Study on Minor Elements in Weld Steel with Submerged Arc Welding Using Fluxes of the System (CaO)-MnO-SiO_2†

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Abstract

Distributions of several non-metallic and alloying elements in low alloy steel welded with SAW method using the fluxes of the system CaO-MnO-SiO_2 were investigated with impulse fusion method and point analysis using IMA. The dependence of nitrogen increment upon CaO content in flux was remarkable and the increment increased with increasing CaO content whereas oxygen increment was scarcely changeable for the flux with constant SiO_2. These dependences were qualitatively interpreted from various properties of slag. However, it was indicated that investigations on fluxless welding process are necessitated in order to clarify the dependence on flux composition. Further, it was suggested that the maldistributions of calcium, aluminium, carbon and sulphur are attributed to the formation of inclusions. Distributions of silicon and manganese showed a little lower content in the middle region, respectively. It was also indicated that mass transfer process during welding must be clarified in order to explain the phenomenon.

1. Introduction

The significance of slag in welding technology is attributed to the fact that submerged arc welding (SAW) and electroslag welding (ESW) methods occupy the great important positions among various welding methods. However, the roles of slag in each method are fairly different. Considering from the metallurgical standpoint, in ESW method, slag-metal reaction is most important factor to decide the properties of weld metal whereas, in SAW method, gas-metal reaction as well as slag-metal one influence on the properties of weld metal. Besides, the gas-metal reaction produces remarkable difficulties for control of the properties of weld metal in SAW.

In iron- and steel-making, the relation between structure of slag and slag-metal reaction has been investigated[1)-4)] and, recently, much detailed information on slag structure was obtained from various methods[5)-8)]. Therefore, it is easily expected that the properties of weld steel with ESW method using a simple silicate slag can considerably be estimated from the information on metallurgical process. On the contrary, the mechanism to decide the properties of weld steel is more complicated because it depends on gas-metal reaction rather than slag-metal one. Further, the gas-metal reaction must be divided into two different processes, that is, air- and arc atomosphere-metal reactions. Furthermore, less information on arc cavity produces many obstacles for controlling the properties of weld steel.

In SAW, oxygen and nitrogen are most trouble elements among non-metallic elements in weld steel. For example, high content of nitrogen beyond a critical value has baneful influences on ductility of weld steel at low temperature or produces blow holes during solidification. High content of oxygen also has great affects on the mechanical properties of weld steel such as Charpy impact value. However, the effect of oxygen in weld steel is more complicated than nitrogen because the effect of soluble oxygen has to be distinguished from that of oxygen contained in the form of inclusion. Further, it is also necessary to clarify the relation between oxygen and fundamental alloying elements such as silicon and manganese because their interralations affect on redistributions of alloying elements. In this study, distributions of non-metallic and alloying elements in low alloy steel, which was welded with SAW method using several fluxes of the system CaO-MnO-SiO_2 and a few commercial fluxes, were investigated with point analysis by IMA and impulse fusion method in order to obtain fundamental information on the problems described

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2. Experimental Procedures

(1) Materials used

Low alloy steel plates (X-52) which dimention are shown in **Fig. 1** were used as substrate material and the results of chemical analysis are shown in **Table 1.** The wire used was a commercial one US-36 (Kobe Steel Co. Ltd.). The fluxes of the system CaO-MnO-SiO_2 and a few commercial fluxes were used and those compositions are shown in **Table 2.** The former were fused-type fluxes which were produced by melting the mixture of limestone, silica sand and MnO_2 in electric furnace with carbon electrode.

(2) Welding method

In this study, bead welding with single electrode was conducted by SAW method because it is main purpose to clarify the effects of flux components. Other various welding conditions were as fixed as possible and the height and width of scattered flux were also fixed to be 3.5 cm and 7.0 cm, respectively. Each fluxes was dried at 300°C for 2 hr before welding. Welding conditions are shown in **Table 3.** Electrode was vertically set for substrate steel and the distance between electrode and substrate was fixed to be 3.0 cm.

