Thermodynamics of Zirconium Deoxidation Equilibrium in Liquid Iron by EMF Measurements

Ryo INOUE,1) Tatsuro ARiyAMA1) and Hideaki SUITO2)

1) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi 980-8577 Japan. 2) Professor Emeritus, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi 980-8577 Japan.

(Received on April 9, 2008; accepted on May 22, 2008)

Thermodynamics of Zr deoxidation equilibrium in liquid iron has been studied at 1 873 K by using ZrO2–9mol%MgO and mullite (3Al2O3·2SiO2) electrolytes coupled with the quantitative analysis of soluble Zr and insoluble Zr as ZrO2 by using a potentiostatic electronic extraction method. The soluble O content for a given soluble Zr content is lower than the previously reported values in the plot of soluble O vs. soluble Zr contents, and the oxygen activity for a given soluble Zr content is higher than the previously reported values. The free energy change of solid Zr dissolution into iron melt: Zr(s) = Zr(1 873 K) is obtained as ΔG° = −153 ± 10 kJ. The interaction coefficients for e°r, r° and r°O are estimated as −70 ± 15, 901 ± 131 and 10 300 ± 1 500, respectively. However, the following interaction coefficients are represented by using a continuous function of logarithms of X, where X=[%sol.Zr]+5.7[%sol.O]+17.1[%sol.Zr]/(2[%sol.Zr]+5.7[%sol.O]):

\[
e_{r}^{°} = -3.70 - 2.20 \ln X - 2.07(\ln X)^2 + (\ln X)^3
\]

\[
r^{°} = dY/dX = (-0.33 + 1.87 \ln X + 3.01(\ln X)^2)/X
\]

\[
r^{°O} = 11.4/(X) = (-3.72 + 21.4 \ln X + 34.3(\ln X)^2)/X
\]

KEY WORDS: Zr deoxidation; mullite; electrolytes; thermodynamics; interaction coefficients.

1. Introduction

Fine oxide particles with an appropriate composition have been utilized for nucleating agents for the phase transformation and the inhibitor of austenite grain growth. For these purposes, fine oxide particles must be dispersed uniformly during deoxidation process. It has been reported that the degree of the critical supersaturation for the formation of ZrO2 is relatively small in comparison with that of Al2O3,3) the ZrO2 particles can be uniformly dispersed without clustering, and they are not pushed out to the liquid Fe in front of the solid/liquid interface.2–4)

Kitamura et al.5) obtained the relationship between total Zr and total O contents at 1 883 to 1 933 K in Fe–0.7 to 74 mass ppm Zr alloys by using a ZrO2–5.5mol%CaO crucible. Busek and Hutla6) reported the same relationship at 2 073 K in Fe–0.02 to 2.68 mass%Zr alloys by using ZrO2 and Al2O3 crucibles. The same relationships in Fe–0.0003 to 0.8mass%Zr alloys are reported at 1 883 to 2 183 K in ZrO2 crucibles by Yamamura and Fuwa.7) It is pointed out that the Zr deoxidation equilibrium has been discussed based on total Zr and total O contents in previous reports; that is, the influence of suspended ZrO2 particles in liquid Fe on this equilibrium has not been taken into considerations.

Because of the suspension of oxide particles in metal, Fruehan8) measured soluble O content in Fe–0.005 to 1.1 mass%Zr alloys, which were melted in ZrO2–4mol%CaO boats at 1 953 K, using neutron activation method and reported the relationship between soluble O and total Zr contents. The oxygen activities in Fe–Zr alloys are measured as a function of total Zr content by ZrO2–MgO,9) ThO2–Y2O3,10) ZrO2–CaO/ThO2–Y2O311) solid electrolytes and fused MgO electrolyte with carbon saturated liquid Fe as a reference electrode.12) In these studies the Zr deoxidation equilibrium has been discussed using total Zr contents, not soluble Zr contents, although the oxygen activities are measured by EMF method.

