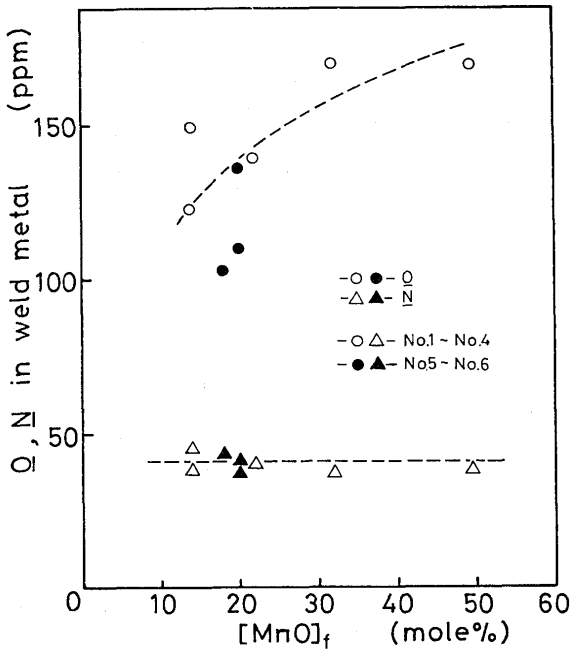

Fig. 4 Oxygen and nitrogen contents in weld metal versus MnO content in flux

content in weld metal is indicated as the amount of MnO is decreased, that is, the amount of CaO is increased. The use of the commercial fluxes shows the same order of oxygen content in weld metal or a somewhat lower value in weld metal, because it contains about 10 mole per cent CaF_2. But the nitrogen content in weld metal is nearly constant irrespective of the flux compositions.

Generally, it is said that the behavior of a flux is connected with a basicity of flux, which is defined as the basic components divided by the acidic components. As basic flux components, following compounds such as CaO, MgO, MnO, FeO, etc. are taken, while SiO_2 and P_2O_5 are classified as acidic components. Although CaO and MnO are considered as the same basic components, but it can understand from **Table 3.** that their ability to determine the oxygen content in weld metal is different.

As an example, the distribution of manganese, oxygen and nitrogen contents in each section of weld

Table 3 Nitrogen and oxygen contents in weld metal

Fluxes	(ppm)	
	N	O
No. 1	38	169
No. 2	37	170
No. 3	40	139
No. 4	45	149
	38	123
No. 5	41	110
	37	136
No. 6	43	103

bead are shown in **Fig. 5**, in the case of flux No. 3. However, the distribution of the other chemical components such as C, Si, P and S was nearly constant, and this was recognized for all of the flux being used. The variation of manganese in each weld section is supposed to be related to the distribution of sulphide and oxide inclusions in weld metal.

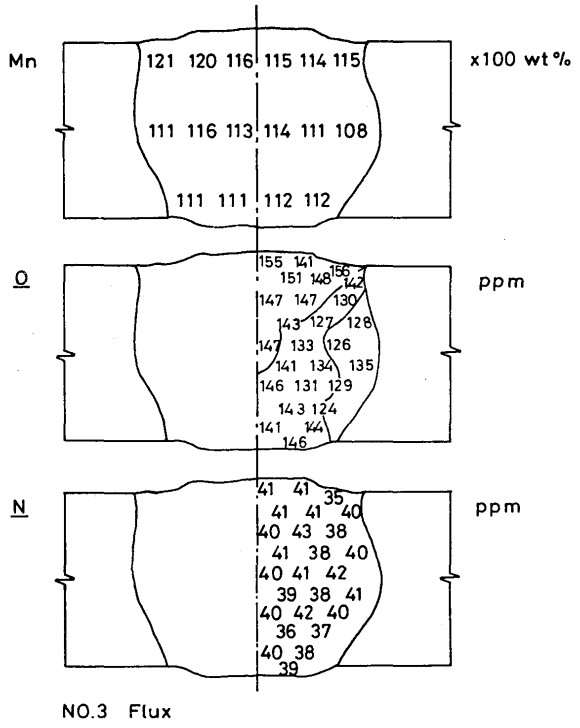

Fig. 5 Distribution of manganese, oxygen and nitrogen contents in a section of weld bead (No. 3 flux)

