Thermodynamic Study on MnO behavior in MgO-saturated Slag containing FeO

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ABSTRACT

In order to understand the behavior of manganese oxide in smelting reduction process, the manganese equilibrium between ironmaking slag containing FeO and silver melt was investigated over the temperature range of 1400-1500℃. The oxygen partial pressure was controlled by CO/CO_2 ratio. Test results on Mn content in silver have been thermodynamically converted into those in supercooled or carbon-saturated iron melts and the activity coefficient of MnO in slag was determined experimentally. The activity of MnO decreased with increasing FeO content in slag. Higher FeO content as well as lower slag basicity resulted in larger equilibrium manganese distribution ratio between slag and iron. The temperature dependence of equilibrium manganese distribution was determined in the temperature range of 1400-1500℃. The relative partial molar heats of solution of MnO and Mn were also experimentally determined.

1. INTRODUCTION

Manganese not only plays an important role in steelmaking process as a deoxidizer but is widely used as an alloying element to affect the mechanical properties of steels. Manganese in steel can reduce the grainboundary embrittlement caused by sulfur and enhance the mechanical properties such as hardenability, strength, hardness and toughness[1]. Manganese is also added in stainless steelmaking process for replacing Ni to stabilize austenitic stainless steel[2].

Presently the manganese content in steel is controlled by addition of ferromanganese into ladle after BOF process. As Fe-Mn is a relatively expensive alloy and its addition causes temperature drop of molten steel, the direct addition of less expensive manganese ore is desirable in the processes of blast furnace, hot metal pretreatment process and BOF. While Mn content of hot metal from a blast furnace process range 0.3 to 0.4%, its content in steel decreases down to 0.1-0.15% due to oxidation loss during hot metal pretreatment and BOF process. The smelting reduction of Mn ore in the processes of hot metal pretreatment or BOF would result in a higher Mn content in steels and save Fe-Mn addition is ladle. For smelting reduction of Mn ore in hot metal pretreatment of BOF process it is necessary to understand the operating and thermodynamic conditions of respective iron and steelmaking processes, as well as the behavior of MnO in slag.

The slag compositions of smelting reduction process are quite different from those of conventional blast furnace processes, previous work on the thermodynamic study of MnO containing slag and the system parameters affecting the reduction reaction of MnO has not been performed sufficiently. The activity measurement of MnO and the interaction of slag components in the $CaO-SiO_2-MnO$ system have been reported to some extent[3-5]. However, no published literature was found for the study on the MgO saturated $CaO-SiO_2-MnO-FeO$ system, which is essential in both hot-metal pretreatment and steelmaking processes. In this study, the thermodynamic behavior of MnO and the role of FeO in the reaction of MnO reduction are discussed in detail. The effects of oxygen potential, temperature, chemical compositions of slags on the equilibrium manganese distribution between slag and iron are also investigated.

2. THERMODYNAMIC BACKGROUND

Using iron melt to study the manganese distribution between slag and metal results in experimental difficulties such as higher working temperature, longer reaction time and variation of carbon content by CO/CO_2 gas mixture. Silver melt instead has merits of lower melting point and insoluble property into both iron and slag. Thermodynamically, it is possible to convert the experimentally measured equilibrium Mn content in Ag to the equilibrium Mn content in supercooled liquid Fe. The activities of MnO and FeO in slag can be determined by measuring the equilibrium Mn content in Ag using a reaction system of electrolytic iron, silver and slag at a fixed oxygen potential.

$$MnO(s) = Mn(l) + 1/2O_2(g) \qquad (1)$$
$$\Delta G° = 97{,}360 - 21.12T(cal/mol)^{2}$$

$$FeO(l) = Fe(s) + 1/2O_2(g) \qquad (2)$$
$$\Delta G° = 57{,}900 - 11.01T(cal/mol)^{6}$$

$$a_{MnO} = \frac{a_{Mn} \cdot p_{O_2}^{1/2}}{K_{(1)}} = \frac{\gamma_{Mn} \cdot X_{Mn} \cdot p_{O_2}^{1/2}}{K_{(1)}} \qquad (3)$$

$$a_{FeO} = \frac{a_{Fe} \cdot p_{O_2}^{1/2}}{K_{(2)}} = \frac{p_{O_2}^{1/2}}{K_{(2)}} \qquad (4)$$

