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SULPHIDE CAPACITIES OF $CaO-Al_2O_3-MgO$ AND $CaO-Al_2O_3-SiO_2$ SLAGS

Mitsutaka HINO*, Susumu KITAGAWA** and Shiro BAN-YA*

* Faculty of Engineering, Tohoku University, Japan

** Formerly Graduate School, Tohoku University.
Now at New Materials Research Laboratories, Nisshin Steel Co., Ltd., Japan

Synopsis: The sulphide capacities of $CaO-Al_2O_3$, $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-SiO_2$ slags were studied at 1823 to 1923K to estimate the sulphur distribution ratio between secondary steelmaking slag and liquid steel.

From the obtained results, it was confirmed that substitution of MgO or SiO_2 for CaO at a given $N_{Al_2O_3}$ decreased the sulphide capacities in both systems of $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-SiO_2$. The evaluated maximum values of sulphur distribution ratio for both slags were higher than 1000 at 1873K on the condition of CaO-saturation if the dissolved aluminium content in steel was assumed to be 0.01mass%.

KEY WORDS: sulphide capacity; sulphur distribution ratio; secondary steelmaking; slag; physical chemistry.

1. Introduction

Various kinds of fluxes for dephosphorization and desulphurization of steel have been developed to produce high purified steel. Practically used flux in secondary steelmaking process is CaO-based flux, and steel is deoxidized with aluminum. As a result, $CaO-Al_2O_3$ slag is formed in the process. $CaO-Al_2O_3$ flux has not been used in the past excepting for the utilization in electro slag remelting process, but a special attention is recently focused on the flux in ladle furnace treatment in secondary steelmaking process. Only a few studies on the physico-chemical properties of the slag have been reported.

The authors have proposed the application of $CaO-Al_2O_3$ flux to the refining in iron- and steelmaking process, and at the first dephosphorization and desulphurization of hot metal and steel with $CaO-Al_2O_3-Fe_xO_y$ flux was studied in our previous works[1,2] to utilize the flux on the oxidizing condition. In the present work, the sulphide capacities of $CaO-Al_2O_3$, $CaO-Al_2O_3-MgO$, into which MgO would be dissolved from the refractories in the secondary steelmaking process, and $CaO-Al_2O_3-SiO_2$ slags, to which SiO_2 would come from the steelmaking slag, were studied to discuss the desulphurization ability of the slags on the reducing condition, in succession to the previous studies.

From the results obtained, the equilibrium sulphur distribution between these slags and liquid steel was discussed on the assumption that the steel would be deoxidized with aluminum.

2. Experimentals

Figure 1 shows the experimental apparatus, which consisted of the purification train of Ar, $Ar-SO_2$ and $CO-CO_2$ gas mixtures, an alumina tube (0.07x0.06x1.00m) as a reaction chamber, and the vertical type Keramax electric resistance furnace (10 kVA) for a heating device, and the quenching zone for samples. Two sets of Pt·6%Rh-Pt·30%Rh thermocouples were used. One of them was inserted between heating elements and the reaction tube and was connected to a temperature controller, and the other was set just above the crucibles to monitor the experimental temperature. The premelted synthetic $CaO-Al_2O_3$, $CaO-Al_2O_3-MgO$ or $CaO-Al_2O_3-SiO_2$ slags of $1x10^{-3}$kg set in three Pt (0.01x0.01m) or two CaO (0.015x0.013x0.015m) crucibles loaded in a MgO protective crucible (0.035x0.030x0.01m) were lifted with a Mo wire up to the hot zone of the reaction tube, and were melted under argon atmosphere of the flow rate of $3.33x10^{-6}m^3/s$.

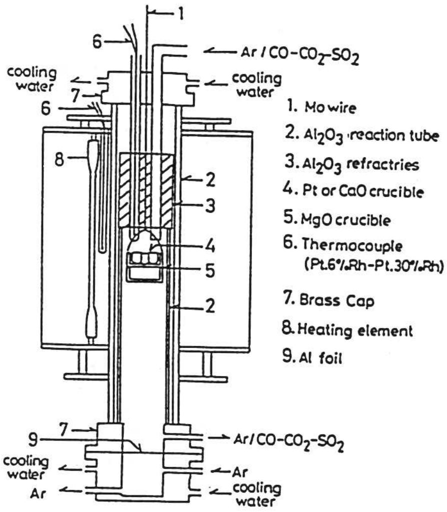

Fig. 1. Schematic diagram of experimental apparatus.

