Manganese Equilibrium between BaO–BaF₂–MnO Fluxes and Ferro-manganese Melts

X. LIU, O. WIJK,¹⁾ R. SELIN²⁾ and J. O. EDSTRÖM³⁾

Division of Process Metallurgy, Royal Institute of Technology, S-100 44 Stockholm, Sweden. 1) Department of Metallurgy, Royal Institute of Technology, S-100 44 Stockholm, Sweden. 2) AGA AB, Business Area Metallurgy, S-181 81 Lidingö, Sweden. 3) Professor Emeritus, Royal Institute of Technology, S-100 44 Stockholm, Sweden.

(Received on September 26, 1994; accepted in final form on December 16, 1994)

The equilibrium distribution ratio of manganese between BaO–BaF₂–MnO slag and Mn(62–73%)–Fe–C_{sat} melt has been determined at 1 573–1 673 K. The effects of slag composition, oxygen partial pressure and temperature on the manganese distribution ratio have been investigated.

The equilibrium manganese distribution ratio was found to increase with oxygen partial pressure and BaO content in the slags. Addition of BaF₂ to BaO–MnO slag provided a beneficial condition to cut down the losses of manganese and enabled to dephosphorize ferro-manganese at a relatively high oxygen partial pressure. At a certain oxygen partial pressure, the molar fraction ratio of BaO to MnO decreased with the increased BaO content in a slag equilibrated with carbon-saturated ferro-manganese.

A high temperature resulted in a low manganese distribution ratio. For a BaO(50%)–BaF₂(47%)–MnO(3%) slag, the effect of temperature on the manganese capacity can be expressed as:

$$\log C_{\text{Mn}^{2+}} = \frac{21\,670}{T} - 3.73$$

The heat of reaction

in the investigated temperature interval was estimated to be –415 kJ/mol.

KEY WORDS: thermodynamics; BaO-based slags; equilibrium manganese distribution; slag chemistry; ferro-manganese.

1. Introduction

With increasing demand for ultra low phosphorus steels with a high fracture toughness and low temperature applications, the removal of phosphorus from these steels or ferro-alloys is very important. Since ferro-manganese is virtually used in all steels to neutralize the harmful effects of sulfur, to alloy steel and to deoxidize, dephosphorization of ferro-manganese has recently been emphasized.^{1,2)} Experimental results so far have shown that CaO and Na₂O based fluxes are not suitable to remove phosphorus from hot metal containing high content of manganese due to their comparatively low refining capacity or evaporation at high temperature. It is also demonstrated that BaO-based flux is a promising reagent. For example, BaO–BaF₂ and BaO–MnO fluxes have been found to possess an extremely high phosphate capacity^{3,4)} at hot metal pretreatment temperature.

When using these reagents to dephosphorize, a high oxygen partial pressure at the interface of slag/metal is favorable. However, since manganese has a high affinity for oxygen, manganese in ferro-manganese will be

oxidized during the dephosphorization process. Besides causing manganese losses, an excessive high MnO content in slags would in general deteriorate the dephosphorization ability of the slags. Therefore, it is very important, from both technical and economical points of view, to diminish the losses of manganese.

Investigations have shown that fluorides in slags can significantly increase the activity coefficient of MnO.⁵⁾ For a BaO–BaF₂ slag containing a high amount MnO, there is very little information on the slag system and the manganese distribution ratio between slag and ferro-manganese. The purpose of the present work is to study the properties of BaO–BaF₂–MnO slag system and to determine the manganese distribution between slag and carbon-saturated ferro-manganese by studies of metal-slag equilibria at 1 573–1 673 K.

2. Experimental

The experimental apparatus was detailed in a previous report.⁶⁾ A vertical furnace tube of dense-sintered Al₂O₃ was heated by four MoSi₂ elements. A graphite crucible

(8% porosity, <0.1% ash) containing metal and slag was supported by a vertically movable cylindrical alumina casting.

Temperature was measured by a thermocouple of Pt-30%Rh/Pt-6%Rh at the bottom center of a crucible and was controlled by a PID regulator. The total maximum error in temperature measurement was estimated to be ± 3 K.

The oxygen partial pressure in the system was controlled by mixing purified argon and carbon monoxide according to the reaction:

$$\Delta G^\circ = -114\,390 - 85.77T \text{ J/mol}^\circ \quad \text{.....(2)}$$

Argon and carbon monoxide were separately purified by passing through a column of "soda lime" and a column of Ascarite (NaOH) to remove carbon dioxide, a column of Dehydrate ($\text{Mg(ClO}_4)_2$) and a bottle of phosphorus pentoxide to remove water. The purified argon was led to a tube furnace containing Mg chips at 853 K to remove residual oxygen. Another tube furnace containing copper was kept at 753 K to remove residual oxygen from carbon monoxide.

