The Study on Sulfur and Nickel Distribution Behavior of Nickel between Fe-Ni alloy and MgO-FeO-SiO$_2$ Slag System

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Abstract: The dissolution behavior of nickel in the MgO-SiO$_2$-FeO slag system was investigated by using the thermodynamic equilibrium technique. Nickel distribution ratio between molten MgO-SiO$_2$-FeO slag and molten Fe-Ni alloy at 1773 K and 1873 K was measured to understand the dissolution mechanism of nickel into the slags. The dependence of oxygen partial pressure and basicity on the distribution of nickel was investigated. Nickel distribution behavior between slag and Fe-Ni alloy increased with higher oxygen partial pressure showing a dependence of 1/2. For basic slag systems near the olivine saturated composition, the nickel distribution ratio increased with higher basicity showing a slope of 1 and for acidic slag systems near the cristobalite saturated composition, the nickel distribution ratio decreased with higher basicity showing a slope of -1. Thus dissolution behavior of nickel in the MgO-SiO$_2$-FeO slag system showed two independent mechanisms similar to that found in the CaO-SiO$_2$-CaF$_2$ system.

The distribution ratio of sulfur between the (CaO)-MgO-FeO-SiO$_2$ slag and Fe-Ni alloy at high temperature was also investigated to understand the refining ability of Ferronickel smelting slag by chemical equilibrating technique. The experimental results indicated that sulfide capacity in terms of the slag composition of MgO-FeO-SiO$_2$ slag and temperature was increased with increasing FeO and CaO contents as well as temperature. And FeO is considered to work as relatively basic component in this slag system that has low basicity. Comparing the effect of components of slag on sulfide capacity, CaO and FeO is considered to be more effective basic oxide than MgO in MgO-FeO-SiO$_2$ slag system while the effect of FeO on sulfide capacity was gradually retarded with increasing CaO. The effect of CaO on MgO solubility of slag and the relationship between sulfide and Ni oxide capacities was also discussed.

Keywords: nickel distribution ratio, basicity, amphoteric behavior, sulfide capacity

1. Introduction

Global extensive use of stainless and specialty steels leads to the supply shortage of nickel ore causing an increase in production coast, which is the main alloying element used to produce stainless and special steels. This increase in nickel ore prices, may make utilizing low grade nickel ores such as laterlite and saprolite a coast alternative to high grade nickel ores such as pentlandite [1]. The Ni content in laterite and saprolite is about 1.5 to 3.2 percent, which results in the slag volume from Ni smelting reduction process to be 25- 35 times that of carbon steel processes. Core technology of Fe-Ni smelting is smelting reduction process between slag and melt in EAF. Therefore, thermodynamic approach for the behavior of Ni and sulfur is essential to ensuring process efficiency and maximizing Ni yield and decreasing impurity like sulfur.

Work done by Pagador *et al.*[2] studied the distribution behavior of minor elements between the nickel based alloy and MgO saturated FeO_x–MgO–SiO_2 or FeO_x–CaO–MgO–SiO_2 slag at 1773 K and 1873 K with controlled oxygen partial pressure ranging from 1025 Pa to 1021 Pa to obtain fundamental information related to nickel smelting. It was found that the values of cobalt distribution ratio between the MgO saturated FeO_x–MgO–SiO_2 slag and Ni–Fe alloy at 1773K are lower than unity and shift downwards with increasing temperature. Jeffes *et al.*[3] reported the effect of temperature between 1623 K and 1723 K in FeO-SiO_2 binary slag system equilibrated by Cu-Ni alloy, and the distribution ratio of Ni and Cu increased with higher FeO content in slag. Nagamori *et al.*[4] evaluated the iso-solubility of Ni in FeO-Fe_2O_3-SiO_2 slag system at 1473 K. The solubility of nickel was proportional to oxygen partial pressure, and the solubility of nickel remarkably increased with higher content of magnetite for Fe/SiO_2=1.97. Yazawa *et al.*[5] measured the distribution ratio of nickel with equilibrating Cu-Ni-Fe alloy and FeO_X-CaO-SiO_2 slags. The distribution ratio showed a u shaped characteristic with increasing C/S (CaO/SiO_2) and a minimum value at C/S=2.

