Fundamental Investigation on Electroslag Welding (Report III) †

– The Effects of CaF_2 Addition to (CaO)-MnO-SiO_2 Fluxes on Inclusion Morphology –

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Abstract

The effects of CaF_2 addition to (CaO)-MnO-SiO_2 fluxes on inclusion morphology were investigated with SEM observation and X-ray microanalysis. Inclusion morphology was scarcely changed by the addition of CaF_2 and main inclusions were (Mn, Fe) (S, O), silicate containing sulphur and iron manganosilicate. The existence ratio of oxide to all inclusions decreased by the addition of CaF_2. However, it was indicated that the existence ratio of main inclusion was more closely related to the composition of parent slag (slag without CaF_2) rather than the content of CaF_2 added.

1. Introduction

It is well known that many sorts of inclusions are detected in steel and various harmful influences are produced from them. Similar phenomena are shown in weld metal and oxide and sulphide are the most trouble inclusions in the case of using low carbon steel as substrate. When alloy elements such as Cr and Nb are contained in steel, carbide and nitride inclusions are generally formed and these inclusions have various effects aparting from the fact whether or not they have good influences on the properties of weld metal.

Generally, it is considered that the addition of fluoride to slag can lower the oxygen potential in slag. As described in the previous papers[1),2)], the addition of CaF_2 is effective to lower the oxygen content in weld metal though the effective amount of CaF_2 depends on slag component. In this study, the effects of CaF_2 addition to silicate slag on inclusion morphologies of oxide, oxysulphide and sulphide were investigated with SEM observation and X-ray microanalysis.

2. Experimental Procedures

Specimens and their notations used in this study were the same ones used in the previous paper[2)]. The experimental conditions of ESW and the compositions of fluxes, wire and substrate steel were also described in the previous paper[2)]. After cutting off specimen pieces from weld metal, they were polished by SiC and ZrO_2 abrasives using water or ethylalcohol as coolant. Then, specimens for SEM observation were prepared by deeply eching them with 5% nital. The conditions of SEM observation were as follows:

Voltage and Current	:	20kV x 100~110μA,
Sensitivity in XMA	:	100 cps,
Type of microscope	:	Hitachi HSM-2B.

3. Results and Discussion

As described above, the effects of CaF_2 addition to two kinds of fluxes ($MnO{\cdot}SiO_2$ and $CaO{\cdot}MnO{\cdot}SiO_2$) on inclusion morphology were investigated by SEM observation and X-ray microanalysis. These results are shown in **Photos. 1-3.** The shape, composition and kind of inclusions were essentially independent upon the addition of CaF_2 and the main inclusions were (Mn, Fe) (S, O), silicate containing sulphur and manganosilicate with iron. Then, SiO_2 (or iron silicate) was also found out as shown in **Photo. 4.**

Subsequently, the ratio of main inclusions was investigated and the result is shown in **Table 1.** The result shows that existence ratio of oxide inclusion is lowered by the addition of CaF_2. This agrees with general consideration in which oxygen potential in slag is lowered by the addition of CaF_2. However, the existence ratio of oxide inclusions was nearly constant in spite of adding different

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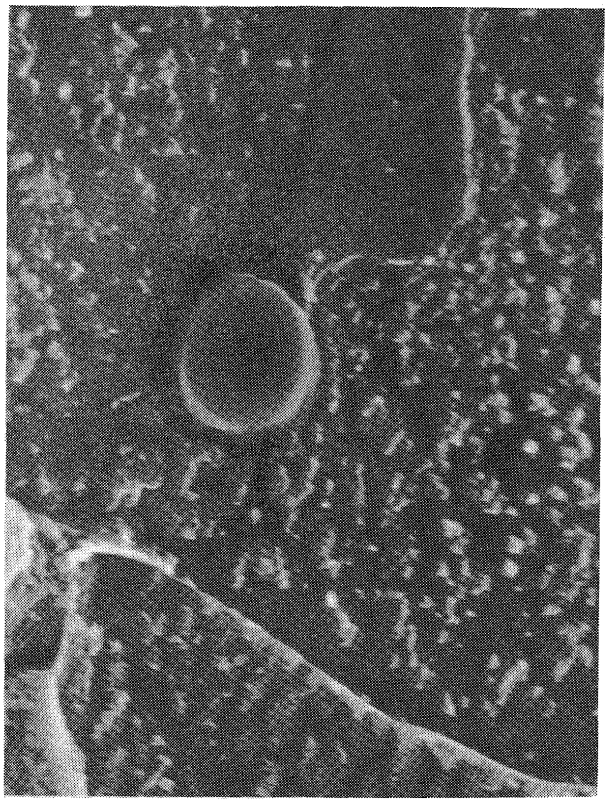


