Thermodynamic Study on Redox Equilibrium of Manganese in $\text{CaO-SiO}_2\text{-Mn}_t\text{O-MgO}_{\text{sat}}$.

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Experiments were carried out to determine the ratio of $\text{Mn}^{3+}/\text{Mn}^{2+}$ at equilibrium in $\text{CaO-SiO}_2\text{-Mn}_t\text{O-MgO}$ slag under various slag compositions and oxygen partial pressures in temperature range of 1350~1450°C. As magnesia crucibles were used, the solubility limit of MgO could also be determined. Results indicate that the $\text{Mn}^{3+}/\text{Mn}^{2+}$ ratio increases with slag basicity as well as with Mn_tO content. The solubility of MgO , on the other hand, decreases as the slag basicity increases and also with increasing Mn_tO content. The ratio $(\%\text{Mn}^{3+})/(\%\text{Mn}^{2+})$ does not change in the oxygen partial pressure between 10^{-12}atm and 10^{-6}atm . At the constant oxygen partial pressure, the value of $\log(\%\text{Mn}^{3+})/(\%\text{Mn}^{2+})$ does not change with the slag basicity less than 0.9. On the other hand, the value of $\log(\%\text{Mn}^{3+})/(\%\text{Mn}^{2+})$ decreases with increasing basicity of slag more than 0.9. Although there is small deviation in the value of $\log(\%\text{Mn}^{3+})/(\%\text{Mn}^{2+})$, the value does not change in the slag composition containing more than 16% Mn_tO . Temperature dependence of the ratio $(\%\text{Mn}^{3+})/(\%\text{Mn}^{2+})$ at $5.1 \times 10^{-9}\text{atm}$ in the temperature range of 1350 to 1450°C can be expressed as follows. From the expression, the reaction enthalpy was calculated to be -75kcal/mol.

$$\log \frac{(\%\text{Mn}^{3+})}{(\%\text{Mn}^{2+})} = \frac{1.64 \times 10^4}{T} - 12.3$$

Keywords : *Manganese, smelting reduction, redox equilibrium, slags, basicity, oxidation state*

I. 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 grain boundary 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 and BOF. While Mn content of hot metal from a blast furnace process ranges 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 in ladle. For smelting reduction of Mn ore in hot metal pretreatment process or 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. A lot of researches on the smelting reduction of Mn ore has been made all over the world.

A lot of papers and technological reports has been published about the thermodynamic behavior of Mn oxide in slags. The majority of the papers mainly deal with measurement of the manganese distribution ratio between slag and metal and the activity coefficient of Mn oxide in slags. Not any researchers place an emphasis on the oxidized

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state of Mn ion in slags. So in this research, the authors wanted to know how Mn ions would change in the valence state with oxygen partial pressure, slag compositions, and temperature.

II. Theoretical background

1. Redox equilibrium of Mn ion in slag

The oxidation-reduction reaction in oxide melt can be formulated like Eq.(1), as has been accepted widely up to now. When x is a positive integer larger than 1, $\text{MnO}_x^{(2x-3)-}$ designates the complex ion between manganic ion (Mn^{3+}) and oxygen ion (O^{2-}) in Eq.(1). On the other hand, when x is a negative integer smaller than -1, Eq.(1) can be simplified to Eq.(2).

where $\text{MnO}_x^{(2x-3)-}$: complex ion

$$K_{(3-1)} = \frac{a_{\text{MnO}_x^{(2x-3)-}}}{a_{\text{Mn}^{2+}} \cdot p_{\text{O}_2}^{1/4} \cdot a_{\text{O}^{2-}}^{(x-\frac{1}{2})}} \quad (3)$$

$$\log \frac{(\% \text{Mn}^{3+})}{(\% \text{Mn}^{2+})} = (x - \frac{1}{2}) \log a_{\text{O}^{2-}} + \frac{1}{4} \log p_{\text{O}_2} + \log \frac{f_{\text{Mn}^{2+}}}{f_{\text{MnO}_x^{(2x-3)-}}} + C \quad (4)$$

$$\log \frac{(\% \text{Mn}^{3+})}{(\% \text{Mn}^{2+})} = (x - \frac{1}{2}) \log a_{\text{O}^{2-}} + \frac{1}{4} \log p_{\text{O}_2} + \log \frac{f_{\text{Mn}^{2+}}}{f_{\text{Mn}^{3+}}} + C \quad (5)$$

