Electrochemical Method for Controlling the Interfacial Oxygen in Molten Fe with ZrO_2 Based Solid Electrolyte

Wook KIM,¹⁾ Dong Joon MIN,¹⁾ Young Seok LEE²⁾ and Joo Hyun PARK³⁾

1) Department of Advanced Materials Engineering, Yonsei University, Shinchon-dong 134, Seodaemun-gu, Seoul, Korea. E-mail: chemical@yonsei.ac.kr

2) Ironmaking Research Group, Technical Research Laboratories, POSCO, Pohang, Korea.

3) School of Materials Science and Engineering, University of Ulsan, Moogeo-dong, Nam-gu, Ulsan, Korea.

(Received on June 25, 2009; accepted on September 3, 2009)

The control of the interfacial oxygen concentration in molten steel by an electrochemical method using ZrO_2 based solid electrolyte was suggested in this study. Oxygen ions were transferred through the solid electrolyte by varying the chemical potential difference and applying an external electric potential between the cathode and the anode. By applying an external electric potential, the oxygen concentration was controlled below 3 ppm at the molten Fe/ ZrO_2 interface. The electrochemical reaction rate of oxygen removal was found to be faster than the estimated diffusion of oxygen through the boundary layer of molten steel. Thus, the slow diffusion of oxygen through the boundary layer creates a steady state oxygen concentration profile, where an oxygen depleted layer at the molten Fe/ ZrO_2 interface is present. The oxygen concentration profile in the boundary layer was confirmed using the Glow Discharge Spectroscopy.

In this study, the oxygen concentration at the interface could be controlled using an electrochemical method of ZrO_2 based solid electrolyte and achieve a steady state at the interface within the liquid phase boundary layer.

KEY WORDS: electrochemical method; ZrO_2 solid electrolyte; interfacial oxygen; oxygen deplete layer.

1. Introduction

Interfacial reaction is an important phenomenon that can determine the rate of almost process issues in the ironmaking and steelmaking process, including pick up of impurities such as nitrogen from the atmosphere, erosion of the refractory, refining, and even nozzle clogging during continuous casting process. The typical interfacial reactions are greatly affected by surface active (surf active) elements such as oxygen and sulfur existing at the interfacial reaction sites. Recent work by Han *et al.*¹⁾ indicated that oxygen contents as low as 10 ppm had inhibited adsorption of nitrogen into molten steel. Several researchers^{2–4)} have demonstrated that surface tension is significantly decreased with small amount of oxygen and thus increase the wettability of molten Fe, the attachment of inclusions, and the likelihood of nozzle clogging. Although the bulk oxygen concentration can be significantly lowered by the high temperature physical chemistry reactions such as precipitation deoxidation, minute concentrations of oxygen at the interface may be important in view of interfacial phenomena. Therefore, there have been some efforts to determine the possibility of further deoxidizing molten metal by an electrochemical method using a solid electrolyte.^{5–10)}

Fischer *et al.*⁵⁾ was one of the first to use an Electro Motive Force (EMF) method to deoxidize steel melt through the electrochemical deoxidation using a solid electrolyte. Rapp *et al.*^{6,7)} applied this electrochemical deoxidation to

an induction-stirred copper melt and achieved oxygen levels below 25 ppm. Iwase *et al.*⁸⁾ used a galvanic method for deoxidizing steel with a one-end closed Calcia Stabilized Zirconia (CSZ) tube immersed into the liquid steel at 1823 K. Due to the open circuit nature of Iwase *et al.*'s experiment, the electrochemical deoxidation has been limited by lower electric conductivity. Pal *et al.*^{9,10)} used a short circuit process for deoxidizing steel in order to increase the cell electric conductivity. The experimental limitations of the above mentioned electrochemical deoxidation processes involves deoxidation of the entire metal bath and concluded that the rate-controlling step was oxygen diffusion across the boundary layer when the bulk oxygen concentration of the melt is low. And although the diffusion boundary layer can be slightly affected to improve mass transfer by violent stirring, the impact is minimal.

