Electrochemical Measurement of Oxygen Diffusivity in Liquid Silver*

By Nobuo SANO,** Shingo HONMA,** and Yukio MATSUSHITA**

Synopsis

A solid electrolyte cell technique different from the popular capillary gas reservoir technique has been developed for the determination of the diffusivity of oxygen in liquid silver. Unsteady oxygen diffusion was detected by measuring the change of the electromotive force with time after the introduction of absorbent oxygen gas into a liquid silver column with a finite length directly in contact with a calcia stabilized zirconia disc at the bottom.

The diffusivity of oxygen was calculated by use of Fick's second law. The relationship between the oxygen diffusivity in liquid silver and temperature from 1 000° to 1 200°C may be expressed by the following expression:

$$D = (3.0 \pm 0.5) \cdot 10^{-3} \exp \frac{-8\,700 \pm 500}{RT} \text{ cm}^2/\text{sec.}$$

I. Introduction

Since Kiukkola and Wagner¹⁾ used a solid electrolyte for the oxygen concentration cell, much effort has been directed to the measurement of thermochemical properties, such as the standard free energy of formation of oxides or sulfides and oxygen partial pressure in gases. This investigation is primarily concerned with the measurement of diffusivity of oxygen in liquid metals, as one of the applications of solid electrolyte to the measurement of transport properties.

II. Principle of the Measurement

Recently Schmalzried proposed²⁾ that diffusivity in solid metals can be determined by measuring the electrical current caused by the steady diffusion of oxygen from any point in the solid metal to the metal electrolyte interface.

The Schmalzried principle appears very attractive, but the disadvantages are obvious, though not serious in liquid systems, considering the different factors involved in using this particular principle. Geometry of the cell, for instance, is an important factor because of the small diffusivity of oxygen in solid electrolyte compared with that in the liquid metals. However, the present authors have developed independently another method treating liquid systems with the use of solid electrolyte.

The principle is schematically represented in Fig. 1. Gaseous oxygen is absorbed into the liquid metal column with length L contained in an alumina tube, the bottom of which is the securely sealed with solid electrolyte (0.85ZrO₂-0.15CaO). In other words the liquid metal rests on the solid electrolyte.

The diffusivity of oxygen can be determined by measuring the change of electromotive force between the metal and the reference electrode with time.

Fig. 1. Principle of the galvanic cell for the measurement of electromotive force change due to unsteady diffusion of oxygen from the top of liquid silver column to the bottom

The oxygen diffusivity in the containing vessel is negligible, compared with that in the liquid metal. According to Utine and Parlee,³⁾ Davenport, Bradshaw, and Richardson,⁴⁾ oxygen in gas and metal is likely to be in equilibrium at the surface. Therefore Fick's second law can be solved with the following conditions.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \dots\dots\dots(1)$$

$$I.C. \quad t = 0 \quad C = 0$$

$$B.C. \quad x = 0 \quad C = C_0$$

$$x = L \quad \partial C / \partial x = 0$$

$$\frac{C_1}{C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left(\frac{-D(2n+1)^2 \pi^2 t}{4L^2} \right) \quad \text{Ref.5)} \quad \dots\dots\dots(2)$$

where C_1 and C_0 are the concentration of oxygen at the bottom of the column and at the gas-metal interface, respectively.

The measured electromotive force is considered to be due to the difference of oxygen potential at the bottom of the bath, $\mu_{O_2}^{Me.}$ and reference electrode, $\mu_{O_2}^{Ref.}$. It is expressed by the following equation

$$\text{e.m.f.} = \frac{RT}{4F} (\mu_{O_2}^{Me.} - \mu_{O_2}^{Ref.}) \quad \dots\dots\dots(3)$$

where F , R , and T are Faraday constant, gas constant, and absolute temperature, respectively.

