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Author(s)	Iwamoto, Nobuya; Nose, Jiro; Naganawa, Yutaka et al.
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Fundamental Investigation on Electro-slag Welding (Report II)†

— Inclusions in Steel Welded using (CaO)-MnO-SiO$_2$ Fluxes —

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

Abstract

Non-metallic inclusions in electro-slag welded steels using several fluxes of the system MnO-SiO$_2$ or CaO-MnO-SiO$_2$ were investigated with X-ray diffraction method and SEM observation. Almost all inclusions were indentified as sulphide (Mn, Fe)S (or oxysulphide (Mn, Fe) (S, O)) and sulphide-silicate duplex or silicate containing sulphur complicatedly. Iron silicate and calcium ferrous sulphide (or oxysulphide) were also found though they were rare. It was concluded that all inclusions attributed to metallurgical origins by several reasons. Relations between flux constituents and species or compositions of inclusion could not be clarified.

1. Introduction

Various non-metallic inclusions in steel are the inevitable products during iron- and steel-making and can be found in a wide variety of shapes, sizes and distributions[1),2),3)]. The importance of non-metallic inclusions is to have a great influence on physical and mechanical properties, and all of them are inclined to lower mechanical properties. Further, it is well established that shape, size and distribution of inclusions show similar effects to quantity of them. In general, the influence of inclusions become greater as the size of them increases.

In iron- and steel-making, most of their origins attribute to air oxidation, chemical erosion of refractories and deoxidation reactions. In welding, especially in submerged arc welding, dragging of slag becomes more important factor instead of chemical erosion of refractories. On the other hand, air oxidation and dragging of slag are minor factors in electro-slag welding and the most significant factor in this process is slag-metal reaction, that is, redistributions of non-metallic elements during the fall of metal drop through molten slag. Of cource, redistributions of alloying elements are also significant because these are closely related to those of non-metallic elements in welded steel.

Harmful inclusions in steel are mainly oxides, sulphides and their complex compounds[1),2)]. For example, it was reported that oxides such as duplex inclusion composed of silicate and alumina have a very harmful effect on tensile fracture of steel. It was also indicated that sulphides show similar effect to tensile fracture[2)]. In low alloy steel, most important sulphide is manganese sulphide and it is well established that three types of MnS can be formed in steel[4),5)] and the morphology is influenced by following factors[6)];

(1) contents of silicon, aluminium and carbon in steel,

(2) cooling rate.

Further, type II MnS, which is fan or chain-like inclusion usually described as eutectic and intergranular, is most harmful for impact value, deep drawing and other mechanical properties[1),7),8)]. However, the deterioration of mechanical properties in weld steel can not always attribute to sulphide because there are a great variety of inclusions in steel and their morphologies and effects are very complex. In this study, the identification of inclusions in a typical low alloy steel, which was welded using several fluxes of the system MnO-SiO$_2$ or CaO-MnO-SiO$_2$, was performed as a serial study of electro-slag welding.

2. Experimental Procedures

The experimental conditions of electro-slag welding and the components of wire, fluxes and substrate steel were described in the previous paper[9)]. Taking cooling rate into consideration, apparent heat input was also fixed as described in the previous paper though it is expected that each flux generates different quantity of

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* Professor
** Nippon Kokan K.K.
*** Research Instructor
**** Research Associate

resistance heat. Specimens used for X-ray diffraction measurement with Debye-Scherrer method were prepared with iodine-methanohol method. The content of iodine was fixed at 10 wt%. During extraction argon was used as atomosphere. The conditions of X-ray diffraction were as follows;

Target: Cr,
Voltage and Current: 35 KV × 10 mA,
Path: Air, Filter: V.

SEM observations were performed on both polished and etched specimens. Polished specimens were prepared according to the schedule shown in Table 1. Etched specimens were prepared by etching these polished specimens with 5% nital after SEM observation. Each etching time was from several seconds to two minutes. The conditions of SEM observation were as follows:

Voltage and Current: 20 KV × 100–110 μA
Tilt angle: 30°
Type of microscope: Hitachi HSM-2B.

3. Results and Discussion

According to the summary by Van Vlack et al.[10)], it was reported that duplex inclusions composed of silicate and sulphide can be formed in low alloy steel because siliceous liquid phase is formed in Fe-Mn-Si-S-O alloys and this phase is generally in contact with solid sulphide. Similar interpretations have been performed by several investigators[6)]. Therefore, it is easily expected that sulphide such as MnS with some FeS and manganosilicate are generally found as inclusions in low alloy steels.