The variation of oxygen content in each weld section shows two characteristics; one shows the higher oxygen content near the water-cooled copper shoe, and the other shows the higher content in the middle of weld metal. The difference of the distribution between two forms is thought as follows. When the weld bead is fairly large, and the molten pool is well stirred, the solidification rate of molten metal near the copper shoe is comparatively rapid, and accordingly the oxide inclusions are likely to be caught in weld metal near that. The oxygen in weld metal is presumed to be precipitated as a very small inclusion. But when the weld bead is small, and the solidification rate is fast throughout weld bead, the higher content of oxygen in the middle of weld metal is reduced to an effect of the base metal dilution. Fairly lower value of the oxygen content of the base metal is in contrast to the oxygen content in weld metal.

On the other hand, the variation of nitrogen contents in each weld section was not recognized, but in weld metal quite near the base metal the lower values of nitrogen content were observed. It is thought that base metal having lower nitrogen content mainly exerted influence on the case.

Base metal dilution was determined by using a graphical integrated method from the end part of weld bead. This is shown in **Fig. 6**. The highest dilution

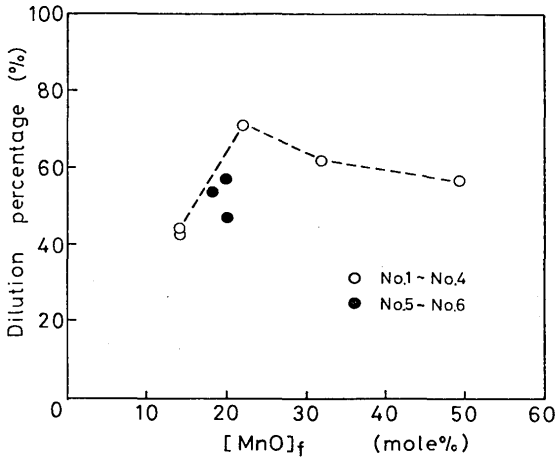

Fig. 6 Base metal dilution versus MnO content in flux

was observed in the use of No. 3 flux containing about 20 mole per cent MnO, and the lowest dilution was obtained in the use of No. 4 flux.

In ESW process the electric resistivity of a flux is an important peoperty. Use of a flux as an ohmic heating source is necessary to produce the weldment. All the experimental fluxes have been designed to have same mole ratio of basic components/acidic components. When MnO was replaced by CaO up to 30

mole per cent, the base metal dilution was increased. On the contrary, at CaO above 30 mole per cent the base metal dilution was decreased. From these results, it is considered that CaO is not as effective to lower a electric resistivity as is MnO.

The average oxygen contents in weld metal were lowered linearly due to the addition of CaF_2 for the experimental fluxes of No. 1 and No. 3. These are shown in **Fig. 7**. Especially, the addition of CaF_2 for

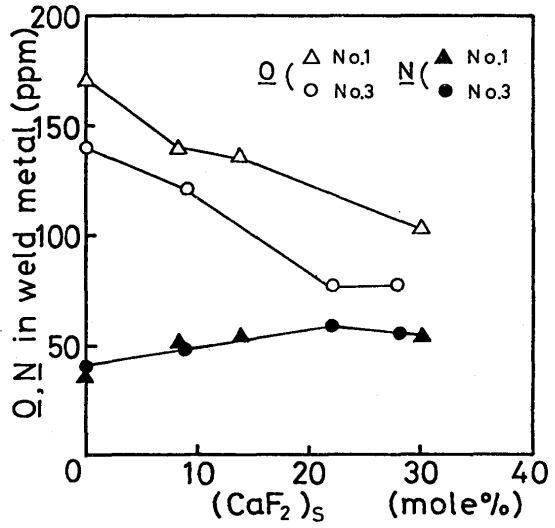

Fig. 7 Effect of CaF_2 addition to the oxygen and nitrogen contents in weld metal

the flux of No. 3 showed the lowest oxygen content as 76 ppm when flux contained above 20 mole per cent CaF_2. In the case of No. 1 flux, lower oxygen content was observed as CaF_2 is increased, but the nitrogen content in weld metal had a tendency to be gradually increased due to the addition of CaF_2. It may be considered to be the effect of introduction of adsorbed nitrogen on CaF_2 particles, because it was mixed to the experimental fluxes mechanically.

