Thermodynamics of Oxygen in Liquid Fe–Cr Alloy Saturated with FeO·Cr₂O₃ Solid Solution

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The equilibrium relation between dissolved Cr and O in liquid high Cr steel has been assessed on the condition of pure solid Cr₂O₃ saturation in our previous paper. Following this, the present work deals with the equilibrium between Cr and O in liquid iron saturated with FeO·Cr₂O₃ solid solution and phase equilibria among liquid Fe–Cr alloy and Cr₂O₃ containing oxides for the full understanding of the thermodynamic behavior of oxygen in liquid Fe–Cr alloy. The free energy of formation of FeO·Cr₂O₃ and activities of the constituents in FeO·Cr₂O₃ solid solution have also been measured by the chemical equilibrium technique at 1823 to 1923 K.

The free energy of formation of FeO·Cr₂O₃ was given by the following equation.

\[ \Delta G^\circ = -307600 + 66.82T \text{ (J/mol)} \quad (1423 \leq T \leq 1923 \text{ K}) \]

The activities of FeO(l) and Cr₂O₃(s) in FeO·Cr₂O₃ solid solution exhibit negative deviation from ideality. The oxide phase in equilibrium with liquid Fe–Cr alloy is not Cr₂O₃ but FeO·Cr₂O₃ solid solution when Cr content in metal is less than the critical Cr content of approximately 7 mass%. The present experimental results are in good accord with the thermodynamic relation between dissolved Cr and O calculated by the parameters which have been proposed in our previous work, if appropriate correction for Cr₂O₃ activity is applied.

KEY WORDS: deoxidation equilibrium; deoxidation product; Fe–Cr alloy; chromium oxide; thermodynamics; iron–chromite solid solution; stainless steel refining.

1. Introduction

Most of steels contain some alloying elements in order to achieve the desired physical, mechanical and chemical properties of final products. The stainless steel is the most typical and valuable high alloyed steel. In the refining process of crude stainless steel, oxidation loss of Cr, which is the major alloying element for the stainless steel, occurs easily from metal to slag due to its less-noble nature. Since Cr is comparatively expensive material, it is very important to improve the yield of Cr in the stainless steel production. Thermodynamic information on the equilibrium between dissolved Cr and O in steel melt is the basic knowledge to control Cr content in the stainless steel. A huge number of studies concerning the Cr and O equilibrium relation have been reported due to such demands, where the Cr content in liquid iron has been up to 50 mass%. Most of researchers have conducted their experiments at high Cr content in metal by using MgO or Al₂O₃ crucible, and they have been analyzed their results by assuming unit activity of Cr₂O₃. It is, however, known that Al₂O₃ forms complete solid solution with Cr₂O₃ and MgO reacts with Cr₂O₃ to form intermediate compound MgO·Cr₂O₃. These facts indicate that the activity of Cr₂O₃ in equilibrium with molten Fe–Cr alloy is lower than unity in their experimental conditions. In direct expression, Cr and O equilibrium in liquid iron has not yet been well established in spite of its industrial importance for stainless steel processing.

With keeping such background in view, the present authors recently assessed the equilibrium relation between dissolved Cr and O in liquid iron saturated with pure solid Cr₂O₃ by using Cr₂O₃ crucible on the condition that the activity of Cr₂O₃ can be precisely defined as unity. Experiments were conducted at the temperature from 1723 to 1923 K in the concentration range of 7 to 46 mass% Cr. As the results, the equilibrium constant of reaction and the interaction parameter between Cr and O in liquid iron were determined as it will be mentioned in the next section, and the activities of Cr and O were well expressed by obtained thermodynamic functions. As shown in Fig. 1, the pre-
dicted oxygen content at constant Cr content under the presence of pure solid Cr$_2$O$_3$ was 100–300 mass-ppm higher than the recommended value by the 19th Committee on Steelmaking, the Japan Society of Promotion of Science (JSPS). Such discrepancy could be attributed to the decrease of Cr$_2$O$_3$ activity in the previous works.