For each experimental run, a synthetic slag mixture, 5–10 grams, was prepared from "pro-analyti" grade chemicals. BaO, MnO and BaF_2 were calcined at 1073 K shortly before the experiments. The manganese alloys (3–5 g with different compositions) were prepared from "pro-analyti" grade chemicals and pre-melted in a graphite crucible under the protection of argon for 18 h. The pre-melted alloys were later used in the experiments to determine the manganese distribution ratio.

Preliminary experiments showed that 18 h were sufficient to reach equilibrium between slags and metal. In all experiments, the crucibles were kept in the furnace for 24 h. Manganese in metal was analyzed by optical emission spectrometry, and carbon by the combustion method. MnO, FeO and BaF_2 in the slags were analyzed by X-ray fluorescence, and BaO by a gravimetric method.

3. Results

The manganese distribution ratio between $\text{BaO-BaF}_2\text{-MnO}$ slags and $\text{Mn(62-73\%)-Fe-C}_{\text{sat}}$ melts, defined as $L_{\text{Mn}} = (\% \text{Mn}) / [\% \text{Mn}]$, is plotted against the BaO content at different oxygen partial pressures and at 1573 K in Fig. 1. Generally speaking, a high BaO content gave a high value of L_{Mn} .

Figure 2 gives the dependence of the manganese distribution ratio between $\text{BaO-BaF}_2\text{-MnO}$ slags and $\text{Mn(62-73\%)-Fe-C}_{\text{sat}}$ melts as function of temperature at $p_{\text{O}_2} = 9.62 \times 10^{-18}$ atm. The manganese distribution ratio decreased with temperature.

4. Discussion

Figure 3 demonstrates the effect of oxygen partial pressure on L_{Mn} between $\text{BaO(43-44wt\%)-BaF}_2\text{-MnO}$ slags and carbon-saturated ferro-manganese ($\% \text{Mn} = 62-73$) at 1573 K. A regression analysis gives the following relationship between $\log L_{\text{Mn}}$ and $\log p_{\text{O}_2}$:

Fig. 1. Manganese distribution ratio between $\text{BaO-BaF}_2\text{-MnO}$ slags and $\text{Mn(62-73\%)-Fe-C}_{\text{sat}}$ melts at 1573 K.

Fig. 2. Effect of temperature on the manganese distribution ratio between $\text{BaO-BaF}_2\text{-MnO}$ slags and carbon-saturated ferro-manganese at $p_{\text{O}_2} = 9.62 \times 10^{-18}$ atm.

$$\log L_{\text{Mn}} = 0.69 \log p_{\text{O}_2} + 10.77 \quad \text{.....(3)}$$

In the experiments, the MnO content in $\text{BaO-BaF}_2\text{-MnO}$ slags gradually increased with the oxygen partial pressure, then the BaF_2 content in the slags was decreased in order to maintain constant concentration of BaO. Thus, L_{Mn} in Eq. (3) was determined at different contents of MnO and BaF_2 .

The valence of manganese in slag affects the distribution ratio of manganese and the properties of the slag. The manganese equilibrium between manganese and pure manganese oxide can be expressed in terms of

Fig. 3. Influence of oxygen partial pressure on the manganese distribution ratio at a given content of BaO in BaO-BaF₂-MnO slag at 1573 K.

reaction (4):

$$\Delta G_4^\circ = -95840 + 20.14T \quad \text{cal/mol}^{(7)} \quad \text{.....(5)}$$

or as:

$$\log L_{\text{Mn}} = \frac{1}{2} \log p_{\text{O}_2} + \log K_6 - \log(a_{\text{O}^{2-}} - f_{\text{Mn}^{2+}}) + \log \gamma_{\text{Mn}} - \log(M_{\text{Mn}} \sum n_{i(m)}) \quad \text{.....(7)}$$

where a_i is activity of i relative to pure substance i ; p_i is partial pressure of i ; K_i is equilibrium constant of reaction (i); γ_i is activity coefficient of i relative to pure substance; f_i is activity coefficient of i relative to 1 wt%; M_i is molar weight of i ; and $n_{i(m)}$ is the molar number of element in metal.

According to Eq. (7), L_{Mn} will increase with lower slag basicity (lower $a_{\text{O}^{2-}}$) and higher oxygen partial pressure.

