Complex Deoxidation Equilibria of Molten Iron by Aluminum and Calcium

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The influence of oxygen potential in molten steel on the steelmaking reactions, such as desulfurization and denitrogenation 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 control the contents of 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 denitrogenation 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. However, the experimental data are not necessarily in 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.

2. Deoxidation Equilibria of Molten Iron by Al and Ca

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

\[ \text{Al}_2\text{O}_3 (s) = 2\text{Al} (\text{mass}%, \text{in Fe}) + 3\text{O} (\text{mass}%, \text{in Fe}) \] ....(1)
\[ \text{CaO} (s) = \text{Ca} (\text{mass}%, \text{in Fe}) + \text{O} (\text{mass}%, \text{in Fe}) \] .......(2)

The equilibrium constants for Eqs. (1) and (2), \( K_{\text{Al}_2\text{O}_3} \) and \( K_{\text{CaO}} \), are given respectively as follows:

\[ \log K_{\text{Al}_2\text{O}_3} = \log \left( \frac{\alpha_{\text{Al}} \cdot \alpha_3}{\alpha_{\text{Al}_2\text{O}_3}} \right) = 11.62 - 45.300 / T \] .......(3)

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.
\[ \log K_{(2)} = \log \left( \frac{a_{\text{Al}} \cdot a_{\text{Ca}}}{a_{\text{CaO}}} \right) = -3.29 - 7.220 / T \]  \hspace{1cm} (4)

where \( a_{\text{Al}}, a_{\text{Ca}}, \text{and} \ a_{\text{O}} \) denote the activities of Al, Ca and O in molten iron relative to the dilute solution, \( a_{\text{Al}_{2}\text{O}_{3}} \) and \( a_{\text{CaO}} \) the activities of \( \text{Al}_{2}\text{O}_{3} \) and \( \text{CaO} \) 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:

\[ a_{\text{Al}} = f_{\text{Al}} \left[ \text{mass}\% \text{Al} \right] \]  \hspace{1cm} (5)

\[ a_{\text{Ca}} = f_{\text{Ca}} \left[ \text{mass}\% \text{Ca} \right] \]  \hspace{1cm} (6)

\[ a_{\text{O}} = f_{\text{O}} \left[ \text{mass}\% \text{O} \right] \]  \hspace{1cm} (7)

The activity coefficient of element \( i \) relative to the dilute solution, \( f_{i} \), is given by

\[ \log f_{i} = \sum_{j} e_{ij} \left[ \text{mass}\% \ j \right] + \sum_{j} \sum_{k} r_{ijk} \left[ \text{mass}\% \ j \right] \left[ \text{mass}\% \ k \right] \]  \hspace{1cm} (8)

where \( e_{ij} \) denotes the first-order mass percent interaction parameter of \( j \) for \( i \), and \( r_{ijk} \) 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 1 873 K by solving Eqs. (1) and (2) simultaneously, using Eqs. (3) through (8) and the activities of \( \text{Al}_{2}\text{O}_{3} \) and \( \text{CaO} \) in CaO–\( \text{Al}_{2}\text{O}_{3} \) system.9,10) In the case of the equilibrium with calcium aluminates (\( \text{CaO} \cdot \text{Al}_{2}\text{O}_{3}(\text{CA}), \text{CaO} \cdot 2\text{Al}_{2}\text{O}_{3}(\text{CA}_{2}), \) or \( \text{CaO} \cdot 6\text{Al}_{2}\text{O}_{3}(\text{CA}_{6}) \)), the activities of \( \text{Al}_{2}\text{O}_{3} \) and \( \text{CaO} \) 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 \( \text{Al}_{2}\text{O}_{3} \) are determined by setting a composition of 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 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 CaO–\( \text{Al}_{2}\text{O}_{3} \) system, the phase diagram for the complex deoxidation equilibria by Al and Ca at 1 873 K is derived 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 \( \text{CaO} \) 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 AI content at the lowering limit of oxygen content is lower under the condition of Al–Ca complex deoxidation saturated with \( \text{CaO} \) in comparison with that saturated with \( \text{CaO} \cdot \text{Al}_{2}\text{O}_{3} \).