As shown in **Fig. 1-(a)**, almost all extracted specimens gave amorphous pattern. However, the diffraction pattern of α-MnS as shown in **Fig. 1-(b)** was obtained from the specimens which were annealed at 1000°C in Ar for 1 hour. Sometimes the pattern due to α-Fe_2O_3 was obtained on account of inadequate experimental conditions. Diffraction patterns due to silicate and other oxide could not detected. As one of these reasons, it can be considered that these oxides were very small. However, strong support could not be obtained from SEM observation as described later.

The typical result of SEM observation on polished specimens was shown in **Fig. 2.** Further, the existence

Table 1 Polishing schedule of specimens

Step	Abrasive	Size of Abrasive	Coolant	Remarks
1	SiC	70 μ	Water	By hand
2	,,	28 μ	,,	,,
3	,,	16 μ	,,	,,
4	,,	10 μ	,,	,,
5	Al_2O_3	1.0 μ	,,	,,
6	,,	0.3 μ	,,	..
7	,,	0.05 μ	,,	,,

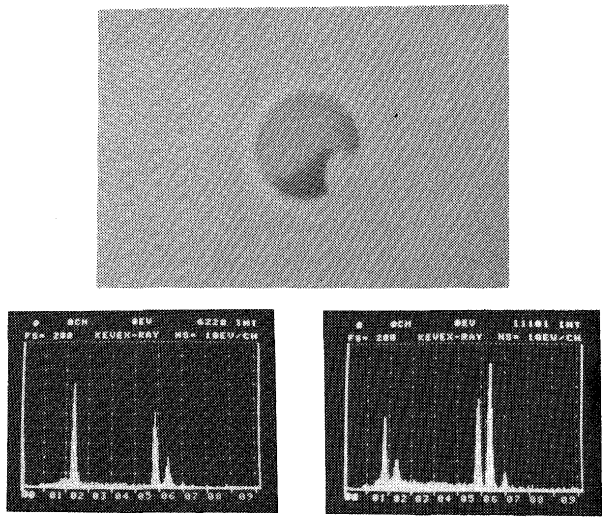

dark region light region

Fig. 2 Typical duplex inclusion in polished speicmen

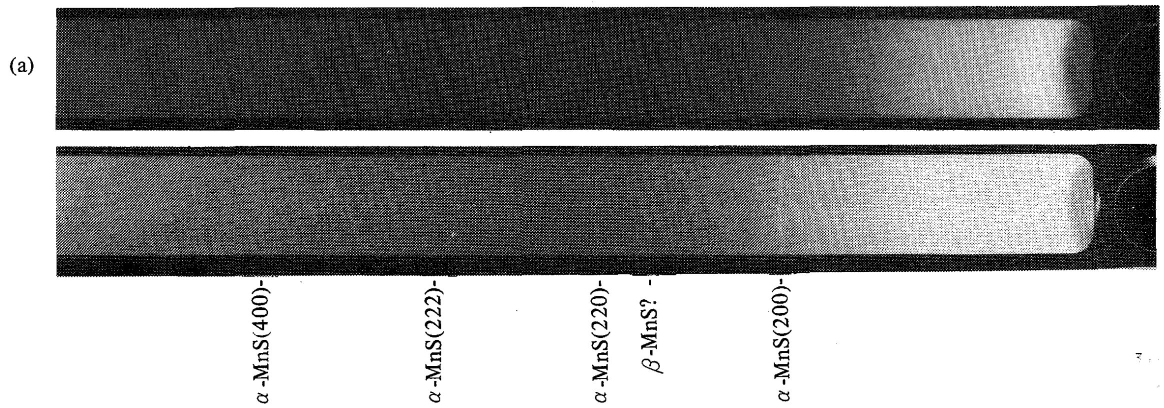


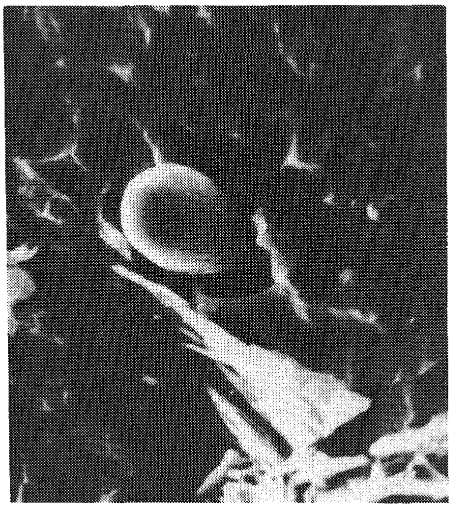
Fig. 1 Typical X-ray diffraction patterns of extracted and annealed specimens