In SAW process the direct transfer of oxygen and nitrogen from an atmosphere to the molten metal is thought to be greatly affected by the arc-cavity. It is thought that CaF_2 additive, which forms a gas of fluorine-compound according to the following reactions,

$$2\ CaF_2+SiO_2=SiF_4\uparrow+2\ CaO$$
$$CaF_2+H_2O=2\ HF\uparrow+\ CaO$$

decreases the partial pressures of oxygen and nitrogen in the arc-cavity. So the decrease of the partial pressures may affect the decreases of oxygen and nitrogen contents in weld metal.

But in ESW process there is no arc-cavity at the steady state welding condition with using the flux as an ohmic heating source. It may be considered that the gas of fluorine-compound reduces the partial pressure of oxygen above the slag surface and accordingly the surface of the electrode wire from atmospheric oxidation. However it seems to be quite all right to consider that the effect of the reduced partial pressure of oxygen above the slag to lower the oxygen content in weld metal is relatively small compared to the other factors, because the shielding effect of the molten slag, whose thickness is about 4–6 cm, seems to be sufficient, and that the effect of the oxidation of the electrode wire to increase the oxygen content in weld metal is also relatively small[1].

It can be considered that in ESW process the changes of physical and chemical properties such as viscosity, interfacial tension, surface tension, electric conductivity, etc. of flux due to the addition of CaF_2 are the main factor to lower the oxygen content in weld metal, and that the change of the slag structure by the addition of CaF_2 is also the main factor, i.e., this change may affect the physical and chemical properties of slag.

The elimination of inclusions from molten metal to molten slag due to the adsorption is accelerated when the following equation is satisfied.[2),3),4)]

$$W_{S-M} < W_{S-I}$$

where: W_{S-M} adhesion energy between molten slag and molten metal
W_{S-I} adhesion energy between molten slag and inclusion

W_{S-M} and W_{S-I} are expressed by the following equations.

$$W_{S-M} = \alpha_S + \alpha_M - \alpha_{S-M}$$
$$W_{S-I} = \alpha_S + \alpha_I - \alpha_{S-I}$$

where α_S, α_M and α_I are the surface tensions of slag, metal and inclusion, respectively. α_{S-M} means the interfacial tension between slag and metal, and α_{S-I} means the interfacial tension between slag and inclusion.

Hence the increase of α_{S-M} and the decrease of α_{S-I} which may be affected by the addition of CaF_2 is indicated to reduce the oxygen in weld metal. The lowered viscosity by CaF_2 additive gives a rapid flow of molten slag, and then the inclusions are quickly brought into molten slag from the interface between slag and metal.

But it is necessary that further studies should be done in order to investigate what the lowering effect of oxygen content in weld metal by CaF_2 additive is.

The distribution of manganese, oxygen and nitrogen contents in each section of weld bead is shown in

Fig. 8, in the case of No. 3 flux containing CaF_2 additive.

