Galvanostatic Polarization Measurements on a Solid Platinum-Alkali Silicate Melts*

By Hideaki SUITO** and Masayasu OHTANI**

Synopsis

Galvanostatic polarization measurements have been made at 1350°C on a solid platinum-molten alkali silicate interface. The overpotential-time curves within 80 μ sec have been analyzed on the assumption that the virtual anodic reaction is the oxygen discharge reaction: $O^{2-} \rightleftharpoons O + 2e$. The exchange current density has been determined as a function of the M_2O/SiO_2 molar ratio ($M=Li, Na$ and K) and the oxygen partial pressure ($P_{O_2}=1, 0.21$ and 0.03 atm). It was found that the exchange current density increases with increasing the M_2O/SiO_2 molar ratio and the oxygen partial pressure. In view of the mass transfer process as the rate-controlling step, the overpotential has been studied by changing the experimental time range (1 msec, 10 msec, 100 msec, 1 sec and 5 sec $\sim$). At the constant M_2O/SiO_2 molar ratio, the slope in the overpotential-square root of time plots was shown to be inversely proportional to the square root of an oxygen pressure. It was also found that the solubility and the square root of the diffusivity product of soluble oxygen increases with the increase of the M_2O/SiO_2 molar ratio and increases in the order lithium, sodium, potassium silicate at the constant M_2O/SiO_2 molar ratio.

I. Introduction

Considering a molten slag as an electrolyte and a metal as an electrode, the slag-metal reaction is essentially electrochemical accompanying the charge transfer reaction. As one of the basic researches to clarify the mechanism for the slag-metal reaction, it is valuable to study the anodic polarization phenomena by means of the electrochemical transient method. Ghosh and King¹⁾ studied the anodic oxygen discharge reaction in lithium silicate melts at 1350°C and observed the evolution of oxygen bubbles on a Pt electrode at high current densities. The anodic polarization at Pt/silicate melts interface was also studied by the potentiostatic method.²⁾ In view of the mass transfer process, the relationship between the current and the inverse square root of time was examined by changing an oxygen pressure. Consequently, Kawakami and Goto²⁾ concluded that the rate of an electrode reaction is controlled by the diffusion of diatomic oxygen molecules dissolved in molten slag. Recently, Emi, *et al.*³⁾ measured the anodic polarization of a Pt electrode in the binary silicate and aluminate melts at 1200° to 1600°C under Ar or O₂ by the potential step method.

In the present work, the kinetics of the oxygen discharge reaction at a Pt/alkali silicate interface were investigated by the transient galvanostatic method. The overpotential-time curves for the different experimental time (100 μ sec $\sim$ 10 sec) were obtained as a function of the slag composition and the oxygen pressure. The results on the kinetic parameters obtained

from this work were compared with those of the previous potentiostatic method.^{2,3)}

II. Experimental

1. Apparatus and Procedure

Lithium, sodium and potassium silicates of M_2O/SiO_2 molar ratios, 3/2, 1, 2/3 and 1/2 were prepared by mixing stoichiometric amounts of A.R. grade alkali carbonate and silica and heating in a Pt crucible for 3 to 5 hr (until the evolution of gas bubbles from the melt ceased) in the temperature range 1300° to 1350°C. Prior to their use, the solidified silicates were stored in a desiccator. The experimental melt of about 75 g was contained in a Pt crucible (40 mm in dia., 40 mm in height). The crucible with melts was heated in a SiC resistance furnace which had a hot zone of 6 cm with a $\pm 2^\circ C$. The temperature was measured with a Pt-Pt/13%Rh thermocouple. The furnace atmosphere was oxygen, air and oxygen-argon gas mixture (3/100), flowing at 500 cm³/min, which had been dried over calcium chloride and silica gel. The schematic diagram of the cell assembly and the circuit is shown in Fig. 1. Three platinum wires (1 or 2 mm in dia.), used as the working electrode (WE), the reference electrode (RE) and the counter electrode (CE) were immersed

Fig. 1. Schematic diagram of the cell assembly and circuit

* Received May 18, 1976.

** Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Katahira, Sendai 980.

vertically by adjusting a precision screw vernier to within 0.5 mm mounted on the top of a reaction tube. After confirming the contact of the electrodes with the surface of the melt by the potentiometric electrometer, two of platinum electrodes were further dipped to 10 mm deep into the molten silicate. It was ensured by measuring emf between each electrodes that the oxygen potential gradient did not exist in the melt, *i.e.*, the equilibration between gas and liquid phase is attained. The emf between a Pt electrode on the surface and that of a 10 mm deep was found to become a constant value (below 5 mV for $P_{O_2}=0.03$ atm and below 3 mV for $P_{O_2}=1$ and 0.21 atm) within 2 to 5 hr, depending on the slag composition. After that, a Pt electrode on the surface was immersed to 10 mm deep and then emfs between two Pt electrodes at 10 mm deep were found to be within 3 mV. Between *CE* and *WE*, the constant current was applied to have the anodic polarization which was assumed to be the oxygen discharge reaction: $O^{2-} \rightleftharpoons O + 2e$. The potential-time curve between *RE* and *WE* was observed. In the experiments that the experimental time of the supplied current was from 100 μ sec to 1 sec, the electrical circuit consists of the function generator (0.01 Hz to 1 MHz: rise time 150 nsec) to supply the constant potential square pulse, the constant current generator and the triggering device to trigger the oscilloscope (20 MHz: rise time 17.5 nsec) for the potential measurement. Also used was the potential recorder to observe the emf between *RE* and *WE* during the experiment. In the experiments that the experimental time is more than 1 sec, it consists of the power source (0~35 mV) which supplied current to the cell through the variable resistance (0.1~100 k Ω), large enough so that the current in the circuit is independent of resistance changes occurring in the cell. The current is measured by the potentiometric voltmeter, which measures the potential drop across the standard resistance of 1 k Ω . Potential-time curves were measured by means of either the oscilloscope or the potential recorder (1 M Ω). The return to the initial potential between *RE* and *WE* which is less than 3 mV was found to be very rapid, after the constant current is cut off.

