MASTER

ACTIVITY AND DIFFUSION OF METALS
IN
BINARY ALUMINUM ALLOYS

BY

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ABSTRACT

To determine the activity of zinc in Zn-Al alloys, the electromotive force (emf) of the cell:

was measured at temperatures between 569.5 K (296.5°C) and 649.5 K (376.5°C). The applicability of a two-suffix Margules equation was demonstrated, in good agreement with theoretical expectations. The diffusion coefficient of Zn in Al determined from a planar diffusion model for the experimental data was about $3 \times 10^{-10} \text{ cm}^2/\text{sec}$ to $2 \times 10^{-9} \text{ cm}^2/\text{sec}$ in the range of temperature studied.

This is higher than that found in the literature. The most plausible reason appears to be the high alumina concentration in the working electrode because of partial oxidation.

Oxidation of the alloying metals was the primary cause of poor alloying between calcium/or zinc and aluminum, thereby frustrating similar measurements at a Ca-Al/or Zn-Al alloy. The literature on the activity of calcium and zinc in aluminum is reviewed.

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CHAPTER I

INTRODUCTION

During the past decades several approaches to advanced batteries with high power density have been successfully developed. Some of these were concerned with the Li-Al¹⁻⁶, Ca-Al systems⁷⁻¹⁵, and the other lithium-containing systems¹⁶⁻²⁵. Lithium, being the most electronegative and one of the lightest elements, has many advantages as a negative electrode material in both ambient and elevated temperature batteries used in the electrical vehicle.

However, lithium is highly corrosive and hygroscopic. Also, lithium dissolves appreciably in the chloride salts used in high temperature cells, causing self-discharge owing to the corresponding increased electronic conduction in molten salt electrolyte⁴. There exists a "de-wetting" tendency³ --- a gradual decrease of the capacity retention of lithium by most matrix materials upon repeated charge-discharge cycling --- which may lead to cell shorting by the lithium globules.

Calcium, an alkaline-earth element, has high abundance, relatively low equivalent weight, and high reaction energy with common positive electrode materials. Its properties, compared with those of lithium (see Table 1)⁹, appear to make calcium a very attractive electrode material.

Table 1. Selected Properties of Calcium and Lithium

	Ca	Li
Abundance, wt % of earth crust	3.63	0.0065
Equivalent Wt., g/g-equiv.	20	6.94
Melting Point, K	1115-1122	452
Boiling Point, K	1760	1590
Density, g/cm ³	1.54	0.534
Decomposition Voltage of Chloride at 773 K (500°C)	3.534	3.646

Calcium, like lithium, also forms compounds with aluminum (CaAl_2 and CaAl_4) that are stable solids at cell operation temperature.

In a few projected processes, Ca-Al electrodes in power-producing cells with very large current density were studied⁷⁻¹³. Previous work by Qafisheh¹⁴ concerned the Ca-Al electrode in acetylide-containing halide melts. Few literature data related to the mass transport and thermodynamic properties of the Ca-Al system at high temperature could be found.

At first, the objective of this research was to obtain thermodynamic data for the calcium-aluminum system. However, the preparation of a suitable Ca-Al alloy was ultimately unsuccessful. Therefore, we chose Zn-Al alloy as

the sample system to gather experience with a model system similar to the Ca-Al system.

The primary objectives of this research were to obtain the preliminary data of zinc-aluminum system by Galvanostatic Intermittent Transient Technique (GITT). Although the coulometric titration technique was introduced more than two decades ago for systematically changing the composition of phases which are employed as electrodes in galvanic cells, this method has been used in only a small number of cases for determining thermodynamic and mass transport properties as a function of the stoichiometry within individual phases. Use of this technique can be especially valuable, however, in the case of phases with narrow composition range. The emf measurements in the electrolyte may provide a better fundamental understanding of the electrochemical behavior of the diffusion coefficient which have been determined by varying the stoichiometric single-phase composition " M_xAl_{1-x} ", where M is the reacting metal and x is the molar fraction of metal M in the binary alloy.

In this thesis, three basic models introduced. First, the cylindrical diffusion model, second, the spherical diffusion model and third, planar diffusion model. From the experimental data, one can obtain by comparison with these assumed models (1) the diffusion coefficient of binary alloy over various composition, and (2) the activity and activity coefficient of zinc.

