Thermodynamic Activity of MnO in CaO–SiO₂–MnO–FeO–MgO Molten Slags

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In order to understand the thermodynamic characteristics of smelting process for high manganese twinning-induced plasticity (TWIP) steel, the activity coefficient of MnO in molten slag of MnO–CaO–SiO₂–FeO–MgO slag system with up to 52 mass% MnO was measured at 1 450°C by the experiments of the manganese equilibrium between liquid silver and molten slag under the mixed gas atmosphere of CO, CO₂ and Ar. The distribution ratio of manganese L_{Mn} between the molten silver and molten slag, and the equilibrium concentration quotient K' were also measured. The effects of MnO, FeO and basicity on the activity coefficient of MnO, the distribution ratio of manganese and the equilibrium concentration quotient were discussed. The activity coefficient of MnO, the distribution ratio of manganese and the equilibrium concentration quotient as a function of the concentration of the components in molten slag were investigated by regression analysis method. The results show that: (a) The Raoultian activity coefficients of MnO in molten slag are less than unity. (b) When the basicity $B = 0.77$ – 1.15 , $MnO = 15.8$ – 52.9 mass% and $FeO = 7$ – 20 mass%, the activity coefficient of MnO increases as MnO content increases, but the L_{Mn} and the K' decrease as MnO content increases. (c) When $B = 0.89$ – 1.08 , $MnO = 43.6$ – 46.9 mass% and $FeO = 7$ – 20 mass%, the activity coefficient of MnO increases as FeO content increases, but the L_{Mn} and the K' decrease as FeO content increases. (d) When $MnO = 40$ – 45 mass%, $FeO = 9$ – 14 mass% and $B = 0.7$ – 1.8 , the activity coefficient of MnO increases as the basicity increases, but the L_{Mn} and the K' decrease as the basicity increases.

KEY WORDS: thermodynamics; activity coefficient; manganese oxide; activity; manganese distribution; concentration quotient; TWIP steel.

1. Introduction

As high manganese TWIP (Twinning-Induced Plasticity) austenitic steel has a good combination of strength and plasticity,¹⁾ it has received great attention in the research field of steel materials for lightweight vehicles. However, lowering the alloying cost of manganese will be one of the technical difficulties for large-scale commercial smelting of high manganese TWIP Steel because of its high content of manganese and high affinity of manganese with oxygen. In order to reduce the smelting cost of high manganese TWIP Steel, a large amount of high carbon ferromanganese is charged into the molten iron before oxygen blowing in the oxidation refining period. A large amount of manganese is oxidized and forms slag with high MnO content at the low temperature during the beginning of oxygen refining. The molten slag formed at this stage is the CaO–SiO₂–MnO–FeO–MgO slag system. The activity of MnO is thus needed to understand the thermodynamics of the reaction of manga-

nese oxidation at this oxygen blowing stage.

Many researchers have studied the thermodynamic properties of MnO in the slag containing MnO. The slag systems studied covered MnO–SiO₂,²⁾ MnO–SiO₂–CaO,^{3,4)} MnO–CaO–Al₂O₃,^{3,5)} MnO–CaO–SiO₂–Al₂O₃,^{3,4)} MnO–CaO–SiO₂–Al₂O₃–FeO ($MnO < 10$ wt%, $FeO < 3$ wt%),⁶⁾ MnO–CaO–SiO₂–Al₂O₃–MgO,⁷⁾ MnO–CaO–SiO₂–MgO,⁴⁾ MnO–CaO–SiO₂–FeO–Fe₂O₃ ($MnO < 21$ wt%, $FeO < 31$ wt%),⁸⁾ MnO–CaO–SiO₂–Al₂O₃–FeO–MgO ($MnO = 3$ – 16 wt%, $FeO = 3$ – 11 wt%),⁹⁾ CaO–MnO–SiO₂–FeO–MgO–P₂O₅ system containing P₂O₅ (hot metal pretreatment,¹⁰⁾ sulphurization of steelmaking slag¹¹⁾), and the slag system containing Cr₂O₃ for stainless steel refining process.¹²⁾ Eom *et al.*⁴⁾ studied the thermodynamic behavior of MnO in the CaO–SiO₂–MnO system, CaO–SiO₂–MnO–Al₂O₃ system and CaO–SiO₂–MnO–MgO system slags without FeO in the reducing process of MnO during the smelting process of high manganese TWIP Steel. Yan *et al.*⁷⁾ studied the thermodynamic behavior of MnO in the CaO–SiO₂–MnO–Al₂O₃–MgO system slags without FeO, where MnO ore is the manganese source and this slags system is involved in