Mn activity coefficient in Ag, γ_{Mn} can be determined by measuring Mn content in Ag at equilibrium between pure solid MnO and Ag. The simultaneous equilibrium among silver, supercooled liquid iron, and pure solid MnO leads to the equality of manganese chemical potential between Ag and supercooled liquid Fe. The manganese activity in Ag becomes the same as that in supercooled liquid Fe for the identical standard state.

$$a_{Mn(in\ Fe)} = a_{Mn(in\ Ag)} \qquad (5)$$

$$X_{Mn(in\ Fe)} = X_{Mn(in\ Ag)} \cdot \frac{\gamma^{\circ}_{Mn(in\ Ag)}}{\gamma^{\circ}_{Mn(in\ Fe)}} \qquad (6)$$

where X_{Mn} represents a mole fraction of Mn in binary solutions. Using Eq. (6), the equilibrium Mn concentration in Fe can be determined from the experimentally measured equilibrium Mn concentration in Ag. The reported value of Raoultian activity coefficien0 of Mn at infinite dilution in Fe, γ°_{Mn} is 1.3 at 1600℃[7]. γ°_{Mn} at other temperatures may be calculated assuming a regular solution model for Fe-Mn solution in the dilute range of Mn concentration.

$$\ln\gamma^{\circ}_{Mn}(T_1) = (T_1/T_2) \cdot \ln\gamma^{\circ}_{Mn}(T_2) \qquad (7)$$

3. EXPERIMENTAL

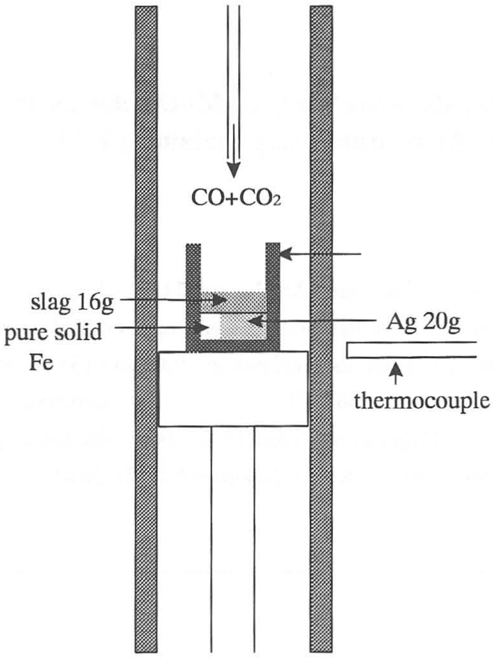

Fig. 1 Schematic diagram of experimental apparatus.

Schematic diagram of experimental apparatus is shown in Fig. 1. The vertical type of SiC resistant electric furnace was employed as a reactor equipped with a mullite tube(ID 60mm). The reaction experiments with Ag, Fe and slag were carried out over the temperature range of 1400-1500℃. The reaction temperature was controlled within ± 2℃ with the aid of a PID controller. The reagent grades of slag components were uniformly mixed by agatar mortar. The $CaCO_3$ was calcinated for 2hr at 1000℃.

A cylinder (8mmϕ, 14mmL) of electrolytic iron weighing 5.5g and Ag chips weighing 20g along with slag powder of 16g were charged into a MgO crucible(25 mm ID and 50 mm L). The slag powder was charged into the crucible so as to cover the two metals. The oxygen partial pressure was controlled by the mixing ratio of CO to CO_2. The purified gas mixture was blown with the total flow rate of 500ml/min using a gas mixing pump(DIGAMIX 2M200) in order to regulate an accurate mixing ratio of CO/CO_2 gases. The flow of Ar gas was maintained before influxing a mixture of CO/CO_2 from the top of the reactor. After the equilibrium of reaction was attained, the crucible was withdrawn and quenched in Ar atmosphere. The compositions of slag samples(CaO, SiO_2, Al_2O_3, MnO, MgO) were determined by the X-ray fluorescent method. The manganese contents in metal sample and FeO in slag sample were determined by the atomic absorption method.

