The Effect of Iron Oxide on Sulphide Capacities of CaO-based Molten Slags

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ABSTRACT

Removing sulphur and phosphorus from molten iron can be expressed by the following reactions, respectively.

$$[S]_{Fe} + (O^{2-})_{slag} = (S^{2-})_{slag} + [O]_{Fe}$$

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

These equations indicate that desulfurization and dephosphorization have opposite oxygen potential conditions. If a small amount of desulfurization slag not removed is carried over to dephosphorization process, the reaction of sulphur mentioned above proceeds toward left hand resulting in increasing sulphur content in molten iron. For better understanding of such re-sulfurization reaction in hot metal pre-treatments, the present study aimed at evaluating the effect of iron oxide on the sulphur distribution ratio between slag and hot metal. To measure sulphide capacities and FeO activities simultaneously at temperatures below the melting point of pure iron, CaO-SiO_2-FeO and CaO-Al_2O_3-FeO ternary molten slags were brought into equilibria with copper-iron-sulphur liquid alloys, and the equilibrium oxygen partial pressures were determined with an electrochemical technique involving the stabilized zirconia solid electrolyte. The experimental results showed that the sulphide capacity increased with an increase in FeO content, and this trend was consistent with the fact that FeO was basic. Although the addition of FeO raised the FeO activity and oxygen potential, the calculated value for sulphur distribution ratio between slag and hot metal increased with increasing FeO content.

INTRODUCTION

In hot metal pre-treatments, impurities of sulphur and phosphorus are removed from liquid iron, and these reactions are given as follows.

$$[S]_{Fe} + (O^{2-})_{slag} = (S^{2-})_{slag} + [O]_{Fe} \qquad (1)$$

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

, where $[\ i\ ]_{Fe}$ and $(\ j\ )_{slag}$ represent chemical species i in liquid iron and j in slag, respectively. According to Equations (1) and (2), it has been well known that the thermochemical conditions for effective desulfurization are high basicity slag and low oxygen potential, while those for efficient phosphorus removal are high basicity slag and high oxygen potential (high FeO activity). Thus, desulfurization and dephosphorization have opposite oxygen potential conditions. When a small amount of desulfurization slag not removed is carried over to dephosphorization process, Reaction (1) proceeds toward left hand resulting in increasing sulphur content in hot metal, because FeO in dephosphorization slag raises oxygen potential. This phenomenon is called re-sulfurization. On the other hand, FeO is a basic oxide and increases sulphide capacities of slags (Richardson and Fincham, 1954; Pierre and Chipman, 1956; Bronson and Pierre, 1981; Shim and Ban-ya, 1982; Nagabayashi, Hino and Ban-ya, 1990; Nzotta, Sichen and Seetharaman, 1999a; Nzotta, Sichen and Seetharaman, 1999b; Jung, 2003). For better understanding of re-sulfurization reaction in hot metal pretreatments, it is necessary to clarify the effect of FeO on sulphur distribution ratio between slag and hot metal, L_S, defined by Equation (3), at temperatures lower than the melting point of pure iron.

$$L_S \equiv \frac{(\%S^{2-})_{slag}}{[\%S]_{Fe}} \qquad (3)$$

In Equation (3), $(\%S^{2-})_{slag}$ and $[\%S]_{Fe}$ represent mass% concentrations of sulphur in slag and liquid iron, respectively.

Sulphide capacity, $C_{S^{2-}}$, is a thermochemical property of slag to hold sulfur as sulfide and is defined based on the following reaction (Fincham and Richardson, 1954; Richardson and Fincham, 1954).

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

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

, where 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 value for $C_{S^{2-}}$ increases when $(a_{O^{2-}})_{slag}$ is high, ie, slag basicity is high, and $(f_{S^{2-}})_{slag}$ is low, ie, slag contains components with high chemical affinity for sulphur. The relationship between L_S and $C_{S^{2-}}$ can be derived as follows. The equilibrium partial pressure of oxygen between slag and liquid iron is fixed by

$$\mathrm{Fe(liquid)} + (1/2)\ \mathrm{O_2(gas)} = \mathrm{(FeO)_{slag}} \tag{6}$$

$$K(6) = \frac{(a_{FeO})_{slag}}{a_{Fe} \cdot P_{O_2}{}^{1/2}} \tag{7}$$

, where $(a_{FeO})_{slag}$ and a_{Fe} represent the activities of FeO in slag and iron, respectively. The dissolution of gaseous diatomic sulphur into liquid iron is given as

$$(1/2)\ \mathrm{S_2(gas)} = \mathrm{[S]_{Fe}} \tag{8}$$

$$K(8) = \frac{[f_S]_{Fe} \cdot [\%S]_{Fe}}{P_{S_2}{}^{1/2}} \tag{9}$$

In Equation (9), $[f_S]_{Fe}$ is the Henrian activity coefficient of sulphur in liquid iron. Combining Equations (3), (5), (7) and (9), we obtain

$$L_S = C_{S^{2-}} \cdot P_{O_2}{}^{-1/2} \cdot \frac{[f_S]_{Fe}}{K(8)} = C_{S^{2-}} \cdot \frac{K(6) \cdot a_{Fe}}{(a_{FeO})_{slag}} \cdot \frac{[f_S]_{Fe}}{K(8)} \tag{10}$$

The values for $C_{S^{2-}}$ have been reported in the CaO-FeO based slags. However, there is still lack of the data at temperatures in hot metal pretreatments. It could be also pointed out here that, when $C_{S^{2-}}$ of FeO-containing slag is measured with the gas-slag equilibrium method based on Equation (4), the oxygen partial pressure, P_{O_2}, should be higher than the equilibrium value between Fe and FeO in order to avoid reducing FeO to form metallic Fe. Such an experimental condition would result in an increase in trivalent iron and then a decrease in slag basicity.

Based on the considerations above, this study aimed at determining $C_{S^{2-}}$ and FeO activities, $(a_{FeO})_{slag}$, in the CaO-SiO$_2$-FeO and CaO-Al$_2$O$_3$-FeO ternary slags under the oxygen partial pressure close to the equilibrium value between Fe and FeO. For this purpose, firstly, the activity coefficients of S and Fe in Cu-Fe-S liquid alloy were determined in order to be used as a reference metal. Subsequently the equilibrium oxygen partial pressures between slag and Cu-Fe-S liquid alloy were measured with an electrochemical technique involving the stabilized zirconia solid electrolyte at 1573 K and 1673 K. In this paper, “ln” and “log” represent natural and common logarithms, respectively.