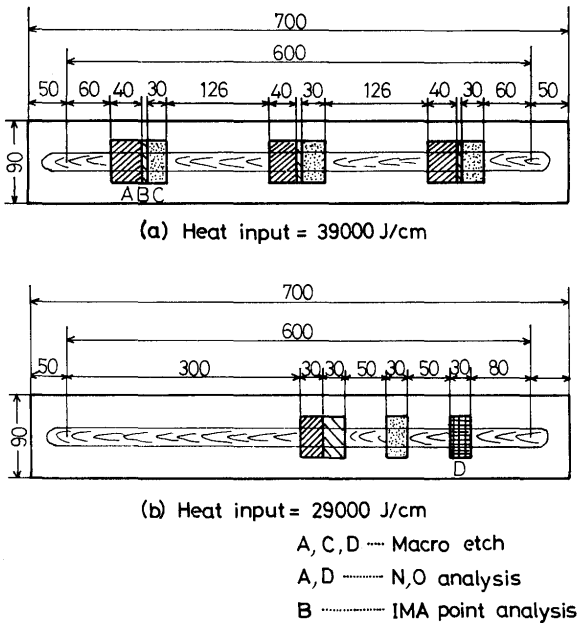

Fig. 1 Sampling positions

Table 3 Welding conditions

	Current	Voltage	Travel speed	Heat input
CMS-1	690±20A	36±2V	50 cm/sec	30×10^3 J/cm
	650±20	40±2	40	39
CMS-2	690±20	36±2	50	30
	650±10	40±2	40	39
CMS-3	690±10	34±2	50	28
	650±10	40±2	40	39
CMS-4	700±20	34±2	50	29
	650±20	40±2	40	39
CF-1	670±30	39±2	50	31
CF-2	650±10	40±2	40	39
CF-3	650±10	40±2	40	39

Table 1 Chemical compositions of substrate steel and filler wire

		C	Si	Mn	P	S	Cu	Nb	Al	N	O
Substrate steel	Ladle	0.129	0.28	1.27	0.013	0.005	0.02	0.025	0.021	——	——
	Check	0.131	0.28	1.24	0.014	0.004	0.02	0.026	0.023	0.0044	0.0011
Filler wire US-36		0.110	0.03	1.88	0.011	0.016	——	——	0.003	0.0043	0.0096

Table 2 Chemical compositions of fluxes

	SiO_2	MnO	CaO	MgO	Al_2O_3	TiO_2	CaF_2
CMS-1	50.38	49.62	——	——	——	——	——
CMS-2	52.20	31.68	16.12	——	——	——	——
CMS-3	52.14	22.29	25.57	——	——	——	——
CMS-4	52.15	14.63	33.22	——	——	——	——
CF-1	44.08	19.86	16.88	5.94	1.60	2.62	9.02
CF-2	42.63	17.77	21.94	6.80	1.80	2.37	6.68
CF-3	26.60	2.32	22.40	11.48	30.67	0.26	6.10

(3) Sampling positions

Sampling positions in every specimen are shown in Fig. 1. Specimens for oxygen and nitrogen analysis and point analysis with IMA were picked from the center of weld steel. In order to examine reproducibility of oxygen and nitrogen analysis results in welding direction, specimens were picked from three different positions as shown in Fig. 1 though only in the case of using flux CMS-2. All specimens in the experiment in which heat input was about 29000 J/cm were picked from the latter half part in weld steel because of less stability of arc just after arc starting.

(4) Point analysis with IMA

Emission processes of secondary ions in ion microprobe analysis are complicated and the number of a released secondary ion delicately influenced by various factors such as incident angle and species of primary ion and specimen properties[9]. In this study, distributions of several non-metallic and alloying elements in weld steel were relatively determined because various factors make quantitative analysis with IMA difficult. Experimental conditions were as follows;

primary ion: Ar^+, beam radius: 250μ,
accelarating voltage: 10 KV,
type of analyzer: Hitachi IMA-SS.

The surface of each specimen was ion-spattered for 10 min before performance of analysis and ion microanalysis was conducted at intervals of 1.0 mm to 1.5 mm.

(5) Analyses of nitrogen and oxygen with impulse fusion method

Each specimen piece with about 20 mm in length was prepared by cutting from weld steel. After its cross section was etched with 2% nital, the piece was sectioned to a lot of small rectangular rods with 1.5 mm square and 20 mm in length. In most cases, twenty small rods or more were obtained. Then, these rods were weighed and analyzed after they were washed with acetone and cleaned with supersonic waves. Analyzer used was a N_2/O_2 determinator (LECO Co. Ltd., Type TC-30).

3. Experimental Results

(1) Effect of flux composition on bead shape

In order to analyze bead shape, the ratio of bead width to penetration depth, W/H, and the quantity $\left[\frac{W}{2}\tan\left(\frac{\alpha+\beta}{2}\right)\right]/H$ were taken as parameters. The latter is called as the parameter of pear-type bead. The relations of bead shape to flux composition are shown in **Figs. 2** and **3.** The ratio W/H is inclined to decrease with increasing CaO content in flux. On the contrary, the quantity of pear-type bead trends to increase as CaO content increases. The latter result shows that

