Thermodynamic Behavior of Manganese Oxide in Lime-based Manganese Smelting Slags

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The thermodynamic behavior of MnO in the CaO–SiO₂–MnO slag system of lower basicity to understand the smelting reduction of silicomanganese was investigated. Experimental results indicated that the activity coefficient of MnO was not affected by MnO content less than 30 mol%. However, it did in fact increase as the MnO content increased beyond 30 mol% because the activity coefficient of MnO is closely associated with the silicate structure. The activity coefficient of MnO also increased with increasing basicity of slag and MgO content because of the free O^{2–} ions that are provided into the slag. On the other hand, the effect of the Al₂O₃ content on the activity coefficient of MnO was analyzed that the structure in the CaO–SiO₂–MnO–Al₂O₃ system changes from that of a Si–O–Si linkage to that of Si–O–Al and Al–O–Al linkages as the content of Al₂O₃ increases. Structural considerations concerning the effect of slag composition on the activity coefficient of MnO are discussed in detail using Fourier transform infrared (FT-IR) spectroscopy. Finally, it is shown that manganese recovery can be increased by increasing the activity coefficient of MnO in the slag.

KEY WORDS: recovery; activity coefficient; manganese oxide; basicity; structure.

1. Introduction

Advanced high-strength steels with high manganese content, such as twinning-induced plasticity (TWIP)-assisted steel, have recently received attention because of their superior mechanical strength and formability.^{1,2)} Manganese is typically added in the form of ferromanganese (FeMn), which is produced either in an electric furnace or a submerged arc furnace using manganese ore or manganese nodules, with carbon as the reductant. During smelting, thermodynamic constraints necessitate the distribution of manganese into the FeMn slag in the form of MnO.³⁾ Because approximately 30–40 wt% MnO is typically present in the HCFMn slag and is recycled by the silicomanganese (SiMn) smelting process, in which a minimization of manganese loss into the slag phase is an important issue to increase the overall efficiency of the smelting process. The possibility of recovering manganese from the manganese smelting slag, of which basicity is relatively high (*i.e.*, CaO/SiO₂ ratio = 1.6), was confirmed by Aleksandrov *et al.*⁴⁾ In order to achieve a higher recovery of manganese, several operating factors such as temperature, oxygen partial pressure, activity of MnO in the slag, and activity of Mn in the alloy should be carefully controlled. Because the activity

of MnO in the slag is known to be a dominant factor in determining the recovery of Mn into the alloy, the activity of MnO in the slag has been estimated by several researchers.^{5–9)}

Abraham *et al.*⁵⁾ estimated the activity of MnO in the CaO–SiO₂–MnO slag system, which increases with an increasing MnO content and CaO/SiO₂ ratio. Furthermore, the effect of basicity was reported by Simeonov and Sano,⁶⁾ showing that the activity coefficient of MnO increases with increasing content of basic oxides such as CaO, BaO, and Na₂O in the highly basic (*i.e.*, CaO/SiO₂ > 3.0) slags. In order to understand the thermodynamic behavior of MnO in steelmaking slag (for which FeO = 5–20 wt% and CaO/SiO₂ ratio > 1.5), the coupled reaction of manganese and iron, viz. (FeO) + [Mn] = (MnO) + Fe, at the slag-metal interface has been investigated.^{7–9)} It has been shown that the equilibrium distribution ratio of Mn, $L_{Mn} = (\%Mn)/[\%Mn]$, decreases as the basicity of slag increases because the ratio of the activity coefficient of oxides $\gamma_{MnO}/\gamma_{FeO}$ increases with increasing basicity. Consequently, the MnO in the slag plays the role of a basic oxide, and thus the activity coefficient of MnO is strongly affected by the basicity of the slag. However, the effect of MgO and Al₂O₃ content on the activity coefficient of MnO in slags with lower amounts of FeO is relatively few, even though it constitutes a very important factor in determining the Mn recovery during the SiMn smelting process.