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the reduction process in high manganese TWIP steel converter smelting. The thermodynamic data on the activity and activity coefficient of MnO in blast furnace slags, steelmaking slags, secondary refining slags, ferromanganese slags and complex slag systems have been accumulated.^{2–33)} The data on the distribution of manganese between the slag and metal have also been accumulated.^{4,6,8–11,20–25,34–41)} In existing studies on MnO-containing slag system with ternary and above-components, the Al₂O₃-containing slag system was most heavily studied while the FeO-containing slag system was least studied. However, MnO-containing slag systems without Al₂O₃ was found in studies that the MnO content in a FeO-containing slag system without P₂O₅ was lower than 21 wt%, and in a slag system containing both FeO and P₂O₅, the MnO content was lower than 28 wt%. If in the early stage of steel refining, a large amount of high carbon ferromanganese is used before oxygen blowing at temperature below 1 500°C, the high manganese content in the molten steel will be oxidized rapidly and thus lead to a quick increase in MnO content. The MnO content in the slag at that time will greatly exceed the MnO content in those studies above. Apparently, due to the low MnO content in the existing research on the thermodynamic behavior of slag containing both MnO and FeO, the existing thermodynamic data will not be used to make accurate thermodynamic analysis for the early stage of high manganese steel smelting.

In present paper, the MnO content in CaO–SiO₂–MnO–FeO–MgO system will be extended to a high MnO range up to 52 wt%. The activity coefficient of MnO in molten slag at 1 450°C and its relationship with the FeO, MnO and the basicity will be investigated by the chemical equilibrium experiment of manganese between liquid silver and CaO–SiO₂–MnO–FeO–MgO molten slag under the mixed gas atmosphere of CO, CO₂ and Ar.

2. Experimental

A pre-mixed slag and a silver flake were melted in a pure iron crucible under argon atmosphere, and then the entire reaction system was equilibrated by holding for enough time under a CO–CO₂ mixed at a given flow rate. The equilibrium of reaction (1) was selected to determine the activity coefficient of MnO in slag.

Figure 1 is a schematic diagram of the experimental apparatus used in this experiment. A SiMo-resistor furnace with mullite tube (120 mm-OD) was used in the experiments. A corundum crucible (85 mm-OD × 100 mm-height) was equipped with three high pure Fe crucibles (35 mm-ID × 35 mm-height). 10 g of metal Ag and 12 g of pre-mixed slag were filled in the Fe crucible. A pure iron is selected as the crucible and a pure Ag as a reference metal. The metal Ag was prepared by 99.9% 3 N grade silver flakes. The slag was prepared by 99.5% MnO, 98% CaO, AR (analytical reagent) grade SiO₂, 98.5% MgO reagents. FeO was prepared by AR grade iron powder and 99.0% Fe₂O₃ at the molar mass of 1:1. The purity of carbon monoxide, carbon dioxide and argon were 99.995%, 99.995% and 99.999%, respectively. A Pt/6% Rh–Pt/30% Rh thermocouples was used to measure the temperature of the molten bath at the bottom of the

Fig. 1. Schematic diagram of the experimental apparatus.

corundum crucible at the furnace bottom. A PID controller was used to control the temperature within $\pm 1^\circ\text{C}$ during the whole melting process.

In the experiments, three iron crucibles filled with metal and slag were placed in the corundum crucible in the center of the resistance furnace. Ar gas had been blown into the top of three iron crucibles in corundum crucible at a flow rate of 150 ml/min to maintain the low oxygen atmosphere during the melting process before the temperature of the crucible reached 1 450°C. After 30 minutes, mixture of CO and CO₂ was introduced to the top of three iron crucibles in the corundum crucible to control the oxygen partial pressure. The flow ratio of CO and CO₂ was 150:1 (at that time $p_{\text{O}_2} = 3.37 \times 10^{-13}$ atm), and the total flow was 151 ml/min. The flow of CO and CO₂ was controlled by mass flow meter respectively. Each gas was sent through a tube filled with silica gel to be dried, then it was mixed in a spherical glass cylinder. The mixed gas was finally passed into the furnace. After introducing CO–CO₂ mixed gas, argon gas flow was adjusted to 50 ml/min. After the temperature had reached 1 450°C, it lasted 30 minutes to make the temperature and composition in the furnace uniform. And then timing started. 24 hours later, the corundum crucible was taken out and was rapidly cooled down in an Ar gas stream. Then the samples were cut. The slag sample, the metal Ag sample and crucible were separated from each other. The composition in metallic silver sample was analyzed by atomic absorption spectrometry. The composition in the slag sample was determined by X-ray fluorescence spectrometry.