In the next chapter a summary of literature data on the binary-alloy system in various cells is given. Chapter III presents the theoretical analysis of the data to obtain diffusion coefficient and thermodynamic properties in the alloys, using the theoretical models introduced above. Chapter IV deals with the experimental work in preparation of binary alloys and with the emf measurement on these alloy systems. Chapter V and VI contain the results and conclusions respectively.

CHAPTER II

LITERATURE SURVEY

In the last fifteen years, many publications have investigated the electrochemical behavior of binary alloys in the molten-salt temperature range. Most of these are concerned with lithium-containing systems¹⁻⁶, and only a few literature references concern alloys of calcium, as used, e.g., in calcium/metal sulfide secondary cells⁷⁻¹⁵. By comparing the physical properties of calcium with those of lithium (see Table 1), we can predict to some degree the electrochemical behavior of the system Ca-Al, and other related binary-alloy systems, from those of the Li-Al system. However, more experimental work is very desirable.

Calcium-Aluminum System

Calcium-Aluminum alloy has many uses in metallurgy. From the phase diagram of the Ca-Al system²⁸⁻³¹ (see Fig. 1), one can see that there is a eutectic Al-CaAl₄ at 7.6 wt. % (5.3 mol. %) calcium at 890 K (617°C), and that CaAl₄ forms by peritectic reaction from CaAl₂ at 970 K (697°C). The solid solubility at eutectic temperature is of the order 0.01 wt. % (0.0067 mol. %) calcium or less. An alloy with 7.6 wt. % calcium, splat cooled, consists of two phases. The density of this system decreases linearly with increasing calcium content, within experimental error.

The thermodynamic properties of solid Ca-Al alloys are listed in the following table. (Table 2)

Figure 1. Phase Diagram of the Calcium-Aluminum System

Table 2. Standard Heat of Formation (ΔH_{st} , in kJ/g-atom) and Heat of Fusion (ΔH_m , in kJ/g-atom) and Entropy of Fusion (ΔS_m , in J/g-atom, K) of Solid Ca-Al Alloys (Ref. 30)

$(1-x) Al_{(s)} + x Ca_{(l)} = Al_{1-x}Ca_x$					
x_{Ca}	Phase	ΔH_{st}	$\Delta H_m, 1352 K$	$\Delta S_m, 1352 K$	
0.20	β	-43.1 (+8.4)*			
0.33	α	-73.3 (+12.6)*	17.6 (+1.3)*	13.02 (+0.92)*	

*Primary Ref.: Kocherov, P.V., Gertman, Y.M. and Gel'D, P.V. 1959. Zh. Neorg. Khim. 4: 1106-1102.

Calcium/Metal Sulfide Cells

Since 1975 calcium-alloy/molten-salt/transient metal sulfide cells are being investigated for use in the second-generation batteries. The development areas include cell chemistry, cell materials, electrode and cell design, and battery and system design. Preto et al.⁷⁻¹² studies calcium/iron sulfide secondary cells and found that the amp-hr efficiency of these cells is very dependent on electrode design and the composition of the electrolyte. With adequate design these cells exhibited good electrode utilization, and a voltage slightly higher than that of comparable lithium cells.

Ross et al.¹¹, compared two important characteristics of the negative electrode compounds with iron current collectors (see Table 3.) They concluded that calcium-

Table 3. Characteristics of Calcium Negative Electrode (Ref. 11)

Compound	Polarization Characteristics	Corrosiveness Toward Iron Current Collectors
Ca-Mg-Si	Excellent	None
CaAl ₂	Fair	Mild
Ca ₂ Si	Fair	Strong

aluminum alloys are not necessarily the best negative electrode material for calcium/metal sulfide cells.