Therefore, in the present study, direct control of the interfacial oxygen concentration by the electrochemical deoxidation method was observed.

2. Experimental

The electrochemical cell and the reaction steps are illustrated in **Fig. 1**. The electrochemical deoxidation consists of 5 steps.^{5–10)}

- ① Diffusion of soluble oxygen through the boundary layer from the bulk to molten Fe/ ZrO_2 interface
- ② Electrode reaction at the molten Fe/ ZrO_2 interface

Fig. 1. Illustration of the deoxidation in the electrochemical cell system and the reaction steps.

- ③ Diffusion of oxygen ions through electrolyte
- ④ Electrode reaction at the ZrO_2 /reference gas interface
- ⑤ Diffusion of oxygen molecules into the bulk of reference gas

The difference of soluble oxygen across the boundary layer and the transfer of oxygen ions across the solid electrolyte are represented by step ① and step ③ in Fig. 1, respectively. The chemical potential of oxygen at the anode was controlled with $P_{\text{O}_2}^{\text{Ref}}$ using various CO_2/CO ratios and the subsequent oxygen partial pressure at the interface, $P_{\text{O}_2}^{\text{Inter}}$, was measured at the cathode. To increase the conductivity of electrons supplied from the anode to cathode, a short-circuit^{9,10)} was applied.

Schematic of experimental apparatus is shown in Fig. 2. A high purity alumina crucible (OD=50 mm, ID=47 mm, and H=70 mm) was charged with 0.08 kg of Ag (99.99%) and 0.27 kg of Fe, the furnace was held at 1823 K in a stream of ultra purified argon gas (99.9999%) in a mullite reaction tube (OD=70 mm, ID=60 mm, and H=1000 mm). Excess moisture and oxygen in the argon gas were removed by passing the gas through a gas purification system of CaSO_4 and a column of magnesium chips heated to 753 K. The temperature of the reaction tube was controlled using a B-type thermocouple placed 2 mm beneath the crucible. This control thermocouple was calibrated with a reference thermocouple placed inside the hot zone of the reaction tube. A solid electrolyte crucible of Magnesia Stabilized Zirconia (MSZ, $\text{ZrO}_2 + 15\% \text{MgO}$) was used (OD=13 mm, ID=10 mm, H=50 mm). The electrochemical cell consisted of an anode/cathode electrode and a solid electrolyte. The anode was the Pt paste layer on the inner side surface of ZrO_2 based electrolyte and the cathode was the molten iron in contact with the ZrO_2 based electrolyte as shown in Fig. 2. The ZrO_2 based electrolyte was cemented and fused at the tip of an alumina tube (OD=10 mm, ID=7 mm, H=1000 mm) at 1273 K. In order to supply the reference gas of CO_2/CO into the solid electrolyte crucible, an inlet gas alumina lance was inserted within the solid electrolyte crucible (OD=5 mm, ID=2 mm, H=1000 mm) placed the outer alumina tube connected to the MSZ crucible. Using a mass flow controller (MFC), 150 cm^3/min of CO/CO_2 reference gas was supplied into the solid electrolyte chamber. Excess moisture and CO_2 from the CO supply gas were removed by passing the gas

Fig. 2. Experimental apparatus.

through a column of CaSO_4 and soda lime.

Using a LECO[®] N/O (TC-300) analyzer, the initial oxygen concentration of electrolytic iron was found to be 150 ppm. The equilibrium reaction of oxygen in molten iron is given below.¹¹⁾

$$\frac{1}{2} \text{O}_{2(\text{gas})} = \underline{\text{O}}, \quad \Delta G = -117300 - 2.9T \text{ (J/mol)} \dots (1)$$

From the equilibrium reaction and the initial oxygen content of 150 ppm at 1823 K, the equilibrium partial pressure of oxygen in molten iron was calculated to be $P_{\text{O}_2}^{\text{Inter}} = 2.1 \times 10^{-11}$ atm. The lead wires of the electrochemical cell were platinum (99.9%) and molybdenum wire (99.9%). The anode Pt wire was attached to the solid electrolyte with a layer of Pt paste. However, the cathode Mo wire could not be directly immersed in the molten iron due to the high solubility of Mo in Fe at 1823 K. Thus, an intermediate layer of silver was incorporated to act as a transport medium for electrons within the molten iron. The details of the experimental conditions are given in Table 1.