EXPERIMENTAL ASPECTS

Activity coefficient of component in Cu-Fe-S alloy

The experimental apparatus and procedures have been described elsewhere (Matsushita *et al*, 2021). Figure 1a schematically shows the experimental setup. An alumina container charged with about 0.5g Cu-Fe-S alloy samples was heated in a mullite reaction tube in which the gas mixtures of Ar + H$_2$ + SO$_2$ were introduced to fix P_{S_2} at 1573 K and 1673 K. The calculation method of the equilibrium partial pressures was based on the conventional thermochemical consideration. The reaction underlying the present experiments is given as

$$(1/2)\ \mathrm{S_2(gas)} = \mathrm{[S]_{Cu}} \tag{11}$$

$$K(11) = \frac{[f_S]_{Cu} \cdot [\%S]_{Cu}}{P_{S_2}{}^{1/2}} \tag{12}$$

$[\%S]_{Cu}$ and $[f_S]_{Cu}$ are the mass content and Henrian activity coefficient of sulphur in Cu-Fe-S liquid alloy. Samples were held at constant temperature under a stream of Ar + H$_2$ + SO$_2$ gas mixture for at least 7 hours, and then moved to the end of the mullite reaction tube with the aid of a nickel rod for quenching. The sulphur contents in alloy samples were analysed with an inductive-coupled plasma spectrometer (ICP-OES, Optima 5300 DV, PerkinElmer Inc.). It was confirmed that 7 hours was long enough for Reaction (11) to reach equilibrium, which was attained from increasing and decreasing sulphur contents in alloy samples. Any unexpected reactions between alloy sample and alumina could not be observed. Temperatures were measured with a Pt-PtRh13 thermocouple placed beside samples and controlled to ±1 K by using a control thermocouple and a PID-type temperature regulator. The overall errors in temperature measurements and control were estimated to be less than ±2 K.

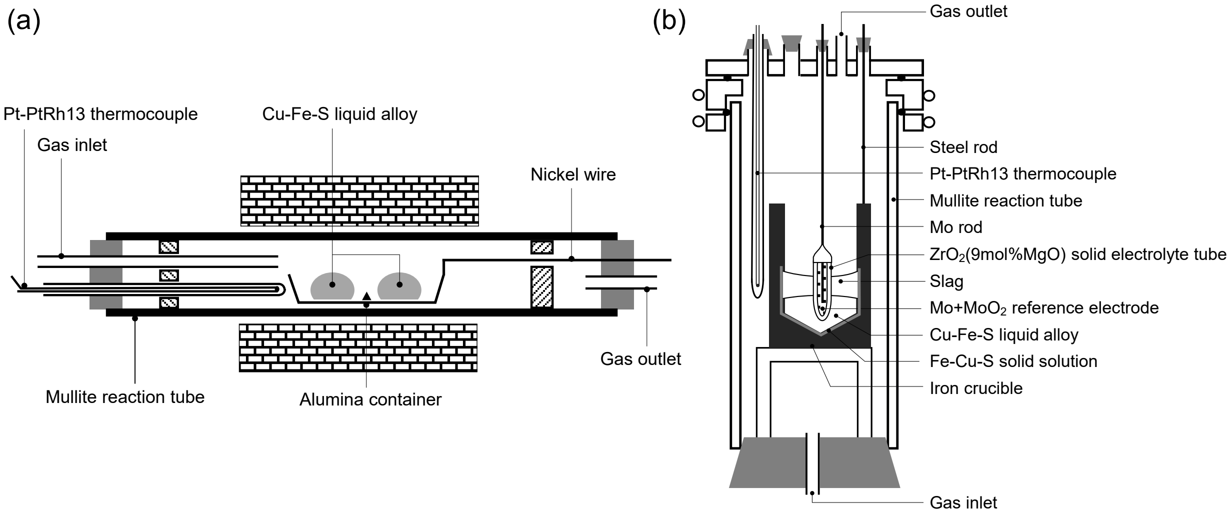

FIG 1 – Experimental apparatus. a – activity coefficient of component in Cu-Fe-S alloy, b – sulphide capacity and FeO activity in slag.

Sulphide capacity and FeO activity in slag

The experimental apparatus has been shown elsewhere (Awaya *et al*, 2023). Figure 1b illustrates the experimental setup. An iron crucible charged with initial Cu-S alloy and powdery slag sample was heated at 1573 K or 1673 K under a stream of purified argon in a SiC resistance furnace. The gas purification train for argon consisted of silica gel, phosphorus pentoxide and magnesium chips held at 823 K. During heating, iron would dissolve into Cu-S alloy to a small extent resulting in a formation of Cu-Fe-S ternary liquid alloy, while Fe-Cu-S solid solution would form on the inner wall of the iron crucible.

The oxygen cell consisted of a zirconia tube stabilized by 9 mol% of magnesia as the solid electrolyte and a Mo + MoO_2 two-phase mixture as the reference electrode. A molybdenum rod was used as an electrical conductor to the reference electrode, while a steel rod soldered to the iron crucible and Cu-Fe-S liquid alloy made electrical contact to the outer electrode of the cell. An oxygen sensor was immersed into Cu-Fe-S liquid alloy to measure the electromotive force (*emf*) between Mo and Fe rods. After the stable value for *emf* could be obtained, the Cu-Fe-S alloy sample was withdrawn by means of a silica sampling tube, and the slag sample was collected by immersing an iron rod into the crucible. The iron rod with the molten slag was pulled out of the furnace and cooled rapidly in air. Then, FeO was added into slag to change the concentration of FeO in slag. In CaO-SiO_2-FeO slags the mole ratio of CaO/SiO_2, X_{CaO}/X_{SiO_2}, was fixed to be 0.53 or 1.1, while the CaO/Al_2O_3 mole ratio, $X_{CaO}/X_{Al_2O_3}$, remained 2 in CaO-Al_2O_3-FeO slags. *Emf* measurements, collecting samples, and adding FeO were repeated during an experimental run.

The open circuit *emf*, E, of the cell used in this study is given by

$$E = \frac{RT}{F}\ln\frac{P_{O_2}(ref.)^{1/4}+P_e{}^{1/4}}{P_{O_2}{}^{1/4}+P_e{}^{1/4}} + E_t \qquad \text{(Schmalzried, 1962)} \qquad (13)$$

, 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 oxygen partial pressure at which the ionic and the *n*-type electronic conductivities are equal. $P_{O_2}(ref.)$ represents the oxygen partial pressures at the reference electrode of Mo + MoO_2. Values for these parameters have been reported as

$$E_t/\mathrm{mV} = -14.69 + 0.0227 \times (T/\mathrm{K}) \qquad \text{(Iwase, Yamada, Ichise and Akizuki, 1984)} \quad (14)$$

$$\log(P_e/\text{atm}) = +\,20.40 - 6.45 \times 10^4/(T/\text{K})$$
(Iwase, Ichise, Takeuchi and Yamasaki, 1984) (15)

$$\log[P_{O_2}(ref.)/\text{atm}] = +8.84 - 30{,}100/(T/\text{K})$$
(Iwase, Yasuda and Mori, 1979) (16)

By using Equations (13) through (16), the equilibrium oxygen partial pressures, P_{O_2}, can be determined between slag and Cu-Fe-S alloy.

