A Phenomenological Investigation on the Control of Oxides at the Interface Using an Electrochemical Cell

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An electrochemical reaction cell using a solid electrolyte was developed to study the thermodynamic and kinetic behavior of interfacial oxides. Al₂O₃ and TiO₂ existing between the Fe alloy melt and the magnesia stabilized zirconia solid electrolyte could be controlled using an electrochemical method of an external direct current at 1823 K. This novel approach could control the electron density near the interface of the oxides and subsequently the interfacial oxygen.

In this study, a direct current of 0.1 ampere resulted in the decomposition of the interfacial oxides and an interfacial oxygen concentration below 3 ppm. Furthermore, morphological observations using EPMA confirmed the interfacial oxide control corresponding to the external electrical potential.

KEY WORDS: interfaces; oxide decomposition; solid electrolyte; electron density; interfacial oxygen.

1. Introduction

Since the pioneering work of Kiukkola et al. on the concept of galvanic cells with solid electrolytes at high temperatures, the fundamental concept of electrochemical reactions through a solid electrolyte have seen many applications including high temperature concentration sensors, electrochemical membranes for solid oxide fuel cell, and electrochemical extractive metallurgy. In particular, stabilized zirconia has received much focus due to its selective permeability of oxygen ions and possible application to electrochemical deoxidation in high temperature extractive metallurgy. Past work on electrochemical deoxidation was controlled on the bulk oxygen concentration change of the molten metal in the bulk and showed the deoxidation rate to be limited by the slow diffusion of oxygen.

However, in a recently published work elsewhere by the present author, the interfacial oxygen concentration between molten Fe and ZrO₂ based solid electrolyte could be controlled using an externally applied DC voltage. An interface oxygen concentration of below 3 ppm could be obtained without significant changes in the bulk oxygen concentration. Some similarities have been observed in the work by Wagner et al. where a solid electrolyte cell of Ni|ZrO₂/9.5 mol% Y₂O₃ (YSZ)|Ni at 1200 K allowed oxygen ion transfer when an external direct current of 0.04 A/cm² was applied. The resulting flux of oxygen ions resulted in the formation of NiO at the Ni|YSZ anode interface. Although the fundamental formation mechanism of oxides using an oxygen ion transfer corresponds with that in the present work, significant differences in the methodology of oxide formation and subsequent decomposition exists. The NiO formation in Wagner’s work was a result of an applied external current and the oxides observed in the present study was a result of the oxygen potential difference from the CO/CO₂ gas mixture equilibrium at the anode. Following the oxide formation, an applied external current was used to decompose the oxides from the oxygen potential gradient at the interface. In addition, the present work on oxide control was done at high temperatures in the molten state unlike the solid state diffusion observed on Wagner’s work.

Recent studies on the interfacial behavior of oxygen in molten steel indicated a decrease in the surface tension of molten steel even at low concentrations in the bulk because of the segregation at the interface. This can be expressed by the thermodynamic relation given by Eq. (1).

\[ \sigma = 1890 - 247[0.5 \ln(1 + 300a_{O}) + 0.5 \ln(1 + 100a_{O})] \ (mN/m) \]

where \( \sigma \) is the surface tension (mN/m) and \( a_{O} \) is the activity of oxygen in molten steel within the Henrian region.

The lower interfacial tension of molten steel due to surface active oxygen can increase the wettability between molten steel and the refractory, and ultimately facilitate the adhesion of oxide inclusions at the interface. Thus, inhibiting the agglomeration of oxide particles at the molten steel/refractory interface is essential in increasing downstream product quality. Furthermore, oxygen in molten steel can readily react with deoxidizing alloying elements forming oxides of Al₂O₃, SiO₂, and TiO₂, which can further interact with the refractory materials.

As mentioned above, surface active oxygen can locally concentrate at the interface and play a major role to form interfacial oxides. It is well known that oxide formation...
occurs when oxygen concentration is above the thermodynamic equilibrium value. However, recent work by Suito et al. suggest the existence of a super-saturation phenomenon required for aluminum oxide formation in molten steel at 1873 K and defined the ratio between the super-saturation concentration and the equilibrium concentration as the critical super-saturation ratio. Due to the necessity of an excess driving potential, aluminum oxide formation in the bulk Fe–Al–O alloy is somewhat difficult even though the bulk oxygen is above the thermodynamic equilibrium concentration. On the other hand, the surface active oxygen at the interface between the molten steel and the refractory can locally increase above the critical super-saturation ratio. In order to inhibit the formation and adhesion of oxide particles at the interface, several chemical and physical methods have been proposed, but the problem of interfacial oxide control has yet to be resolved.

Therefore, in the present study, a novel approach using an electrochemical potential cell in molten steel was implemented to elucidate and control the behavior of interfacial oxides.