In a similar study, Jung *et al.*⁸⁾ found that the distribution of manganese achieved equilibrium in 8 hours in the equilibrium experiment of 5 g CaO–SiO₂–FeO–MnO slag and 10 g Ag at 1 673 K under a CO/CO₂ gas mixture. The reaction system achieved equilibrium in 22 hours in another similar experiment of the author. Therefore, the equilibrium time of the reaction used in present study was 24 h.

3. Results

Table 1 shows the equilibrium concentration of compo-

Table 1. Equilibrium concentrations of metal and slag and the activity coefficient of MnO and FeO at 1 450°C.

No.	Composition of Metal		Composition of Slag (mass pct)					$\gamma_{\text{MnO(s)}}$	a_{MnO}	$\gamma_{\text{FeO(l)}}$
	[mass%Mn] _{in Ag}	$x_{\text{Mn in Ag}}$	MnO	FeO	SiO ₂	CaO	MgO			
1	0.065	0.00128	15.79	24.39	32.70	20.24	9.94	0.227	0.029	0.251
2	0.10	0.00196	28.77	9.95	33.25	19.35	10.57	0.191	0.045	0.612
3	0.21	0.00411	46.07	7.03	27.01	13.20	10.84	0.249	0.095	0.864
4	0.48	0.00933	52.92	16.38	17.05	8.23	10.44	0.481	0.216	0.363
5	0.22	0.00431	43.63	9.00	25.07	12.40	12.05	0.272	0.100	0.665
6	0.25	0.00490	44.93	10.07	23.04	11.83	12.49	0.300	0.113	0.595
7	0.29	0.00568	44.76	15.91	21.76	9.27	12.15	0.350	0.131	0.377
8	0.30	0.00587	45.04	18.64	20.36	7.43	12.70	0.359	0.136	0.322
9	0.47	0.00919	46.88	20.06	18.59	6.49	13.56	0.547	0.212	0.303
10	0.19	0.00372	48.27	23.84	15.46	4.46	13.34	0.213	0.086	0.252
11	0.13	0.00255	46.78	28.92	14.16	2.46	12.24	0.147	0.059	0.203
12	0.22	0.00431	41.29	9.75	28.24	10.50	11.20	0.283	0.100	0.605
13	0.25	0.00490	42.34	11.99	19.39	16.76	11.41	0.316	0.113	0.497
14	0.33	0.00646	41.71	9.51	18.82	20.71	11.71	0.430	0.149	0.636
15	0.36	0.00704	42.36	7.18	18.31	22.32	13.26	0.471	0.163	0.859
16	0.40	0.00782	43.04	12.85	20.46	17.20	9.60	0.498	0.181	0.464
17	0.47	0.00919	40.12	13.31	19.81	20.45	9.73	0.633	0.212	0.452
18	0.55	0.01074	40.36	13.84	17.60	21.54	10.04	0.737	0.248	0.435

nents in metal and slag when the metal-slag-gas reaction system achieves equilibrium. The activity coefficient and the activity of MnO and FeO in slag are also listed in the table.

The equilibrium constant K_1 in reaction (1) can be deduced from the standard Gibbs free energy changes ΔG° of reaction (2)–(4).

So, the standard Gibbs free energy changes of the reaction (1) can be calculated from Eq. (5).

The equilibrium constant of the reaction (1) can be written as:

$$K_1 = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{a_{\text{Mn}}}{a_{\text{MnO}}} = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{\gamma_{\text{Mn}} x_{\text{Mn}}}{\gamma_{\text{MnO}} x_{\text{MnO}}} \quad \dots (6)$$

Where, p is the partial pressure of component, atm; x is the mole fraction of the component; γ_{Mn} and γ_{MnO} are the Raoultian activity coefficients of Mn in liquid silver and MnO in molten slag, respectively; K_1 is the equilibrium constant of the reaction (1), which is equal to the equilibrium constant of reaction (5) under these selected standard states of activ-

ity. The derived equilibrium constant K_1 is:

$$\lg K_1 = -\frac{6\,269}{T} - 0.05 \quad \dots (7)$$

Since the mole fraction of Mn in liquid Ag is very low (as shown in Table 1), Mn in liquid Ag can be considered to obey Henry's law, the Raoultian activity coefficient γ_{Mn} of Mn in liquid Ag in Eq. (6) can be calculated by the Raoultian activity coefficient of Mn at infinite dilution in liquid Ag, γ_{Mn}° , which has been given by Shim *et al.*,³³⁾ as shown in Eq. (8).

$$\log \gamma_{\text{Mn(in Ag(l))}}^\circ = -\frac{2\,132}{T} + 1.088 \quad (33) \quad \dots (8)$$

The activity coefficient of MnO in molten slag can be obtained from Eq. (6), which can be calculated from Eq. (9).