On the other hand, it is well known that the liquid Fe–Cr alloy is in equilibrium with FeO·Cr$_2$O$_3$ at lower Cr content in metal. The critical Cr concentration, [%Cr]$_{critical}$, at which the equilibrium oxide phase changes from FeO·Cr$_2$O$_3$ to Cr$_2$O$_3$, has been theoretically revealed in our previous work$^{13}$ as 6.31, 6.82 and 7.24 mass% at 1 823, 1 873 and 1 923 K, respectively. This result indicates that the oxide phase in equilibrium with liquid Fe–Cr alloy is not Cr$_2$O$_3$, but FeO·Cr$_2$O$_3$ if Cr content in metal is lower than these critical Cr contents. Cr$_2$O$_3$ can not be in equilibrium with liquid Fe–Cr alloy at the steelmaking temperature from the phase diagram of Fe–Cr–O system.$^{12}$ It is also known that FeO·Cr$_2$O$_3$ has relatively wide solid solution range from approximately 70 mass% Cr$_2$O$_3$ in FeO–Cr$_2$O$_3$ binary, almost stoichiometric composition at pure Cr$_2$O$_3$ saturation, to 43 mass% Cr$_2$O$_3$ coexisted with liquid FeO–Cr$_2$O$_3$ slag as shown in Fig. 2.$^{14}$ Therefore, the activities of Cr$_2$O$_3$ and FeO·Cr$_2$O$_3$ in FeO·Cr$_2$O$_3$ solid solution in equilibrium with liquid Fe–Cr alloy should decrease from unity at Cr$_2$O$_3$ saturation with decreasing Cr content in metal from [%Cr]$_{critical}$. However, most of previous works have not considered the change of the activity of Cr$_2$O$_3$ or FeO·Cr$_2$O$_3$ in FeO·Cr$_2$O$_3$ phase.

The objective of the present work is the establishment of the thermodynamic knowledge of oxygen in liquid Fe–Cr alloy saturated with FeO·Cr$_2$O$_3$ solid solution and phase equilibria among liquid Fe–Cr alloy and Cr$_2$O$_3$ containing oxides at steelmaking temperature. The free energy of formation of FeO·Cr$_2$O$_3$, FeO, Cr$_2$O$_3$, and FeO·Cr$_2$O$_3$ solid solution)–(liquid Ag–Fe–Cr alloy)–(CO–CO$_2$ gas mixture) at steelmaking temperature. The free energy of formation of FeO·Cr$_2$O$_3$ was studied by some of present authors. However, their experimental temperature was limited in 1 423 to 1 723 K, so that the precise free energy value at steelmaking temperature is necessary to understand the thermodynamic behavior of FeO·Cr$_2$O$_3$ solid solution. No literature on activities of the constituents in FeO·Cr$_2$O$_3$ solid solution is available. Finally, the equilibrium relation between dissolved Cr and O in liquid iron was measured by the conventional sampling method at 1 823–1 923 K and [Cr]=[%Cr]$_{critical}$, where liquid metal was expected to be in equilibrium with FeO·Cr$_2$O$_3$ solid solution.

2. Thermodynamic Basis

The chemical reaction between Cr and O in liquid iron and its equilibrium constant are given by Eqs. (1) and (2).

$$\log K_i = \log(k_i^C \cdot h_i^O \cdot a_{Cr}) = \log(\gamma_i^{Fe} \cdot [\%Cr]_i \cdot [\%O]_i/\gamma_i^{Cr} \cdot [\%Cr]_i \cdot [\%O]_i)$$

$$= \log K_i^C + 2 \log f_{Cr} + 3 \log f_{O} - \log a_{Cr}$$

$$= \log K_i^C + 2e_i^{C} [\%Cr] + 2e_i^{O} [\%O] + 3e_i^{Cr} [\%Cr]$$

$$+ 3e_i^{O} [\%O] - \log a_{Cr}$$

Where, $K_i$, $a$, $h$, $f$, $C_i$ and $e_i$ denote the equilibrium constant, the Raoultian activity, the Henrian activity, the Henrian activity coefficient, the deoxidation product (=[C]/[O]) and interaction parameter between $i$ and $j$, respectively. The standard states of $h_C$ and $h_O$ in Eq. (2) are infinite dilute solution for Cr and O in liquid iron, and that of $a_{Cr}$ is pure solid. $e_i^{C}$ can be estimated as zero,$^{11}$ and $e_i^{O}$ and $e_i^{Cr}$ are also given by the following equations$^{11}$ among the parameters in Eq. (2).

$$e_i^{C} = -1750/T + 0.76$$

$$e_i^{O} = 3.25e_i^{C} - 0.01$$

The present authors have determined $\log K_i$ and $e_i^{C}$ in their
previous work\textsuperscript{13} as Eqs. (5) and (6).

\[
\log K_f = -36.200 + T/16.1 \quad (1823 \text{ K} < T < 1923 \text{ K}) \quad \ldots (5)
\]

\[
e_	ext{O}^c = -123/T + 0.034 \quad (\text{mass}\% \text{ Cr} < 46, \ 1823 \text{ K} < T < 1923 \text{ K}) \quad \ldots (6)
\]

