Thermodynamic Assessment of MnO and FeO Activities in FeO–MnO–MgO–P₂O₅–SiO₂(–CaO) Molten Slag

Sun-Joong KIM,^{1)*} Jun TAKEKAWA,²⁾ Hiroyuki SHIBATA,³⁾ Shin-ya KITAMURA,³⁾ Katsunori YAMAGUCHI⁴⁾ and Youn-Bae KANG⁵⁾

1) JSPS Postdoctoral Fellow, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 Japan. 2) Formerly Graduate School of Engineering, Tohoku University. Now at Nippon Steel & Sumitomo Metal Corporation, 3 Hikari, Kashima, 314-0034 Japan. 3) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 Japan. 4) Iwate University, 4-3-5 Ueda, Morioka, 020-8511 Japan. 5) Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, San 31, Hyojadong, Pohang, Kyungbuk, 790-784 Republic of Korea.

(Received on February 27, 2013; accepted on May 15, 2013)

The activity coefficients of MnO and FeO in an FeO–MnO–MgO–P₂O₅–SiO₂(–CaO) slag system were measured on the basis of the equilibrium between Ag and molten slag at 1 673 K under a controlled atmosphere. On the basis of experimental results, the activity coefficients of MnO and FeO in this multicomponent slag were evaluated using a regular solution (RS) model, FactSage, and an empirical formula. In the case of the RS model, the interaction energies and conversion factors to fit the calculated values to experimental results were reassessed. By the use of the empirical formula, FactSage and the regular solution model of present work, the activity coefficient ratio of MnS and FeS in a Fe–Mn–O–S matte that was equilibrated with a FeO–MnO–MgO–P₂O₅–SiO₂ slag system was evaluated. When the RS model was used to calculate the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio decreased slightly with an increase in the $X_{\text{MnS}}/X_{\text{FeS}}$ ratio. In contrast, when the empirical formula and FactSage were used, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio was almost constant when the $X_{\text{MnS}}/X_{\text{FeS}}$ ratio was increased.

KEY WORDS: recycling; steelmaking slag; manganese; interaction energy; regular solution model; manganese sulfide; iron sulfide.

1. Introduction

A proper amount of Mn when used as an alloying element improves the mechanical properties of steel. Despite the important role of Mn and growth in its consumption in steelmaking, no recycling strategy for realizing stable Mn resources has been investigated. The amount of Mn wasted in slag is almost equal to the amount of Mn consumed in the steelmaking process.^{1–3)} The authors have proposed an innovative process to recover Mn in the form of an Fe–Mn alloy without any P by sulfurization of steelmaking slag. One of advantages of this process is that the sulfurization of steelmaking slag can separate P from Mn.

In order to understand the behavior of Mn and Fe during the sulfurization of molten slag, the equilibrium between an Fe–Mn–O–S matte and FeO–MnO–MgO–P₂O₅–SiO₂ slag system has been investigated.³⁾ When matte and slag are assumed to be pure sulfide and pure oxide, respectively, the equilibrium of Mn and Fe between matte and slag are governed by following equations:

$$\frac{\gamma_{\text{FeS}}}{\gamma_{\text{MnS}}} = K_1 \times \left(\frac{X_{\text{FeO}}}{X_{\text{MnO}}} \times \frac{\gamma_{\text{FeO}}}{\gamma_{\text{MnO}}} \right) \times \frac{X_{\text{MnS}}}{X_{\text{FeS}}} \quad \dots\dots\dots (2)$$

where X_{FeO} and X_{MnO} are the mole fractions of FeO and MnO in the slag, respectively; and X_{FeS} and X_{MnS} are the mole fractions of FeS and MnS in the matte, respectively; and γ_{FeO} , γ_{MnO} , γ_{FeS} and γ_{MnS} are the activity coefficients of FeO, MnO, FeS and MnS. For efficient recovery of Mn from slag, the conditions for decreasing the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio in the Fe–Mn–O–S matte have to be clarified. The value of this ratio can then be estimated using the $\gamma_{\text{FeO}}/\gamma_{\text{MnO}}$ ratio for molten slag. However, thermodynamic data for the FeO–MnO–MgO–P₂O₅–SiO₂ slag system has not been sufficiently investigated because steelmaking slag containing P normally also contains CaO. In addition, although the activity coefficients of MnO and FeO in slag could be calculated using a regular solution (RS) model⁴⁾ and FactSage,⁵⁾ the calculation results for the two models showed different values of the $\gamma_{\text{FeO}}/\gamma_{\text{MnO}}$ ratio for the same slag composition. Therefore, the γ_{MnO} and γ_{FeO} values for the FeO–MnO–MgO–P₂O₅–SiO₂ slag system should be measured to evaluate the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio for the Fe–Mn–O–S matte in Eq. (2).³⁾