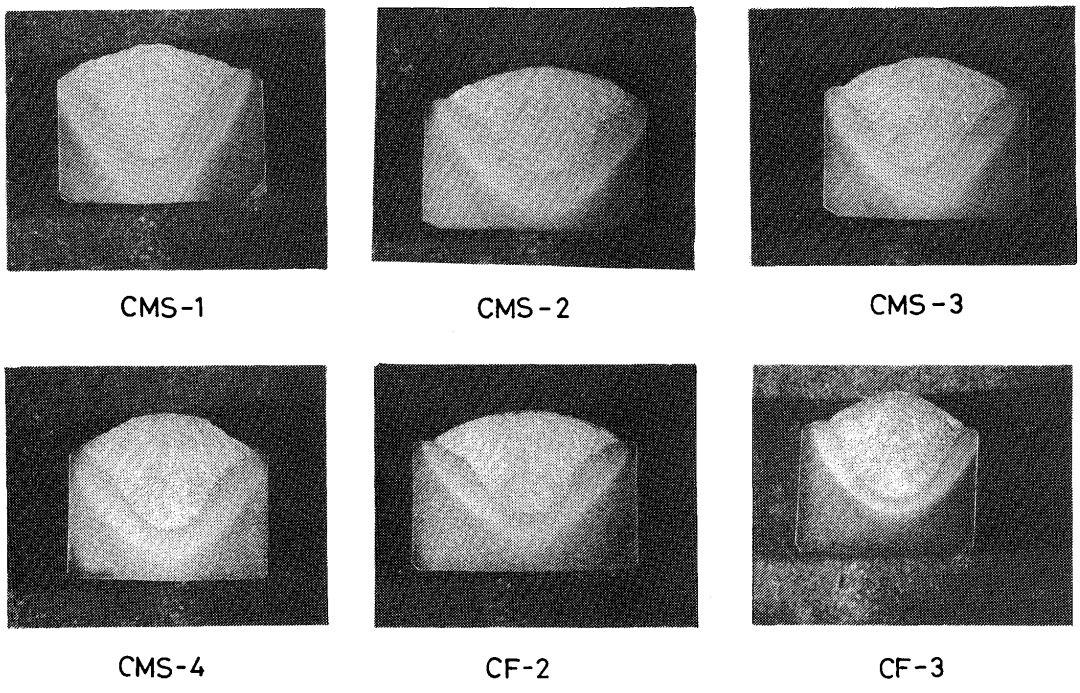

Photo. 1 Metallographic pictures of cross sections etched with 2% nital

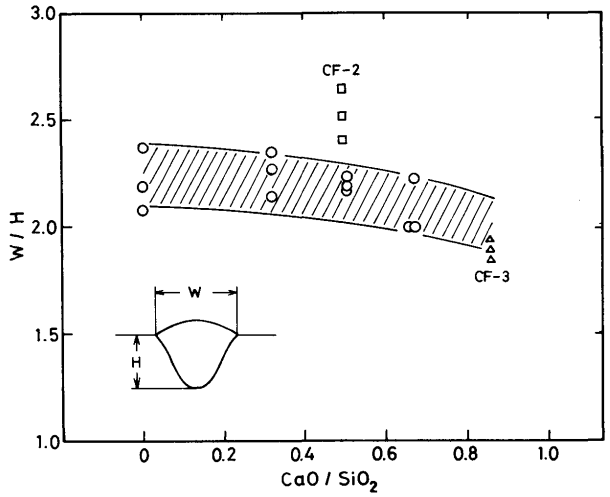

Fig. 2 The relation between the ratio of bead width to penetration depth and CaO/SiO_2 ratio

