ACTIVITY MEASUREMENT OF THE CONSTITUENTS IN SECONDARY STEELMAKING SLAG

Mitsutaka HINO*, Shin-ichiro KINOSHITA**,
Yasuhiro EHARA***, Hiroyasu ITOH****
and Shiro BAN-YA*****

* Faculty of Engineering, Tohoku University, Aoba-ku, Sendai, Miyagi 980-77 Japan

** Formerly Graduate Student, Tohoku University, now Chita Works, Aichi Steel Works Ltd., Tohkai, Aichi 476 Japan

*** Formerly Graduate Student, Tohoku University, now Kinuura Works, Nippon Metal Industry Co., Ltd., Hekinan, Aichi 447 Japan

**** Formerly Research Student, Tohoku University, now Kuzuu Works, Yoshizawa Lime Industry, Kuzuu, Aso, Tochigi 327-05 Japan

***** Professor Emeritus, Tohoku University, now Akita National College of Technology, Iizima, Akita, Akita 011 Japan

SUMMARY

The chemical equilibrium among $CaO-Al_2O_3$, $CaO-Al_2O_3-CaF_2$ or $CaO-Al_2O_3-MgO$ slag, molten copper, graphite crucible and CO was observed at steelmaking temperature. The activities of CaO, Al_2O_3 and MgO in these slags were determined based on the free energy changes of reactions among the four phases and the activities of Ca, Al and Mg in liquid copper.

The sulphur distribution between these slags and liquid steel is discussed based on the result obtained and sulphide capacities of these slags reported by the authors.

1. INTRODUCTION

CaO-based fluxes are direct charged to liquid steel with deoxidizer to control oxygen and sulphur contents, and the composition and shape of nonmetallic inclusion in the final steel products. As $CaO-CaF_2$, $CaO-Al_2O_3$ and $CaO-Al_2O_3-CaF_2$ systems have high basicity and low melting point, these are the major slags for desulphurization in the ladle refining. $CaO-Al_2O_3-MgO$ system is also basic to clarify the effect of contamination by erosion of refractories on physico-chemical properties of CaO-based fluxes. Therefore, the most important data for the determination of oxygen and sulphur contents in metal is the equilibrium relation between the deoxidizer and oxygen in metal with the activity of deoxidation products in $CaO-Al_2O_3$ based slags such as $CaO-Al_2O_3-CaF_2$ and $CaO-Al_2O_3-MgO$ slags in the secondary refining process.

The activities of constituents in $CaO-Al_2O_3$, $CaO-Al_2O_3-CaF_2$ and $CaO-Al_2O_3-MgO$ slags were studied at 1823 to 1923K to estimate the sulphur distribution ratios between these slags and liquid iron in the secondary steelmaking process.

From the obtained results, it was confirmed that the evaluated maximum values of sulphur distribution ratio between these slags and liquid iron were higher than 1000 at 1873K on the condition of CaO-saturation if the dissolved aluminum content in liquid iron was assumed to be 0.01mass%, based on the combination of the observed results for the sulphide capacities and activities of Al_2O_3 in these slags.

2. EXPERIMENTAL

Figure 1 shows the experimental apparatus for the activity measurement of the constituents in slag. $CaO-Al_2O_3$ based slag and Cu-Al alloy melts in a graphite crucible were reacted with atmospheric pressure of CO for 30h. The crucible holding samples were quenched in water with impinging Ar after attainment to equilibrium.

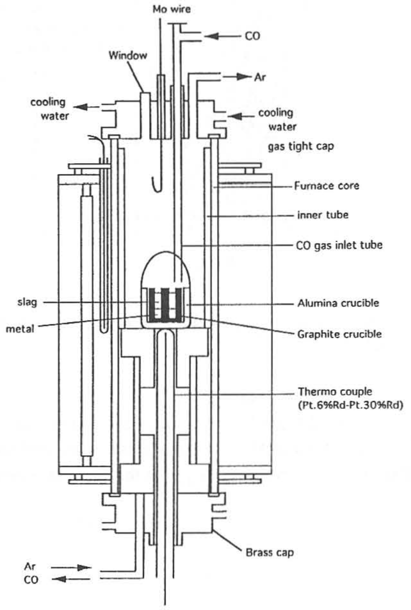

Fig. 1. Experimental apparatus for activity measurement of the constituents in slag.

