

New Developments in High Temperature Processing of Steels and Related Materials Leading the Sustainable Society, and Key Properties of High Temperature Melts

Note

# Effect of Iron Oxide on Sulfide Capacities of CaO–SiO<sub>2</sub>–FeO and CaO–Al<sub>2</sub>O<sub>3</sub>–FeO Ternary Systems

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Towards steelmaking processes which are compatible with the sustainable society, re-sulfurization reaction in hot metal pretreatments needs to be suppressed as much as possible. To evaluate the effects of iron oxide on the sulfur distribution ratio between FeO-containing slag and hot metal, sulfide capacities and FeO activities were measured in CaO–SiO<sub>2</sub>–FeO and CaO–Al<sub>2</sub>O<sub>3</sub>–FeO ternary liquid slags. Although the FeO activity and oxygen potential increased, the addition of FeO raised sulfide capacity drastically and resulted in an increase in the calculated value for distribution ratio of sulfur.

KEY WORDS: sulfide capacity; activity; iron oxide; sulfur distribution ratio; re-sulfurization.

## 1. Introduction

In steelmaking process, sulfur and phosphorus are often removed from hot metal before decarburization. The chemical reactions of desulfurization and dephosphorization are expressed as follows.

$$[S]_{hot metal} + (O^{2^{-}})_{slag} = (S^{2^{-}})_{slag} + [O]_{hot metal} \dots \dots \dots (1)$$

$$[P]_{hot metal} + (3/2)(O^{2-})_{slag} + (5/2)(FeO)_{slag} = (PO_4^{3-})_{slag} + (5/2) Fe(liquid) \qquad \dots (2)$$

, where  $[i]_{\text{hot metal}}$  and  $(j)_{\text{slag}}$  represent chemical species *i* in hot metal and *j* in slag, respectively. According to Eqs. (1)

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and (2), desulfurization and dephosphorization have opposite oxygen potential conditions. When a small amount of desulfurization slag is carried over to dephosphorization process, S in slag would return to hot metal since FeO in dephosphorization slag raises FeO activity and oxygen potential. When the production of CaO, which is one of the most commonly used desulfurization agents, emits carbon dioxide, it is important for the sustainable society to use CaO effectively and suppress the re-sulfurization reaction. For better understanding of re-sulfurization in hot metal pre-treatments, it is necessary to evaluate sulfur distribution ratio between FeO-containing slag and hot metal at temperatures below the melting point of pure Fe.

The sulfur distribution ratio between slag and hot metal,  $L_S$ , is expressed by

$$L_{S} \equiv \frac{\left(mass\% S^{2-}\right)_{slag}}{\left[mass\% S\right]_{hot\ metal}} \qquad (3)$$

, where  $(mass\%S^{2^-})_{slag}$  and  $[mass\%S]_{hot metal}$  represent mass% concentrations of S in slag and hot metal, respectively. Sulfide capacity,  $C_{S^{2^-}}$ , is a thermochemical property of slag to hold S as sulfide and is defined based on Reaction (4).<sup>1,2)</sup>

$$(1/2) S_2(gas) + (O^{2-})_{slag} = (S^{2-})_{slag} + (1/2) O_2(gas) \dots (4)$$

$$C_{S^{2-}} \equiv \left(mass\%S^{2-}\right)_{slag} \cdot \frac{P_{O_2}^{1/2}}{P_{S_2}^{1/2}} = K(4) \cdot \frac{\left(a_{O^{2-}}\right)_{slag}}{\left(f_{S^{2-}}\right)_{slag}} \dots (5)$$

In Eq. (5),  $P_i$  is the partial pressure of gaseous specie *i*, *K*(4) is the apparent equilibrium constant of Reaction (4),  $(a_{O^{2-}})_{slag}$  is the activity of  $O^{2-}$  and  $(f_{S^{2-}})_{slag}$  is the activity coefficient of  $S^{2-}$  in slag. The relationship between  $L_S$  and  $C_{S^{2-}}$  can be obtained as follows. The dissolution of gaseous diatomic S into hot metal is given as

$$(1/2) S_2(gas) = [S]_{hot metal}$$
.....(6)

$$\log K(6) = -1.22 + 7\ 054 / (T / K)^{3} \dots (8)$$

 $[f_S]_{hot metal}$  in Eq. (7) is the Henrian activity coefficient of S in hot metal. Combining Eqs. (3), (5) and (7), we have

$$L_{S} = C_{S^{2-}} \cdot P_{O_{2}}^{-1/2} \cdot \frac{[f_{S}]_{hot metal}}{K(6)} \dots \dots \dots \dots (9)$$

To evaluate  $L_S$ , the present study aimed at measuring  $C_{S^{2-}}$  of FeO-containing slag.

