Equilibrium Partitions of Manganese and Phosphorus between BaO–BaF₂ Melts and Carbon Saturated Fe–Mn Melts

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The phosphorus and manganese partition ratios between BaO–BaF₂–MnO fluxes and Fe–Mn–C_{satd.} alloys were measured at temperatures ranging from 1473 to 1573 K in a CO atmosphere.

The phosphorus partition ratio increases with increasing BaO content of the fluxes. This ratio for the BaO–BaF₂–MnO system is smaller than that for the BaO–BaF₂ system because of the strong interaction between manganese and phosphorus in molten iron. The temperature dependence of the phosphorus partition ratio was found to decrease with increasing temperature. The effect of manganese on the phosphorus content of carbon saturated iron melts is also discussed.

The manganese partition ratio increases with increasing BaO content of the fluxes and with decreasing temperature. The manganese oxide in fluxes is likely to behave as an acidic oxide for the BaO–BaF₂ system where BaO acts as a strongly basic oxide.

KEY WORDS: steelmaking; thermodynamics; BaO–BaF₂ flux; manganese; phosphorus; Fe–Mn–C_{satd.} melts.

1. Introduction

There has been a growing emphasis on removing impurities such as phosphorus from hot metal to extremely low levels for the production of ultra pure steels. Hot metal treatments have been developed in order to remove phosphorus and sulfur from hot metal, optimizing steelmaking processes. The most common reagents for this purpose are CaO-bearing fluxes because of their low prices and high refining capacities. Soda ash is capable of simultaneously removing sulfur and phosphorus at relatively lower oxygen potentials and has high refining capacities. However, it easily attacks refractory and evaporates during the treatment. The thermodynamics of BaO bearing melts has been studied in order to refine chromium containing hot metal using BaO–BaF₂ fluxes. The refining capability of the BaO–BaF₂ system has been found to be similar to that of the Na₂O bearing system and to be much higher than that of CaO bearing melts.

Recently manganese ores have been used as an oxidizer in the hot metal treatment to enhance manganese yield for the production of high manganese steel during subsequent BOF treatment. If BaO–BaF₂ flux have high dephosphorizing ability for refining Fe–Mn–C melts, they could be used in the production of high manganese steels with high manganese yield. However, there are few thermodynamic data for manganese in the BaO–BaF₂ system. Consequently, it is the purpose of the present work to determine the thermodynamics of phosphorus and manganese partition ratios between BaO–BaF₂

melts and carbon saturated Fe–Mn alloys.

2. Experimental

A chemical equilibration technique was employed in order to measure the equilibrium partition ratios of phosphorus and manganese between BaO–BaF₂ melts and carbon saturated Fe–Mn alloys. Measurements of phosphorus and manganese partition ratios were conducted separately. Three grams of mixtures of reagent grade BaO and BaF₂ were equilibrated with two grams of carbon saturated Fe–Mn alloys in a graphite crucible (O.D. 21 mm, I.D. 11 mm, Height 65 mm) in a CO atmosphere at the temperatures from 1473 to 1573 K. In the case of the measurement of manganese partition ratio, the initial manganese content of the fluxes ranged from 0 to 1 mass% and the initial manganese content of the carbon saturated Fe–Mn alloys changed from 0 to 21 mass%. In measuring phosphorus partition ratio, the initial phosphorus content of BaO–BaF₂–MnO melts ranged from 0.05 to 1 mass% and the initial phosphorus content of the carbon saturated Fe–8mass%Mn–P alloy ranged from 0 and 5 mass%. Equilibrium was approached from two directions, namely, oxidation and reduction of phosphorus and manganese. Analysis of phosphorus was conducted by molybdenum blue colorimetry and manganese was determined by atomic absorption spectroscopy. The carbon saturated Fe–Mn alloys were prepared by melting electrolytic iron and manganese in a graphite crucible in a CO atmosphere at the experimental temperatures.

3. Results and Discussion

Figure 1 shows the relationship between the manganese content of BaO-BaF₂-MnO melts and that of carbon saturated Fe-Mn alloys at 1573 K for various BaO contents of the melts. Manganese content of the slag has a linear relationship with that of the metal. This indicates that the manganese partition ratio is constant up to about 40 mass% of Mn in the metal. Therefore, the manganese content of the slags does not have any effect on the partition of manganese between BaO-BaF₂-MnO melts and carbon saturated Fe-Mn melts.