Sulfur removal in iron-making and steel-making process is now of even more importance than in the past because of the increasing demand for extremely clean steels. In order to understand the desulfurization phenomena and process control, it is important that the sulfide capacities of slags are well known. To achieve this, a number of sulfide capacity measurements have been carried out earlier. Since most steelmaking slags contain certain amount of FeO, knowledge of the sulfide capacities of FeO containing slags is valuable to metallurgical industry. However, very few experimental studies have been carried out for the FeO containing slag systems due to the experimental difficulties. For low sulfide capacity of Fe-Ni smelting slag, additional desulfurization process is required. Considering large slag volume of the process and plausibility of maximizing desulfurization efficiency by enhancing sulfide capacity of slag, it is necessary to understand thermodynamic equilibrium of slag and molten metal in EAF in terms of process optimization.

Nzotta *et al.*[6] measured the sulfide capacity with equilibrating gas and FeO-SiO_2 slag or CaO-FeO slag. In this study, amphoteric activity of FeO by basicity is confirmed thus FeO acts as basic oxide and affinity between Fe^{2+} and sulfur is verified. Turkdogan *et al.*[7] reported relationship between sulfide capacity and acidic oxides concentration in terms of ionic theory. Nzotta *et al.*[8] measured the sulfide capacity with equilibrating gas and FeO-SiO_2-(CaO)-(MgO) slag at 1673 K ~ 1923 K. Shim *et al.*[9] measured the distribution ratio of sulfur with equilibrating Fe and CaO-MgO-Fe_tO-SiO_2 slag at 1823 K ~ 1973 K. Sulfide capacity was dominated by basicity and amphoteric FeO. Seo *et al.*[10] reported sulfide capacity of CaO-MgO-SiO_2–Al_2O_3-FeO slag at 1773 K was increased with additive content of FeO.

Although much work has already been done, the slag systems were too limited to adapt the result to low grade nickel ore refining. Therefore, in this study, the dissolution mechanism of nickel and sulfur, the effect of FeO and basicity were redefined in the MgO-SiO_2-FeO slag system typical of low grade ore range at 1873 K.

2. Experimental

A Tamman furnace(Fig. 1) with a C-type(W-5 mass% Re/ W-26 mass% Re) thermocouple was used for the equilibration of a Fe-20 mass% Ni alloy and (CaO)-MgO-SiO_2-FeO slag melts. A proportional integral differential (PID) controller was used to maintain the temperature within 2 K. Regent grade chemicals of MgO, SiO_2 and FeO were uniformly mixed with an agate mortar. The mixed powder were charged in the Pt crucible and pre-melted in the induction furnace under an Ar gas atmosphere for 3 hours. The composition of pre-melted slags was confirmed by using the XRF. Reagent grade chemical of Ni (Kanto chemical, purity=99.9%) and Fe (Kanto chemical, purity=99.9%) were mixed with a ratio of 1:4 and melted by a induction furnace under Ar(purity=99.9999%) . After homogenizing for 3 hours, the alloy was quenched and analyzed by XRF (X-Ray Fluorescence Spectroscopy). The composition was identical before and after melting. 5g of Fe-20 mass% Ni alloy and 3g of slag were charged into magnesia and silica crucible (14 mm-OD, 10 mm-ID and 40 mm-L). The reaction tube was sufficiently purged with Ar gas before each experiment, and maintained at a flow rate of 400 sccm during the experiment. The partial pressure of oxygen (p_{O2}) was fixed by Fe-FeO equilibrium [11] at the slag/metal interface previously mentioned lay equation (1) to (2).