In the present study, the γ_{MnO} and γ_{FeO} values for the FeO–MnO–MgO–P₂O₅–SiO₂ slag system with/without CaO were measured on the basis of the equilibrium between the slag

* Corresponding author: E-mail: ksjoong@mail.tagen.tohoku.ac.jp
DOI: <http://dx.doi.org/10.2355/isijinternational.53.1325>

and Ag at 1 673 K. The influence of slag basicity on γ_{FeO} and γ_{MnO} was also investigated by controlling the (MgO + CaO)/SiO₂ ratio in molten slag. The values of γ_{MnO} and γ_{FeO} were compared with those calculated using the RS model, FactSage, and an empirical equation. The relationship between the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ and $X_{\text{MnS}}/X_{\text{FeS}}$ ratios for the Fe–Mn–O–S matte was then estimated.

2. Experimental Method

Figure 1 shows the experimental setup used in this study. A furnace equipped with a Kanthal Super heating element and an alumina reaction tube (inner diameter: 42 mm; height: 1 000 mm) was used. The temperature of the furnace was measured using a Pt–6%Rh/Pt–30%Rh thermocouple and was maintained at $1\,673 \pm 5$ K.

Approximately 10 g silver shots (purity: 99.9%) were charged on 5 g slag powder in an Fe crucible (SS400; inner diameter: 21 mm; height: 45 mm). The slag powder was prepared from a mixture of reagent-grade MnO, MgO, Ca₃(PO₄)₂, SiO₂, CaO, Fe, and Fe₂O₃ powders. The appropriate amount of FeO in the slag was achieved by mixing the Fe and Fe₂O₃ powders in a carefully maintained mole ratio of 1:1. CaO in the slag was prepared using CaCO₃ powder calcined at 1 273 K for more than 3 h in air.

Table 1 lists the initial compositions of the slag. Slag compositions S1–S6 did not contain CaO and these compositions were similar to those in the previous experiment in which the equilibrium between the Fe–Mn–O–S matte and FeO–MnO–MgO–P₂O₅–SiO₂ slag was investigated.³⁾ The ratios of MgO and SiO₂ content, and MgO and MnO content were varied among compositions S1–S6. For comparison, slag compositions S7–S9 that contained CaO were also investigated and the ratio of CaO and SiO₂ content was varied among these compositions.

A CO/CO₂ gas mixture and Ar gas were supplied through the gas inlet of the Al₂O₃ tube. These gases were dehydrated by passing them through a glass tube filled with P₂O₅, as shown in Fig. 1. Before putting the slag sample into the furnace, Ar gas was flown into the furnace at a rate of about 150×10^{-6} m³/min for 15 min to maintain the atmosphere in the furnace in its initial state. After that, the CO/CO₂ gas mixture was flown into the furnace. The partial pressure of oxygen (P_{O_2}) in the furnace was controlled to be between

10^{-13} and 10^{-11} by changing the mixing ratio of CO and CO₂ in the gas mixture. The relation between P_{O_2} and the $P_{\text{CO}}/P_{\text{CO}_2}$ ratio can be represented by the following equations:

$$K_3 = \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}^2 \cdot P_{\text{O}_2}} \quad (4)$$

$$P_{\text{O}_2} = \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2 \cdot \frac{1}{K_3} \quad (5)$$

Table 1. Initial compositions of slag.

No.	Initial Composition / mass%						CaO/SiO ₂
	FeO	MnO	MgO	P ₂ O ₅	SiO ₂	CaO	
S1	20	20	10	5	45	–	–
S2	20	20	15	5	40	–	–
S3	20	20	20	5	35	–	–
S4	20	25	10	5	40	–	–
S5	20	25	15	5	35	–	–
S6*	20	25	15 + MgO rod	5	35	–	–
S7	17	6	15	3	39	20	0.5
S8	10	6	15	5	32	32	1
S9	7	6	15	5	31	36	1.2

*: Slag S6 was saturated with MgO by putting a MgO rod in the slag as shown in Fig. 1.

Fig. 1. Experimental setup.

Fig. 2. Variations of FeO contents and Mn distribution between Ag and slags of (a) FeO–MnO–MgO–P₂O₅–SiO₂ or (b) FeO–MnO–MgO–P₂O₅–SiO₂–CaO as a function of experimental time at 1 673K for a log P_{O_2} value of –11.

In **Table 2**, the flow rates of CO and CO₂ and the calculated values of P_{O₂} at 1 673 K are listed. The flow rates of CO and CO₂ were in the range 130–139 × 10^{−6} m³/min and 0.9–9.8 × 10^{−6} m³/min, respectively.