The Ca-Al voltammetry results were essentially the same in LiCl-14.5 mol. % KCl-31 mol. % CaCl₂ at 773 K(500°C) and in LiCl-37 mol. % KCl-9 mol. % CaCl₂ at 758 K(485°C)¹². A voltammogram from the study in the former electrolyte is shown in Fig. 2. In addition to the Ca-Al doublet, which is also found in the NaCl-CaCl₂ electrolyte, a LiAl peak is clearly evident on the cathode side. It is present because of incomplete utilization of the aluminum by calcium reactions, which leaves some aluminum available for LiAl formation. The peak is absent on discharge because the LiAl reacts with CaCl₂ in the electrolyte to form LiCl and the calcium-aluminum compounds; disregarding the actual stoichiometry this can be written schematically as:

As the working electrode was cycled, the LiAl peak became

Figure 2. Voltammogram for 200 mg Aluminum in LiCl-KCl- CaCl_2 at 773 K (500°C)

smaller relative to the calcium peaks, thereby indicating that breakup of the initially coarse aluminum particles permitted the calcium reaction to proceed more readily.

Roche¹³ tested Li-Al-Zn electrodes and showed that their performance of Ca-Al and Ca-Al-Zn electrodes. He found that zinc had no effect on the utilization of aluminum electrode.

Thermodynamics of Calcium-Aluminum Alloy Formation

By the hydrogen titration method (HTM)¹⁵ Veleckis investigated the thermodynamics and the phase diagram of calcium-aluminum binary alloys and derived the temperature dependance of the calcium activity from the measured partial pressures of hydrogen in equilibrium with calcium and calcium alloy. (see Table 4)

Table 4. Equations for Hydrogen Pressure, Calcium Activity, and Cell Potential for the Two-Phase Fields of Ca-Al System (Ref. 15)

Property	(Al + CaAl ₄)	(CaAl ₄ + CaAl ₂)
P _{H₂} (KPa)	$6.013 \times 10^{-7} \exp(-9,157T^{-1})$	$2.88 \times 10^{-8} \exp(-11,206T^{-1})$
a _{Ca}	$13.07 \exp(-12,121T^{-1})$	$2.726 \exp(-10,072T^{-1})$
Emf(mV)*	$522.2 - 0.01107T \text{ (K)}$	$433.9 - 0.04321T \text{ (K)}$
Ca/Ca ⁺⁺ /Ca-Al.		

* Emf(V) = $-(RT/2F) \ln a_{Ca}$

The equations for the standard free energy of formation of CaAl_2 and CaAl_4 were found to be:

$$\text{CaAl}_2: \Delta G_f^0 \text{ (kJ/mol)} = -92.1 + 14.8 \times 10^{-3} T \quad (2.2.)$$

$$\text{CaAl}_4: \Delta G_f^0 \text{ (kJ/mol)} = -100.7 + 21.2 \times 10^{-3} T \quad (2.3.)$$

Thermodynamics of Calcium-Carbide and Calcium-Carbon Compounds

Bonomi et al.³² investigated the free energy of formation of CaC_2 and its activity in molten salt solution. Using a potential relaxation technique in a cell at 873~973 K (600~700°C),

$\text{Fe, Li-Ca(alloy)/LiCl-CaCl}_2$ eut. $\text{CaC}_2/\text{C(s), Fe}$
they found that a potential plateau at 470 mV which they took to represent CaC_2 formation was very well in agreement with $\Delta G_f^0(\text{CaC}_2)$ predicted from the literature ($\Delta G_f^0 = -90.85$ kJ/mol. at 973 K). The activity coefficient of CaC_2 in molten-salt was found to decrease with increasing concentration.

However, in Qafisheh's work¹⁴ the ΔG_f^0 of CaC_2 calculated from emf measurements in a cell

with the Ca-Al system as a reference electrode, was -131.6 kJ/mol. at 823 K (550°C). Since the ΔG_f^0 value obtained by Qafisheh was much more negative than the other literature values, the intercalation reaction

may have occurred in his experiment.

Since Qafisheh had one estimated value of ΔG_f^0 (CaAl_4)

available, it is of interest to recalculate his data for ΔG_f^0 (CaC_2) using the thermodynamic data for CaAl_2 and CaAl_4 found by Veleckis¹⁵. Veleckis' data for CaAl_4 are shown as following:

$$\Delta S^0 = -21.2 \times 10^{-3}, \quad \text{kJ/mol, K} \quad (2.5.)$$

$$\Delta H_f^0 = -100.7, \quad \text{kJ/mol} \quad (2.6.)$$

$$E = 521.77 - 0.11T \text{ (K)} \quad (2.7.)$$

Calculated from these equations we obtain the potential and the activity of CaAl_4 as given in Table 5.