$$\gamma_{\text{MnO}} = \frac{1}{K_1} \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{\gamma_{\text{Mn}}^\circ x_{\text{Mn}}}{x_{\text{MnO}}} \quad \dots (9)$$

The activity coefficient and activity value of MnO in the experimental slag are listed in Table 1. It can be seen that the obtained value of activity coefficient of MnO is less than 1, which is the same as the research results of Woo *et al.*⁵⁾ on MnO–SiO₂–Al₂O₃ slag system, Yan *et al.*⁷⁾ on MnO–CaO–SiO₂–Al₂O₃–MgO slag system and Ding *et al.*¹⁴⁾ on MnO–CaO–SiO₂–MgO slag system, indicating that the activity of MnO shows a strong negative departure from Raoult's law. This is also the same with Kim *et al.*'s research¹¹⁾ on FeO–MnO–MgO–P₂O₅–SiO₂–(CaO) slag system, where MnO is higher than 6.9 wt%. However, Jung *et al.*'s research⁹⁾ on CaO–SiO₂–Al₂O₃ (10 wt%)–MnO (3–16 wt%)–FeO (10

wt%)–MgO_{sat} slag system, Kim *et al.*'s research¹¹⁾ on slag with MnO lower than 6.6 wt% and Morales and Fruehan's research¹⁵⁾ on CaO–SiO₂–MnO–FeO–P₂O₅–MgO_{sat} slag system all reported that MnO activity showed strong positive deviation from Raoult's law.

4. Discussions

4.1. Activity Coefficient of MnO

4.1.1. Effect of MnO on Activity Coefficient of MnO

The effect of MnO on activity coefficient of MnO at 1450°C is shown in **Fig. 2**. The activity coefficient of MnO, γ_{MnO} , increased with its own concentration when $B = 0.77$ – 1.15 and $\text{FeO} = 7$ – 20% . The combined effect of MnO, basicity and FeO on the activity coefficient of MnO were much stronger than the individual effects of MnO, basicity and FeO on the activity coefficient of MnO. This result is very similar to the investigative results of Woo *et al.*,⁵⁾ Yan *et al.*,⁷⁾ and Kim *et al.*¹¹⁾ This tendency is similar to the research results of Abraham *et al.*²⁾ and Eom *et al.*⁴⁾ This may be related to the change in the structure of the molten slag which will be affected by composition of slag, basicity and their interactions.

4.1.2. Effect of FeO on Activity Coefficient of MnO

It is shown from **Fig. 3** that the activity coefficient of MnO increases with the FeO increasing when the slag basicity is 0.89 – 1.08 and $\text{MnO} = 43.6$ – 46.9% . And when the slag basicity is 1.31 – 1.94 and $\text{MnO} = 40.1$ – 43% , the activity coefficient of MnO changes in V-shape, and reaches the lowest point at 42.34% MnO, 12% FeO and 1.45 of the basicity. This is an interesting phenomenon and needs further research.

4.1.3. Effect of Basicity on Activity Coefficient of MnO

As MnO is a basic oxide, the activity coefficient of MnO increases with the basicity increasing, $B = (\text{mass}\% \text{CaO} + \text{mass}\% \text{MgO}) / \text{mass}\% \text{SiO}_2$, as shown in **Fig. 4**. This law is consistent with previous studies findings.^{4,10,11,15,16)} This result is the same as that of Yan *et al.*⁷⁾ when the basicity B is higher than 0.7 with CaO–SiO₂–MnO–MgO– 20% Al₂O₃.

4.1.4. The Relationship between Activity Coefficient of MnO and Component Concentration

Based on the discussion above, each component and basicity in molten slag interact with each other, and the effect of interaction on MnO activity coefficient complicates the change of activity coefficient of MnO. By considering the effects of the components and the interaction between FeO and MnO, a complex quadratic functional relationship is obtained by multiple quadratic regression using all data in Table 1, as shown in Eq. (10).

$$\begin{aligned} \log \gamma_{\text{MnO}} = & 1.359 + 0.0205(\% \text{MnO}) + 0.138(\% \text{FeO}) + 0.119(\% \text{SiO}_2) \\ & - 0.148(\% \text{CaO}) - 0.627(\% \text{MgO}) + 3.821 \times 10^{-5}(\% \text{MnO})^2 \\ & - 0.00337(\% \text{FeO})^2 - 0.00251(\% \text{SiO}_2)^2 + 0.00542(\% \text{CaO})^2 \\ & + 0.0255(\% \text{MgO})^2 - 0.00106(\% \text{MnO})(\% \text{FeO}) \pm 0.0794 \\ & (\alpha = 0.05, R = 0.969, \text{Adj.} R^2 = 0.826) \end{aligned} \quad (10)$$

Where, α is the significance level; R is correlation coefficient; $\text{Adj.} R^2$ is the adjusted coefficient of determination; the concentration of the component, ($\%i$), is the mass per-

Fig. 3. Effect of FeO on activity coefficient of MnO.