The sample was maintained at 1 673 K for the desired holding time, after which it was removed from the furnace and quenched in water. **Figures 2(a)** and **2(b)** show the change in the FeO content in the slag and change in the distribution ratio of Mn between the slag and Ag phases, respectively, with the holding time. In these experiments, the temperature and log P_{O₂} were maintained at 1 673 K and −11, respectively. **Figures 2(a)** and **2(b)** show the results for the FeO–MnO–MgO–P₂O₅–SiO₂ and FeO–MnO–MgO–P₂O₅–SiO₂–CaO slag systems, respectively. As shown in this figure, the FeO content and Mn distribution ratio became constant after 24 h in both slag systems. Therefore, these preliminary experiments confirmed that the reaction achieved equilibrium at 1 673 K after 24 h.

The slag sample was collected carefully by grinding the

quenched sample. Particles of Fe and pieces of Fe crucible in the slag sample were removed by magnetic treatment and chemical treatment using a solution of bromine and methanol (1:20, *vol* ratio). After removing the slag residues from the surface of the Ag sample, about 0.3 g the sample was made by cutter and dissolved in a HNO₃ solution for chemical analysis. The concentrations of Fe, Mn, Mg, Ca, and P in each slag sample were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP–AES, Optima 3300, Perkin Elmer). The concentrations of FeO, MnO, MgO, and P₂O₅ were calculated assuming them to be in stoichiometric compositions, and the SiO₂ content was calculated by subtracting the sum of the masses of these components from 100 (total mass%). In the case of FeO–MnO–MgO–P₂O₅–SiO₂–CaO slag system, the SiO₂ content was measured using the alkali-fusion and gravimetric methods. The concentration of Mn in Ag was analyzed using ICP–AES. An acid solution was prepared by mixing deionized water and HNO₃ in a 1:1 ratio. Twenty milliliters of this

Table 2. Experimental results for metal and slag.

Sample no.	logP _{O₂}	Flow rate (10 ^{−6} m ³ /min)		Slag type*	Metal		Slag (mass%)								γ _{FeO}	γ _{MnO}
		CO	CO ₂		{mass% Mn}	X {Mn}**	FeO	MnO	MgO	P ₂ O ₅	SiO ₂	CaO	FeO _{1.5} ***			
1	−11.0	130	9.8	S1	0.015	0.0003	36.25	20.63	9.38	0.64	33.10		0.90	0.980	0.194	
2				S2	0.018	0.0004	30.80	19.92	15.21	0.99	33.07		0.89	1.202	0.253	
3				S3	0.024	0.0005	26.33	20.85	19.81	1.52	31.50		0.95	1.454	0.313	
4				S4	0.021	0.0004	27.88	21.45	8.29	1.25	41.14		0.41	1.266	0.261	
5				S5	0.026	0.0005	24.95	25.98	17.87	1.14	30.05		1.07	1.525	0.276	
6				S6	0.025	0.0005	26.14	25.47	16.75	1.45	30.19		1.06	1.440	0.266	
7	−12.0	137	2.7	S1	0.023	0.0004	25.04	20.63	9.38	0.26	44.68		0.15	0.379	0.080	
8				S2	0.030	0.0007	18.03	19.92	15.21	0.20	46.63		0.12	0.550	0.137	
9				S3	0.036	0.0007	16.67	20.85	19.81	0.91	41.76		0.17	0.608	0.132	
10				S4	0.034	0.0007	22.81	25.20	9.13	0.48	42.37		0.19	0.415	0.096	
11				S5	0.049	0.0009	15.63	25.98	17.87	0.26	40.26		0.19	0.643	0.142	
12				S6	0.059	0.0011	12.76	27.26	17.38	0.34	42.26		0.14	0.786	0.163	
13	−13.0	139	0.9	S1	0.022	0.0004	18.09	18.61	9.21	0.18	53.91		0.03	0.173	0.028	
14				S2	0.036	0.0007	16.57	18.80	13.93	0.30	50.39		0.05	0.193	0.047	
15				S3	0.048	0.0009	11.67	19.97	19.17	0.40	48.80		0.04	0.283	0.060	
16				S4	0.049	0.0010	14.21	25.23	9.95	0.14	50.47		0.04	0.220	0.047	
17				S5	0.064	0.0012	9.16	25.91	15.22	0.11	49.59		0.03	0.353	0.060	
18				S6	0.088	0.0017	10.31	24.20	16.05	0.15	49.29		0.04	0.315	0.089	
C-01	−11.0	130	9.8	S7	0.019	0.0004	19.28	6.94	15.10	2.51	41.38	21.04	0.48	2.075	0.845	
C-02				S8	0.040	0.0008	8.16	6.41	14.73	4.70	30.36	33.53	0.39	4.598	1.775	
C-03				S9	0.047	0.0009	6.37	6.40	14.30	4.93	30.10	36.52	0.40	5.948	2.119	
C-04	−12.0	137	2.7	S7	0.037	0.0007	8.11	8.30	16.84	0.87	44.52	23.61	0.11	1.309	0.360	
C-05				S8	0.115	0.0022	2.73	6.53	16.33	4.16	33.78	35.87	0.06	3.781	1.387	
C-06				S9	0.152	0.0030	1.94	6.19	15.76	4.21	32.85	38.85	0.09	5.358	1.953	
C-07	−13.0	139	0.9	S7	0.088	0.0017	3.70	9.22	17.78	0.08	47.55	25.02	0.03	0.954	0.259	
C-08				S8	0.221	0.0043	1.93	7.15	16.96	2.26	37.39	39.69	0.03	1.870	0.850	
C-09				S9	0.268	0.0053	1.31	5.74	16.14	3.12	33.37	39.37	0.13	2.595	1.219	