When oxygen gas is used as the reference electrode, the relation

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** Department of Metallurgy, University of Tokyo, Bunkyo-ku, Tokyo 113.

$$\mu_{O_2}^{Ref.} = \mu_{O_2}^0 + RT \ln P_{O_2}^{Ref.} \quad (4)$$

holds and when Henry's law is applicable to the behavior of oxygen in liquid metal,

$$C_1 = K P_{O_2}^{1/2} \quad (5)$$

then

$$\mu_{O_2}^{Me.} = \mu_{O_2}^0 + 2RT \ln C_1/K \quad (6)$$

When the partial pressure of absorbent oxygen gas is equal to that of the reference gas, the following relation is obtained.

$$\begin{aligned} \mu_{O_2}^{Ref.} &= \mu_{O_2}^0 + RT \ln P_{O_2}^{Ab.} \\ &= \mu_{O_2}^0 + 2RT \ln C_0/K \quad (7) \end{aligned}$$

Substituting Eqs. [6] and [7] to Eq. [3] gives

$$e.m.f. = (RT/2F) \ln C_1/C_0 \quad (8)$$

Equation (8) expresses the relationship between the measurable electromotive force and C_1/C_0 which is related to Dt/L^2 by Eq. (2). However, direct determination of Dt/L^2 from Eq. (2) is apparently cumbersome. This can be facilitated by a plot Dt/L^2 vs. C_1/C_0 with the aid of electronic computer. Thus, measuring the electromotive force change with time after the introduction of absorbent oxygen gas, one can determine the diffusivity of oxygen in metal.

III. Experimental

Liquid silver was chosen for the application of the above mentioned principle for the following reasons:

- i) Low melting temperature
- ii) No formation of oxide under one atmosphere of oxygen
- iii) Availability of data by other methods for comparison
- iv) Applicability of Henry's law to oxygen in liquid silver.⁶⁾

The schematic diagram of the apparatus is shown in Fig. 2. The cell consists of alumina tube (I.D. 5 mm) with the solid electrolyte disc (0.85ZrO₂-0.15CaO) securely sealed with glass (12w/oNa₂O, 20w/oA₂O₃, 68w/oSiO₂) at the bottom. The experimental temperature and the subsequent expansion of both alumina and solid electrolyte were the deciding factors in determining the composition of the glass.

Perfect seal between the tube and the disc was of prime consideration and this was checked by vacuum pump before every diffusion run. Stainless steel (25%Cr-20%Ni, 1 mm ϕ) was used as lead wire for silver electrode,⁶⁾ and platinum wire for the reference electrode. Thermoelectric force between both electrodes was measured for correction. Mulite tube (I.D. 22 mm) enclosed the cell to maintain the oxygen pressure of the reference to be one atmosphere. The furnace consists of double heating system with nichrome winding and the temperature distribution within a length of 5 cm was not more than $\pm 2^\circ\text{C}$ by controlling the outer heating system.

The weighed silver granules of 99.9% purity was melted in the above mentioned cell and deoxidized by

A. Electrode (25%Cr-20%Ni stainless steel wire)	J. Absorbent oxygen
B. Quartz tube for absorbent oxygen (I.D. 3 mm)	K. Water cooled brass head
C. Rubber stopper	L. Control thermocouple (Pt-Pt 13% Rh)
D. Alumina tube (I.D. 5 mm)	M. Alumina tube (I.D. 42 mm)
E. Reference electrode (Pt wire)	N. Heating element (nichrome wire)
F. Liquid silver	O. Alumina tube (I.D. 22 mm)
G. Glass	P. Alumina tube support
H. Stabilized zirconia disc (12 mm ϕ)	Q. Oxygen for reference electrode
I. Refractory	

Fig. 2. Schematic cross section of apparatus

purified hydrogen down to -700 mV which corresponds to $C/C_0 \approx 10^{-5}$. Then the melt was kept under argon about ten minutes for flushing hydrogen gas. After no leakage of oxygen from the exterior was ascertained by the possible change of electromotive force

in this time, oxygen absorbent gas was introduced at 40 ml/min through a quartz tube (I.D. 3 mm), the tip of which was placed 2 cm above the surface of the melt. This flow rate had been found to satisfy two conditions: (1) keeping the melt motionless and (2) eliminating gaseous diffusion control. Initial movement of the potentiometer indicated fifteen or twenty seconds after introduction of oxygen was regarded as the reference point. The oxygen partial pressure of the purified hydrogen and argon gas were found to be 10^{-22} and 10^{-15} atm, respectively. The electromotive force was recorded continuously by high impedance EMF recorder until almost saturation with absorbent oxygen (-10 mV) was attained (Fig. 3). Usually it took about 150 min.