The deoxidation product of liquid Fe–Cr alloy is finally given by Eq. (7) which can be derived from the combination of Eqs. (2) to (6).

\[
\log K_i' = -36.200 + T/16.1 - (-369/T + 0.102)[\% \text{ Cr}] - (-649.5/T + 2.481)[\% \text{ O}]/\log a_{Cr_2O_3} \quad \ldots (7)
\]

Bold solid lines in Fig. 1 denote equilibrium relation between Cr and O calculated from Eq. (7) with unit activity of Cr$_2$O$_3$. Equation (7) well explains the observed ones in the Cr content range of Fig. 1.

3. Principle of Chemical Equilibrium Technique

3.1. Determination of Free Energy of Formation of FeO·Cr$_2$O$_3$

Liquid Ag was equilibrated with a crucible made by FeO·Cr$_2$O$_3$+Cr$_2$O$_3$ mixture or FeO·Cr$_2$O$_3$ solid solution under CO–CO$_2$ gas mixture for the measurement of the free energy of formation of FeO·Cr$_2$O$_3$ and activities of the constituents in FeO·Cr$_2$O$_3$ solid solution.

When the crucible of FeO·Cr$_2$O$_3$+Cr$_2$O$_3$ mixture is used, the equilibrium of the system can be represented by Eq. (8), where the oxygen partial pressure in the system, $P_{O_2}$ (atm), can be fixed by CO–CO$_2$ gas mixture according to Eq. (10).

\[
\text{Fe(l)} + 1/2 \text{O}_2(g) + \text{Cr}_2\text{O}_3(s) = \text{FeO·Cr}_2\text{O}_3(s) \quad \ldots (8)
\]

\[
\Delta G_{8}^\circ = -RT \ln K_{14} = -RT \ln \frac{a_{\text{FeO·Cr}_2\text{O}_3}}{a_{\text{Fe(l)}}^{1/2} a_{\text{Cr}_2\text{O}_3(s)}} \quad \ldots (9)
\]

\[
\text{CO(g)} + 1/2 \text{O}_2(g) = \text{CO}_2(g) \quad \ldots (10)
\]

\[
\Delta G_{10}^\circ = -RT \ln K_{16} = -RT \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}}^{1/2} P_{O_2}} \quad -280658 + 85.298T \quad \ldots (11)
\]

Where, $a_{\text{FeO·Cr}_2\text{O}_3}$ is the activity of FeO·Cr$_2$O$_3$ of which standard state is FeO·Cr$_2$O$_3$ saturated with Cr$_2$O$_3$ and $a_{\text{Fe(l)}}$ denotes the activity of Fe in liquid Ag relative to its pure liquid. Since both of the activities of FeO·Cr$_2$O$_3$ and Cr$_2$O$_3$ are unity on this experimental condition, Eq. (12) can be simply derived from Eq. (9):

\[
K_s = \frac{1}{a_{\text{Fe(l)}}^{1/2} a_{\text{Cr}_2\text{O}_3(s)}} = \frac{1}{\gamma_{\text{Fe(l)}} X_{\text{Fe(l)}} a_{\text{Cr}_2\text{O}_3(s)} P_{O_2}^{1/2}} \quad \ldots (12)
\]

Where, $\gamma_{\text{Fe(l)}}$ and $X_{\text{Fe(l)}}$ are the activity coefficient and the mole fraction of Fe in liquid Ag, respectively. It is known that the activity of Fe in liquid Ag obeys Henry’s law due to its small solubility,\textsuperscript{15,17,18} and this results in the following equation, where $a_{\text{Fe}}$ is equal to unity at solubility limit, $X_{\text{Fe}}^{\text{sat}}$.

\[
a_{\text{Fe}} = \gamma_{\text{Fe}} \cdot X_{\text{Fe}} = \frac{X_{\text{Fe}}}{X_{\text{Fe}}^{\text{sat}}} \quad \ldots (13)
\]

Solubility of Fe can be measured by equilibrating liquid Ag with liquid Fe under an inert atmosphere. Therefore, the free energy of formation of FeO·Cr$_2$O$_3$ can be determined by the measurement of Fe solubility in liquid Ag at given $P_{O_2}$ and temperature.