In a typical experimental method based on Reaction (4) to measure  $C_{S^{2-}}$ , the content of S is analyzed in slag equilibrated with gas phase where  $P_{O_2}$  and  $P_{S_2}$  are fixed. Figure 1 shows the reported conditions of  $P_{O_2}$  and temperature to determine  $C_{S^{2-}}$  of FeO-containing slags with the gasslag equilibrium method.<sup>1,4–12</sup> To avoid reducing FeO and



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Fig. 1. Experimental condition of oxygen pressure and temperature to determine sulfide capacity of FeO-containing slag.

forming metallic Fe in slag,  $P_{O_2}$  should be higher than the equilibrium value between Fe and FeO. Although the analyzed contents of Fe<sup>3+</sup> in slag were not available in some literatures, such conditions would result in increasing Fe<sup>3+</sup> and then decreasing slag basicity, and then there would be a possibility to underestimate  $C_{S^{2-}}$ . At temperature higher than the melting point of pure Fe, the values for  $C_{S^{2-}}$  can be also measured by equilibrating slag with liquid Fe.13-16) For the determinations of  $C_{S^{2-}}$  of FeO-containing slags at temperatures below the melting point of Fe, the present authors suggested Cu-Fe-S liquid alloy saturated with Fe-Cu-S solid solution as reference metal phases,<sup>17)</sup> and measured  $C_{S^{2-}}$  of the CaO–SiO<sub>2</sub>–FeO ternary slag at 1 573 K.<sup>18)</sup> In this study, the measurements were extended to the CaO-SiO<sub>2</sub>-FeO system at 1 673 K and the CaO-Al<sub>2</sub>O<sub>3</sub>-FeO system at 1 573 K. The equilibrium  $O_2$  partial pressures between slag and Cu-Fe-S liquid alloy were measured with an electrochemical technique involving the stabilized zirconia solid electrolyte. The chemical reaction underlying the present experiments can be expressed by

$$\left[S\right]_{Cu-Fe-S} + (O^{2^{-}})_{slag} = (S^{2^{-}})_{slag} + (1/2) O_2(gas) \dots (10)$$

## 2. Experimental Apparatus

The starting materials were Fe, Fe<sub>3</sub>O<sub>4</sub>, CaCO<sub>3</sub>, SiO<sub>2</sub> and Cu obtained from Nacalai Tesque, Inc., Kyoto, Japan. FeO was prepared by heating Fe + Fe<sub>3</sub>O<sub>4</sub> mixture (1:1 mole ratio) at 1 273 K for 8 hours under a stream of Ar + H<sub>2</sub> + H<sub>2</sub>O gas mixture where  $P_{O_2}$  was fixed to be  $1.7 \times 10^{-14}$  atm. CaO was obtained by heating CaCO<sub>3</sub> at 1 573 K for 4 hours, and SiO<sub>2</sub> was used after dried at 413 K. To make initial Cu–S alloy, Cu was melted in a molybdenum crucible at 1 573 K under a stream of Ar + 30%H<sub>2</sub> + 0.2%SO<sub>2</sub> gas mixture where  $P_{S_2}$  was controlled to be  $4 \times 10^{-6}$  atm.