The slags were submitted to chemical analysis for sulphur, which was based upon conventional combustion method using self-made equipment. The concentrations of the other elements in the slag and alloy samples were determined with ICP-OES.

EXPERIMENTAL RESULTS AND DISCUSSION

Activity coefficient of component in Cu-Fe-S alloy

Equation (12) can be rewritten as

$$\log[\%S]_{Cu} = (1/2)\log P_{S_2} - \log[f_S]_{Cu} + \log K(11) \tag{17}$$

, where $[\%i]_{Cu}$ represents the mass content of *i* in Cu-Fe-S liquid alloy. Equation (17) indicates that, when the Henrian activity coefficient of S in Cu-Fe liquid alloy, $[f_S]_{Cu}$, is constant at infinite dilute solution of sulphur, a plot of $\log[\%S]_{Cu}$ against $\log P_{S_2}$ is linear with a slope of $1/2$ and an intercept of $-\log[f_S]_{Cu} + \log K(11)$. Such plots at 1573 K and 1673 K are shown in Figure 2. As seen in this figure, a linear relation could be observed at a constant temperature and a fixed $[\%Fe]_{Cu}/[\%Cu]_{Cu}$ mass ratio, and the slope of each line was close to $1/2$. When the standard state of S in Cu-Fe liquid alloy is taken to be S in molten Cu at 1 mass% solution, $[f_S]_{Cu}$ in Cu-S alloy ($[\%Fe]_{Cu} = 0$) is unity, and the intercept of the regression line corresponds to $\log K(11)$. Therefore, from the intercepts of the regression lines for Cu-S alloys, the values for $\log K(11)$ were determined as follows.

$$\log K(11) = 2.74 \pm 0.03 \quad \text{at 1573 K} \tag{18}$$

$$\log K(11) = 2.55 \pm 0.01 \quad \text{at 1673 K} \tag{19}$$

$$\Delta G°(11) = G_S(1\%\ \text{S in Cu}) - (1/2)G_{S_2} = -RT\ln K(11) \tag{20}$$

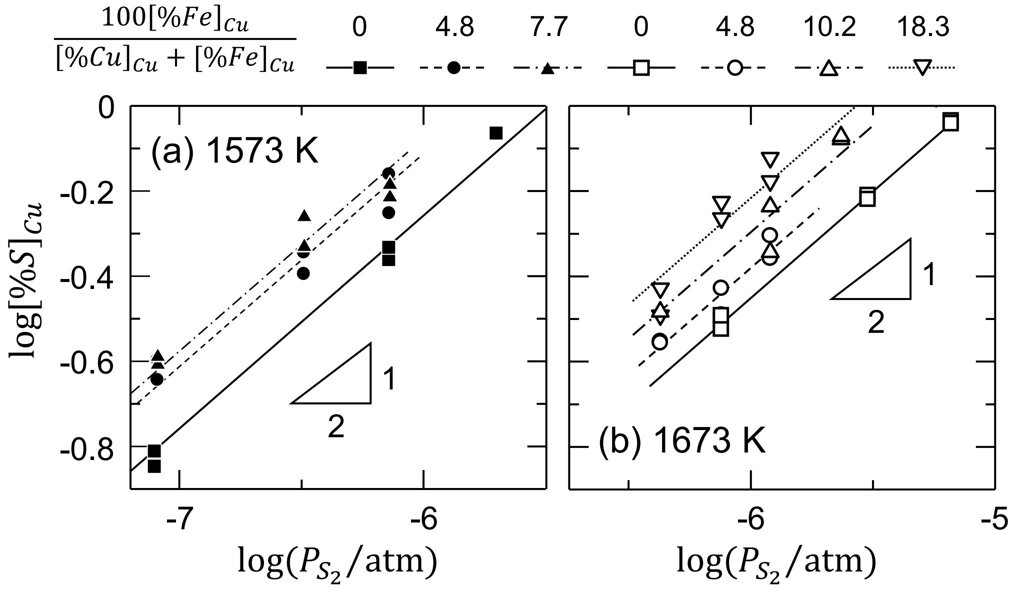

FIG 2 – Relation between $\log[\%S]_{Cu}$ in Cu-Fe-S liquid alloy and $\log P_{S_2}$.

Figure 3 shows that the present results of $\Delta G°(11)$ plotted against temperature were in good agreement with those reported by Alcock (Alcock, 1958) and Ohta *et al* (Ohta, Kubo and Morita, 2003) and were not inconsistent with the other literature data (Umetsu, 1950; Yagihashi and Sato, 1962; Sigworth and Elliott, 1974a).

Combining Equations (17) to (19), we have

$$\log[\%S]_{Cu} = (1/2)\log P_{S_2} - \log[f_S]_{Cu} + 2.74 \pm 0.03 \quad \text{at 1573 K} \qquad (21)$$

$$\log[\%S]_{Cu} = (1/2)\log P_{S_2} - \log[f_S]_{Cu} + 2.55 \pm 0.01 \quad \text{at 1673 K} \qquad (22)$$

Substituting values for the intercepts of the regression lines into Equations (21) and (22), $\log[f_S]_{Cu}$ could be derived. Figure 4 shows $\log[f_S]_{Cu}$ plotted against $[\%Fe]_{Cu}$ with the Cu-Fe binary phase diagram (Okamoto, 2010). As seen in this figure, $\log[f_S]_{Cu}$ decreased with an increase in iron content. The standard Gibbs energy change of the dissolution of gaseous sulphur into liquid Fe, $\Delta G°(8)$, has been reported as follows, and is also illustrated in Figure 3.

$$\Delta G°(8) = G_S(1\%\ \mathrm{S\ in\ Fe}) - (1/2)G_{S_2} \qquad (23)$$

$$\Delta G°(8)/\mathrm{J\cdot mol^{-1}} = -135100 + 23.43 \times (T/\mathrm{K}) \qquad \text{(Sigworth and Elliott, 1974b)} \ (24)$$

By extrapolating $\Delta G°(8)$ to temperature below the melting point of pure iron, it could be considered that $\Delta G°(8)$ is lower than $\Delta G°(11)$. This is consistent with the negative value for $\log[f_S]_{Cu}$, because both properties indicate that the chemical affinity between Fe and S is stronger than that between Cu and S.