Fig. 2. Effect of MnO on activity coefficient of MnO.

Fig. 4. Effect of basicity on activity coefficient of MnO.

centage.

According to the p-value (the probability that H_0 in the t test is true) of regression analysis, the order of the effect of each component on activity coefficient of MnO from strong to weak is FeO^2 , CaO^2 , CaO , MgO , FeO , MgO^2 , SiO_2 , SiO_2^2 , the interaction of MnO and FeO, MnO and MnO^2 . With the Eq. (10), the activity coefficient of MnO in the slag can be estimated at 1450°C in the range of slag composition in this study.

According to the quadratic formula proposed by Banya,⁴²⁾ Woo *et al.*⁵⁾ gave the quadratic relationship between the logarithm of the activity coefficient of MnO and the concentrations of components for the MnO– SiO_2 – Al_2O_3 melt at 1823 K. The influence of the first-order term of the concentration of each component is not considered. Sobandi *et al.*¹⁰⁾ showed a first-order regression relationship between the logarithm of the activity coefficient of MnO and the concentration ratio of ‘free basic oxides’ to SiO_2 in the slag for CaO–MnO– SiO_2 – $\text{PO}_{2.5}$ –(MgO, FeO) slag system. Kim *et al.*¹¹⁾ proposed a multiple linear regression relationship between the logarithm of the activity coefficient of MnO and concentration of each component for the MnO–MgO– P_2O_5 – SiO_2 –(CaO) slag system.

4.2. Distribution Ratio of Mn between Molten Slag and Liquid Silver

The distribution ratio of manganese between the CaO– SiO_2 –FeO–MnO–MgO slags and the liquid silver under the conditions of this study can be derived from the equilibrium constant (Eq. (6)) of reaction (1).

$$L_{\text{Mn in slag/silver}} = \frac{(\text{mass}\% \text{MnO})}{[\text{mass}\% \text{Mn}]_{\text{in Ag}}} = \frac{C_1}{K_1} \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{f_{\text{Mn}}}{\gamma_{\text{MnO}}} \dots (11)$$

Where, L_{Mn} is the distribution ratio of Mn; f_{Mn} is the Henrian activity coefficient of Mn in liquid silver for the 1 mass% standard state. It can be seen from Table 1 that the concentration of Mn in liquid silver is very low, it can be considered that the manganese in liquid silver obeys Henry’s law, so the activity coefficient of Mn in liquid silver f_{Mn} is unity. The term C_1 is a stoichiometric constant that depends on slag composition, the concentration conversion from the mass percent of MnO to mole fractions and the standard state conversion from the Henrian activity coefficient of Mn to the Raoultian activity coefficient.

Figures 5–7 show the effect of MnO, FeO and basicity B ($B = (\text{mass}\% \text{CaO} + \text{mass}\% \text{MgO})/\text{mass}\% \text{SiO}_2$) on the distribution ratio of Mn in slag and liquid silver, respectively.

The effect of MnO in the slag on the Mn distribution ratio is more complicated, as shown in Fig. 5. L_{Mn} decreases with MnO increasing when $B = 0.77$ – 1.15 , but L_{Mn} increases with MnO increasing when $B = 1.31$ – 1.94 . In the experimental, CO gas with a fixed CO/CO₂ ratio and flow rate caused both FeO and MnO to be continuously reduced, and made the MnO in the slag and the distribution ratio of manganese continuously decrease. At that time, the manganese in the liquid silver was oxidized by FeO in slag, and made the MnO in slag and the distribution ratio of manganese increase. When the temperature and the standard state of the activity of the substances participating in the reaction were determined, the equilibrium constants of the above

Fig. 5. The effect of MnO on the distribution ratio of Mn.

Fig. 6. The effect of FeO on the distribution ratio of Mn.

Fig. 7. The effect of basicity on the distribution ratio of Mn.

two reactions were unchanged. But the activity coefficient of MnO, γ_{MnO} , increases with MnO increasing when $B = 0.77$ – 1.15 (see Fig. 2). So, the equilibrium of the reduction reaction of MnO reduced by CO will proceed in the direction of reduction of MnO, and the equilibrium concentration of MnO decreases. The oxidation reaction of Mn by FeO proceeds in the direction of generating Mn, so that the equi-

librium MnO content is reduced. Therefore, the manganese distribution ratio decreases with MnO increasing. It is also easy to explain this result from Eq. (11). When the basicity $B = 1.31\text{--}1.94$, the activity coefficient of MnO decreases with MnO increasing (see Fig. 2), so the opposite result is obtained. Data obtained in this work are in general agreement with that obtained by Kim,¹¹⁾ and the result obtained by Jung⁸⁾ when MnO is higher than 12%, but much smaller than that obtained by Jung⁸⁾ when MnO is lower than 10%. The concentration of the components, the basicity and the interaction between various components and the basicity in the slag also have effect on the L_{Mn} than that of MnO.

