Investigation on the Decomposition of Al_2O_3 Using an Electrochemical Method

Dong Ju SHIN and Dong-Joon MIN*

Yonsei University 262 Seongsanno, Seodaemun-Gu, Seoul, 120-749 Korea.

(Received on September 28, 2012; accepted on December 11, 2012)

When the chemical potential of dissolved oxygen in a Fe–Al–O alloy is above the super-saturation level, Al_2O_3 inclusions will be precipitated; electrochemical reaction analysis can provide explanations of the kinetic and thermodynamic mechanisms in the formation and decomposition of Al_2O_3 . In this study, an external potential was supplied to the electrochemical system consisting of electrodes and a MgO-stabilized ZrO_2 electrolyte in order to control interfacial oxygen levels and oxide inclusions in Fe–Al–O alloys of 30, 70, 170, 560 and 1 500 ppm Al at 1 823 K. Critical levels of interfacial oxygen concentration were kinematically determined by concentration overvoltage using the Tafel relationship and the Nernst equation. From these experiments, the formation of Al_2O_3 requires interfacial and crystallization energy. Also energy for decomposition of Al_2O_3 should be needed the energy to break Al–O bonding and to dissociate into the Fe melt. The results of the formation and decomposition of Al_2O_3 at the interface between the Fe–Al–O alloy and solid electrolyte are indicated in scanning electron microscope (SEM) images and through electroprobe microscope analyzer (EPMA) analysis.

KEY WORDS: electrochemistry; oxide inclusion control; deoxidation; critical oxygen concentration; crystallization and binding energy.

1. Introduction

The detrimental effects of non-metallic oxide inclusions in steels products and processes are well-known.¹⁾ Oxide inclusions, which are precipitated during deoxidation reactions in the steelmaking process, can cause nozzle clogging in continuous casting and lowers the quality of the steel resulting in decreased mechanical properties.²⁾ Thus, the control of inclusions in steel is essential to ensure product quality. According to recent work by Kim and Sohn³⁾ regarding the formation of oxide inclusions, such as Al_2O_3 , the exchange of oxygen ions determines the formation and decomposition of Al_2O_3 inclusions at the interface.

Using the pioneering work of Kiukkola and Wagner,⁴⁾ several studies have been conducted concerning the control of oxygen activity in high temperature systems using solid electrolytes including those related to the steelmaking process.^{5–7)} Fischer and other researchers reported that the degree of deoxidation possible from the use of electromotive force (EMF) methods in liquid metals was limited owing to the slow bulk diffusion of oxygen.^{8–10)} Kim *et al.*¹¹⁾ reported that the local interfacial oxygen concentration could be kept below 3 ppm by applying an external voltage using a ZrO_2 -based solid electrolyte at high temperatures and showed the interfacial oxygen concentration is a major factor in the formation of oxide inclusions.

In other work regarding thermodynamic relationship

between aluminum and oxygen in molten Fe, Fruehan¹²⁾ and Dimitrov *et al.*¹³⁾ were able to analyze the activity of oxygen in a Fe–Al–O alloy using galvanic cells and found to coincide with the thermodynamic reaction mechanisms with soluble aluminum. Seo *et al.*¹⁴⁾ modeled the equilibrium relationship between aluminum and oxygen in molten Fe at 1 873 K by calculating thermodynamic values such as the interaction coefficient and the equilibrium constant. Although the thermodynamic conditions for Al_2O_3 formation were well documented, Suito *et al.*^{15,16)} reported that additional oxygen is required to actually nucleate and grow the oxide inclusions, and introduced the concept of differing super-saturation ratios for different oxides. In accordance with Suito *et al.*,¹⁶⁾ Kim and Sohn³⁾ confirmed the formation of oxide inclusions and further suggested the possibility of decomposing the oxide inclusion by supplying an external current through the use of an electrochemical cell. This novel process verified the decomposition reaction of Al_2O_3 , but did not focus on a wide range of aluminum concentration needed for inclusion decomposition and was limited to apply in typical steelmaking compositions.