3. RESULTS AND DISCUSSION

3.1. Activities of The Constituents in Slag

The activity of the each constituent in the slag, for example can be estimated from the free energy changes of the reactions (1), (3) and (5) and the activities of dissolved elements in liquid Cu, of which data were quoted from literatures[1)-4)].

$$Al_2O_3(s) + 3C(gr.) = 2Al(\textit{in liq. Cu}) + 3CO(g) \quad (1)$$

$$\Delta G_1^{\circ} = 1\,323\,700 + 573.65T \ (J) \quad (2)$$

$$CaO(s) + C(g) = Ca(\textit{in liq. Cu}) + CO(g) \quad (3)$$

$$\Delta G_3^{\circ} = 517\,380 - 191.67T \ (J) \quad (4)$$

$$MgO(s) + C(g) = Mg(\textit{in liq. Cu}) + CO(g) \quad (5)$$

$$\Delta G_5^{\circ} = 517\,380 - 191.67T \ (J) \quad (6)$$

3.1.1. $CaO-Al_2O_3$ Slag

The activity of $Al_2O_3(s)$ in $CaO-Al_2O_3$ slag was determined at 1823, 1873 and 1923K by the above-mentioned method in the present work, and that of CaO(*s*) was estimated by the application of quadratic formalism. The activities of $Al_2O_3(s)$ and CaO(*s*) in $CaO-Al_2O_3$ binary system obtained in the present work is shown in **Fig. 2**, where the other reported results are compared with ours at 1873K. These do not agree with each other. Direct measurement of $a_{Al_2O_3}$ is only the present work.

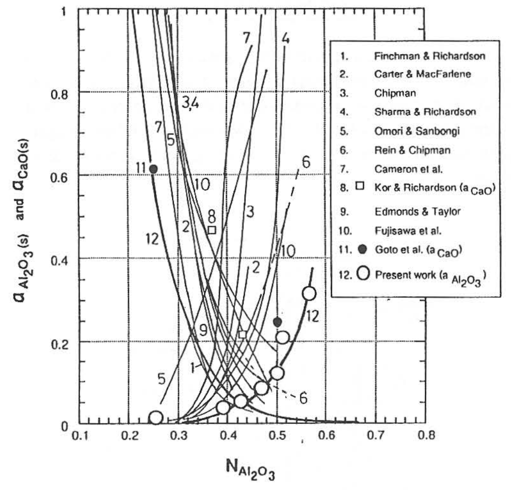

Fig. 2. Activities of $Al_2O_3(s)$ and $CaO(s)$ in $CaO-Al_2O_3$ slag at 1873K.

3.1.2. $CaO-Al_2O_3-CaF_2$ Slag

$a_{Al_2O_3}$ in $CaO-Al_2O_3-CaF_2$ slag was determined at 1873K by the above-mentioned method in the present work, and the result is shown **Fig. 3**. No literature on $a_{Al_2O_3}$ in this slag has been reported.

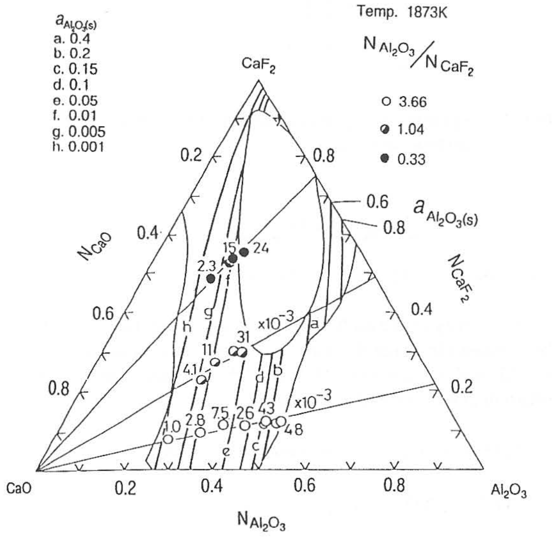

Fig. 3. Iso-activity curves of $Al_2O_3(s)$ in $CaO-Al_2O_3-CaF_2$ slag at 1873K. Open circle: experimental composition. Numerical values show $a_{Al_2O_3}$.