With these values one can calculate the thermodynamic properties of CaC_2 vs. Ca^0 in Ca-Al system from Qafisheh's data as shown in Table 6.

Table 5. Standard Gibbs Free Energy and Emf Values of CaAl_4 vs. Ca^0

Temperature K(°C)	ΔG_f^0 (kJ/mol.)	a	E (mV)
823 (550)	-83.25	5.23×10^{-6}	+431.4
873 (600)	-82.19	1.22×10^{-5}	+425.9
923 (650)	-81.13	2.58×10^{-5}	+420.4
973 (700)	-80.07	5.05×10^{-5}	+414.9

Lithium Alloys

The emf values of the cell

Table 6. Standard Enthalpy, Entropy and Free Energy of Formation of CaC_2 vs. Ca^0 and C (From Qafisheh's data by recalculation)

Temperature K(°C)	ΔH_f^0 (kJ/mol.)	ΔS^0 (J/mol., K)	ΔG_f^0 (J/mol.)
823 (550)	-232.2	-199.3	-122.2
873 (600)	-231.7	-199.3	-111.7
923 (650)	-232.2	-199.3	-102.4
973 (700)	-230.0	-199.3	- 92.1

were measured by Yao et al.¹. They found the emf to be independent of the composition up to 47% lithium in lithium alloy and dependent on temperature in a linear relation:

$$E = 451.07 - 0.2202T \quad (\sigma = 0.3) \quad (2.8.)$$

where E is in millivolts, T in K(555~668 K, or 282~389 °C) and σ is the standard deviation.

Selman et al.³ measured the emf of the cell

and found (i) a steep decrease in emf as the lithium fraction in the alloy exceeded 48% lithium; (ii) No significant emf discontinuity at 67% lithium (i.e. Li_2Al); In related work Selman⁶ observed that in the $(\alpha+\beta)$ region the emf shows a linear temperature dependence,

$$E(\text{mV}) = 474.37 - 0.2565T \quad (\sigma = 0.3) \quad (2.9.)$$

where T is in K. (T = 651~857 K, or 378~584 °C)

Weppner et al.^{4,5,19-24} used two different electrochemical transient techniques --- the potentiostatic intermittent transient technique (PITT) and the galvanostatic intermittent transient technique (GITT) --- to measure the chemical diffusion coefficient, the standard Gibbs free energy, enthalpy and entropy of formation in lithium-containing alloys as a function of stoichiometry by parallel-plane, single-phase diffusion modelling.

Wen et al.^{4,5} investigated the thermodynamic properties of LiAl, the solubility and chemical diffusion of lithium in aluminum using the electrochemical cell:

over a temperature range from 688 to 873 K (415~600 °C). They found that the emf of the single β -phase Li-Al lies between 300 to 700 mV at 688 K (415°C) relative to pure lithium and this corresponds to a lithium activity increasing from 0.0063 to 0.31 over the phase stability range from 46.8 to 55.0 wt.% lithium. The solubility limit of lithium in aluminum α -phase was found to decrease from 13.8 wt.% lithium at 868 K (595°C) to 8.0 wt.% at 668 K (395°C). On the lithium deficit side of the ideal β stoichiometry (LiAl), the chemical diffusion coefficient increases with decreasing lithium concentration, becoming about 10^{-4} cm²/sec near the phase boundary. These data at the lithium-poor phase-boundary of β -phase fit the relation:

$$D = 0.155 \exp(-119.2 \text{ kJ/mol/RT}), \text{cm}^2/\text{sec} \quad (2.10.)$$

In both the lithium-bismuth and lithium-tin systems²⁰⁻

²⁴, the excess chemical potential, Δu^E , of lithium in the alloys was derived as a function of temperature and composition for the compounds Li_3Sb and Li_3Bi with a narrow composition range.

The theoretical (maximum) specific energies for lithium cells with tin and bismuth electrodes were quite high at about 643 K (370°C); and the Gibbs free energies of the compounds existing in the systems Li-Sb and Li-Bi were shown to be linearly temperature-dependent over a narrow range of stoichiometric composition.