*: Slag compositions at the initial stage are listed in Table 1.

**: X {Mn} denotes the mol fraction of Mn in Ag.

***: FeO_{1.5} content values are calculated using Eq. (7).

acid solution was added to about 0.3 g Ag sample, and the mixture was then heated at about 373 K for 1 h. No residue was observed on a filter paper after filtration of this solution.

3. Results

3.1. Equilibrium between Ag and FeO–MnO–MgO–P₂O₅–SiO₂(–CaO) Slag System

Table 2 lists the measured chemical compositions of Ag and slag. Samples 1–18 indicate the results for the equilibrium between Ag and the FeO–MnO–MgO–P₂O₅–SiO₂ slag system. Samples C01–C09 indicate the results for the equilibrium between Ag and the FeO–MnO–MgO–P₂O₅–SiO₂–CaO slag system. In Table 2, the listed concentration of FeO_{1.5} in the slag was calculated using Eq. (6), assuming the activity coefficient ratio of FeO/FeO_{1.5} to be unity. On the basis of this assumption, the equilibrium relation given in Eq. (6) can be rewritten as Eq. (7) and the mole fractions of FeO and FeO_{1.5} can be calculated using log P_{O₂}. Moreover, the mole fraction of total Fe can be obtained from chemical analysis.

$$\begin{aligned} \text{FeO}_{1.5}(\text{R.S.}) &= \text{FeO}(\text{R.S.}) + 1/4\text{O}_2(\text{g}) \\ \Delta G^\circ(\text{J/mol})^{(4)} &= 126\,820 - 53.01T \end{aligned} \quad (6)$$

$$RT \ln K_6 = RT \ln (X_{\text{FeO}} / X_{\text{FeO}_{1.5}}) + 1/4 RT \ln P_{\text{O}_2} \quad (7)$$

Since the calculated concentration of FeO_{1.5} was below 1.07 mass%, as listed in Table 2, most of the Fe oxide in the slag can be considered to be FeO. Therefore, in the present study, the analyzed value of Fe was converted to FeO by

Fig. 3. Influence of the oxygen partial pressure on the FeO concentration (a) and distribution ratio of Mn (L_{Mn}) (b). The initial concentration of FeO in S1–S6 slag is 20 mass%. S6 slag was saturated with MgO by putting a MgO rod in the slag as shown in Fig. 1. In the case of S7, S8 and S9, the initial concentrations of FeO are 17, 10 and 7, respectively.

using a stoichiometric relation.

Figures 3(a) and 3(b) show the effect of P_{O₂} on the FeO concentration and distribution ratio of Mn (L_{Mn}), respectively. The value of L_{Mn} can be calculated using the following equation:

$$L_{\text{Mn}} = \frac{\text{mass\% MnO in slag}}{\text{mass\% Mn in silver phase}} \quad (8)$$

Although the initial composition of FeO did not change in each slag, the FeO content increased upon increasing P_{O₂}. In addition, L_{Mn} also increased with an increase in P_{O₂}. **Figure 4** shows the effect of slag basicity on FeO concentration and L_{Mn} for a log P_{O₂} value of –11. The slag basicity is expressed by the following equation:

$$\text{Slag basicity} = \frac{\text{\%CaO} + \text{\%MgO}}{\text{\%SiO}_2} \quad (9)$$

It is clear that both FeO concentration and L_{Mn} decreased with an increase in the slag basicity.

