Complex Deoxidation Equilibria of Molten Iron by Aluminum and Calcium

Kenji TAGUCHI, Hideki ONO-NAKAZATO,¹⁾ Tateo USUI,¹⁾ Katsukiyo MARUKAWA,²⁾ Ken KATO³⁾ and Hiroaki KOSAKA⁴⁾

Graduate Student and JSPS Research Fellow, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan.

1) Course of Materials Science and Engineering, Division of Materials Science and Manufacturing, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan.

2) Center for Advanced Science and Innovation, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871 Japan.

3) Heraeus Electro-Nite Japan, LTD., 1-7-40 Mishimae, Takatsuki, Osaka 569-0835 Japan.

4) TOYO Engineering and Research Center Co., Ltd., 2-2-1 Kasuga, Ibaraki, Osaka 567-0031 Japan.

(Received on June 17, 2005; accepted on July 20, 2005)

The influence of oxygen potential in molten steel on the steelmaking reactions, such as desulfurization and denitrogenization by fluxes, is very significant, and it is important to control oxygen content of the molten steel. The use of the strong deoxidizing agents, such as Al and Ca, is effective for decreasing oxygen content of steel, and several researches on the complex deoxidation have been carried out. However, the experimental data do not necessarily accord with the thermodynamically calculated ones, because the reliable thermodynamic data on Ca deoxidation of molten iron are unavailable. In the present study, the complex deoxidation equilibria of molten iron by Al and Ca have been examined at 1 873 K. The oxygen activity in molten iron deoxidized by Al and Ca has been measured by an electro motive force (EMF) method at 1 873 K. The Al–Ca complex deoxidation equilibria are presented, and the validity is confirmed from the present experimental results and the previous ones in the literature on the complex deoxidation by Al and Ca. The Al–Ca deoxidation equilibria presented in the present study can represent the relationship of Fe–Al–Ca–O system more properly than the previously reported ones.

KEY WORDS: complex deoxidation; aluminum; calcium; oxygen activity; EMF method; steelmaking; CaO; Al₂O₃.

1. Introduction

In recent years, with an increase of demands for ultra clean steel, the more exact control of the contents of impurity elements in steel has been required. It has become necessary to decrease and to control the contents of the impurities in steel under a few mass ppm. In particular, the influence of oxygen potential in molten steel on the steelmaking reactions, such as desulfurization and denitrogenization by fluxes, is very significant; it is important to control oxygen content of the molten steel. The use of the strong deoxidizing agents, such as Al and Ca, is effective for decreasing oxygen content of steel. The complex deoxidation by Al and Ca is considered to be more effective, and several investigations on the complex deoxidation have been carried out.^{1,2)} However, the experimental data are not necessarily in accord with the thermodynamically calculated ones, because the thermodynamic data on Ca deoxidation equilibrium of molten iron are considered not to be reliable enough, which may be caused by the difficulty of the measurements. For this reason, it is necessary to re-examine the complex deoxidation equilibria of molten iron by Al and Ca, around a few to 10 mass ppm oxygen, in particular. Recently, the single deoxidation equilibrium by Al or Ca was investigated

by Itoh *et al.*^{3,4)} In the present study, the complex deoxidation equilibria of molten iron by Al and Ca are calculated at 1 873 K, using the thermodynamic data by Itoh *et al.* The oxygen activity in molten iron deoxidized by Al and Ca is measured by an electro motive force (EMF) method, and the validity of the Al–Ca complex deoxidation equilibria derived in the present study is discussed from the present and previous experimental results^{1,2)} on the complex deoxidation by Al and Ca.

2. Deoxidation Equilibria of Molten Iron by Al and Ca

The deoxidation reactions of molten iron by Al and Ca are represented by

The equilibrium constants for Eqs. (1) and (2), $K_{(1)}$ and $K_{(2)}$, are given respectively as follows^{3,4)}:

$$\log K_{(1)} = \log \left(\frac{a_{\text{Al}}^2 \cdot a_{\text{O}}^3}{a_{\text{Al}_2\text{O}_3}} \right) = 11.62 - 45\,300/T \dots\dots\dots(3)$$

$$\log K_{(2)} = \log \left(\frac{a_{\text{Ca}} \cdot a_{\text{O}}}{a_{\text{CaO}}} \right) = -3.29 - 7220/T \dots\dots(4)$$

where a_{Al} , a_{Ca} and a_{O} denote the activities of Al, Ca and O in molten iron relative to the dilute solution, $a_{\text{Al}_2\text{O}_3}$ and a_{CaO} the activities of Al_2O_3 and CaO relative to the pure solid, respectively, and T the absolute temperature (K). The activities of Al, Ca, and O in molten iron are defined as follows:

$$a_{\text{Al}} = f_{\text{Al}}[\text{mass}\% \text{Al}] \dots\dots\dots(5)$$

$$a_{\text{Ca}} = f_{\text{Ca}}[\text{mass}\% \text{Ca}] \dots\dots\dots(6)$$

$$a_{\text{O}} = f_{\text{O}}[\text{mass}\% \text{O}] \dots\dots\dots(7)$$

The activity coefficient of element i relative to the dilute solution, f_i , is given by⁵⁾

$$\log f_i = \sum_j e_i^j [\text{mass}\% j] + \sum_j \sum_k r_i^{(j,k)} [\text{mass}\% j][\text{mass}\% k] \quad (j \leq k) \dots\dots(8)$$

where e_i^j denotes the first-order mass percent interaction parameter of j for i , and $r_i^{(j,k)}$ the second-order mass percent interaction parameter between j and k for i . The values for the interaction parameters used in the present study are shown in **Table 1**. The interaction parameters between the two of Al, Ca and O are different from each other in the literatures.^{3,4,6-8)} In the present study, the values reported by Itoh *et al.* are used, because they can reasonably explain the experimental results of the single deoxidation of Al or Ca over a wider concentration range, and are considered to be one of the most reliable data at present. The complex deoxidation equilibria by Al and Ca are calculated at 1873 K by solving Eqs. (1) and (2) simultaneously, using Eqs. (3) through (8) and the activities of Al_2O_3 and CaO in $\text{CaO}-\text{Al}_2\text{O}_3$ system.^{9,10)} In the case of the equilibrium with calcium aluminates ($\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA), $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA_2), or $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ (CA_6)), the activities of Al_2O_3 and CaO are estimated from the standard Gibbs energies of formation of those oxides reported by Hallstead,¹¹⁾ which are shown in **Table 2**. The relationship among the contents of Al, Ca, and O is investigated as follows:

1. The activities of CaO and Al_2O_3 are determined by setting a composition of $\text{CaO}-\text{Al}_2\text{O}_3$ system.
2. By assuming an arbitrary oxygen content of molten iron, the relationship between Al and Ca contents which satisfies the equilibrium of Eq. (1) is calculated from Eqs. (3), (5), (7) and (8).
3. Similarly, the relationship between Al and Ca contents which satisfies the equilibrium of Eq. (2) is calculated by using Eqs. (4), (6), (7) and (8).
4. The composition of molten iron in equilibrium with the setting composition of $\text{CaO}-\text{Al}_2\text{O}_3$ system can be determined from the intersection of the relationships between Al and Ca contents in Steps 2 and 3.
5. The calculations in Steps 2 to 4 are repeated at oxygen contents ranging from 10^{-5} to 10^{-2} mass%.

By repeating the above calculations over all compositions of $\text{CaO}-\text{Al}_2\text{O}_3$ system, the phase diagram for the complex deoxidation equilibria by Al and Ca at 1873 K is derived

Table 1. The interaction parameters for Fe-Al-Ca-O system at 1873 K used in the present study.

i	j	e_i^j	r_i^j	$r_i^{(i,j)}$	Ref.
Al	Al	0.0430	—	—	6)
	Ca	-0.047	—	—	6)
	O	-1.98	40	-0.0284	4)
Ca	Al	-0.072	—	—	6)
	Ca	-0.002	—	—	6)
	O	-780	650000	-90000	3)
O	Al	-1.17	-0.01	47.4	4)
	Ca	-313	-18000	520000	3)
	O	-0.174	—	—	6)

Table 2. Activities of Al_2O_3 and CaO in the coexistence of two solid phases.

Equilibrium phase	$a_{\text{Al}_2\text{O}_3}$	a_{CaO}
(a) $\text{Al}_2\text{O}_3(\text{s}) + \text{CaO} \cdot 6\text{Al}_2\text{O}_3$	1	3.28×10^{-3}
(b) $\text{CaO} \cdot 6\text{Al}_2\text{O}_3 + \text{CaO} \cdot 2\text{Al}_2\text{O}_3$	0.811	0.0115
(c) $\text{CaO} \cdot 2\text{Al}_2\text{O}_3 + \text{CaO} \cdot \text{Al}_2\text{O}_3$	0.30	0.084

Fig. 1. Complex deoxidation equilibria of molten iron by Al and Ca at 1873 K.