Besides Eqs. (4) and (6), a reaction of type:

$$\log L_{\text{Mn}} = \frac{3}{4} \log p_{\text{O}_2} + \left(x - \frac{3}{2}\right) \log a_{\text{O}^{2-}} - \log f_{\text{MnO}_x^{(2x-3)-}} + \log K_8 + \log \gamma_{\text{Mn}} - \log(M_{\text{MnO}_x} \sum n_{i(m)}) \quad \text{.....(9)}$$

may be considered.^{8,9)} L_{Mn} should here increase with higher slag basicity and higher oxygen partial pressure. If manganese in slag exists as $\text{MnO}_x^{(2x-3)-}$, a slope of 0.75 between $\log L_{\text{Mn}}$ and $\log p_{\text{O}_2}$ should be obtained at a fixed slag composition.

Ahundov *et al.*³⁾ studied the manganese distribution ratio between BaO-BaF₂-MnO slag and Fe-8%Mn-C_{sat}

melt. From the fact that the manganese distribution ratio increases with the BaO content in the slag, they draw the conclusion that manganese oxide in the slag behaves as an acidic oxide.

In CaO-CaF₂-SiO₂-MnO slags,¹⁰⁾ at a certain content of CaF₂ the manganese distribution decreases significantly with increasing the (%CaO/SiO₂) ratio, which indicates that in this case MnO in the slags should act as a basic component. However, at a given content of SiO₂ in the same slag, when replacing CaO by CaF₂, a phenomenon similar to a BaO-BaF₂-MnO slag appears, *i.e.* substitution of CaF₂ for CaO lowers the manganese distribution. Therefore, the conclusion that manganese oxide in this type of slag has an acidic function is questionable.

The parameter before $\log p_{\text{O}_2}$ in Eq. (3) is 0.69. For a fixed slag composition it should be close to 0.5. The obtained value may be accounted for by the overall effect of both increasing oxygen partial pressure and decreasing the BaF₂ content on the manganese distribution ratio. It is certain that some manganese ions appear acidic in the slag, especially at a high oxygen partial pressure and a high slag basicity according to reaction (8).

The existing manganese in the slags may be divided into Mn^{II+} and Mn^{III+}. The role of Mn^{III+} in slags can be represented in terms of ionic reaction (10):

where x is an integer with a value higher than 1.

This suggests that Mn^{III+} in slags would combine oxygen ions to form acidic ions, which results in a decrease of the slag basicity. Therefore, high content of Mn^{III+} in a slag is not favorable to dephosphorization. Under the conditions of a low oxygen partial pressure and a low slag basicity, the existence of Mn^{III+} in the slags should be low and possibly negligible. But at a high oxygen partial pressure and a high slag basicity, the effect of Mn^{III+} should be noted.^{9,11)} Because of the low oxygen partial pressure used in the present study, only Mn^{II+} was considered. The fact that the addition of SiO₂ to a BaO-BaF₂-MnO slag results in an increase of manganese distribution⁶⁾ also supports that Mn^{II+} in the slag is predominant. Experimental results,¹²⁾ showing that manganese in BaO-MnO slag mainly exists as Mn^{II+} even at a higher BaO content and higher oxygen partial pressure compared to the present study, also corroborate the discussion above.

A study¹³⁾ on equilibrium distribution of manganese between CaO-CaF₂-MnO slags and metal showed that manganese in the slags principally exists as Mn^{II+} and that MnO in the slags has a strongly positive deviation from ideal behavior. Similar to BaO-BaF₂-MnO slags, as the CaO content increases, the manganese distribution ratio increases. This implies that with increasing the BaF₂ or CaF₂ content in the slags, $f_{\text{Mn}^{2+}}$ is increased so high that the value of $a_{\text{O}^{2-}} - f_{\text{Mn}^{2+}}$ in Eq. (7) still increases even though the value of $a_{\text{O}^{2-}}$ decreases.

By using the experimental data shown in Fig. 1 and regression analysis, the manganese distribution ratio between BaO-BaF₂-MnO slags and carbon-saturated ferro-manganese can be expressed in terms of Eq. (11):

Fig. 4. Influence of BaF_2 on X_{MnO} in $\text{BaO-BaF}_2\text{-MnO}$ slags equilibrated with $\text{Mn(62-73\%)-Fe-C}_{\text{sat}}$ melts at 1573 K.

$$\log L_{\text{Mn}} = 0.666 \log p_{\text{O}_2} + 3.947 X_{\text{BaO}} + 8.622 \quad \dots (11)$$

where X_i is the molar fraction of i .