3.2. Determination of Activities of the Constituents in FeO·Cr$_2$O$_3$ Solid Solution

When the crucible of FeO·Cr$_2$O$_3$ solid solution is used, the equilibrium of the system can be achieved as Eqs. (14) to (17).

\[
\text{Fe(l)} + 1/2 \text{O}_2(g) = \text{FeO(l)} \quad \ldots (14)
\]

\[
\Delta G_{14}^\circ = -RT \ln K_{14} = -RT \ln \frac{a_{\text{FeO(l)}}}{a_{\text{Fe(l)}}^{1/2} P_{O_2}^{1/2}} \quad -235800 + 47.44T \quad (J/mol)^{16} \quad \ldots (15)
\]

\[
2 \text{Cr(s), in liquid Ag) + 3/2 O}_2(g) = \text{Cr}_2\text{O}_3(s) \quad \ldots (16)
\]

\[
\Delta G_{16}^\circ = -RT \ln K_{16} = -RT \ln \frac{a_{\text{Cr}_2\text{O}_3(s)}}{a_{\text{Cr(s)}}^{3/2} P_{O_2}^{3/2}} \quad = -1120700 + 256.38T \quad (J/mol)^{16} \quad \ldots (17)
\]

Since $P_{O_2}$ is evaluated from CO$_2$/CO ratio in the gas mixture, activities of FeO and Cr$_2$O$_3$ in FeO·Cr$_2$O$_3$ solid solution can be determined from the equilibrium contents and activity coefficients of Fe and Cr in liquid Ag.

The solubility of Cr in liquid Ag is small at steelmaking temperature but it would not enough low to assume Henry’s law.\textsuperscript{18-21} Therefore, the activity coefficient of Cr was determined in the present work from the equilibrium of liquid Ag with pure solid Cr$_2$O$_3$ and CO–CO$_2$ gas mixture. The activity of Cr$_2$O$_3$ is unity in this experiment, so that the activity coefficient of Cr can be determined from Eq. (17) with equilibrium Cr content in Ag and CO$_2$/CO ratio in the gas mixture. Therefore, activities of FeO and Cr$_2$O$_3$ in FeO·Cr$_2$O$_3$ solid solution can be estimated from the contents of Fe and Cr in liquid Ag based on Eqs. (15) and (17), when Ag–Fe–Cr alloy is melted in fixed composition of FeO·Cr$_2$O$_3$ solid solution under a given ratio of CO$_2$/CO gas mixture.

4. Experiments

4.1. Chemical Equilibrium Technique

Experimental details have been described elsewhere.\textsuperscript{15} Approximately 4 g of Ag–Fe–Cr alloy was charged in the crucible of FeO·Cr$_2$O$_3$+Cr$_2$O$_3$ mixture or FeO·Cr$_2$O$_3$ solid solution and set in a Mo cage. The appropriate initial concentrations of Fe and Cr in the master alloy were given based on the preliminary experiments in order to minimize the amount of Fe and Cr transfer between the liquid Ag and the crucible. After setting the crucible assembly in the hot zone of the LaCrO$_3$ electric resistance furnace which was already controlled at the desired temperature, the reaction tube was sealed and the atmosphere was quickly changed from Ar to a given ratio of CO–CO$_2$ gas mixture. Subsequently, the crucible assembly was held for 4 h to attain equilibrium. The holding time was confirmed in prelimi-
nary experiments. The experimental temperature (1823, 1873 or 1923 K) was monitored by 6% Rh/Pt–30% Rh/Pt thermocouple located just below the crucible. Then the crucible was quenched by withdrawing from the chamber and impinging He. The quenched Ag specimen was dissolved into nitric acid, and contents of Fe and Cr were determined by the Induction Coupled Plasma Spectroscopy (ICP). Compositions of FeO·Cr2O3 and Cr2O3 phases in equilibrium with the metal phase were determined by electron probe micro-analyzer (EPMA). Fe2O was prepared by sintering an equimolar mixture of electrolytic Fe and reagent-grade Fe2O3 powder in an iron crucible at 1373 K under Ar stream for 6 to 8 h. This Fe2O and reagent of Cr2O3 powder were well mixed at the aimed ratio to form FeO·Cr2O3 saturated with FeO·Cr2O3 solid solution, pressed into tablet, sintered at 1673 K for 18 h under Ar in two stages, ground and again sintered twice in CO–50%CO2 atmosphere at 1673 K for 6 h. For the measurement of ΔG°, Fe2O and Cr2O3 powder were mixed with 20 mol% Cr2O3 in excess from stoichiometric composition of FeO·Cr2O3. Formation of FeO·Cr2O3 was confirmed by an X-Ray diffraction method. Then the crucible was formed by a rubber press technique from these oxide powder.