Therefore, this study assesses not only the condition of interfacial oxygen activity using electrochemical methods for decomposing oxide inclusions in a wide range Fe–Al–O alloys, but also determines the kinetic mechanism of the decomposition at 1 823 K using MSZ (magnesia stabilized zirconia) as solid electrolyte.

* Corresponding author: E-mail: chemical@yonsei.ac.kr

DOI: <http://dx.doi.org/10.2355/isijinternational.53.434>

2. Experimental Methods and Procedure

2.1. Experimental Setup

A schematic diagram of the experimental apparatus used in the experiment is shown in Fig. 1(a). The alumina crucible (OD: 50 mm, ID: 44 mm, and H: 70 mm) is charged with 0.2 kg of Fe–Al–O alloy and 0.085 kg of Ag (purity: 99.99%) and situated within the hot zone of vertical electric resistance furnace at 1823 K. Five samples with varying compositions of Fe, Al, and O, which is used in this study are provided in Table 1. The present work basically focuses on three regions at the interface between the electrolyte and melt. One region is the supply of oxygen using a reference gas to the interface up to the supersaturation point described by Suito *et al.*¹⁶⁾ The second region is the partial decomposition of the Al_2O_3 by applying an external potential. The third region is the complete decomposition of the Al_2O_3 by

Fig. 1. (a) Experimental apparatus, (b) The reaction steps at the interface between Reference gas region and Fe–Al–O melt and electrochemical construction.

Table 1. Experimental composition of the Fe–Al–O melt in the present study.

Experiment number	Initial content before melting (ppm)		Oxygen concentration of melt before applying external voltage (ppm)
	Al	O	
S 1	30	104	238
S 2	70	63	100
S 3	170	23	327
S 4	560	11	235
S 5	1 500	27	450

applying an external potential below the equilibrium point. At each region to obtain the samples for further EDS analysis, the samples are furnace cooled while applying the as-needed external potential corresponding to the end point of the experiment. Details of the experimental set-up and procedure have been provided elsewhere.³⁾

2.2. Cell Construction and Electrochemical Measurements

The electrochemical cell used here can be described schematically in Fig. 1(b).

$P_{\text{O}_2}^{\text{Ref}}$ and $a_{\text{O}}^{\text{Ref}}$ are the oxygen pressure and activity in the reference gas, and $P_{\text{O}_2}^{\text{Int}}$ and $a_{\text{O}}^{\text{Int}}$ are the oxygen pressure and activity at the Fe–Al–O melt–electrolyte interface, respectively. By measuring the cell potential (E_{cell}), the oxygen activity at the interface can be calculated using the Nernst equation, which can be expressed for a cell with supplied external potential as¹⁷⁾

$$E_{\text{apply}} - I_{\text{ion}} R_{\text{ion}} = E_{\text{cell}} = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}^{\text{Int}}}{P_{\text{O}_2}^{\text{Ref}}} = \frac{RT}{4F} \ln \frac{a_{\text{O}}^{\text{Int}}}{a_{\text{O}}^{\text{Ref}}} \dots (1)$$

where F is Faraday's constant ($F = 96\,450 \text{ C/mol}$), E_{apply} is the external potential (V), I_{ion} is the ionic current (A), and R_{ion} is the ionic resistance (Ω).

The MSZ electrolyte is immersed into the molten Fe–Al alloy to a depth of approximately 1.5 mm, and the electric potential of the cell is measured at intervals of 0.3 s using a digital multimeter (Keithley Co., Model 2000 DMM). An external potential is applied to the circuit with a sourcemeter (Keithley Co., 2400 Sourcemeter). The cell current is read by applying an external voltage from the sourcemeter at a frequency of 7.5 Hz. The applied potentials have magnitudes within a region between 0.2 and 0.65 V.