Weppner and Huggins²⁰⁻²⁴ utilized the GITT method to determine lithium transport in the Li_3Sb and Li_3Bi systems, and got relative high values for the chemical diffusion coefficients ($2 \times 10^{-5} \text{ cm}^2/\text{sec}$ for Li_3Sb and $10^{-4} \text{ cm}^2/\text{sec}$ for Li_3Bi at about 643 K) with high lithium deficit and increased markedly when approaching ideal stoichiometry. These coefficients were linear functions of the reciprocal of the absolute temperature.

Sabounji et al.²⁵ used a coulometric titration technique to characterize the intermetallic compounds in the lithium-lead system by a electrochemical cell:

where the left-hand electrode consisted of a two-phase alloy (either two solid phases or a solid and liquid phase) and served as a secondary reference electrode as well as a source of lithium. They measured the emf's of voltage-

plateaus and the thermodynamic properties of the compounds in the system are shown in the following tables. (see Table 7 and 8)

Table 7. Electromotive Forces (mV) vs. Pure Liquid Lithium in the Li-Pb System (Ref. 25)

Equilibrium	Emf (mV)	Temperature Range (K)
LiPb + Pb(soln)	917.282 - 0.60925T	653 ~ 723
Li ₈ Pb ₃ + Pb(soln)	715.565 - 0.47500T	773 ~ 823
Li _{1+δ} Pb + Li ₈ Pb ₃ *	521.591 - 0.21724T	653 ~ 723
Li ₈ Pb ₃ + Li ₃ Pb	365.794 - 0.14011T	653 ~ 823
Li ₃ Pb + Li ₇ Pb ₂	283.627 - 0.06870T	653 ~ 823
Li _{7+ξ} Pb + Li ₂₂ Pb ₅ *	179.441 - 0.13463T	653 ~ 823

* The symbols δ and ξ refer to the range of the solid solution around the LiPb and Li₇Pb₂ compounds, respectively.

Table 8. Thermodynamic Properties of the Compounds in the Li-Pb System*(Ref. 25)

Compounds	$\Delta H_f^0 \pm 0.3$ kJ/g-atom	$\Delta S_f^0 \pm 1$ J/g-atom, K	$\Delta G_f^0(T=750 \text{ K})$ kJ/g-atom
LiPb	-34.755	-11.192	-26.361
Li ₈ Pb ₃	-41.094	-14.340	-30.339
Li ₃ Pb	-40.606	-14.267	-29.906
Li ₇ Pb ₂	-39.134	-13.417	-29.071
Li ₂₂ Pb ₅	-35.750	-12.575	-26.319

* The thermodynamic properties of formation are estimated for the reaction:

Zinc-Aluminum System

The phase diagram of the aluminum-zinc system²⁸⁻³¹ is shown in Fig. 3. For aluminum-rich alloys of this system in the meta-stable state, the structure of the alloys corresponds to the dotted line in Fig. 4. It follows from the figure that the field of the homogeneous β -solid solution becomes much narrower in this case. It was found that the boundary of β -solid solution is shifted under pressure towards a decrease solubility of zinc in aluminum. According to these references²⁸⁻³¹, The concentration of the β -solid solution, resulting from the application of pressure, is retained at room temperature, and when the alloys are heated without the application of pressure, It rises very slowly (even at 623 K), gradually approaching the equilibrium concentration of the β -solid solution under atmosphere pressure.

In the work of Hilliard et al.²⁶, the thermodynamic data in solid aluminum-zinc solution exhibited a large positive deviation from Raoult's law, and this deviation increased with decreasing temperature. (see Table 9)

Rudman et al.²⁷ had thermodynamic calculation with X-ray results in aluminum-zinc solid solution. The X-ray data indicate that the atoms have almost identical sizes and there is no strain energy contribution between aluminum and zinc atoms.