$$\mathrm{Fe(l)} + \frac{1}{2}\mathrm{O_2(g)} = \mathrm{FeO(l)} \tag{1}$$

$$p_{\mathrm{O_2}} = \left(\frac{a_{\mathrm{FeO}}}{\mathrm{K}\cdot a_{\mathrm{Fe}}}\right)^2 \tag{2}$$

where a_{i} is the activity of component i. The activity of Fe (a_{Fe}) in the Fe-Ni alloy was reported by Belton *et al.* [12] and the activity of FeO (a_{FeO})in the slag was calculated by using the regular solution model after Ban-Ya *et al.* [13]. The crucible containing the slag and metal was placed within an alumina holder to prevent damage in the case of slag leakage and equilibrated. All gases were purified by passing through calcium sulfate, soda lime, silica gel and magnesium turnings at 753K. After the equilibration experiment, the crucible was quenched with Ar flow. The sample was removed from the crucible, and the slag and metal was crushed separately. Ni in the metal was analyzed by AAS (Atomic Absorption Spectroscopy, Shimadzu, AA-6601 F/G) and each component in the slag was analyzed by XRF

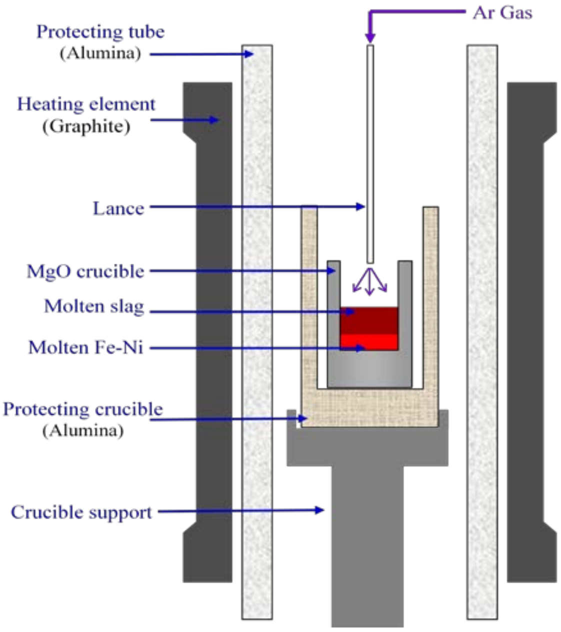

Fig .1 Experimental apparatus

3. Results and discussion

3.1 Distribution ratio of Ni

The relationship between the distribution ratio of Ni and (wt.%MgO/wt.%SiO_2) ratio is represented in Fig.2. As shown in Fig.2, L_{Ni} decreases with increased (wt.%MgO/wt.%SiO_2) ratio under SiO_2 saturated condition. This is due to the existence of Ni as a Ni^{2+} ion in a SiO_2 saturated system. Thus, L_{Ni} decreases with increased of MgO/SiO_2 ratio. On the other hand, L_{Ni} increases with increased MgO/SiO_2 ratio due to the existence of Ni as NiO_2^{2-} in MgO saturated system.

Fig.3 shows the relationship between the distribution ratio of Ni and FeO concentration. The distribution ratio of Ni increases with increased FeO concentration, regardless of MgO or SiO_2 saturated conditions. As shown from the dissolution mechanism, both reaction mechanism has the same proportional tendency to the oxygen potential.

Consequently, the dissolution reaction of Ni into MgO-SiO_2-FeO melts has a different behavior dependent upon the saturated condition and each mechanism could be constructed as follows:

$$\mathrm{Ni} + \frac{1}{2}\mathrm{O_2(g)} + \mathrm{O^{2-}} = \mathrm{NiO_2^{2-}(slag)} \qquad \text{(Olivine saturated)} \qquad (3)$$

$$\mathrm{Ni} + \frac{1}{2}\mathrm{O_2(g)} = \mathrm{NiO_2^{2-}(slag)} + \mathrm{O^{2-}(slag)} \qquad (\mathrm{SiO_2}\ \text{saturated}) \qquad (4)$$