It has been established that ZrO2 particles dispersed in iron are completely extracted by using a potentiostatic electronic extraction method with non-aqueous electrolyte solutions.13) In the present study the thermodynamics of Zr deoxidation equilibrium has been studied by using the following method: The oxygen activities are measured at 1 873 K by ZrO2–9mol%MgO and mullite probes and soluble Zr contents are estimated from the subtraction of insoluble Zr contents as ZrO2 particles from total Zr contents. These ZrO2 particles correspond to those suspended in liquid Fe, not those precipitated during cooling.
2. Basic Consideration of EMF Measurements

2.1. ZrO$_2$–9mol%MgO Solid Electrolyte

It is well known that ZrO$_2$ type solid electrolyte is used for an oxygen sensor by which oxygen activity in a molten metal can be electrochemically measured. In the presence of soluble Zr in metal, the local equilibrium given by Eq. (1) is established at molten metal/ZrO$_2$ type solid electrolyte interface.

\[ \text{Zr} + 2O^* = \text{ZrO}_2 \text{ (in solid-electrolyte) } \] ............(1)

The local oxygen activity, \( a_O \), is written by oxygen potential, \( P_O \), as

\[ a_O = K_O (P_O)^{1/2} \] ............(2)

where \( K_O \) is the equilibrium constant of the reaction: 1/2 \( O_2 \) = \( O^* \).

The electrochemical oxygen concentration cell can be expressed as

\[ \text{Mo, Cr}–\text{Cr}_2\text{O}_3/\text{solid electrolyte (SE)/O}_2 \] ............(3)

The relationship between EMF value obtained from the above cell and the local oxygen potential is given by

\[ E = RT/F \log \left \{ \frac { P_O (\text{Cr}–\text{Cr}_2\text{O}_3)^{1/4} + P_d (\text{SE})^{1/4} } { (P_O)^{1/4} + P_d (\text{SE})^{1/4} } \right \} \] ............(4)

where \( P_O (\text{Cr}–\text{Cr}_2\text{O}_3) \) is calculated from the standard free energy of the formation of \( \text{Cr}_2\text{O}_3 (s) \): \( \Delta G^{\circ}_{\text{Cr}_2\text{O}_3} = -1110.1 + 0.24737 \text{Tk/mol}^{14} \) and \( P_d (\text{SE}) \) is defined as oxygen partial pressure at equal ionic and excess electronic conductivity depending on the temperature and the type and composition of the electrolyte. In the present study, Janke and Fischer's value$^{(5)}$ given by Eq. (5) is used for ZrO$_2$–9mol%MgO electrolyte.

\[ \log P_d (\text{ZR-9M}) = 29.43 - 74.370/ T (\text{Pa}) \] ............(5)

The following relationship with respect to oxygen activity and EMF, \( E \), can be derived from Eqs. (2), (4) and (5) as

\[ a_O = K_O \left \{ \frac { P_O (\text{Cr}–\text{Cr}_2\text{O}_3)^{1/4} + P_d (\text{ZR-9M})^{1/4} } { (P_O)^{1/4} + P_d (\text{ZR-9M})^{1/4} } \right \}^{1/2} \] ............(6)

where \( R \) is the gas constant, \( F \) is the Faraday constant and \( K_O \) is obtained from \( \Delta G^{\circ}_{\text{Zr}_2\text{O}_3} = -117 - 0.00297 \text{Tk/mol}^{16} \).

In the case of Zr deoxidation in which the oxygen activity, \( a_O \), is determined by the Zr/ZrO$_2$ (s) equilibrium, the \( a_O \) value at molten metal/solid electrolyte interface is equal to the \( a_O \) value in molten metal.

2.2. Mullite (3Al$_2$O$_3$·2SiO$_2$) Electrolyte

It has been shown in our previous study that the activities of Al$^{17}$ and Si$^{18}$ in liquid iron can be measured by using a mullite electrolyte. If soluble Al and Si are not present in molten metal, mullite electrolyte works simply as an oxygen sensor such as a stabilized ZrO$_2$ sensor. If mullite is used as an oxygen concentration cell given by Eq. (3), the EMF value is given by

\[ E = RT/F \log \left \{ \frac { P_O (\text{Cr}–\text{Cr}_2\text{O}_3)^{1/4} + P_d (\text{SE})^{1/4} } { (P_O)^{1/4} + P_d (\text{SE})^{1/4} } \right \} \] ............(7)

The \( P_d (\text{SE}) \) for a mullite probe is measured as

\[ \log P_d (\text{mullite}) = 59.33 - 137 \text{000} / T (\text{Pa})^{19} \] ............(8)