Furthermore, Abraham *et al.*⁵⁾ have reported that the

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activity coefficient of MnO in the CaO–SiO₂–MnO ternary system is closely associated with the SiO₂ content. This can be explained by the fact that the manganese (Mn²⁺) tends to associate with O²⁻ and/or SiO₄⁴⁻ ions in the silicate structure. The organic relationships between the silicate structure and the thermodynamic properties of oxide melts such as the mixing free energy of silicates and sulfide capacity have been reported.^{10,11)} In particular, Park^{12,13)} demonstrated that the sulfide capacity is strongly affected by the structure of the CaO–SiO₂–MnO system, and that the excess free energy of MnO is inversely proportional to the degree of polymerization by employing Raman spectra analysis in conjunction with a computational thermodynamic assessment. Therefore, the influence of the silicate structure on the activity coefficient of MnO should be thoroughly investigated.

In the present study, the effects of the MnO content, basicity (CaO/SiO₂ ratio), as well as the MgO and Al₂O₃ content on the activity coefficient of MnO in the CaO–SiO₂–MnO(–Al₂O₃, MgO) slag systems, are investigated. To understand the structural aspects of the slag, which influences the thermodynamic behavior of MnO, Fourier transform infrared (FT-IR) spectroscopy is employed using quenched slag samples.

2. Experimental Methods and Procedures

2.1. Experimental

A thermochemical equilibration technique was used for measuring the activity coefficient of MnO in the CaO–SiO₂–MnO(–MgO, Al₂O₃) slag in equilibrium with a molten Cu or Fe–C melt. A vertical super kanthal (MoSi₂) furnace with a mullite reaction tube was used, as shown in Fig. 1. The temperature was controlled within ±2 K by using a calibrated R-type (Pt-13 mass% Rh/Pt) thermocouple and a proportional integral differential controller. The slag samples were prepared using reagent-grade SiO₂, MnO, MgO, Al₂O₃, and CaCO₃. CaCO₃ was calcined to CaO by heating at 1 273 K for 6 h. 5 g of the slag sample and 5 g of the Cu or Fe–C system were placed in a molybdenum or graphite crucible, respectively (15 mm ID × 18 mm OD × 50 mm H), and the oxygen partial pressure was controlled (which is described in detail in the following sections). Equilibration times of 12 h for slag/Cu under a CO–CO₂

atmosphere (CO/CO₂ = 9/1), and 24 h for slag/Fe–C under a CO gas atmosphere coexisted with C, were determined from preliminary experiments.

After equilibration, the samples were removed from the furnace and quenched by Ar flushing. The metal and slag were carefully separated and then analyzed. The carbon content of the metals after the experiments was determined using a C/S combustion analyzer (C/S, CS-200; LECO, St. Joseph, MI, USA). The concentration of Mn in the metal was measured with an inductively coupled plasma optical emission spectrometer (ICP-OES; Agilent Technologies, Santa Clara, CA, USA). The slag composition was determined using X-ray fluorescence spectroscopy (XRF, S4 Explorer; Bruker AXS, Madison, WI, USA); the equilibrium compositions are listed in Tables 1 and 2. The slag structure was then investigated by Fourier transform infrared (FT-IR) spectroscopy (Spectral00; Perkin-Elmer, Waltham, MA, USA). The details for glass sample preparation and FT-IR analysis procedures are provided elsewhere.¹⁴⁾

2.2. Determination of Activity Coefficient of MnO in CaO–SiO₂–MnO Slag

The activity coefficient of MnO in the CaO–SiO₂–MnO ternary slag was measured by equilibrating the slag and molten Cu using a Mo crucible under a CO–CO₂ atmosphere (CO/CO₂ = 9/1) at 1 773 K, for which the oxygen partial pressure was $p_{O_2} = 2.75 \times 10^{-10}$ atm. The equilibrium reaction and the activity coefficient of MnO in the slag can be expressed as follows:¹⁵⁾

$$\gamma_{\text{MnO}} = \gamma_{\text{Mn}}^\circ \cdot \frac{[X_{\text{Mn}}]}{(X_{\text{MnO}})} \cdot \frac{p_{\text{CO}_2}}{p_{\text{CO}}} \cdot \frac{1}{K_1}, \quad (2)$$

where γ_{MnO} is the activity coefficient of MnO in the slag, γ_{Mn}° is the activity coefficient of Mn in molten Cu, and X_{MnO} and X_{Mn} are the mole fractions of MnO in the slag and Mn in the alloy, respectively. The activity coefficient of Mn in molten Cu was measured by Jung¹⁶⁾ to be $\gamma_{\text{Mn}}^\circ = 0.324$ at 1 773 K. The activity coefficient of MnO estimated by Eq. (2) in the present study agrees well with previous results⁵⁾ measured by the equilibration between Pt foil and CaO–SiO₂–MnO slag at 1 773 K, as shown in Fig. 2. The activity coefficient of MnO was measured by equilibrating the slag and molten Cu in the present study.