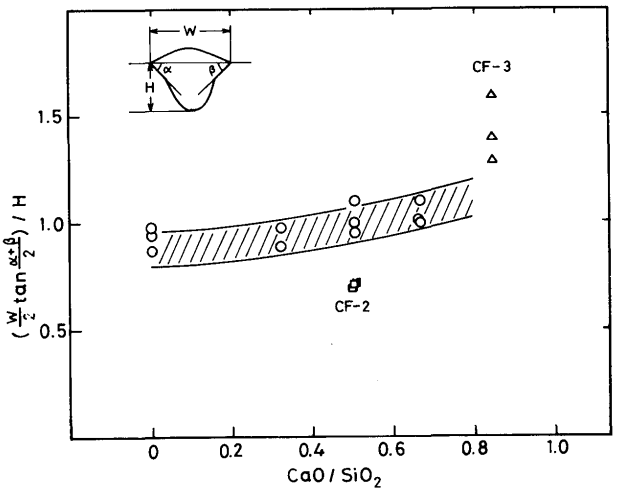

Fig. 3 The relation between pear-type bead parameter and CaO/SiO_2 ratio

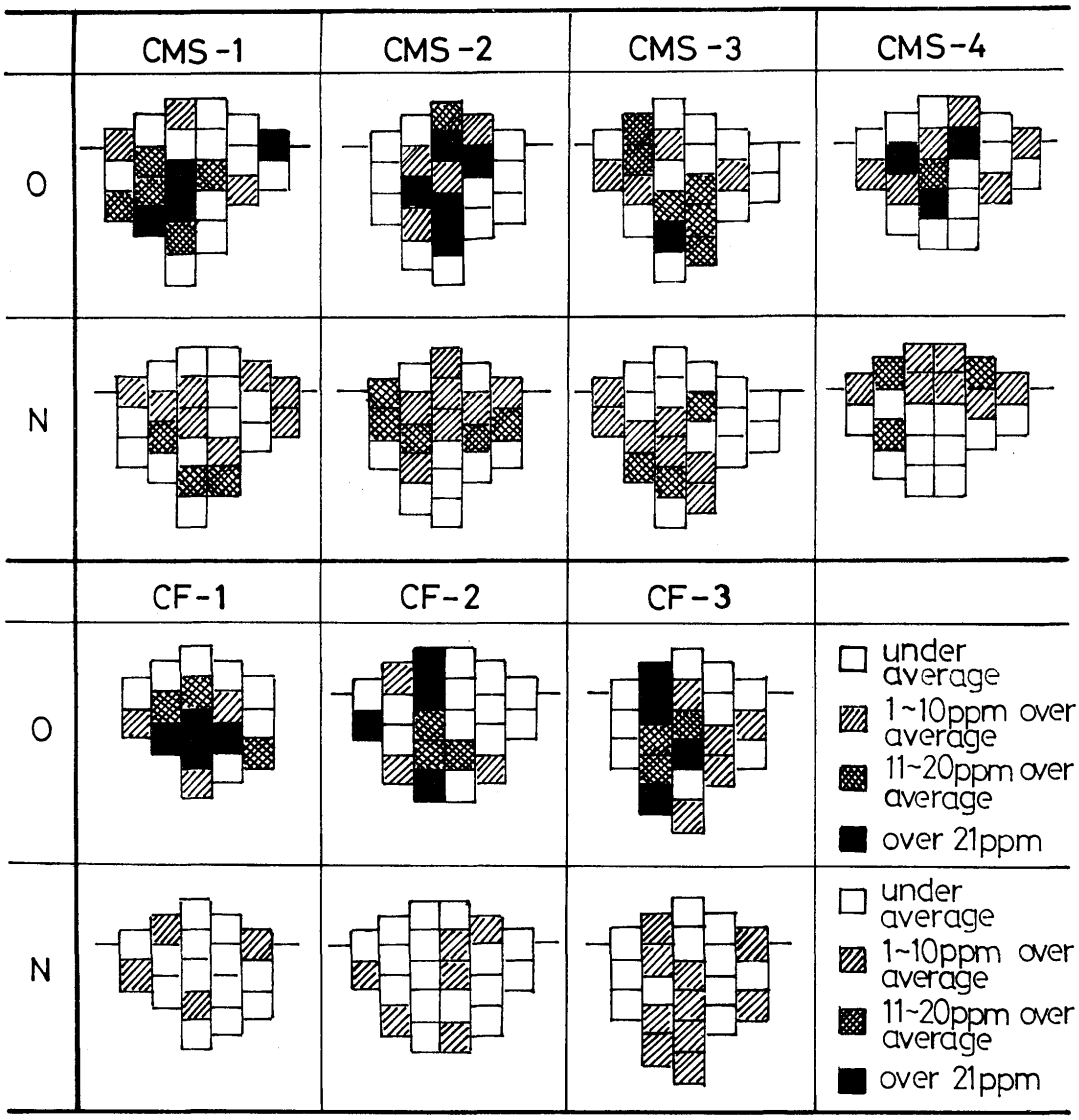

Fig. 4 Distributions of oxygen and nitrogen in weld steel with impulse fusion method