In the absence of soluble Al and Si, the oxygen activity at electrolyte/molten metal interface which is equal to that in molten metal is expressed as follows:

\[ a_O = K_O \left \{ \frac { P_O (\text{Cr}–\text{Cr}_2\text{O}_3)^{1/4} + P_d (\text{mullite})^{1/4} } { (P_O)^{1/4} + P_d (\text{mullite})^{1/4} } \right \}^{1/2} \] ............(9)

3. Experimental

3.1. Procedure

By using a vertical resistance furnace with LaCrO$_3$ heating bars, the EMF measurements were carried out at 1873 K under ultra high-purity Ar flow (150 cm$^3$/min) which was passed through a purification train of Mg(ClO$_4$)$_2$ and P$_2$O$_5$, followed by deoxidation with Ti (934 K) and Mg (728 K) and dehydration with P$_2$O$_5$. The mixture of pure iron and Fe–10mass%Zr alloy was melted in ZrO$_2$–11mol%CaO crucible and an appropriate amount of Fe–10mass%Zr alloy was additionally charged into the melt using a quartz tube. The melt was stirred by a ZrO$_2$–11mol%CaO rod for 30 s every 20 min in order to attain the Zr+2O=ZrO$_2$ equilibrium. After 2 h, a plug-type ZrO$_2$–9mol%MgO probe (φ4.0×10 mm) shown in Fig. 1(a) and the Mo rod (φ3 mm) inserted in the ZrO$_2$–11mol%CaO tube, which are preheated above the melt, are simultaneously dipped into the melt for 1 min to measure the oxygen activity. Then, a mullite probe (φ4.5×φ2.5×40 mm) shown in Fig. 1(b) was dipped into the melt for 1 min to measure the oxygen activity. After the EMF measurements, the crucible containing the sample was removed from the furnace and quenched rapidly in a He gas stream, followed by water-quenching. In order to avoid the air involvement during the removal of crucible from the furnace, the rate of Ar flowing from the bottom of the furnace was increased up to 2000 cm$^3$/min.

3.2. Chemical Analysis

Soluble Zr and insoluble Zr as ZrO$_2$ were analyzed by the potentiostatic electronic extraction method.$^{13}$ The non-

![Fig. 1. Schematic illustration of plug type ZrO$_2$–9mol%MgO (a) and tube type mullite (b) probes.](image-url)
aqueous electrolyte was 10%AA (10v/v% acetylacetone–1w/v% tetramethylammonium chloride–methanol). Electrolyte was filtered after extraction using a PTFE membrane filter with the open pore size of 0.1 μm. The metal sample after extraction was washed with methanol using an ultrasonic vibrator, and then the methanol was also filtered using the same filter. The residue obtained by drying the mixture of filtrate and HCl was dissolved by aqua regia, and the content of Zr, which corresponds to soluble Zr, was determined by using inductively coupled plasma-mass spectrometry (ICP-MS). The residue on the filter was fused with Na2CO3 and B2O3, followed by leaching with HCl and the content of insoluble Zr as ZrO2 particles was also determined by ICP-MS. Total oxygen content in metal was determined within ±1 mass ppm by inert gas fusion-infrared absorptiometry.

4. Results and Discussion

4.1. Relationship between Zr and O Contents

The experimental results for EMF, O activity, and metal composition are summarized in Table 1. Total Zr contents are plotted against total O contents in Fig. 2, together with the previously reported relationships between total Zr and total O contents5–7,11) and that between total Zr and soluble O contents.8) In the present experiments a metal sample was rapidly quenched so that both size and amount of the particles precipitated during cooling are significantly small compared with those present in molten metal as deoxidation product. This was confirmed by the following two methods:

i) The insoluble Zr was analyzed by using two stages filtering technique in which the polycarbonate film filters with the open pore size of 1 and 0.05 μm were used. The insoluble Zr content on the filter with the open pore size of 0.05 μm (second stage) was negligible compared with that on the filter with the open pore size of 1 μm (first stage).

ii) The volume fraction of the inclusion particles was obtained from the SEM observation of extracted particles on the film filter with the open pore size of 0.05 μm. The volume fraction of the particles with the size below 0.5 μm was much smaller than that above 0.5 μm.