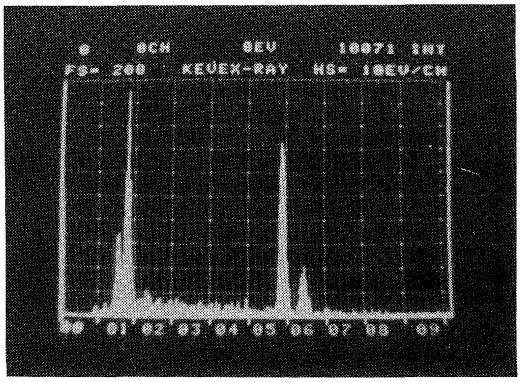
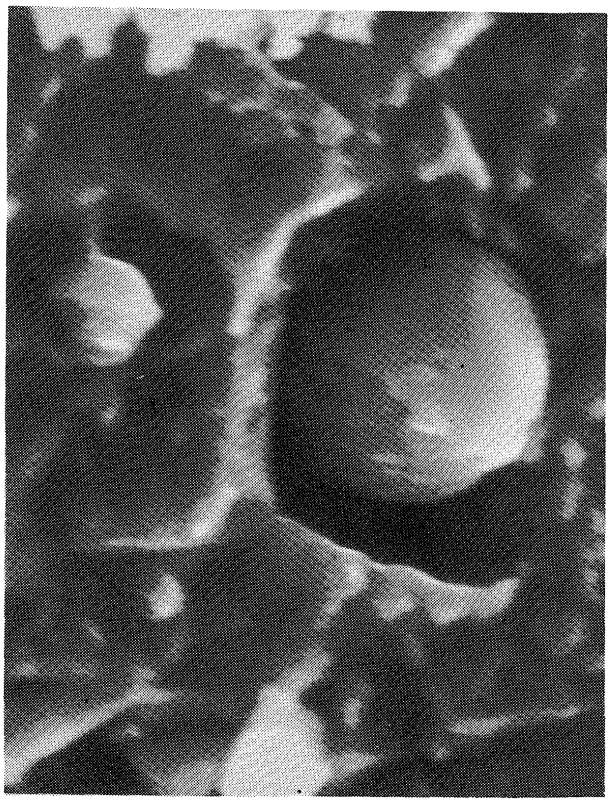
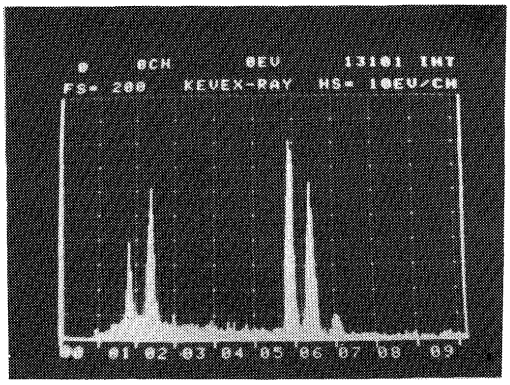
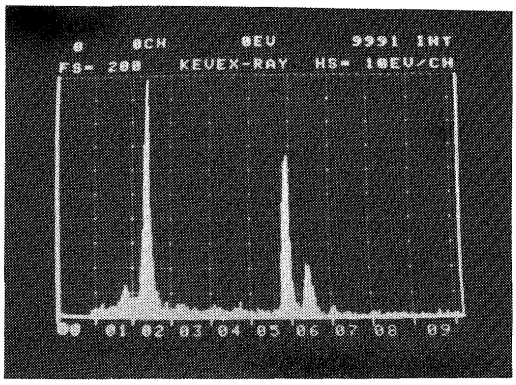


Photo. 1 Typical oxide inclusion in ESW metal using (CaO)-MnO-SiO_2 flux with CaF_2 (x5000)