For the measurement of Fe solubility in liquid Ag and preparation of Ag–Fe or Ag–Cr master alloy, 5 to 30 g of reagent grade of Ag was melted together with a piece of electrolytic Fe or Cr in Al2O3 crucible under purified Ar atmosphere for 12 to 24 h. The aimed composition of Ag–Fe or Ag–Cr master alloy was obtained as solid Fe or Cr saturated Ag by adjusting the melting temperature.

4.2. Sampling Method

Experimental equipment and procedure are identical with that of our earlier work on the Cr–O equilibrium in liquid iron saturated with Cr2O3. Approximately 70 g of pre-melted Fe–Cr alloy was charged in a Cr2O3 crucible manufactured in our laboratory from the reagent grade of Cr2O3 powder. This crucible was set in an induction furnace and the metal was heated under purified Ar atmosphere. The metal specimen was melted for enough time to reach equilibrium (90 min) at the aimed constant temperatures of 1823, 1873 or 1923 K. Temperature measurement was conducted by a calibrated infrared radiation pyrometer. Then, approximately 6 g of metal sample was sucked with a quartz tube and quenched in water. The contents of Cr and O in the quenched samples were determined by ICP and LECO, respectively. The cross section of Cr2O3 crucible quenched after the experiment was analyzed by EPMA and XRD.

5. Experimental Results

5.1. Free Energy of Formation of FeO·Cr2O3

Table 1 and Fig. 3 show the solubility of liquid Fe into liquid Ag as a function of 1/T. The solubility of solid Fe observed by the authors15,17,18 are also shown in this figure for the comparison. The solubility of liquid Fe into liquid Ag was in the range from 3900 to 4300 mass-ppm at 1823 to 1923 K and the solubility increased with increasing temperature. The results of the present work were in good agreement with the ones observed by Tsujita.17 As it was realized from Fig. 3, solubility of Fe in liquid Ag was not a simple linear function of 1/T in the higher and lower temperature range of melting point of Fe. However, almost linear relation was found between logarithmic solubility and 1/T within the experimental error in the higher and lower temperature range than the melting point of Fe, respectively, and regression analysis gave Eq. (18) for the solubility of liquid Fe in liquid Ag.

\[
\log(\text{mass-ppm Fe})_{\text{Ag}} = -1455/T + 4.39 \quad \text{(18)}
\]

Equation (18) was used for the calculation of \(a_{\text{Fe}(s)}\) in liquid Ag in the present work.

Table 2 and Fig. 4 represent the effect of oxygen partial pressure on Fe or Cr content in liquid Ag in equilibrium with the crucible of FeO·Cr2O3+Cr2O3 mixture. The activities of FeO·Cr2O3 and Cr2O3 were both unity and the activity coefficients of Fe and Cr in liquid Ag were considered as constant values due to sufficiently low concentration on this experimental condition, so that the following relation could be derived from Eqs. (12) and (17).

\[
\ln X_{\text{Fe}} = -\ln K_8 - \ln \gamma_{\text{Fe}(s)} - \frac{1}{2} \ln P_{\text{O}_2} \quad \text{...........(19)}
\]

\[
\ln X_{\text{Cr}} = -\ln K_{16} - \ln \gamma_{\text{Cr}(s)} - \frac{3}{4} \ln P_{\text{O}_2} \quad \text{...........(19)}
\]

Equation (19) means that the plot of \(\ln X_{\text{Fe}}\) or \(\ln X_{\text{Cr}}\) against \(\ln P_{\text{O}_2}\) should be linear and its slope should be \(-1/2\) or \(-3/4\). As it is seen from Fig. 4, the slopes are very close to the theoretical values, which indicates that the equilibrium among liquid Ag–Fe–Cr alloy, crucible of FeO·Cr2O3+Cr2O3 mixture and CO–CO2 gas is well established in the present work. Since \(K_{16}\) is known value from the free energy of formation of Cr2O3(s), the activity coefficient of Cr in liquid Ag can also be determined from the results of Fig. 4. The results are represented in Fig. 5 together with other lit-
The activity coefficient of solid Cr observed in the present work is given as a linear function of the reciprocal of temperature.

$$\log \gamma_{\text{Cr}(s)} = \frac{3400}{T} + 0.175 \quad \text{(20)}$$

Allen\(^{19}\) has reported that the solubility of Cr in liquid Ag is relatively small and logarithmic solubility is in proportional to \(1/T\). If we assumed the Henry’s law up to the solubility limit of solid Cr in liquid Ag, the activity coefficient of Cr can be evaluated from Allen’s data by Eq. (21).

