Equilibrium Distribution Ratios of Phosphorus and Chromium between BaO–MnO Melts and Carbon Saturated Fe–Cr–Mn Alloys at 1 573 K

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The phosphorus, manganese, and chromium distribution ratios between BaO–MnO fluxes and liquid Fe–Cr–Mn–C_{satd.} alloys have been measured at 1 573 K by using a chemical equilibration technique. The distribution ratio of phosphorus between BaO–MnO fluxes and liquid Fe–Cr–Mn–C_{satd.} alloys decreases and those of chromium and manganese are nearly constant with increasing chromium content of the metal. With increasing the BaO content of flux the phosphorus distribution ratio is found to increase. The chromium distribution slightly increases and that of manganese decreases at the same time. The possibility of dephosphorization of Fe–Cr–Mn–C_{satd.} melts by using BaO–MnO fluxes is discussed.

KEY WORDS: steelmaking; thermodynamics; BaO–MnO system; Fe–Cr–Mn–C_{satd.} alloy; distribution ratio; phosphorus; chromium; manganese.

1. Introduction

When CaO bearing fluxes are applied to oxidative dephosphorization of chromium containing hot metals, chromium may be preferentially oxidized. Accordingly, the flux with high basicity is required to avoid it. Watanabe *et al.*¹⁾ reported that BaO–MnO flux has a strong dephosphorization ability and is applicable to dephosphorization of Fe–Mn–C_{satd.} alloys, suggesting that this flux may be also used for dephosphorization of chromium containing hot metal. In the present study, the phosphorus, chromium, and manganese distribution ratios between the BaO–MnO fluxes and Fe–Cr–Mn–C_{satd.} alloys have been measured at 1 573 K in a CO atmosphere.

2. Experimental

A chemical equilibration technique was employed for the measurement of phosphorus, chromium, and manganese distribution between the BaO–MnO fluxes and molten Fe–Cr–Mn–C_{satd.} alloys at 1 573 K. The experimental procedure is similar to what was described in the previous paper.¹⁾ Six grams of these fluxes containing 10 to 40 mass% MnO, 1.5 mass% Cr₂O₃, and 1 mass% phosphorus were equilibrated with 2.5 g of molten Fe–Cr–Mn–C_{satd.} alloys containing up to 13 mass% Cr and 16 to 31 mass% Mn in a dense graphite crucible (12 mm ID, 22 mm OD, 55 mm height). A graphite crucible with the sample placed in a graphite holder was held in an electric furnace. Temperature was

controlled within the range of ± 0.5 K. The time for equilibration was 16 h, which had been preliminarily determined to be sufficient. A purified CO was flowed with the rate of 2.5×10^{-6} m³/s. The oxygen partial pressure of the system controlled by reaction (1) was 2.80×10^{-12} Pa at 1 573 K in the present experiments.

$$\Delta G^\circ = -114\,400 - 85.77\,T \text{ [J/mol]} \quad \dots\dots\dots(2)$$

The flux sample was prepared from reagent-grade BaO, BaHPO₄, MnCO₃, and Cr₂O₃. The MnCO₃ chemicals were decomposed to MnO at 1 173 K in an argon atmosphere before mixing the reagents in a desired proportion. After equilibration, the graphite crucible was withdrawn from the furnace and the samples were quenched in an argon flow. Phosphorus in the flux and metal was determined by molybdenum blue colorimetry. Chromium in the flux and metal was determined by diphenylcarbazide colorimetry, titration with potassium permanganate, respectively. Manganese contents of the flux and metal were analyzed by titration with potassium permanganate. Barium oxide in the flux was analyzed by gravimetry. Carbon contents were determined by LECO* combustion analyzer.

3. Results and Discussion

3.1. Phosphorus Distribution

Experimental results for the distribution ratios of

* LECO is a trademark of LECO Corporation, St. Joseph, MI, U.S.A.