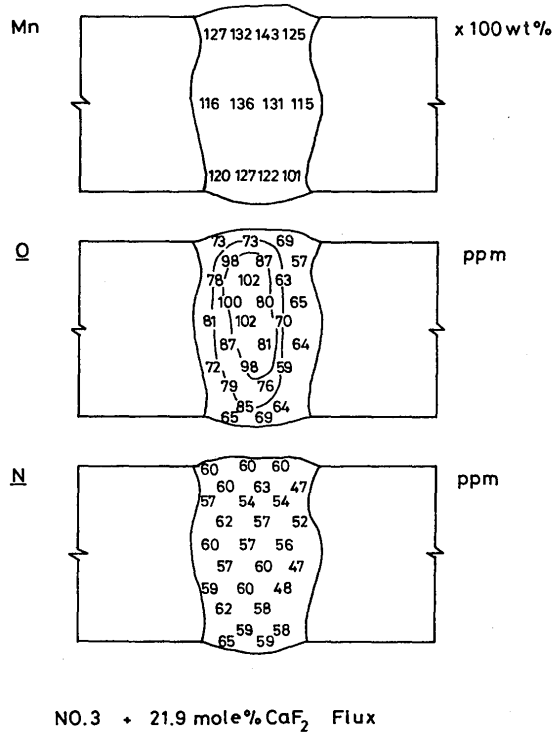

Fig. 8 Distribution of manganese, oxygen and nitrogen contents in a section of weld bead (No. 11 flux)

The decrease of base metal dilution was remarkably affected as the amount of CaF_2 was increased. This is shown in **Fig. 9**. In particular, the addition of CaF_2

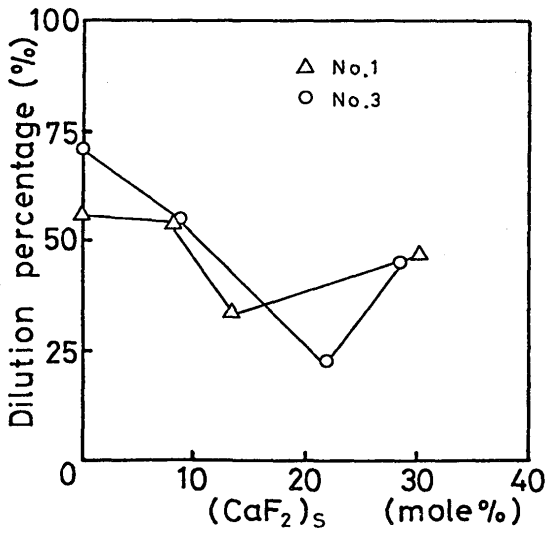

Fig. 9 Dependence of base metal dilution due to the CaF_2 addition

to the flux of No. 3 lowered the base metal dilution which was found to go through a minimum (about 20 mole per cent CaF_2) with increasing CaF_2 content, and it was varied from 70 per cent to 25 per cent.