$$\gamma_{\text{Cr}(s)} = 1/X_{\text{Cr}}^\text{sat} \quad \text{(21)}$$

Figure 4 represents the free energy of formation of Fe\(_2\)O\(_3\) from Fe\(_s\), O\(_2\)(g) and Cr\(_2\)O\(_3\)(s) as a function of temperature.

$$\Delta G_{23}^\circ = -12{,}040.17 - 6.55843T - 3.6751551 \times 10^{-21}T^3 \quad (J/mol) \quad \text{(24)}$$

Hino et al.\(^{15}\) have determined \(\Delta G_{22}^\circ\) with the same experimental technique of the present work and they obtained the following temperature function of \(\Delta G_{22}^\circ\) at the temperature from 1423 to 1723 K.

$$\Delta G_{22}^\circ = -307{,}600 + 66.82T \pm 6800 \quad (J/mol) \quad (1423 K < T < 1723 K) \quad \text{(25)}$$

\(\Delta G_{22}^\circ\) determined in the present work is in good agreement with Eq. (25) as demonstrated in Fig. 6. Therefore, it is concluded that Eq. (25) can be used at the steelmaking temperature up to 1923 K.

5.2. Activities of the Constituents in FeO·Cr\(_2\)O\(_3\) Solid Solution

The activities of Fe\(_t\)O\(_l\) and Cr\(_2\)O\(_3\)(s) in FeO·Cr\(_2\)O\(_3\) solid solution observed by the chemical equilibrium technique are summarized in Table 3 and plotted in Fig. 7 as a function of Cr\(_2\)O\(_3\) content in the solid solution. The number \(r\) in Eqs. (14) and (15) was approximated as unity due to the small deviation of iron oxide composition from stoichiometry for the calculation of \(a_{\text{Fe}_t\text{O}}\). There is no literature information on the activities in FeO·Cr\(_2\)O\(_3\) solid solution. According to the phase diagram of Fe\(_t\)O–Cr\(_2\)O\(_3\) binary system, Fe\(_t\)O–26mol% (43mass%) Cr\(_2\)O\(_3\) solid solution is in equilibrium with Fe\(_t\)O–6mol% (12mass%) Cr\(_2\)O\(_3\) liquid at 1873 K. If we assumed ideal solubility for liquid phase, the activities of Fe\(_t\)O\(_l\) and Cr\(_2\)O\(_3\)(s) on such condition are
0.94 and 0.06, respectively. These values are also represented in Fig. 7. As it is seen in Fig. 7, both activities of Fe$_3$O and Cr$_2$O$_3$ exhibit negative deviation from ideality. These results give us an important indication that the activity of Cr$_2$O$_3$ would quickly decrease from unity when Cr content in metal is lower than [%Cr]$_{critical}$.

5.3. Cr–O Equilibrium in Liquid Iron Equilibrated with FeO·Cr$_2$O$_3$ Solid Solution

Experimental results on the Cr–O equilibrium in liquid iron coexisted with FeO·Cr$_2$O$_3$ solid solution are listed in Table 4. Figure 8 shows the equilibrium relation between Cr and O contents at different temperatures observed in the present work by the sampling method together with other literature values$^{2,9,11}$ including our previous work.$^{13}$ The equilibrium relation in the present work is compared in this figure with those in unit activity of Cr$_2$O$_3$(s), which is calculated by Eq. (7) and is shown by dashed lines. The present results obtained for Cr concentration less than [%Cr]$_{critical}$ did not agree with the calculated ones. This indicates that the equilibrium oxide phase is not pure solid Cr$_2$O$_3$ in the present work even by the use of Cr$_2$O$_3$ crucible. The equilibrium relation between Cr and O coexisted with pure solid FeO·Cr$_2$O$_3$ can also be calculated by Eq. (26) based on unit activity of FeO·Cr$_2$O$_3$(s), where Eq. (26) and its free energy change can be obtained by the combination of Eqs. (1), (2), (22)–(24), (28) with Eq. (29). The activity of Fe(l) is calculated for the estimation by the model proposed by Anderson.$^{31}$

$$\text{FeO·Cr}_2\text{O}_3(s) = \text{Fe}(l) + 2\text{Cr} + 4\text{O} \quad \text{.........(26)}$$
The results are represented by dotted lines in Fig. 8. It is obvious that the present observed results are still much lower than this relation. This deviation means that FeO·Cr₂O₃ formed at the metal–crucible interface is not stoichiometric compound due to the dissolution of FeO into FeO·Cr₂O₃ when the iron of which Cr content is less than [%Cr]critical is melted in a Cr₂O₃ crucible at steelmaking temperature.