and is described in **Fig. 1**. The dependencies of oxygen content and oxygen activity on aluminum content for the complex deoxidation by Al and Ca saturated with $\text{CaO} \cdot \text{Al}_2\text{O}_3$ or CaO are respectively compared with those for the single deoxidation by Al in **Figs. 2(a)** and **2(b)**. It is found from **Fig. 2(a)** that the Al content at the lowering limit of oxygen content is lower under the condition of Al-Ca complex deoxidation saturated with CaO in comparison with that saturated with $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

3. Experimental

The high purity electrolytic iron was put in an alumina

Fig. 2. Effect of oxygen content and activity on aluminum content under several deoxidation conditions at 1873 K.

crucible (38-mm o.d., 45-mm height, 30-cm³ volume) and was inductively heated in Ar–H₂ mixture. After the temperature reached 1873 K, hydrogen gas was blown onto the metal surface at a flow rate of 250 cm³/min (s.t.p.) for 1 h. After deoxidation, aluminum was added, and the sample was held for 5 min. Then, the sample was quickly cooled, and Fe–Al alloy ([mass ppm O]=10–15) was prepared. The preparation of CaO–(CaO·Al₂O₃)_{satd.} slag and the experiments were conducted by using the electric resistance furnace consisted of MoSi₂ heating elements. The slag of CaO–(CaO·Al₂O₃)_{satd.} was made by mixing reagent grades of CaO and Al₂O₃ at the molar ratio of 1 to 1 in a carbon crucible at 1873 K in an argon atmosphere. The prepared Fe–Al alloy weighing 60 g and CaO–(Al₂O₃·CaO)_{satd.} slag weighing 5–6 g were placed in an alumina crucible (25-mm o.d., 20-mm i.d., 120-mm length), and was held for 1.5 h at 1873 K in an argon atmosphere. Then, the oxygen activity in molten alloy was measured by an electro motive force (EMF) method by using the oxygen sensor shown in Fig. 3. The constitution of the oxygen sensor is as follows:

The solid electrolyte of the oxygen sensor is a magnesia stabilized zirconia (ZrO₂–8mol%MgO (MSZ)), and the reference substances are the reagent grades of Nb and NbO at a molar ratio of 9 to 1. The molybdenum rod (3-mm o.d.) and wire (1-mm o.d.) are used as contact leads to the melt and the reference substances, respectively. After the experiment, aluminum and calcium contents of the metal samples were analyzed by an inductively coupled plasma (ICP) emission spectrometry.

4. Results and Discussion

4.1. Measurement of Oxygen Activity in Molten Iron

The experimental results are summarized in Table 3. The variation of the electro motive force, E (V), with time is ex-

Fig. 3. Schematic cross section of oxygen sensor used in the present study.

Table 3. The aluminum and calcium contents of molten iron, electro motive force and oxygen activity.

No.	[mass%Al]	[mass ppm Ca]	E (mV)	$a_{\text{O}} \times 10^4$
1	0.032	<3	15.5	3.2
2	0.050	<3	-7.0	2.1
3	0.050	<3	3.0	2.6
4	0.098	<3	-10.1	2.0
5	0.300	<3	-13.9	1.9
6	0.570	<3	-45.0	0.99
7	0.570	<3	-55.0	0.79
8	0.865	<3	-38.8	1.1

Fig. 4. Variation of electro motive force with time for Run Nos. 1, 4 and 8.

emplified in Fig. 4. The E values become almost constant after about 20 s, and oxygen activity in molten alloy, a_{O} , is determined by the following equations:

$$a_{\text{O}} = K_{(11)} \left((P_{\text{e}}'^{1/4} + P_{\text{O}_2(l)}^{1/4}) \exp \left(\frac{EF}{RT} \right) - P_{\text{e}}'^{1/4} \right) \dots (10)$$

$$\frac{1}{2} \text{O}_2 (\text{g}) = \underline{\text{O}} (\text{mass\%, in Fe}) \dots (11)$$

Fig. 5. Effect of aluminum content on oxygen activity in molten iron at 1873 K.

Fig. 6. Effect of calcium content on oxygen activity in molten iron at 1873 K.