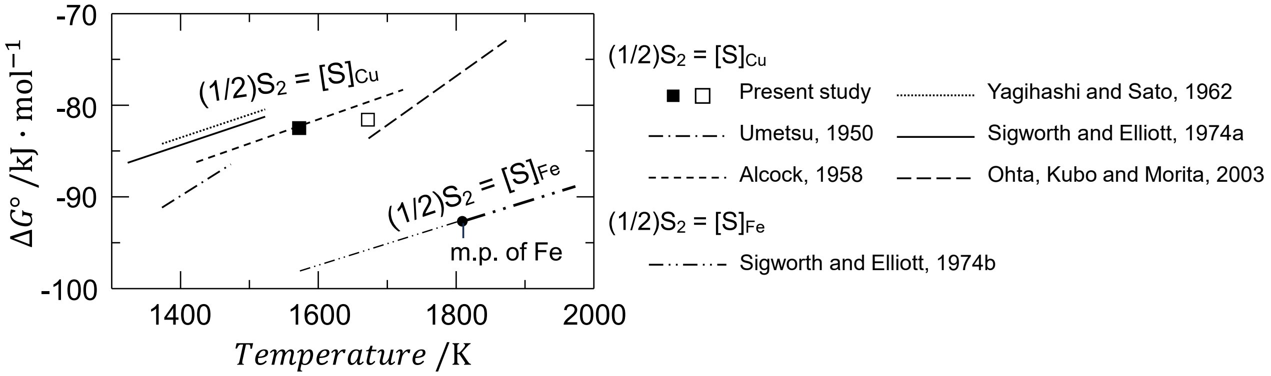

FIG 3 – Standard Gibbs energy change of the dissolution of gaseous sulphur into liquid metal.

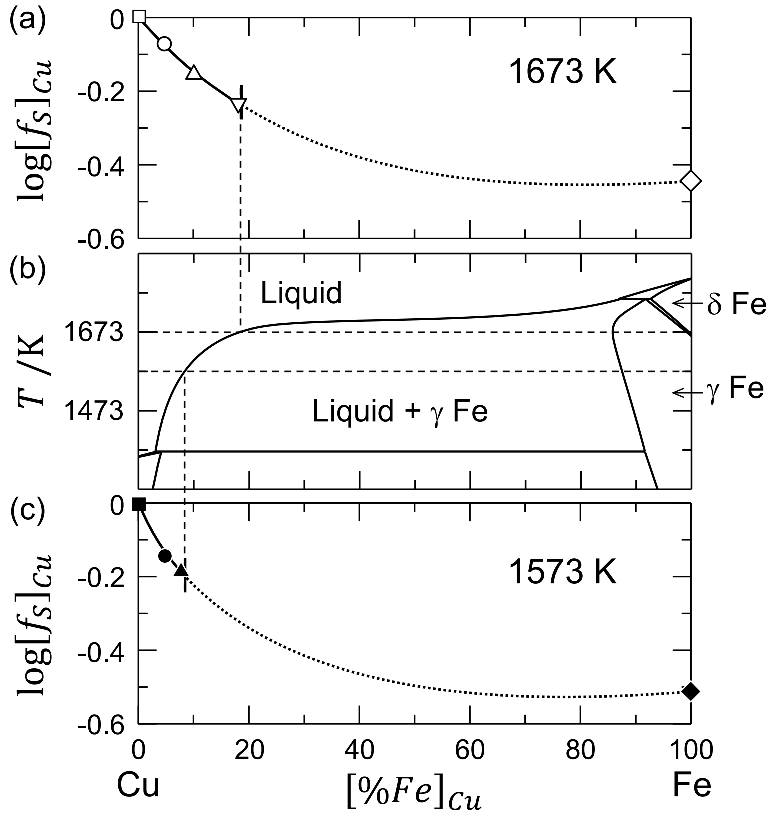

FIG 4a – Henrian activity coefficient of sulphur in Cu-Fe-S liquid alloy at 1673 K, b – Cu-Fe binary phase diagram (Okamoto, 2010), c – Henrian activity coefficient of sulphur in Cu-Fe-S liquid alloy at 1573 K.

When the standard state is taken to be S in molten Cu at $[\%S]_{Cu} = 1$, the Henrian activity coefficient of S in liquid Fe at $[\%S]_{Fe} = 1$ is given by

$$RT\ln[f_S]_{Fe} = G_S(1\%\text{ S in Fe}) - G_S(1\%\text{ S in Cu}) = \Delta G°(8) - \Delta G°(11) \text{ at } [\%S]_{Fe} = 1 \quad (25)$$

By inserting Equations (18), (19) and (24) into Equation (25), the Henrian activity coefficient of S in hypothetical liquid Fe, $[f_S]_{Fe}$, can be calculated as follows, and they are plotted on Figures 4a and 4c.

$$\log[f_S]_{Fe} = -0.52 \quad \text{at 1573 K} \quad (26)$$

$$\log[f_S]_{Fe} = -0.44 \quad \text{at 1673 K} \quad (27)$$

By connecting smoothly the present experimental results and $\log[f_S]_{Fe}$ given in Equations (26) and (27), the relations between $\log[f_S]_{Cu}$ at definite dilute sulphur concentration and $[\%Fe]_{Cu}$ in hypothetical homogeneous Cu-Fe liquid alloys at 1573 K and 1673 K can be drawn by dotted curves in Figures 4a and 4c, respectively. In this paper, the following quadratic formulae can be recommended tentatively.

$$\log[f_S]_{Cu} = -3.18 \times 10^{-2} \times [\%Fe]_{Cu} + 8.90 \times 10^{-4} \times {[\%Fe]_{Cu}}^2 \quad \text{at 1573 K} \quad (28)$$

$$\log[f_S]_{Cu} = -1.67 \times 10^{-2} \times [\%Fe]_{Cu} + 2.23 \times 10^{-4} \times {[\%Fe]_{Cu}}^2 \quad \text{at 1673 K} \quad (29)$$

When the standard state of iron in Cu-Fe-S liquid alloy is taken to be pure solid iron, the activity coefficient of iron, $[\gamma_{Fe}]_{Cu}$, is formulated by

$$\ln[\gamma_{Fe}]_{Cu} = \ln[\gamma_{Fe}°]_{Cu} + \varepsilon_{Fe}^{Fe} \cdot [X_{Fe}]_{Cu} + \rho_{Fe}^{Fe} \cdot {[X_{Fe}]_{Cu}}^2 + \varepsilon_{Fe}^{S} \cdot [X_S]_{Cu} \quad (30)$$

, where $[X_i]_{Cu}$ is the mole fraction of *i*, ε_i^j and ρ_i^j are the first- and second-order interaction parameters in liquid copper. In Equation (30), $[\gamma_{Fe}°]_{Cu}$ represents the activity coefficient of iron when the iron activity obeys Henry's law and is obtainable by using the standard Gibbs energy change of the dissolution of iron into molten copper as follows.