This relation clearly shows the effect of oxygen partial pressure and the BaO content.

It should be mentioned that the experiment carried out by Watanabe *et al.*⁴⁾ shows that the slag is saturated with MnO when $\text{BaO-BaF}_2\text{-MnO}$ slag is in equilibrium with carbon-saturated $\text{Fe-40\%Mn}$ melt at $p_{\text{O}_2} = 2.76 \times 10^{-17}$ atm and at 1573 K. However, in the present study, according to Fig. 1, it is certain that MnO in the slags was not saturated even though the manganese content in $\text{Mn-Fe-C}_{\text{sat}}$ melts was up to 67% at the same conditions. The reason for the difference is not clear.

The content of MnO as a function of BaF_2 in $\text{BaO-BaF}_2\text{-MnO}$ slags equilibrated with $\text{Mn(62-73\%)-Fe-C}_{\text{sat}}$ melts at different oxygen partial pressures and at 1573 K is given in Fig. 4. As discussed above, the action of BaF_2 in the slag is similar to that of CaF_2 to some extent. Many studies on the action of CaF_2 in slags on dephosphorization have been carried out. It has been suggested that CaF_2 should contribute to dephosphorization by forming $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ and stabilizing $\text{Ca}_3(\text{PO}_4)_2$,¹⁴⁾ and that fluoride ions in slag can replace oxygen in phosphate ions¹⁵⁾ to form PO_3F^{2-} and in SiO_2 network to form F-Si bonds,¹⁶⁾ which releases oxygen ions and enhances dephosphorization. In a similar way, it can be expected that the addition of BaF_2 into BaO-MnO slag decreases the losses of manganese enabling ferro-manganese refining to be performed at a relatively high oxygen pressure and enhances the dephosphorizing reaction.

Figure 5 shows the effect of increasing BaO content on the ratio of $X_{\text{BaO}}/X_{\text{MnO}}$ in $\text{BaO-BaF}_2\text{-MnO}$ slags equilibrated with $\text{Mn(62-73\%)-Fe-C}_{\text{sat}}$ melts at 1573 K. At a fixed oxygen partial pressure, a high BaO content

Fig. 5. Relationship between $X_{\text{BaO}}/X_{\text{MnO}}$ and X_{BaO} in $\text{BaO-BaF}_2\text{-MnO}$ slags equilibrated with $\text{Mn(62-73\%)-Fe-C}_{\text{sat}}$ melts at 1573 K.

Fig. 6. Influence of the BaO and CaO contents on activity coefficient of MnO in different slag systems.
1: $\text{CaO-CaF}_2\text{-MnO}$, $X_{\text{MnO}} = 0.005$, 1773 K (Ref. 5);
2: $\text{CaO-CaF}_2\text{-MnO}$, $X_{\text{MnO}} = 0.24$, 1773 K (Ref. 5);
3: $\text{CaO-CaF}_2\text{-MnO}$, 1773 K (Ref. 13); 4: $\text{BaO-BaF}_2\text{-MnO}$, 1573 K (Ref. 3); 5: $\text{CaO-CaF}_2\text{-MnO-SiO}_2$, 1573 K (Ref. 10); 6: $\text{BaO-BaF}_2\text{-MnO}$, 1573 K (Ref. 28).

gave a low ratio of $X_{\text{BaO}}/X_{\text{MnO}}$, which indicates that the increasing rate of molar fraction of MnO is faster than that of BaO. The decreasing rate of $X_{\text{BaO}}/X_{\text{MnO}}$ at a high oxygen partial pressure is lower than that at a low oxygen partial pressure. Using BaCO_3 as dephosphorizing reagent, Lee¹⁾ found that a high ratio of $X_{\text{BaO}}/X_{\text{MnO}}$

in BaO–MnO slag results in a high dephosphorization degree. The phosphorus distribution ratio generally increases with the molar fraction of BaO in BaO–BaF₂–MnO slag,⁶⁾ which implies that a low equilibrium value of $X_{\text{BaO}}/X_{\text{MnO}}$ in the ternary slag is beneficial to dephosphorization.

