4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

FUNDAMENTAL STUDY ON THE CONDITION OF DEOXIDATION FOR MOLTEN STAINLESS STEEL BY FLUX ADDITION

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Synopsis: In order to obtain high properties for stainless steels, the oxygen content is required to be low and the inclusions to be deformable. A fundamental study on deoxidation with flux for stainless steel in 2-500kg scale was made .

Using CaO based flux and no aluminium addition , lower the refining temperature and lower the activity of SiO_2 were effective to lower the oxygen content. The rate of deoxidation increased with increasing the intensity of stirring energy. And the activity ratio of $aCr_2O_3/aSiO_2$ should be lowered to decrease the composition of (Cr_2O_3) in inclusions to make inclusions deformable.

Key words: clean steel, stainless steel, deoxidation with flux , slag equilibrium, inclusions , gas bubbling

1. Introduction

New steel products with extremely low oxygen content have shown excellent material properties; for example , the lower oxygen content in bearing steels give the higher fatigue life. This is also true for stainless steels, which are used for various parts in many industrial fields. Recently the demand for cleanliness of stainless steel has become severe . In order to obtain high resistance to fatigue , the oxygen content is required to be sufficiently low . To obtain the high deformability of deep drawing , inclusions are required to be deformable, so inclusions with high melting point such as high Al_2O_3 and Cr_2O_3 should be avoided. Therefore, refining techniques to decrease the amount of inclusions and to control the shape of inclusions are important.

There have been some researches on inclusions of stainless steel for the relation of deoxidizer and inclusions [1], and for the calculation of inclusion composition at the solidification [2),3)]. But there have not many researches on lowering the amount of inclusions and to decrease the composition of Al_2O_3 and Cr_2O_3 in inclusions. So a fundamental study on deoxidation using flux and no aluminum addition , was made.

2. Experimental procedures

Fundamental experiments of two scale were made , one was the experiment of 2 kg scale , and the other was 500 kg scale . They were made to aim at lowering the oxygen content and controlling the shape of inclusions.

2.1 Experiments of 2 kg scale

Schematic apparatus and experimental conditions are shown in Fig.1 and Table 1 respectively. Experiments were carried out to investigate the influence of flux and Si content on the achieved value of oxygen content and inclusions. After a flux was added to the molten stainless steel, the melt was kept at a predetermined temperature for about an hour . And in case of shape control of inclusions , the melt was cooled and

solidified in a crucible at about 50 K/min of cooling rate . The solidified steel was supplied for samples for the analysis of metal content and inclusions.

2.2 Experiments of 500 kg scale

Schematic apparatus and experimental conditions are shown in Fig.2 and Table 2 respectively. Experiments were carried out to investigate the influence of Ar gas flow rate and temperature on the deoxidation rate. After a flux was added to the molten stainless steel, the melt was stirred by Ar gas for slag-ageing about 15 minutes. And the melt was kept at a constant temperature , changes of oxygen content and inclusions were studied during this period.

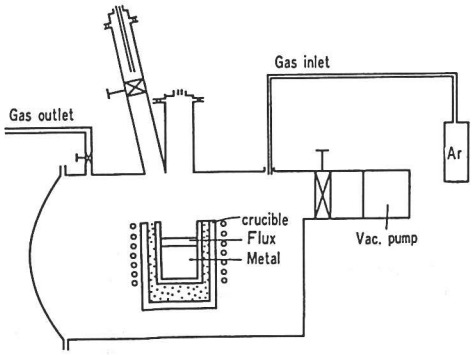

Fig.1 Schematic diagrams of apparatus

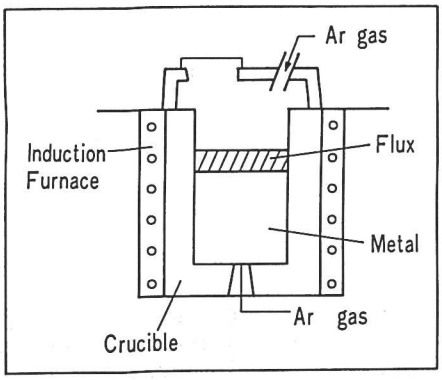

Fig.2 Schematic diagrams of apparatus

Table 1 Experimental conditions

Furnace	5 kg VIF
Crucible	MgO
Metal	C: 0.08/0.1, Si: 0.08/0.49, Mn: 0.9/0.95, Cr: 17.9/18.1, Ni: 8.0/8.1, Sol Al: ≦0.001, Fe: bal (wt %) 2kg
Flux	A: 73 CaO, 14 CaF_2, 13 SiO_2, 0 Al_2O_3; B: 50, 0, 40, 10; C: 81, 14, 5, 0 (wt %) 30kg/T
Atmosphere	Ar 1.013×10^5 Pa
Temperature	1723 ~ 1923 K