2.3. Calculation of the Oxygen Concentration and Analysis

$P_{\text{O}_2}^{\text{Int}}$ can be determined from Eq. (1) as

$$P_{\text{O}_2}^{\text{Int}} = P_{\text{O}_2}^{\text{Ref}} \exp \left(\frac{4FE_{\text{cell}}}{RT} \right) \dots (2)$$

By calculating pressure of oxygen at the interface from Eq. (2), the concentrations of oxygen (in either ppm or wt%) can be found from the activity using the reactions

To calculate the oxygen concentration at the interface, the

Table 2. Interaction coefficient (e_i^j) of elements dissolved in liquid steel.^{19–21)}

i	j	
	Al	O
Al	$63.0/T + 0.011$	$-34\,740/T + 11.95$
O	$-20\,600.0/T + 7.15$	$-1\,750/T + 0.734$

interaction coefficient of aluminum with respect to oxygen in the Fe–Al–O alloy is required. The interaction coefficients of the dissolved elements in liquid steel have been previously calculated in the literature.^{20–22} **Table 2** shows the values of the interaction coefficients of aluminum and oxygen in liquid Fe–Al–O used in this study as a function of temperature.

Interfacial oxide inclusions are analyzed using a scanning electron microscope (SEM, JEOL JSM-7001F) and an electro-probe microscope analyzer (EPMA, Oxford). The alloy composition of the samples are identified using an inductively coupled plasma–optical emission spectrometer (ICP-OES, Agilent Technologies 700 series) to detect aluminum and a N/O determinator (LECO Co., TC-300) for oxygen.

3. Results and Discussions

3.1. Rate-controlling Step during the Deoxidation of Electrolytic Fe with O

According to previous study,³⁾ the oxygen activity is the most important factor in controlling oxide inclusions at the interface. To determine the rate-controlling step, an external voltage was applied from 0.1 to 0.7 V in 0.1 V intervals to the cell in order to deoxidize a sample of electrolytic Fe containing 120 ppm oxygen. These preliminary experiments allow the fundamental understanding of the rate controlling steps of transported oxygen species through the electrochemical cell. Based on previous studies to determine the rate-controlling steps of deoxidation processes,^{9–11)} there are five steps as shown schematically in Fig. 1(b).

- Diffusion of oxygen molecules into the CO/CO₂ reference gas region
- Electrochemical reaction at the solid electrolyte/reference gas interface
- Oxygen ion migration through the solid electrolyte
- Electrochemical reaction at the solid electrolyte/molten Fe interface
- Oxygen species diffusion from the bulk of the molten Fe to the solid electrolyte/molten Fe interface

To maintain a continuous reaction an excess potential of

Fig. 2. The relationship between overpotential and current density in electrolytic Fe with O.

the rate controlling step needs to be provided. This excess potential is called overvoltage (η) defined by Eq. (5).

$$\eta = E - E_0 \quad (5)$$

E is the external potential (V) and E_0 is the zero current cell potential (V), respectively. In the present study, it is assumed that the bulk diffusion of oxygen molecules into the reference gas (A) and electrochemical reaction at the solid electrolyte/reference gas interface (B) are fast and at equilibrium compared to other steps. When an external potential is applied to the cell, the rate controlling kinematic mechanism can be determined from the amount of the overvoltage according to the Tafel relationship.²³⁾ **Figure 2** shows the current density of the cell as a function of overvoltage showing three distinct regions including—a region of activation overvoltage where is electrochemical reaction at the solid electrolyte/molten Fe interface, a region of ohmic overvoltage (the Tafel region) where is oxygen ion migration through the solid electrolyte, and a region of concentration overvoltage where is oxygen species diffusion from the bulk of the molten Fe to the solid electrolyte/molten Fe interface—that are distinguishable from each other at their inflection points. A more detailed explanation of the Tafel behavior will be discussed in the following sections.