Activities of $CaO(s)$ and $CaF_2(l)$ were estimated by the application of quadratic formalism to observed activities of $CaO(s)$ in $CaO-CaF_2$ slag by Edmunds and Taylor[5] and in $CaO-Al_2O_3-CaF_2$ slag in the present work. The estimated values are shown in **Fig. 4**, and these values agree fairly with those reported by Edmunds and Taylor, and by Zaitsez et al..[6]

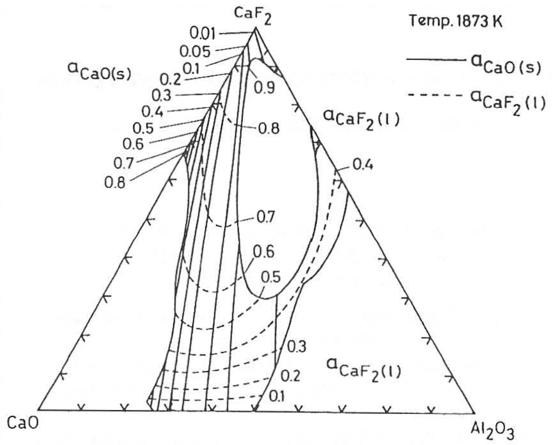

Fig. 4. Iso-activity curves of $CaO(s)$ and $CaF_2(l)$ in $CaO-Al_2O_3-CaF_2$ slag at 1873K.

3.1.3. $CaO-Al_2O_3-MgO$ Slag

activities of the constituents in $CaO-Al_2O_3-MgO$ slag were determined by the above-mentioned method in the present work, and the result at 1873K is shown **Fig 5**. $a_{Al_2O_3}$ in this system was reported by Kalyanram and Bell[7] at 1773K.

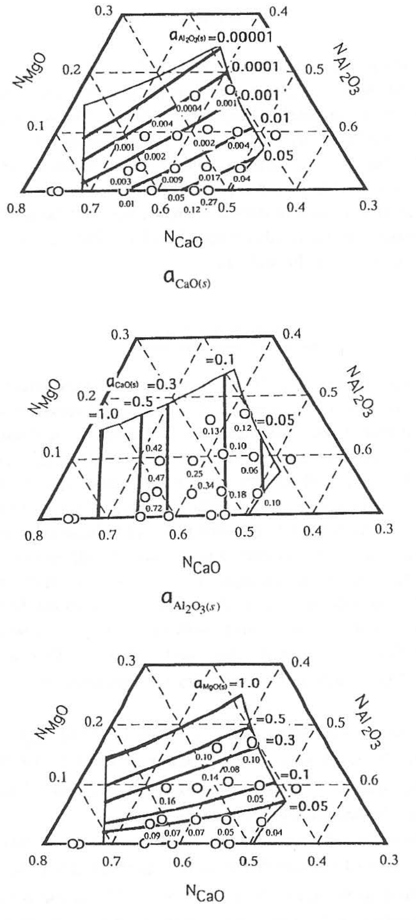

Fig. 5. Iso-activity lines of the constituents in $CaO-Al_2O_3-MgO$ slag at 1873K. Open circle: experimental composition. Numerical values show activity of each constituent.

3.2. Deoxidation by Aluminum with CaO-based Slag

In many cases, an aluminium is used with the addition of burnt lime or CaO-based fluxes in the ladle refining process to control the oxygen and sulphur contents and the composition of nonmetallic inclusion in the final steel products. Therefore, the most important data for the determination of oxygen content in metal is the equilibrium relation between aluminium and oxygen in metal with the activity of $Al_2O_3(s)$ in the CaO-based slags.

The equilibrium relation of Al-deoxidation of liquid steel can be written as follows, [8]

$$(Al_2O_3)(s) = 2[Al] + 3[O] \tag{7}$$

$$\log K_3 = -64\,000/T + 20.57. \tag{8}$$

The deoxidation of liquid iron with aluminium is expressed by the following relation at 1873K.

$$a^2_{Al(\%)} \cdot a^3_{O(\%)} = 2.51\text{x}10^{-14} \cdot a_{Al_2O_3} \tag{9}$$

The very low value of $a_{Al_2O_3}$ was found to be $a_{Al_2O_3}=1\text{x}10^{-3}$ at the near saturation of CaO in the $CaO\text{-}Al_2O_3$ slag and $CaO\text{-}Al_2O_3\text{-}CaF_2$ slag at 1873K, as shown in Figs. 2 and 3.