Since the difference of manganic ion cannot be made by ionic species in chemical analysis, $(\% \text{MnO}_x^{(2x-3)-})$ is usually replaced by $(\% \text{Mn}^{3+})$. Therefore, $(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$ is denoted by Eq.(4) at constant temperature. Here C is a constant value which contains the equilibrium constant of Eq.(1). According to Eq.(4), in case of x larger than 1, manganic ion Mn^{3+} forms complex ion. The ratio $(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$ increases with the activity of oxygen ion in slag, which is an indicator of basicity and increases with oxygen partial pressure as shown in Eq.(2). If the values $\log(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$ are plotted over $\log p_{\text{O}_2}$, the slope should be 1/4 according to Eq.(4). When Mn ions exist in the form of free manganic free

cations, the activity coefficient of Mn anion complexes $f_{\text{MnO}_x^{(2x-3)-}}$ in Eq.(4) will be replaced by $f_{\text{Mn}^{3+}}$ as shown in Eq.(5). Contrary to Eq.(4), for Eq.(5) the ratio $(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$ decreases with increasing the oxygen activity. Combination of Eq.(1) and Eq.(2) results in Eq.(6), which indicates that will form anion complexes, $(\% \text{MnO}_x^{(2x-3)-})$ in basic slags where free oxygen ions are provided sufficiently and the manganic ions Mn^{3+} are favored in acidic slags. This indicates that Mn_2O_3 is an amphoteric oxide.

2. Activity coefficient of Mn oxide in slag

Equilibrium of manganese between copper-manganese alloys and slag containing MnO can be expressed by Eq.(7), with the equilibrium constant $K_{(7)}$. The activity coefficient of MnO in slag can be expressed by Eq.(9).

$$\Delta G^\circ = -95,840 + 20.14 T \text{ [cal/mol] } \quad (4)$$

$$K_{(7)} = \frac{a_{\text{MnO}(\text{s})}}{a_{\text{Mn}(\text{l})} \cdot p_{\text{O}_2}^{1/2}} \quad (8)$$

$$\gamma_{\text{MnO}} = \frac{K_{(7)} \cdot \gamma_{\text{Mn}}^\circ \cdot X_{\text{Mn}} \cdot p_{\text{O}_2}^{1/2}}{X_{\text{MnO}}} \quad (9)$$

Here a_{MnO} is the activity of MnO with reference to solid MnO, X_{Mn} the mole fraction of manganese in copper-manganese alloys, and γ_{Mn} the activity coefficient of Mn in copper. The activity coefficients of manganese in copper in the temperature range between 1350°C and 1450°C were calculated using the activity coefficient of manganese in copper at 1300°C measured by Hultgren and Desai⁽⁵⁾, assuming that Cu-Mn alloy forms a regular solution. The activity coefficients of Mn in Cu at other temperatures can be calculated through the constant $RT \ln \gamma$.

III. Experimental

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 experiment between Cu and slag was carried out over the temperature range of 1350–1450°C. The reaction temperature was controlled within $\pm 2^\circ\text{C}$ with the aid of a PID controller. The reagent grades of slag components

Fig. 1 Schematic diagram of experimental apparatus.