Table 2 Existence ratio of inclusion containing sulphur

Specimen No.	no sulphur	containing sulphur	remark
1-1	4	18	
2-2	8	16	
3-2	4	20	
4-2	1	19	less content
5-2	3	17	
6-2	3	15	

of sulphur was investigated as shown in **Table 2.** From these results, it can be seen that most of inclusions were sulphide and sulphide-silicate duplex or silicate containing sulphr complicatedly. SEM observation on etched specimens gave more clear informations on the identification of inclusions. These results are shown in **Figs. 3, 4, 5** and **6.** As shown in Fig. 3, all sulphide inclusions clearly were type I MnS with some FeS. Therefore, cooling rate of weld metal seems to be very slow. According to the result by Mohla[6], cooling rate in this experiment corresponds to 2–5 °C/sec or below. However, it may be expected that type I MnS can be produced at somewhat higher cooling rate if cooperative effects of carbon and silicon are taken into consideration.

It was recertified from SEM observation on etched specimens that most of oxide inclusions were manganosilicate containing some sulphur. As shown in Fig. 4, manganosilicate inclusions looked more whitish than sulphide because of their less conductivity and their dimentions was somewhat, but not remarkably, smaller than that of sulphides. This result is contradictry to the result with extraction method and, therefore, the necessity of further investigations with extraction method is suggested. Perfect identification of these sulphide and silicate is very difficult because MnO, FeO, MnS and FeS can generally be soluble each other[11],[12]. Practically, it is impossible to determine the chemical formulas of these inclusions but the formulas such as (Mn,Fe) (S,O) and $[(\mathrm{Mn,Fe})(\mathrm{S,O})]_x[\mathrm{SiO_2}]_y$ would be better expressions. In order to discuss in more detail, the precise measurement of lattice constant or state analysis of each element in



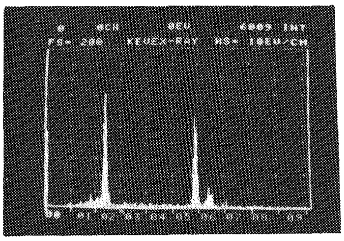
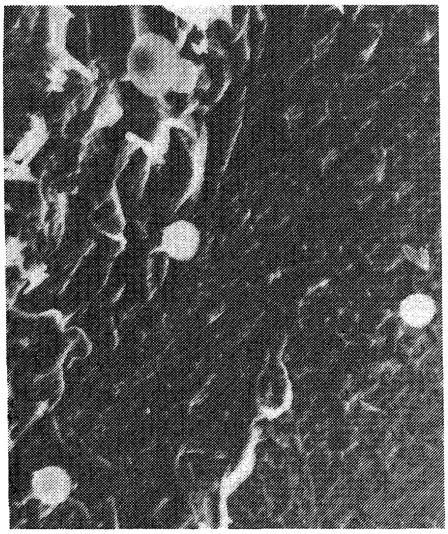


Fig. 3 Typical inclusion identified as (Mn,Fe)S or (Mn,Fe) (S,O)



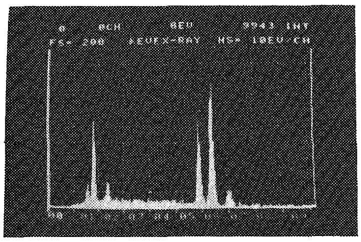


Fig. 4 Typical inclusion identified as manganosilicate containing sulphur

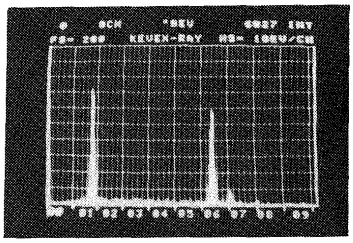


Fig. 5 The inclusion identified as iron silicate (from specimen 2–2)

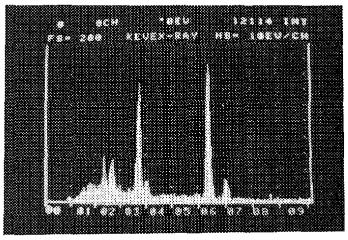


Fig. 6 The inclusion identified as (Ca,Fe)S or (Ca,Fe) (S,O) (from specimen 4–2)

inclusions are necessitated.

Furthermore, a few another inclusions were found as shown in Figs. 5 and 6 and these inclusions were very rare. It was supposed that the inclusion in Fig. 5 was formulated as $(FeO)_x(SiO_2)_y$ and accidentally formed by the reaction between iron oxide and SiO_2 in the region containing no MnO. On the other hand, the inclusion with much calcium was identified as calcium ferrous sulphide (Ca,Fe) (S,O) from the result of X-ray energy spectrum. In general, the origin of the large inclusions containing calcium is regarded as the result of the dragging of slag. For example, such inclusions are often found in submerged-arc welded steels. From following reasons, however, it was suggested that the inclusion containing calcium did not attribute to the dragging of slag;

(1) the inclusion was not silicate but sulphide or oxysulphide

(2) the inclusion was fairly small.