4. RESULTS AND DISCUSSION

4.1 Mn Activity Coefficient in Ag

20g of Ag and a disk type of MnO weighing 3g were charged into a MgO crucible and held at 1450℃ for 24hr under CO/CO_2 atmosphere with p_{O_2} of 1.63×10^{-9}atm. Mn content in Ag after the experimental was analyzed and a value of 4.32×10^{-4} in terms of mole fraction was obtained.

$$\gamma^{\circ}_{Mn} = \frac{K_{(1)}}{X_{Mn}\cdot p_{O_2}^{1/2}} \qquad (8)$$

Substituting the equilibrium Mn content into Eq. (8), the Raoultian activity coefficient of Mn at infinite dilution in Ag was determined as 0.527 at 1450℃.

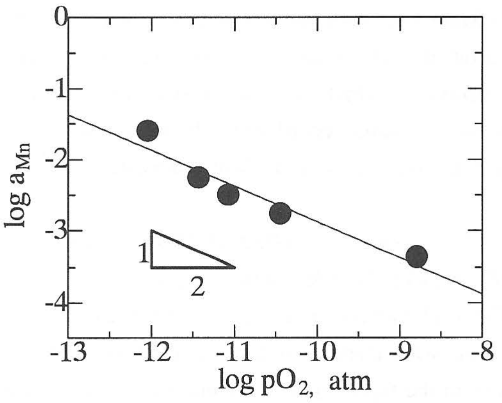

Fig. 2 The relationship between Mn activity in liquid Ag equilibrium with pure solid MnO and oxygen partial pressures at 1723K.

The activity of Mn, a_{Mn} was obtained from the Mn content assuming the constant value of γ°_{Mn}=0.527. The oxygen partial pressure was varied from 3.72×10^{-12} to 1.63×10^{-9}atm. Fig. 3 shows the dependence of manganese activity in Ag on oxygen partial pressure. The slope of the line in Fig. 2 estimated as -0.52 by regression is in good agreement with the theoretical value -0.5 from Eq. (3). This result indicates that manganese in slag exists as Mn^{2+} and the reaction (1) reaches equilibrium within 24hr.

4.2 MnO Reduction

Slag containing CaO, SiO_2, Al_2O_3, MnO weighing 20g and Cu weighing 10g were held at 1500℃ in a MgO crucible under the oxygen partial pressure of 2.71×10^{-12} atm.

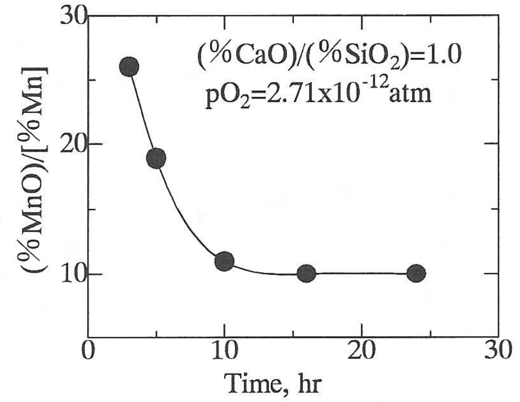

Fig. 3 Variation of manganese distribution between CaO-SiO_2-Al_2O_3(10%)-MnO(5%)-$MgO_{sat.}$(17%) and Cu melt with respect to reaction times at 1773K.

The results in Fig. 3 indicated that equilibrium was reached in about 18hr. Cu was chosen instead of Ag, since Ag has lower melting point and is was chosen for the study to be sure to reach equilibrium.

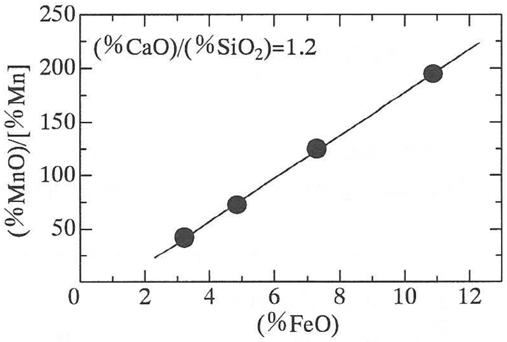

Fig. 4 Equilibrium manganese distribution between CaO-SiO_2-Al_2O_3-MnO(5%)-FeO(3-11%)-$MgO_{sat.}$ and molten iron as a function of FeO content at 1723K.