3.2. Rate-controlling Step during the Deoxidation of Fe–Al–O Alloy

Figure 3 shows the current density of the cell as a func-

Fig. 3. The relationship between overpotential and current density in Fe–Al–O alloy.

tion of overvoltage for Fe–Al–O alloys with 30, 70, 170, 560 and 1 500 ppm of aluminum similar to Fig. 2, three distinct regions are observed.

Region 1 identified as the “activation overvoltage”²⁴⁾ is the region, where the electrochemical reaction at the interface between the ZrO₂ electrolyte and the Fe–Al–O melt is rate determining. The reaction can be expressed as the following.

With sufficient external potential, the oxygen in the melt can overcome the activation barrier for Eq. (6), resulting in higher ionic current. The disparate starting current densities are the result of differences in the oxygen concentration between the reference gas and the Fe–Al–O melt/electrolyte interface just prior to applying the external potential as presented in Table 1. Thus, Fig. 3 shows wide range of measured current densities at different initial aluminum content. It should be noted that the oxygen chemical potential of the reference gas is higher than that at the interface of the Fe–Al–O melt and the ZrO₂ electrolyte just prior to applying an external potential and the oxygen ions can transfer reversibly from the reference gas region to the interface.

Region 2 identified as the “ohmic overvoltage” is the region, where the electric resistance to the oxygen ion migration within the solid electrolyte and electron movement within electrode materials are rate-controlling.²⁵⁾ In the ohmic overvoltage region, Ohm’s law is obeyed and can be defined as²⁴⁾

$$\eta_{\text{ohm}} = jR \dots\dots\dots (7)$$

where j and R denote the current density (mA/cm²) and resistance (Ω) in the cell, respectively. R incorporates various components, including the electrode resistance, contact resistance, and electrolyte resistance. The overall resistance, however, is dominated by the electrolyte resistance term, and the others can be neglected. The slope in Region 2 represents the inverse of the value of the electrolyte resistance, and the average value of 3.0 Ω is similar to the resistance of the ZR-15M solid electrolyte material of 2.5 Ω used in this experiment.

Region 3 has a different rate-determining step from that of Regions 1 and 2. It is called the “concentration overvoltage”. The concentration overvoltage is dominated by slow diffusion of oxygen species from the Fe–Al–O bulk to the interface. Once the overall reaction is being controlled by the liquid phase bulk mass transport effects, the oxygen concentration at the interface between the electrolyte and the Fe–Al–O melt cannot go lower than a critical value, even when the applied potential is continuously increased. Since there are no activated oxygen atoms that can react at the interface through slow diffusion of oxygen from the bulk, current density levels out, as observed in Fig. 3. The relationship between overvoltage and current density within the concentration overvoltage region is²⁵⁾

$$\eta_{\text{conc}} = \frac{RT}{\alpha nF} \ln \left(1 - \frac{j}{j_L} \right) \dots\dots\dots (8)$$

where α is the transfer coefficient ($\alpha = 1$),²⁵⁾ n is the number of transferred electrons ($n = 4$),^{8–11,16)} R is the gas constant ($R = 8.314 \text{ J/mol}\cdot\text{K}$), j is the current density, and j_L is the limiting current density (mA/cm²). The oxygen chemical

potential does not change, and the critical concentration of oxygen for decomposition of Al₂O₃ is determined at the beginning of Region 3 using the Nernst equation.

3.3. Effect of Oxygen Concentration at the Interface on Al₂O₃ Formation and Decomposition

The equilibrium reaction for formation of Al₂O₃ in the iron melt is given by,^{21,26)}

However, based on previous work by Suito *et al.*,¹⁶⁾ a supersaturation oxygen activity is necessary for the formation of Al₂O₃. The supersaturation ratio can be defined as

$$S_{\text{Al}_2\text{O}_3}^\circ = (a_{\text{Al}}^2 \cdot a_{\text{O}}^3)_{\text{ss}} / (a_{\text{Al}}^2 \cdot a_{\text{O}}^3)_{\text{eq}} \dots\dots\dots (10)$$

Figures 4(a) and 4(b) show the equilibrating relationship between oxygen content and aluminum content in a molten Fe alloy at equilibrium, as provided by several studies.^{12–14,16)} This relationship indicates a critical supersaturation ratio value of ($\log S_{\text{Al}_2\text{O}_3}^\circ = 3.5$) as proposed by Suito *et al.*¹⁶⁾ The experimental group with (1), (4) and (7) correspond to S1. The experimental group with (2), (5) and (8) correspond to

Fig. 4. (a) Interfacial O and Al concentration by formation of Al₂O₃, (b) Interfacial O and Al concentration by decomposition of Al₂O₃.