$$K_{(11)} = \exp\left(\left(\frac{117\,000}{T} + 2.89\right)/R\right) \dots\dots\dots(12)$$

$$P_e' = \exp\left(56.17 - \frac{171\,051}{T}\right) \dots\dots\dots(13)$$

where F denotes Faraday constant ($=96.5$ kC/mol), $K_{(11)}$ the equilibrium constant of Eq. (11),⁸⁾ P_e' the electronic conductivity parameter (atm),¹²⁾ $P_{O_2(l)}$ the equilibrated oxygen partial pressure at the reference electrode (atm),¹³⁾ and R the gas constant ($=8.314$ J/(mol·K)). Oxygen activities in the molten iron, which are obtained from the experimental results equilibrated with $\text{CaO}-(\text{Al}_2\text{O}_3 \cdot \text{CaO})_{\text{satd.}}$ slag, are plotted as a function of aluminum content in Fig. 5. The calculated curve is also shown in Fig. 5 under the same deoxidation condition. The experimental values of oxygen activity are in good accord with the calculated curves, which suggests that the Al–Ca complex deoxidation equilibria derived in the present study are valid. Moreover, the calculated oxygen activity is drawn as a function of calcium content in Fig. 6. As shown in Table 3, the calcium contents of the metal samples are below 3 mass ppm in all experiments, and it was impossible to analyze the calcium content exactly. The range of the oxygen activity measured in the present study is from 0.79×10^{-4} to 3.2×10^{-4} . It is found from Fig. 6 that the calcium content corresponding to the measured oxygen activities is about 1 mass ppm, which is also in reasonable agreement with the experimental results.

Table 4. The experimental conditions for Al–Ca complex deoxidation investigated by Suito *et al.*'s group.

	Temperature	Sample	[mass ppm N or S]
Kimura <i>et al.</i> ¹⁾	1873K	Fe–Ca–Al–O–N	1.5–106
Inoue <i>et al.</i> ²⁾		Fe–Ca–Al–O–S	10–483

Fig. 7. Relationship between Al and O contents of molten iron equilibrated with $\text{CaO}-(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{\text{satd.}}$ or $\text{CaO}_{\text{satd.}}-\text{Al}_2\text{O}_3$ slag at 1873 K.

4.2. Complex Deoxidation by Al and Ca

The experiments on Ca–Al deoxidation equilibria of molten iron using $\text{CaO}-(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{\text{satd.}}$ and $\text{CaO}_{\text{satd.}}-\text{Al}_2\text{O}_3$ slags were carried out at 1873 K by Kimura *et al.*¹⁾ and by Inoue *et al.*²⁾ The experimental conditions are tabulated in Table 4, and the results are plotted in Fig. 1. It is found that the relationship of Al and Ca contents equilibrated with $\text{CaO}-(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{\text{satd.}}$ slag investigated by Kimura *et al.* reasonably agrees with the relationship derived in the present study; Ca content increases with increasing Al content along the solid curve saturated with CA. Most of other experimental data are found in the liquid phase region. In Inoue *et al.*'s experiments, molten iron contains 10 to 483 mass ppm sulfur, which may explain the disagreement with the present calculation. The relationships between Al and O contents of molten iron are shown in Figs. 7(a) and 7(b) from the results equilibrated respectively with $\text{CaO}-(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{\text{satd.}}$ and $\text{CaO}_{\text{satd.}}-\text{Al}_2\text{O}_3$ slags by Kimura *et al.*¹⁾ and Inoue *et al.*²⁾ The oxygen contents are calculated from the measured oxygen activities in the present study using Eq. (7) on the assumption of $[\text{mass ppm Ca}] = 1$, which are also plotted in Fig. 7(a). The dashed curves in Fig. 7 represent the equilibrium ones for Eq. (1) described by Suito *et al.*'s group,^{1,2)} using the thermodynamic data^{8,14)} shown in Table 5. The calculations are conducted by taking into account the atomic interactions shown in Table 5 and the activity of Al_2O_3 in $\text{CaO}-\text{Al}_2\text{O}_3$ slag. With increasing Al content up to about 1 mass%, the discrepancy is found to become larger between the results of equilibrium experiments and the calculated results. On the other hand, the solid curves in Fig. 7 represent the relationships of Al and O contents derived in the present study. It is found that the solid curve is in good agreement with the present and previ-

Table 5. The equilibrium constant for the reaction of $\text{Al}_2\text{O}_3(\text{s})=2\text{Al}+3\text{O}$ and the interaction parameters used by Suito *et al.*'s group.

Equilibrium constant $\log K_{(1)}^{(14)}$	Interaction parameters ⁸⁾			
	<i>i</i>	<i>j</i>	e_i^j	r_i^j
$20.2 - 62800/T$	Al	Al	0.045	-0.001
		O	-6.6	-
	O	Al	-3.9	1.7
		O	-0.20	-

Fig. 8. Relationship between Ca and O contents of molten iron equilibrated with $\text{CaO}-(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{\text{satd.}}$ or $\text{CaO}_{\text{satd.}}-\text{Al}_2\text{O}_3$ slag at 1 873 K.

ous experimental results equilibrated with $\text{CaO}-(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{\text{satd.}}$ slag at higher Al content from 0.1 to 1 mass% Al, in particular. In Fig. 7(b), the solid curve is not drawn over the range above 0.06 mass% Al, because Eqs. (3) and (4) could not be solved simultaneously at the higher concentrations. The solid curve also reasonably agrees with the experimental results equilibrated with $\text{CaO}_{\text{satd.}}-\text{Al}_2\text{O}_3$ slag in the described concentration range below about 0.06 mass% Al.