Figure 2 shows the dependence of the partition ratio of manganese on the BaO content of the BaO-BaF₂ system at 1473, 1523 and 1573 K. The manganese content of the fluxes ranged from 0.007 to 0.5 mass% and manganese content of the carbon saturated Fe-Mn alloys ranged from 0.4 to 10 mass%. The manganese partition ratio increases with increasing BaO content and it increases more than 100 times when the BaO content changes from 5 to 60 mass%. This means that the manganese partition ratio increases as the slag becomes more basic.

Figure 3 shows the dependence of the phosphorus partition ratio on the BaO content of BaO-BaF₂-MnO fluxes in a CO atmosphere at 1573 K, the manganese

content of metals being kept at 8 mass%. The partition ratio increases with increasing BaO content. The phosphorus content of BaO-BaF₂-MnO melts ranged from 0.03 to 0.5 mass% and the phosphorus content of the carbon saturated Fe-8mass%Mn-P alloy ranged from 0.004 to 0.5 mass%. The maximum manganese content of the flux was about 2 mass%. Hara, Tsukihashi and Sano¹⁾ have measured the phosphorus partition between BaO-BaF₂ melts and carbon saturated iron melts at 1573 K in a CO atmosphere. Their results are also shown in Fig. 3 for comparison with the present results. Since the carbon saturated Fe-Mn alloys were used in the present study, the phosphorus partition of the present study is lower than that of Hara *et al.* because of the interaction of manganese and phosphorus in the metal.

The temperature dependences of manganese and phosphorus partition ratios between BaO-BaF₂ melts (mass% BaO/mass% BaF₂ = 59/41) and carbon saturated Fe-8mass%Mn alloy between 1473 and 1573 K are shown in Fig. 4 as expressed by Eqs. (1) and (2), re-

Fig. 1. Relationship between manganese content of Fe-Mn-C_{satd.} melts and BaO-BaF₂-MnO fluxes at 1573 K.

Fig. 2. Manganese partition ratio between Fe-Mn-C_{satd.} alloy and BaO-BaF₂-MnO melts as a function of BaO content at 1473, 1523 and 1573 K.

Fig. 3. Phosphorus partition ratio between Fe-8mass%Mn-C_{satd.} alloy and BaO-BaF₂-MnO melts as a function of BaO content at 1573 K.

Fig. 4. Temperature dependence of phosphorus and manganese partition ratio between BaO-BaF₂ melts (mass% BaO/mass% BaF₂ = 59/41) and Fe-8mass%Mn-C_{satd.} alloy between 1473 and 1573 K.

spectively.

$$\log \frac{(\text{mass\% P})}{[\text{mass\% P}]} = \frac{5670}{T} - 2.16 \quad \text{.....(1)}$$

$$\log \frac{(\text{mass\% Mn})}{[\text{mass\% Mn}]} = \frac{12700}{T} - 8.90 \quad \text{.....(2)}$$

Both partition ratios decrease with increasing temperature. The heat of the reaction expressed by Eq. (3) can be calculated from the slope of the lower straight line in Fig. 4, as $\Delta H^\circ = -357 \text{ kJ/mol}$ after correcting for the CO reaction from Eq. (5).

$$\Delta G^\circ = -114400 - 85.77T \text{ (J/mol)}^{(2)} \quad \text{.....(5)}$$

The Gibbs free energy of the reaction (3) is expressed by Eq. (6).

$$\Delta G^\circ = -357000 + 63.49T \text{ (J/mol)}^{(2,3)} \quad \text{.....(6)}$$

The ΔH° in Eq. (6) agrees well with the measured one, -357 kJ/mol , which corresponds that the heat of dissolution of MnO in BaO-BaF₂-MnO melts is very small.

The activity coefficient of MnO for the BaO-BaF₂-MnO system can be calculated as follows. The reaction of manganese between BaO-BaF₂-MnO melts and carbon saturated Fe-Mn alloy is expressed by Eq. (7).