Table 1. Experimental results for the distribution ratios of phosphorus, chromium, and manganese between molten Fe–Cr–Mn–C_{satd.} alloy and the BaO–MnO fluxes at 1 573 K.

No.	[%P]	[%Cr]	[%Mn]	[%C]	(%P)	(%Cr)	(%Mn)	(%BaO)	L_P	L_{Cr}	L_{Mn}
1	0.00160	0.00	19.7	5.84	0.966	0.00	12.1	82.2	604	—	0.614
2	0.00184	1.34	24.3	5.18	0.891	0.166	12.1	82.2	484	0.124	0.498
3	0.00235	4.83	24.9	5.85	0.590	0.529	10.7	84.0	251	0.110	0.430
4	0.00214	6.37	22.0	6.05	1.13	1.39	10.9	81.4	528	0.218	0.495
5	0.00359	7.50	25.9	5.60	0.849	0.932	12.4	80.7	236	0.124	0.479
6	0.0620	8.78	17.5	4.96	0.898	0.879	14.1	78.5	145	0.100	0.806
7	0.0582	9.22	24.4	6.40	1.45	0.488	13.4	78.7	249	0.0529	0.549
8	0.00497	10.0	18.9	5.86	0.904	1.14	12.0	80.8	182	0.114	0.635
9	0.00940	12.7	21.5	5.27	0.608	1.07	11.6	82.1	65.0	0.0843	0.540
10	0.00981	13.2	23.4	6.13	0.987	2.18	12.4	78.6	101	0.165	0.530
11	0.0198	8.51	38.5	5.90	1.13	0.381	23.3	66.9	57.1	0.0448	0.605
12	0.0617	7.89	29.8	6.84	1.49	0.747	17.8	72.6	241	0.0947	0.597
13	0.00847	9.50	29.9	5.00	1.12	0.634	17.7	74.7	132	0.0667	0.592
14	0.0101	9.78	28.0	5.98	1.26	0.734	17.4	74.7	125	0.0751	0.621
15	0.00235	8.39	31.4	6.20	0.874	0.923	15.2	77.2	372	0.110	0.484
16	0.00209	10.5	19.7	6.40	1.01	1.09	8.23	85.5	483	0.104	0.418
17	0.00177	9.50	16.6	5.74	1.16	1.47	7.39	85.7	655	0.155	0.445
18	0.00136	9.11	16.0	6.54	0.992	0.791	6.68	88.0	729	0.0868	0.417

Fig. 1. Phosphorus distribution ratios between the 80mass% BaO–MnO flux and Fe–Cr–[17 to 26mass%]Mn–C_{satd.} alloy at 1 573 K as a function of chromium content of the alloy at the oxygen partial pressure of 2.80×10^{-12} Pa.

phosphorus, chromium, and manganese between BaO–MnO fluxes and Fe–Cr–Mn–C_{satd.} alloys at 1 573 K are listed in Table 1. Experiments 1 to 10 were conducted at constant manganese content and experiments 11 to 18 were done at constant chromium content of metal. However, since it is difficult to keep constant manganese or chromium content in the present experimental conditions, manganese and chromium contents are ranging from 17 to 26 mass% and from 7.9 to 10.5 mass%, respectively.

The effect of chromium content of molten Fe–Cr–Mn–C_{satd.} alloy on the phosphorus distribution ratios ($L_P = (\text{mass\% P})/(\text{mass\% P})$) between the 80mass%BaO–MnO flux and a molten Fe–Cr–[17 to 26mass%]Mn–C_{satd.} alloy at 1 573 K is shown in Fig. 1. They decrease

Fig. 2. Phosphorus distribution ratios between the BaO–MnO flux and Fe–[7.9 to 10.5mass%]Cr–Mn–C_{satd.} alloy at 1 573 K as a function of BaO content of the flux at the oxygen partial pressure of 2.80×10^{-12} Pa.

with increasing chromium content of the metal. Since the chromium oxide content of flux is less than 3.19 mass% in the present results the effect of chromium oxide on the activity of phosphorus in the flux may be ignored. Therefore, the interaction parameter between phosphorus and chromium in the Fe–Cr–[17 to 26 mass%]Mn–C_{satd.} alloy, $e_{P \text{ at } C_{\text{satd.}}}^{\text{Cr}}$, can be obtained as -0.063 at 1 573 K from the slope of the line in Fig. 1.