The effect of FeO content in slag on the equilibrium Mn distribution between slag and molten iron in Fig. 4 indicated that the Mn distribution increases with FeO content in slag in linear relationship. The oxygen potential was changed from 9.1×10^{-13} to 3.6×10^{-11} atm according to the variation of FeO content in slag. The equilibrium Mn distribution increases with FeO content, resulting in a less efficient MnO reduction at a higher FeO content.

$$\underline{Mn} + (FeO) = (MnO) + Fe \qquad (9)$$

$$\frac{X_{MnO}}{X_{Mn}} = K_{(9)} \cdot \gamma_{Mn} \cdot \frac{\gamma_{FeO}}{\gamma_{MnO}} \cdot X_{FeO} \tag{10}$$

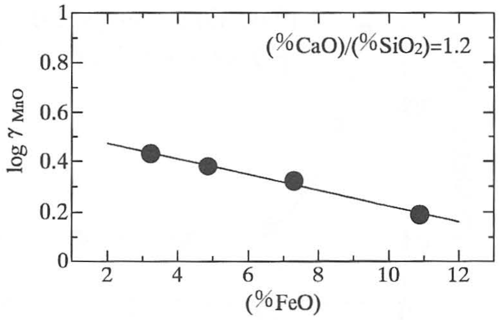

Fig. 5 Variation of activity coefficients of MnO in CaO-SiO_2-Al_2O_3-MnO(5%)-FeO(3-11%)-$MgO_{sat.}$ as a func-tion of FeO content at 1723K.

The value of γ_{Mn} in Eq. (10) is the same as that of γ°_{Mn} as the Mn content in molten iron is in the Henrian range. The results in Fig. 4, a linear relationship between MnO/Mn and FeO, indicate a constant value of $\gamma_{FeO} / \gamma_{MnO}$ range. As shown in Fig. 5, when FeO content in slag decreases from 3 to 11%, the activity coefficient of MnO decreases from 2.7 to 1.5 is an indicator of the interaction parameter.

$$\varepsilon^{(FeO)}_{MnO} = \frac{\partial \ln \gamma_{MnO}}{\partial X_{FeO}} \tag{11}$$

The negative value of the interaction parameter indicates that FeO in this slag system acts as an acidic component.

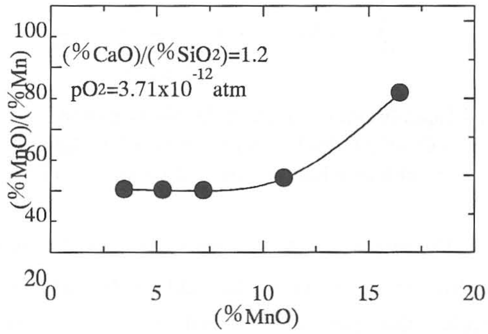

Fig. 6 Equilibrium manganese distribution between CaO-SiO_2-Al_2O_3(10%)-MnO(3-16%)-FeO(10%)-$MgO_{sat.}$ and molten iron as a function of MnO content at 1723K.

As shown in Fig. 6, the Mn distribution does not change up to 12% but increases above 12% over the MnO concentration range investigated at a fixed oxygen partial pressure of 3.7×10^{-12}atm.

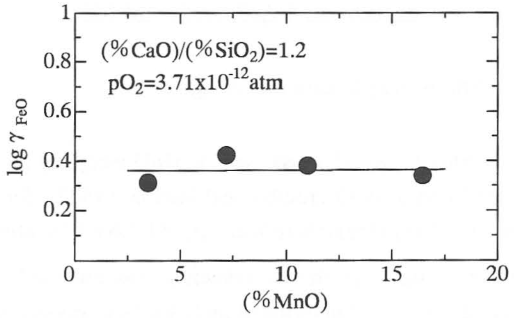

Fig. 7 Variation of activity coefficients of FeO in CaO-SiO_2-Al_2O_3(10%)-MnO(3-16%)-FeO(10%)-$MgO_{sat.}$ as a funtion of MnO content at 1723K.

$$K_{(1)} = \frac{\gamma_{Mn} \cdot X_{Mn} \cdot p_{O_2}^{1/2}}{\gamma_{MnO} \cdot X_{MnO}} \tag{12}$$

Noting that γ_{Mn} is a constant in dilute solution range, the activity coefficient of MnO shows a constant value up to 12% MnO, but drops down beyong 12% MnO content. This indicates that the amount of MnO reduction increases in proportion to MnO content in slag, but the reduction efficiency of MnO according to the more addition into the slag starts to decrease at the MnO concentration of 12%.