3.2. Evaluation of Activity Coefficients of MnO and FeO

The equilibrium relation between Mn in Ag and MnO in the slag can be expressed by the following equations:

$$\begin{aligned} \text{Mn}(\text{l}) + 1/2\text{O}_2 &= \text{MnO}(\text{l}), \\ \Delta G^\circ(\text{J/mol})^{(6)} &= -356\,650 + 64.800T \end{aligned} \quad (10)$$

$$K_{10} = \frac{a_{\text{MnO}}}{a_{\text{Mn}} \cdot P_{\text{O}_2}^{1/2}} \quad (11)$$

$$\gamma_{\text{MnO}} = \frac{\gamma_{\text{Mn}} \cdot X_{\text{Mn}} \cdot P_{\text{O}_2}^{1/2} \cdot K_{10}}{X_{\text{MnO}}} \quad (12)$$

where γ_{Mn} , K_{10} , P_{O₂}, X_{Mn} , and X_{MnO} are the activity coefficient of Mn in Ag, equilibrium constant, partial pressure of oxygen, mole fraction of Mn in the Ag phase, and mole fraction of MnO in the slag, respectively. Moreover, γ_{Mn} is given by the following equation:⁷⁾

$$\log \gamma_{\text{Mn}} = -\frac{358}{T} - 0.0178 \quad (13)$$

When P_{O₂} is known from experimental conditions, γ_{MnO} can

Fig. 4. Effect of slag basicity on FeO concentration and Mn distribution between slag/silver when log P_{O₂} is –11.

be obtained by putting the measured values of X_{Mn} , and X_{MnO} in Eq. (12).

On the other hand, the equilibrium between Fe(s) and FeO in the slag is governed by the following equation:

The activity of Fe(s) is unity because Ag is saturated with Fe by using an Fe crucible. Equation (14) can then be expressed as follows:

$$K_{14} = \frac{a_{\text{FeO}}}{P_{\text{O}_2}^{1/2}} \quad \text{..... (15)}$$

$$\gamma_{\text{FeO}} = \frac{P_{\text{O}_2}^{1/2} \cdot K_{14}}{X_{\text{FeO}}} \quad \text{..... (16)}$$

where γ_{FeO} , K_{14} , P_{O_2} , and X_{FeO} indicate the activity coefficient of FeO, equilibrium constant, partial pressure of oxygen, and mole fraction of FeO in the slag, respectively. γ_{FeO} can be obtained using Eq. (16) and X_{FeO} . When P_{O_2} is low, P_2O_5 in the slag is reduced, and reduced P can be dissolved in the Fe crucible. However, the activity of solid Fe can be assumed to be unity because the solubility of P in solid Fe is below 2 mass% according to the Fe–P binary phase diagram⁸⁾ at 1673 K.

The obtained values of γ_{MnO} and γ_{FeO} are listed in Table 2. **Figures 5(a)** and **5(b)** show the effect of slag basicity and FeO content on γ_{FeO} and γ_{MnO} , respectively. As can be seen in these figures, both γ_{FeO} and γ_{MnO} increased with an increase in the basicity. Moreover, when the basicity was constant, both γ_{FeO} and γ_{MnO} increased with an increase in the FeO content. **Figure 6** shows the effect of slag basicity on the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio; this ratio was almost constant in spite of any change in the basicity.

4. Discussion

4.1. Thermodynamic Assessment of γ_{MnO} and γ_{FeO}

The values of γ_{MnO} and γ_{FeO} for molten slag were calculated using a RS model and FactSage. Ban-ya⁴⁾ employed the RS model to calculate the activity and activity coefficient of oxides in molten slag on the basis of interaction energies between cations. The activity coefficient of a component i , $\gamma_{i\text{RS}}$, in a multicomponent regular solution can be expressed as

$$RT \ln \gamma_{i\text{RS}} = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \quad \text{..... (17)}$$

where α_{ij} denotes the interaction energies between the cation of i component and the cation of j component; and X_j is the mole fraction of j component. From Eq. (17), the reference state of i indicates a hypothetical liquid oxide of a regular nature. Therefore, γ_i for a real slag can be obtained using the following equation:

$$RT \ln \gamma_i = RT \ln \gamma_{i\text{RS}} + \mathbf{I} \quad \text{..... (18)}$$

Here, $\mathbf{I}$ is a conversion factor for γ_i of a hypothetical liquid oxide and that of a real solution in a multicomponent slag. From Eqs. (17) and (18), the interaction energies and conversion factor are very important parameters for formulating

Fig. 5. Influence of slag basicity and FeO concentration on activity coefficients of FeO (a) and MnO (b).

Fig. 6. Comparison of $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ in FeO–MnO–MgO–P₂O₅–SiO₂ (–CaO) slag system as a function of slag basicity at 1673 K.

the activity coefficients of components in molten slag. The interaction energies between cations as calculated by Ban-ya⁴⁾ and Suito and Inoue⁹⁾ are listed in Table 3.