S2. The experimental group with (3), (6) and (9) correspond to S3. At the initial chemical composition shown as the gray dashed line just below the supersaturation line in Fig. 4(a), the interfacial oxygen at constant aluminum content increases following Route 1 by supplying oxygen from the reference gas to the interface between molten Fe–Al–O and MgO–ZrO₂ solid electrolyte. Once the oxygen content reaches the supersaturation line, Al₂O₃ starts to form. As Al₂O₃ forms by increasing oxygen content at the interface by electrochemically, the aluminum concentration decreases and the interfacial oxygen concentration maintains the supersaturation line in the direct following Route 2. In this route, aluminum is heavily consumed at the interface owing to the crystallization of Al₂O₃ due to the slow diffusion of aluminum from the bulk to the interface. The interfacial concentration of oxygen, however, increases gradually since oxygen is supplied continuously from the reference gas. This behavior of oxygen and aluminum can be verified by work of Suito *et al.*¹⁶⁾ Morphological observations for (1), (2) and (3) were done and verified the formation of Al₂O₃ as shown in Figs. 5(1), 5(2) and 5(3), respectively. The schematic of the Al₂O₃ formation presented in Fig. 6(a).

After Al₂O₃ formation was achieved above the supersaturation line, separate experiments were done to confirm the decomposition reaction of Al₂O₃. By supplying an external potential of 0.3 to 0.4 V to the cell, the oxygen concentration

decreases and starts to decompose the as-formed Al₂O₃ at the interface as shown in Fig. 4(b). Morphological observations of samples (4), (5) and (6) revealed partially decomposed Al₂O₃ at the interface in Figs. 5(4), 5(5) and 5(6), respectively. The schematic of the partial Al₂O₃ decomposition is presented in Fig. 6(b).

At higher external potentials above 0.4V, the measured oxygen concentration drops below the equilibrium line for Al₂O₃ and full Al₂O₃ decomposition is observed, which were confirmed from the morphological observations of samples 7, 8 and 9 in Figs. 5(7), 5(8) and 5(9), respectively. It should be noted that the measured interfacial oxygen concentration has a critical limiting value due to the limitation of bulk liquid phase mass transport from the Fe–Al–O melt. Thus, the effects of an external potential no longer has an impact on the decomposition of Al₂O₃ at the interface above a critical potential value. The schematic of the fully decomposed and mass transport limiting reaction is shown in Fig. 6(c). The critical oxygen concentration can be obtained by the Nernst equation given in Eq. (11),

$$P_{O_2}^{\text{critical}} = P_{O_2}^{\text{Ref}} \cdot \exp\left(-\frac{nFE_{\text{critical}}}{RT}\right) \dots\dots\dots(11)$$

where E_{critical} is the measured critical cell potential. When Al₂O₃ is decomposed with an external potential, the critical oxygen content of the present study seems to correspond

Fig. 5. Al₂O₃ formation and decomposition by SEM images.

Fig. 6. The scheme of (a) Al₂O₃ formation, (b) Partial Al₂O₃ decomposition, and (c) Full Al₂O₃ decomposition.

Fig. 7. Line scanning of Al and O by EPMA analysis for (a) formation of Al_2O_3 , (b) decomposition of Al_2O_3 .

with the work of Kim and Sohn³⁾ in Fig. 4(b). Although the plots of the critical oxygen contents are similar to the equilibrium or supersaturation line, additional data in a broader range is needed to definitively define the critical oxygen line.