Previous works on electrochemical cell reactions incorporated the methodologies of direct periodic melt samplings⁸⁾ or cell current measurements^{9,10)} to detect melt oxygen concentration in the bulk. In the present study, the cell potential (E^{cell}) was continuously measured for obtaining the oxygen concentration at the Fe melt/ ZrO_2 interface ($P_{\text{O}_2}^{\text{Inter}}$) calculated by using Eq. (2).

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

where F is the Faraday's constant ($F = 96487 \text{ C/mol}$), $P_{\text{O}_2}^{\text{Ref}}$

Table 1. Experimental parameters.

Sample Number	CO ₂ /CO ratio	$P_{O_2}^{Ref}$ (atm)	External Applied EMF (V)
NEV-P8	3/5	2.7×10^{-8}	0.0
NEV-P9	1/5	3.0×10^{-9}	0.0
NEV-P10	1/10	7.6×10^{-10}	0.0
NEV-P11	1/50	3.3×10^{-11}	0.0
NEV-P12	1/100	7.6×10^{-12}	0.0
EV-P8	3/5	2.7×10^{-8}	0.20–0.58
EV-P9	1/5	3.0×10^{-9}	0.20–0.58
EV-P10	1/10	7.6×10^{-10}	0.20–0.58
EV-P11	1/50	3.3×10^{-11}	0.20–0.58
EV-P12	1/100	7.6×10^{-12}	0.20–0.58

(Fe weight: 0.27 kg, Initial oxygen content: 0.015 ± 0.002 mass%)

and $P_{O_2}^{Inter}$ are the partial pressures (atm) of oxygen in the reference gas and in the melt, respectively. The oxygen partial pressure in the reference gas was controlled by passing a defined CO₂/CO gas volume ratio using the following reaction (3).¹¹⁾

The voltage between the two electrodes was measured using a Keithly 2000 multi-meter at a 2 Hz interval and an external electric potential was applied using a Keithly 2400 power supply.

The solid electrolyte crucible was immersed into the molten iron up to 20 mm below the topline of the melt 30 min after the reaction hot zone reached 1823 K. The potential difference of the cell was then measured for 3500 s. Following the measurement of the potential variation, the furnace was cooled down and the oxygen concentration in the bulk and its profile in the boundary layer of the sample were measured using the LECO® N/O (TC-300) analyzer and the Glow Discharge Spectroscopy (LECO® GDS 850A), respectively. The stability of the interface between molten Fe and ZrO₂ was analyzed using the Electro Probe Microscope Analyzer (EPMA, JEOL JXA8100).

3. Results and Discussion

3.1. Changes of the Interfacial Oxygen Concentration with Oxygen Partial Pressure under No External Electric Potential

The dependence of the interfacial oxygen concentration on the oxygen partial pressure is shown in Fig. 3. The oxygen partial pressure at the anode is controlled by varying the CO₂/CO ratio in the reference gas through the MSZ solid electrolyte crucible. Results show the change in oxy-

Fig. 3. Dependence of interfacial oxygen concentration with time at different oxygen partial pressure of reference gas.

gen concentration at the Fe melt/ZrO₂ interface. For experiments NEV-P8, NEV-P9, and NEV-P10, the oxygen ions are transferred from the reference gas to the Fe melt/ZrO₂ interface resulting in the increase of oxygen concentration at the interface. However for experiments NEV-P11 and NEV-P12, the oxygen ions are transferred from the Fe melt/ZrO₂ interface to the reference gas. This suggests that the movement of oxygen ions is closely related to the difference in oxygen potential of the electrochemical cell. A higher oxygen partial pressure at the anode directs the flow of oxygen ions towards the cathode and *vice versa*. The interfacial oxygen concentration changed rapidly within 1500 s after the electrochemical cell was immersed into the Fe melt and converged to a constant value dependent on oxygen partial pressure of the reference gas.