3. Results

The effect of the MnO content on the activity coefficient of MnO at 1 773 K is shown in Fig. 2. The activity coefficient of MnO, γ_{MnO} , is not affected by its own concentration up to about 30 mol% MnO, beyond which it slightly increases at a CaO/SiO₂ ratio of 0.54. This tendency is very similar to Abraham *et al.*'s result,⁵⁾ in which the inflection point is dependent on the CaO/SiO₂ ratio. This possibly originates from the fact that the structure of the slag melt is affected by the CaO/SiO₂ ratio.

The effect of the modified basicity (B), which is defined as the (%CaO + %MgO + %FeO)/%SiO₂ ratio on the activ-

Fig. 1. Schematic diagram of the experimental apparatus for smelting reduction.

Table 1. Experimental result for the composition of slag and Cu.

No.	Crucible	Gas	Base metal	(mol%)								
				alloy	slag							
				Mn	CaO	SiO ₂	MnO	CuO	MoO ₃	MgO	Al ₂ O ₃	C/S
1				0.0283	31.94	59.24	8.47	0.25	0.08	–	–	0.54
2				0.0716	28.66	54.22	16.82	0.21	0.09	–	–	0.53
3				0.0694	28.97	53.61	17.07	0.27	0.08	–	–	0.54
4				0.1064	25.98	47.48	26.00	0.37	0.17	–	–	0.55
5				0.138	24.10	44.71	30.66	0.31	0.22	–	–	0.54
6				0.2065	22.88	41.22	35.12	0.35	0.37	–	–	0.56
7				0.379	19.25	34.84	44.78	0.33	0.79	–	–	0.55
8				0.6826	15.59	28.64	53.43	0.35	1.99	–	–	0.54
9				0.0341	36.68	56.22	6.82	0.21	0.07	–	–	0.65
10				0.0769	43.63	49.25	6.61	0.20	0.31	–	–	0.89
11	Mo	CO–CO ₂	Cu	0.0811	48.39	44.50	6.80	0.14	0.17	–	–	1.09
12				0.129	52.61	39.94	6.92	0.11	0.42	–	–	1.32
13				0.0447	35.19	50.94	6.69	0.19	0.05	6.93	–	0.69
14				0.0476	31.52	46.50	6.75	0.26	0.09	14.88	–	0.68
15				0.0526	28.80	43.29	6.27	0.15	0.26	21.23	–	0.67
16				0.0774	26.53	38.97	6.09	0.11	0.28	28.03	–	0.68
17				0.0451	35.50	53.61	6.93	0.28	0.22	–	3.47	0.66
18				0.0511	34.03	50.68	6.96	0.41	0.79	–	7.14	0.67
19				0.0629	33.02	47.77	7.41	0.37	0.18	–	11.24	0.69
20				0.07	30.96	46.43	7.52	0.17	0.22	–	14.69	0.67
21				0.0753	28.03	42.58	8.19	0.20	0.05	–	20.96	0.66
22				0.0698	27.52	41.09	7.80	0.26	0.08	–	23.25	0.67

Table 2. Experimental result for the composition of slag and Fe–Mn–Si–C.

(mol%)													
No.	Crucible	Gas	Base metal	alloy			slag						
				Mn	C	Si	CaO	SiO ₂	MnO	FeO	MgO	Al ₂ O ₃	C/S
1	C	C–CO	Fe	4.68	17.93	6.06	38.03	51.43	10.28	0.27	–	–	0.74
2				4.35	17.67	6.57	42.17	49.27	8.34	0.22	–	–	0.86
3				4.79	18.58	6.02	48.08	45.40	6.35	0.17	–	–	1.06
4				5.39	20.32	4.45	54.61	41.98	3.27	0.14	–	–	1.30
5				5.65	18.58	3.45	34.08	50.70	14.74	0.48	–	–	0.67
6				6.56	19.24	1.67	31.55	48.56	19.41	0.48	–	–	0.65
7				12.23	19.99	1.41	27.81	44.80	27.01	0.37	–	–	0.62
8				4.26	18.49	3.98	34.72	48.27	8.49	0.18	8.33	–	0.72
9				4.17	18.56	4.16	31.13	45.70	6.92	0.17	16.08	–	0.68
10				4.38	19.20	2.71	28.45	43.41	5.24	0.16	22.74	–	0.66
11				4.04	19.72	2.23	25.59	40.92	3.91	0.15	29.44	–	0.63
12				4.60	18.15	3.95	37.41	50.22	8.23	0.19	–	3.95	0.74
13				4.61	19.31	3.95	35.41	49.71	7.31	0	–	7.57	0.71
14				4.48	19.52	3.04	34.48	48.01	5.53	0.20	–	11.78	0.72
15				3.89	18.65	3.21	34.36	46.10	3.97	0.28	–	15.28	0.75
16				3.80	19.76	4.49	31.84	47.13	5.25	0.241	–	15.54	0.68
17				4.16	14.30	3.77	31.71	43.69	3.82	0.24	–	20.53	0.73