The atmosphere was changed from Ar to the given mixed ratio of $CO-CO_2-SO_2-Ar$ gas mixtures of the flow rate of $2.5x10^{-6}m^3/s$, and the samples were held for 4 - 6h at 1823, 1873 or 1923K until the attainment to equilibrium. At the end of run, the MgO crucible containing the samples in Pt or CaO crucibles was lowered with the Mo wire to a water-cooled chamber of Ar atmosphere to quench the samples. The slags were separated from quenched crucibles, and the contents of CaO, Al_2O_3, MgO, SiO_2 and S in the slags were determined by chemical analysis.

The Pt crucibles were hand-made from Pt foil , of which thickness was $5x10^{-5}$m, by forge welding, and the CaO and MgO crucibles were bought from a market. The gas mixtures were supplied by two kinds of cylinder of CO_2-50.1vol%CO and Ar-1.987vol%SO_2.

3. Experimental Results

The principal equilibrium reaction between gas and slag is represented by Eq. (1) in this experiment.

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

Richardson[3] assumed the Henrian behaviour of sulphur in slag because of the low solubility, and defined the following sulphide capacity to discuss the physico-chemical property of slag.

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

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

3.1. Sulphide Capacity of $CaO-Al_2O_3$ Slag

Figure 2 shows the sulphide capacities of homogeneous and CaO-saturated $CaO-Al_2O_3$ melts obtained at 1823, 1873, 1923K. The experimental errors of C_S caused by chemical analysis of sulphur are shown in Fig. 2. The numerical value of C_S in this slag increased with increasing temperature and concentration of CaO, and the lower the temperature was, the more the value of C_S increased with increasing N_{CaO}.

The C_S in $CaO-Al_2O_3$ slag has been studied at 1923K by Fincham and Richardson[3], at 1923 and 1873K by Ozturk and Turkdogan[4], at 1873K by Schürmann *et al.*[5] on the condition of CaO or $CaO\cdot 2Al_2O_3$ saturation, and at 1823K by Carter and Macfarlane[6], Sharma and

Richardson[7], Cameron *et al.*[8], and Kor and Richardson[9]. They are also shown in Fig. 2, and agree well with the C_S obtained in the present work.

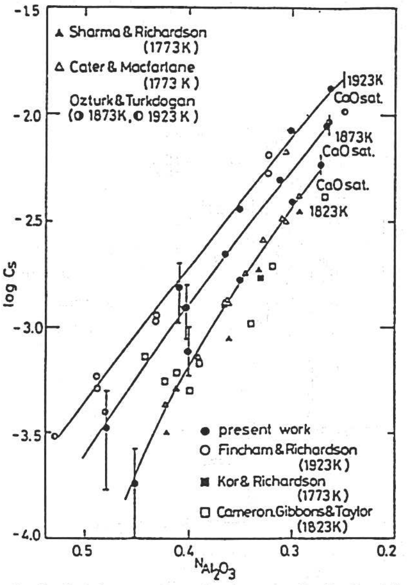

Fig. 2. Sulphide capacities of $CaO-Al_2O_3$ slag.

3.2. Sulphide Capacity of $CaO-Al_2O_3-MgO$ Slag

The sulphide capacities of homogeneous and CaO-saturated $CaO-Al_2O_3-MgO$ melts were determined at 1823, 1873 and 1923K on the condition of the given ratios of N_{CaO}/N_{MgO}, molar ratio of CaO to MgO, as 10/0, 9/1 and 8/2. The observed iso-sulphide capacity curves at 1873K are shown in Fig. 3. The experimental composition is marked in Fig. 3 by ●. The numerical values in Fig. 3 show $-\log C_S$. It was found in Fig. 3 that the iso-C_S curves were almost parallel to the liquidus of CaO in this slag system, and the numerical values of C_S increased with CaO content. Figure 3 shows that MgO has not equivalent effect to CaO on the sulphide capacity, and the same behaviour has been observed in oxygen[10,11], phosphorus[12,13] and sulphur distribution[14] between slag and metal in our previous works.