### 2. Experimental

A schematic of the experimental apparatus is shown in Fig. 1. 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–M alloy (M = Al or Ti), 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 CaSO4 and a column of Mg 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, ZrO2 + 15%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 MSZ crucible and a solid electrolyte. The anode was the Pt paste layer on the inner side surface of MSZ crucible and the cathode was the molten steel in contact with the MSZ crucible as shown in Fig. 1. The MSZ crucible 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 CO2/CO (ratio of 1/50) into the solid electrolyte chamber, an inlet gas alumina lance (OD = 5 mm, ID = 2 mm, H = 1000 mm) was inserted within the outer alumina tube connected to the MSZ crucible. Using a mass flow controller (MFC), 150 cm3/min of CO2/CO reference gas was supplied into the solid electrolyte chamber. Excess moisture and CO2 from the CO supply gas were removed by passing the gas through a column of CaSO4 and soda lime.

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 and Table 2.

Previous researches on electrochemical cell reactions incorporated the methodologies of direct periodic melt samplings or cell current measurements to detect melt oxygen concentration in the bulk. Unlike the bulk periodic measurements, the cell potential (E_{cell}) of the present study is continuously measured for obtaining the oxygen concentration at the molten steel/MSZ interface (P_{O2}^{Int}) calculated by using Eqs. (2) and (3).

![Fig. 1. Scheme of the experimental apparatus.](image-url)
Where $F$ is the Faraday’s constant ($F = 96.487 \text{ C/mol}$), $E^{\text{ex}}$ is an external electric potential (V), $I^{\text{ion}}$ is the ionic current (A), $R^{\text{ion}}$ is the ionic resistance ($\Omega$) in the electrochemical cell, $P^{\text{Ref}}_{O_2}$ and $P^{\text{Inter}}_{O_2}$ are the partial pressures (atm) of oxygen in the reference gas and at the interface, respectively. The actual experiments measure $E^{\text{cell}}$, which is used to deduce $P^{\text{Inter}}_{O_2}$.

The oxygen partial pressure in the reference gas was controlled by passing a defined CO$_2$/CO gas volume ratio using the following reaction (4).26)

$$\text{CO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \quad \Delta G_T = -117300 - 2.9T \quad \text{(J/mol)}$$

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. To determine the equilibrium oxygen concentration at the interface of the electrochemical potential cell at 1823 K, the equilibrium dissolution reaction into the melt given below was used.27)

$$\frac{1}{2} \text{O}_2 = \text{O}_{(\text{Fe})} \quad \Delta G = -117300 - 2.9T \quad \text{(J/mol)}$$

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.

In the present study, two specific groups of experiments were described to study the behavior of the oxide inclusions at the interface with an external electric potential. The first group of experiments was done to observe the formation of oxide inclusion with the specific controlled oxygen potential. The second group of experiments, which applied an external DC voltage and direct current, were done to observe the decomposition of oxide inclusions at the interface. The detail of the experimental conditions for the first group is given in Table 1. In order to control the oxygen concentration for the first group of experiments, an external DC voltage is continuously applied during the experiment before submerging the cell into the molten steel.

For the second group of experiments to observe the decomposition of oxide inclusions, two sets of experiments (set 2, 3) were performed and the details of the experimental conditions are given in Table 2. The first experiment (Exp 2-1) in set 2 is done in the absence of external electric potential. The second experiment (Exp 2-2) in set 2 is done under an external direct current (DC) voltage after 2500 s. The third experiment (Exp 2-3) in set 2 is done under an external direct current after 2500 s. The experiments of set 3 follow the same procedure.

After the experiment, the oxide inclusions at the interface were identified using the Electro Probe Microscope Analyzer (EPMA, JEOL JXA8100). The compositions of the Fe–M alloys were determined using Optical Emissive Spectrometer (OES, LAB-S) before and after the experiment.

### 3. Results and Discussion

The dependence of the oxygen concentration as a function of aluminum concentration in the Fe alloy is shown in Fig. 2. The oxygen partial pressure at the anode (reference gas/Pt paste) can be controlled according to Eq. (3) by passing the reference gas of CO$_2$/CO continuously through the MSZ solid electrolyte crucible. The oxygen partial pressure at the interface between molten Fe alloy and MSZ is controlled by an external electric potential as previously dis-
cussed in detail elsewhere. In Fig. 2, the dash lines are the critical super-saturation line by Suito et al. using an EMF method and the equilibrium line between aluminum and oxygen determined by previous researchers. The reaction of aluminum oxide ($\text{Al}_2\text{O}_3$) was expressed as follow.