Table 2 Experimental conditions

Furnace	500 Kg IF
Crucible	MgO
Metal	C: 0.09/0.10, Si: 0.4/0.6, Mn: 0.97/1.05, Cr: 18.0/18.8, Ni: 7.9/8.5, Sol Al: ≦0.001, Fe: bal (wt %) 450kg
Flux	CaO-CaF_2-SiO_2 30kg/T
Atmosphere	Ar 1.013×10^5 Pa
Temperature	1833, 1763 K
Stirring gas	Ar $0 \sim 50 \times 10^{-3}$ Nm^3/min

3. Results and discussion

3.1 Lower the oxygen content

3.1.1 [Si]-[O] equilibrium

Experiments of 2 kg scale were made to study on Si-O equilibrium with flux C , and the results were plotted in Fig.3. The value of SiO_2 activity of flux was estimated from iso-activity diagram of CaO-CaF_2-SiO_2[4], and the lines were calculated by equation (1)[5].

$$SiO_2 = \underline{Si} + 2\underline{O}$$
$$\log K = \log(a_{Si}a_{O}^2/a_{SiO_2})$$
$$= -30110/T + 11.4 \quad \cdots\cdots\cdots (1)$$

Experimental data were closed to the calculated line. Though the value of $aSiO_2$[4] was measured at 1723K, it was applied to the data at 1873K . In case of regular solution

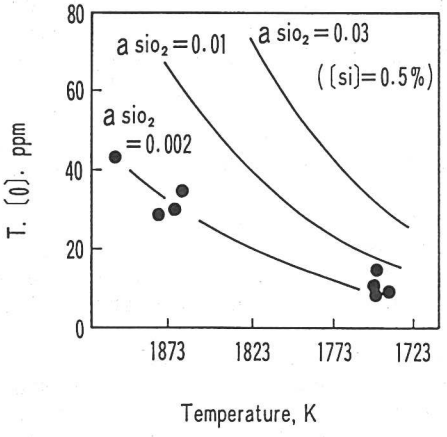

Fig.3 Relation between T.[O] and temperature

model, activity of slag is not strongly influented by temperature, so this results were assumed to be reasonable.

It could be obtained the value of oxygen content about 10 ppm at low temperature , its value was as low as that obtained by special melting methods such as vacuum arc remelting and electro slag remelting.

It was found that to lower the refining temperature and to decrease the actvity of SiO_2 were effective to lower the oxygen content according to the thermochemical estimation .

3.1.2 Oxygen content and inclusions

Experiments of 500 kg scale were made, and behaviors of oxygen content at 1833K and 1763K are shown in Fig.4 and Fig.5 respectively. The values of equilibrium oxygen content ,[O]e were calculated from the equation (1), and $aSiO_2$ was estimated from the iso-diagram of $CaO-CaF_2-SiO_2$ [4]. From these Fig.4 and 5, the apparent rate constant of deoxidation, Ko was defined by following equation (2).

$$d[O]/dt = -Ko([O]-[O]e) \qquad .....(2)$$

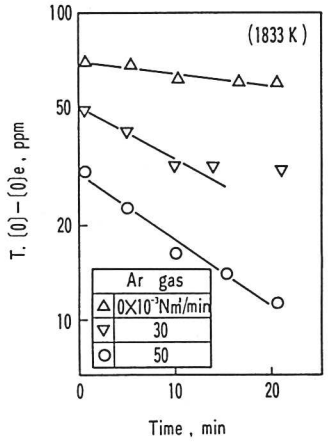

Fig.4 Change in T.[O] content (1833K)

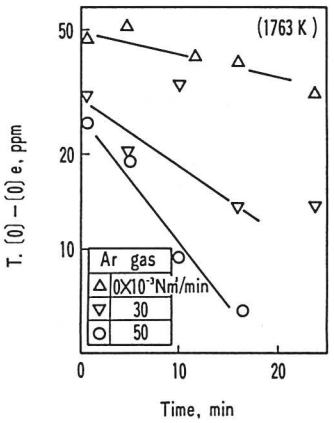

Fig.5 Change in T.[O] content (1763K)

Typical inclusions are shown in Fig.6, the diameter of inclusions were mostly smaller than 2μm. Sometimes there observed the inclusions whose diameter are larger than 10 μm in the steel manufactured in the plant. It is thought that there exist some primary inclusions which had not been fully removed from the steel in case of the plant .