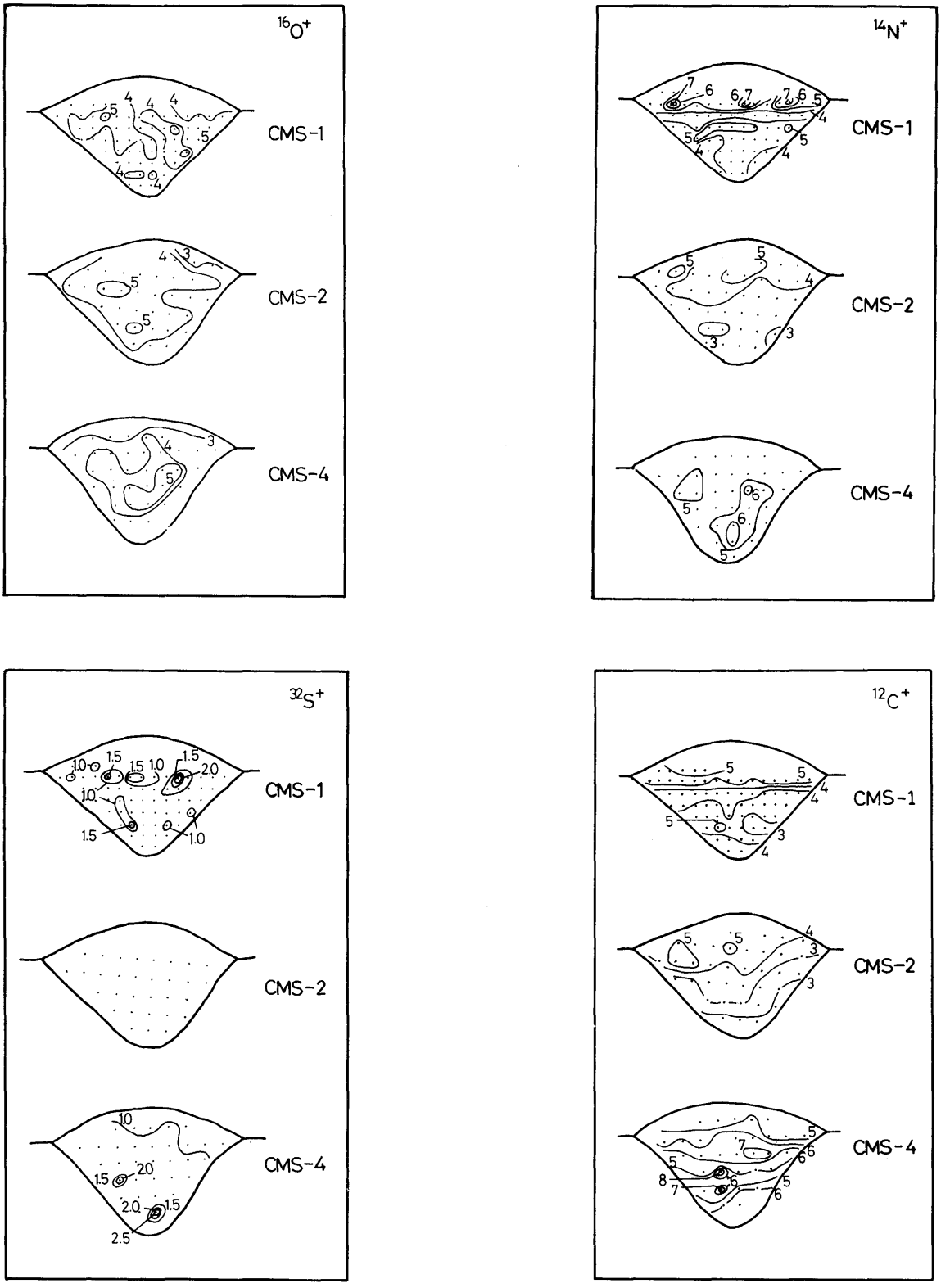

Fig. 5 Distributions of oxygen, nitrogen, sulphur and carbon in weld steel with point analysis using IMA (every numeral is shown relatively)

bead shape become more round with increasing CaO content. **Photo. 1** shows the cross sections of these beads etched with 2% nital.

(2) Distributions of non-metallic elements

Among non-metallic elements in welded steel with submerged arc welding method, oxygen and nitrogen shows remarkable change in content. Therfore, the distributions of oxygen and nitrogen were mainly investigated in this study. The results of these distributions with impulse fusion method and point analysis by IMA are shown in **Figs. 4** and **5.** The remarkable change in the distribution of oxygen was not detected from the result of point analysis by IMA whereas fairly detectable difference is shown from the result with impulse fusion method.

Dependences of increments in oxygen and nitrogen upon CaO content in flux are shown in **Figs. 6** and **7.** As CaO content increases, nitrogen content increases from 90 ppm to 220 ppm whereas oxygen content in weld steel was nearly constant or inclined to decrease a little. Further, the inclination of increment in nitrogen content seems to be independent upon the quantity of heat input.

Subsequently, the distributions of sulphur and carbon, which were investigated with IMA, are shown in Fig. 5. Though higher region of sulphur content was locally found out, it can be considered that the distribution of sulphur is almost homogenious after welding. The distribution of carbon has an inclination such that its concentration becomes higher along ripple line in weld steel. Further, the region of higher carbon content was also detected though its localization was not so clear as in the case of sulphur.

(3) Distributions of alloying elements

In this study, distributions of silicon, manganese, calcium and aluminium were investigated from following reasons;

1) silicon and manganese are main alloying elements in low carbon or alloy steel.
2) aluminium is one of the most popular deoxidizer and alumina is easily mixed into flux as impurity.
3) in most cases, calcium can be used as the indicator to judge whether inclusion is attributed to slag dragging or not.

Distributions of these elements obtained in this study are shown in **Fig. 8.** As shown in this figure, the distributions of silicon and manganese are in contrast to those of calcium and aluminium. The regions of high aluminium and calcium are locally detected and, in some cases, these regions were located at nearly same position.

On the contrary, the gradients of concentration in silicon and manganese distributions were essentially inclined to lie parallel to the direction of fusion line though their elements were maldistributed, respectively.