It is worthy of special mention in the measurement of activity of $Al_2O_3(s)$ in CaO-based slags that the $a_{Al_2O_3}$ in $CaO\text{-}Al_2O_3\text{-}MgO$ slag shows the minimum value at the saturation with both CaO and MgO, as shown in Fig.5. The minimum value of $a_{Al_2O_3}$ was found to be $a_{Al_2O_3}=1\text{x}10^{-6}$ at 1873K. It was found, therefore, that the extremely low oxygen steel can be refined with the Al-deoxidation in combination of $CaO_{sat.}\text{-}MgO_{sat.}\text{-}Al_2O_3$ slag or the use of dolomite refractories.

Figure 6 shows the practical example of Al-deoxidation of liquid iron alloy in a dolomite crucible. In this measurement, the iron alloy was melted in dolomite crucible having various ratio of MgO under argon atmosphere at 1873K, and 0.5% aluminum was added to liquid metal. As seen in Fig. 7, the large amount of Mg was dissolved into metal by the reduction of MgO in the crucible, and the oxygen concentration in metal was extremely low. This facts can be explained by the data of Fig. 5.

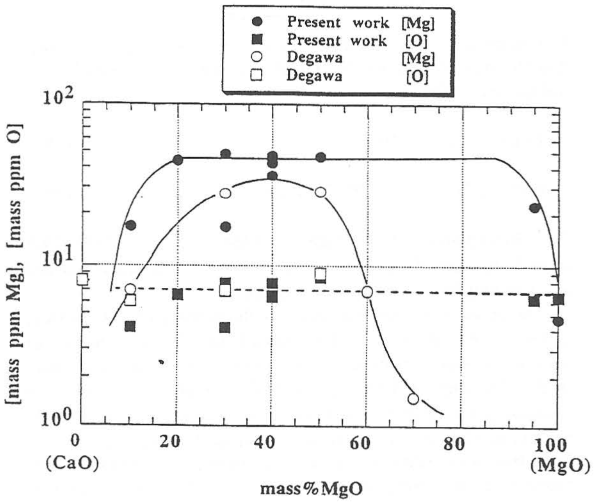

Fig. 6. Oxygen, Magnesium and Aluminum contents in liquid iron in a dolomite crucible after Al-deoxidation at 1873K.

3.3. Sulphur Distribution between Secondary Refining Slag and Liquid Steel

The equilibrium reaction between gas and slag is represented by Eq. (10).

$$(1/2)S_2(g) + (O^{2-}) = (S^{2-}) + (1/2)O_2(g) \tag{10}$$

Richardson et al.[9] assumed the Henrian behavior of sulphur in slag, and defined the following sulphide capacity to express a physicochemical property of slag.

$$C_S = (\text{mass\%S})(P_{O_2}/P_{S_2})^{1/2} \tag{11}$$

Where, (mass%S) denotes the mass% of sulphur in slag.

The following relations are known.[8]

$$[O] = (1/2)O_2(g) \tag{12}$$

$$\log\{P_{O_2}{}^{1/2}/a_{O(\%)}\} = -6\,070/T - 2.10 \tag{13}$$

$$[S] = (1/2)S_2(g) \tag{14}$$

$$\log\{P_{S_2}{}^{1/2}/a_{S(\%)}\} = -6\,535/T - 0.964 \tag{15}$$

By the combination of Eqs. (11), (13) and (15), the distribution of sulphur between slag and metal is derived as follows,

$$\log\{(\%S)/a_{S(\%)}\} = \log C_S - \log a_{O(\%)} - 465/T + 1.174 \tag{16}$$

Therefore, the low sulphur steel can be produced when high sulfide capacity slag is used with strong deoxidation at higher temperature. An aluminum is used together with CaO-based fluxes for this purpose as mentioned before. Therefore, the sulphur distribution ratio, $L_S=(\%S)/[\%S]$, between secondary steelmaking slag and liquid iron could be estimated by Eq.(17) based on sulphide capacity, C_S, and $a_{Al_2O_3}$ in the slags, by combination of Eqs. (8) and (16).