Fig. 2. The effect of MnO concentration on activity coefficient of MnO in CaO-SiO₂-MnO system at 1773 K.

Fig. 3. The effect of slag basicity on the activity coefficient of manganese in CaO-SiO₂-MnO(-MgO) at 1773 K.

ity coefficient of MnO is shown in Fig. 3. The activity coefficient of MnO increases as a function of the modified basicity, indicating that MnO is a basic oxide in the slag. There are qualitatively similar tendencies in the works of Abraham *et al.*,⁵⁾ Jung *et al.*,¹⁷⁾ Sobandi *et al.*,¹⁸⁾ and the present authors for a modified basicity region of lower than 1.5. However, Suito and Inoue⁸⁾ as well as Simeonov and Sano⁶⁾ carried out experiments at the higher modified basicity region of $B > 2.0$. It is interesting that the basicity dependency of γ_{MnO} is different in accordance with slag system. The basicity dependency of γ_{MnO} in the CaO-SiO₂-MnO(-MgO) system is more significant than that in the FeO-⁸⁾ or CaF₂-⁶⁾ systems.

The effects of MgO and Al₂O₃ on the activity coefficient of MnO in the CaO-SiO₂-MnO-MgO and CaO-SiO₂-MnO-Al₂O₃ slags at CaO/SiO₂ = 0.67 are shown in Fig. 4. The activity coefficient of MnO increases with increasing content of MgO and Al₂O₃ up to about 20 mol%. Meanwhile, the effect of MgO on the activity coefficient of MnO is magnified at higher MgO region due to changing from the (pseudo-) wollastonite primary area to the diopside primary area, where phases are the silicate structure. Otherwise, in case of Al₂O₃ containing slag system, the activity coefficient of MnO decrease with increasing content of Al₂O₃ at higher Al₂O₃ region because the (pseudo-) anorthite primary area of the aluminosilicate structure is changed to the (pseudo-) Al-spinel primary area of the aluminate structure. Thus, the dominant reason for this behavior is independent from thermodynamic and structural viewpoints. In point of fact, the MgO simply provides free O²⁻ ions into the slag as likely as CaO, resulting in the depolymerization of silicate melts. However, the effect of Al₂O₃ is more complicated than the effect of MgO in view of the aluminosilicate structure. Moreover, the activity coefficient of MnO in the CaO-SiO₂-MnO-Al₂O₃ system decreases for Al₂O₃ contents greater than about 20 mol% because the Mn²⁺ ions are balanced with aluminate anions at higher Al₂O₃ region. A more detailed analysis of the structural effect of MgO and Al₂O₃ on γ_{MnO} is discussed in the following section.

Fig. 4. The effect of mole fraction of MgO and Al₂O₃ on the activity coefficient of MnO in CaO-SiO₂-MnO(-MgO, Al₂O₃) at 1773 K.