No literature on C_S of this slag has been reported.

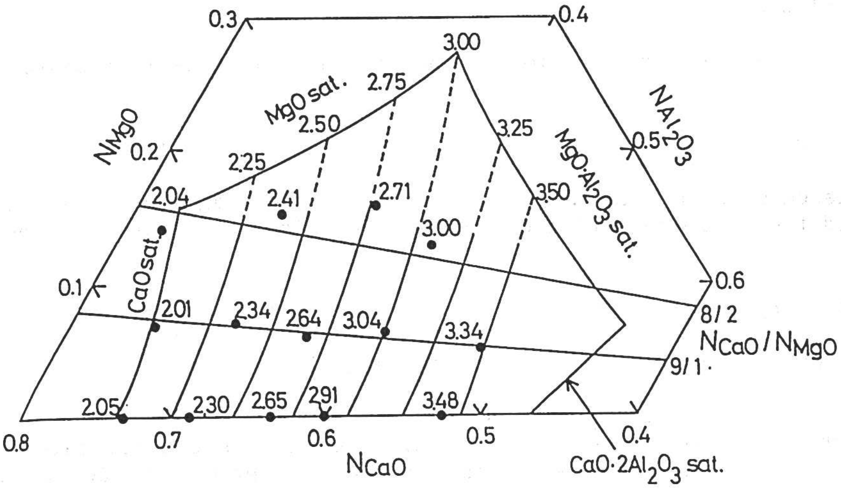

Fig. 3. Iso-sulphide capacity curves for $CaO-Al_2O_3-MgO$ slags at 1873K. ● : experimental composition. Numerical values show $-\log C_S$.

3.3. Sulphide Capacity of $CaO-Al_2O_3-SiO_2$ Slag

The sulphide capacity of homogeneous, CaO- and $2CaO \cdot SiO_2$-saturated $CaO-Al_2O_3-SiO_2$

melts were determined at 1873K on the condition of N_{CaO}/N_{SiO_2} of 10/0, 9/1 and 8/2. The melts corresponding to N_{CaO}/N_{SiO_2} of 10/0 and 9/1 were saturated with CaO, and the melt to N_{CaO}/N_{SiO_2} of 8/2 was saturated with $2CaO\cdot SiO_2$ in higher basic composition. The observed iso-sulphide capacity curves at 1873K are shown in **Fig. 4**. The experimental composition is marked also in this figure by ●. The numerical values in Fig. 4 show $-\log C_S$. It was found in this figure that the iso-C_S curves were almost parallel to the liquidus of CaO, and the numerical values of C_S increased with CaO content in this system, too.

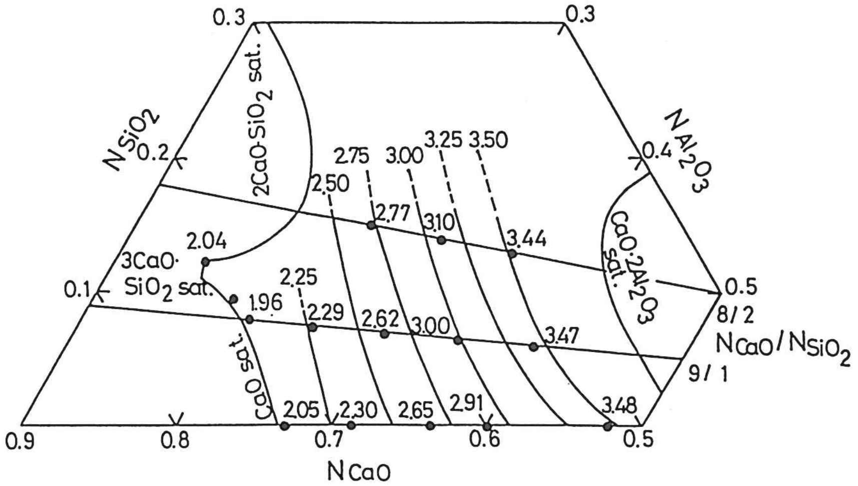

Fig. 4. Iso-sulphide capacity curves for $CaO-Al_2O_3-SiO_2$ slags at 1873K. ● : experimental composition. Numerical values show $-\log C_S$.