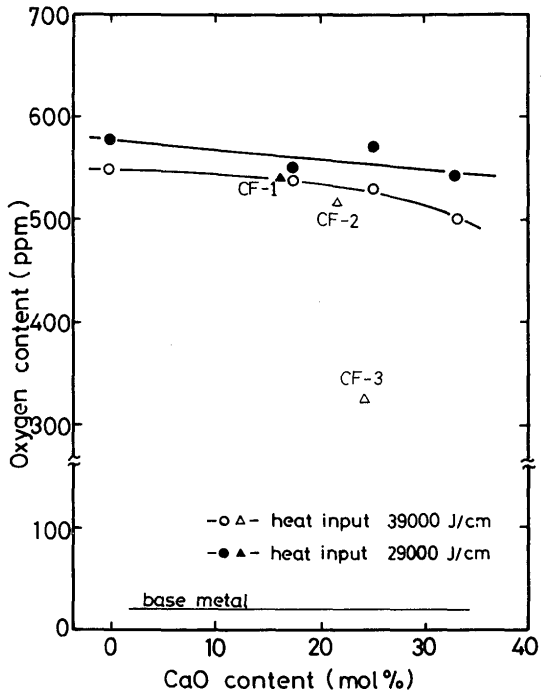

Fig. 6 Dependence of oxygen content in weld steel upon CaO content in flux

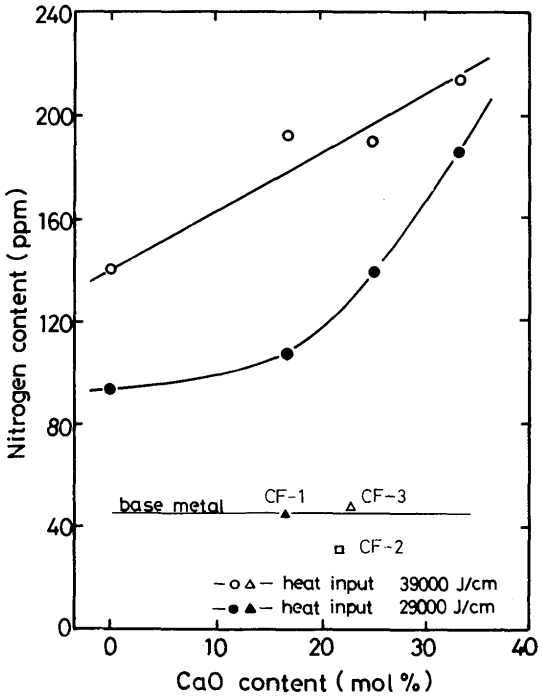

Fig. 7 Dependence of nitrogen content in weld steel upon CaO content in flux

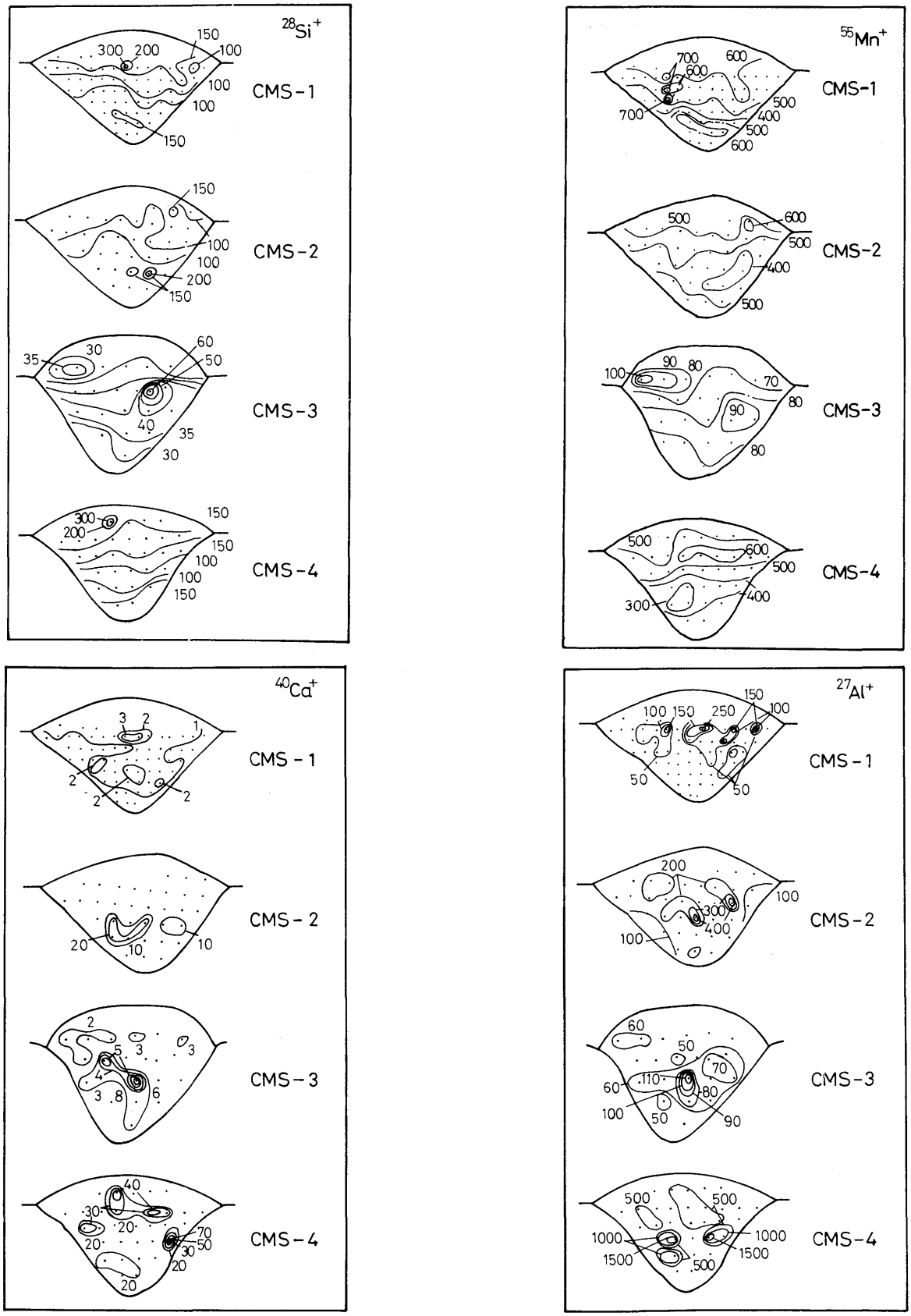

Fig. 8 Distributions of silicon, manganese, calcium and aluminium in weld metal with point analysis using IMA (every numeral is shown relatively)

4. Discussions

Although bead shape depends on various operating conditions such as current, voltage and travel speed, it can be considered that main factor in this study are the interfacial tensions among substrate metal, molten slag and metal because other operating conditions were constant. If these interfacial tensions are expressed as shown in **Fig. 9,** following relation is introduced;

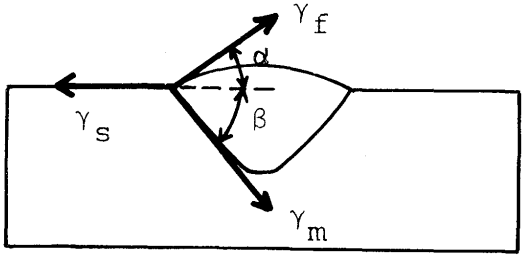

Fig. 9 Schematic diagram of the relation among interfacial tensions in the weldment

$$\gamma_s=\gamma_f\cos\alpha+\gamma_m\cos\beta \quad (1)$$

$$\cos\alpha=\frac{\gamma_s-\gamma_m\cos\beta}{\gamma_f} \quad (2)$$

Now, if it can be assumed that heat consumption by flux is independent on flux composition and nearly equal amount of steel is welded in every case, it can be presumed that the temperature of molten steel during welding is nearly same in every case because of constant heat input. Accordingly, it is possible to regard $\gamma_m \cos\beta$ as constant in equation (2). Besides, in the case of constant SiO_2, both γ_s and γ_f increase with increasing CaO content and then the increment of γ_f is larger than that of γ_s. Therefore, with increasing CaO content, α decreases and the ratio W/H also decreases apparently. Such consideration is supported by the data of Ferrera et al.[10]. The parameter of pear-type bead shape can be considered to depend upon only slag composition because other experimental conditions were hold as constant. The fact that parameter increased with increasing CaO content would originate in the increment of viscosity in CaO-MnO-SiO_2 slag.