The experimental apparatus and procedure have been reported elsewhere.<sup>18)</sup> Hence only a brief description is given in this paper. Initial Cu–S alloy and powdery slag sample were heated in an Fe crucible up to the experimental temperature under a stream of purified Ar. The gas purification train to remove moisture and remaining  $O_2$  in Ar consisted of silica gel, phosphorus pentoxide and magnesium chips held at 823 K. During heating, Fe would dissolve into

Cu–S alloy to a small extent resulting in a formation of Cu– Fe–S liquid alloy, while Fe–Cu–S solid solution would form on the inner wall of the Fe crucible. Temperatures were measured with a Pt-PtRh13 thermocouple placed beside the Fe crucible.

The oxygen sensor consisted of a zirconia tube stabilized by 9 mol% of magnesia as the solid electrolyte and a twophase mixture of  $Mo + MoO_2$  as the reference electrode. A Mo rod was used as an electrical conductor to the reference electrode, while a steel rod soldered to the Fe crucible made electrical contact to the outer electrode of the cell. After the value for electromotive force, emf, remained stable, the Cu-Fe-S alloy sample was withdrawn by means of a silica tube and the slag sample was collected by immersing an iron rod. Then, FeO was added to slag phase to change the slag composition. In CaO-SiO2-FeO slags the mole ratio of CaO/SiO<sub>2</sub>,  $X_{CaO}$  /  $X_{SiO_2}$ , was fixed to be 0.53 or 1.1, while the CaO/Al<sub>2</sub>O<sub>3</sub> mole ratio,  $X_{CaO} / X_{Al_2O_3}$ , remained 2 in CaO-Al<sub>2</sub>O<sub>3</sub>-FeO slags. During one experimental run, the emf measurements, collecting samples, and adding FeO were repeated at a fixed  $X_{CaO} / X_{SiO_2}$  or  $X_{CaO} / X_{Al_2O_3}$  and a constant temperature. All slag samples were homogeneous liquid at the experimental temperature. The collected slag samples were submitted to chemical analysis for S, which was based upon conventional combustion method.<sup>19)</sup> The concentrations of the other elements in the slag and alloy samples were determined with ICP-OES.

The relationship between the open circuit *emf* of the cell and the  $O_2$  partial pressure is given by<sup>20)</sup>

, where  $E_t$  is thermo-*emf* between Mo(+) and Fe(-), R is the gas constant, T is temperature, F is the Faraday constant, and  $P_e$  is the O<sub>2</sub> partial pressure at which the ionic and the *n*-type electronic conductivities are equal.  $P_{O_2}(ref.)$ represents the O<sub>2</sub> partial pressures at the reference electrode of Mo + MoO<sub>2</sub>. Values for these parameters have been reported as

$$E_t / mV = -14.69 + 0.0227 \times (T / K)^{210} \dots (12)$$

$$\log(P_e / \operatorname{atm}) = +20.40 - 6.45 \times 10^4 / (T / K)^{22} \dots (13)$$

 $\log \left[ P_{O_2} \left( ref. \right) / \text{atm} \right] = +8.84 - 3.01 \times 10^4 / \left( T / \text{K} \right)^{23} \dots (14)$ 

The equilibrium O<sub>2</sub> partial pressures between slag and Cu– Fe–S alloy,  $P_{O_2}$ , can be calculated from Eqs. (11) through (14).

### 3. Experimental Results and Discussion

The reaction of the dissolution of gaseous diatomic sulfur into Cu–Fe–S liquid alloy is given as

$$(1/2) S_2(gas) = [S]_{Cu-Fe-S}$$
 .....(15)

, where  $[f_S]_{Cu-Fe-S}$  and  $[mass\%S]_{Cu-Fe-S}$  represents the

Henrian activity coefficient and content of S in Cu–Fe–S liquid alloy. Substituting Eq. (16) into Eq. (5), we have

$$C_{S^{2-}} = \left(mass\%S^{2-}\right)_{slag} \cdot P_{O_2}^{1/2} \cdot \frac{K(15)}{[f_s]_{Cu-Fe-S} \cdot [mass\%S]_{Cu-Fe-S}}$$
.....(17)

When the standard state of S is taken to be S in liquid Cu at 1 mass% solution, K(15) and  $[f_S]_{Cu-Fe-S}$  are obtainable in the literature<sup>17)</sup> as follows.