The values for the interaction parameter at 1 573 K are reported by Kanzaki *et al.*,²⁾ Takiguchi *et al.*,³⁾ and Hara *et al.*⁴⁾ as -0.037 , -0.039 , and -0.085 , respectively. The value in the present study is in fairly good agreement with the foregoing ones.

The phosphorus distribution ratios between the BaO–MnO flux and molten Fe–[7.9 to 10.5mass%]Cr–Mn–C_{satd.} alloy at 1 573 K are shown by solid circles in Fig. 2 as a function of BaO content of the flux. These distribution ratios for various chromium contents can be calibrated to the values for 9.0 mass% Cr by using the interaction parameter at carbon saturation, $e_{P \text{ at } C_{\text{satd.}}}^{\text{Cr}}$,

Fig. 3. Chromium distribution ratios between the 80mass% BaO-MnO flux and Fe-Cr-[17 to 26mass%]Mn-C_{satd.} alloy at 1573 K as a function of chromium content of the alloy at the oxygen partial pressure of 2.80×10^{-12} Pa.

Fig. 4. Chromium distribution ratios between the BaO-MnO flux and Fe-[7.9 to 10.5mass%]Cr-Mn-C_{satd.} alloy at 1573 K as a function of BaO content of the flux at the oxygen partial pressure of 2.80×10^{-12} Pa.

obtained from the results shown in Fig. 1. The modified distribution ratios are shown in Fig. 2 by open circles. They increase with increasing BaO content of the flux. This is due to an increase in basicity of the flux as MnO is replaced by BaO, since BaO is more basic than MnO.

3.2. Chromium Distribution

The chromium distribution ratios ($L_{Cr} = (\text{mass\% Cr})/(\text{mass\% Cr})$) between the 80mass% BaO-MnO flux and molten Fe-Cr-[17 to 26mass%]Mn-C_{satd.} alloy at 1573 K are shown in Fig. 3 as a function of chromium content of the alloy. They slightly decrease with increasing chromium content of the metal. The chromium distribution ratios between the flux and molten Fe-[7.9 to 10.5mass%]Cr-Mn-C_{satd.} alloy at 1573 K are shown in Fig. 4 as a function of BaO content of the flux, increasing with increasing BaO content. Since the distribution ratios of phosphorus are much larger than those of chromium, the BaO-MnO flux can be said to be suitable for the oxidative dephosphorization treatment of Fe-Cr-Mn-C melts without a significant loss of chromium.

The reaction of chromium between the molten fluxes

Fig. 5. Activity coefficient of $CrO_{1.5}$ for the BaO-MnO system at 1573 K compared with that for the BaO-BaF₂ system.

and alloys and its equilibrium constant, K , are expressed by Eqs. (3) and (5).

$$\Delta G^\circ = -556\,000 + 124\,T \text{ [J/mol]}^{5)} \quad \dots\dots\dots(4)$$

$$K = \frac{a_{CrO_{1.5}}}{a_{Cr} \cdot P_{O_2}^{3/4}} = \frac{\gamma_{CrO_{1.5}} \cdot X_{CrO_{1.5}}}{\gamma_{Cr} \cdot X_{Cr} \cdot P_{O_2}^{3/4}} \quad \dots\dots\dots(5)$$

where a_i and γ_i are the activity and activity coefficient of component i relative to pure solid component, respectively, X_i is the mole fraction of component i , and P_{O_2} is the partial pressure of oxygen.