IV. Results and Discussion

Figures 3 and 4 show the change of electromotive force and the converted Dt/L^2 value with time at 1202°C , respectively. The slope of the straight line gives D/L^2 . The change from -300 to -10 mV was mainly used for the diffusivity determination because the initial significant drop of electromotive force from -700 to -300 mV corresponds to too small a change of oxygen concentration. The height of the melt was estimated by weight, the diameter of the alumina tube and the known density data of liquid silver as a function of temperature.⁷⁾

Least square treatment of the results gave the following relation.

Fig. 3. Change of electromotive force with time at 1202°C

Fig. 4. Dimensionless quantity Dt/L^2 as a function of time at 1202°C

$$D = (3.0 \pm 0.5) \cdot 10^{-3} \exp \frac{-8700 \pm 500}{RT} \text{ cm}^2/\text{sec}$$

The Arrhenius plots of D between 1000° and 1200°C in Fig. 5 are compared with data obtained by Mizukar, Grace, and Parlee⁸⁾ which were measured by the capillary gas reservoir method. Both findings agree fairly well in spite of the difference in the principle of measurement, the scattering in this work is much less and it appears that the electrochemical method is more satisfactory in determining the diffusivity of oxygen in some liquid metals. However, this inference needs to be supported by more experimental data for which authors are presently undertaking in liquid lead and copper.

Fig. 5. Arrhenius plots of D vs. $10^4/T^\circ\text{K}$

Masson and Whiteway¹²⁾ also measured the oxygen diffusivity in liquid silver by use of a stabilized zirconia tube. They claimed that the oxygen potential of only the bottom of liquid column contained in the tube can be detected, when a long column of melt is used and the reference electrode is placed near the bottom across the electrolyte. However, it is considered that the result is sensitive to the geometry of the cell and the error due to the internal current in the electrolyte is essential.

The present authors checked their concept by use of a tube with 5 mm of I.D. (Fig. 6) instead of a disc described above, keeping the experimental conditions

Fig. 6. A use of $\text{ZrO}_2 (+\text{CaO})$ tube instead of a disc in Fig. 1

unchanged otherwise. The platinum wire for reference electrode was wound around the tube at 8 mm above the bottom.

Suppose the convection of the bath was sufficient to give a uniform distribution of oxygen in the melt or the electromotive force detected the *mean concentration* of oxygen in the melt (Assumption I), then the electromotive force would follow the curve (a) in Fig. 7 which was calculated as follows:

$$\text{e.m.f.} = \frac{RT}{2F} \ln \frac{\bar{C}}{C_0} = \frac{RT}{2F} \ln \frac{\int_0^L C dx}{C_0 L} \dots\dots\dots (9)$$

$$\frac{\bar{C}}{C_0} = \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left(-\frac{D(2n+1)^2 \pi^2 t}{4L^2} \right) \right] \dots\dots\dots \text{Ref.5)} \quad (10)$$

where $\bar{C}$ denotes the mean oxygen concentration along the diffusional direction from the top to the bottom of the column and the numerical value of D obtained by use of a disc (0.96×10^{-4} cm²/sec) was used.

The curve (b) in Fig. 7 shows the behavior of oxygen in terms of the electromotive force if the melt was granted motionless and the *mean oxygen potential* along the diffusional direction was indicated (Assumption II). The curve (b) was calculated as follows.

$$\text{e.m.f.} = \frac{RT}{2F} \ln \frac{\bar{C}}{C_0} = \frac{RT}{2F} \int_0^L \ln \frac{C}{C_0} \frac{dx}{L} \dots\dots\dots \text{Ref.12)} \quad (11)$$

where $\ln C/C_0$ denotes the mean of $\ln C/C_0$ which was obtained by help of electronic computer for lack of analytical solution. This corresponds to the calculation of external voltage when batteries with the *same* internal resistance are connected in parallel.