$$\log K(15) = 2.74 \pm 0.03$$
 at 1573 K .....(18)

$$\log K(15) = 2.55 \pm 0.01$$
 at 1 673 K .....(19)

$$\log[f_{S}]_{Cu-Fe-S} = -3.18 \times 10^{-2} \times [mass\% Fe]_{Cu-Fe-S} +8.90 \times 10^{-4} \times [mass\% Fe]_{Cu-Fe-S}^{2} \dots (20)$$
at 1573 K

$$\log[f_{S}]_{Cu-Fe-S} = -1.67 \times 10^{-2} \times [mass\% Fe]_{Cu-Fe-S} +2.23 \times 10^{-4} \times [mass\% Fe]_{Cu-Fe-S}^{2} \dots (21)$$
at 1673 K

Equations (17) to (21) indicate that  $C_{S^{2-}}$  can be determined by using the measured values for  $(mass\% S^{2-})_{slag}$ ,  $[mass\% S]_{Cu-Fe-S}$ ,  $[mass\% Fe]_{Cu-Fe-S}$  and  $P_{O_2}$ .

**Figures 2**(a) to 2(d) show the logarithmic value for  $C_{S^2}$ -plotted against the mole fraction of FeO,  $(X_{FeO})_{slag}$ , in CaO–SiO<sub>2</sub>–FeO slag. The results at 1 573 K illustrated in Figs. 2(a) and 2(c) were reported by the present authors.<sup>18)</sup> At a fixed  $X_{CaO} / X_{SiO_2}$  and a constant temperature,  $C_{S^2}$ - increased with an increase in  $(X_{FeO})_{slag}$ ; this was consistent with what was reported in the literature<sup>2,4,9,10,14,16)</sup> based on FeO being a basic oxide. It could be also observed that  $C_{S^2}$ - increased as  $X_{CaO} / X_{SiO_2}$  increased at a fixed  $(X_{FeO})_{slag}$ .

**Figures 3**(a) and 3(b) give the relation between logarithmic value for  $C_{S^{2-}}$  of CaO–SiO<sub>2</sub>–FeO slag and reciprocal temperature for comparisons of the results by the present authors with the literature data.<sup>1,24–29)</sup> At  $X_{CaO} / X_{SiO_2} = 1.1$ , the present values for  $C_{S^{2-}}$  of CaO–SiO<sub>2</sub>–FeO slag coexisting with Cu–Fe–S liquid alloy in an Fe crucible were very close to those measured with a gas-slag equilibrium method.<sup>10)</sup> On the other hand, the latter were lower than the former at  $X_{CaO} / X_{SiO_2} = 0.53$ . These trends implied that the effect of O<sub>2</sub> pressure on slag basicity through Fe<sup>3+</sup> would be evident when slag basicity was low. As illustrated in Fig. 1, the values for  $P_{O_2}$  measured in the present experiments were



Fig. 2. Experimental and calculation results at 1 573 K and 1 673 K. (a) to (c) logarithmic value of sulfide capacity, (d) to (f) FeO activity, (g) to (i) logarithmic value of sulfur distribution ratio between slag and hot metal.



Fig. 3. Logarithmic value of sulfide capacity plotted against reciprocal temperature.

lower than the O<sub>2</sub> pressure conditions adopted in a gas-slag equilibrium method.<sup>1,4–12</sup> Although  $Fe^{2+}/Fe^{3+}$  ratios in the present slags could not be analyzed, it has been reported that the proportion of  $Fe^{2+}$  in total iron was over 87% in CaO–SiO<sub>2</sub>–FeO molten slag coexisting with metallic iron at 1 573 K.<sup>30</sup>