The oxygen content as ZrO2 particles is estimated from insoluble Zr content by assuming that all particles are present as primary inclusion particles in molten metal. Soluble oxygen contents are obtained from the balance between total O content and O content as oxides. These values are also given in Table 1. The relationships between soluble Zr and soluble O contents are shown in Fig. 3, together with the previously reported.5–8,11) It can be seen that the present soluble O contents for a given Zr content are lower than the previous results except for the values reported by Buzek and Hulta.6)

4.2. Relationships between Total Zr Content and Oxygen Activity

The oxygen activities measured by ZrO2–9mol%MgO probe and mullite probe are plotted against soluble Zr content in Fig. 4. It can be seen that the oxygen activities obtained in both probes agree well each other in the range of Zr content below 600 ppm, but those by ZrO2-type probe are slightly lower than those by mullite probe in the range above 600 ppm. This is explained by the fact that the oxygen activities measured by ZrO2 type probe correspond to

| [sol.Zr] (ppm) | [isol.Zr] (ppm) | [O]m.e.(ZrO2) (ppm) | [Total O] (ppm) | [sol.O] (ppm) | ZrO2–9mol%MgO | Mullite | [ZrO2–9mol%MgO] | [Mullite] |
|---------------|----------------|-------------------|----------------|-------------|---------------|--------|----------------|---------|
| 1.2           | 52.6           | 18.5              | 65.6           | 47.1        | 42±3          | -2.339 | -46±5          | -2.342  |
| 18.4          | 0.8            | 0.3               | 5.1            | 4.8         | 126±2         | -3.445 | 156±2          | -3.462  |
| 23.7          | 5.0            | 1.7               | 7.0            | 5.3         | 128±3         | -3.460 | 143±5          | -3.391  |
| 42.1          | 1.4            | 0.5               | 5.5            | 5.0         | 153±3         | -3.661 | 191±1          | -3.653  |
| 61.3          | 11.1           | 3.9               | 8.5            | 4.6         | 168±7         | -3.783 | 190±3          | -3.656  |
| 128           | 1.9            | 0.7               | 5.0            | 4.3         | 190±0         | -3.986 | 253±2          | -4.024  |
| 335           | 18.0           | 6.3               | 10.6           | 4.3         | 215±0         | -4.239 | 270±3          | -4.128  |
| 583           | 2.5            | 0.9               | 5.0            | 4.1         | 223±2         | -4.328 | 269±7          | -4.119  |
| 1150          | 3.2            | 1.2               | 6.0            | 4.8         | 221±1         | -4.299 | 259±9          | -4.065  |
| 2450          | 27.6           | 9.6               | 16.5           | 6.9         | 207±6         | -4.164 | 258±2          | -4.055  |

[Table 1. Experimental results for metal composition, EMF and oxygen activity.]

Fig. 2. Relationships between total O and total Zr contents.
the local equilibrium value obtained at molten metal/solid electrolyte interface, which can be determined by Eq. (3).

The oxygen activities measured by ThO₂–Y₂O₃ solid electrolyte and fused MgO electrolyte are shown in Fig. 4 for comparison, indicating that these oxygen activities for a given soluble Zr content are lower than the present values.

4.3. Thermodynamic Values in Zr Deoxidation

a) Interaction Coefficients Determined by Electrolyte Probe

The activity coefficient of oxygen, \( f_O \), relative to an infinite dilute solution of 1 mass% standard state can be written as

\[
\log f_O = e_O [\% \text{sol. O}] - e_O [\% \text{sol. Zr}]^{1.4} \tag{10}
\]

where \( e_O \) and \( r_{O,Zr} \) are expressed as

\[
\log f_O = e_O [\% \text{sol. O}] - e_O [\% \text{sol. Zr}]^{1.4} \tag{11}
\]

From Eq. (10) to Eq. (13), we have the following relation:

\[
\log f_O^{Zr} [\% \text{sol. Zr}] = e_O^{Zr} [\% \text{sol. Zr}]^{1.4} \tag{12}
\]

The values for the left-hand side of Eq. (14) are plotted against those for the second term without \( r_{O,Zr} \) on the right-hand side in Fig. 5 by using the \( e_O^{Zr} \) value (0.20) reported by Sigworth and Elliott. Although the data points scatter, the \( e_O^{Zr} \) and \( r_{O,Zr} \) values are obtained from the intercept and slope, respectively. These values determined by a regression analysis are summarized in Table 2 together with the \( r_{O,Zr} \) value from Eq. (13), and those obtained in previous studies are listed in Table 2.

b) Equilibrium Constant Determined from Soluble Zr and O Contents

The Zr deoxidation reaction is written as

\[
\text{ZrO}_2(s) = \text{Zr} + 2\text{O}_2 \tag{15}
\]