The experimentally obtained electromotive force also shown in Fig. 7, however, disagrees with either of the two predictions. The disagreement with curve (a) is natural because the melt was maintained motionless. The disagreement with curve (b) shows the

Fig. 7. Change of electromotive force with time at 1 000°C

importance of the information on the exact location dependence of internal resistance in the solid electrolyte. However, the internal resistance can not be estimated theoretically, because it is complicatedly dependent on the thickness of the electrolyte tube, the length of the tube in contact with the melt, the position of the reference electrode, electric conductivity of the tube material used, porosity of the electrolyte, and so on. Consequently it is concluded that the use of solid electrolyte *tube* should be rejected for kinetic measurements when oxygen potential difference exists along the direction of diffusion.

Therefore, the diffusivity value of 3.41×10^{-4} cm²/sec indicated in Fig. 8 based on the assumption II is erroneous. It was found to be four times bigger than the experimental value 0.96×10^{-4} cm²/sec obtained earlier with solid electrolyte disc.

During the preparation of this manuscript Rickert and El Miligy⁹⁾ reported their results, using the Schmalzried principle as mentioned above (galvanostatic and potentiostatic methods). Their measurements are expressed as follows

$$D = 2.63 \times 10^{-3} \exp(-7300/RT) \text{ cm}^2/\text{sec}$$

and also plotted in Fig. 5. Rickert's values are 40 to 60% higher than the present results. The reason for the difference is not yet well understood.

Fig. 8. Dimensionless quantity Dt/L^2 as a function of time at 1 000°C

V. Conclusion

(1) The proposed electrochemical method appears to be more satisfactory than the conventional capillary gas reservoir or chemical analysis methods in the following respects:

- i) Only the ratio of concentration to any reference is necessary in the determination of the diffusivity values.
- ii) Direct measurement in the liquid state
- iii) Simple experimental procedure
- iv) Good reproducibility of data.

(2) The following relation was found from experimental results between the temperature 1 000° and 1 200°C

$$D = (3.0 \pm 0.5) \cdot 10^{-3} \exp \frac{-8700 \pm 500}{RT} \text{ cm}^2/\text{sec.}$$

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REFERENCES

- 1) K. Kiukkola and C. Wagner: *J. Electrochem. Soc.*, **104** (1957), 308.
- 2) H. Schmalzried: *Arch. Eisenhüttenw.*, **39** (1968), 531.
- 3) M. T. Utine and N. A. Parlee: *Trans. TMS-AIME*, **242** (1968), 1458.
- 4) W. G. Davenport, A. V. Bradshaw, and F. D. Richardson: *J. Iron Steel Inst.*, **205** (1967), 1034.
- 5) J. Crank: *The Mathematics of Diffusion*, London, Oxford University Press, (1956).
- 6) C. Diaz, C. R. Masson, and F. D. Richardson: *Trans. Inst. Min. Metall.*, **75** (1956), 183.
- 7) G. Urbain and L. D. Lucas: *The Physical Chemistry of Metallic Solution and Intermetallic Compounds*, Vol. 2, 4E, London, Her Majesty's Stationery Office, (1959).
- 8) E. A. Mizukar, R. E. Grace, and N. A. D. Parlee: *Trans. Am. Soc. Metals*, **56** (1963), 101.
- 9) H. Rickert and A. A. El Miligy: *Z. Metallk.*, **59** (1968), 635.
- 10) N. A. D. Parlee and H. Seibel: *Trans. TMS-AIME*, **233** (1965), 1923.
- 11) L. R. Velho, N. M. El-Tayeb, J. Gani, and N. A. D. Parlee: *Trans. TMS-AIME*, **254** (1969), 184.
- 12) C. R. Masson and S. G. Whiteway: *Can. Met. Quarterly*, **6** (1967), 199.