Figures 3(a) and 3(b) also show  $C_{S^{2-}}$  for the CaO–SiO<sub>2</sub>–MgO,<sup>24)</sup> CaO–SiO<sub>2</sub>–AlO<sub>1.5</sub><sup>1,25–27)</sup> or CaO–SiO<sub>2</sub>–CaF<sub>2</sub><sup>28,29)</sup> ternary liquid slags which contains MgO, AlO<sub>1.5</sub> or CaF<sub>2</sub> at the same concentration as FeO in the CaO–SiO<sub>2</sub>–FeO ternary slag. At a fixed  $X_{CaO} / X_{SiO_2}$ , replacing MgO, AlO<sub>1.5</sub> or CaF<sub>2</sub> with the same amount of FeO raises  $C_{S^{2-}}$  significantly. In Fig. 3(c), the present results of CaO–Al<sub>2</sub>O<sub>3</sub>–FeO system are compared with that of CaO–Al<sub>2</sub>O<sub>3</sub> binary system estimated by the model that gives the relation between sulfide capacity and optical basicity.<sup>31)</sup> As seen in this figure, the addition of FeO to CaO–Al<sub>2</sub>O<sub>3</sub> system forms homogeneous liquid slag at lower temperature and raises sulfide capacity. According to Eq. (5), these results indicate that FeO raises  $C_{S^{2-}}$  by not only increasing slag basicity,  $(a_{O^{2-}})_{slag}$ , but also decreasing  $(f_{S^{2-}})_{slag}$ .

A number of models to calculate  $C_{S^{2-}}$  were reviewed by Kang.<sup>32)</sup> In this discussion, the present results of  $C_{S^{2-}}$  were compared with the values calculated with Optical Basicity Model<sup>33,34)</sup> and KTH Model.<sup>10)</sup> Young *et al.*<sup>33)</sup> and Zhang et al.<sup>34)</sup> derived the formulae to give the relations between  $C_{S^{2-}}$  and optical basicity available for FeO-containing slags. Nzotta *et al.* suggested the prediction model of  $C_{S^{2-}}$ (KTH Model) in which both effects of FeO on not only  $(a_{O^{2-}})_{slag}$  but also  $(f_{S^{2-}})_{slag}$  were taken into account.<sup>10</sup> Since some of data used for the parameter optimization in these models were measured with a gas-slag equilibrium method,<sup>10,33,34)</sup> there would be a possibility to underestimate  $C_{S^{2-}}$  slightly. Figures 2(a) to 2(e) show that, although the model calculations were lower than the present results in CaO-SiO<sub>2</sub>-FeO system at  $X_{CaO}$  /  $X_{SiO_2}$  = 0.53, they were in good agreement with each other in CaO-SiO2-FeO system at  $X_{CaO}$  /  $X_{SiO_2}$  = 1.1 and in CaO–Al<sub>2</sub>O<sub>3</sub>–FeO system at  $X_{CaO} / X_{Al_2O_3} = 2.$ 

Next, let us consider oxygen potential through FeO activi-

ties in slags. The reaction of iron between slag and Cu–Fe–S liquid alloy is formulated as

$$[Fe]_{Cu-Fe-S} + (1/2) O_2(gas) = (FeO)_{slag} \dots (22)$$

$$K(22) = \frac{(a_{FeO})_{slag}}{[\gamma_{Fe}]_{Cu-Fe-S} \cdot [X_{Fe}]_{Cu-Fe-S} \cdot P_{O_2}^{1/2}} \dots \dots (23)$$

$$\log K(23) = -2.20 + 11750 / (T / K)^{21} \dots (24)$$

The standard states of Fe in Cu–Fe–S alloy and FeO in slag are taken to be pure solid Fe and pure non-stoichiometric liquid FeO coexisting with pure solid Fe, respectively. By using the thermochemical data,<sup>35–37)</sup> the activity coefficients of iron,  $[\gamma_{Fe}]_{Cu-Fe-S}$ , at 1 573 K and 1 673 K are expressed as

$$\ln[\gamma_{Fe}]_{Cu-Fe-S} = 2.92 + (-6.88) \cdot [X_{Fe}]_{Cu-Fe-S} + (-6.29) \cdot [X_S]_{Cu-Fe-S} \dots (25)$$
at 1 573 K

$$\ln[\gamma_{Fe}]_{Cu-Fe-S} = 2.76 + (-9.48) \cdot [X_{Fe}]_{Cu-Fe-S} + 14.36 \cdot [X_{Fe}]_{Cu-Fe-S}^{2} \dots (26) + (-3.25) \cdot [X_{S}]_{Cu-Fe-S}$$
at 1.673 K