Fig. 2 The variation of $\log[(\%Mn^{3+})/(\%Mn^{2+})]$ and $(\%MnO)/[\%Mn]$ between $CaO-SiO_2-MnO-MgO_{sat}$ and Cu melt with respect to reaction times at $1400^\circ C$.

were uniformly mixed by agatar mortar. The $CaCO_3$ was calcinated for 2 hours at $1,000^\circ C$. Cu chips weighing 10g along with slag powder of 6g were charged into a MgO crucible (18mm ID and 45mm L). 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 200ml/min using a gas mixing pump (DIGAMIX 2M200). After the equilibrium of reaction was attained, the crucible was withdrawn and quenched in argon atmosphere, followed by water quenching. The compositions of slag samples (CaO, SiO_2, MnO, MgO) were

determined by the X-ray fluorescent method. The analysis of $(\%Mn^{3+})$ were carried out using ortho-phenanthroline absorption spectroscopy where the slag samples are dissolved into oxygen free HCl solution to which some amount of iron (II) ammonium sulfate solution is added under Ar flow. The manganese contents in metal sample was determined by the atomic absorption method.

IV. Results and Discussion

Slags containing CaO, SiO_2, MnO weighing 6g and Cu weighing 10g were held at $1400^\circ C$ in a MgO crucible under the oxygen partial pressure of 5.12×10^{-9} atm. Although the redox equilibrium of Mn ion in slag reached in 4 hours as shown in Fig. 2. The Mn distribution ratio between slag and metal took 12 hours to reach equilibrium. Therefore, the equilibrium time was determined to be 12 hours in this experiment.

The effect of oxygen partial pressure on the ratio $(\%Mn^{3+})/(\%Mn^{2+})$ may be seen in Fig. 3. The slope of this graph was expected to be 0.25. But the slope of the graph in this experiment is 0.017 and the ratio $(\%Mn^{3+})/(\%Mn^{2+})$ does not change in the oxygen partial pressure between 10^{-12} and 10^{-6} atm. This result is compared with the slope measured by Tamura and Sano⁽³⁾ in slag $CaO-SiO_2-MnO$ at the oxygen partial pressure between 10^{-2} and 1atm. The theoretical value of the slope, 0.25 in the graph between $\log[(\%Mn^{3+})/(\%Mn^{2+})]$ and oxygen partial pressure can be obtained under the assumption that the activity coefficients of manganous cation Mn^{2+} and anion complex $MnO_x^{(2x-3)-}$ does not change with oxygen partial pressure⁽⁶⁾. In the Mn^{3+}/Mn^{2+} equilibrium, the linearity with a slope of 0.25 was reported in the range of $\log P_{O_2} = -4 \sim 0$ in the field of glass chemistry⁽⁷⁾. The result in Fig.3 can be explained by the possibility that the value of $\log(fMn^{2+}/fMnO_x^{(2x-3)-})$ can decrease with increasing oxygen partial pressure in the very low oxygen partial pressure between 10^{-12} and 10^{-6} atm.

The results in Fig. 4 indicate that the saturated solubility of MgO decreases with increasing the basicity of slag defined by the ratio $(\%CaO)/(\%SiO_2)$ in the slag containing about 25% MnO. When the value of the basicity of slag increases from 0.6 to 1.4, the saturated solubility of MgO decreases from 14 to 3%. This indicates that MgO behaves as a strong basic oxide in the slag.

Fig. 3 Dependence of the ratio $(\%Mn^{3+})/(\%Mn^{2+})$ on the partial pressure of oxygen in $CaO-SiO_2-25\%MnO-8.5\%MgO_{sat}$ at $1400^\circ C$.

Fig. 5 Dependence of the ratio $(\%Mn^{3+})/(\%Mn^{2+})$ on basicity $(\%CaO)/(\%SiO_2)$ in $CaO-SiO_2-MnO-MgO_{sat}$ at $1400^\circ C$.

Fig. 4 Change of $(\%MgO)_{sat}$ as a function of $(\%CaO)/(\%SiO_2)$ in $CaO-SiO_2-25\%MnO-MgO_{sat}$ at $1400^\circ C$.