The top of a Pt wire (15 mm length) was replaced by a new Pt wire by welding after every measurements at the constant slag composition and the oxygen pressure. The accuracy in the depth of the immersion was also ascertain to within 0.5 mm by the change in surface shine of the wetted Pt wire. The overpotential which is the difference between the potential and IR drop was read by photographing the oscilloscope trace. IR drop in each run was determined by applying high currents of 10, 15 and 20 mA within 80 μ sec. Three different currents were chosen in each experimental condition so that the overpotential may not exceed to 30 to 40 mV. The measurement was made at 1350°C throughout the experiment.

2. Preliminary Experiment

The effect of the depth of immersion (5, 10, 15 and

20 mm), the size of a Pt anode (1, 2 and 5 mm in dia.) and the applied current on the potential-time relationship has been studied in the preliminary experiment. Hence, potential-time curves were shown to be corresponded to the current densities corrected for the geometric area of the wetted Pt anode. In addition, the effect of the applied current on the potential-time curve was also ignored. The accuracy of the geometric area of the wetted electrode increases with the increase of the depth of immersion, but the longer time is necessary in order to equilibrate the melt with the gas phase. Thus, in the present work, the depth of the electrodes was chosen as the 10 mm deep. The thicker diameter of a Pt electrode is preferable in order to solve the unsteady state diffusion equation under the condition of semi-infinite linear diffusion which will be discussed later in detail, but a Pt wire with the diameter of 1 and 2 mm was used in the present work. The results of the present preliminary experiments lead to the conclusion that the oxygen discharge reaction: $O^{2-} \rightleftharpoons 1/2O_2(g) + 2e$ at the three phase boundary (Pt-gas-slag) may be neglected.

III. Results and Discussion

1. Rate-controlling Process

When the constant current is applied to the system, the virtual charge transfer reaction at the Pt/silicate anode surface will presumably be given as follows:

where, O_{ad} denotes an adsorbed oxygen on the Pt surface. In case of the anodic polarization at low current densities, an oxygen may not diffuse into a solid platinum, but may be soluble in molten silicate melt by the following chemical reaction process:

where, (O) is the dissolved oxygen in melt. (The type of an oxygen dissolved will be described later in detail.) Oxygen ions O^{2-} and dissolved oxygen (O) transport to the anode surface and to the bulk, respectively by the mass transfer process. However, these processes described above will be different depending on the experimental conditions such as the current densities and the slag composition. That is, at high current densities discussed by Ghosh and King,¹⁾ the evolution of oxygen gas bubbles will be observed instead of Eq. (2).

Oxygen bubbles due to Eq. (3) react with a solid platinum and a passive oxide film is formed on the surface.¹⁾ Since the concentration of alkali silicate melts less basic than the orthosilicate composition, it is more likely to consider that free oxygen ions O^{2-} may be available near the anode surface by the following polymerization reaction such as:

In the present work, the potential-time relationships have been obtained from the polarization measurement at low current densities, *i.e.*, no evolution of an oxygen gas and no formation of an oxide film. For the cases of the charge transfer, the mass transfer and the mixed controlling processes, the kinetic parameters were derived from the analysis of the potential-time curves obtained.

1. The Charge Transfer Process

In early period of time when the constant current is applied, the mass transfer process is assumed to be ignored. Then, considering the charge of the electrical double layer capacity *C*, the overpotential η -time *t* relationship may be written:

$\eta = i_T R_f \{1 - \exp(-t/CR_f)\} \dots\dots\dots(5)$

where, *R_f* is the charge transfer reaction resistance and *i_T* is the current density. Substituting η_i (*i*=1, 2, 3) at *t_i* into Eq. (5), *R_f* may be derived from the solution of three simultaneous equations. *R_f* was obtained in the experimental time range of 80 μ sec for three different currents of 5, 10 and 15 mA. One of the results plotting *i_TR_f* against time *t* is given in Fig. 2. The derivation of *R_f* has been described in detail elsewhere.⁴⁾ The exchange current density *i_o* for the oxygen discharge reaction given by Eq. (1) is written:

$i_o = \frac{RT}{2F_1} \cdot \frac{1}{R_f} \dots\dots\dots(6)$

where, *R* is the gas constant and *F₁* is the Faraday constant (23 060 cal·v⁻¹·equivalent⁻¹). The results of *i_o* is listed in Table 1. It can be seen from Table 1 that the values of *i_o* increase with increasing the oxygen pressure and the M₂O/SiO₂ molar ratio. Furthermore, they increase in the order lithium, sodium and potassium silicates at the constant oxygen pressure and the slag composition. It is not apparent from the present work whether the dependence of *i_o* on the cationic species may be due to the change of

the rate constant of Eq. (1) in its standard state, or the change of the concentration of free oxygen ions O²⁻, and of soluble oxygen (O).