Since the equilibrium constant of reaction (7) is shown by Eq. (8), the activity coefficient of MnO in BaO-BaF₂ melts is given by Eq. (9)

$$K = \frac{(\gamma_{\text{MnO}} \cdot X_{\text{MnO}}) \cdot a_{\text{C}}}{(\gamma_{\text{Mn}} \cdot X_{\text{Mn}}) \cdot P_{\text{CO}}} \quad \text{.....(8)}$$

$$\gamma_{\text{MnO}} = \left(\frac{K \cdot \gamma_{\text{Mn}} \cdot P_{\text{CO}}}{a_{\text{C}}} \right) \cdot \left(\frac{X_{\text{Mn}}}{X_{\text{MnO}}} \right) \quad \text{.....(9)}$$

where γ_i is the activity coefficient of component i relative to pure substance, a_{C} is the activity of carbon relative to graphite, X_i is the mole fraction of component i , and P_i is the partial pressure of gaseous component i .

In the present study, the a_{C} is unity and the partial pressure of CO is 1 atm ($1.013 \times 10^5 \text{ Pa}$). The equilibrium constant can be calculated from the ΔG° of Eq. (7) for pure substances which is given by Eq. (10).

$$\Delta G^\circ = -242600 + 149.3T \text{ (J/mol)}^{(2,3)} \quad \text{.....(10)}$$

The activity coefficient of manganese in carbon saturated iron is 0.510 at 1573 K according to Simeonov and Sano.⁽⁴⁾ The values at various temperatures are estimated by a regular solution approximation. Substituting these values into Eq. (9), the activity coefficient of MnO for the BaO-BaF₂-MnO system was obtained as shown in Fig. 5. They decrease with increasing BaO content. Very slight

Fig. 5. Activity coefficient of MnO for the BaO-BaF₂ system at 1473, 1523 and 1573 K compared with that for CaO bearing systems. 1: Smith and Davis, CaO-CaF₂-MnO, 1773 K, $X_{\text{MnO}}=0.005$, 2: Smith and Davis, CaO-CaF₂-MnO, 1773 K, $a_{\text{MnO}}=0.24$, 3: Inoue and Suito, CaO-CaF₂, 1773 K, 4: Simeonov and Sano, CaO-CaF₂-16mass% SiO₂, 1573 K.

temperature dependence of activity coefficient of MnO was observed.

Tsukihashi, Matsumoto, Hyodo, Yukinobu and Sano⁽⁵⁾ measured the manganese partition between carbon saturated iron melts and Na₂O-SiO₂ fluxes at 1473 K. With increasing the basicity of fluxes, the manganese partition ratio decreases. Simeonov and Sano have studied the thermodynamic properties of manganese for lime based fluxes containing MnO, BaO and Na₂O and reported that the manganese partition ratio decreased as CaO content increased. Also, the substitution of BaO by CaO decreases the manganese partition ratio, indicating that BaO is more basic than CaO. Inoue and Suito⁽⁶⁾ measured the equilibrium manganese partition ratios between soda and lime based fluxes and carbon saturated iron. They showed that for the Na₂O-SiO₂ system, with increasing Na₂O, the manganese partition ratio decreased. From these measurements, it can be seen that the manganese partition decreases when the basic component increases in the fluxes.

Conversely, the manganese partition ratio increases as the slag becomes basic for the BaO-BaF₂ system in the present study. For the CaO-CaF₂ and CaO-CaF₂-SiO₂ systems Inoue and Suito⁽⁶⁾ and Simeonov and Sano⁽⁴⁾ measured the manganese partition ratio, respectively. It increased when the CaF₂ was substituted by CaO. This behavior of manganese partition is similar to that for the BaO-BaF₂-MnO system of the present study. Smith and Davis⁽⁷⁾ observed the same tendency for the CaO-CaF₂ system. The activity coefficient of MnO for the CaO-CaF₂ system is shown in Fig. 5 together with that for the BaO-BaF₂ system. Since MnO activity for the CaF₂-MnO system deviates positively from the ideal solution behavior,⁽⁷⁾ it is also expected that in the case of BaO-BaF₂ system, the fluorine ion in flux melts enhances the activity coefficient of MnO as BaF₂ content of fluxes increases.