\[
\text{Al}_2\text{O}_3(s) = 2\text{Al}(l) + \frac{3}{2} \text{O}_2(g),
\]

\[
\Delta G^\circ = 1687 \, 240 - 326.87 \, (\text{J/mol}) \quad ...........(6)
\]

The super-saturation ratio of $\text{Al}_2\text{O}_3$ ($S_{\text{Al}_2\text{O}_3}$) in Suito’s result expressed as \( \left( \frac{a^{2l}_{\text{Al}} \cdot a_{\text{O}}^{3}}{a_{\text{Al}}^{2l} \cdot a_{\text{O}}^{3}} \right)^{\text{ss}} \) indicated a critical super-saturation (\( \log S_{\text{Al}_2\text{O}_3}^\circ \)) value of 3.5 in Fig. 2. When the oxygen concentration at the interface is below the equilibrium value for a specific aluminum concentration as in region III (Fig. 2(d)), the aluminum oxide cannot be formed at the interface due to thermodynamic constraints. Some aluminum oxide particles did line up at a virtually single point on the interface toward the Fe alloy, which will be discussed later in detail. When the oxygen concentration at the interface is higher than the equilibrium value as in region II, the $S_{\text{Al}_2\text{O}_3}$ is higher than unity, but lower than the critical value (\( \log S_{\text{Al}_2\text{O}_3}^\circ = 3.5 \)). A small amount of aluminum oxide did precipitate at the interface as shown in Fig. 2(b) and 2(c). Higher oxygen concentration at the interface above the critical super-saturation ratio as in region I accelerate the oxidation of aluminum in molten Fe alloys. Through an electrochemical method, the oxygen concentration and formation of oxide at the interface between molten steel and ZrO$_2$ solid electrolyte could be controlled.

The rope shape attachments at the interface as shown in Fig. 2(d) were verified to be minute particles of Al$_2$O$_3$. These particles were lined up from a single point as shown in Fig. 3. The direct cause of adhesion at that particular point has yet to be determined, but may be related to the lowering of the surface energy at the interface by long-range and capillary attraction between particles as discussed by Shibata et al. regarding Al$_2$O$_3$ agglomeration. Moreover, considering the interface between Fe alloy and MSZ, oxygen concentration is lower than the Fe alloy bulk due to electrochemical deoxidation and thus the corresponding surface tension is higher at the interface than the bulk as indicated by Eq. (1).

Thus, adhesion of oxide particles on a bare surface with high surface energy of the interface may be difficult, but adhesion on existing adhered particles maybe easier to attach onto. Further work should be done to determine this point adhesion on the bare surface of the interface.

**Figure 4** shows the results of the electrochemical reactions to control the oxygen concentration at the interface for the Fe–[0.039wt%Al] melt. The detailed composition of the Fe alloy is given in Table 3. Due to the gradient of oxygen partial pressure between the anode and the cathode, oxygen ions transfer through the solid electrolyte toward the lower oxygen partial pressure. The oxygen concentration at the interface increases with time up to the expected equilibrium oxygen concentration at 1823 K. The expected equilibrium oxygen concentration can be calculated from the measured cell potential, which was 0.03 V. From the measured cell potential and incorporating Eqs. (3) and (5), the expected equilibrium oxygen concentration was 190 ppm. There are three distinct lines depending upon the applied external DC voltage and a direct current. Line (a) is a result of no external electric potential and direct current, line (b) shows the result of an applied DC voltage of 0.52 V after 2500 s, and line (c) shows the result of an applied direct current of 0.1 A after 2500 s. From the measurements of the cell potential, the oxygen concentration could be determined; details of which have been provided elsewhere.
When an external DC voltage is applied, no apparent change in the oxygen concentration at the interface is observed (line b). However, application of an external direct current results in a significant decrease in the oxygen concentration at the interface (line c) below 3 ppm.

Using the oxygen partial pressure in the reference gas ($P_{\text{O}_2}^{\text{Ref}} = 3.06 \times 10^{-11} \text{ atm}$) and Eq. (5), the equilibrium oxygen concentration at the interface was estimated to be $C_{\text{O}}^{\text{Inter}} = 194$ ppm between the Fe alloy and the ZrO$_2$. Since the minimum value for stable aluminum oxide formation with the specific Fe alloy melt is well below 194 ppm, it is likely that the formation of aluminum oxide at the interface is thermodynamically favorable. The optical interfacial state after 2500 s was also visually verified to have an oxide layer.