The relationships between Ca and O contents of molten iron are shown in Figs. 8(a) and 8(b) from the results equilibrated respectively with $\text{CaO}-(\text{CaO} \cdot \text{Al}_2\text{O}_3)_{\text{satd.}}$ and $\text{CaO}_{\text{satd.}}-\text{Al}_2\text{O}_3$ slags by Kimura *et al.*¹⁾ and Inoue *et al.*²⁾ The solid curves in Fig. 8 show the relationships of Ca and O contents estimated in the present study under each deoxidation condition. In Fig. 8, the relationships of Ca and O contents are also in reasonable agreement with the solid curves estimated in the present study. In Fig. 7(b), the relationship of Al and O contents could not be described over the concentration range above 0.06 mass% Al; the validity of the experimental results equilibrated with $\text{CaO}_{\text{satd.}}-\text{Al}_2\text{O}_3$ slag could not be evaluated at the higher Al concentrations.

With respect to the relationship of Ca and O contents described in Fig. 8(b), the experimental results reasonably agree with the relationship derived in the present study. From these examinations, it is found that the complex deoxidation equilibria of molten iron by aluminum and calcium derived in the present study are considered to be valid.

5. Conclusions

The oxygen activity in molten iron deoxidized by Al and Ca has been measured by an EMF method at 1 873 K, and the complex deoxidation equilibria of molten iron by aluminum and calcium have been examined. The conclusions are as follows:

- (1) The complex deoxidation equilibria of molten iron by aluminum and calcium are described by applying the reliable thermodynamic data on the single deoxidation of molten iron by aluminum or calcium.
- (2) The validity of the Al-Ca complex deoxidation equilibria presented in the present study is confirmed from the present and previous experimental results on the complex deoxidation by Al and Ca, and the relationship of Fe-Al-Ca-O system can be represented more properly than previously reported ones.

Acknowledgments

The authors wish to thank Mr. K. Terauchi in Heraeus Electro-Nite Japan, LTD., for his kind help in making the oxygen sensor. Helpful discussion with Prof. I. Katayama of Osaka University is also gratefully acknowledged. This study was financially supported by JFE 21st Century Foundation.

REFERENCES

- 1) T. Kimura and H. Suito: *Metall. Mater. Trans. B*, **25B** (1994), 33.
- 2) R. Inoue and H. Suito: *Steel Res.*, **65** (1994), 403.
- 3) H. Itoh, M. Hino and S. Ban-ya: *Tetsu-to-Hagané*, **83** (1997), 695.
- 4) H. Itoh, M. Hino and S. Ban-ya: *Tetsu-to-Hagané*, **83** (1997), 773.
- 5) C. H. Lupis: *Chemical Thermodynamics of Materials*, Elsevier Science Publishing Co., Inc., New York, (1983), 255.
- 6) The 19th Committee on Steelmaking, The Japan Society for the Promotion of Science: *Steelmaking Data Sourcebook*, Gordon and Breach Science Publishers, New York, (1988), 280, 282.
- 7) J. D. Seo, S. H. Kim and K. R. Lee: *Steel Res.*, **69** (1998), 49.
- 8) G. K. Sigworth and J. F. Elliot: *Met. Sci.*, **8** (1974), 298.
- 9) T. Fujisawa, M. Yamauchi and H. Sakao: *CAMP-ISIJ*, **1** (1988), 1115.
- 10) The 19th Committee on Steelmaking, The Japan Society for the Promotion of Science: *Chemical Properties of Molten Slags*, ed. by S. Ban-ya and M. Hino, ISIJ, Tokyo, (1991), 38.
- 11) B. Hallsteadt: *J. Am. Ceram. Soc.*, **73** (1990), 15.
- 12) D. Janke: *Arch. Eisenhüttenwes.*, **46** (1975), 477.
- 13) JANAF Thermochemical Tables, 3rd ed., ed. by M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Fruip, R. A. McDonald and A. N. Syverud: *J. Phys. Chem. Ref. Data*, **14** (1985), Supl. No. 2, 1601, 1608.
- 14) J. F. Elliott, M. Gleiser and V. Ramakrishna: *Thermochemistry for Steelmaking*, Vol. II, Addison-Wesley, Reading, MA, (1963), 547.