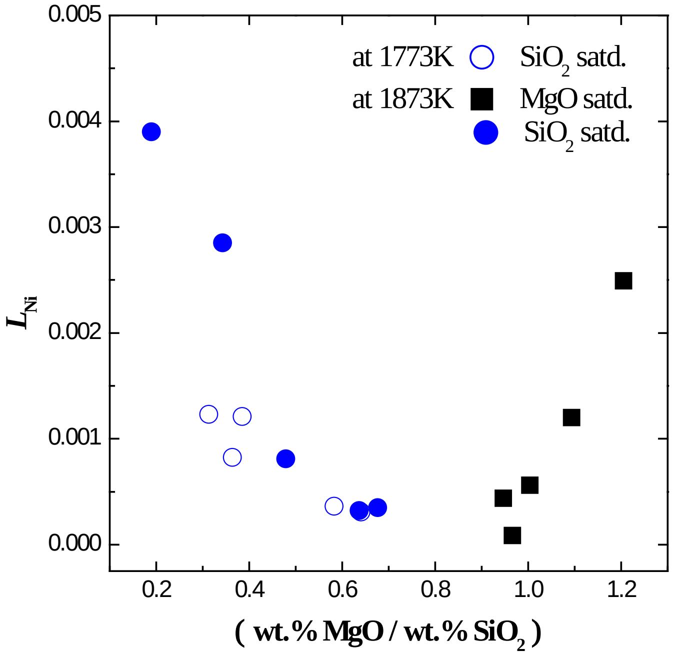

Fig.2 Effect of wt.%MgO/wt.%SiO_2 on the Ni distribution.

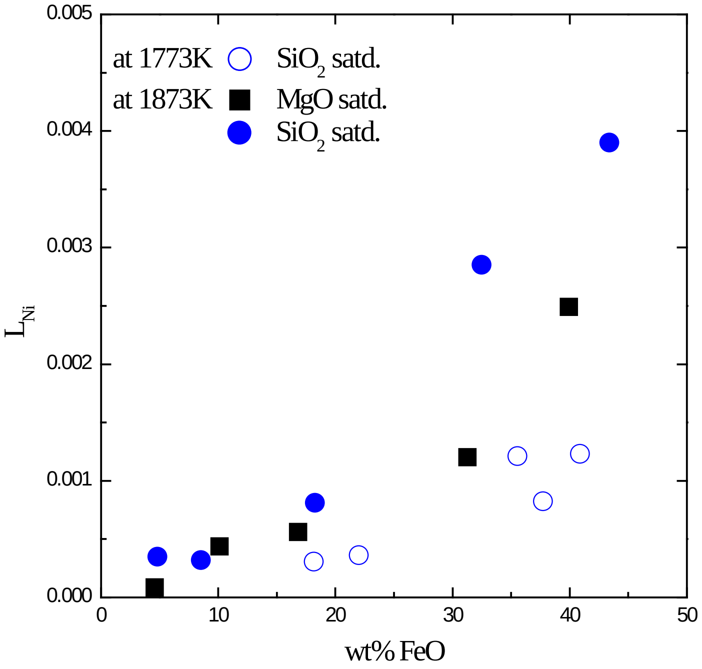

Fig.3 Effect of FeO content on the Ni distribution.

3.2 Sulfide capacity

Sulfur in slag would be stabilized in the form of sulfide in steelmaking process and the following expression.

$$[S] + (O^{2-}) = (S^{2-}) + \frac{1}{2}O_2 \tag{5}$$

$$L_S = \frac{(wt\%S^{2-})}{[wt\%S]} = \frac{C_S \cdot f_{[S]}}{a_{[O]}} = \frac{K_S \cdot f_S \cdot a_{(O^{2-})}}{p_{O_2}^{\frac{1}{2}} \cdot f_{(S^{2-})}} \tag{6}$$

$$C_{S^{2-}} = \frac{K_{(5)} \cdot a_{O^{2-}}}{f_{S^{2-}}} = \frac{(\%S^{2-})}{[\%S] \cdot f_S} \cdot p_{O_2}^{\frac{1}{2}} \tag{7}$$

where $K(5)$ is the equilibrium constant of Eq. (5), $a_O{}^{2}-$ and $f_S{}^{2}-$ are, respectively, the activity of free $O^{2}-$ and the activity coefficient of $S^{2}-$ ions in slag, and p_{O2} is the partial pressure of oxygen.

Fig.4 shows the relationship between the distribution ratio of sulfur and FeO concentration. Sulfur distribution ratio in terms of the slag composition of MgO-FeO-SiO_2 slag was increased with increasing FeO. The concentration of free oxygen ion increases due to substitution of MgO by FeO under acidic conditions. And FeO is considered to work as relatively basic component in this slag system that has low basicity. Comparing the effect of components of slag on sulfide capacity, FeO is considered to be more effective basic oxide than MgO in MgO-FeO-SiO_2 slag system.