4. Discussion

4.1. Structure of the CaO-SiO₂-MnO Slag

The activity coefficient of MnO in silicate melts is known to be affected by silicate structure because the relative stability of oxide components in multicomponent silicate melts is strongly dependent on the degree of polymerization and the network-modifying role of cations.²⁰⁾ The non-bridging oxygen (NBO) in silicate melts can be categorized into the following units: Q⁴ (NBO/Si = 0, fully polymerized), Q³ (NBO/Si = 1, sheet), Q² (NBO/Si = 2, chain), Q¹ (NBO/Si = 3, dimer), and Q⁰ (NBO/Si = 4, monomer). A singly charged site Q³ provides a site for one M⁺, whereas the doubly charged site Q² may accommodate one M²⁺, or two M⁺ cations. Furthermore, divalent cations M²⁺ of large

ionic radius should preferentially occupy the more open Q^3 sites, whereas the smaller M^{2+} cations will favor the higher charge concentration offered by the Q^2 sites.²¹⁾ Because the ionization potential of Ca^{2+} ($Z/r^2 = 2$) is lower than that of Mn^{2+} ($Z/r^2 = 2.4$ to 3.0 , depending on the electron's spin),²¹⁾ the Ca^{2+} ion is charge balanced with two open O^- ions, whereas the Mn^{2+} ion is balanced with two adjacent corner-shared O^- ions.²⁰⁾

The relationship between the activity coefficient of MnO and the relative abundance of structural units in the CaO–SiO₂–MnO slag system is shown in Fig. 5.²⁰⁾ According to Park,²⁰⁾ the silicate structure is depolymerized by the addition of MnO in the CaO–SiO₂–MnO (CaO/SiO₂ ratio = 0.5) system. In particular, the relative fraction of the Q^2 unit increases dramatically with the increasing MnO concentration. Since Mn^{2+} should be balanced with Q^2 corner-shared O^- ions, free Mn^{2+} cations should be nearly unchanged in spite of increasing MnO concentration. Thus, the activity coefficient of MnO is almost constant. Then, the activity coefficient of MnO increases by increasing the content of MnO because the relative fraction of the Q^2 unit drastically decreases for MnO content greater than about 35 mol%. A more detailed analysis for the depolymerization reaction of silicate melts by the addition of MnO is available in previous study.²⁰⁾

The IR transmittance of the CaO–SiO₂–7mol%MnO slag is shown as a function of the wavenumbers (cm^{-1}) at various CaO/SiO₂ ratios in Fig. 6. In general, the bands at 1150–750 cm^{-1} and 480 cm^{-1} correspond to the symmetric Si–O stretching vibration with various NBO/Si and the rocking bridging oxygen vibration mode of the Si–O–Si bond, respectively. The IR bands in the former range are categorized into four groups (*i.e.*, 1090, 990, 920, and 870 cm^{-1}), which are typically assigned to NBO/Si = 1, 2, 3, and 4,^{14,20,22,23)} respectively. The symmetric Si–O stretching bonds at 1150–800 cm^{-1} for the CaO/SiO₂ ratio = 0.65 system shift to 1150–730 cm^{-1} for the CaO/SiO₂ ratio = 1.32 system. The shifting of the symmetric Si–O stretching bands

towards the lower wavenumbers indicates that the NBO/Si = 4 (Q^0) unit becomes more pronounced by increasing the CaO/SiO₂ ratio. This means that the silicate network is more depolymerized by increasing the CaO/SiO₂ ratio. This is similar to Park's result,²⁰⁾ in which analysis of the Raman spectra shows that the Q^2 and Q^0 units gradually increase with an increasing CaO/SiO₂ ratio in the CaO–SiO₂–MnO slag. Therefore, an increase in the fraction of free O^{2-} ions that results from increasing the CaO/SiO₂ ratio is a dominant factor affecting the activity coefficient of MnO in the CaO–SiO₂–MnO slag system.

4.2. Structure of the CaO–SiO₂–MnO–MgO(–Al₂O₃) Slag

The symmetric Si–O stretching bonds at about 1150–800 cm^{-1} extend to about 1150–760 cm^{-1} with increasing MgO content as shown in Fig. 7(a), indicating that the silicate network is more depolymerized at higher MgO content. The activity coefficient of MnO in the CaO–SiO₂–MnO–MgO system increases as the MgO content increases (Fig. 4) because the MgO behaves as a basic oxide. Moreover, the fraction of free Mn^{2+} cations from the network-modifying role increases with increasing MgO content because the silicate units are charge-balanced with plenty of Mg^{2+} and Mn^{2+} ions.²⁴⁾