$$\log L_S = \log C_S - (1/3)\log a_{Al_2O_3} + (2/3)\log[\%Al]$$
$$+ 21\,168/T - 5.703 \tag{17}$$

The sulphur distribution ratio between secondary refining slags and liquid steel make clear from the reported sulphide capacities by the present authors and $a_{Al_2O_3}$ in the CaO-base slags in the present works.

3.2.1. $CaO\text{-}Al_2O_3$ Slag

It is understood from Figs. 2, 3 and Eq. (16) that the very high values of L_S (=(%S)/[%S]) = 100-1000 can be expected at the oxygen activity of $a_{O(ppm)} = 5$ in the $CaO_{sat.}\text{-}CaF_2$ and the $CaO_{sat.}\text{-}Al_2O_3$ systems at 1873K. This is the reason why ultra low sulphur steel can be refined in the ladle refining processes by the combination of Al-deoxidation with the addition of CaO-based fluxes.

The addition of the CaO-based fluxes and aluminum is also effective to remove the sulphur in Fe-Ni alloy.

3.2.2. $CaO\text{-}Al_2O_3\text{-}CaF_2$ Slag

From these observed results of $a_{Al_2O_3}$ shown in Fig. 3, and C_S[10] in $CaO\text{-}Al_2O_3\text{-}CaF_2$ slag, the L_S was estimated at 1873K by Eq. (17) on the assumption that dissolved aluminum content in liquid iron was 0.01mass%, and it is shown in **Fig. 7**.

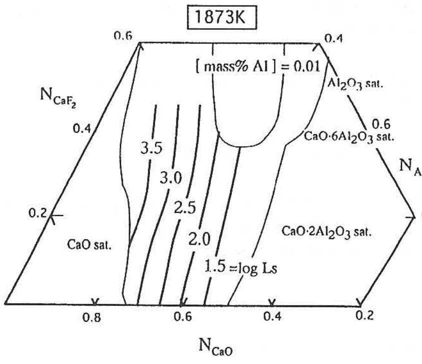

Fig. 7. Iso-sulphur distribution ratio between CaO-Al_2O_3-CaF_2 slag and liquid iron at 1873K. Numerical values show logL_S.

3.2.3. CaO-Al_2O_3-MgO Slag

It is worthy of special mention in the measurement of activity of Al_2O_3 in CaO-based slags that the $a_{Al_2O_3}$ in CaO-Al_2O_3-MgO slag shows the minimum value at the saturation with both CaO and MgO, as shown in Fig. 5. From these observed results of $a_{Al_2O_3}$ and C_S[11] in CaO-Al_2O_3-MgO slag, the L_S may attain to more than 10000 at the saturation with dolomite on the assumption that dissolved aluminum content in liquid iron is 0.01mass%, as shown in **Fig. 8**.

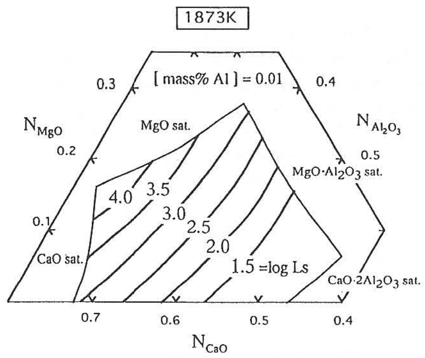

Fig. 8. Iso-sulphur distribution ratio between CaO-Al_2O_3-MgO slag and liquid iron at 1873K. Numerical values show logL_S.

Generally speaking, it is theoretically possible to obtain higher sulphur distribution ratio when stronger deoxidizer than aluminum is applied to liquid steel with CaO-based fluxes in saturation of CaO.

However, about only 200 of sulphur distribution ratio was obtained as shown in **Fig. 9**,[12] when liquid iron was equilibrated with CaO-Al_2O_3-MgO slag under argon atmosphere in the experiment at steelmaking temperatures, because the slag contained about 1 mass% Fe_tO after all our efforts.