$$\text{Fe(pure solid)} = [\text{Fe}]_{\text{Cu}} \quad (31)$$

$$\Delta G°(31)/\text{J}\cdot\text{mol}^{-1} = 54270 - 47.45 \times (T/\text{K}) = -RT\ln\frac{100\cdot M_{Cu}}{[\gamma_{Fe}°]_{Cu}\cdot M_{Fe}}$$

(Sigworth and Elliott, 1974a) (32)

, where M_i is the atomic weight of *i*; $M_{Fe} = 55.847$ and $M_{Cu} = 63.546$. Based on Equation (32) and the literature data on $[\gamma_{Fe}]_{Cu}$ (Taniguchi, Morita and Sano, 1997; Hasegawa, Wakimoto and Iwase, 2002), the values for $[\gamma_{Fe}°]_{Cu}$, ε_{Fe}^{Fe} and ρ_{Fe}^{Fe} can be estimated as follows.

$$\ln[\gamma_{Fe}°]_{Cu} = 2.92 \quad \text{at 1573 K} \quad (33)$$

$$\varepsilon_{Fe}^{Fe} = -6.88 \quad \text{at 1573 K} \quad (34)$$

$$\rho_{Fe}^{Fe} = 0 \quad \text{at 1573 K} \quad (35)$$

$$\ln[\gamma_{Fe}°]_{Cu} = 2.76 \quad \text{at 1673 K} \quad (36)$$

$$\varepsilon_{Fe}^{Fe} = -9.48 \quad \text{at 1673 K} \quad (37)$$

$$\rho_{Fe}^{Fe} = 14.36 \quad \text{at 1673 K} \quad (38)$$

Equations (28) and (29) indicate that the first-order interaction coefficients, e_S^{Fe}, at 1573 K and 1673 K are -3.18×10^{-2} and -1.67×10^{-2}, respectively. Therefore, the values for ε_{Fe}^{S} can be derived as

$$\varepsilon_{Fe}^{S} = \varepsilon_{S}^{Fe} = 230 \cdot \frac{M_{Fe}}{M_{Cu}} \cdot (-3.18 \times 10^{-2}) + \frac{M_{Cu} - M_{Fe}}{M_{Cu}} = -6.29 \quad \text{at 1573 K} \quad (39)$$

$$\varepsilon_{Fe}^{S} = \varepsilon_{S}^{Fe} = 230 \cdot \frac{M_{Fe}}{M_{Cu}} \cdot (-1.67 \times 10^{-2}) + \frac{M_{Cu} - M_{Fe}}{M_{Cu}} = -3.25 \quad \text{at 1673 K} \quad (40)$$

Then, inserting Equations (33) to (40) into Equation (30), the formulae of $[\gamma_{Fe}]_{Cu}$ are given as follows.

$$\ln[\gamma_{Fe}]_{Cu} = 2.92 + (-6.88) \cdot [X_{Fe}]_{Cu} + (-6.29) \cdot [X_S]_{Cu} \quad \text{at 1573K} \quad (41)$$

$$\ln[\gamma_{Fe}]_{Cu} = 2.76 + (-9.48)\cdot[X_{Fe}]_{Cu} + 14.36\cdot{[X_{Fe}]_{Cu}}^{2} + (-3.25)\cdot[X_S]_{Cu} \quad \text{at 1673K} \qquad (42)$$

TABLE 1 –Experimental results of sulphide capacity and FeO activity.

$(\boldsymbol{X_{FeO}})_{slag}$	$\log\left(\frac{P_{O_2}}{\text{atm}}\right)$	$(\%\boldsymbol{S^{2-}})_{slag}$	$[\%\boldsymbol{S}]_{Cu}$	$[\%\boldsymbol{Fe}]_{Cu}$	$\log C_{S^{2-}}$	$(\boldsymbol{a_{FeO}})_{slag}$	$\log L_S$
CaO-SiO$_2$-FeO, 1573 K, $X_{CaO}/X_{SiO_2} = 0.53$							
0.212	-11.49	0.094	0.339	9.56	-3.34	0.310	-0.831
0.411	-11.17	0.147	0.264	9.86	-2.87	0.455	-0.531
0.437	-10.96	0.161	0.200	9.61	-2.61	0.578	-0.375
0.546	-10.78	0.194	0.112	9.38	-2.19	0.718	-0.048
CaO-SiO$_2$-FeO, 1573 K, $X_{CaO}/X_{SiO_2} = 1.1$							
0.202	-11.19	0.239	0.610	9.22	-3.05	0.415	-0.667
0.449	-10.87	0.182	0.163	10.98	-2.41	0.659	-0.229
0.478	-10.81	0.206	0.156	11.83	-2.29	0.717	-0.150
0.475	-10.79	0.201	0.139	10.78	-2.25	0.729	-0.119
0.552	-10.75	0.172	0.087	10.80	-2.10	0.761	0.014
CaO-SiO$_2$-FeO, 1673 K, $X_{CaO}/X_{SiO_2} = 0.53$							
0.270	-10.48	0.058	0.245	11.42	-3.16	0.291	-0.826
0.425	-9.90	0.162	0.202	11.74	-2.33	0.573	-0.297
0.768	-9.55	0.179	0.048	9.62	-1.51	0.820	0.366
CaO-SiO$_2$-FeO, 1673 K, $X_{CaO}/X_{SiO_2} = 1.1$							
0.213	-10.29	0.088	0.423	20.41	-3.03	0.411	-0.850
0.290	-10.01	0.156	0.401	19.32	-2.63	0.559	-0.580
0.409	-9.88	0.236	0.286	18.84	-2.24	0.650	-0.257
0.361	-9.96	0.178	0.385	23.07	-2.50	0.630	-0.505
0.473	-9.84	0.198	0.201	20.92	-2.13	0.705	-0.181
0.560	-9.81	0.186	0.127	20.59	-1.94	0.730	-0.011
CaO-Al$_2$O$_3$-FeO, 1573 K, $X_{CaO}/X_{Al_2O_3} = 2$							
0.229	-11.40	0.182	0.169	8.57	-2.72	0.335	-0.246
0.682	-10.83	0.501	0.171	7.94	-2.01	0.628	0.190
0.313	-11.45	0.633	0.197	8.68	-2.27	0.316	0.230
0.616	-10.90	0.472	0.133	7.71	-1.97	0.575	0.272
0.521	-11.04	0.559	0.183	8.30	-2.09	0.500	0.208
0.417	-11.19	0.599	0.208	8.32	-2.19	0.420	0.183
0.371	-11.21	0.251	0.096	9.34	-2.23	0.432	0.136

Sulphide capacity and FeO activity in slag

Substituting Equation (12) into Equation (5), we have

$$C_{S^{2-}} = (\%S^{2-})_{slag} \cdot {P_{O_2}}^{1/2} \cdot \frac{K(11)}{[f_S]_{Cu} \cdot [\%S]_{Cu}} \tag{43}$$

Equations (28), (29) and (43) indicate that $C_{S^{2-}}$ can be determined by using the measured values for $(\%S^{2-})_{slag}$, $[\%S]_{Cu}$, $[\%Fe]_{Cu}$ and P_{O_2}. The experimental results are summarized in Table 1.