Using the interaction parameters in Mn–Fe–C solutions⁶⁾ and Eq. (4), the effect of BaO in BaO–BaF₂–MnO slags at 1573 K on the calculated activity coefficient of MnO, relative to pure solid MnO is illustrated in Fig. 6. The results obtained by other investigators are also plotted in the figure as comparison. As indicated in the figure, a high BaO or CaO content in fluoride containing slags gives a low activity coefficient of MnO. MnO activity coefficient obtained in the present study is lower than that by other investigators, especially at a high content of BaO. The reason may be the difference of MnO content in the slags. The relationship between the activity coefficient of MnO and the BaO content in the present investigated slag composition can be approximately represented as:

$$\log \gamma_{\text{MnO}} = 2.049 - 0.042(\% \text{BaO}) + 1.58 \cdot 10^{-4}(\% \text{BaO})^2 \quad \text{.....(12)}$$

In the regular solution model dealing with reciprocal salt mixtures suggested by Flood, Forland and Grjotheim,¹⁷⁾ both cations and anions were assumed to be randomly distributed over their respective ion position. According to their theory, the energy required to create the random state was equated with the free energy change of a reaction, e.g. of the type:

$$\Delta G_{1573\text{K}}^\circ = 48\,800 \text{ cal/mol}^{7,18,19)}$$

The MnO activity coefficient relative to pure solid MnO can be calculated by Eq. (14) if only the nearest-neighbor interactions are considered.

$$a_{\text{MnO}} = X_{\text{Mn}^{2+}} X_{\text{O}^{2-}} \exp \left(X'_{\text{Ba}^{2+}} X'_{\text{F}^-} \frac{\Delta G_{13}^\circ}{RT} \right) \exp \left(\frac{\Delta G_{15}^\circ}{RT} \right) \quad \text{.....(14)}$$

$$\text{MnO}(\text{s}) = \text{MnO}(\text{l}) \quad \text{.....(15)}$$

$$\Delta G_{15}^\circ = 13\,000 - 6.317T \text{ cal/mol}^{19)} \quad \text{.....(16)}$$

where X is the ionic fraction according to Temkin, e.g. $X_{\text{O}^{2-}} = n_{\text{O}^{2-}} / (n_{\text{O}^{2-}} + n_{\text{F}^-})$, and X' is the equivalent ionic fraction, e.g. $X'_{\text{F}^-} = n_{\text{F}^-} / (2n_{\text{O}^{2-}} + n_{\text{F}^-})$.

Calculation shows that this model gives the value of MnO activity ten to several hundred times higher than the experimental results at 1573 K. The difference between the calculated and observed results decreases with increasing BaO content in the slags. If the next-nearest-neighbor interactions are taken into account, the activity of MnO can be calculated by:

$$a_{\text{MnO}} = X_{\text{Mn}^{2+}} X_{\text{O}^{2-}} \exp \left\{ \frac{X'_{\text{Ba}^{2+}} X'_{\text{F}^-}}{RT} [\Delta G_{13}^\circ + k_{\text{O-Ba-F}}(X'_{\text{F}^-} - X'_{\text{O}^{2-}}) + k_{\text{Mn-F-Ba}}(X'_{\text{Ba}^{2+}} - X'_{\text{Mn}^{2+}})] + (k_{\text{O-Mn-F}} X'_{\text{F}^-} + k_{\text{Mn-O-Ba}} X'_{\text{Ba}^{2+}}) \right\}$$

$$\cdot (X'_{\text{Mn}^{2+}} X'_{\text{F}^-} + X'_{\text{Ba}^{2+}} X'_{\text{O}^{2-}})] \left\{ \exp \left(\frac{\Delta G_{15}^\circ}{RT} \right) \right\} \quad \text{.....(17)}$$

where k_{i-j-k} is an interaction parameter in a solution with a common ion j .

According to Lumsden,²⁰⁾ the polarizability of the common ion is the most important single factor in determining the value of k that primarily reflects two types of electrostatic forces—simple coulombic interaction and polarization of one ion surrounded by different ions of the opposite sign—and non-polar (van der Waals or London) contributions to the interaction energy.

Using the BaO activity data in a BaO–BaF₂ solution²¹⁾ and BaO fusion free energy,¹⁸⁾ the activity coefficient of BaO relative to pure liquid state could be approximately expressed as:

$$RT \ln \gamma_{\text{BaO}} = -7\,480(X'_{\text{F}^-})^2 \quad \text{.....(18)}$$