### Table 1. Interaction parameters for Fe–Al–Ca–O system

|   | \( \text{Fe} \) | \( \text{Al} \) | \( \text{Ca} \) | \( \text{O} \) |
|---|-----------------|----------------|----------------|---------|
| \( e_{ij} \) | \( 0.043 \) | \( -0.047 \) | \( -0.002 \) | \( -0.174 \) |
| \( r_{ijk} \) | \( -1.98 \) | \( -870 \) | \( -313 \) | \( -0.174 \) |

### Table 2. Activities of \( \text{Al}_{2}\text{O}_{3} \) and \( \text{CaO} \) in the coexistence of two solid phases

| Equilibrium phase | \( a_{\text{Al}_{2}\text{O}_{3}} \) | \( a_{\text{CaO}} \) |
|-------------------|-----------------|-----------------|
| (a) \( \text{Al}_{2}\text{O}_{3}+\text{CaO} \) | \( 1 \) | \( 3.28 \times 10^{-3} \) |
| (b) \( \text{CaO} \cdot \text{Al}_{2}\text{O}_{3}+\text{CaO} \cdot \text{Al}_{2}\text{O}_{3} \) | \( 0.811 \) | \( 0.0115 \) |
| (c) \( \text{CaO} \cdot \text{Al}_{2}\text{O}_{3}+\text{CaO} \cdot \text{Al}_{2}\text{O}_{3} \) | \( 0.30 \) | \( 0.084 \) |

![Fig. 1. Complex deoxidation equilibria of molten iron by Al and Ca at 1873 K.](image-url)
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)ₙₙd slag and the experiments were conducted by using the electric resistance furnace consisted of MoSi₂ heating elements. The slag of CaO–(CaO·Al₂O₃)ₙₙd 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)ₙₙd slag 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:

(I) Mo, Nb/NbO | O₂/(MSZ) | (II) Mo, O (in Fe) .....(9)

The solid electrolyte of the oxygen sensor is a magnesia stabilized zirconia (ZrO₂–8mol%MgO (MSZ)), and the reference substances are the regent 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 exemplified in Fig. 4. The E values become almost constant after about 20 s, and oxygen activity in molten alloy, a₀, is determined by the following equations:

\[ a_\text{O}_0 = K_{i11} \left( P_{\text{O}_2}^{\text{1/4}} + P_{\text{O}_2}^{\text{1/4}} \right) \exp \left( \frac{EF}{RT} \right) - P_{\text{O}_2}^{\text{1/4}} \]  

\[ \frac{1}{2} \text{O}_2 (g) = \text{O} \text{(mass%}, \text{ in Fe}) \] .........(11)
where $F$ denotes Faraday constant ($=96.5$ kC/mol), $K_{(11)}$, the equilibrium constant of Eq. (11), $P^*_e$ the electronic conductivity parameter (atm), $P_{g}$ the equilibrated oxygen partial pressure at the reference electrode (atm), $T$ the gas constant ($=8.314$ J/(mol·K)), $R$ the molten iron, which are obtained from the experimental results equilibrated with CaO–(Al$_2$O$_3$·CaO)$_{satd}$ 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 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.

4.2. Complex Deoxidation by Al and Ca

The experiments on Ca–Al deoxidation equilibria of molten iron using CaO–(CaO·Al$_2$O$_3$)$_{satd}$ and CaO$_{satd}$–Al$_2$O$_3$ slags were carried out at 1 873 K by Kimura et al. and by Inoue et al. 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 CaO–(CaO·Al$_2$O$_3$)$_{satd}$ 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 CaO–(CaO·Al$_2$O$_3$)$_{satd}$ and CaO$_{satd}$–Al$_2$O$_3$ slags by Kimura et al. and Inoue et al. The oxygen contents are calculated from the measured oxygen activities in the present study using Eq. (7) on the assumption of [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, using the thermodynamic data shown in Table 5. The calculations are conducted by taking into account the atomic interactions shown in Table 5 and the activity of Al$_2$O$_3$ in CaO–Al$_2$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 previous experimental results.
ous experimental results equilibrated with CaO–(CaO·Al₂O₃)_{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 CaO_{satd.}–Al₂O₃ 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 CaO–(CaO·Al₂O₃)_{satd.} and CaO_{satd.}–Al₂O₃ slags by Kimura et al.\(^ {11}\) and Inoue et al.\(^ {12}\). 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 CaO_{satd.}–Al₂O₃ 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.

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