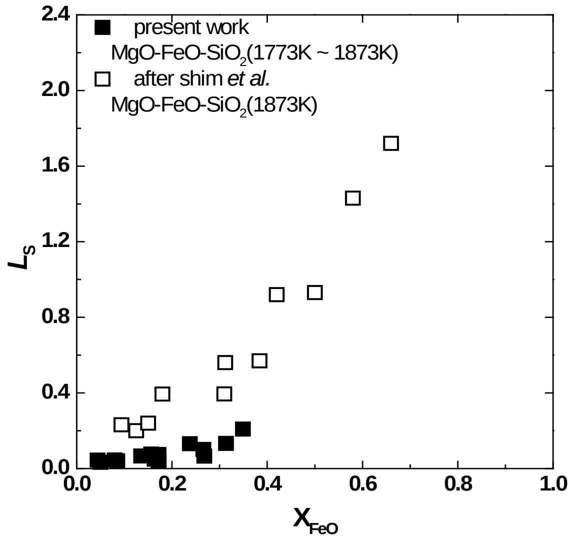

Fig.4 Effect of FeO content on the Sulfur distribution ratio [9]

Fig.5 shows the relationship between the sulfide capacity and CaO concentration. The experimental results indicated that sulfide capacity in terms of the slag composition of CaO-MgO-FeO-SiO_2 slag was increased with increasing CaO contents as well as FeO contents. Comparing the effect of components of slag on sulfide capacity, CaO and FeO is considered to be more effective basic oxide than MgO in MgO-FeO-SiO_2 slag system while the effect of FeO on sulfide capacity was gradually retarded with increasing CaO. The relative contributions of oxides to sulfide capacity can be estimated by consideration of the equilibrium constants of specific MO/MS equilibria. Selected values of CaO/CaS, FeO/FeS, and MgO/MgS equilibria are shown in the following expression.

$$\mathrm{FeO(S)} + \frac{1}{2}\mathrm{S_2} = \mathrm{FeS(S)} + \frac{1}{2}\mathrm{O_2} \qquad \mathrm{K} = 3.16 \times 10^3 \tag{8}$$

$$\mathrm{MgO(S)} + \frac{1}{2}\mathrm{S_2} = \mathrm{MgS(S)} + \frac{1}{2}\mathrm{O_2} \qquad \mathrm{K} = 0.0162 \times 10^3 \tag{9}$$

$$\mathrm{CaO(S)} + \frac{1}{2}\mathrm{S_2} = \mathrm{CaS(S)} + \frac{1}{2}\mathrm{O_2} \qquad \mathrm{K} = 2.67 \times 10^3 \tag{10}$$

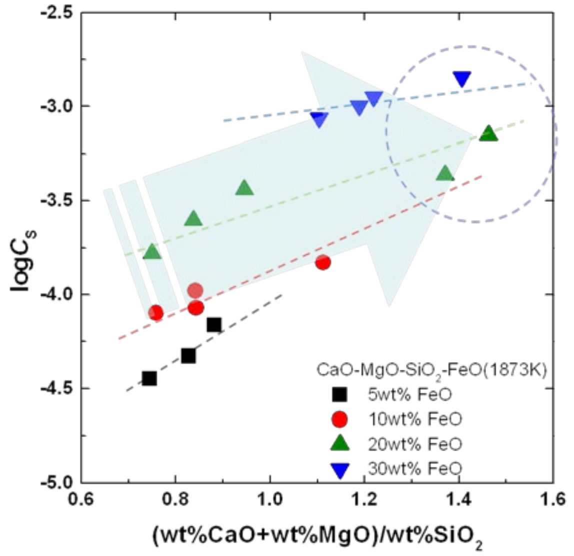

Fig.5 Effect of CaO content on the sulfide capacity

4. Conclusions

Ni yield and desulfurization of ferronickel smelting slag has been measured by chemical analysis. In this study is performed the investigation on the effect of oxygen potential and basicity on the distribution of nickel. Furthermore, the effect of FeO and CaO contents on the sulfide capacity is investigated to derive optimization operating conditions of Ni yield at ferro-nickel smelting reduction process. And the thermodynamic behavior was able to derive the following results.