The change of $\log(\%Mn^{3+})/(\%Mn^{2+})$ is plotted as a function of the basicity of slag. At the constant oxygen partial pressure, the value of $\log(\%Mn^{3+})/(\%Mn^{2+})$ does not change with the slag basicity less than 0.9. This result can be explained by the exchange reaction between manganic cations and manganic anion complexes using the principle applied in the redox equilibrium between ferric and ferrous ions⁽⁸⁾.

Fig. 6 Dependence of the activity coefficient of MnO on basicity $(\%CaO)/(\%SiO_2)$ in $CaO-SiO_2-25\%MnO-MgO_{sat}$ at $1400^\circ C$.

Because there are not enough oxygen ions available to make the following reactions below reach the equilibrium state in the basicity region of slag less than 0.9. It is thought that the total amount of manganic cations which can be analyzed is constant.

On the other hand, since the oxygen ions are provided sufficiently for the reactions above and x is a negative value in the basicity region of slag more than 0.9, manganic and manganous equilibrium is accomplished according to Eq.(2). That is, since the sufficient supply of oxygen ions makes the reaction of Eq.(2) proceed to the left, it is thought that the value of $\log(\%Mn^{3+})/(\%Mn^{2+})$ decreases with increasing the basicity of slag more than 0.9. From this experimental result, it can be concluded that the reduction of manganic ion into manganous ion is promoted in the basicity of slag more than at least 0.9.

The results in Fig. 6 indicate that the activity coefficient of MnO increases from 0.25 to 1.5 when the basicity of slag increases from 0.6 to 1.4 at the given experimental conditions. Therefore, it can be concluded that MnO behaves as a basic oxide in the slag of this experiment. From the results in Fig. 5, in the basicity region of more than 0.9, that is, in the region where x of Eq.(5) is a negative value, the decrease in the value of $(x-1/2)\log a_{O^{2-}}$ overwhelms the increase of the activity coefficient of MnO. This result supports the experimental result in Fig. 5 that as the basicity of slag increases, the activity coefficient of manganous cations increases and the activity coefficient of manganic cations decreases, which is caused by formation of manganic anion complexes.

Fig. 7 Change of $(\%MgO)_{sat}$ as a function of $(\%MnO)$ in $CaO-SiO_2-MnO-MgO_{sat}$ at $1400^\circ C$.

The results in Fig. 7 indicate that the saturated

solubility of MgO slightly decreases from 9.7 to 6.5% with increasing $(\%MnO)$ from 8 to 36% under the oxygen partial pressure, $5.12 \times 10^{-9} atm$ at $1400^\circ C$. As compared with the case in Fig. 4, the amount of the solubility decrease of MgO is not as large as that in Fig. 4 where $(\%CaO)/(\%SiO_2)$ changes as experimental variable. This indirectly indicates that CaO is more basic than MnO in this slag.

Fig. 8 Dependence of the ratio $(\%Mn^{3+})/(\%Mn^{2+})$ on $(\%MnO)$ in $CaO-SiO_2-MnO-MgO_{sat}$ at $1400^\circ C$.

Fig. 9 Dependence of the activity coefficient of MnO as a function of $(\%MnO)$ in $CaO-SiO_2-MnO-MgO_{sat}$ at $1400^\circ C$.

The graph in Fig. 8 indicates that the

concentration of Mn_2O in slag has influence on the value of $\log(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$. Although there is small deviation in the value of $\log(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$, the value does not change in the slag composition containing more than 16% Mn_2O . This experimental result may be explained by Fig. 9 which denote the change of the activity coefficient of MnO in terms of $(\% \text{Mn}_2\text{O})$. The activity coefficient of MnO greatly increases in the slag composition more than 16% Mn_2O . According to Eq.(5), the decrease of $\log a_{\text{O}_2}$ cancels out the increase of the activity coefficient of MnO by addition of basic oxide MnO in the slag composition where x is a negative value smaller than -1 . Therefore, the value of $\log(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$ almost remains unchanged in the slag containing more than 16% Mn_2O .