This was not consistent with the results of Iwase *et al.*,⁸⁾ where the change of oxygen concentration in Fe melt of the bulk with time was extremely slow even though the oxygen partial pressure of the reference gas was lower than the present investigation. The main reason for the slow rate in oxygen variation was likely due to the experimental procedure of sampling in the bulk of the melt and not at the interface or near the boundary layer. And since the bulk diffusion of oxygen ions is slow, measurement of the bulk oxygen concentration with time will result in very slow changes in oxygen concentration. The results in present study indicate, a higher rate of oxygen concentration change at the Fe melt/ZrO₂ interface by the cell potential (E^{cell}). Since the oxygen partial pressure in the reference gas was kept constant by a continuous constant flow of fixed CO₂/CO gas mixture, the decrease in cell potential could be correlated with the change of oxygen partial pressure at Fe melt/ZrO₂ interface.

As demonstrated in past studies,^{5–10)} the soluble oxygen diffusion across the boundary layer was the rate limiting step of the electrochemical deoxidation at low oxygen concentrations. As a result, the overall deoxidation rate of the bulk was slow and minimal approximately 2.2×10^{-6} wt%/s.⁷⁾ Similar results with bulk oxygen concentration were also verified in this study, but detailed observation at

the interface revealed a more significant impact on the variation of the oxygen concentration. Furthermore, the control of oxygen partial pressure using CO/CO₂ gas ($P_{O_2}^{Ref}$) mixtures allowed the direct control of oxygen concentration at the interface. Details are given below.

Figure 4 shows the oxygen partial pressure in the steady state at the Fe melt/ZrO₂ interface ($P_{O_2}^{Inter}$) as a function of the oxygen partial pressure in the reference gas ($P_{O_2}^{Ref}$). Results show that there is a linear relationship between the $P_{O_2}^{Inter}$ and the $P_{O_2}^{Ref}$ with a slope of unity. From the results of Fig. 4, the driving force of oxygen ion transfer is related to the initial difference of the oxygen potential between the anode and the cathode. With time, the oxygen concentration of the interface reaches a steady state and thus the driving force becomes smaller and the reaction rate slower.

In **Fig. 5**, the rate of oxygen ion transfer through the

Fig. 4. The terminal oxygen partial pressure at the Fe melt/ZrO₂ interface with different oxygen partial pressure of reference gas.

Fig. 5. The rate of oxygen ion transfer through the solid electrolyte (k^{Ion}) and the rate of soluble oxygen diffusion through the boundary layer (k^{Diff}) with interfacial oxygen concentration.

solid electrolyte and the rate of soluble oxygen diffusion through the boundary layer as a function of the interfacial oxygen concentration. These rates can be deduced from previous work by Iwase *et al.*⁸⁾ and the experimental data obtained in this study. Iwase *et al.*⁸⁾ demonstrated that the rate of oxygen removal by an electrochemical reaction and the rate of oxygen supply to the interface by diffusion can be expressed by the following,

$$-\frac{dN(O^{2-})}{dt} = -\bar{A} \frac{\sigma_{ion} RT}{2F^2 L} \times \left[\ln \left\{ 1 + \left(\frac{P_{\theta}}{P_{O_2}^{Inter}} \right)^{1/4} \right\} - \ln \left\{ 1 + \left(\frac{P_{\theta}}{P_{O_2}^{Ref}} \right)^{1/4} \right\} \right] \dots \dots \dots (4)$$

where σ_{ion} is the ionic conductivity of solid electrolyte ($\Omega^{-1} \text{cm}^{-1}$), $\bar{A}$ is the mean area (cm^2), L is the thickness of solid electrolyte (cm), P_{θ} is the oxygen partial pressure at which the ionic conductivity is equal to the n -type electronic conductivity. More details of P_{θ} has been provided by Iwase *et al.*⁸⁾ in the expression for the transfer number of ions (t_{ion}).