The equilibrium constant of Eq. (15), \( K_{Zr} \), is expressed by using the apparent equilibrium constant, \( K'_{Zr} \) (=[\%sol. Zr]·[%sol. O]²) and the respective activity coefficients as follows:

\[
K_{Zr} = a_{Zr} a_{O}^2 = K'_{Zr} f_{Zr} f_{O}^2 \tag{16}
\]

The activity coefficients of Zr \( (f_{Zr}) \) and O \( (f_{O}) \) can be written by using the first-order and second-order interaction coefficients as
The relationships between $e_i$ and $e_j$, between $r_i$ and $r_j$ and between $r^O_i$ and $r^O_j$ are expressed by Eqs. (19), (20) and (13), respectively. \[ \log f_{Zr} = e^O_{Zr}[\%sol.Zr] + e^O_O[\%sol.O] + r^O_{Zr}[\%sol.Zr] \cdot [\%sol.O] \] \[ \log f_O = e^O_O[\%sol.Zr] + e^O_O[\%sol.O] + r^O_O[\%sol.Zr] \cdot [\%sol.O] \] The relationships between $e_i$ and $e_j$, between $r_i$ and $r_j$ and between $r^O_i$ and $r^O_j$ are expressed by Eqs. (19), (20) and (13), respectively. \[ e^O_{Zr} = e^O_O M_{Zr}/M_O = 5.7 e^O_{Zr} \] \[ r^O_{Zr} = r^O_O (M_{Zr}/M_O)^2 = 32.5 r^O_{Zr} \] By using the values for $e^O_{Zr}$, $r^O_{Zr}$ and $r^O_O$ obtained in Sec. 4.3(a), the $K_{Zr}$ values are calculated from Eq. (13) and Eqs. (16) to (20). These values are plotted against soluble Zr contents in Fig. 6 and the experimental and thermodynamically calculated values obtained at 1873 K in previous studies are summarized in Table 3. It is clear from Fig. 6 that the present $K_{Zr}$ (~9.83 ± 0.28) is about the average value of the previous values and independent of soluble Zr content.

The combination of the $\Delta G^\circ$ for 1/2 $O_2$ and $\Delta G^\circ_{21}$ for the reaction given by Eq. (21) leads to the standard free energy change of the dissolution of solid Zr into molten iron.

\[ \Delta G^\circ_{22} = 1081 - 0.17647T (kJ) \] \[ \Delta G^\circ_{21} = Zr(s) + 2O_2(g) \]

From the $\Delta G^\circ_{22}$ value, the Henrian activity coefficient at 1873 K can be derived. This value and the $\Delta G^\circ_{22}$ value are given in Table 4, together with the reported values. The following relationship is derived from Eqs. (13) and (20) to (23)

\[ \log (K_{Zr}/K^*_{Zr}) = e^O_{Zr}[\%sol.Zr] - 2 e^O_O[\%sol.O] + r^O_{Zr}[\%sol.Zr] + 5.7 e^O_O[\%sol.O] \]

The term on the left-hand side of Eq. (23) denoted by $Y$ is plotted against the second term without $r^O_{Zr}$ on the right-hand side of Eq. (23) denoted by $X$ in Fig. 7. In this plot the

| e^O_{Zr} | r^O_{Zr} | r^O_O | Temp.(K) | [% Zr] |
|---|---|---|---|---|
| Buzek et al. | -0.44 | - | - | 1873 | 0.01–1.9 |
| Janke and Fischer | -0.5–2.0 | - | - | 1873 | 0.0009–1.7 |
| Kitamura et al. | -2.1 | - | 1883–1983 | 0.00097–0.0074 |
| Buzek and Hutka | -4.5 | - | 1873 | 0.01–0.2 |
| Yamamura and Fuwa | -5.7 | - | 1883 | 0.0006–0.8 |

This work
from EMF: -70 ± 15 | 901 ± 131 | 10300 ± 1500 | 1873 | 0.0001–0.08
from [sol.Zr] and [sol.O]: Eq. (26) | Eq. (25) | Eq. (27) | 1873 | 0.0001–0.7 |

| e^O_{Zr} | r^O_{Zr} | r^O_O | Temp.(K) | [% Zr] |
|---|---|---|---|---|
| Buzek et al. | 0.53 | - | - | 1873 | 0.0001–0.7 |
| Janke and Fischer | 0.5–2.0 | - | - | 1873 | 0.0009–1.7 |
| Kitamura et al. | -2.1 | - | 1883–1983 | 0.00097–0.0074 |
| Buzek and Hutka | -4.5 | - | 1873 | 0.01–0.2 |
| Yamamura and Fuwa | -5.7 | - | 1883 | 0.0006–0.8 |

Table 2. Interaction coefficients of $e^O_{Zr}$, $r^O_{Zr}$ and $r^O_O$.