The activity coefficient of $CrO_{1.5}$ of the flux may be calculated by substituting the chromium contents of the flux and alloy into Eq. (5). The activity coefficient of chromium in the Fe-Cr-Mn-C_{satd.} alloy was estimated by using Eq. (6), which was derived by extrapolating the value for the activity coefficient of chromium at 1813 K obtained by Ohtani⁶⁾ to the value at 1573 K, assuming regular solution behavior and combining it with the interaction parameter between chromium and manganese, ϵ_{Cr}^{Mn} , measured by the present investigation which is described later.

$$\ln \gamma_{Cr} = -23.9 \frac{X_{Cr} \cdot X_C}{(1 - X_C)^2} + \epsilon_{Cr}^{Mn} \cdot X_{Mn} \quad \dots\dots\dots(6)$$

The activity coefficient of $CrO_{1.5}$ at 1573 K is shown as a function of BaO content of the flux in Fig. 5. Its value decreases with increasing the BaO content of flux. Hara *et al.*⁴⁾ reported the activity coefficient of $CrO_{1.5}$ in the BaO-BaF₂ system at 1573 K which is also shown in Fig. 5 in comparison with the present results. The chromium contents of slag in the present study are about 1 mass% which is the same as that for the BaO-BaF₂ system. The activity coefficient of $CrO_{1.5}$ in the BaO-MnO system is smaller than that in the BaO-BaF₂ system at large BaO contents. This indicates that fluorine has a function to enhance the activity coefficient of $CrO_{1.5}$.

Fig. 6. Manganese distribution ratios between the 80mass% BaO-MnO flux and Fe-Cr-[17 to 26mass%]Mn-C_{satd.} alloy at 1573 K as a function of chromium content of the alloy at the oxygen partial pressure of 2.80×10^{-12} Pa.

There exists a compound, $3\text{BaO} \cdot \text{Cr}_2\text{O}_3$ in the BaO-Cr₂O₃ system at 1573 K according to the phase diagram.⁷⁾ Therefore, a possibility of the formation of $3\text{BaO} \cdot \text{Cr}_2\text{O}_3$ in the present study is discussed as follows. Recently, the standard Gibbs energy of reaction (7) has been measured by Kobayashi *et al.*⁸⁾ as Eq. (8). The equilibrium constant is expressed by Eq. (9).

$$\Delta G^\circ = -1260000 + 282T \text{ [J/mol]}^{(8)} \quad \dots\dots\dots(8)$$

$$K = \frac{a_{3\text{BaO} \cdot \text{Cr}_2\text{O}_3}}{a_{\text{BaO}}^3 \cdot a_{\text{Cr}}^2 \cdot P_{\text{O}_2}^{3/2}} \quad \dots\dots\dots(9)$$

Since the chromium content of the Fe-Cr-Mn-C_{satd.} alloy lies between 0 and 13mass% in the present investigation, the maximum activity of chromium is about 0.04 according to Eq. (6). Therefore, the maximum activity of $3\text{BaO} \cdot \text{Cr}_2\text{O}_3$ is calculated as 0.3 at BaO saturation and no $3\text{BaO} \cdot \text{Cr}_2\text{O}_3$ may be formed during the experiments.

3.3. Manganese Distribution

The manganese distribution ratios ($L_{\text{Mn}} = (\text{mass\% Mn})/(\text{mass\% Mn})$) between the 80mass%BaO-MnO flux and molten Fe-Cr-[17 to 26mass%]Mn-C_{satd.} at 1573 K are shown in Fig. 6 as a function of chromium content of the molten alloy. They remain almost constant with increasing chromium content of the metal. The value for the interaction parameter between manganese and chromium at carbon saturation in Fe-Cr-[17 to 26mass%]Mn-C_{satd.} alloy, $e_{\text{Mn at C}_{\text{satd.}}}^{\text{Cr}}$, is obtained to be 0.00 at 1573 K within the accuracy of the present study from the regression line shown in Fig. 6. Therefore, the effect of chromium content on the manganese content can be ignored. The value for the interaction parameter, $e_{\text{Mn}}^{\text{Cr}}$, is also reported to be 0.0039 up to 3.2mass% Cr in molten alloy at 1843 K by Mukai *et al.*⁹⁾ and is estimated to be 0.0015 at 1573 K assuming regular solution behavior, which is in good agreement with the present result.