Figures 5a and 5b show the logarithmic value for $C_{S^{2-}}$ plotted against the mole fraction of FeO, $(X_{FeO})_{slag}$, in CaO-SiO$_2$-FeO slag at 1573 K and at 1673 K, respectively. The value for $C_{S^{2-}}$ increased with an increase in the CaO/SiO$_2$ mole ratio at a fixed $(X_{FeO})_{slag}$ and a constant temperature. The present result that $C_{S^{2-}}$ increased with an increase in $(X_{FeO})_{slag}$ was consistent with what was reported in the literatures based on FeO being a basic oxide (Richardson and Fincham, 1954; Pierre and Chipman, 1956; Bronson and Pierre, 1981; Shim and Ban-ya, 1982; Nagabayashi, Hino and Ban-ya, 1990; Nzotta, Sichen and Seetharaman, 1999a; Nzotta, Sichen and Seetharaman, 1999b; Jung, 2003). Figures 5a and 5b also show the values for $\log C_{S^{2-}}$ calculated by using the prediction model (Nzotta, Sichen and Seetharaman, 1999b). Although the parameters in this model were optimized by the data in a temperature range of 1673 K to 1923 K, the present experimental results at 1573 K and 1673 K were not inconsistent with the calculated values.

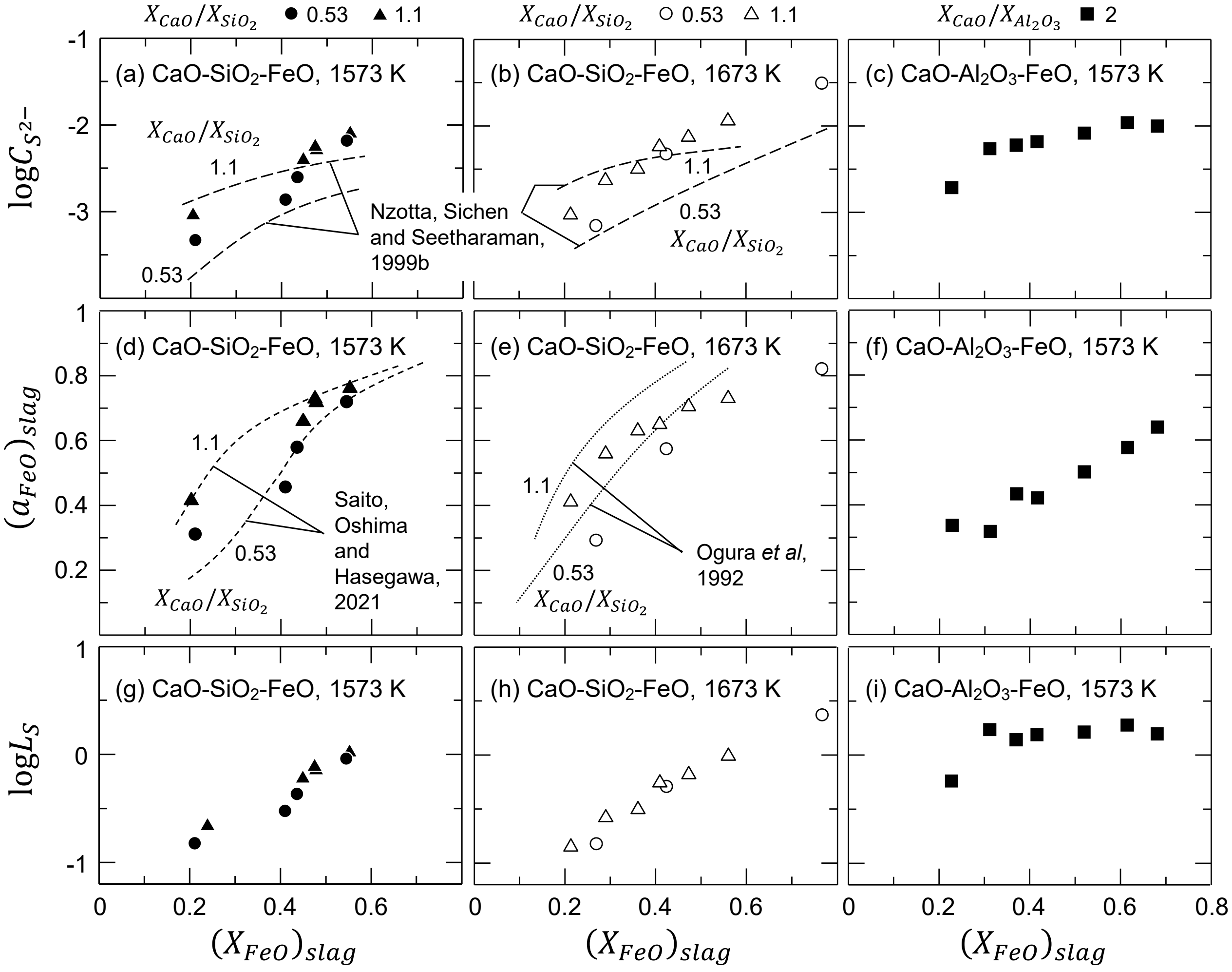

FIG 5 – Experimental and calculation results at 1573 K and 1673 K. a-c – logarithmic value of sulphide capacity, d-f – FeO activity, g-i – logarithmic value of sulphur distribution ratio between slag and hot metal.