Alumina is known to substitute for tetrahedral sites in aluminosilicate melts when the sum of charge-balancing basic oxides is higher than the content of Al₂O₃.^{25–28)} In Fig. 7(b), the relative fraction of $[AlO_4]$ -tetrahedra increases with the increasing content of Al₂O₃ as a result of the fact that the band at 800–600 cm^{-1} , which corresponds to the $[AlO_4]$ -tetrahedral bond,^{22,23)} becomes more pronounced as the Al₂O₃ content increases. The alternating arrangement of Al and Si is a manifestation of Loewenstein's aluminum-avoidance rule,²⁹⁾ which states that Al–O–Al linkages between aluminate tetrahedra are energetically unfavorable compared to the Si–O–Al linkage. Thus, the aluminosilicate structure, *i.e.*, the Si–O–Al linkage, should increase with

Fig. 5. The relationship between activity coefficient of MnO and abundance of structural units in CaO–SiO₂–MnO slag system.²⁰⁾

Fig. 6. IR-transmittance of the CaO–SiO₂–MnO slag system as a function of wavenumber at different CaO/SiO₂.

Fig. 7. IR-transmittance of (a) CaO-SiO₂-MnO-MgO and (b) CaO-SiO₂-MnO-Al₂O₃ slag system (C/S=0.67) as a function of wavenumber.

increasing [AlO₄]-tetrahedra in the CaO-SiO₂-MnO-Al₂O₃ system, viz. (Si-O-Si) + (Al-O-Al) = 2(Si-O-Al).¹⁰⁾ Seifert³²⁾ reported that the proportions of ring types in melts, which are the Si-O-Si, Si-O-Al, and Al-O-Al linkages, depend on the Al/(Al+Si) ratio in the CaAl₂O₄-SiO₂ system. According to this article, the Si-O-Si linkage (six-membered SiO₂ rings) decreases, whereas the Si-O-Al linkage (four-membered Al₂Si₂O₈²⁻ rings) increases with Al₂O₃ content up to an Al/(Al+Si) ratio of 0.67. Also, the Al-O-Al linkage (six-membered Al₂O₄²⁻ rings) appears and increases above an Al/(Al+Si) ratio of 0.4. The Al-O-Al linkage increases dramatically above an Al/(Al+Si) ratio of 0.67, whereas the Si-O-Al linkage decreases with the increasing Al/(Al+Si) ratio. Therefore, the structure in the CaO-SiO₂-MnO-Al₂O₃ system should change from that of the Si-O-Si linkage to that of the Si-O-Al and Al-O-Al

linkages with increasing Al₂O₃ content.

In the CaO-SiO₂-MnO system, Mn²⁺ is able to occupy the Q² site, whose glass structure in this case is dominated by the Si-O-Si linkage³⁰⁾ because the [MnO₆] cage is smaller than the [CaO₆] cage.¹¹⁾ In the CaO-SiO₂-MnO-Al₂O₃ system, Mn²⁺ is favorable to occupy the Q² site as before. The Si-O-Al linkage formed by the Al₂O₃ content is balanced with Ca²⁺, whose glass structure is dominated by a series of glasses of the formula CaAl₂O₄·nSiO₂ (n = 1, 2, 4, 6, 12, depending on the Si/Al ratio)²⁴⁾ because of the preference of Si-O-Al linkage with alkali cations.²⁸⁾ Therefore, the number of free Mn²⁺ cations increases with increasing content of Al₂O₃ because the Si-O-Si linkage decreases as the Al₂O₃ content increases.³²⁾ In this way, the activity coefficient of MnO increases with the increasing Al₂O₃ content (Fig. 4) owing to an increase in the number of free Mn²⁺ cations, which results from changing the silicate melt to an aluminosilicate melt. However, the activity coefficient of MnO decreases with increasing Al₂O₃ content above 20 mol% Al₂O₃ because the Al-O-Al linkages (Al₂O₄²⁻), which are charge-balanced with Mn²⁺ to increase the activity of MnAl₂O₄,^{31,33)} appear above 20 mol% Al₂O₃, which corresponds to about Al/(Al+Si) = 0.4 in present slag system.