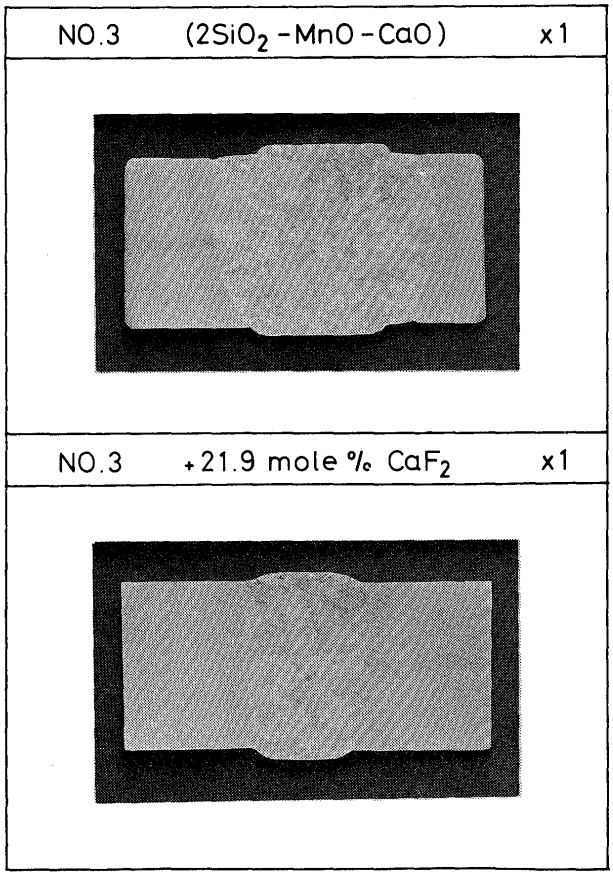

Photo 1 Decrease of base metal dilution due to the CaF_2 addition

However it seemed to be increased in the case of above 25 mole per cent CaF_2 addition. This was also observed for the addition of CaF_2 to the flux of No. 1. The decrease of the base metal dilution which may be interpreted as a decrease of the electric resistivity due to the CaF_2 addition seems to be related to the behavior of CaF_2 in slag.

The depth of the molten weld metal[5] may be considered to influence the raising of the inclusions which is ruled by the Stoke's law. It seems to depend on the size of the molten pool and then seems to be related to the base metal dilution. Therefore the decrease of the base metal dilution due to the CaF_2 addition may be thought to cause to lower the oxygen content in weld metal.

Charpy V-notch test in weld metal was carried out at several temperatures. This is shown in **Fig. 10**. Weld metal toughness examined in connection with the oxygen content in weld metal changed by using