Furthermore, Ban-ya *et al.*¹⁰⁾ reported the conversion factors for FeO and MnO by comparing the measured values of $a_{\text{FeO(l)}}$ for an FeO–SiO₂ system and $a_{\text{MnO(l)}}$ for a MnO–SiO₂ system, respectively, with the values calculated using the RS model. The conversion factors for FeO and MnO are expressed by the following equations:

Table 3. Interaction energies between cations for regular solution model.

ion-ion	Ref. 4) (J)	Ref. 9) (J)	Present work (J)	ion-ion	Ref. 4) (J)	Ref. 9) (J)	Present work (J)
Fe ²⁺ –Mn ²⁺	7 110	0	7 110	Si ⁴⁺ –Mg ²⁺	–66 940	–127 612	–127 612
Fe ²⁺ –Ca ²⁺	–31 380	–50 208	–31 380	Si ⁴⁺ –Ca ²⁺	–133 890	–271 960	–271 960
Fe ²⁺ –Si ⁴⁺	–41 840	–41 840	–41 840	Mg ²⁺ –Ca ²⁺	–100 420	18 828	–100 420
Fe ²⁺ –Mg ²⁺	33 470	12 845	12 845	P ⁵⁺ –Fe ²⁺	–31 380	12 845	12 845
Mn ²⁺ –Ca ²⁺	–92 050	–16 736	–16 736	P ⁵⁺ –Mn ²⁺	–84 940	–108 784	–84 940
Mn ²⁺ –Si ⁴⁺	–75 310	–76 776		P ⁵⁺ –Mg ²⁺	–37 660	–134 725	–37 660
		–100 416	–100 416	P ⁵⁺ –Ca ²⁺	–251 040		–251 040
Mn ²⁺ –Mg ²⁺	61 920	–23 849	–23 849	P ⁵⁺ –Si ⁴⁺	83 860		83 860

Fig. 7. Comparison of activity coefficients of FeO (a) and MnO (b) between the measured values and the calculated values by using the interaction energies of Refs. 4) and 9) listed in Table 3. Conversion reactions of FeO and MnO were Eqs. (21) and (22).

From Eqs. (19) and (20), the conversion reactions for FeO and MnO at 1 673 K can be derived as follows:

$$a_{\text{FeO(l)}} = 1.278a_{\text{FeO(RS)}} \quad \text{..... (21)}$$

$$a_{\text{MnO(l)}} = 0.952a_{\text{MnO(RS)}} \quad \text{..... (22)}$$

where $a_{\text{FeO(l)}}$, $a_{\text{MnO(l)}}$, $a_{\text{FeO(RS)}}$, and $a_{\text{MnO(RS)}}$ are the activities of FeO and MnO in molten slag and regular solution, respectively.

Figure 7 shows a comparison of activity coefficients of FeO (a) and MnO (b) between the measured values in Table 2 and the calculated values by using the interaction energies

Fig. 8. Comparison of activity coefficients of FeO (a) and MnO (b) between the modified interaction energies of measured values and the calculated values by using the present work in Table 3. In Fig. (a), the conversion reactions of γ_{FeO} were used by Eqs. (21) and (23). And the conversion reactions of γ_{MnO} were used by Eqs. (22) and (24) in Fig. (b).

of Refs. 4) and 9) shown in Table 3. As shown in Fig. 7(a), although the calculated values of γ_{FeO} based on Ref. 4) were closer to the measured γ_{FeO} values than those based on Ref. 9), the calculated values do not meet the experimental values. Moreover, in the case of γ_{MnO} values too (Fig. 7(b)), although the calculation values based on Ref. 9) were closer to the measured values than those based on Ref. 4), the calculated values do not meet the experimental values. Therefore, to estimate the γ_{FeO} and γ_{MnO} values for the slag system used in this study, a revision of the interaction energy is necessary. In the present study, interaction energies were chosen so that the calculated values of γ_{FeO} and γ_{MnO} would be close to the experimental values. As the results, the interaction energies for Fe²⁺ and P⁵⁺ cations listed in Ref. 4) were used except the interaction energies for P⁵⁺–Fe²⁺ and Fe²⁺–Mg²⁺.

For the interaction energies for Mn^{2+} and $\text{Si}^{4+}\text{--Mg}^{2+}$, $\text{Si}^{4+}\text{--Ca}^{2+}$, and $\text{Fe}^{2+}\text{--Mg}^{2+}$, the values listed in Ref. 9) were used. In the case of $\text{Mg}^{2+}\text{--Ca}^{2+}$ and $\text{P}^{5+}\text{--Fe}^{2+}$, the sign of the interaction energy listed in Ref. 4) is different from that listed in Ref. 9). On the basis of the dependence of each component on the activity coefficient, for $\text{Mg}^{2+}\text{--Ca}^{2+}$, the value listed in Ref. 4) was used, and for $\text{P}^{5+}\text{--Fe}^{2+}$, that listed in Ref. 9) was used. The interaction energies used in the present study are listed in Table 3.