$$t_{ion} = \frac{P_{\theta}^{-1/4}}{P_{\theta}^{-1/4} + P_{O_2}^{-1/4}} \dots \dots \dots (5)$$

According to Iwase's work transfer number of ions was expected above 0.95 at the minimum $P_{O_2} = 7.6 \times 10^{-12}$ atm for the present study. At the condition of higher $P_{O_2} = 2.7 \times 10^{-8}$ atm, t_{ion} was to be closed to approximately unity thus the solid electrolyte could be regarded as an ionic conductor. Furthermore, the present work incorporated a short-circuit in the electrochemical cell using an external lead wire. And the oxygen transfer did not depend on the residual electronic conductivity in the stabilized zirconia solid electrolyte^{9,10)} which was previously explained. Therefore, in this study, the t_{ion} of the cell was to be closed unity and the addition of the external short-circuit should allow the current cell to behaves as a perfect ionic conductor and Eq. (4) could be modified with Eqs. (1) and (2) as below,

$$\begin{aligned} -\frac{dN(O^{2-})}{dt} &= -\bar{A} \frac{\sigma_{ion} E^{cell}}{2FL} = -\bar{A} \frac{\sigma_{ion}}{2FL} \frac{RT}{4F} \ln \frac{P_{O_2}^{Inter}}{P_{O_2}^{Ref}} \\ &= -\bar{A} \frac{\sigma_{ion}}{2FL} \frac{RT}{4F} \ln \left(\frac{a_O}{K_1} \right) \\ &= -\bar{A} \frac{\sigma_{ion}}{2FL} \frac{RT}{4F} \ln \left\{ \frac{55.85[\%O]_i}{P_{O_2}^{Ref} K_1 (16 + 39.85[\%O]_i)} \right\} \equiv k^{Ion} \end{aligned} \dots \dots \dots (6)$$

where $[\%O]_i$ is the oxygen concentration at the interface (wt%), K_1 is the equilibrium constant of Eq. (1), k^{Ion} was defined as the rate of oxygen ion transfer at the interface (mol/s). According to Eq. (6), the oxygen ion transfer is directly proportional to the cell potential as function of $[\%O]_i$

and other terms in Eq. (6) are fixed value at each experimental conditions in present study. A decrease in the cell potential results in a lower rate of oxygen ion transfer. The rate of soluble oxygen transfer through a boundary layer (k^{Diff} , mol/s) was defined by Eq. (7).

$$\frac{dN(\text{O})}{dt} = \frac{\alpha_{\text{O}}^{\text{Fe}} \rho}{1600} \{ [\% \text{O}]_{\text{b}} - [\% \text{O}]_{\text{i}} \} \equiv k^{\text{Diff}} \quad \text{.....(7)}$$

where $\alpha_{\text{O}}^{\text{Fe}}$ is the mass transfer coefficient ($(1.6 \pm 0.4) \times 10^{-4}$ cm/s),⁸⁾ ρ is the density of melt (g/cm³), $[\% \text{O}]_{\text{b}}$ is the oxygen concentration in bulk (wt%). In Eq. (7), the driving force of soluble oxygen diffusion from the bulk molten Fe is the difference in oxygen concentration between the bulk and the interface. And since the soluble bulk oxygen is constant, the driving force for the diffusion across the boundary layer is dependent on the soluble oxygen concentration at the interface.

In Fig. 5, the solid bold line is the diffusive rate of soluble oxygen transfer through the boundary layer as a function of $[\% \text{O}]_{\text{i}}$ according to Eq. (7). Other lines are the calculated rate of oxygen ion transfer according to Eq. (6) at different oxygen partial pressures in the reference gas. The intersections between the solid bold line and the other lines are marked with a solid square symbol. This intersection symbolizes the oxygen concentration balance between the rate of soluble oxygen diffusion and the rate of oxygen ion transfer and the subsequent attainment of steady state. Comparison of the oxygen concentration of the intersection agrees well with experimental measurements at steady state in the previous Fig. 3 and is given in Table 2.