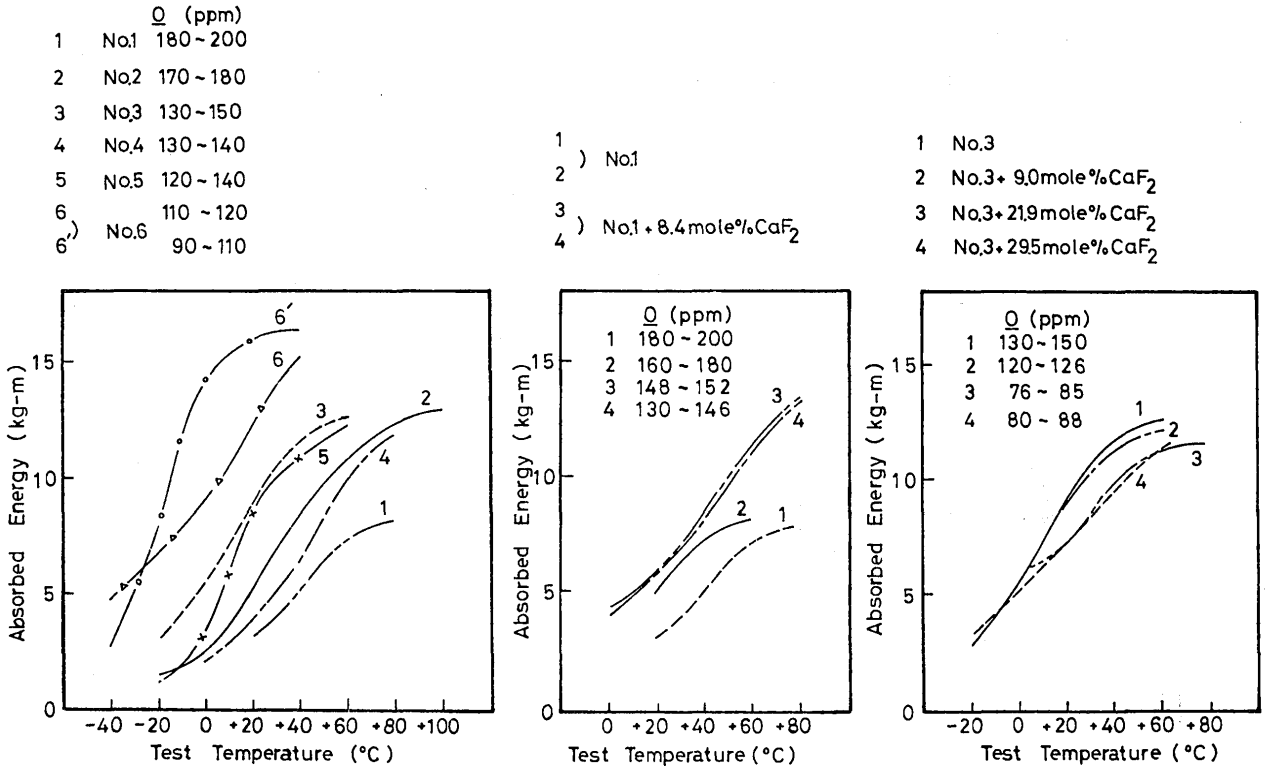

Fig. 10 Weld metal impact curves for ESW welds in the as-weld condition

various fluxes. The best result on absorbed energy was obtained in the case of No. 6 flux, and it seems to be caused by a appropriate flux/electrode combination.

Exclusive of the case of No. 4 flux and the case of CaF_2 addition to the No. 3 flux, lowering the oxygen content in weld metal was effective to obtain the better weld toughness. However, it must be considered that weld metal toughness is not depend on the oxygen content in weld metal only, but also depend on the contents of impurities such as nitrogen, sulpfur and phosphorus in weld metal. This thought is supported from that good weld metal toughness was not obtained regardless of the lowered oxygen content in weld metal when the base metal dilution was small. The base metal dilution may be considered to be connected with the solidification rate, the growth direction of the dendrite and the size and form of the inclusions in weld metal. Hence it is considered that absorbed energy in weld metal seems to be related to the product of oxygen, nitrogen, sulphur and phosphorus contents which is divided by the base metal dilution. This is shown in **Fig. 11**. This figure shows a good straight line relationship.

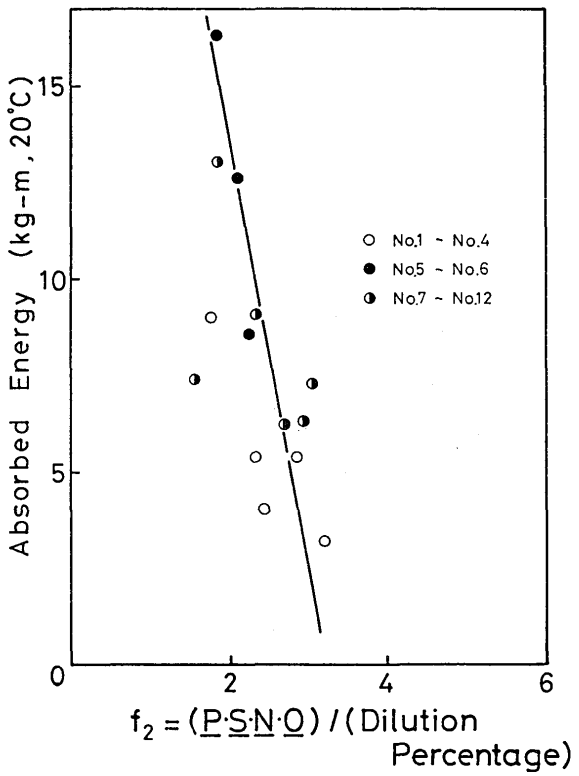

Fig. 11 Relation between absorbed energy in weld metal and f_2

The metallic manganese and silicon contents in weld metal were calculated from the analytical contents of the base metal and electrode wire with including the base metal dilution. The difference between analytical value in weld metal and calculated one was taken as ordinate, and the MnO content of flux was taken as

abscissa. The result is shown in **Fig. 12**. It is seen that the recovery of metallic silicon in weld metal was