Emi, *et al.*³⁾ obtained *i_o* from the potential step measurement of the anodic polarization of a Pt electrode in sodium silicate melts. Our values of *i_o* are in good agreement with those of Emi, *et al.*

2. Mixed Controlling Step with the Charge Transfer and the Mass Transfer Processes

R_f obtained in III.1.1 was almost independent of the experimental time within 80 μ sec, but it was found that the mass transfer process is operative as the time increases, *i.e.*, *R_f* changes with time. When both the charge transfer and the mass transfer processes are assumed to be the rate-controlling step, the relationship between the overpotential and the current density can be expressed as follows:⁵⁾

$i_T = i_o \left\{ \frac{C_{O^{2-}}}{C_{O^{2-}}} \exp\left(\frac{2\alpha F_1 \eta}{RT}\right) - \frac{C_O}{C_O} \exp\left(\frac{-2(1-\alpha) F_1 \eta}{RT}\right) \right\} \dots\dots\dots(7)$

where, α : the transfer coefficient
 $C_{O^{2-}}$ and C_O : the concentration of O²⁻ (g-ion/cm³) and (O) (g-atom/cm³) at the electrode interface, respectively
 $C_{O^{2-}}$ and C_O : the concentration of O²⁻ (g-ion/cm³) and (O) (g-atom/cm³) in the bulk, respectively.

Equation (7) is derived on the assumption that the concentration of O²⁻ and (O) is dilute, *i.e.*, the activity of O²⁻ and (O) is equal to the concentration of O²⁻ and (O), respectively. The migration of oxygen ions (or silicate anions) under an electric field may be neglected, since the transport number of alkali cation was unity in alkali silicate melts. The concentration of O²⁻ and (O) at the electrode interface can be obtained from the solution of Fick's second law, assuming that the diffusion of O²⁻ and (O) in molten silicate is the semi-infinite linear diffusion. Then, $C_{O^{2-}}$ and C_O are given as follows under the approximate conditions described in Appendix (A):

$C_{O^{2-}} = C_{O^{2-}} - \frac{i \sqrt{t}}{F_2 \sqrt{\pi} \sqrt{D_{O^{2-}}}} \dots\dots\dots(8)$

Table 1. Exchange current density *i_o* (mA/cm²)

	<i>P_{O₂}</i> (atm)	3/2	1/1	2/3	1/2
Li ₂ O/SiO ₂	1	185	180	160	135
	0.21	150	150	120	130
	0.03	130	120	105	110
Na ₂ O/SiO ₂	1	505	240	170	135
	0.21	310	200	140	155
	0.03	230	145	135	125
K ₂ O/SiO ₂	1	—	290	240	230
	0.21	—	290	225	230
	0.03	—	155	140	150

Fig. 2. Plot of *i_TR_f* against time *t* (Pt electrode 1 mmφ)

$$^{\circ}C_0 = C_0 + \frac{i\sqrt{t}}{F_2\sqrt{\pi}\sqrt{D_0}} \quad \dots\dots\dots(9)$$

where, F_2 : the Faraday constant (96 487 coulomb/mol)
 D_0 and $D_{O^{2-}}$: the diffusivity of (O) and O^{2-} , respectively.

These diffusivities imply the interdiffusivities given by the notations $D_{O-(M_2O-SiO_2)}$ and $D_{M_2O-SiO_2}$, respectively. If, however, the concentration of (O) and O^{2-} is dilute, these interdiffusivities are identical to the tracer diffusivities. By substituting Eqs. (8) and (9) into Eq. (7), one can write

$$\eta = \frac{RT}{2F_1} \left\{ \frac{i}{i_0} + \frac{im\sqrt{t}}{F_2\sqrt{\pi}} \right\} \quad \dots\dots\dots(10)$$

where,

$$m = 1/C_0\sqrt{D_0} + 1/C_{O^{2-}}\sqrt{D_{O^{2-}}}$$

with the approximate conditions

$$\frac{2\alpha F_1 \eta}{RT} \ll 1, \quad \frac{i\sqrt{t}}{F_2\sqrt{\pi}C_0\sqrt{D_0}} \ll 1, \quad \frac{i\sqrt{t}}{F_2C_{O^{2-}}\sqrt{D_{O^{2-}}}} \ll 1$$

Equation (10) indicates that m and i_0 can be obtained from the slope and the intersect in the $\eta-t^{1/2}$ plot, respectively, if the experimental conditions satisfy the approximate conditions of Eq. (10) and Eqs. (A-6) and (A-7) in Appendix (A). But, actually, the $\eta-t^{1/2}$ plot shows the convex downwards curve at the time range of 1 msec. Although the linear relationship was obtained at the time range of 10 msec, some values of i_0 calculated from the intersect at $t=0$ were shown to be small negative. This may be due to the fact that the double layer charging current still flows within 10 msec. Emi, *et al.*³⁾ reported that the diffusive mass transfer process becomes predominant after 100 msec (in many cases 10 msec). Their observation is in good agreement with that of the present study.

Figure 3 illustrates one of the experimental results plotting the overpotential against the square root of time. One may see from Fig. 3 that the intersect of the line A (time range of 10 msec) at $t=0$ is slightly negative, but the intersects of the lines B and C (time range of 100 msec) are both positive. The value of i_0 determined from Eq. (6) was found to be approximately in accord with that obtained from these intersects. Therefore, the approximate conditions would be satisfied in the measurement of 100 msec. However, the determination of i_0 by Eq. (10) is not adequate in this work, since the intersect at $t=0$ obtained by the extrapolation was not accurate enough to calculate the i_0 value.