Subsequently, SEM observation on welded steel using a few commertial fluxes was performed in order to compare with results of welded steel using fluxes of the system MnO-SiO_2 or CaO-MnO-SiO_2. Typical inclusions are shown in **Fig. 7.** Almost all inclusions were manganese sulphide containing iron and silicate with sulphur. As shown in X-ray energy spectrum, titanium oxide was detected in silicate inclusion. Thus, it is suggested that addivite component such as TiO_2 and Al_2O_3 is inclined to be contained as a component of inclusion. It can be easily imagined that the inclination is related to their free energy of formation[13]. As indicated in this study, however, it can easily be considered that basic oxide such as CaO or MgO can be scarcely contained in inclusion and, if contained, they are contained in the form of any compound in most cases. Thus, free energy of formation of simple oxide seems to be not so closely related to the composition of inclusion. It is fully expected that activity of component oxide, distribution of metallic element between molten steel and slag and slag structure are complicatedly related to the constituent and type of inclusion. In further investiga-

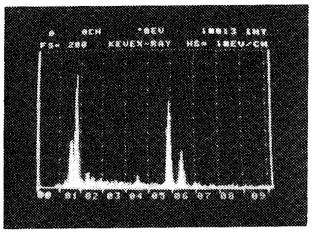


Fig. 7 Typical inclusion identified as manganosilicate containing titanium (It is shown by white spot. Another inclusions are sulphide (Mn,Fe)S.)

tion, therefore, it is necessary to clarify the influence of fourth additive oxide (or fluoride) on the constituent, shape and type of inclusion according to the result obtained using simple silicate flux.

4. Summary

Non-metallic inclusions in electro-slag welded steel using several fluxes of the system MnO-SiO_2 or CaO-MnO-SiO_2 were investigated with X-ray diffraction measurement and observation by SEM equipped with XMA. Almost all inclusions were sulphide or oxysulphide formulated as (Mn,Fe)S or (Mn,Fe) (S,O) and sulphide-silicate duplex such as $(Mn,Fe)S$-$[(Mn,Fe)O]_x [SiO_2]_y$ or silicate containing sulpher complicatedly. Ferrous silicate and calcium ferrous sulphide (or oxysulphide), which were formulated as $(FeO)_x \cdot (SiO_2)_y$ and (Ca,Fe)S (or (Ca,Fe) (S,O)), were also found though they were rare. It was concluded that all inclusions did not attribute to the dragging of slag but to the metallurgical origins such as slag-molten steel reaction, deoxidation and desulpherization by following reasons;

1) oxide inclusions, even if sulphur was contained in them, did not contain calcium which originated in the dragging of slag in most cases.
2) Inclusions containing calcium were not silicate or other oxides but sulphide or oxysulphide.
3) All inclusions were fairly small.

Titanium was detected in the inclusions of the welded steel using a few commertial fluxes. In this study, however, such phenomenon could not be interpreted because the effects of additive oxides on the constituents of inclusions were not investigated. Therefore, the relationship between flux constituent, especially fourth additive oxide, and the composition of inclusion must be clarified in further investigation.

References

1) C. E. Sims: Trans. AIME, 215 (1959), p. 367.
2) K. Narita and T. Itoh: Research and Development (Kobe Steel Eng. Rept.), 16 (1967), p. 226 (in Japanese).
3) E. T. Turkdogan and R. A. Grange: JISI, 208 (1970), p. 482.
4) T. J. Baker and J. A. Charles: JISI, 210 (1972), p. 702.
5) T. J. Baker: "Sulphide Inclusions in Steel", p. 135, Proc. Intl. Symp., 1974 (Port Chester, New York), ASM.
6) P. P. Mohla and J. Beech: JISI, 207 (1969), p. 177.
7) T. J. Baker and J. A. Charles: JISI, 210 (1972), p. 680.
8) T. J. Baker and J. A. Charles: JISI, 211 (1973), p. 187.
9) N. Iwamoto, J. Nose, Y. Naganawa, Y. Tsunawaki and Y. Makino: JWRI, 6 (1977), p. 23.
10) L. H. Van Vlack, O. K. Riegger, R. J. Warrick and J. M. Dahl: Trans. AIME, 221 (1961), p. 220.
11) R. G. Wells: "Sulphide Inclusions in Steel", p. 123, Proc. Intl. Symp., 1974 (Port Chester, New York), ASM.
12) R. Kiessling and C. Westman: JISI, 203 (1965), p. 377.
13) F. D. Richardson and J. H. E. Jeffes: JISI, 160 (1948), p. 261.