Figure 8 shows a comparison between the measured (Table 2) and calculated values of γ_{FeO} (a) and γ_{MnO} (b); the calculated values were obtained using the interaction energies of the present study listed in Table 3. The comparison of γ_{FeO} values shown in Fig. 8(a) is represented using the conversion reactions given by Eqs. (21) and (23). Similarly, in Fig. 8(B), the comparison of γ_{MnO} values is represented by the conversion reactions given by Eqs. (22) and (24). Despite revising the interaction energies, the values of γ_{FeO} and γ_{MnO} calculated using Eqs. (21) and (22)⁴⁾ were higher than the measured values. Kim and Song¹¹⁾ reported that the a_{FeO} values calculated using the interaction energies proposed by Ban-ya⁴⁾ were larger than the measured a_{FeO} values for a slag saturated with MgO. They also suggested that it is necessary to change the conversion factor for its application to their slag system. Therefore, to fit the calculated values to the measured ones, the values of $a_{\text{FeO(RS)}}$ and $a_{\text{MnO(RS)}}$ at 1 673 K were changed according to the following equations:

$$a_{\text{FeO(1)}} = 0.37a_{\text{FeO(R.S.)}} \quad \text{..... (23)}$$

$$a_{\text{MnO(1)}} = 0.74a_{\text{MnO(R.S.)}} \quad \text{..... (24)}$$

Fig. 9. Comparison of activity coefficients of FeO (a) and MnO (b) between the measured values and the calculating values by Factsage⁵⁾ and regular solution model of present work.

As shown in Fig. 8, the γ_{FeO} and γ_{MnO} values calculated using Eqs. (23) and (24) achieved a linear correspondence with the measured values.

Figure 9 shows a comparison between the measured and calculated values of γ_{FeO} (a) and γ_{MnO} (b) for the FeO–MnO–MgO–P₂O₅–SiO₂ slag system; the calculated values were obtained using the RS model (present study) and FactSage.⁵⁾ The γ_{FeO} values calculated using FactSage corresponded well with the measured values; however, the γ_{MnO} values calculated using FactSage were larger than the measured values.

The purpose of this research is to evaluate the γ_{FeO} and γ_{MnO} values for a slag that was equilibrated with matte in a previous study.³⁾ For achieving this, the application of a general model, *i.e.*, RS model or FactSage, is not imperative. As the slag composition and temperature of this study were close to those in the previous study, for precise estimation, multiple linear regression analyses were conducted. The empirical equations for the FeO–MnO–MgO–P₂O₅–SiO₂ slag system (**Fig. 10**) were obtained as follows:

$$\begin{aligned} \log \gamma_{\text{FeO}} = & 0.013(\% \text{FeO}) + 0.016(\% \text{MnO}) + 0.016(\% \text{MgO}) \\ & - 0.018(\% \text{P}_2\text{O}_5) - 0.026(\% \text{SiO}_2) \end{aligned} \quad \text{..... (25)}$$

$$\begin{aligned} \log \gamma_{\text{MnO}} = & 0.005(\% \text{FeO}) + 0.007(\% \text{MnO}) + 0.011(\% \text{MgO}) \\ & - 0.022(\% \text{P}_2\text{O}_5) - 0.032(\% \text{SiO}_2) \end{aligned} \quad \text{..... (26)}$$

Fig. 10. Comparison of activity coefficients of FeO (a) and MnO (b) between the measured values of FeO–MnO–MgO–P₂O₅–SiO₂ slag system and the calculated values by Multiple Linear Regression Analysis.

Fig. 11. Comparison of activity coefficients of FeO (a) and MnO (b) between the measured values of FeO–MnO–MgO–P₂O₅–SiO₂–CaO slag system and the calculated values by Multiple Linear Regression Analysis.

The empirical equations for the FeO–MnO–MgO–P₂O₅–SiO₂–CaO slag system (Fig. 11) were obtained as follows:

$$\log \gamma_{\text{FeO}} = -0.011(\% \text{FeO}) - 0.012(\% \text{MnO}) - 0.007(\% \text{MgO}) + 0.200(\% \text{P}_2\text{O}_5) + 0.009(\% \text{SiO}_2) - 0.007(\% \text{CaO}) \quad (27)$$

$$\log \gamma_{\text{MnO}} = 0.009(\% \text{FeO}) - 0.003(\% \text{MnO}) + 0.014(\% \text{MgO}) - 0.022(\% \text{P}_2\text{O}_5) - 0.032(\% \text{SiO}_2) + 0.025(\% \text{CaO}) \quad (28)$$

4.2. Activity Coefficient Ratio for Mn and Fe in Fe–Mn–O–S Matte

On the basis of the slag composition used in our previous study,³⁾ the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio for the FeO–MnO–MgO–P₂O₅–SiO₂ slag system equilibrated with matte was calculated using a RS model with modified parameters, FactSage, and an empirical formula.