The comparisons of the present results with the literature data were conducted in Figures 6a and 6b. In the CaO-SiO$_2$-FeO ternary slags of the same CaO/SiO$_2$ mole ratio and $(X_{FeO})_{slag}$, the present values for $C_{S^{2-}}$ measured at 1573 K and 1673 K were agreement with those at higher temperatures (Nzotta, Sichen and Seetharaman, 1999b). It could be concluded that $C_{S^{2-}}$ in the CaO-SiO$_2$-FeO ternary slag decreased with an increase in reciprocal temperature. This agrees with the knowledge that the desulfurization reaction proceeds more easily at higher temperatures. Figures 6a and 6b also shows $C_{S^{2-}}$ for the CaO-SiO$_2$-MgO (Nzotta *et al*, 1997), CaO-SiO$_2$-AlO$_{1.5}$ (Fincham and Richardson, 1954; Abraham and Richardson, 1960; Berryman, Sommerville and Ishii, 1988; Drakaliysky, Sichen and Seetharaman, 1997) or CaO-SiO$_2$-CaF$_2$ (Uo *et al*, 1989; Ferguson and Pomfret, 1989) ternary liquid slags which contains MgO, AlO$_{1.5}$ or CaF$_2$ at the same concentration as FeO in the CaO-SiO$_2$-FeO ternary slag. As seen in this figure, replacing MgO, AlO$_{1.5}$ or CaF$_2$ with FeO at a fixed CaO/SiO$_2$ mole ratio raises $C_{S^{2-}}$ significantly.

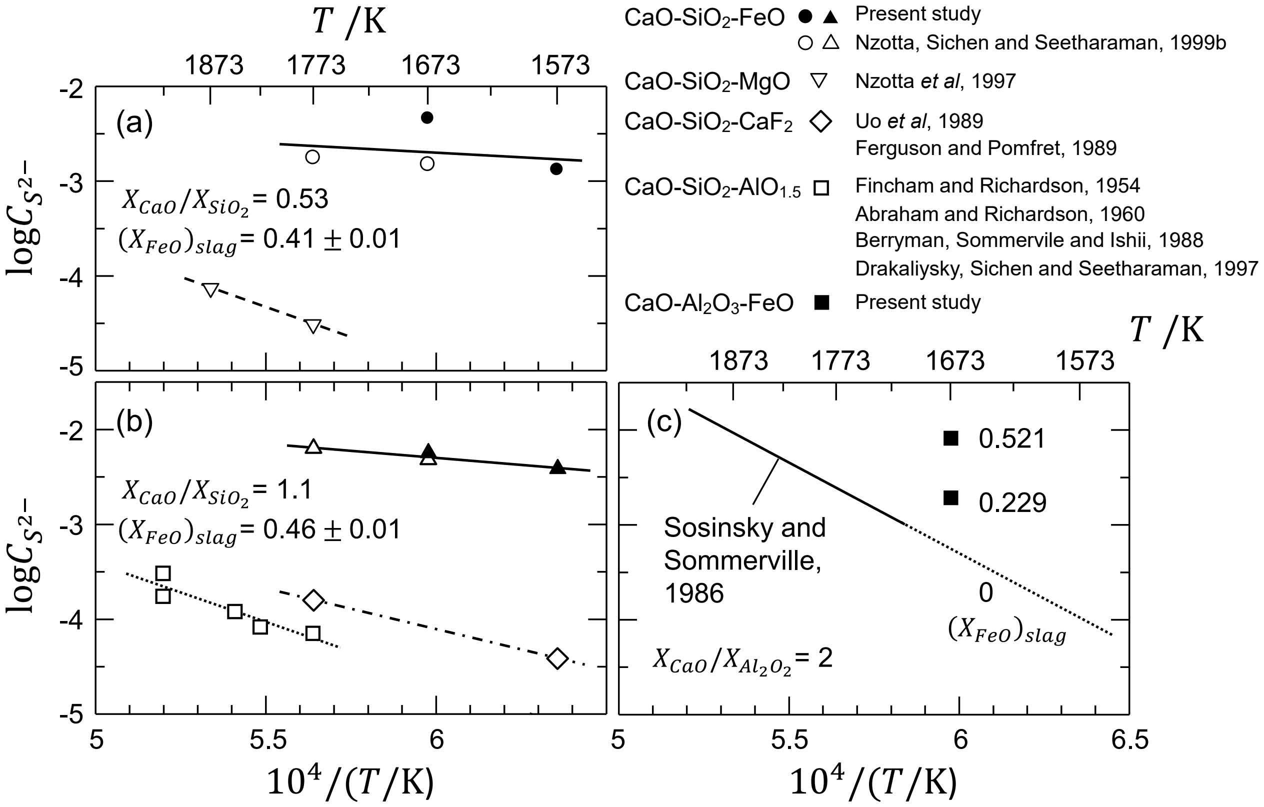

FIG 6 – Logarithmic value of sulphide capacity plotted against reciprocal temperature.

Figure 5c shows that $\log C_{S^{2-}}$ increased with an increase in $(X_{FeO})_{slag}$ in CaO-Al$_2$O$_3$-FeO slag at 1573 K. Figure 6c illustrates the present measured values for $\log C_{S^{2-}}$ with the literature data on CaO-Al$_2$O$_3$ binary system (Sosinsky and Sommerville, 1986). At 1573 K, CaO-Al$_2$O$_3$ binary oxide of $X_{CaO}/X_{Al_2O_3} = 2$ does not melt, while CaO-Al$_2$O$_3$-FeO ternary slag becomes homogeneous liquid with higher sulphide capacity than that of CaO-Al$_2$O$_3$ binary slag.

The reaction of iron between slag and Cu-Fe-S liquid alloy is formulated as

$$[\mathrm{Fe}]_{\mathrm{Cu}} + (1/2)\ \mathrm{O_2(gas)} = (\mathrm{FeO})_{\mathrm{slag}} \qquad (44)$$

$$K(44) = \frac{(a_{FeO})_{slag}}{[\gamma_{Fe}]_{Cu} \cdot [X_{Fe}]_{Cu} \cdot {P_{O_2}}^{1/2}} \qquad (45)$$

$$\log K(44) = -2.20 + 11750/(T/\mathrm{K}) \quad \text{(Iwase, Yamada, Ichise and Akizuki, 1984)} \quad (46)$$

The standard states of Fe in Cu-Fe-S liquid alloy and FeO in slag are taken to be pure solid iron and pure non-stoichiometric liquid FeO coexisting with pure solid iron. The value for $(a_{FeO})_{slag}$ can be calculated from Equations (41), (42), (45) and (46) with the measured values for $[X_{Fe}]_{Cu}$, $[X_S]_{Cu}$ and P_{O_2}. The experimental results are listed in Table 1, and the relation between $(a_{FeO})_{slag}$ and $(X_{FeO})_{slag}$ is illustrated in Figures 5d, 5e and 5f with the activity curves reported in the literatures (Ogura *et al*, 1992; Saito, Oshima and Hasegawa, 2021); the present results are not inconsistent with the literature data.