Fig. 10 Change of $(\% \text{MgO})_{\text{sat}}$ in the temperature range of 1350 to 1450°C in CaO-SiO_2 -(22~24% Mn_2O)- MgO_{sat} .

The results in Fig. 10 indicate that the measurement of the saturated solubility of MgO was carried out over the temperature range from 1350 to 1450°C under the given oxygen partial pressure, $5.1 \times 10^{-9} \text{ atm}$. When the temperature increases from 1350 to 1450°C, the MgO saturation increases from 5 to 11%. It is thought that this result is due to the increase of the slag fluidity accompanied by the temperature increase. The change in solubility of MgO results in the slight change of $(\% \text{Mn}_2\text{O})$ which is dilution effect by dissolution of MgO crucible into the slag.

Because the temperature dependence of redox equilibrium of Eq.(1) is denoted in the form of

Eq.(11), the reaction enthalpy of Eq.(1) can be calculated from the experimental results measured at various temperatures.

$$\frac{\partial \log(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})}{\partial (1/T)} = \frac{-\Delta H^\circ}{2.303R} + C'' \quad (11)$$

Fig. 11 Dependence of the ratio $(\% \text{Mn}^{3+})/(\% \text{Mn}^{2+})$ on temperature in CaO-SiO_2 -(22~24% Mn_2O)- MgO_{sat} .

Fig. 12 Change of the activity coefficient of MnO in the temperature range of 1375 to 1450°C in CaO-SiO_2 -(22~24% Mn_2O)- MgO_{sat} .

The results in Fig. 11 indicate that

$\log(\%Mn^{3+})/(\%Mn^{2+})$ slightly decreases with increasing temperature from 1375 to 1450°C at constant oxygen partial pressure and basicity. From the slope of the straight line given by the linear regression, the reaction enthalpy for Eq.(2) is calculated to be -314kJ/mol(=-75kcal/mol). That is, the heat energy of 314kJ is released when 1 mol of manganous cations are oxidized to 1 mol of manganic cations in the given slag. This value can be compared with the reaction enthalpy -230kJ/mol(=-55kcal/mol) measured by Johnston⁽⁹⁾ in $Na_2O \cdot 2SiO_2$ glass in the temperature range of 1000 to 1300°C.

The results in Fig. 12 indicate that the activity coefficient of MnO increases with temperature at the constant oxygen partial pressure. The increase of the activity coefficient of MnO is only due to the increase of the saturated solubility of MgO which behaves as a strong basic oxide in this slag.

V. Conclusions

The redox equilibrium between manganic and manganous cations in $CaO-SiO_2-Mn_2O-MgO_{sat}$ has been investigated in the temperature range of 1350~1450°C and the following results are obtained.

(1) The ratio $(\%Mn^{3+})/(\%Mn^{2+})$ does not change in the oxygen partial pressure between 10^{-12} and 10^{-6} atm. This result is compared with the slope measured by Tamura and Sano in slag $CaO-SiO_2-Mn_2O$ at the oxygen partial pressure between 10^{-2} and 1atm.

(2) At the constant oxygen partial pressure, the value of $\log(\%Mn^{3+})/(\%Mn^{2+})$ does not change with the slag basicity less than 0.9. On the other hand, the value of $\log(\%Mn^{3+})/(\%Mn^{2+})$ decreases with increasing basicity of slag more than 0.9.

(3) Although there is small deviation in the value of $\log(\%Mn^{3+})/(\%Mn^{2+})$, the value does not change in the slag composition containing more than 16% Mn_2O .

(4) Temperature dependence of the ratio $(\%Mn^{3+})/(\%Mn^{2+})$ at 5.1×10^{-9} atm in the temperature range of 1350 to 1450°C can be expressed as follows.

$$\log \frac{(\%Mn^{3+})}{(\%Mn^{2+})} = \frac{1.64 \times 10^4}{T} - 12.3$$

From this expression, the reaction enthalpy for Eq.(2) is calculated to be -314kJ/mol

(=-75kcal/mol).

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