Table 3. Equilibrium constant for Zr deoxidation: ZrO$_2(s)$ = Zr + 2O plotted against soluble Zr content.

Table 4. The Henrian activity coefficient and standard free energy of solution of zirconium in liquid iron: Zr(s) = Zr (1 mass% solution).

| $\gamma^\circ_{1873}$ | $\Delta G^\circ$ (kJ/mol) | $\Delta G^\circ$ at 1873 K (kJ/mol) |
|---|---|---|
| Elliott et al. | 0.011 | -53600–50.2T | -148 |
| Sigworth and Elliott | 0.043 | -34700–50.0T | -128 |
| This work | 0.0088 | -153±10 |
log $K_Zr = -9.98 (1873 K)$ value is estimated from the reported value of $\Delta G^0_{Zr,O} (\text{kJ})$ and $\Delta G^0_{O,Zr} (\text{kJ})$

The relationships between $Y$ and $X$ are calculated from the experimental results obtained by other researchers and the results are shown in Fig. 8. The $e^0_{O,Zr}$ and $r^0_{O,Zr}$ values obtained in Sec. 4.3(a) are substituted into the right-hand side of Eq. (23). These results are represented by a broken line in Fig. 7, in which this line falls on the experimental line only in the limited range. A similar trend observed in Figs. 7 and 8 is obtained in the Ca deoxidation equilibrium of liquid Fe by Ohta and Suito, who found that $Y$ can be expressed approximately by a continuous function of $\ln X$ in the present Zr deoxidation $Y$ can be expressed as

$$Y = -4.028 - 0.327 \ln X + 0.937 \ln X^2 + (\ln X)^3 \ldots \ldots (24)$$

This relation is given by the solid line in Fig. 7, indicating that the data points fall on this line in the whole range.

The $e^0_{O,Zr}$ and $r^0_{O,Zr}$ values are obtained from Eqs. (25) and (26), respectively, which are developed previously in the Ca deoxidation equilibrium.

$$r^0_{O,Zr} = dY/dX = \{-0.33 + 1.87 \ln X + 3.01(\ln X)^2\}/X \ldots \ldots (25)$$

$$e^0_{O,Zr} = Y - X(dY/dX) = -3.70 - 2.20 \ln X - 2.07(\ln X)^2 + (\ln X)^3 \ldots \ldots \ldots (26)$$

and the $r^0_{O,Zr}$ value is obtained from Eq. (13) as

$$r^0_{O,Zr} = 11.4 r^0_{O,Zr} = (-3.72 + 21.4 \ln X + 34.3(\ln X)^2)/X \ldots \ldots \ldots \ldots (27)$$

The $e^0_{O,Zr}$, $r^0_{O,Zr}$ and $r^0_{O,Zr}$ values represented by Eqs. (25) to (27), respectively, are listed in Table 2. The relationships between soluble O and soluble Zr contents at $1873 K$ are obtained by using $\log K_Zr = -9.98 (1873 K)$ and these $e^0_{O,Zr}$, $r^0_{O,Zr}$ and $r^0_{O,Zr}$ values. The results are shown in Fig. 3 by the solid line which explains well all experimental data points. For the comparison, those calculated by using $\log K_Zr = -9.98 (1873 K)$ and the $e^0_{O,Zr}$, $r^0_{O,Zr}$ and $r^0_{O,Zr}$ values, which were obtained in Sec. 4.3(a), are also shown in Fig. 3 by the gray solid line. This line corresponds to the experimental data points at $\% sol. Zr < 0.06$.

5. Conclusions

Thermodynamics of Zr deoxidation has been studied at $1873 K$ from the measurement of oxygen activities using ZrO$_2$ type and mullite probes, coupled with the soluble and insoluble Zr contents analyzed by using a potentiostatic electric extraction method. The conclusions obtained are summarized as follows:

(1) The soluble O content for a given soluble Zr content is lower than the previous soluble O content in a plot of total Zr vs. total O contents.