3. The Mass Transfer Process

The rate of the electrode reaction is regarded as limited by only the mass transfer process after a period of time when the double layer capacity is completely charged. Then, the overpotential is expressed as a function of time, (see Appendix (B))

$$\eta = \frac{RTi\sqrt{t}m'}{2F_1F_2\sqrt{\pi}} \quad \dots\dots\dots(11)$$

$$m' = 1/C_0\sqrt{D_0} + 1/C_{M_2O}\sqrt{D_{M_2O-SiO_2}}$$

Comparison of Eqs. (10) and (11) indicates that the slope in $\eta-t^{1/2}$ plot is identical when C_{M_2O} is equal to $C_{O^{2-}}$. This will be discussed in detail later. With the increase of the experimental time, it is expected that the actual diffusion process would be deviated from the linear diffusion. This limitation of the experimental time is particularly dependent of the diameter of a Pt anode. Since a Pt electrode with 1 and 2 mm ϕ was used in the present work, the experimental time should be chosen as less than about one second in order to have the linear relationship in $\eta-t^{1/2}$ plot. (see Appendix (C))

Figure 4 shows one of the results on $\eta-t^{1/2}$ plot for the time range from 1 to 15 sec. In Fig. 5, the slopes in $\eta-t^{1/2}$ plot for three different current densities are plotted against the logarithm of the time range of measurement. As shown in Fig. 5, the slopes obtained are considered to be almost independent of the time range of measurement from 10 msec to 1 sec, but one may see that the slopes decrease significantly after one second. The slopes were not obtained after 5 sec because of the nonlinearity of the $\eta-t^{1/2}$ plot as shown in Fig. 4. This nonlinearity may also be explained by the effect of the natural convection, but it is more likely interpreted in the present experiment by the deviation from the semi-infinite linear diffusion as explained by Appendix (C). The $\eta-t^{1/2}$ plot for the measurement of 1 and 4 sec as shown in Fig. 4 apparently shows the linearity, but the values of i_0 calculated from the intersects of these two lines are not in agreement with i_0 from Eq. (6). This is due to the effect of the deviation from the linear diffusion. In

- A: $K_2O \cdot 2SiO_2$, $P_{O_2}=1$ atm, 6.07 mA/cm²
- B: $3Li_2O \cdot 2SiO_2$, $P_{O_2}=0.03$ atm, 1.52 mA/cm²
- C: $3Na_2O \cdot 2SiO_2$, $P_{O_2}=0.21$ atm, 4.55 mA/cm²

Fig. 3. Overpotential-square root of time relationships for the platinum anode (2 mm ϕ)

Fig. 4. Overpotential-square root of time relationships for the platinum anode (2 mm ϕ) in $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ composition at $P_{\text{O}_2} = 1$ atm—0.46 mA/cm², 0.30 mA/cm² and 0.15 mA/cm²

Fig. 5. Plot of $\eta/\sqrt{t} \cdot i$ against logarithm of the experimental time range for $\text{Na}_2\text{O} \cdot \text{SiO}_2$ composition

the present work, the slopes in the time range from 10 msec to 1 sec were found to be nearly constant regardless of the alkali cation, the slag composition and the oxygen pressure.

From the results of Emi, *et al.*³⁾ by the potential step method (electrode dia. 2 mm), the linear relationship between i and $t^{-1/2}$ deviates after about 4 sec. They explain this deviation by the natural convection of the melt. On the other hand, from the potentiostatic work of Kawakami and Goto²⁾ (electrode dia. 1 mm), the linear relationship between i and $t^{-1/2}$ was obtained for an extended period of time (20~200 sec).

2. Kinetic Parameters

The values of m' are calculated as a function of the slag composition and the oxygen pressure from the

Fig. 6. Plot of $1/C_{\text{O}}\sqrt{D_{\text{O}}} + 1/C_{\text{M}_2\text{O}}\sqrt{D_{\text{M}_2\text{O-SiO}_2}}$ ($=m'$) against $P_{\text{O}_2}^{-1/2}$ for $\text{Li}_2\text{O-SiO}_2$ system

Fig. 7. Plot of $1/C_{\text{O}}\sqrt{D_{\text{O}}} + 1/C_{\text{M}_2\text{O}}\sqrt{D_{\text{M}_2\text{O-SiO}_2}}$ ($=m'$) against $P_{\text{O}_2}^{-1/2}$ for $\text{Na}_2\text{O-SiO}_2$ system

Fig. 8. Plot of $1/C_{\text{O}}\sqrt{D_{\text{O}}} + 1/C_{\text{M}_2\text{O}}\sqrt{D_{\text{M}_2\text{O-SiO}_2}}$ ($=m'$) against $P_{\text{O}_2}^{-1/2}$ for $\text{K}_2\text{O-SiO}_2$ system

slope of $\eta-t^{1/2}$ plot. Figures 6 to 8 show the variation of m' with $P_{\text{O}_2}^{-1/2}$ in the systems $\text{Li}_2\text{O-SiO}_2$, $\text{Na}_2\text{O-SiO}_2$ and $\text{K}_2\text{O-SiO}_2$. It can be seen from Figs. 6 to 8 that the experimental results obtained from a Pt electrode of 1 mm dia. systematically differ from those of 2 mm dia., but this systematic scattering is not due to the difference in the diameter of a Pt

electrode, since no effect of a Pt electrode dia. on the potential-time curve was observed in the present preliminary experiment. Hence, these scattering would be caused by the use of the different mother slag for the experiment of 1 and 2 mm ϕ .