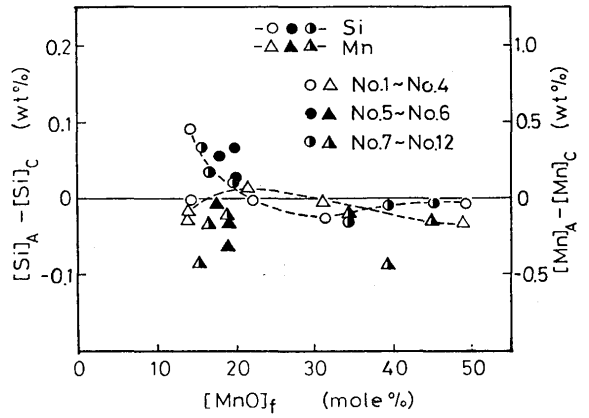

Fig. 12 Dependences of Mn and Si on MnO content in flux

accelated with reducing the amount of MnO below 30 mole per cent, but above 30 mole per cent the recovery became nearly zero, while the recovery of metallic manganese in weld metal was always recognized under the zero line except 20–30 mole per cent MnO. These suggest to correspond with the increase of the MnO content in slag and the decrease of the SiO_2 content in slag.

According to Zeke,[6),7)] the influence of the flux on the chemical composition of the weld metal or on metallurgical process during welding can be expressed, using "silicon reduction intensity coefficient" KIR_{Si} and "manganese reduction intensity coefficient" KIR_{Mn} which are the metallurgical characteristics of the flux, respectively.

The metallurgical characteristics KIR_{Si} and KIR_{Mn} are calculated from the chemical analysis of the flux as follows.

$$KIR_{Si}=nO^{2-}_{CH}\times N_{SiO_2}\times(1-\sqrt[3]{N_{MnO}})$$

$$KIR_{Mn}=\sqrt{N_{MnO}}\times(1-\sqrt{KIR_{Si}})$$

where $nO^{2-}_{CH}=\sum mR_2O+\sum mRO-(2mSiO_2+2mTiO_2+mAl_2O_3)$

N molar broken number
m mole number (in 100 g of flux or slag)
R_2O univalent metal oxides
RO divalent metal oxides

From these equations, KIR_{Si} and KIR_{Mn} were calculated, and KIR_{Si} versus the analytical value of metallic silicon in weld metal is shown in **Fig. 13**, and KIR_{Mn} versus the analytical value of metallic manganese in weld metal is shown in **Fig. 14**, respectively. The lines in these figures express the equilibrium content of silicon and manganese in weld metal as proposed by Zeke. Experimental results indicate a comparatively