The C_S of this slag in high SiO_2 concentration, for which the chemical property of ironmaking slag has been discussed, has been studied by Fincham and Richardson[3] Carter and Macfarlane[6], Cameron *et al.*[8], Kalyanram *et al.*[15], and Abraham and Richardson[16]. The literature on C_S of this slag in low SiO_2 concentration, which might have been considered in the secondary steelmaking process, has never been reported.

4. Discussion

The $CaO-Al_2O_3$ flux has been recently utilized in the secondary steelmaking process as a ladle furnace treatment. MgO is dissolved from the refractories and BOF steelmaking slag is brought into the $CaO-Al_2O_3$ melt. Therefore, it is very important in practice to discuss the refining ability of $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-SiO_2$ slags.

From the results obtained, the sulphur distribution between slag and metal is discussed in case that the $CaO-Al_2O_3$ flux is practically used.

The reactions of dissolution of O_2 and S_2 into liquid iron are expressed by Eqs. (3)-(6).

$$1/2O_2(g) = \underline{O} \quad \cdots\cdots (3)$$

$$\log K_3 = \log\{a_O/P_{O_2}^{1/2}\} = 6\ 070/T + 0.210\ [17] \quad \cdots\cdots (4)$$

$$1/2S_2(g) = \underline{S} \quad \cdots\cdots (5)$$

$$\log K_5 = \log\{a_S/P_{S_2}^{1/2}\} = 6\ 535/T - 0.964\ [17] \quad \cdots\cdots (6)$$

The following equation is obtained from Eqs. (2), (4) and (6).

$$\log\{(\text{mass\%})/a_S\} = \log C_S - \log a_O - 465/T + 1.174 \quad \cdots\cdots (7)$$

a_S is assumable as mass% of sulphur in liquid iron, [mass%S], because the concentration of sulphur discussed in the present work is very low. Therefore, it is possible to calculate the sulphur distribution ratio between slag and liquid iron, L_S = (mass%S)/[mass%S], with Eq. (7) based on the observed C_S and temperature, if one can estimate the activity of oxygen in liquid iron equilibrated with the slag.

The activity of oxygen in liquid iron would be determined by the following reaction, when the liquid iron is equilibrated with $CaO-Al_2O_3-MgO$ or $CaO-Al_2O_3-SiO_2$ slag, in which MgO or SiO_2 concentration is low, in secondary steelmaking process.

$$2\underline{Al} + 3\underline{O} = (Al_2O_3) \quad \cdots\cdots (8)$$

$$\log K_8 = \log[a_{Al_2O_3}/\{a_{Al}^2 \cdot a_O^3\}] = 64\ 900/T - 20.63\ [17] \quad \cdots\cdots (9)$$

Where, a_{Al} was assumable as [mass%Al] because of the very low concentration of aluminum and oxygen in liquid iron deoxidized with aluminum in secondary steelmaking process.

The $a_{Al_2O_3}$ for $CaO-Al_2O_3-MgO$ slag was determined at 1773K by Kalyanram and Bell[18], and that for $CaO-Al_2O_3-SiO_2$ was studied at 1823K by Cameron *et al.*[8], Kay and Taylor[19], at 1823 and 1873K by Rein and Chipman[20], and at 1903K by Sanbongi and Omori[21]. The $a_{Al_2O_3}$ derived from a_{SiO_2} by Kay and Taylor[19] is quoted in the present study, because the authors believe that their result is the most reliable among many investigations on the a_{SiO_2} in $CaO-SiO_2$ slag. These two values of $a_{Al_2O_3}$ interpolated to $CaO-Al_2O_3$ binary slag agreed well with the reported by Chipman[22].