The value of $k_{\text{O-Ba-F}}$ ($-7\,480 \text{ J}$) is reasonably more negative than $k_{\text{O-Ca-F}} = -7\,070 \text{ J}$,²²⁾ since Ba^{2+} ion is more polarizable than Ca^{2+} ion. This polarization effect lowers the energy of the mixture, which leads to negative deviation from ideality.^{23,24)} $k_{\text{Mn-O-Ca}}$ was estimated to be $-92\,048 \text{ J}$.²⁵⁾ The value of $k_{\text{Mn-O-Ba}}$ should be more negative than $-92\,048 \text{ J}$ because of the larger size of Ba^{2+} ion than Ca^{2+} ion. A smaller interaction would almost certainly arise with fluoride ion because it is less polarizable than O^{2-} (0.77 compared with $2.76 \text{ \AA}^3$). Contribution of $k_{\text{O-Mn-F}}$ to the MnO activity is probably less important than other interaction parameters and can be neglected. Of course, between two dissimilar cations or anions there is probably a non-polar contribution of a positive energy, which partly counterbalances the polarization effect. But for the interaction parameters considered here, the non-polar contributions seem unimportant.

Substitution of values of $k_{\text{O-Ba-F}} = -7\,480$ and $k_{\text{Mn-O-Ba}} = -92\,048 \text{ J}$ into Eq. (17) substantially reduces the calculated MnO activity, but it still cannot bring the calculated and observed activities together. At low contents of BaO in the mixtures, the calculated results could be 60 times higher than the observed values. In this case, the term $k_{\text{Mn-F-Ba}}(X'_{\text{Ba}^{2+}} - X'_{\text{Mn}^{2+}})$ in Eq. (17) may considerably affect the calculated results. It seems clear that the random mixing condition is not met in the slags.

Because of the high value of ΔG° for reaction (13), there remains the possibility that the Mn^{2+} ions tend to cluster around the O^{2-} ions and Ba^{2+} ions around the F^- ions, which probably can result in immiscibility in the mixture of BaF₂ and MnO. As might be expected, the activity coefficient of MnO is strongly lowered by the addition of BaO which is reasonably miscible with MnO²⁾ and BaF₂.²¹⁾

There are several approaches to measure the ability of a flux to absorb manganese. Besides the manganese distribution ratio and MnO activity coefficient in the flux discussed above, the manganese capacity is a very important factor to judge the ability of slag absorbing

Fig. 7. Manganese capacity of BaO-BaF₂-MnO slags at 1573 K.

manganese. Using Eq. (6), it is defined as:

$$C_{Mn^{2+}} = \frac{(\%Mn^{2+})}{p_{O_2}^{1/2} a_{Mn}} = \frac{K_6}{a_{O_2} f_{Mn^{2+}}} \quad \text{.....(19)}$$

where a_{Mn} is activity of manganese relative to pure liquid state.

The relationship between the manganese capacity and the manganese distribution ratio can be expressed as:

$$\log C_{Mn^{2+}} = \log L_{Mn} - \log \gamma_{Mn} - \frac{1}{2} \log p_{O_2} + \log(\sum n_{i(m)}) + 1.74 \quad \text{.....(20)}$$

According to the definition, the manganese capacity is only dependent on the slag composition and temperature. Combination of Eqs. (4) and (19) gives the relationship between the manganese capacity and the activity coefficient of MnO (relative to pure solid MnO):

$$\log C_{Mn^{2+}} = -\log \gamma_{MnO} + \log(\sum n_{i(s)}) + \frac{20944}{T} - 2.65 \quad \text{.....(21)}$$

where $n_{i(s)}$ is the molar number of compound i in slags.

By neglecting the existence of Mn^{III+} in the studied slags, the dependence of the calculated manganese capacity on the BaO content in BaO-BaF₂-MnO system at 1573 K is given in Fig. 7. The maximum value of $\log C_{Mn^{2+}}$ in the slags is about 10.5. It is less than 11 obtained in CaO_{sat}-CaF₂-SiO₂ slags²⁶⁾ and 11.05 in Na₂O (60 wt%)-based slags.¹³⁾ The tendency of the change of the manganese capacity is the same as that in the CaO-CaF₂-MnO system,^{5,13)} i.e. with increasing fluoride content, the manganese capacity is decreased. The following equation was obtained by a linear regression analysis:

$$\log C_{Mn^{2+}} = 2.78 \log X_{BaO} + 11 \quad \text{.....(22)}$$

Fig. 8. Relationship between the phosphate and manganese capacities and BaO content in BaO-BaF₂-MnO slags at 1573 K.