Fig. 7 shows the effect of MnO content on activity coefficient of FeO under the same experimental condition as in Fig.6. The activity coefficient of FeO tends to be nearly constant with respect to the variation of MnO content. Based on the Eq. (10), it is evident that the equilibrium Mn distribution represents a constant value at a fixed concentration of FeO because the ratio of $\gamma_{FeO} / \gamma_{MnO}$ does not change with increasing MnO content up to 12%. This finding confirms thermodynamically that the manganese distribution is independent of MnO content over the given concentration range. The inconsistency of the interaction parameters obtained from the results in Figs. 5 and 7 seems to arise from the effects of the variation of the concentration of the other slag constituents.

The effects of basicity index, (CaO+0.3 MgO)/SiO_2 on the equilibrium manganese distribution may be seen in Fig. 8. Since the equilibrium manganese quotient decreases with increasing basicity at a fixed oxygen potential, the ratio of $\gamma_{FeO} / \gamma_{MnO}$ will also decrease according to Eq. (10).

The temperature dependence of equilibrium Mn

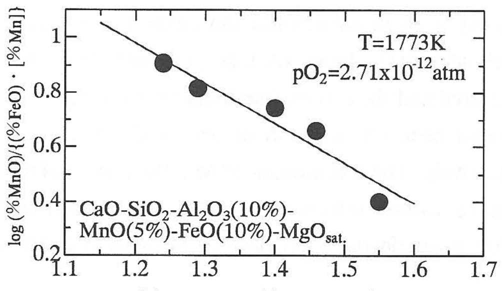

Fig. 8 Relationship between the equilibrium Mn quotient and the slag basicity, $(\%\mathrm{CaO} + 0.3\%\mathrm{MgO})/(\%\mathrm{SiO_2})$.

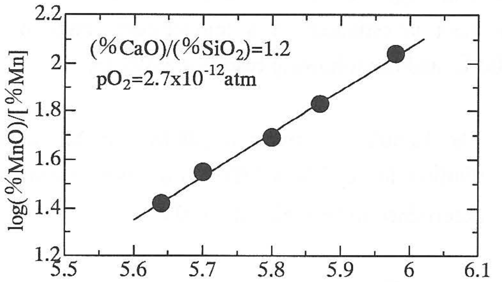

Fig. 9 Temperature dependence of manganese distribution ratio between $\mathrm{CaO\text{-}SiO_2\text{-}Al_2O_3(10\%)\text{-}MnO(5\%)\text{-}FeO(10\%)\text{-}MgO_{sat.}}$ and molten iron.

distribution at the oxygen partial pressure of 2.7×10^{-12}atm is shown in Fig. 9. The equilibrium Mn distribution decreases with increasing temperature as expressed by Eq. (13):

$$\log\frac{(\%\mathrm{MnO})}{[\%\mathrm{Mn}]} = \frac{18040}{\mathrm{T}} - 8.76 \qquad (13)$$

Although experiments were carried out over the temperature range from 1400 to 1500℃, it can be reasonably extrapolated up to 1600℃ to estimate the equilibrium Mn distribution for the identical slag system. The partial molar heats of solution of Mn in Fe-Mn and MnO in this slag system can be estimated from the relation between partial molar Gibbs free energy and activity for a specified component.