Figure 7 shows the EPMA line scanning analysis for aluminum and oxygen for S3 (170 ppm Al) when Al_2O_3 is formed and decomposed. Figure 7(a) shows significant aluminum content present at the interface between the melt and the MSZ solid electrolyte compared to the bulk of the sample. Oxygen content also seems to be significantly higher at the interface suggesting Al_2O_3 formation. Figure 7(b) indicates similar analysis, but correspond to decomposition of Al_2O_3 considering the contents of aluminum and oxygen spread evenly across the sample.

3.4. Critical External Potential for Decomposition of Al_2O_3

From the aforementioned effect of an external potential for Al_2O_3 decomposition, there is a characteristic critical potential value where the reaction is controlled by the liquid phase mass transport of oxygen to the interface. Above this critical external potential, the interfacial oxygen concentration is unaffected. **Figure 8** shows the interfacial oxygen concentration as a function of external voltage. The initial oxygen concentration decreases with higher external voltage. Depending on the composition of the sample, the critical external voltage varies and the final critical oxygen content at the interface is determined. The critical values are provided in **Table 3**. From the present work, the supply of an external potential can control the interfacial oxygen concentration at levels below the equilibrium oxygen content and thus either inhibit the formation of Al_2O_3 or decompose existing Al_2O_3 at the interface.

3.5. Characteristic Energy for Formation and Decomposition of Al_2O_3

According to works of Suito *et al.*,^{16,27)} it was speculated

Fig. 8. Interfacial oxygen concentration by external voltage.

Table 3. Critical oxygen concentration at the interface and critical external potential.

Sample number	[ppm O] _{crit} ^{Int}	Critical External potential (V)
S 1	11.3	0.4
S 2	6.5	0.5
S 3	2.0	0.55
S 4	1.7	0.6
S 5	3.0	0.5

that Al_2O_3 formation requires an excess free energy in liquid steel up to the supersaturation point. Assuming that the required excess free energy for Al_2O_3 formation consists of an interfacial and crystallization term, supersaturation free energy ($\Delta G_{\text{Al}_2\text{O}_3}^{\text{ss}}$) can be recognized as follows:

$$\Delta G_{\text{Al}_2\text{O}_3}^{\text{ss}} = \Delta G_{\text{interfacial}} + \Delta G_{\text{crystallization}} \quad \dots\dots\dots (12)$$

The formation of Al_2O_3 represents a change in state of soluble aluminum and oxygen in molten steel to a state of solid Al_2O_3 in molten steel, where a solid-liquid two phase exists from a single liquid phase. A randomly mixed aluminum and oxygen atom in molten steel rearranges into the form of Al_2O_3 having a defined ordered crystal structure.^{28,29)} Creation of a new phase involves the interfacial energy, $\Delta G_{\text{interfacial}}$ and a crystallization energy, $\Delta G_{\text{crystallization}}$, to form an ordered crystal structure from a random mixed state.

In the present work, this supersaturation Gibbs free energy is provided by the applied electric energy and calculated using the Nernst equation.

$$\Delta G_{\text{Al}_2\text{O}_3}^{\text{ss}} = -RT \ln \left(\frac{P_{\text{O}_2}^{\text{Ref}}}{P_{\text{O}_2}^{\text{initial}}} \right) = -nFE \quad \dots\dots\dots (13)$$

where $P_{\text{O}_2}^{\text{initial}}$ is the initial oxygen pressure at the interface between electrolyte and Fe–Al–O melt, and E is the initial cell electric potential. The energy for formation Al_2O_3 in each experimental sample is calculated by multiplication of right terms in Eq. (13) and is shown in **Table 4**. In several past literatures,^{30,31)} the interfacial energy for Al_2O_3 nucleation in liquid Fe is approximately 1.2 J/m². Assuming that particle of Al_2O_3 is spherical and has 0.3–5 μm ,^{30,32)} the total

Table 4. The additional energy for formation and decomposition of Al₂O₃.