Figure 9 is an example of the microscopic view of the metal–Cr₂O₃ crucible interface observed on the present experimental condition of [%Cr]critical. Similar EPMA mapping image of Fe–36.6mass%Cr alloy/Cr₂O₃ crucible interface taken in our previous work is also presented in Fig. 10 for the comparison. Since Cr content in metal was higher than [%Cr]critical in our previous work, no intermediate phase was observed between the metal and crucible, and liquid Fe–Cr alloy was always in equilibrium with pure solid Cr₂O₃ on such condition. Contrarily, an intermediate oxide phase formed at the metal–Cr₂O₃ crucible and the
concentration gradient of Fe and Cr was clearly observed in
the intermediate oxide phase in the present work as shown
in Fig. 9. Though the composition of this intermediate
phase at Cr₂O₃ crucible interface was that of FeO·Cr₂O₃ at
Cr₂O₃ saturation, the FeO content in FeO·Cr₂O₃ at the in-
terface with metal phase was definitely higher than the sto-
ichiometric as shown in Fig. 9. This means that the activity
of Cr₂O₃ or FeO·Cr₂O₃ in the equilibrium oxide phase with
liquid Fe–Cr alloy is less than unity.

6. Discussions

6.1. Phase Equilibria between Liquid Fe–Cr Alloy and
FeO·Cr₂O₃ Solid Solution

Liquid Fe–Cr alloy was found to be in equilibrium with
FeO·Cr₂O₃ solid solution on the present experimental con-
ditions where Cr content in metal was less than [%Cr] critcal.
If we assumed the local equilibrium at metal–FeO·Cr₂O₃
solid solution interface in Fig. 9, the composition of
FeO·Cr₂O₃ solid solution in equilibrium with liquid metal
can be evaluated by extrapolating the concentration profiles
of Fe and Cr to metal/oxide interface. Figure 11 shows the
relation between Fe/Cr ratio (mass ratio) in FeO·Cr₂O₃
solid solution in equilibrium with liquid Fe–Cr alloy and Cr
content in metal. The Fe/Cr ratio did increase with decreasing
Cr content in metal corresponding to the dissolution of
FeO into FeO·Cr₂O₃. The relation in Fig. 11 was converted
to Fe–Cr–FeO–Cr₂O₃ phase diagram as illustrated in Fig.
12. It was confirmed that liquid Fe–Cr alloy was in equilib-
rium with non-stoichiometric FeO·Cr₂O₃ solid solution in
the range of [%Cr] < [%Cr] critcal and the tie-lines between
metal and oxide phases were drawn as shown in Fig.12.

![Figure 10. EPMA mapping images of Fe and Cr in the cross sec-
tion of Cr₂O₃ crucible equilibrated with liquid Fe–
36.6 mass%Cr alloy at 1873 K.](image)

![Figure 11. Composition of FeO·Cr₂O₃ solid solution in equilibri-
um with liquid Fe–Cr alloy as a function of Cr content
in metal, where local equilibrium at metal–oxide inter-
face was assumed.](image)

![Figure 12. Phase relation between liquid Fe–Cr alloy and FeO·Cr₂O₃ solid solution in Fe–Cr–O ternary phase diagram,
where tie-lines between two phases were determined by assuming local equilibrium between metal and oxide
phase.](image)
The equilibrium relation between dissolved Cr and O at lower Cr content in liquid iron can be estimated by Eq. (7) with taking the change of activity of Cr$_2$O$_3(s)$ in FeO·Cr$_2$O$_3$ solid solution shown in Fig.13 into account. The results are drawn as bold solid lines in Fig. 8 together with the observed results in the present work.

7. Conclusions

The free energy of formation of FeO·Cr$_2$O$_3$ and activities of the constituents in FeO·Cr$_2$O$_3$ solid solution have been directly measured by the chemical equilibrium technique at 1 823 to 1 923 K. The free energy of formation of FeO·Cr$_2$O$_3$ is given by the following formula.

$$
\Delta G^\circ = -307600 + 66.82T \text{ } (\pm 6800) \text{ } (\text{J/mol})
$$

(1 423–1 923 K)

The activities of Fe$_{0.5}$(l) and Cr$_2$O$_3(s)$ in FeO·Cr$_2$O$_3$ solid solution exhibit negative deviation from ideality.