The behavior of MnO deviates positively from that of an ideal solution similar to the CaO–CaF₂ system. Generally both MnO and BaO are considered to be basic oxides, but in the present case MnO seems to act as an acidic oxide in the BaO–BaF₂ system where BaO behaves as a strongly basic oxide.

This behavior can be explained by Eq. (11) assuming the existence of manganate ions in slags.

Further experiments would be required to confirm this reaction to determine the ionic species of manganese by changing the partial pressure of oxygen.

The partition ratio of phosphorus in the present system is lower than that without manganese as shown in Fig. 3. The first order interaction coefficient between manganese and phosphorus, e_{P}^{Mn} , can be estimated from these results as follows. The activity coefficient of manganese in carbon saturated iron is expressed by Eq. (12).

$$\log f_{\text{P}} = e_{\text{P}}^{\text{C}} \cdot [\text{mass}\% \text{ C}] + e_{\text{P}}^{\text{P}} \cdot [\text{mass}\% \text{ P}] + e_{\text{P}}^{\text{Mn}} \cdot [\text{mass}\% \text{ Mn}] \dots\dots\dots(12)$$

where f_{P} is the activity coefficient of phosphorus in carbon saturated Fe–Mn melts, e_{P}^i is the interaction coefficient between P and i component, $[\text{mass}\% i]$ is the mass% of component i in iron melts. The logarithmic value of the ratio of phosphorus partition ratio for Fe–C–0%Mn to that of 8% Mn alloys in Fig. 3 corresponds to the term $e_{\text{P}}^{\text{Mn}} \cdot [\text{mass}\% \text{ Mn}]$ in Eq. (12). The e_{P}^{Mn} values calculated from the data shown in Fig. 3 ranged from -0.16 to -0.25 at 1 573 K when carbon saturated Fe–8mass%Mn alloy was used. Ban-ya, Maruyama and Kawase⁸⁾ measured the effect of various elements on the activity coefficient of phosphorus in liquid iron and obtained -0.032 as the e_{P}^{Mn} at 1 673 K. Schenck *et al.*⁹⁾ observed that e_{P}^{Mn} is 0 at 1 873 K.

The value obtained in the present study is more negative than those of other investigators. It must be noted that the e_{P}^{Mn} of the present study is derived only at a certain composition of iron alloy, namely carbon saturated Fe–8mass%Mn melts.

4. Conclusions

The phosphorus and manganese partitions between BaO–BaF₂–MnO fluxes and Fe–Mn–C alloys were measured at temperatures ranging from 1 473 to 1 573 K in a graphite crucible in a CO atmosphere and the following results have been obtained.

(1) Phosphorus partition ratio increases with increas-

ing BaO content of the fluxes. This ratio for the BaO–BaF₂–MnO system is smaller than that for the BaO–BaF₂ system because of the interaction between manganese and phosphorus in molten alloys.

(2) The phosphorus partition ratio decreases with temperature. The temperature dependence of partition ratio between BaO–BaF₂ melts ($\text{mass}\% \text{ BaO} / \text{mass}\% \text{ BaF}_2 = 59/41$) and carbon saturated Fe–8mass%Mn alloy is expressed as follows.

$$\log \frac{(\text{mass}\% \text{ P})}{[\text{mass}\% \text{ P}]} = \frac{5\,670}{T} - 2.16 \dots\dots\dots(13)$$

(3) The manganese partition ratio increases with increasing BaO content of fluxes and decreasing the temperature. The temperature dependence of partition ratio between BaO–BaF₂ melts ($\text{mass}\% \text{ BaO} / \text{mass}\% \text{ BaF}_2 = 59/41$) and carbon saturated Fe–8mass%Mn alloy is expressed as follows.

$$\log \frac{(\text{mass}\% \text{ Mn})}{[\text{mass}\% \text{ Mn}]} = \frac{12\,700}{T} - 8.90 \dots\dots\dots(14)$$

Manganese oxide in fluxes behaves apparently as an acidic oxide for the BaO–BaF₂ system where BaO behaves as a strongly basic oxide.

(4) The interaction coefficient between manganese and phosphorus, e_{P}^{Mn} , ranges from -0.16 to -0.25 at 1 573 K for carbon saturated Fe–8mass%Mn melts.

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