Sample Number	Formation	Decomposition
	Additional energy (kJ/mol)	Additional energy (kJ/mol)
S 1	85.5	150.2
S 2	99.4	169.1
S 3	127.3	210.2
S 4	140.0	210.0
S 5	86.8	192.9

surface energy by the mole of Al₂O₃ has range of about 18.4–306 J/mol, which is comparably negligible. Therefore, most of the excess free energy to form Al₂O₃ in the melt is the crystallization energy.

Accurate calculation of the energy for decomposition of Al₂O₃ by dividing the compound into elements is difficult. Energy difference between the supersaturation and the equilibrium state is calculated to be 125 kJ/mol. ($RT \ln S_{\text{Al}_2\text{O}_3}^\circ = 8.314 \cdot 1873 \cdot 2.303 \cdot 3.5 = 125 \text{ kJ/mol}$) However, not all of the Al₂O₃ can be decomposed due to the thermodynamic limitations of the reaction. If the excess free energy is supplied beyond the thermodynamic equilibrium position, Al₂O₃ will fully decompose and maintain a local oxygen and aluminum concentration different from the equilibrium oxygen and aluminum contents. The energy for decomposition of Al₂O₃ can be obtained from supplied electric energy to the electrochemical cell. Therefore decomposition energy is calculated using the Nernst equation and this is similar to the calculation for supersaturation Gibbs free energy above.

$$\Delta G_{\text{Al}_2\text{O}_3}^{\text{decom}} = -RT \ln \left(\frac{P_{\text{O}_2}^{\text{Ref}}}{P_{\text{O}_2}^{\text{critical}}} \right) = -nF\Delta E_{\text{critical}} \quad \dots (14)$$

$\Delta E_{\text{critical}}$ is the external potential as interfacial oxygen concentration reaches the critical value. Each calculated value by multiplying right terms in Eq. (14) is different from every sample and is indicated in Table. 4. The energy for decomposition of Al₂O₃ ranges from about 150 to 210 kJ/mol which is greater than an excess energy for formation of Al₂O₃. For decomposition of Al₂O₃ and subsequent dissolution of aluminum and oxygen into molten Fe–Al–O, the energy includes the energy needed to break the Al–O binding energy and the dissolute energy of aluminum and oxygen into the Fe melt.

4. Conclusions

In the present study, both the formation and the decomposition of Al₂O₃ have been observed as a result of supplying an external potential in a wide range Fe–Al–O alloys. The results obtained are summarized as follows:

(1) Oxide inclusions are formed as the oxygen potential reaches a critical supersaturation state, which has been defined as $\log S_{\text{Al}_2\text{O}_3}^\circ = 3.5$ by Suito *et al.*

(2) Three kinetic mechanisms are involved in applying an external potential to the cell in order to decompose oxide inclusions: activation overvoltage, ohmic overvoltage, and concentration overvoltage. The rate determining steps of these are, respectively, electrochemical reaction, diffusion of oxygen ions through the ZrO₂ electrolyte, and diffusion

of oxygen atoms from the bulk Fe–Al–O melt to the interface.

(3) As-formed interfacial oxide inclusions can be decomposed by maintaining, via an critical external potential, a critical interfacial oxygen concentration lower than equilibrium value.

(4) Formation of oxide inclusions at the interface require supersaturation energy which consists of interfacial and crystallization energies for formation Al₂O₃. Energy for decomposition of Al₂O₃ is indicted as binding energy to break the Al–O and dissolution energy of Al and O into the Fe melt. In this study, these energies for formation were found to be approximately 90 kJ/mol, whereas for decomposition, it was about 150–210 kJ/mol.

Acknowledgement

This work was supported by the “Brain Korea 21 (BK 21) Project.” We gratefully acknowledge the additional financial support from the Division of Humantronics Information Materials (The YONSEI University of Seoul, Korea). The authors greatly appreciate the discussion and guidance provided by Professor I. Sohn at Yonsei University.