It can be concluded from the excellent linear relationships between m' and $P_{O_2}^{-1/2}$ that an oxygen dissolves in molten silicate, not as a diatomic molecule, but as an atom, as the $C_{M_2O} (D_{M_2O-SiO_2})^{1/2}$ term is constant at the fixed slag composition. This conclusion about a soluble oxygen in molten slag is different from the interpretation of Kawakami and Goto.²⁾ They explained in some detail the type of the physically dissolved oxygen. The present authors agree with their explanation, but their result (Fig. 6 in Ref. 2)) is more reasonably explained by considering, not a diatomic molecule, but an atom as a dissolved oxygen. It is more reasonable to consider that an oxygen dissolves as a diatomic molecule when slag is equilibrated with an oxygen gas, but from the present experimental conditions, *i.e.*, an atomic oxygen is produced at the interface by the anodic polarization, it is suggested that an oxygen dissolves as an atom. But the further work is necessary in order to draw the definite conclusions.

Each intersect by extrapolating the line of the constant slag composition to the point at which the oxygen pressure is infinite is corresponding to the $C_{M_2O} (D_{M_2O-SiO_2})^{1/2}$ term for each slag composition. These results of $C_{M_2O} (D_{M_2O-SiO_2})^{1/2}$ term are summarized in Table 2. The $C_O (D_O)^{1/2}$ terms calculated graphically from Figs. 6 to 8 are tabulated in Table 3 as a function of the slag composition and the oxygen pressure. Figure 9 shows the relationship between the $C_O (D_O)^{1/2}$ term and the slag composition of N_{SiO_2} under 0.21 atm.

The dependence of $C_O (D_O)^{1/2}$ and $C_{M_2O} (D_{M_2O-SiO_2})^{1/2}$ terms on the slag composition will be discussed in the

following.

Ghosh and King¹⁾ studied the anodic polarization at Pt/lithium silicate melt interface at 1350°C by the galvanostatic method. They obtained the steady state overpotential within about 1 sec, and which was plotted against the logarithm of the applied current density. But in the present experimental time range of about 1 sec, the overpotential was explained by the unsteady state mass transfer process. This different observation for the overpotential-time relationship arises from the current density used, *i.e.*, they employed the high current densities which result in the higher overpotential than the present one (40 mV). The steady state overpotential was also observed regardless of the experimental time in the present preliminary experiment by the use of the high current densities such as those of Ghosh and King.¹⁾ Their results indicate that the overpotential increases with decreasing Li_2O/SiO_2 molar ratio and the oxygen pressure at the constant current density. This is qualitatively in agreement with the present results.

We will consider the results on the relationship between the $C_O (D_O)^{1/2}$ term and the slag composition shown in Fig. 9. The $C_O (D_O)^{1/2}$ term decreases with decreasing M_2O/SiO_2 molar ratio and increases in the order lithium, sodium and potassium silicates. The effect of the alkali cations on the $C_O (D_O)^{1/2}$ term was found to be very small in the composition more acidic than $M_2O/SiO_2=2/3$. Table 3 indicates that the $C_O (D_O)^{1/2}$ term decreases with decreasing the oxygen pressure. The permeability and the diffusivity of dissolved oxygen as diatomic molecules in molten slag have been measured by the oxygen concentration cell and the galvanic cell, independently and from these two quantities, the solubility of an oxygen was calculated.⁶⁾ Consequently, the values of D_{O_2} and C_{O_2} decrease with the decrease of PbO/SiO_2 molar ratio in $PbO-SiO_2$ system. Their dependence of the $C_{O_2} (D_{O_2})^{1/2}$ term on the slag com-

Table 2. The results of $C_{M_2O}(D_{M_2O-SiO_2})^{1/2}$ as a function of slag compositions: $C_{M_2O}(D_{M_2O-SiO_2})^{1/2} \times 10^8$

M_2O/SiO_2	3/2	1/1	2/3	1/2
Li_2O/SiO_2	4.0	1.0	0.54	0.42
Na_2O/SiO_2	20	2.0	0.61	0.38
K_2O/SiO_2	—	13	2.3	1.1

Table 3. Solubility and square root of diffusivity of soluble oxygen product: $C_O \sqrt{D_O} \times 10^8$

	P_{O_2} (atm)	3/2	1/1	2/3	1/2
Li_2O/SiO_2	1	3.8	2.9	1.8	1.5
	0.21	1.8	1.3	0.83	0.67
	0.03	0.68	0.48	0.32	0.25
Na_2O/SiO_2	1	17	5.9	1.8	1.5
	0.21	7.1	1.7	0.83	0.69
	0.03	2.6	0.69	0.32	0.27
K_2O/SiO_2	1	—	33	4.2	2.2
	0.21	—	17	1.9	1.0
	0.03	—	6.7	0.72	0.38

Fig. 9. Dependence of $C_O \sqrt{D_O}$ on the slag composition N_{SiO_2} at $P_{O_2}=0.21$ atm for Li_2O-SiO_2 , Na_2O-SiO_2 and K_2O-SiO_2 systems

position was in agreement with the present results, although their results are limited in the high concentration of PbO.

We will consider the results on the relationship between C_{M_2O} ($D_{M_2O-SiO_2}$)^{1/2} term and the slag composition listed in Table 2.