1. The present researches have been carried out to understand the dissolution mechanism of nickel in the MgO-SiO_2-FeO slag system.

Basic Region: $\mathrm{Ni} + \frac{1}{2}\mathrm{O_2(g)} + \mathrm{O^{2-}} = \mathrm{NiO_2^{2-}(slag)}$ (M/S>0.54)

$$\mathrm{C_{NiO_2^{2-}}} = \mathrm{L_{Ni}} \cdot \frac{1}{\gamma_{\mathrm{Ni}} \cdot p_{\mathrm{O_2}}^{1/2}}$$

Acidic Region: $\mathrm{Ni} + \frac{1}{2}\mathrm{O_2(g)} = \mathrm{NiO_2^{2-}(slag)} + \mathrm{O^{2-}(slag)}$ (M/S<0.54)

$$\mathrm{C_{Ni^{2+}}} = \mathrm{L_{Ni}} \cdot \frac{1}{\gamma_{\mathrm{Ni}} \cdot p_{\mathrm{O_2}}^{1/2}}$$

2. Relatively, in lower basicity region, the distribution ratio of sulfur increases with additive content of FeO. And sulfide capacity also increases with additive CaO. Affinity between Ca and S is much stronger than that between Mg and S.

References

[1] B. Terry. Extractive Metallurgy of nickel. *John Wiley & Sons*,1987, 21(2), p8-50.

[2] R. U. Pagador, M. Hino, K. Itaki. Distribution of minor elements between MgO saturated FeO_x-MgO-SiO_2 or FeO_x-CaO-MgO-SiO_2 slag and nickel alloy. *Material Transaction*, 1999, 40(3), p225-232.

[3] J. H. E. Jeffes, J. R. Taylor. *Institution of Mining and Metallurgy*, 1975, p136-148.

[4] M. Nagamori. Oxidic dissolution of nickel in fayalite slag and thermodynamics of continuous converting of nickel-copper matte. *Metallurgical Transactions*, 1974, 5, p539-549.

[5] A. Yazawa, Y. Takada, S. Kanesaka. Equilibria between FeO_x-CaO-SiO_2 slag and liquid Cu-Ni-Fe alloy. *25th Annual Conference of Metallurgists*, 1986, p185-202.

[6] M. M. Nzotta, Du Sichen, S. Seetharaman. Sulphide Capacities of "FeO”- SiO_2, CaO-"FeO", and "FeO"-MnO Slags. *ISIJ Int*, 1999, 39(7), p.657-663.

[7] E. T. Turkdogan. *JISI*, 1952, 171, p64.

[8] M. M. Nzotta, Du Sichen, S. Seetharaman. A Study of the Sulfide Capacities of Iron-Oxide Containing Slags. *Metall. Mater. Trans. B*, 1999, 30B, p909-920.

[9] J. D. Shim, S. Ban-Ya. Equilibria of Sulfur between Liquid Iron and Fe_tO-SiO_2-CaO-MgO Slags Saturated with MgO. *Tetsu to Hagane*, 1982, 68(2), p251-260.

[10] J. D. Seo, S. H. Kim. The Sulfide capacity of CaO-SiO_2-Al_2O_3-MgO(-FeO) smelting slags. *steel research international*, 1999, 70(6), p203-208.

[11] E. T. Turkdogan. Physical Chemistry of High Temperature Technology., 1980(New York), Academic Press, p1-24.

[12] G. B. Belton, R. J. Fruehan. The Determination of Activities by Mass Spectrometry. I. The Liquid Metallic Systems Iron-Nickel and Iron-Cobalt. *J. Phys. Chem*, 1967, 71(5), p1403-1409.

[13] S. Ban-YA. Mathematical Expression of Slag-Metal Reactions in Steelmaking Process by Quadratic Formalism Based on the Regular Solution Model. *ISIJ Int*, 1993, 33(1), p2-11.