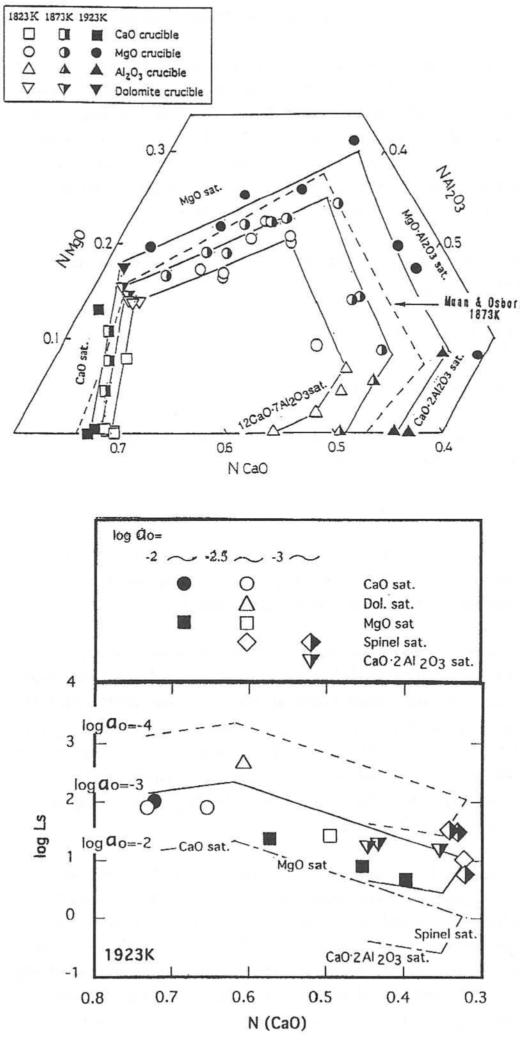

Fig. 9. Observed sulphur distribution ratio between CaO-Al_2O_3-MgO slag and liquid iron at 1873K.

It became clear from the discussion of the experimental results that the oxygen content in liquid iron was determined by the following equilibrium.[8]

$$Fe_tO(l) = tFe(l) + [O] \qquad (18)$$

$$\log\{a_{O(\%)}/a_{Fe_tO}\} = -6\,150/T + 2.60 \qquad (19)$$

This shows that it is very tough to realize more than 10000 of LS even if any kind of slag is used, unless the Fe_tO in slag is reduced to extremely low concentration in plant.

Therefore, it is important to know the activity of Fe_tO in slag, in which the content of Fe_tO is almost 1 mass%, for discussion of sulphur distribution between secondary steelmaking slag and liquid steel. The observed activity of Fe_tO in CaO-Al_2O_3-SiO_2 slag containing less than 5 mass% Fe_tO by the present authors,[13] do not agree with the recent reported values by Lee and Suito.[14] From this discrepancy, the activity measurement of Fe_tO in CaO-based slag containing small amount of Fe_tO became important study.

4. CONCLUSIONS

The activities of the constituents in slags were determinated steelmaking temperature from the chemical equilibrium experiment among $CaO-Al_2O_3$, $CaO-Al_2O_3-CaF_2$ or $CaO-Al_2O_3-MgO$ slag, molten copper, graphite crucible and CO. And the sulphur distribution between these slags and liquid steel is discussed based on the result obtained and sulphide capacities of these slags reported by the authors.

The main findings in this study are briefly summarized as follows:

1) The deoxidizing power of aluminum is exceedingly enhanced by addition of CaO-based fluxes saturated with CaO.

2) Sulphur content in steel is greatly lowered by addition of CaO-based fluxes in strongly reducing condition.

3) The maximum value of more than 1000 was gotten at CaO-saturated composition for all slags in the present work on the assumption that dissolved aluminum content in liquid iron was 0.01mass%.

4) When MgO and CaF_2 were dissolved into the $CaO-Al_2O_3$ slag, the desulphurization ability of the slag became stronger than that of $CaO-Al_2O_3$ slag. Especially, more than 10000 of L_S was evaluated on the condition of dolomite saturation on the assumption that dissolved aluminum content in liquid iron was 0.01mass%.

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