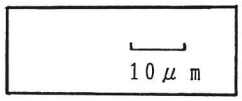

Fig.6 Typical inclusions

Changes in number of inclusions are shown in Fig.7. Inclusions were observed by use of an optical microscope (x800,3.5mm^2 area). Number of inclusions decreased with time , same as to the behavior of oxygen content. Since these small inclusions were estimated to be secondary inclusions formed during cooling time and solidification, the values of chemical analyses were seemed to be the soluble oxygen .

The composition of inclusions were SiO_2 -MnO-Cr_2O_3 type,analyzed by using the SEM and the EPMA. There were not observed the composition of CaO or MgO , which considered to be formed from contamination of slag and refractory.

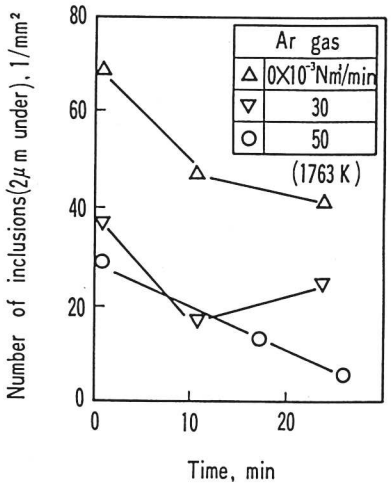

Fig.7 Change in number of inclusions (2μm under)

3.1.3 Deoxidation rate

It is assumed that the site of deoxidation with flux is the slag-metal interface ,equation (2) can be rewritten to equation (2)'.

$$d[O]/dt=-k_mA/V([O]-[O]e) \quad .....(2)'$$

where k_m:apparent metal-side mass transfer coefficient of oxygen,

V:volume of metal,

A:slag-metal interfacial area

On the other hand, the surface area of slag-metal was calculated from diameter of crucible, its area was defined to S. Fig.8 shows the relation between k_mA/S and the stirring energy $\dot{\varepsilon}$, which were calculated by Sundberg's equation[6] for gas bubbling and Ohnishi's equation[7] for electromagnetic induction respectively.

The values of k_mA/S were not influented by temperature, and these values increased in proportion to $\dot{\varepsilon}^{1/2}$. There had been some studies[8),9)] on relation between k_m and $\dot{\varepsilon}$, and it was said that k_m increased in proportion to $\dot{\varepsilon}^{1/3}$ or $1/2$. Since experimental result was close to these values , deoxidation reaction with flux was seemed to determined by the step of mass transfer of oxygen in metal.

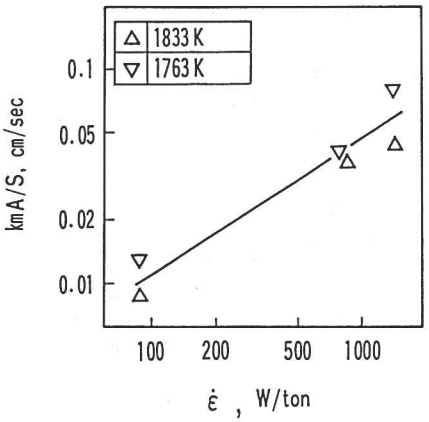

Fig.8 Relation between Km/S and $\dot{\varepsilon}$

3.2 Shape control of inclusions

3.2.1 Oxygen content and inclusions

Experiments of 2 kg scale were made .The relation between oxygen and [Si] contents is shown in Fig.9. The activities of SiO_2 were calculated by equation (1), and the values of SiO_2 activity of flux A and B were estimated from iso-activity diagram of $CaO-CaF_2-SiO_2$[4] and $CaO-SiO_2-Al_2O_3$[10] respectively. The values of the chemical analysis were total oxygen, but these total oxygen content were close to the calculated lines, so these chemical analyses seemed to be almost soluble oxygen.

Most of inclusions were smaller than 2μm, and number of inclusions decreased with decreasing oxygen content in Fig.10, so the observed inclusions were correspond to oxygen contents measured by chemical analysis.