The increment of oxygen content in weld steel with SAW method would be attributed to following causes;

(1) the chemical reaction between molten slag and molten steel,
(2) dragging of slag,
(3) oxidation of molten steel by atomosphere,
(4) dissolution of oxygen which originates in the decomposition of compounds containing oxygen under arc atomosphere.

Considering the results in ESW using the fluxes of the system CaO-MnO-SiO_2[11], it can be supported that the increment of oxygen attributed to slag-metal reactions is 200 ppm at most. Therefore, the rest of oxygen increment would be attributable to the described effects of (2) to (4). Although the discussion on inclusion is not performed in this paper, scanning electron microscope observation suggested that larger inclusions due to slag dragging were rare. Thus, it is expected that second effect is small unless these large inclusions decompose into small inclusions.

Subsequently, the information on standard free energy of formation of each slag component suggests that CaO is most stable and MnO is most unstable in the slag of the system CaO-MnO-SiO_2. Accordingly, oxygen content in weld steel will be inclined to decrease as CaO content in slag becomes rich. Further, the large difference of standard free energy between CaO and MnO must produce the remarkable dependency of oxygen content on CaO content. As shown in Fig. 6, the inclination is consistent with experimental result. However, only a slight decrease was shown in the experimental result. This would be attributable to the fact that silica content is 50 mole% and the difference of standard free energy of formation between SiO_2 and MnO is fairly small.