4.3. Examination of Manganese Distribution between CaO-SiO₂-MnO(-MgO, Al₂O₃) Slag and Molten Fe-Mn-Si-C

The equilibrium between CaO-SiO₂-MnO(-MgO, Al₂O₃) slag and the Fe-C melt was carried out under a strongly reducing atmosphere to simulate the smelting reduction of MnO in the silicomanganese slag. Equilibrium compositions are listed in Table 2. The results from the equilibrium test indicated that manganese and silicon were distributed between metal and slag phases because MnO and SiO₂ follow the couple reaction at the slag/metal interface, which is given by:³⁴⁻³⁷⁾

The distribution ratio of Mn between the slag and Fe-Mn-Si-C can be obtained by Eq. (4):

$$\log L_{\text{Mn}} = \log \left(\frac{X_{\text{MnO}}}{X_{\text{Mn}}} \right) = \log \left(\frac{\gamma_{\text{Mn}}}{\gamma_{\text{MnO}}} \right) + \frac{1}{2} \log \left(\frac{a_{\text{SiO}_2}}{a_{\text{Si}}} \cdot \frac{1}{K_1} \right), \quad (4)$$

where X_{Mn} and γ_{Mn} are the mole fraction and activity coefficient of Mn in the Fe-Mn-Si-C, respectively, a_{SiO_2} is the activity of SiO₂ in the slag, and a_{Si} is the activity of Si in Fe-Mn-Si-C.

The logarithmic value of the Mn distribution ratio (L_{Mn}) is inversely proportional to the logarithmic value of the γ_{MnO} as shown in Fig. 8. As mentioned in previous section 3, the γ_{MnO} is obtained by the equilibrium between molten slag and Cu. Since FeO concentration is lesser than 0.5 mol% in present work, the effect of FeO would be ignored.⁹⁾ Moreover, Fig. 8 indicates the correlation between γ_{MnO} and the degree of reduction for MnO in slag as an index of the recovery of Mn. Accordingly, the degree of Mn reduction

Fig. 8. Dependence of the γ_{MnO} on the distribution ratio or degree of reduction of MnO between CaO-SiO₂-MnO(-MgO, Al₂O₃) slag and Fe-Mn-Si-C at 1773 K.

can be defined as follows:

Degree of Mn reduction (%)

$$= \frac{W_{\text{slag}}^{\text{initial}} \times \text{wt}\% \text{MnO}_{\text{in slag}}^{\text{initial}} - W_{\text{slag}}^{\text{final}} \times \text{wt}\% \text{MnO}_{\text{in slag}}^{\text{final}}}{W_{\text{slag}}^{\text{initial}} \times \text{wt}\% \text{MnO}_{\text{in slag}}^{\text{initial}}} \times 100, \quad (5)$$

where W_{Metal} and W_{Slag} are the weight of the metal and slag, respectively, and M_i is the molecular mass of component i . The degree of Mn reduction increases linearly with increasing activity coefficient of MnO.

5. Conclusions

In order to understand the thermodynamic behavior of MnO in slag, the activity coefficient of MnO was measured in the molten CaO-SiO₂-MnO(-MgO, Al₂O₃) slag system at 1773 K using molten Cu. The concept of modified basicity was employed in this measurement, and its effect was compared with that in various other slag systems. On the basis of the results of our study, we may draw the following conclusions.

(1) The activity coefficient of MnO in the CaO-SiO₂-MnO slag system is influenced by the MnO contents of the slag and slag composition (basicity and additional elements).

(2) The activity coefficient of MnO is not affected by its own concentration up to about 30 mol% MnO because Mn²⁺ should be balanced with Q² corner-shared O⁻ ions, beyond which it slightly increases at a CaO/SiO₂ ratio of 0.54.

(3) The activity coefficient of MnO increases with an increase in the modified basicity, which is represented by the (CaO+MgO+FeO)/SiO₂ ratio, because an increase in the fraction of free O²⁻ ions is a dominant factor in affecting the activity coefficient of MnO in the CaO-SiO₂-MnO(-MgO) slag system.

(4) The activity coefficient of MnO is affected by the

Al₂O₃ content because the structure in the CaO-SiO₂-MnO-Al₂O₃ system should be changed from that of the Si-O-Si linkage to that of the Si-O-Al and Al-O-Al linkages with the increasing content of Al₂O₃. The activity coefficient of MnO increases with the increasing Si-O-Al linkage and decreases with the increasing Al-O-Al linkage because Mn²⁺ can be charge balanced with the Q² site dominated by the Si-O-Si and Al-O-Al linkages.

(5) The degree of Mn reduction increases linearly with increasing activity coefficient of MnO in the CaO-SiO₂-MnO(-MgO, Al₂O₃) slag system in equilibrium with the Fe-Mn-Si-C.

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