, where  $[X_i]_j$  represents the mole fraction of *i* in liquid *j*. The activities of FeO in slag,  $(a_{FeO})_{slag}$ , can be calculated from Eqs. (23) through (26) with the measured values for  $[X_{Fe}]_{Cu-Fe-S}$ ,  $[X_S]_{Cu-Fe-S}$  and  $P_{O_2}$ . The relation between  $(a_{FeO})_{slag}$  and  $(X_{FeO})_{slag}$  is illustrated in Figs. 2(f), 2(g) and 2(h). At a fixed  $X_{CaO} / X_{SiO_2}$  or  $X_{CaO} / X_{Al_2O_3}$ ,  $(a_{FeO})_{slag}$  increased as  $(X_{FeO})_{slag}$  increased, and the present results were not inconsistent with the activity curves reported in the literature.<sup>30,38</sup>

Finally, the distribution ratios of S between slag and hot metal,  $L_S$ , were evaluated from the experimental results of  $C_{S^{2-}}$  and  $(a_{FeO})_{slag}$ . The O<sub>2</sub> partial pressure between slag and hot metal is fixed by

$$\left[\mathrm{Fe}\right]_{\mathrm{hot metal}} + (1/2) \mathrm{O}_{2}(\mathrm{gas}) = (\mathrm{FeO})_{\mathrm{slag}} \dots \dots \dots (27)$$

$$\log K(27) = -2.59 + 12\ 470\ /\ (T\ /\ K)\ ^{21,39}\ \dots\dots(29)$$

Substituting Eq. (28) into Eq. (9), we obtain

$$L_{S} = C_{S^{2-}} \cdot \frac{K(27) \cdot [a_{Fe}]_{hot metal}}{(a_{FeO})_{slag}} \cdot \frac{[f_{S}]_{hot metal}}{K(6)} \dots \dots (30)$$

According to Eq. (30), sulfide capacity and FeO activity have completely opposite effects on sulfur distribution ratio, although both of  $C_{S^{2-}}$  and  $(a_{FeO})_{slag}$  increase with an increase in  $(X_{FeO})_{slag}$  as already mentioned. In this discussion, it was assumed that hot metal was Fe–C–S liquid alloy,  $[a_{Fe}]_{hot metal}$ obeyed Raoult's law and  $[f_S]_{hot metal}$  did not depend on [mass%S]<sub>hot metal</sub> due to low sulfur concentration. Figures 2(i), 2(j) and 2(k) show  $L_S$  calculated by substituting measured values for  $C_{S^{2-}}$  and  $(a_{FeO})_{slag}$  into Eq. (30). The result that  $L_S$  increased as  $(X_{FeO})_{slag}$  increased indicated that the effect of increasing sulfide capacity by adding FeO would be greater than the effect of increasing FeO activity. It will be an important subject to quantitatively evaluate the effects of FeO on slag basicity,  $(a_{O^{2-}})_{slag}$ , and  $(f_{S^{2-}})_{slag}$  in Eq. (5) to clarify the reason why FeO raised sulfide capacity.

### 4. Conclusion

Towards environmentally friendly steelmaking processes, re-sulfurization reaction in hot metal pre-treatments needs to be suppressed. To evaluate the sulfur distribution ratio between FeO-containing slag and hot metal, sulfide capacities and FeO activities in the CaO-SiO2-FeO and CaO-Al<sub>2</sub>O<sub>3</sub>-FeO ternary slags were measured under the conditions where slags coexisted with metallic iron at temperatures below the melting point of pure iron. The present values for sulfide capacities of the CaO-SiO<sub>2</sub>-FeO and CaO-Al<sub>2</sub>O<sub>3</sub>-FeO slags increased as FeO content increased and were significantly larger than those of the CaO-SiO<sub>2</sub>-MgO, CaO-SiO<sub>2</sub>-AlO<sub>1.5</sub> and CaO-SiO<sub>2</sub>-CaF<sub>2</sub> ternary systems. The addition of FeO resulted in an increase in the distribution ratio of sulfur calculated between FeOcontaining slag and hot metal, although the FeO activity and oxygen potential rose.

#### **Statement for Conflict of Interest**

The authors declare that they have no conflict of interest.

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