In the investigation of Kawakami and Goto²⁾ who studied the anodic polarization of a Pt anode in the molten slag (PbO-SiO₂, Na₂O-SiO₂ and Na₂O-GeO₂) by the potentiostatic method, they indicate by the calculation that the molar quantity of M₂O transferred through the interface is much smaller than M₂O present in the bulk melt because of the extremely small current density used. Consequently, they assume that the latter term in Eq. (B-2), *i.e.*, $(RT/2F_1) \ln {}^o a_{M_2O}/a_{M_2O}$ may be neglected. However, in the present work, the C_{M_2O} ($D_{M_2O-SiO_2}$)^{1/2} term decreases with decreasing M₂O/SiO₂ molar ratio as is listed in Table 2. The extent of this decrease is in the order lithium, sodium and potassium silicates.

Now we discuss the validity of the assumption involved in Eq. (11).

As a result of the concentration gradient of M₂O between the interface and the bulk, the activity of M₂O at the interface changes with time as the anodic polarization proceeds. We obtain Eq. (B-3) in *Appendix* (B), assuming that the activity coefficient at the interface is equal to that in the bulk. But it is obvious from the behavior of a_{M_2O} in the binary alkali silicate melt that this assumption is not valid. If this assumption is valid under the present experimental conditions, the latter term in Eq. (B-2) can be neglected as pointed out by Kawakami and Goto. Actually, however, this term was found not to be neglected in this work as already shown in Figs. 6 to 8. This contradiction may be more reasonably explained by introducing the ionic concept to the melt. That is, the ratio of ${}^o a_{M_2O}$ to a_{M_2O} may be reduced to the ratio of ${}^o N_{O^{2-}}$ to $N_{O^{2-}}$ when the Temkin's model of ideal ionic mixing is applicable. Then we obtain Eq. (B-11) instead of Eq. (11) as explained in *Appendix* (B). The activity of M₂O in the binary silicate melt by this model is expressed by the anionic fraction of free oxygen ions O²⁻ which do not mean the oxygen bonded with the total cations present. In other words, $C_{O^{2-}}$ is different from C_{M_2O} . Although the latter term in Eq. (B-2) was neglected by Kawakami and Goto, it is not always acceptable in the alkali metal oxides-silica system, *i.e.*, the concentration of the free oxygen ion O²⁻ is extremely low at the composition more acidic than the orthosilicate composition.

Finally, we examine the validity of the Temkin's model.

Belton, *et al.*⁷⁾ observed from the experiment of vaporization measurement that cation in $xNa_2O \cdot (1-x)SiO_2 - xK_2O \cdot (1-x)SiO_2$ system may not behave ideally. Accordingly, C. Wagner⁸⁾ pointed out that the assumption of constant activities of the cations in the system M₂O-SiO₂ is not valid and the error cannot be estimated since it is not possible to determine experimentally the activity of ionic species. This

deviation from the Temkin's model depends on the slag composition as well as the cationic species present. But this assumption about the activity of cation seems to be valid in the present experimental condition of the small current density. Actually, however, the concentration of O²⁻ ions in alkali silicate melts decreases considerably with the decrease of M₂O/SiO₂ molar ratio and is extremely low at the composition more acidic than the orthosilicate composition. Thus it may be possible to consider that O²⁻ ions would be produced by the polymerization reaction such as Eq. (4) in the vicinity of the electrode.

IV. Summary

(1) By means of galvanostatic measurement within 80 μ sec, the exchange current density assumed for the oxygen discharge reaction $O^{2-} \rightleftharpoons O + 2e$ has been obtained. Consequently, i_0 increases with increasing the oxygen pressure and M₂O/SiO₂ molar ratio, and increases in the order lithium, sodium and potassium silicates at the constant M₂O/SiO₂ molar ratio and the oxygen pressure.

(2) In view of the mass transfer process as the rate-controlling step, $\eta-t^{1/2}$ curve has been obtained at the constant M₂O/SiO₂ molar ratio as a function of the oxygen pressure. Consequently, the slope in $\eta-t^{1/2}$ plot at the constant slag composition is inversely proportional to the square root of the oxygen pressure.

(3) The solubility and diffusivity product $C_0 (D_0)^{1/2}$ term has been obtained graphically in $\eta-t^{1/2}$ diagram, assuming that (O) in molten slag transport by the diffusive mass transport process. Consequently, the product $C_0 (D_0)^{1/2}$ increases with the increases of M₂O/SiO₂ molar ratio and increases in the order lithium, sodium and potassium silicates at the constant M₂O/SiO₂ ratio.

(4) The term $C_{M_2O} (D_{M_2O-SiO_2})^{1/2}$ has been discussed in view of the Temkin's concept of ideal ionic melts.

Acknowledgements

The authors are indebted to Mr. K. Serata (Tohoku Metal Ind., Ltd.) for his valuable discussion. Financial support was provided by the grant from the Ministry of Education (S. 50. 2-085028).

REFERENCES

- 1) A. Ghosh and T. B. King: *Trans. Met. Soc. AIME*, **245** (1969), 145.
- 2) M. Kawakami and K. S. Goto: *Met. Trans.*, **4** (1973), 1097; *Tetsu-to-Hagane*, **59** (1973), 196.
- 3) T. Emi, T. Sakuraya and K. Sanbongi: *Metal-Slag-Gas Reactions and Processes*, ed. by Z. A. Foroulis and W. W. Smeltzer, The Electrochem. Soc., Toronto, (1975), 87.
- 4) H. Suito, K. Serata and M. Ohtani: *Metal-Slag-Gas Reactions and Processes*, ed. by Z. A. Foroulis and W. W. Smeltzer, The Electrochem. Soc., Toronto, (1975), 170.
- 5) A. D. Graves, G. J. Hills and D. Inman: *Advances in Electrochemistry and Electrochemical Engineering*, IV, ed. by P. Delahay, Interscience, New York, (1966), 117.
- 6) M. Sasabe and K. S. Goto: *Met. Trans.*, **5** (1974), 2225.
- 7) G. R. Belton, U. V. Choudary and D. R. Gaskell: *Physical Chemistry of Process Metallurgy*, The Richardson Con-