Sulphur distribution ratio between slag and hot metal

In this section, the distribution ratios of sulphur between slag and hot metal, L_S, were calculated from the experimental results of $C_{S^{2-}}$ and $(a_{FeO})_{slag}$. When the standard states of a_{Fe} and $(a_{FeO})_{slag}$

are taken as pure liquid iron and pure non-stoichiometric liquid FeO, the equilibrium constant of Reaction (6) is given as (Iwase, Yamada, Ichise and Akizuki, 1984; Kubaschewski, Alcock and Spencer, 1993)

$$\log K(6) = -2.59 + 12470/(T/\mathrm{K}) \quad (47)$$

Assuming that hot metal is Fe-C-S liquid alloy, a_{Fe} obeys Raoult's law and $[f_S]_{Fe}$ does not depend on $[\%S]_{Fe}$ due to low sulphur concentration, a_{Fe} and $[f_S]_{Fe}$ can be formulated as follows.

$$a_{Fe} = 1 - [X_C]_{Fe} - [X_S]_{Fe} \quad (48)$$

$$\log[f_S]_{Fe} = e_S^C[\%C]_{Fe} \quad (49)$$

$[X_i]_{Fe}$ and $[\%i]_{Fe}$ represent the mole fraction and mass content of *i* in Fe-C-S liquid alloy, respectively. Thus, the value for L_S can be obtained inserting Equations (47) through (49) into Equation (10) with the measured data on $C_{S^{2-}}$ and $(a_{FeO})_{slag}$. The calculation results are listed in Table 1 and shown in Figures 5g, 5h and 5i. In both of CaO-SiO_2-FeO and CaO-Al_2O_3-FeO ternary slags, L_S increased with an increase in $(X_{FeO})_{slag}$. These results mean that the effect of increasing $C_{S^{2-}}$ by adding iron oxide would be greater than the effect of increasing $(a_{FeO})_{slag}$.

Figure 7 shows the comparisons of L_S for CaO-SiO_2-FeO and CaO-SiO_2-CaF_2 ternary slags which occur at homogeneous liquid at 1573 K. The solid triangle for the CaO-SiO_2-FeO system indicates L_S when P_{O_2} is fixed by FeO in slag and Fe in hot metal. On the other hand, the open rhombus for the CaO-SiO_2-CaF_2 system gives L_S at P_{O_2} fixed by C in hot metal and CO gas of 1 atm. As seen in this figure, the value for L_S for CaO-SiO_2-FeO slag is lower than that for CaO-SiO_2-CaF_2 slag, because $C_{S^{2-}}$ of CaO-SiO_2-FeO slag is 2 orders of magnitude larger than $C_{S^{2-}}$ of CaO-SiO_2-CaF_2 slag (see Figure 6), but P_{O_2} fixed by FeO + Fe is more than 5 orders of magnitude larger than P_{O_2} fixed by C + CO.

The oxygen partial pressure between slag and hot metal in the practical operation is considered to take values between the Fe/FeO equilibrium and the C/CO equilibrium and is here assumed to be $\log(P_{O_2}\,/\,\mathrm{atm}) \fallingdotseq -13$ based on the study by Negishi *et al* (Negishi *et al*, 2023). In Figure 7, L_S for the CaO-SiO_2-FeO ternary system at $\log(P_{O_2}\,/\,\mathrm{atm}) = -13$ is shown by an open triangle and is almost equal to L_S for the CaO-SiO_2-CaF_2 ternary system. It is noteworthy that the relationship between $\log L_S$ and $\log P_{O_2}$ is linear with a slope of (–1/2) considering Equation (10).

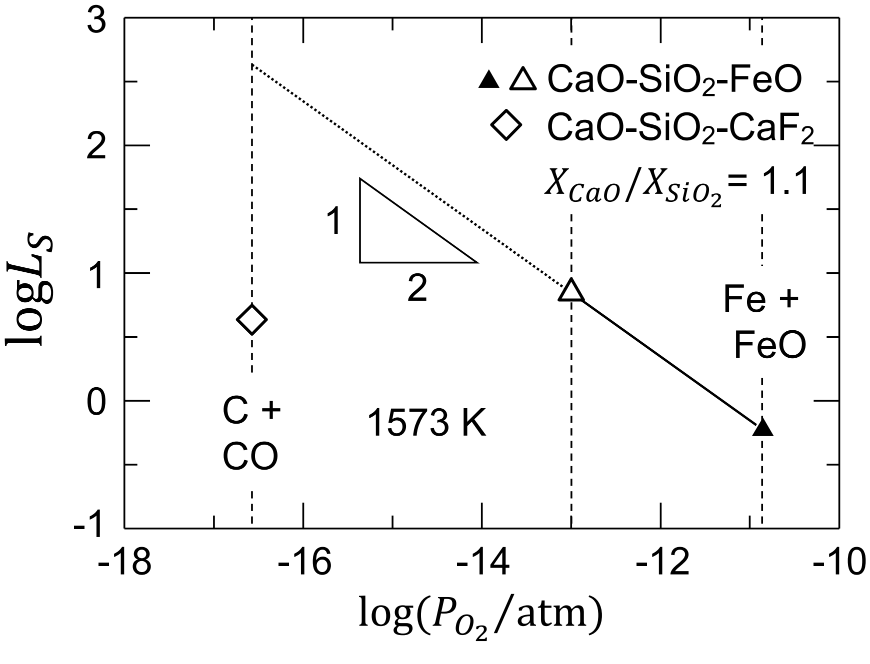

FIG 7 – Relation between $\log C_{S^{2-}}$ and $\log P_{O_2}$ at 1573 K.

CONCLUSIONS

For better understanding of re-sulfurization reaction in hot metal pre-treatments, the present study aimed at evaluating the effect of iron oxide on the sulphur distribution ratio between slag and hot metal by measuring sulphide capacities and FeO activities in the CaO-SiO_2-FeO and CaO-Al_2O_3-FeO ternary slags simultaneously at 1573 K and 1673 K. The activity coefficients of components were also determined in Cu-Fe-S liquid alloy used as a reference metal. The results are summarized as follows.

The Herian activity coefficient of sulphur in Cu-Fe-S liquid alloy decreased with an increase in iron content. This indicated that the chemical affinity between iron and sulphur would be stronger than that between copper and sulphur.

The trend that the sulphide capacities in the CaO-SiO_2-FeO and CaO-Al_2O_3-FeO ternary slags increased with an increase in FeO content was consistent with the fact that FeO was a basic oxide.

The value for sulphide capacity of the CaO-SiO_2-FeO system was significantly larger than those of the CaO-SiO_2-MgO, CaO-SiO_2-$AlO_{1.5}$ and CaO-SiO_2-CaF_2 ternary systems.

At 1573 K, CaO-Al_2O_3-FeO ternary slag becomes homogeneous liquid with higher sulphide capacity than that of CaO-Al_2O_3 binary slag.

Although the addition of FeO raised the FeO activities in the CaO-SiO_2-FeO and CaO-Al_2O_3-FeO ternary slags, the calculated sulphur distribution ratios increased with increasing FeO content.

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