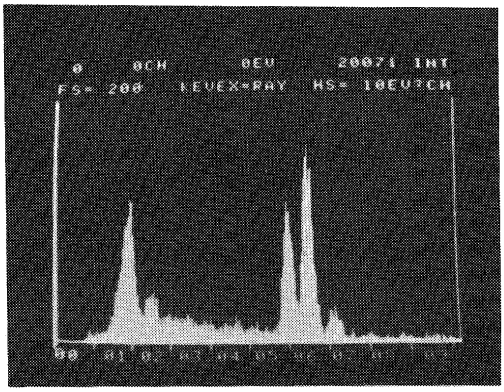


upper region



lower region

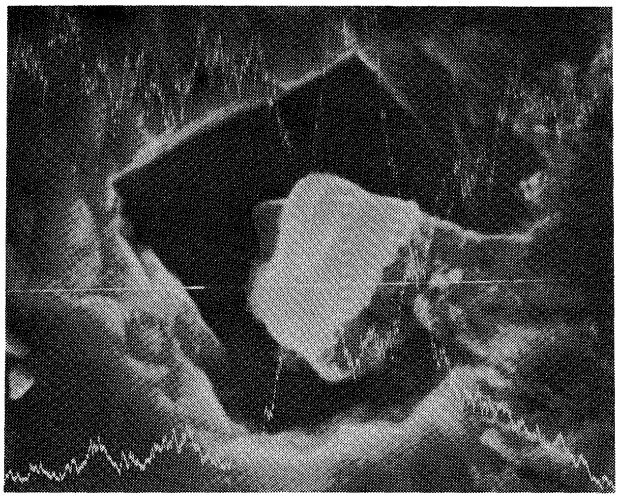
Photo. 2 Typical duplex inclusion in ESW metal using (CaO)-MnO-SiO_2 flux with CaF_2 [from No. 7 specimen] (x15000)



Spectrum from the largest inclusion

Photo. 3 Typical inclusion of silicate containing sulphur in ESW metal using (CaO)-MnO-SiO_2 flux with CaF_2 (x3000)

Fe



Si

Photo. 4 The inclusion identified as SiO_2 or iron silicate (x15000)

content of CaF_2. According to the previous studies[1),3)], it is indicated that all fluorine ion is not effective to breaking Si-O bond in silicate when fluoride of 30 mol% or over is added to silicate. In other words, fluorine ion changes a certain state to another in the vicinity of 20 mol%. Taking the result into consideration, it is reasonable to interpret that only the addition of initial several percentage CaF_2 is effective to lowering the existence ratio of oxide inclusions. This disagreement in the quantity of CaF_2 is maybe due to the difference of slag composition between in this study and in the previous study. In addition, physical effects such as the difference of viscosity may superimpose on chemical effects.

Similar tendency was shown in the relation of existence ratio between sulphide and silicate containing sulphur. That is, the dependences of these inclutions on additive amount of CaF_2 were scarecely recognized and the quantity of sulphide increased with increasing CaO content in slag. The result can be related to sulphide

Table 1 The existence ratio of inclusions detected in ESW metal using (CaO)-MnO-SiO_2 flux with CaF_2.

Specimen No.	CaF_2 Content	(Mn, Fe) (S, O)	Silicate Containing Sulphur	Silicate
No. 1	0.0%	34%	45%	21%
No. 7	8.3%	38%	50%	12%
No. 8	19.5%	28%	61%	11%
No. 9	31.0%	34%	50%	16%
No. 3	0.0%	29%	54%	17%
No. 10	13.0%	43%	49%	8%
No. 11	16.3%	45%	48%	6%
No. 12	30.9%	36%	54%	11%

capacity C_s $(=(\%S)\frac{p_{O_2}}{p_{S_2}})$. The value of C_s in the slag of the system MnO-SiO_2 is larger than that in the system CaO-SiO_2[4),5)]. Therefore it is suggested that the formation of sulphide is easier with increasing CaO content in slag. Another interpretation can be performed on the basis of sulphur solubilities in these slags. As is general, it has been considered that to decrease the solubility of sulphide is to increase the activity coefficient. According to Sharma and Richardson[6)], activity coefficient of sulphide in the slag of the system CaO-SiO_2 is several times as large as that in the system MnO-SiO_2. Therefore, the amount of sulphide separated from slag becomes larger as the content of CaO in slag increases because the solubility of sulphide in slag decreases with increasing CaO content. The interpretation shows good agreement with the result shown in table 1 but the interpretation is not always reasonable when a large amount of CaF_2 is added to slag.

Thus, it is concluded that inclusion morphology in weld metal essentially depends upon oxygen potential and sulphide solubility of slag used. In order to decide the clear relation between inclusion morphology and slag properties or other conditions, however, further investigations using various fluxes are required because only two series of fluxes were used in this study.

4. Summary

The effects of CaF_2 addition to two manganosilicate fluxes on inclusion morphology were investigated with SEM observation and X-ray microanalysis. Inclusion morphology was almost similar to that in the case of using manganosilicate fluxes without CaF_2 and it was indicated that main inclusions were (Mn, Fe) (S, O), silicate containing sulphur and manganosilicate with iron. It was also shown that the existence ratio of these inclusions were scarcely dependent upon additive CaF_2 content and were related to the composition of parent slag which is manganosilicate with no CaF_2. The ratio of oxide inclusions was influenced by the addition of CaF_2 but it can be considered that the addition of several percentage CaF_2 is effective to lowering the quantity of oxide inclusions because the ratio of oxide inclusions was nearly constant in spite of increasing CaF_2 content. However, inclusion morphology in weld metal using various fluxes must be investigated because existence ratios of various inclusions are influenced by chemical properties of slag as well as physical properties such as viscosity. Further, structural investigations on inclusion are necessitated.

References

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