$$\mathrm{Mn(l)} = \underline{\mathrm{Mn}}$$

$$\log a_{\mathrm{Mn}} = \frac{\Delta\overline{\mathrm{H}}_{\mathrm{Mn}}}{2.303\mathrm{RT}} - \frac{\Delta\overline{\mathrm{S}}_{\mathrm{Mn}}}{2.303\mathrm{R}} \qquad (14)$$

$$\mathrm{MnO(s)} = (\mathrm{MnO})$$

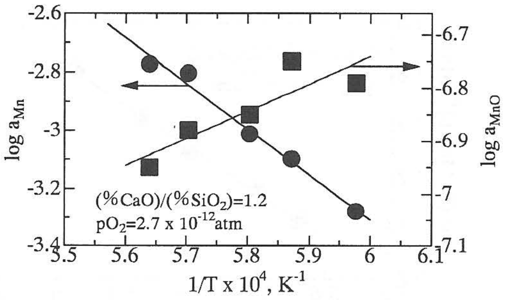

Fig. 10 Temperature dependence of Mn and MnO activities in molten iron and $\mathrm{CaO\text{-}SiO_2\text{-}Al_2O_3(10\%)\text{-}MnO(5\%)\text{-}FeO(10\%)\text{-}MgO_{sat.}}$

$$\log a_{\mathrm{MnO}} = \frac{\Delta\overline{\mathrm{H}}_{\mathrm{MnO}}}{2.303\mathrm{RT}} - \frac{\Delta\overline{\mathrm{S}}_{\mathrm{MnO}}}{2.303\mathrm{R}} \qquad (15)$$

where $\Delta\overline{\mathrm{H}}_i$ and $\Delta\overline{\mathrm{S}}_i$ are the partial molar heat and entropy of solution for species i, respectively. The value of $\log a_i$ is expressed by a linear function of the reciprocal of the absolute temperature for the given metal or slag compositions and the slope gives a relative partial molar heat of solution of i. The activity of manganese oxide and Mn were plotted as a function of temperature in Fig. 10. From the values of slopes, it can be obtained that the relative partial molar heats of solution of MnO and Mn are 115.1 kJ/mol(27.4 kcal/mol) and -300.3 kJ/mol(-71.5 kcal/mol), respectively.

4.3 Carging Amount of Mn oxide

The activity coefficient of Mn in carbon saturated iron at other temperatures was also estimated using a regular solution model with the value of activity coefficient, 0.51, which was determined at 1300℃ by Sano et al[8]. From the similar formula like Eq. (6), the equilibrium Mn concentration in carbon saturated iron can be determined based on the manganese equilibrium Mn content in Ag.

Fig. 11 shows the temperature dependence of equilibrium Mn distribution at $p_{O_2}=2.7\times10^{-12}$ atm. The results can be expressed by the Eq. (16).

$$\log\frac{(\%\mathrm{MnO})}{[\%\mathrm{Mn}]} = \frac{17400}{\mathrm{T}} - 8.78 \qquad (16)$$

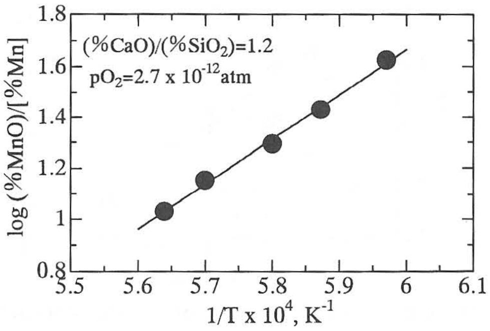

Fig. 11 Temperature dependence of manganese distribution ratio between CaO-SiO$_2$-Al$_2$O$_3$(10%)-MnO(5%) -FeO(10%)-MgO$_{sat.}$ and carbon saturated iron.

The charging amount of Mn oxide can be predicted for a given equilibrium Mn content in carbon saturated iron in terms of mass balance between slag and metal. Under the conditions of the smelting reduction process employing the same slag system as in this study at 1550℃, the relation between the charging amount of manganese oxide and the equilibrium Mn content in carbon saturated iron was derived for the system comprising 1 ton of metal and 100kg of slag.

$$W_{MnO}(kg) = 1000([\%Mn]/100) \times (70.94/54.94) + 100(5.82[\%Mn]/100) \qquad (17)$$

On the other hand, the following Eq. (18) can be derived to determine the charging amount of MnO for a given equilibrium Mn content in carbon free iron at 1550℃ by extrapolating Eq. (13).

$$W_{MnO}(kg) = 1000([\%Mn]/100) \times (70.94/54.94) + 100(13.8[\%Mn]/100) \qquad (18)$$

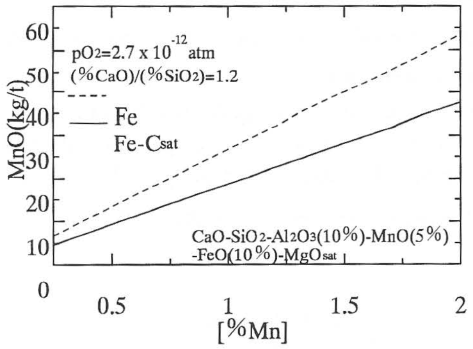

Fig. 12 The amount of MnO required to achieve a given equilibrium Mn content in Fe-C$_{sat}$ and pure Fe for the smelting reduction of MnO at 1823K.