3.2. Dependence of Oxygen Concentration at the Interface on the External Electric Potential

There are two driving forces for electrochemical reactions using a solid electrolyte. One deals with chemical potential through the control of oxygen partial pressure as previously described and the other deals with an external electric potential which will be discussed in the following section. Similar to Fisher *et al.*,⁵⁾ a direct current (DC) electric potential was applied as shown in Fig. 2. The effect of an applied electric potential on the oxygen concentration at the interface is shown in Fig. 6. This oxygen concentration could be deduced from a modified Nernst equation given below⁸⁾

$$E^{\text{ex}} - I^{\text{ion}} R^{\text{ion}} = E^{\text{cell}} = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}^{\text{Inter}}}{P_{\text{O}_2}^{\text{Ref}}} \quad \text{.....(8)}$$

where E^{ex} is an external electric potential (V), I^{ion} is the ionic current (A), and R^{ion} is the ionic resistance (Ω) in the electrochemical cell.

The external electric potential was applied at t_0 in Fig. 6. The applied voltage at each of the five regions is given in Table 3. When the external electric potential of 0.30 V is applied in Region II, the oxygen concentration at the Fe melt/ZrO₂ interface changed from 1410 ppm (the steady state oxygen concentration equilibrated with $P_{\text{O}_2}^{\text{Ref}} = 3.0 \times 10^{-9}$ atm) to 11 ppm within 0.5 s and maintained at 11 ppm. An increase of the external voltage to 0.36 V further drops

Table 2. Comparison of the interface oxygen concentration at steady state between the experimental results and the calculated values.

	NEV-P8	NEV-P9	NEV-P10	NEV-P11	NEV-P12
Experimental (ppm)	2730	1500	250	120	22
Intersection (ppm)	2324	1433	319	106	28

Fig. 6. The interfacial oxygen concentration change with external electrical potential (DC voltage) applying and critical oxygen concentration at the interface.

Table 3. Applied voltage to control the interfacial oxygen concentration shown in Fig. 5.

	Region I	Region II	Region III	Region IV	Region V
Applied External Voltage	0.00	0.30	0.36	0.42	0.46-0.58

the oxygen concentration to approximately 6 ppm and maintained at 6 ppm until the next change in applied voltage. The results indicate that the change in oxygen concentration at the interface is rapid unlike the slow response of the bulk measurements carried out by the sampling on periodically⁸⁾ or by the calculation of the oxygen flux from the cell current.^{9,10)} Thus, although the control of the bulk oxygen concentration is difficult, the control of the interface oxygen concentration is likely to be possible. Further stepwise changes in the applied external potential resulted in a stepwise decrease of oxygen concentration at the Fe melt/ZrO₂ interface until a critical value of $C_{\text{O}}^{\text{Cr}} \leq 3$ ppm. This critical oxygen content will be discussed in detail later.

The dependence of the oxygen partial pressure at the interface as a function of external EMF is shown in Fig. 7. The slopes of the individual experiments indicate a slope of approximately -11.05 . This is consistent with the slope calculated from the modified Nernst equation, Eq. (8). In addition, each individual experiment conducted with a constant electric potential showed varying degrees in the critical cell potential, but the critical oxygen concentration were identical.

Fig. 7. The change of interfacial oxygen partial pressure caused by external electrical potential applying.

3.3. The Oxygen Depleted Layer at the Fe Melt/ZrO₂ Interface and the Oxygen Profile Layer of the Boundary Layer

In Fig. 6 and Fig. 7, a critical oxygen content was observed when an external electric potential for 0.3 to 0.58 V was applied. Fischer *et al.*⁵⁾ showed the external voltage needed for decomposition of ZrO₂ at 1873 K was 7.5 V. Since the maximum applied electric potential for this study was 0.58 V, it was much lower than the 7.5 V limit and was expected to have negligible effects on the breakdown of the solid electrolyte. Visual observations of the interface using the Electron Probe Microscopic Analyzer (EPMA) also confirmed the stability of the interface. Results of the line scanning EPMA is shown in Fig. 8. No zirconium was detected in the Fe melt and no blackening phenomena¹³⁾ was observed in the ZrO₂.