The effect of FeO in the slag on the distribution ratio of Mn is shown in Fig. 6. The distribution ratio of Mn decreases with FeO increasing when $B = 0.89\text{--}1.08$ and $\text{MnO} = 43.63\text{--}46.88\%$. As γ_{MnO} increases with FeO increasing (see Fig. 3), L_{Mn} decreases with FeO increasing from Eq. (11). But Kim's *et al.*¹¹⁾ and Jung *et al.*⁸⁾ got the opposite results. And when the slag basicity is $1.31\text{--}1.94$ and $\text{MnO} = 40.1\text{--}43\%$, L_{Mn} changes with FeO in an inverted V shape from Eq. (11) because the activity coefficient of MnO changes with FeO in V-shape, and reaches the highest point at 42.34% MnO, 12% FeO and 1.45 of the basicity (see Fig. 3).

Because the activity coefficient of MnO increases with the basicity increasing (see Fig. 4), the distribution ratio of Mn decreases with the increase of basicity B when $\text{MnO} = 40\text{--}45\%$ and $\text{FeO} = 9\text{--}14\%$, as shown in Fig. 7. The data of L_{Mn} and its change trend agree with that obtained by Kim.¹¹⁾

Considering the effect of the concentration of each component in molten slag and its interaction, a quadratic regression relationship of the distribution ratio of Mn with the components can be obtained under the condition in this study, as shown in Eq. (12).

$$\begin{aligned} \log L_{\text{Mn in slag/silver}} = & -0.0689 - 0.0169(\% \text{MnO}) - 0.135(\% \text{FeO}) - 0.115(\% \text{SiO}_2) \\ & + 0.1531(\% \text{CaO}) + 0.6352(\% \text{MgO}) - 3.843 \times 10^{-5}(\% \text{MnO})^2 \\ & + 0.00338(\% \text{FeO})^2 + 0.00251(\% \text{SiO}_2)^2 - 0.00543(\% \text{CaO})^2 \\ & - 0.0256(\% \text{MgO})^2 + 0.00107(\% \text{MnO})(\% \text{FeO}) \pm 0.0797 \\ & (\alpha = 0.05, R = 0.968, \text{Adj.} R^2 = 0.824) \end{aligned} \quad (12)$$

4.3. Equilibrium Concentration Quotient of Oxidation Reaction of Mn by FeO

Since the slag contained a large amount of FeO, the oxidation reaction of Mn in the liquid silver by the FeO in molten slag would occur.

$$K' = \frac{(\text{mass}\% \text{MnO})}{[\text{mass}\% \text{Mn}]_{\text{Ag}} (\text{mass}\% \text{FeO})} = K_{13} C_{13} f_{\text{Mn}} \frac{\gamma_{\text{FeO}}}{a_{\text{Fe}} \gamma_{\text{MnO}}} \quad (14)$$

Where, $K'_{\text{Mn in slag/silver}}$ can be defined as the equilibrium concentration quotient of the reaction (13); γ_{FeO} is the Raoultian activity coefficient of FeO in molten slag.

Figures 8–10 show the effects of MnO, FeO and basicity B ($B = (\text{mass}\% \text{CaO} + \text{mass}\% \text{MgO})/\text{mass}\% \text{SiO}_2$) on the

equilibrium concentration quotient K'_{Mn} respectively.

It can be seen from the Fig. 8 that the effect of MnO in the slag on the equilibrium concentration quotient K'_{Mn} is also complicated. The equilibrium concentration quotient, K'_{Mn} , is similar to that result obtained by Kim¹¹⁾ and by Jung.⁸⁾ The change of K'_{Mn} can also be explained by Eq. (14) and the effect of MnO on activity coefficient of MnO (see Fig. 2).

It can be shown from Fig. 9 that the equilibrium concentration quotient K'_{Mn} decreases with FeO increasing. Similar to the distribution ratio of manganese, the change of the K'_{Mn} is the results of the competition between the reduction of MnO in slag by CO and the oxidation of Mn in silver by FeO. Not only the concentration of the components in the slag, but also the basicity of the slag affect the K'_{Mn} .