- ference, The Institute of Mining and Metallurgy, London, (1974), 247.
- 8) C. Wagner: *Met. Trans.*, **6B** (1975), 405.
 - 9) T. Kambara and I. Tachi: *Bull. Chem. Soc. Japan*, **25** (1952), 135.
 - 10) C. Wagner: *Advances in Electrochemistry and Electrochemical Engineering*, IV, ed. by P. Delahay and C. W. Tobias, Interscience, New York, (1966), 1.
 - 11) H. J. S. Sand: *Phil. Mag.*, **1** (1900), 45.
 - 12) H. S. Carslaw and J. C. Jaeger: *Conduction of Heat in Solids*, Oxford University Press, (1959), 338.
 - 13) P. J. Koros and T. B. King: *Trans. Met. Soc. AIME*, **224** (1962), 299.

Appendix

(A) The concentration of O^{2-} and (O) at the electrode interface as a function of time can be derived from the solution of the Fick's second law with respect to the following initial and boundary conditions:

Initial Condition: $t = 0, x \geq 0$

$${}^{\circ}C_0 = C_0, \quad {}^{\circ}C_{O^{2-}} = C_{O^{2-}} \dots\dots\dots (A-1)$$

Boundary Condition: $t = 0, x = 0$

$$D_0 \partial C_0 / \partial x = k_1 {}^{\circ}C_{O^{2-}} - k_2 {}^{\circ}C_0 = -D_{O^{2-}} \partial C_{O^{2-}} / \partial x \dots (A-2)$$

where, k_1 and k_2 are the rate constant of the forward and the backward reaction of Eq. (1), respectively. Then, ${}^{\circ}C_{O^{2-}}$ and ${}^{\circ}C_0$ are given⁹⁾ as follows:

$${}^{\circ}C_{O^{2-}} = C_{O^{2-}} - \frac{k_1 C_{O^{2-}} - k_2 C_0}{\lambda \sqrt{D_{O^{2-}}}} \{1 - \exp(\lambda^2 t) \operatorname{erfc}(\lambda \sqrt{t})\} \dots\dots\dots (A-3)$$

$${}^{\circ}C_0 = C_0 + \frac{k_1 C_{O^{2-}} - k_2 C_0}{\lambda \sqrt{D_0}} \{1 - \exp(\lambda^2 t) \operatorname{erfc}(\lambda \sqrt{t})\} \dots\dots\dots (A-4)$$

where,

$$\begin{aligned} \lambda &= k_1 / \sqrt{D_{O^{2-}}} + k_2 / \sqrt{D_0} \\ &= \frac{i_0}{2F_2} \left[\frac{\exp(2\alpha F_1 \eta / RT)}{{}^{\circ}C_{O^{2-}} \sqrt{D_{O^{2-}}}} + \frac{\exp\{-2(1-\alpha)F_1 \eta / RT\}}{{}^{\circ}C_0 \sqrt{D_0}} \right] \end{aligned} \dots\dots\dots (A-5)$$

Equations (A-3) and (A-4) are now reduced to Eqs. (8) and (9), respectively, with the following assumption.

$$\lambda \sqrt{t} \ll 1 \dots\dots\dots (A-6)$$

$$k_1 C_{O^{2-}} - k_2 C_0 \doteq k_1 {}^{\circ}C_{O^{2-}} - k_2 {}^{\circ}C_0 = i / 2F_2 \dots\dots (A-7)$$

(B) As the transport number of the cation in alkali silicates is unity, the overpotential between *RE* and *WE* is given by the following expression:¹⁰⁾

$$\eta = \frac{RT}{2F_1} \ln \left(\frac{P_{O_2}^{WE}}{P_{O_2}^{RE}} \right)^{1/2} - \frac{1}{2F_1} (\mu_{M_2O}^{WE} - \mu_{M_2O}^{ME}) \dots (B-1)$$

where, subscripts *WE* and *RE* denote the working electrode and the reference electrode, respectively. When an oxygen gas is dissolved in molten slag as an atomic form, Eq. (B-1) would now become:

$$\eta = \frac{RT}{2F_1} \ln \frac{{}^{\circ}C_0}{C_0} - \frac{RT}{2F_1} \ln \frac{{}^{\circ}a_{M_2O}}{a_{M_2O}} \dots\dots\dots (B-2)$$

where, ${}^{\circ}a_{M_2O}$ and a_{M_2O} represent the activity of M_2O at the electrode interface and in the bulk, respectively.