The exact reason for the above-mentioned critical value of the oxygen concentration at the interface was not clearly understood yet. But the depletion of the reactant at the interface may play a role in determining this critical oxygen content. Once an external electric potential was supplied, differences in the k^{lon} and k^{Diff} occurred, which accelerated the transfer of oxygen ions. Thus, the oxygen concentration at the interface was rapidly reduced, but will not drop beyond the critical oxygen content due to the depletion of oxygen.

The oxygen concentration profile in the boundary layer with respect to the distance from the interface is shown in Fig. 9 using the Glow Discharge Spectrometer (GDS). The results were compared with solution of the Fick's 2nd law using initial and boundary conditions given below,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{for } x, t \geq 0 \quad \dots\dots\dots(9)$$

$$C(x, t) = \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad \dots\dots\dots(10)$$

$$\text{Initial condition: } C(x, 0) = 150 \text{ ppm for } x \geq 0 \quad \dots\dots\dots(11)$$

Fig. 8. The image of SEM and the result of line scan by EMPA.

Fig. 9. The oxygen concentration profile with a distance from the interface analyzed by GDS and the calculated result of Fick's 2nd law of diffusion.

$$\text{Boundary condition: } C(\infty, t) = 150 \text{ ppm, } C(0, t) = 2.24 \text{ ppm} \quad \dots\dots\dots(12)$$

The interfacial oxygen concentration was approximately below 3.0 ppm, the oxygen concentration in the bulk was set at 150 ppm, t was set to 60 s (setting time for cooling in the furnace from 1823 to 1773 K), the diffusion coefficient D was $D = 1.56 \times 10^{-1} \text{ cm}^2/\text{s}$ ¹⁷⁾ and the thickness of the boundary layer was 400 μm based on the GDS analysis.

The results of the GDS analysis are in good correspondence with the error function solution of the Fick's 2nd law. This seems to support the assumption of deficiency in oxygen reactants as the limiting factor for achieving a critical oxygen concentration at the interface although higher external electric potential applying.

Furthermore, The Tafel relationship¹⁵⁾ can be used to identify the mass transfer limitation to the electrode kinetics when an external potential is supplied. As it is well known, the Tafel plot shows the rate determining step of oxygen diffusion and its effect on the electrochemical deox-

Fig. 10. The Tafel plot of this study to identify a mass transfer effect to the electrode kinetics.

idation rate with the molten Fe cathode. The Tafel equation for a large over potential (η) is given below.

$$\eta = \frac{RT}{\alpha nF} \ln i_0 - \frac{RT}{\alpha nF} \ln i \dots\dots\dots(13)$$

where η is the over potential (V), i_0 is the exchange current density (A/cm²), i is the current density (A/cm²), and α is the transfer coefficient. A typical result of Tafel plot for experimental data of present study was shown in Fig. 10. In the Tafel region from 0.18 to 0.32 V, the current density increased linearly with the over potential. This suggests that a reversible reaction occurs without mass transfer. However, above 0.32 V external electric potential the slope of the Tafel plot become non-linear, which suggests the start point of a mass transfer limited current.¹²⁾ Further increases in the over potential will result in a limit to the current density, which implies that above a certain external potential the rate of deoxidation will converge to a critical value reached at 0.52 V in present study. Therefore, it seems reasonable that a critical oxygen concentration exists at the interface and higher values in external potential will have limited effect.