The equilibrium relation between Cr and O in liquid iron coexisted with FeO·Cr$_2$O$_3$ solid solution and phase equilibrium between liquid Fe–Cr alloy and Cr$_2$O$_3$ containing oxide have been observed at 1 823 to 1 923 K for the assessment of thermodynamics of oxygen dissolved in liquid Fe–Cr alloy at steelmaking temperature. The oxide phase in equilibrium with liquid Fe–Cr alloy is not Cr$_2$O$_3$ but FeO·Cr$_2$O$_3$ solid solution when Cr content in metal is less than the critical Cr content of approximately 7 mass%. The present experimental results are in good accord with the relation between Cr and O calculated by the thermodynamic parameters, which have been proposed in our previous work, if appropriate correction for Cr$_2$O$_3$ activity was applied.

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REFERENCES

1) Steelmaking Data Sourcebook: The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking, Gordon and Breach Science Pub., New York, NY, (1988).
2) H. M. Chen and J. Chipman: Trans. Am. Soc. Met., 38 (1947), 70.
3) D. C. Hilty, W. D. Forgeng and R. L. Folkman: Trans. AIME, 203 (1955), 253.
4) E. T. Turkdogan: J. Iron Steel Inst., 178 (1954), 278.
5) H. Sakao and K. Sano: J. Jpn. Inst. Met., 38 (1962), 236.
6) R. J. Fruehan: Trans. Metall. Soc. AIME, 245 (1969), 1215.
7) Y. Nakamura, T. Ohno and K. Segawa: Trans. Iron Steel Inst. Jpn. Suppl., 11 (1971), 456.
8) Y. Nakamura and M. Uchimura: Trans. Iron Steel Inst. Jpn., 13 (1973), 343.
9) D. Janke and W. A. Fischer: Arch. Eisenhüttenwes., 47 (1976), 147.
10) M. Heinz, K. Koch and D. Janke: Steel Res., 60 (1989), 246.
11) S. Dimitrov, H. Wenz, K. Koch and D. Janke: Steel Res., 66 (1995), 39.
12) E. M. Levin, C. R. Robbins and H. F. McMurdie: Phase Diagrams for Ceramists, Vol. 1, Am. Ceram. Soc., Columbus, OH, (1964).
13) T. Itoh, T. Nagasaka and M. Hino: *ISIJ Int.*, **40** (2000), 1051.
14) P. V. Riboud and A. Muan: *Trans. AIME*, **230** (1964), 88.
15) M. Hino, K. Higuchi, T. Nagasaka and S. Ban-ya: *ISIJ Int.*, **35** (1995), 851.
16) M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud: JANAF Thermochemical Tables, 3rd ed., Amer. Chem. Soc. & Amer. Inst. of Phys. for National Bureau of Standards, Midland, MI, (1985).
17) K. Tsujita: Master thesis, Graduate School of Engineering, Tohoku University, (1989).
18) C. Wang, J. Hirama, T. Nagasaka and S. Ban-ya: *ISIJ Int.*, **31** (1991), 1292.
19) B. C. Allen: *Trans. Metall. Soc. AIME*, **239** (1967), 1026.
20) Y. Kobayashi, K. Morita and N. Sano: *ISIJ Int.*, **36** (1996), 1009.
21) J.-H. Park, D.-J. Min and C.-H. Rhee: *ISIJ Int.*, **38** (1998), 1287.
22) A. T. Dinsdale: *Calphad*, **15** (1991), 317.
23) F. G. Boericke and W. M. Bangert: U. S. Bureau of Mines, (1945), Rep. No. 3813.
24) F. D. Richardson, J. H. E. Jeffes and G. Withers: *J. Iron Steel Inst.*, **166** (1950), 213.
25) W. Kunmann, D. B. Rogers and A. Wold: *J. Phys. Chem. Solids*, **24** (1963), 1535.
26) T. Katsura and A. Muan: *Trans. Metall. Soc. AIME*, **230** (1964), 77.
27) I. D. Tretjakov and H. Schmalzried: *Ber. Bunsenges. Phys. Chem.*, **69** (1965), 396.
28) K. T. Jacob and C. B. Alcock: *Metall. Trans. B*, **6B** (1975), 215.
29) K. Nagata and R. Murohashi: *CAMP-ISIJ*, **3** (1990), 940.
30) I. Barin and O. Knacke: Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, (1973).
31) J.-O. Andersson: *Metall. Trans. A*, **19A** (1988), 627.