In the CaO-Na₂O-CaF₂-SiO₂ system double saturated with CaO and 3CaO·SiO₂ at 1573 K, the linear relationship between phosphate and manganese capacities is found.²⁶⁾ Using the data of the phosphate capacity⁶⁾ of BaO-BaF₂-MnO slags, it was found that no simple linear relationship existed between phosphate and manganese capacities (the phosphate capacity is defined as $C_{PO_4^{3-}} = (\%PO_4^{3-})/p_{O_2}^{5/4} p_{P_2}^{1/2}$). The relation between the phosphate and manganese capacities at a given temperature can be written as:

$$\log[C_{PO_4^{3-}} \cdot (C_{Mn^{2+}})^{3/2}] = -\frac{3}{2} \log f_{Mn^{2+}} - \log f_{PO_4^{3-}} + \text{const.} \quad \text{.....(23)}$$

The value of $f_{PO_4^{3-}}$ is expected to be lowered by increasing BaO content. Since the increase of BaO content resulted in a decrease of BaF₂ content at a given oxygen partial pressure and temperature, the value of $f_{Mn^{2+}}$ would decrease with BaO content. It means that the value in the left hand of the Eq. (23) would increase with the content of BaO. Figure 8 revealing the relationship between the phosphate and manganese capacities and BaO content in BaO-BaF₂-MnO slags at 1573 K confirms the above discussion.

As shown in Fig. 2, a high temperature causes a low manganese distribution ratio at same content of BaO. In Fig. 9, the manganese capacity is plotted against inverse of temperature for a BaO(50%)-BaF₂(47%)-MnO(3%) slag. The relationship between the manganese capacity and temperature can be obtained from regression analysis on experimental results:

$$\log C_{Mn^{2+}} = \frac{21670}{T} - 3.73 \quad \text{.....(24)}$$

The heat of reaction (25):

Fig. 9. Influence of temperature on the manganese capacity of a BaO(50%)-BaF₂(47%)-MnO(3%) slag.

can be calculated from the relationship between the manganese capacity and temperature using Van't Hoff's equation.

$$-\Delta H_{25}^\circ = R \frac{\partial \ln C_{Mn^{2+}}}{\partial (1/T)} + R \frac{\partial \ln \gamma_{MnO}}{\partial (1/T)} \quad \text{.....(26)}$$

and

$$\Delta H_{25} = \Delta H_{25}^\circ + \Delta \bar{H}_{MnO} \quad \text{.....(27)}$$

$$\Delta H_{25} = -R \frac{\partial \ln C_{Mn^{2+}}}{\partial (1/T)} \quad \text{.....(28)}$$

where ΔH_{25}° is the standard enthalpy of reaction (25); and $\Delta \bar{H}_{MnO}$ is the partial molar enthalpy of dissolution of MnO in the BaO(50%)-BaF₂(47%)-MnO(3%) slag.

Substitution of Eq. (24) into Eq. (28) yields:

$$\Delta H_{25} = -415 \text{ kJ/mol} \quad \text{.....(29)}$$

Simeonov and Sano¹⁰⁾ estimated the enthalpy of reaction (25) to be -222 kJ/mol for a CaO-CaF₂-SiO₂-MnO slag and Tsukihashi *et al.*²⁷⁾ determined it to be -247 kJ/mol for a Na₂O-SiO₂-MnO slag. Recently, Ahundov *et al.*³⁾ evaluated the enthalpy to be -357 kJ/mol for a BaO-BaF₂-MnO (%BaO/%BaF₂=49/51) slag in the temperature range of 1473–1573 K, which is in agreement with the result obtained in the present study. Comparing the enthalpy of reaction (25) for oxidation with different slags, it implies that the effect of temperature on the manganese distribution ratio in BaO-BaF₂-MnO slag is much stronger than that in CaO-CaF₂-SiO₂-MnO and Na₂O-SiO₂-MnO slags.

5. Conclusions

The equilibrium distribution ratio of manganese between BaO-BaF₂-MnO slag and carbon-saturated ferro-

manganese has been determined at 1573–1673 K. Using the experimental data, the manganese capacity has been calculated. The following conclusions can be drawn:

(1) The manganese distribution ratio between BaO-BaF₂-MnO slag and carbon-saturated ferro-manganese increases with oxygen partial pressure and BaO content. At 1573 K, the manganese distribution ratio can be expressed as:

$$\log L_{Mn} = 0.666 \log p_{O_2} + 3.947 X_{BaO} + 8.662$$

(2) BaF₂ not only acts as a fluxing agent but it also increases the activity coefficient of MnO in BaO-BaF₂-MnO slag, which provides a beneficial condition to cut down the losses of manganese and enables dephosphorization of ferro-manganese at a relatively high oxygen partial pressure.

(3) In BaO-BaF₂-MnO slag equilibrated with carbon-saturated ferro-manganese, at constant oxygen partial pressure the ratio of molar fraction of MnO to BaO increases with increasing BaO content.