Figure 12 shows a comparison between the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ values for matte obtained by putting the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratios obtained from the three methods in Eq. (2). In spite of the different methods used to calculate the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratios, we obtained similar values of the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio than those of previous results.³⁾ When the RS model was used to calculate the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio decreased slightly with

Fig. 12. Relationship between the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ and $X_{\text{MnS}}/X_{\text{FeS}}$ in Fe–Mn–O–S matte. The $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio in FeO–MnO–MgO–P₂O₅–SiO₂ slag were calculated by empirical formula, FactSage and RS model of present work.

an increase in the $X_{\text{MnS}}/X_{\text{FeS}}$ ratio. In contrast, when the empirical formula and FactSage were used, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio was almost constant when the $X_{\text{MnS}}/X_{\text{FeS}}$ ratio was increased. For a constant $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio in Eq. (2), the $X_{\text{MnS}}/X_{\text{FeS}}$ ratio for matte can be improved by increasing the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio for slag. On the basis of the present study, it can be concluded that γ_{MnO} and γ_{FeO} increase with an increase in slag basicity. Therefore, the effect of slag basicity on the distribution of Mn and Fe between the Ca–Fe–Mn–O–S matte and multicomponent slag should be investigated.

5. Conclusions

The values of γ_{MnO} and γ_{FeO} for a FeO–MnO–MgO–P₂O₅–SiO₂–(CaO) slag system were measured on the basis of the equilibrium between Ag and molten slag at 1 673 K under a controlled atmosphere. For obtaining the relationship between the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ and $X_{\text{MnS}}/X_{\text{FeS}}$ ratios for matte, γ_{MnO} and γ_{FeO} for the multicomponent slag were evaluated using the regular solution model, FactSage, and an empirical formula. The following conclusions were obtained:

(1) Both γ_{MnO} and γ_{FeO} increased with an increase in slag basicity. Moreover, when slag basicity was kept constant, both γ_{MnO} and γ_{FeO} increased upon increasing the FeO concentration in slag. However, the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio was constant against changes in slag basicity.

(2) The values of γ_{MnO} and γ_{FeO} for the multicomponent slag with/without CaO were evaluated using a regular solution model, FactSage, and an empirical formula. In the case of the RS model, the interaction energies and conversion factors to fit the calculated values to the experimental results were reassessed.

(3) By the used of the empirical formula, FactSage and the regular solution model of present work, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio for the Fe–Mn–O–S matte equilibrated with the FeO–MnO–MgO–P₂O₅–SiO₂ slag was evaluated. When the RS model was used to calculate the $\gamma_{\text{MnO}}/\gamma_{\text{FeO}}$ ratio, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio decreased slightly with an increase in the $X_{\text{MnS}}/X_{\text{FeS}}$ ratio. In contrast, when the empirical formula and FactSage were used, the $\gamma_{\text{MnS}}/\gamma_{\text{FeS}}$ ratio was almost constant when the $X_{\text{MnS}}/X_{\text{FeS}}$ ratio was increased.

Acknowledgement

The authors appreciate the financial support of the Japan Society for the Promotion of Science (21360367), Grant-in-Aid for Scientific Research (B), the Sumitomo Foundation, and the Steel Industry Foundation for the Advancement of Environmental Protection Technology.

REFERENCES

- 1) S.-J. Kim, T. Hotta, H. Shibata, S. Kitamura and K. Yamaguchi: Proc. of the 6th European Slag, EUROSLAG Publication, Madrid, Spain, (2010), 183.
- 2) S.-J. Kim, H. Shibata, N. Maruoka, S. Kitamura and K. Yamaguchi: *High Temp. Mater. Proc.*, **30** (2011), 425.
- 3) S.-J. Kim, H. Shibata, J. Takekawa, S. Kitamura, K. Yamaguchi and Y.-B. Kang: *Metall. Mater. Trans.*, **43B** (2012), 1069.
- 4) S. Ban-ya: *ISIJ Int.*, **33** (1993), 2.
- 5) C. W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melançon, A. D. Pelton, C. Robelin and S. Petersen: *Calphad*, **33** (2009), 295.
- 6) O. Knacke, O. Kubaschewski and K. Hesselmann: Thermochemical Properties for Inorganic Substances, 2nd ed., Springer-Verlag, Verlag Stahleisen, Berlin-New York, (1991).
- 7) S.-M. Jung, C.-H. Rhee and D.-J. Min: *ISIJ Int.*, **42** (2002), 63.
- 8) M. Hansen and K. Anderko: Constitution of Binary Alloys, McGraw-Hill, New York, (1965).
- 9) H. Suito and R. Inoue: *Tetsu-to-Hagané*, **70** (1984), 533.
- 10) S. Ban-ya, M. Hino and N. Yuge: *Tetsu-to-Hagané*, **71** (1985), 853.
- 11) S.-H. Kim and B. Song: *Metall. Mater. Trans.*, **30B** (1999), 435.