In another perspective, due to the change in the concentration of surfactive oxygen at the interface, the interfacial tension may have been significantly modified with the electrochemical deoxidation. According to Jimbo *et al.*,²⁾ the surface tension of molten steel varies with small amount of oxygen at 1823 K and can be expressed as Eq. (14),

$$1950 - \sigma = 291 \ln[1 + 130a_{O_2}] \text{ mN/m} \dots\dots\dots(14)$$

where σ is the surface tension and a_{O_2} is the activity of oxygen in molten steel. In present study, the interfacial tension of molten steel seems to be 1318 mN/m before the electrochemical deoxidation which was calculated value from Eq. (14) with an initial oxygen concentration of 150 ppm. After electrochemical deoxidation, it could be increased to 1879 mN/m with decreasing oxygen concentration at the interface to approximately 2.2 ppm according to Eq. (14). Thus, the electrochemical deoxidation at the interface can

be used to control the interfacial tension of molten Fe. Furthermore, Shibata *et al.*¹⁶⁾ demonstrated that the engulfment of an inclusion into an advancing solid/liquid interface during solidification is determined by a force balance. Two of these forces correspond to the interfacial tension of molten steel with solid inclusion. It can thus be inferred that inclusions move due to the existence of a gradient in interface tension and the direction of movement is toward the lower value. As a result of the present study, the interfacial tension can be increased when an external electric potential is applied to deoxidize the interface as mentioned above. Therefore, a high interfacial tension layer at the interface may inhibit inclusion attachment onto the interface between molten steel and a refractory.

4. Summary

In this study, the oxygen concentration at the interface could be controlled using an electrochemical potential method. The interfacial oxygen concentration could be controlled with variations in the oxygen partial pressure difference within the electrochemical cell. The transfer of oxygen ions through the solid electrolyte was spontaneous and reversible. Using an external EMF, the local interfacial oxygen concentration could be controlled below 3 ppm. This critical oxygen concentration was related to the local depletion of soluble oxygen at the interface and visually confirmed using GDS.

Acknowledgments

The authors would like to express their thanks to Ph. D. J. M. Park and O. D. Kwon, POSCO technical laboratory. This study was supported by POSCO and the Brain Korea 21 (BK21) Project the Division of the Humantronics Information Materials. In addition, the authors gratefully acknowledge Prof. I. Sohn at Yonsei University and Prof. J. H. Lee at Korea University.

REFERENCES

- 1) S. M. Han, J. H. Park, S. M. Jung, J. H. Park and D. J. Min: *ISIJ Int.*, **49** (2009), 487.
- 2) I. Jimbo and A. W. Cramb: *ISIJ Int.*, **32** (1992), 26.
- 3) G. R. Belton: *Metall. Trans. B*, **24B** (1993), 241.
- 4) B. J. Keene, K. C. Mills, J. W. Bryant and E. D. Hondros: *Can. Metall. Q.*, **21** (1982).
- 5) W. A. Fisher and D. Janke: *Scr. Metall.*, **6** (1972), 923.
- 6) K. E. Oberg, L. M. Freidman, W. M. Boorstein and R. A. Rapp: *Metall. Trans. B*, **4B** (1973), 61.
- 7) R. R. Odle and R. A. Rapp: *Metall. Trans. B*, **8B** (1976), 581.
- 8) M. Iwase, M. Tanida, A. Mclean and T. Mori: *Metall. Trans. B*, **12B** (1981), 517.
- 9) Z. Hasham, U. Pal and K. C. Chou: *J. Electrochem. Soc.*, **142** (1995), 469.
- 10) S. Yuan, U. B. Pal and K. C. Chou: *J. Am. Ceram. Soc.*, **79** (1996), No. 3, 641.
- 11) B. Deo and R. Boom: *Fundamentals of Steelmaking Metallurgy*, Prentice Hall International, Hertfordshire, (1993), 52.
- 12) A. J. Bard and L. R. Faulker: *Electrochemical Methods*, John Wiley & Sons, New York, (1980), 105.
- 13) J. Janek and C. Korte: *Solid State Ionics*, **116** (1999), 181.
- 14) M. H. Song, S. M. Han, G. S. Choi, D. J. Min and J. H. Park: *Metall. Trans. A*, **40A** (2009), 495.
- 15) J. Tafel: *Z. Physik. Chem.*, **50A** (1905), 641.
- 16) H. Shibata, H. B. Yin, S. Yoshinaga, T. Emi and M. Suzuki: *ISIJ Int.*, **38** (1998), 149.
- 17) K. Suzuki and T. Mori: *Tetsu-To-Hagane*, **57** (1971), 2291.