It can be shown from Fig. 10, the equilibrium concentration quotient decreases with the basicity B increasing when $\text{MnO} = 40\text{--}45 \text{ mass}\%$ and $\text{FeO} = 9\text{--}14 \text{ mass}\%$. The result obtained in this work agrees with that obtained by Kim *et al.*¹¹⁾ and by Jung *et al.*⁸⁾

The equilibrium concentration quotient is regressed on the concentration of components under the condition in this study, as shown in Eq. (15).

Fig. 8. The effect of MnO on the equilibrium concentration quotient.

Fig. 9. The effect of FeO on the equilibrium concentration quotient.

Fig. 10. The effect of basicity on the equilibrium concentration quotient.

$$\begin{aligned}
 K'_{\text{Mn in slag/silver}} = & -313.024 + 4.792(\% \text{MnO}) - 1.664(\% \text{FeO}) - 5.237(\% \text{SiO}_2) \\
 & + 7.407(\% \text{CaO}) + 23.105(\% \text{MgO}) - 0.0319(\% \text{MnO})^2 \\
 & + 0.113(\% \text{FeO})^2 + 0.170(\% \text{SiO}_2)^2 - 0.183(\% \text{CaO})^2 \\
 & - 0.854(\% \text{MgO})^2 - 0.00446(\% \text{MnO})(\% \text{FeO}) \pm 1.681 \\
 & (\alpha = 0.05, R = 0.992, \text{Adj.} R^2 = 0.953)
 \end{aligned} \quad (15)$$

4.4. Estimation of the Distribution Equilibrium of Mn between Molten Iron and CaO–SiO₂–MnO–FeO–MgO Slags

In ferrous metallurgy, the distribution equilibrium of Mn between molten iron and molten slag can be expressed as:

$$\begin{aligned}
 K'_{\text{Mn in slag/iron}} &= \frac{(\text{mass}\% \text{MnO})}{[\text{mass}\% \text{Mn}]_{\text{in Fe}} (\text{mass}\% \text{FeO})} \quad (17) \\
 &= K_{16} C_{16} f_{\text{Mn}} \frac{\gamma_{\text{FeO}}}{\gamma_{\text{MnO}}}
 \end{aligned}$$

Based on the activity in liquid silver, the following reactions and their thermodynamic data, the activity of manganese in molten iron can be estimated.

$$\Delta G_{18}^\circ = 4084 - 38.16 T, \text{ J} \cdot \text{mol}^{-1} \quad (19)$$

$$\Delta G_{20}^\circ = RT \ln \left(\frac{M_{\text{Ag}}}{100 M_{\text{Mn}}} \gamma_{\text{Mn}}^\circ \right) = -40822 - 11.85 T \quad (21)$$

Subtraction of Eq. (20) from Eq. (18) obtains Eq. (22) and the standard free energy change.

$$\Delta G_{22}^\circ = 44906 - 26.31 T, \text{ J} \cdot \text{mol}^{-1} \quad (23)$$

$$\log K_{22} = \log \left(\frac{f_{\text{Mn in Fe}} [\text{mass}\% \text{Mn}]_{\text{in Fe}}}{[\text{mass}\% \text{Mn}]_{\text{in Ag}}} \right) = -\frac{2345}{T} + 1.37 \quad (24)$$

And

$$[\text{mass}\% \text{Mn}]_{\text{in Fe}} = \frac{[\text{mass}\% \text{Mn}]_{\text{in Ag}} K_{22}}{f_{\text{Mn in Fe}}} \quad (25)$$

The reaction product iron is solid iron in reaction (13), but liquid iron in reaction (16), so the free energy change of the process of the Eq. (26) needs to be considered:

$$\Delta G_{26}^\circ = 13800 - 7.6 T, \text{ J} \cdot \text{mol}^{-1} \quad (27)$$

The distribution ratio of manganese between molten slag and molten iron can be deduced.

$$\begin{aligned}
 \log L_{\text{Mn in slag/iron}} &= \log \frac{(\text{mass}\% \text{MnO})}{[\text{mass}\% \text{Mn}]_{\text{in Fe}}} \\
 &= \log \frac{(\text{mass}\% \text{MnO}) f_{\text{Mn in Fe}}}{[\text{mass}\% \text{Mn}]_{\text{in Ag}} K_{22}} \quad (28) \\
 &= \log L_{\text{Mn in slag/silver}} + \log f_{\text{Mn in Fe}} \\
 &\quad - \log K_{22} + \log K_{26}
 \end{aligned}$$

The equilibrium concentration quotient of reaction (16) can be deduced.