(2) The present oxygen activity for a given soluble Zr content is higher than the previous oxygen activity in a plot of oxygen activity and Zr content.

(3) The free energy change of dissolution of solid Zr: $Zr(s) = Zr^{3+}$ at $1873 K$ is obtained as $\Delta G^0_{Zr} = -153 \pm 10\text{kJ}$.

(4) Although the interaction coefficients of $e^0_{O,Zr} = -70 \pm 15$, $r^0_{O,Zr} = 901 \pm 131$ and $r^0_{O,Zr} = 10300 \pm 1500$ are estimated, the observed relationships between soluble O and soluble Zr contents cannot be well explained by these interaction coefficients. Therefore, it is recommended to use the following interaction coefficients represented by a continuous function of $\ln X$, where $X = [\% sol. Zr] + [5.7[\% sol. O]] + 17.1[\% sol. Zr] + [5.7[\% sol. O]]$.

$$e^0_{O,Zr} = -3.70 - 2.07(\ln X)^2 + (\ln X)^3$$

$$r^0_{O,Zr} = -3.72 + 21.4 \ln X + 34.3(\ln X)^2$$

REFERENCES

1) G. Li and H. Suito: ISIJ Int., 37 (1997), 762.
2) H. Suito and H. Ohta: ISIJ Int., 46 (2006), 33.
3) T. Sawai, M. Wakoh, Y. Ueshima and S. Mizoguchi: ISIJ Int., 32 (1992), 169.
4) H. Ohta and H. Suito: ISIJ Int., 46 (2006), 22.
5) O. Kitamura, S. Ban-ya and T. Fuiwa: 2nd Japan–USSR Joint Symp. on Physical Chemistry of Metallurgical Processes, ISIJ, Tokyo, 2008.
6) Z. Busek and A. Hutla: Sammelbuch der Bergbau-Hochschule, Os-
trava, 3, (1965), 383.
7) M. Yamamura and T. Fuwa: Tetsumo-Hagané, 59 (1973), S52.
8) R. J. Fruehan: Metall. Mater. Trans., 5 (1974), 345.
9) H. Vorwerk, H. Gerdor and H-U. Lindenber: Stahl Eisen, 96
(1976), 611.
10) A. Jacquemot, C. Gatellier and M. Olette: IRSID Report Re.109,
(1974).
11) D. Janke and W. A. Fischer: Arch. Eisenhüttenwes., 47 (1976), 195.
12) E. B. Teplitskiy and L. P. Vladimirov: Izv. VUZ. Cernaya Metall.,
(1973), No. 3, 5.
13) H. Ohta and H. Suito: ISIJ Int., 46 (2006), 14.
14) I. Barin: Thermochemical Data of Pure Substance, VCH, Weinheim,
New York, (1989).
15) D. Janke and W. A. Fischer: Arch. Eisenhüttenwes., 46 (1975), 755.
16) G. K. Sigworth and J. F. Elliott: Met. Sci., 8 (1974), 298.
17) H. Suito, R. Inoue and A. Nagatani: Steel Res., 63 (1992), 419.
18) R. Inoue and H. Suito: Trans. JSS, 22 (1995), 51.
19) A. Nagatani, R. Inoue and H. Suito: J. Appl. Electrochem., 22
(1992), 859.
20) Z. Busek, M. Macoszek and J. Szlauer: Hutn. Listy, 8 (1972), 547.
21) S. W. Cho and H. Suito: ISIJ Int., 34 (1994), 265; 764.
22) J. Chipman: Basic Open Hearth Steelmaking, 3rd ed., ed. by G.
Derge, American Institute of Mining, Metallurgical and Petroleum
Engineers, New York, (1964), 678.
23) J. F. Elliott, M. Gleiser and V. Ramakrishna: Thermochemistry for
Steelmaking, The American Iron and Steel Institute, Vol. 2, Addi-
son-Wesley Pub. Co., Massachusetts, USA, (1963).
24) G. Kinne, A. F. Vischkarev and V. I. Javoiskij: Izv. VUZ. Cernaya
Metall., (1963), No. 5, 65.
25) M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frueip, R. A.
McDonald and A. N. Syverud: J. Phys. Chem. Ref. Data, 14 (1985),
Suppl. 1.
26) H. Ohta and H. Suito: ISIJ Int., 43 (2003), 1293.