(4) The manganese distribution ratio between BaO-BaF₂-MnO slags and carbon-saturated ferro-manganese decreases with increasing temperature at a given slag composition. For a BaO(50%)-BaF₂(47%)-MnO(3%) slag, the dependence of manganese capacity on temperature is represented by:

$$\log C_{Mn^{2+}} = \frac{21670}{T} - 3.73.$$

The enthalpy of reaction:

is estimated to be -415 kJ/mol .

(5) A high content of BaO in BaO-BaF₂-MnO slags gives a high manganese capacity. In the investigated slag compositions, the maximum of manganese capacity is about 3.2×10^{10} .

Acknowledgment

The financial support of the Swedish National Board for Industrial and Technical Development (NUTEK) is gratefully acknowledged.

REFERENCES

- 1) Y. E. Lee: Proc. of the Sixth Int. Iron and Steel Congress, Nagoya, 1, (1990), 327.
- 2) M. Fujita, H. Katayama, A. Yamamoto and M. Matsui: *Tetsu-to-Hagane*, **74** (1988), 816.
- 3) N. Ahundov, F. O. F. Tsukihashi and N. Sano, *ISIJ Int.*, **31** (1991), 685.
- 4) Y. Watanabe, K. Kitamura, I. P. Rachev, F. Tsukihashi and N. Sano: *Metall. Trans.*, **24B** (1993), 339.
- 5) P. N. Smith and M. W. Davies: *Trans. Inst. Min. Metall. Sect. C*, **80** (1971), 87.
- 6) X. Liu: Dephosphorization of ferro-manganese under oxidizing conditions, Ph. D. thesis, TRITA-PT-93-01, KTH, Stockholm, Sweden, (1993).
- 7) E. T. Turkdogan: Physical Chemistry of High Temperature Technology, Academic Press, New York, (1980), 7.
- 8) A. Paul and D. Lahiri: *J. Am. Ceram. Soc.*, **49** (1966), 565.
- 9) W. D. Johnston: *J. Am. Ceram. Soc.*, **48** (1965), 184.
- 10) S. R. Simeonov and N. Sano: *Trans. ISIJ*, **25** (1985), 1116.
- 11) W. H. Park and H. Suito: *Tetsu-to-Hagane*, **77** (1991), 31.
- 12) S. C. Shim, F. Tsukihashi and N. Sano: *Metall. Trans.*, **24B**

- (1993), 333.
- 13) R. Inoue and H. Suito: *Trans. ISIJ*, **24** (1984), 816.
- 14) N. Sano: The Elliott Symp., Cambridge, MA, USA, (1990), 163.
- 15) M. Iwase: The 122-123 Nishiyama Memorial Seminar, "Thermodynamics of Oxide-Halide Melts", ISIJ, February, (1988), 63.
- 16) G. J. W. Kor: *Metall. Trans.*, **8B** (1977), 107.
- 17) H. Flood, T. Forland and K. Grjotheim: *Z. Anorg. Allg. Chem.*, **276** (1954), 289.
- 18) O. Kubaschewski and C. B. Alcock: *Metallurgical Thermochemistry*, 5th Ed., Pergamon Press, New York, (1979), 326, 330.
- 19) I. Barin and O. Knacke: *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, (1973), 470.
- 20) J. Lumsden: *Thermodynamics of Molten Salt Mixtures*, Academic Press, New York, (1966), 74.
- 21) T. Hara, F. Tsukihashi and N. Sano: *Tetsu-to-Hagané*, **76** (1990), 352.
- 22) A. J. Hawkins, S. G. Meherali and M. W. Davies: *J. Iron Steel Inst.*, **209** (1971), 646.
- 23) M. Blander: *Molten Salt Chemistry*, ed. by M. Blander, New York, (1964), 127.
- 24) M. Blander: *Molten Salt Chemistry*, ed. by G. Mamantov and R. Marassi, Boston, (1987), 17.
- 25) S. Ban-ya and M. Hino: *Tetsu-to-Hagané*, **73** (1987), 476.
- 26) F. Tsukihashi, A. Tagaya and N. Sano: *Trans. Iron Steel Inst. Jpn.*, **28** (1988), 164.
- 27) F. Tsukihashi, F. Matsumoto, T. Hyodo, M. Yukinobu and N. Sano: *Tetsu-to-Hagané*, **71** (1985), 823.
- 28) Y. Watanabe, K. Kitamura, I. P. Rachev, F. Tsukihashi and N. Sano: *Metall. Trans.*, **24B** (1993), 339.