If the activity coefficient of M_2O at the interface is assumed to be equal to that of M_2O in the bulk in the present work, one can write:

$$\ln \frac{{}^{\circ}a_{M_2O}}{a_{M_2O}} \doteq \ln \frac{{}^{\circ}N_{M_2O}}{N_{M_2O}} \dots\dots\dots (B-3)$$

where, ${}^{\circ}N_{M_2O}$ and N_{M_2O} represent the mole fraction of M_2O at the interface and in the bulk, respectively in the present binary system M_2O - SiO_2 . In addition, one further assumes that the ratio of ${}^{\circ}N_{M_2O}$ to N_{M_2O} can be reduced to the ratio of ${}^{\circ}C_{M_2O}$ to C_{M_2O} in the present experimental condition of the small current density where ${}^{\circ}C_{M_2O}$ (mole/cm³) and C_{M_2O} (mole/cm³) denote the concentration of M_2O at the interface and in the bulk, respectively. The change of M_2O concentration at the interface with time can be obtained, assuming one-dimensional diffusion in a semi-infinite medium and under the following conditions.

$$\begin{aligned} D_0 \partial C_0 / \partial x &= -D_{M_2O-SiO_2} \partial C_{M_2O} / \partial x (= i / 2F_2) \\ t &> 0, \quad x = 0 \dots (B-4) \end{aligned}$$

$${}^{\circ}C_0 = C_0, \quad {}^{\circ}C_{M_2O} = C_{M_2O} \quad t = 0, \quad x \geq 0 \dots (B-5)$$

Then, one obtains the following equations.¹¹⁾

$${}^{\circ}C_{M_2O} = C_{M_2O} - \frac{i \sqrt{t}}{2F_2 \sqrt{\pi} \sqrt{D_{M_2O-SiO_2}}} \dots\dots (B-6)$$

$${}^{\circ}C_0 = C_0 + \frac{i \sqrt{t}}{2F_2 \sqrt{\pi} \sqrt{D_0}} \dots\dots\dots (B-7)$$

Upon substitution of Eqs. (B-6) and (B-7) into Eq. (B-2), it follows that:

$$\begin{aligned} \exp(2F_1 \eta / RT) - 1 &= \frac{i \sqrt{t}}{F_2 \sqrt{\pi}} \left(\frac{1}{C_0 \sqrt{D_0}} \right. \\ &\quad \left. + \frac{1}{C_{M_2O} \sqrt{D_{M_2O-SiO_2}}} \right) \dots (B-8) \end{aligned}$$

If $2F_1 \eta / RT \ll 1$, Eq. (B-8) is reduced to Eq. (11).

On the other hand, referring to Temkin's concept of ideal ionic melts, one obtain:

$$\ln \frac{{}^{\circ}a_{M_2O}}{a_{M_2O}} \doteq \ln \frac{{}^{\circ}N_{O^{2-}}}{N_{O^{2-}}} \dots\dots\dots (B-9)$$

where, ${}^{\circ}N_{O^{2-}}$ and $N_{O^{2-}}$ denote the anionic fraction of O^{2-} at the interface and in the bulk, respectively. One may assume that the ratio of ${}^{\circ}N_{O^{2-}}$ to $N_{O^{2-}}$ can be reduced to the ratio of ${}^{\circ}C_{O^{2-}}$ to $C_{O^{2-}}$ if the total number of anions and the density at the interface are equal to those in the bulk, respectively in the present experimental condition of the small current density. Then, one can obtain as follows:

$${}^{\circ}C_{O^{2-}} = C_{O^{2-}} - \frac{i \sqrt{t}}{2F_2 \sqrt{\pi} \sqrt{D_{M_2O-SiO_2}}} \dots\dots (B-10)$$

Substituting Eqs. (B-7) and (B-10) into Eq. (B-2), one obtain if $2F_1 \eta / RT \ll 1$

$$\eta = \frac{RT i \sqrt{t}}{2F_1 F_2 \sqrt{\pi}} \left(\frac{1}{C_0 \sqrt{D_0}} + \frac{1}{C_{O^{2-}} \sqrt{D_{M_2O-SiO_2}}} \right) \dots (B-11)$$

(C) When one may consider the cylindrical diffusion with the initial condition given by Eq. (A-2) and the boundary condition given by Eq. (B-4), the concentration of M_2O and (O) at the electrode surface may be written as Eqs. (C-1) and (C-2), if $Dt/a^2 \ll 1$, where a is the electrode radius,

$$^oC_O = C_O + \frac{i}{2F_2} \left(\frac{t}{D_O} \right)^{1/2} \left[\frac{2}{\sqrt{\pi}} - \frac{1}{2} \left(\frac{D_O t}{a^2} \right)^{1/2} + \dots \right] \quad \text{.....(C-1)}$$

$$^oC_{M_2O} = C_{M_2O} - \frac{i}{2F_2} \left(\frac{t}{D_{M_2O-SiO_2}} \right)^{1/2} \left[\frac{2}{\sqrt{\pi}} + \frac{1}{2} \left(\frac{D_{M_2O-SiO_2} t}{a^2} \right)^{1/2} - \dots \right] \quad \text{.....(C-2)}$$

When Eqs. (C-1) and (C-2) are compared with Eqs.

(8) and (9), it is apparent that the following approximate conditions are necessary in order to satisfy the semi-infinite linear diffusion.

$$2/\sqrt{\pi} \gg \sqrt{D_O t}/2a, \quad 2/\sqrt{\pi} \gg \sqrt{D_{M_2O-SiO_2} t}/2a \quad \text{.....(C-3)}$$

The values of D_O and $D_{M_2O-SiO_2}$ have not been obtained so far in the alkali silicate melts, but in the present work, the diffusivity of a dissolved oxygen as a diatomic molecule in the $PbO-SiO_2$ system⁶⁾ was used to evaluate the experimental time. The tracer diffusivity of oxygen in the system $CaO-SiO_2-Al_2O_3$ measured by Koros and King¹³⁾ was used for the value of $D_{M_2O-SiO_2}$, assuming the order of magnitude in the interdiffusivity $D_{M_2O-SiO_2}$ is equal to that of the tracer diffusivity.