Fig. 12 shows the amount of Mn oxide required to achieve a given equilibrium Mn content in Fe-C$_{sat.}$ and Fe melts at 1550℃ based on Eqs. (17) and (18). The carbon saturated and the carbon free irons with 1% equilibrium Mn content need the addition of Mn oxide of 18 and 26kg, repectively. The less amount of Mn oxide is required for the case of carbon saturated iron, because carbon in Fe-Mn solution can decrease the value of Mn activity coefficient.

5. CONCLUSION

Manganese equilibrium distribution between molten iron and MgO saturated CaO-SiO$_2$-Al$_2$O$_3$-FeO-MnO slag has been investigated in a temperature range of 1400-1500℃ and the following results are obtained.

(1) The Raoultian activity coefficient of Mn at infinite dilution in Ag-Mn solution γ°_{Mn} was experimentally determined to be 0.527 at 1450℃.

(2) The equilibrium manganese distribution increases with increasing FeO content. However, it does not change with the variation of MnO content up to 12% but increases beyond 12%. The reduction efficiency of MnO with the more addition into the slag starts to decrease at the MnO content of 12%.

(3) The value of manganese equilibrium distribution decreases with increasing basicity. Experimental results indicate that FeO acts as an acidic oxide in the slag system investigated.

(4) Temperature dependence of equilibrium manganese distribution at p_{O_2}=2.7×10^{-12}atm in the temperature range of 1400 to 1500℃ can be expressed as follows:

for supercooled liquid irons,

$$\log\frac{(\%MnO)}{[\%Mn]} = \frac{18040}{T} - 8.76$$

for carbon saturated irons,

$$\log\frac{(\%MnO)}{[\%Mn]} = \frac{17400}{T} - 8.78$$

These expressions can reasonably predict the charging amount of Mn oxide required for a given Mn content through extrapolation.

REFERENCES

1. W. H. Cubberly et al, ″ Machining Characteristics of Steels″ , Metals Handbook Vol. 1, American Society for Metals, Metals Park, Ohio, 1978, pp. 565-585.

2. H. E. McGannon et al, ″ Stainless Steels″ , The making, Shaping and Treating of Steel , Association of Iron and Steel Engineers, Pittsburgh, Pennsylvania, 1985, pp. 1333-1362.

3. A. Muan and E. F. Osborn, ″ Four-Component Systems″ , Phase Equilibrium among Oxides in Steelmaking, Addison-Wesley, Massachusettes, 1965, pp. 103-142.

4. N. Tiberg and A. Muan, ″ Activity-Composition Relations at 1100℃ in the System Calcium Oxide-Iron Oxide-Manganese Oxide in Contact with Metallic Iron″ , Metall. Trans., Vol. 1, 1970, pp. 435-439.

5. S. Uchida, F. Tsukihashi, and N. Sano, ″ The Phase Relations of the CaO-MnO-SiO_2 system in Connection with the Smelting Reduction of Manganese Ore″ , Tetsu-to-Hagane, Vol. 77, 1991, pp. 490-495.

6. E. T. Turkdogan, ″ Selected Thermodynamic Functions″ , Physical Chemistry of High Temperature Technology, Academic Press, New York, NY, 1980, pp. 1-26.

7. E. T. Turkdogan, ″ Physicochemical Properties of Metals and Alloys″ , Physical Chemistry of High Temperature Technology, Academic Press, New York, NY, 1980, pp. 60-129.

8. S. Simeonov and N. Sano, ″ Manganese Equilibrium Distribution between Carbon-saturated Iron Melts and Lime Based Slags Containing MnO, BaO, and Na_2O″ , Trans. ISIJ, Vol. 25, 1985, pp. 1116-1121.