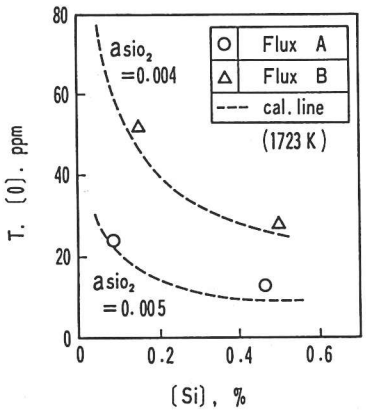

Fig.9 Relation between T.[O] and [Si] content

3.2.2 Composition of inclusions

The composition of inclusions were SiO_2-MnO-Cr_2O_3 in this study, the relation between composition of inclusions and oxygen content is shown in Fig.11. With increasing oxygen content, (MnO) and (Cr_2O_3) in inclusions increased, but (SiO_2) decreased.

Other oxides -for example Al_2O_3,CaO,MgO- in inclusions were not observed.

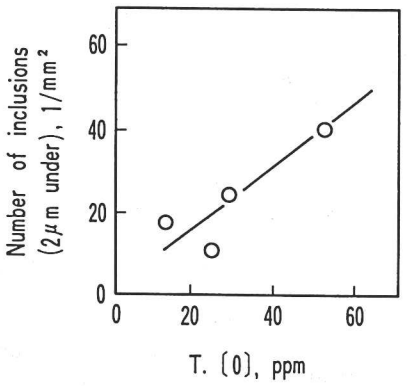

Fig.10 Relation between number of inclusions(2μm under) and T.[O] content

3.2.3 Thermochemical consideration

Composition of (Cr_2O_3) in inclusions decreased with decreasing the ratio of $aCr_2O_3/aSiO_2$ calculated by metal composition at the liquidus temperature in Fig.12. The data of thermochemical

equilibrium of [Si]-[O] was used by equation (1),and [Cr]-[O] equilibrium was used by equation (3)[5] respectively.

$$Cr_2O_3 = 2\underline{Cr} + 3\underline{O}$$
$$\log K = \log(a_{Cr}^2 a_O^3 / a_{Cr_2O_3}) = -44040/T + 19.42 \quad \text{.....(3)}$$

To lower the ratio of $a_{Cr_2O_3}/a_{SiO_2}$ was effective to decrease the composition of (Cr_2O_3) in inclusions.

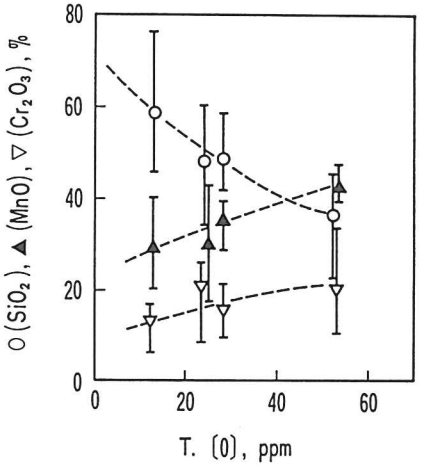

Fig.11 Relation between composition of inclusions and T.[O] content

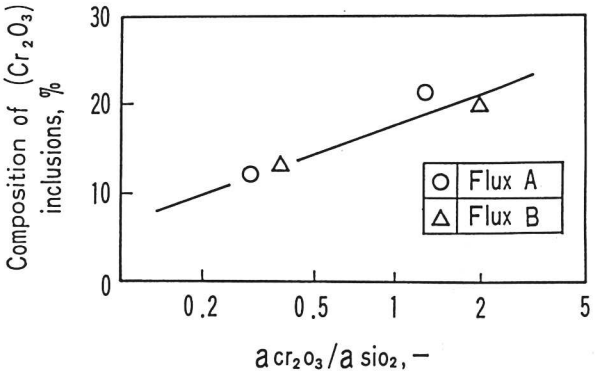

Fig.12 Relation between (Cr_2O_3) in inclusions and $a_{Cr_2O_3}/a_{SiO_2}$

4. Conclusion

Fundamental study on deoxidation using CaO based flux and no aluminum addition for stainless steel was made. The results of this study were as follows.

1) To lower the refining temperature and to lower the activity of SiO_2 were effective to lower the oxygen content.
2) The deoxidation rate was not influented by temperature , and the rate increased with increasing the intensity of stirring energy .
3) The activity ratio of $a_{Cr_2O_3}/a_{SiO_2}$ should be lowered to decrease the composition of (Cr_2O_3) in inclusions.

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