The manganese distribution ratios between the BaO-

Fig. 7. Manganese distribution ratios between the BaO-MnO flux and Fe-[7.9 to 10.5mass%]Cr-Mn-C_{satd.} alloy at 1573 K as a function of BaO content of the flux at the oxygen partial pressure of 2.80×10^{-12} Pa.

Fig. 8. Activity of MnO for the BaO-MnO system at 1573 K.

MnO flux and molten Fe-[7.9 to 10.5mass%]Cr-Mn-C_{satd.} alloy at 1573 K are shown in Fig. 7. Since the interaction between chromium and manganese can be ignored, the manganese distribution ratios shown in Fig. 7 hold regardless of chromium content of the metal. They slightly decrease with increasing BaO content of the flux.

The reaction of manganese between the flux and alloy and its equilibrium constant are expressed by Eqs. (10) and (12).

$$\Delta G^\circ = -357000 + 63.49T \text{ [J/mol]}^{(5)} \quad \dots\dots\dots(11)$$

$$K = \frac{a_{\text{MnO}}}{\gamma_{\text{Mn}} \cdot X_{\text{Mn}} \cdot P_{\text{O}_2}^{1/2}} \quad \dots\dots\dots(12)$$

where γ_{Mn} is the activity coefficient of Mn relative to pure liquid Mn and a_{MnO} is the activity of MnO relative to pure liquid MnO.

The activity coefficient of manganese in the molten alloy was estimated by combining the activity of manganese for a Fe-Mn-C alloy reported by Dresler¹⁰⁾

with the interaction parameter, $e_{\text{Mn at } C_{\text{satd.}}}^{\text{Cr}}$. The activity of MnO in the BaO–MnO system relative to liquid MnO at 1573 K is shown in Fig. 8.

Shim *et al.*¹¹⁾ determined the activity of MnO in the BaO–MnO system at 1573 K by equilibrating molten silver with BaO–MnO fluxes in a CO–CO₂ atmosphere, which is shown in Fig. 8 together with the present results. The activity of MnO observed in the present study is smaller than that of Shim *et al.* Since the partial pressure of CO₂ is as high as 6.28 and 16.9 kPa in their experiments, CO₂ dissolved into the flux must have enhanced the activity of MnO due to that the dissolved CO₂ weaken the interaction between BaO and MnO in their case.

4. Conclusions

In order to obtain the thermodynamic knowledge about oxidative dephosphorization of the Fe–Cr–Mn–C_{satd.} alloy, phosphorus, chromium, and manganese distribution ratios between BaO–MnO fluxes and those alloys were measured at 1573 K. The following conclusions may be drawn from the findings in the present study.

(1) A Fe–Cr–Mn–C_{satd.} alloy can be dephosphorized by using the BaO–MnO flux without substantial oxidation of chromium. However, dissolution of a large amount of manganese into the alloys can not be avoided.

(2) The distribution ratios of phosphorus between the BaO–MnO fluxes and Fe–Cr–Mn–C_{satd.} alloy de-

crease and those of chromium and manganese remains unchanged with increasing chromium content of the metal. The following interaction parameters at carbon saturation in Fe–Cr–[17 to 26mass%]Mn–C_{satd.} alloys were obtained at 1573 K.

$$e_{\text{P at } C_{\text{satd.}}}^{\text{Cr}} = -0.063, e_{\text{Mn at } C_{\text{satd.}}}^{\text{Cr}} = 0.00$$

(3) The phosphorus distribution ratio increases with increasing BaO content of the flux. That of chromium slightly increases and that of manganese slightly decreases.

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