Without an external electric potential, the oxide inclusions formed due to the increase in the interfacial oxygen concentration, which was also confirmed through EPMA analysis as shown in Fig. 5(a). Al$_2$O$_3$ layer is clearly observed at the interface. MgO is also observed in the interface, which likely originated from the Mg in MSZ considering Mg is not present in the Fe alloy given in Table 2. When an external voltage is applied after 2500 s, as shown in Fig. 4 line (b) the oxygen concentration at the interface, which was 180 ppm, is relatively unaffected. The corresponding morphological observation could be obtained in Fig. 5(b). Al$_2$O$_3$ clusters still exist, but the MgO clusters seem to have been decomposed. The direct cause of this selective decomposition has yet to be fully understood and will need further study. With the application of an external direct current ($I_{\text{ex}}$) of 0.1 A after 2500 s, the interfacial oxygen concentration decreases from 194 ppm to approximately 3 ppm as shown in Fig. 4 line (c). The morphology of the interface verified the absence of an oxide layer between the Fe alloy and the MSZ shown in Fig. 5(c). The lower oxygen concentration at the interface and the absence of an oxide layer suggests the decomposition of the oxide after the external direct current was applied.

Both the measured cell potential and the interface oxygen concentration are plotted in Fig. 6 as a function of the applied external direct current. The oxygen concentration at the interface decreased with external direct current. When an external direct current lower than 0.075 A is applied, the oxygen concentration at the interface could not drop below the thermodynamic equilibrium oxygen concentration of the Al$_2$O$_3$/Al reaction at aluminum concentration of 393 ppm. With direct current higher than 0.075 A, interfacial oxygen concentration decreased to a level as low as 3 ppm shown in Fig. 6. To maintain a clean interface without oxide inclusions and also to decompose already exiting oxide inclusions, the oxygen concentration at the interface must be maintained below the thermodynamic equilibrium oxygen concentration dependent upon the specific deoxidizer such as Al or Ti. According to many previous researches, the maximum value of soluble oxygen con-
centration without oxide precipitation is below 6 ppm. Thus in the present work, the interfacial oxygen concentration of less than 3 ppm with an external direct current of 0.1 A should inhibit and decompose oxides.

Details of the decomposition mechanism of interfacial oxides under an external direct current are shown in Fig. 7. Before applying the direct current, the oxygen ion transfers from the anode to the cathode. At the interface, the deoxidizing element in the Fe–M melt reacts with the transferred oxygen ion expressed as Eq. (9) and the excess electrons evolved through Eq. (7) are transferred through the external short-circuit as shown in Fig. 7(a). The interfacial oxide formation can be expressed using the following ionic reactions.

\[
\begin{align*}
M \rightarrow M^{z+} + ze^- & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quad.
The supply of oxygen through the solid electrolyte results in TiO$_2$ and Al$_2$O$_3$ formation before the external electric potential is applied, which was also verified from the EPMA spot analysis and SEM micrograph in Fig. 9(a) and. Since the interfacial oxygen concentration, which migrated from the anode to the cathode, is higher than the equilibrium value, the Ti (368 ppm) and Al (45 ppm) in molten Fe reacts with the interfacial oxygen to form oxide at the interface between Fe alloy and ZrO$_2$ solid electrolyte. When significant amounts of inclusion are formed, the electrochemical reaction can be inhibited due to the coverage of oxide at the interface. Similar to the results with Al$_2$O$_3$, an external DC voltage did not affect the decomposition of TiO$_2$ formed at the interface as shown in Fig. 9(b). However, application of a direct current accelerated the decomposition of the oxide at the interface as shown in Fig. 9(c).

Furthermore, the approximate ionization energies of Mg, Al, and Ti for oxide formation are given in Table 4.$^{29,30}$ As can be seen, the values increase from MgO to Al$_2$O$_3$ suggesting that the dissolution sequence should be initiated with MgO followed by TiO$_2$ and Al$_2$O$_3$ which was verified from the morphological studies observed in Fig. 5 and Fig. 9.

4. Conclusion

In this study, the oxide inclusion at the interface between Fe alloy melt and MSZ solid electrolyte could be controlled by an electrochemical method. Using an external electrical potential, the excess electrons accumulated near the interface of the oxide inclusions resulting in the disturbance of the local electrical neutrality. In order to dissipate the excess electrons and ensure the electrical neutrality at the interface, the oxygen within the oxide was ionized with the excess electrons and subsequently removed from the interface between Fe alloy melt and MSZ by an electrochemical deoxidation.

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Table 4. Ionization energies for oxide formation.$^{29,30}$

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ionization energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deoxidizer</td>
<td>Oxygen</td>
</tr>
<tr>
<td>MgO</td>
<td>2188.4</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>8796.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>10277.2</td>
</tr>
</tbody>
</table>

Fig. 8. The interfacial oxygen concentration change with time. (a) No external V and I, (b) External Voltage applying, and (c) External Current applying.

Fig. 9. Ti oxide formation and decomposition at the interface and final oxygen concentration at the interface.
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