It was assumed in this paper that the values of $a_{Al_2O_3}$ for $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-SiO_2$ slags were independent of temperature, because there were a few studies on the temperature dependency of the $a_{Al_2O_3}$ for both slags as the above-mentioned. On this assumption, the values of $a_{Al_2O_3}$ were read at given $N_{CaO}/N_{Al_2O_3}$ ratios from the iso-activity curves of Al_2O_3 in $CaO-Al_2O_3-MgO$ and $CaO-Al_2O_3-SiO_2$ slags, and the activity of oxygen was evaluated at 1873K by Eq. (9) with a fixed concentration of aluminum in the liquid iron. As a result, the sulphur distribution ratio between slag and metal, L_S, could be estimated by Eq. (10), based on the observed C_S shown in Figs. 3 and 4.

$$\log L_S = \log C_S - (1/3)\log a_{Al_2O_3} + (2/3)\log[\text{mass\%Al}] + 21\ 168/T - 5.703 \quad \cdots\cdots (10)$$

The value of sol[Al] was assumed to be 0.01mass% in the present work. The result of above-mentioned estimation is shown in **Fig. 5.** The estimated value of L_S between slag and liquid iron increased gradually in $CaO-Al_2O_3-MgO$ slag with increasing N_{MgO}, and decreased considerably in $CaO-Al_2O_3-SiO_2$ with increasing N_{SiO_2}. The value of L_S increased with increasing $N_{CaO}/N_{Al_2O_3}$ ratio in both slags within the experimental composition range of N_{MgO} and N_{SiO_2} of 0.12, and the maximum value of about 1000 was gotten at CaO-saturated composition, where the value of L_S did not decrease even if SiO_2 content increased in $CaO-Al_2O_3-SiO_2$ slag. However, the value decreased with increasing N_{SiO} at $2CaO\cdot SiO_2$ saturated-composition.

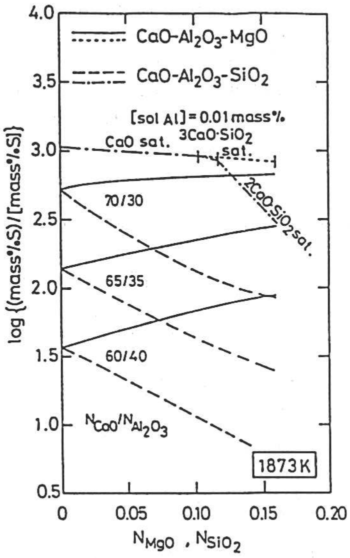

Fig. 5. Comparison of the change of sulphur distribution ratio between $CaO-Al_2O_3$ slag and liquid iron by addition of MgO or SiO_2 to the slag at 1873K.

Based on the above-mentioned discussion, it is carefree that MgO is dissolved into

CaO-Al_2O_3 slag from refractories when liquid steel is desulphurized in secondary steelmaking process. But every effort must be made to prevent SiO_2 from mixing in the slag. It is important eventually that the $N_{CaO}/N_{Al_2O_3}$ ratio is made to increase as considerably as possible and the slag composition is made to approach CaO-saturation for getting strong desulphurization effect.

5. Conclusions

The chemical equilibrium between CO-CO_2-SO_2-Ar gas mixtures and CaO-Al_2O_3, CaO-Al_2O_3-MgO, CaO-Al_2O_3-SiO_2slags has been studied to determine the sulphide capacities of these slags, and the followings have been confirmed from the results obtained.

(1) The sulphide capacities of these slags increased with increasing temperature and the concentration of CaO.

(2) The sulphide capacities decreased when MgO or SiO_2 was substituted for CaO in CaO-Al_2O_3 slag on the condition of a constant $N_{Al_2O_3}$, and the decreasing rate in CaO-Al_2O_3-SiO_2 slag was larger than that in CaO-Al_2O_3-MgO slag.

(3) When MgO was dissolved into the CaO-Al_2O_3 slag at a constant $N_{CaO}/N_{Al_2O_3}$ ratio, the desulphurization ability of the slag became a little stronger than that of CaO-Al_2O_3 slag. On the other hand, the ability decreased markedly when SiO_2 was dissolved into the CaO-Al_2O_3 slag. The CaO-saturated slag in both CaO-Al_2O_3-MgO and CaO-Al_2O_3-SiO_2 systems at a given N_{CaO}/N_{MgO} or N_{CaO}/N_{SiO_2} ratio showed the strongest desulphurization ability, where the increase of MgO and SiO_2 contents did not result in the decrease of the ability.

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