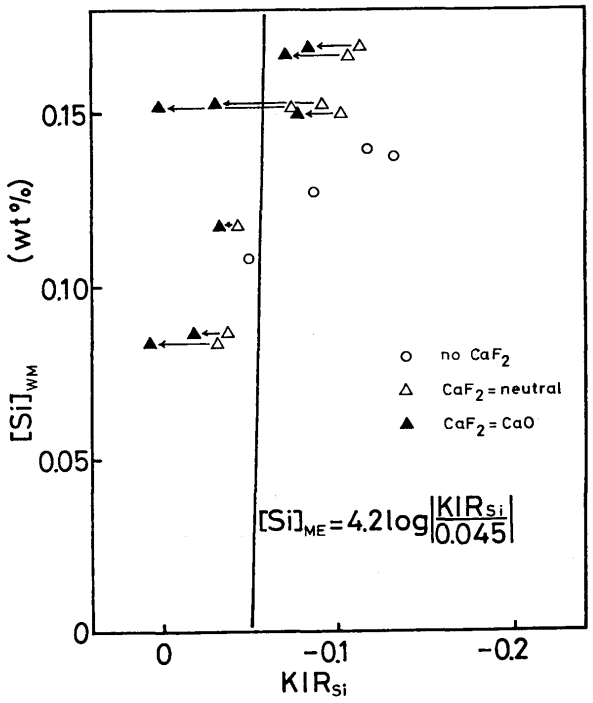

Fig. 13 Relation between silicon content in weld metal and KIR_{Si}

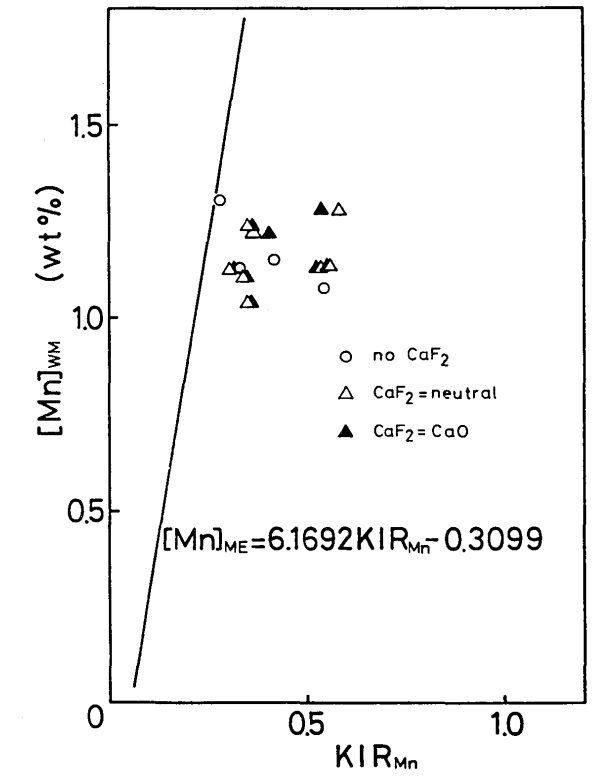

Fig. 14 Relation between manganese content in weld metal and KIR_{Mn}

good agreement with the equilibrium content in weld metal.

It is considered that the additional CaF_2 to the slag affects KIR_{Si} and KIR_{Mn} playing such two roles as follows. (1) CaF_2 is equivalent to CaO in slag. (2) CaF_2 is neutral and then plays a dilution effect in slag. From Fig. 13, the effect of CaF_2 may be considered to vary according to the chemical compositions of flux and the quantity of CaF_2 addition.

Further studies are desired to investigate the morphology of the inclusion in weld metal, the relationship between impact strength and structure of weld metal, and the main effect of CaF_2 addition to lower the oxygen content in weld metal.

4. Summary

The effect of the constitutional change in the CaO-MnO-SiO_2 ternary system and the role of CaF_2 addition on the characteristic of welding fluxes were investigated by using ESW process. The decrease of oxygen content in weld metal was observed with increasing the amount of CaO, but the nitrogen content was nearly constant. The distribution of manganese and oxygen contents in each weld section was recognized, and these are supposed to be related to the distribution of sulphide and oxide inclusions in weld metal. The oxygen content in each weld section showed higher value near the water-cooled copper shoe and in the middle of weld metal. The oxygen content in weld metal was lowered linearly due to the addition of CaF_2, and the lowest oxygen content as 76 ppm was obtained when flux contained above 20 mole per cent CaF_2. In ESW process, the changes of physical and chemical properties of the product can be considered to be the main factor to lower the oxygen content in weld metal. The decrease of the base metal dilution was remarkably affected by the CaF_2 addition in flux, and found to go through a minimum (about 20 mole per cent CaF_2). It can be considered that weld metal toughness was related not to oxygen only, but to the product of impurities' contents in weld metal and also affected by the base metal dilution. The manganese and silicon contents in weld metal indicated a comparatively good agreement with the equilibrium content. It is considered that CaF_2 added to the slag played two roles as follows: (1) CaF_2 is equivalent to CaO, and (2) CaF_2 is neutral. These roles were considered to vary with the chemical compositions of flux and the quantity of CaF_2 addition.

References

1) Ю.В. Латаш and Б.И. Медовар: ЭЛЕКТРОШЛАКОВЫЙ ПЕРЕПЛАВ (Japan and USSR correspond., Wakayama, 1974), p. 77 (in Japanese)
2) Ibid., p. 28
3) D. A. R. Kay: 1st Intl. Symp. ESR., (1967), II
4) M. M. Klynev and R. J. Prmfret: JISI, 209 (1971), p. 962
5) M. Wahlster and H. Spitzer: Stahl u. Eisen, 92 (1972), p. 961
6) J. Zeke: JJWS, 39 (1970), p. 118 (translated in Japanese by I. Masumoto and K. Tamaki)
7) J. Zeke: IIW Document No. XII-629-76