$$\begin{aligned}
 \log K'_{\text{Mn in slag/iron}} &= \log \frac{(\text{mass}\% \text{MnO})}{[\text{mass}\% \text{Mn}]_{\text{in Fe}} (\text{mass}\% \text{FeO})} \\
 &= \log \frac{(\text{mass}\% \text{MnO}) f_{\text{Mn in Fe}}}{(\text{mass}\% \text{FeO}) [\text{mass}\% \text{Mn}]_{\text{in Ag}} K_{22}} \\
 &= \log K'_{\text{Mn at slag/silver}} + \log f_{\text{Mn in Fe}} - \log K_{22} + \log K_{26} \quad (29)
 \end{aligned}$$

The distribution ratio of manganese between the molten iron and CaO–SiO₂–MnO–FeO–MgO slags can be obtained by combining Eqs. (28) and (12). And the equilibrium concentration quotient of the oxidation reaction of manganese in molten iron by FeO in molten slag can be obtained by combining Eqs. (29) and (15).

4.5. Activity Coefficient of FeO

The equation for calculating the activity coefficient of FeO in molten slag can be derived from the equilibrium constant of reaction (30), which can be calculated from the standard Gibbs free energy changes ΔG° of reaction (31)–(34).

$$\Delta G^\circ = -256061 + 53.68 T, \text{ J} \cdot \text{mol}^{-1} \quad (31)$$

$$\Delta G^\circ = -114391 - 85.77 T, \text{ J} \cdot \text{mol}^{-1} \quad (32)$$

$$\Delta G^\circ = -395346 - 0.54 T, \text{ J} \cdot \text{mol}^{-1} \quad (33)$$

So, the standard Gibbs free energy changes of the reaction (30) can be calculated from Eq. (35).

The equilibrium constant of the reaction (30) can be written as:

$$K_{30} = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{a_{\text{Fe}}}{a_{\text{FeO}}} = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{1}{\gamma_{\text{FeO}} x_{\text{FeO}}} \quad \dots\dots\dots (36)$$

Where, K_{30} is the equilibrium constant for the reaction (30); γ_{FeO} is the Raoultian activity coefficients of FeO in molten slag; In the case of a pure iron crucible, $a_{\text{Fe}} = 1$. The derived equilibrium constant K_{30} is:

$$\lg K_{30} = \frac{2\,021}{T} - 2.045 \quad \dots\dots\dots (37)$$

The activity coefficient of FeO in molten slag can be obtained from Eq. (36), which can be calculated from Eq. (38).

$$\gamma_{\text{FeO}} = \frac{1}{K_{30}} \cdot \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{1}{x_{\text{FeO}}} \quad \dots\dots\dots (38)$$

The activity coefficients of FeO in each slag sample of the experimental slags are listed in Table 1. It can be seen that the obtained values of activity coefficient of FeO are less than one, which are the same as in research results from Kojima *et al.*¹⁶⁾ and Fujim *et al.*¹⁷⁾ on FeO–MnO–SiO₂ slag system, and Eissa *et al.*¹⁸⁾ on FeO–TiO₂–CaO–Al₂O₃ slag system, indicating that the activity of FeO shows a strong negative departure from Raoult's law. However, the other researchers^{11,43)} obtained the result: FeO activity showed strong positive deviation to Raoult's law.

5. Conclusions

The activity coefficients of MnO in molten slag of MnO–CaO–SiO₂–FeO–MgO at 1 450°C were measured by the experiments of chemical equilibrium of manganese between liquid silver and molten slag under the mixed gas atmosphere of CO, CO₂ and Ar. The distribution ratio of manganese between the molten silver and molten slag, and the equilibrium concentration quotient of the reduction reaction of ferrous oxide by manganese were also measured. The activity coefficient of MnO, the distribution ratio of manganese and the equilibrium concentration quotient as a function of the concentration of the components in molten slag were investigated by a quadratic regression analysis method.

(a) The Raoultian activity coefficients of MnO in molten slag are less than unity. This indicates that MnO shows a negative deviation from the Raoultian law in this slag system.

(b) When the basicity $B = 0.77\text{--}1.15$, MnO = 15.8–52.9 mass% and FeO = 7–20 mass%, the activity coefficient of MnO increases as MnO content increases, but the distribution ratio of Mn and the equilibrium concentration quotient decrease as MnO content increases.

(c) When $B = 0.89\text{--}1.08$, MnO = 43.6–46.9 mass% and FeO = 7–20 mass%, the activity coefficient of MnO increases as FeO content increases, but the distribution ratio of Mn and the equilibrium concentration quotient decrease as FeO content increases.

(d) When MnO = 40–45 mass%, FeO = 9–14 mass% and $B = 0.7\text{--}1.8$, the activity coefficient of MnO increases

as the basicity increases, but the distribution ratio of Mn and the equilibrium concentration quotient decrease as the basicity increases.

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