REFERENCES

- G. H. Kim and I. Sohn: *J. Non-Cryst. Solid*, **358** (2012), 1530.
- J. H. Park, D. J. Kim and D. J. Min: *Metall. Trans. A*, **43A** (2012), 2316.
- W. Kim and I. Sohn: *ISIJ Int.*, **51** (2011), 63.
- K. Kiukkola and C. J. Wagner: *J. Electrochem. Soc.*, **104** (1957), 379.
- E. L. Courtright, R. W. Knoll, G. R. St. Pierre and R. A. Rapp: *Oxid. Met.*, **38** (1992), 267.
- K. E. Oberg, L. M. Friedman, R. Szwarc, W. M. Boorstein and R. A. Rapp: *J. Iron Steel Inst.*, **210** (1972), 359.
- M. Iwase and A. McLean: *Solid State Ionics*, **5** (1981), 571.
- W. A. Fischer and D. Janke: *Scr. Metall.*, **6** (1972), 923.
- M. Iwase, M. Tanida, A. Mclean and T. Mori: *Metall. Trans. B*, **12B** (1981), 517.
- Z. Hasham, U. Pal and K. C. Chou: *J. Electrochem. Soc.*, **142** (1995), 469.
- W. Kim, D. J. Min, Y. S. Lee and J. H. Park: *ISIJ Int.*, **49** (2009), 1882.
- R. J. Fruehan: *Metall. Trans. B*, **1** (1970), 3403.
- S. Dimitrov, A. Weyl and D. Janke: *Steel Res.*, **66** (1995), 3.
- J. D. Seo, S. H. Kim and K. R. Lee: *Steel Res.*, **69** (1998), 49.
- H. Suito, H. Inoue and R. Inoue: *ISIJ Int.*, **31**(1991), 1381.
- G. Li and H. Suito: *ISIJ Int.*, **37** (1997), 762.
- K. E. Oberg, L. M. Friedman, W. M. Boorstein and R. A. Rapp: *Metall. Trans. B*, **4B** (1973), 61.
- E. T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York/London, (1980), 5, 7, 22.
- B. Deo and R. Boom: *Fundamentals of Steelmaking Metallurgy*, Prentice Hall International, Hertfordshire, (1993), 52.
- S. K. Choudhary, S. Chandra and A. Ghosh: *Metall. Trans. B*, **36B** (2005), 59.
- J. F. Elliott, M. Gleiser and V. Ramakrishna: *Thermochemistry for Steelmaking*, Addison-Wesley, Boston, (1963).
- The Japan Society for the Promotion of Science: *Steelmaking Data Sourcebook*, Gordon & Breach Science Publishers, New York, (1988), 280.
- J. Tafel: *Z. Physik. Chem.*, **50A** (1950), 641.
- A. J. Bard and L. R. Faulkner: *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, (1980), 101.
- A. J. Bard, G. Inzelt and F. Scholz: *Electrochemical Dictionary*, Springer, New York, (2008), 108, 466.
- G. K. Sigworth and J. F. Elliott: *Met. Sci.*, **8** (1974), 298.
- H. Suito: The E. T. Turkdogan Symp. On Fundamentals and Analysis of New and Emerging Steelmaking Technologies, Iron and Steel Soc., TMS-AIME and U.S. Steel Group of USX Corp., Pittsburgh, PA, (1994), 141.
- J. W. Mullin: *Crystallization* 4th ed., Elsevier Ltd., MA, (2001).
- E. V. Khamskii: *Crystallization from Solutions*, Consultants Bureau, New York, (1969).
- M. Wakoh and N. Sano: *ISIJ Int.*, **47** (2007), 627.
- J. Tanabe and H. Suito: *Metall. Mater. Trans. B*, **26B** (1995), 95.
- H. Shibata, H. Yin, S. Yoshinaga, T. Emi and M. Suzuki: *ISIJ Int.*, **38** (1998), 149.