Effect (3) may replace the shielding effect of slag. If the assumption is reasonable, it can be considered that shielding effect is estimated by diffusion of oxygen from atomosphere to molten metal. However, it is impossible to discuss the shielding effect because the investigations on diffusion coefficient of oxygen in molten slag is very rare. Besides, in SAW process, it is not so important to consider the diffusion of oxygen on account of very rapid solidification. Therefore, it may be reasonable to interpret the oxygen increment by oxygen activity in slag rather than diffusion process. However, oxygen activity in the slag of the system CaO-MnO-SiO_2 is unknown. If the oxygen increment can be discussed by activity of MnO, a_{MnO}, instead of oxygen activity, the distribution of oxygen to molten steel would be apt to be suppressed with increasing CaO content because a_{MnO} becomes small with increasing CaO content[11]. Such consideration roughly gives good agreement to the result shown in Fig. 6. Conclusively, it is suggested that slight remarkable dependency of oxygen increment on slag composition can be explainable from stabilities of component oxides and activity of MnO.

As is general, the increase of nitrogen in weld steel

are responsible for two following processes. One is the direct process in which nitrogen is transfered from nitrogen-rich slag to molten steel and the other is attributable to the direct reaction between molten steel and nitrogen in atomosphere. Dissolution of nitrogen into slag is enhanced by following factors;

(1) atomosphere is reducible[12),13)],
(2) the existence of carbon[14)],
(3) basicity of slag is small[13)].

The effects of (1) and (2) can scarcely be expected in welding process performed in this study. However, the absorption of carbon dioxide at the surface of flux may be considered as one of the reasons for the elevation of nitrogen content. In general, the richness of lime in flux is likely to cause the absorption of carbon dioxide. Hence, the existence of carbon may be possible providing absorbed carbon dioxide can decompose under arc atomospere. Thus, the inclination of the nitrogen increment may be explainable from the dependence of absorbed carbon dioxide upon flux composition. Subsequently, the formation of silanol on the surface of flux may be responsible for the introduction of hydrogen. However, it is questionable whether the formation of silanol is effective on the formation of gaseous hydrogen because silanol decomposes at fairly lower temperature (100–200 °C).

A slight effect due to slag composition can be expectable because the basicity of slag become more acidic with increasing MnO content. Therefore, the decrement of nitrogen must be expectable with increasing CaO content because the solubility of nitrogen increases with increasing the basicity of slag. However, reverse inclination was obtained as shown in Fig. 7. Thus, it can be concluded that the increment of nitrogen does not depend on chemical dissolution of nitrogen gas into slag.

The direct effect of air on the elevation of nitrogen and oxygen in weld steel was not discussed in this study. However, viscosity of slag may give a very significant information on the increments of oxygen and nitrogen if the direct reaction of molten steel to atomosphere can be more suppressed as slag becomes less viscous. Further, it would be reasonable that this effect is discussed from the results of the investigation on fluxless welding processes.

The condensation of sulphur and carbon in each distribution map is likely to be attributable to the formation of sulphide[15)] and carbide, respectively. The formation of sulphide was detected with SEM observation though it was rare, and, in most cases, these compounds seem to be in the form of (Fe, Mn) (S, O). Although the most possible carbide seems to be NbC, the identification was not performed in this study. Further investigation on inclusion is desired.

The formation of inclusion also seems to produce the condensation of calcium and aluminium as shown in their distribution maps. Although similar tendency was detected in the distributions of silicon and manganese, these elements were not so maldistributed than calucium and aluminium. This would be due to the fact that manganosilicate inclusions were fairly homogeneously distributed and these inclusions are very small. Further, it was detected that these elements are apt to show lower content in the middle layer of weld steel because of redistributions of these elements.

5. Summary

Distributions of several non-metallic and alloying elements in low alloy steel welded with SAW method using fluxes of the system CaO-MnO-SiO_2 were investigated by impulse fusion method and point analysis using IMA. The increment of oxygen in weld steel was inclined to decrease a little with increasing the content of CaO in flux. The dependency of oxygen increment was qualitatively interpreted from the stability of each component oxide and activity of MnO. Subsequently, the remarkable dependency of nitrogen increment on CaO content was detected. It was suggested that the phenomenon may be supported by the dependency of absorbed carbon dioxide or the formation of silanol on flux component. However, these interpretations did not come to be confirmed from the results in this study. Further, it was suggested that viscosity of slag may give significant information on the increments of nitrogen and oxygen.

Maldistributions in carbon and sulphur can be considered to originate in the formation of inclusions such as carbide or sulphide. Similar results in calcium and aluminium were obtained. Distributions in silicon and manganese showed a little lower content in the middle region, respectively. This would be attributable to the redistributions of these elements during melting.

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