Gödeny³³ measured the diffusion coefficient of Zn⁶⁵ in Al-Zn solid solution over a range of 0 to 60 wt.% zinc

Figure 3. Phase Diagram of the Zinc-Aluminum System

Figure 4. Diagram of Meta-Stable State of the System Zn-Al in the Range of Aluminum Rich Alloy

Table 9. Thermodynamic Properties of Solid Zn-Al Alloys at 625 K (Ref. 26,30)

x_{Zn}	Phase	ΔG_f° (kJ/g-atom)	ΔH_f° (kJ/g-atom)	ΔS° (J/g-atom,K)	ΔG^E (kJ/g-atom)	ΔS^E (J/g-atom,K)
0.1	α	-0.61	1.30	3.06	1.08	0.33
0.2		-0.71	2.22	4.69	1.88	0.54
0.3		-0.73	2.85	5.69	2.45	0.63
0.4		-0.73	3.18	6.24	2.76	0.63
0.5		-0.73	3.27	6.36	2.87	0.63
		(± 0.15)	(± 0.63)	(± 1.05)	(± 0.15)	(± 1.05)
0.6		-0.69	3.18	6.20	2.80	0.63
0.645	α	-0.65	3.14	6.03	2.72	0.63
0.979	β	-0.15			0.38	

between 588 K(315°C) and 923 K(650°C) (see Fig. 5) In Gmelins Handbuch³⁴, the diffusion coefficient of zinc in aluminum between 673 K(400°C) and 722 K(449°C) are in the range of 10^{-10} to 12×10^{-10} cm²/sec from 0 to 18 wt.% zinc. (see Fig. 6)

Hässner³⁵ investigated the diffusion of Zn⁶⁵ in sintered aluminum containing 13.0 wt.% oxide. The effective diffusion coefficient of Zn⁶⁵ in temperature range 379 ~ 873 K(106 ~ 600°C) can be expressed as follows:

$$D = 109 \exp(-37.3/RT) + 0.88 \exp(-30.9/RT) + 43.7 \cdot 10^{-5} \exp(-13.7/RT), \text{ cm}^2/\text{sec} \quad (2.12)$$

Figure 5. Concentration Dependence of Zn^{65} Diffusivity in Al-Zn Solid Solutions

Figure 6. Concentration Dependence of Zinc in Aluminum
Between 722 K (449°C) and 673 K (400°C)

CHAPTER III

THEORETICAL ANALYSIS

Determination of Activity from Emf Measurements

For the purpose of illustration, consider that one has the following galvanic cell

where A_yB is a general formula which can denote the one-phase solid electrode in question, y is the A/B ratio, and A serves as a source or sink of the electroactive species

A:

Under equilibrium conditions, the open circuit potential of above cell, E , provides a measure of the activity of A, a_A , in the electrode A_yB , since

$$-Z_A F E = RT \ln a_A \quad (3.2.)$$

where Z_A , F , R , and T are the charge number of the electroactive species A in the electrolyte phase, the Faraday constant, the gas constant, and the absolute temperature in K, respectively. The activity coefficient γ_A is expressed as follows:

$$\gamma_A = \frac{a_A}{x_A} \quad (3.3.)$$

where x_A is the molar fraction of species A in the alloy A_yB .

The composition of binary solid A_yB can be systematically changed by passing a current I through the cell. After equilibration following a period of constant-current

passage (current pulse), the change of stoichiometry, Δx_A , is directly related to the concentration difference between the surface concentration and the initial concentration, $(C_s - C_0)$, by the following expression

$$\Delta x_A = V_M (C_s - C_0) = Q/Z_A F n_B = It/Z_A F n_B \quad (3.4.)$$

where V_M is, the molar volume of the electrode sample. Q represents the total charge transferred during the titration corresponding to the potential step E and n_B is the number of moles of the non-electroactive component B. I and t are the current and time interval during titration.

Assume that the activity coefficient obeys the two-suffix Margules equation³⁶

$$RT \ln \gamma_A = A x_B^2 = A(1-x_A)^2 \quad (3.5.)$$

valid mixtures of molecules which are similar in size, shape and chemical nature, where A is an empirical constant with units of energy, the so-called interaction characteristics of components A and B, which depends linearly on the temperature but not on the composition. If there exists a regular solution behavior, this constant can be expressed as follows:

$$A = A' RT \quad (3.6.)$$

where A' is an empirical constant.

Hence Eq. (3.2.) can be expressed as:

$$-Z_A FE = RT \ln x_A + A(1-x_A)^2 \quad (3.7.)$$

or,

$$-Z_A FE/RT = \ln x_A + A'(1-x_A)^2 \quad (3.8.)$$

One can determine x_A from E by Eq. (3.7.) or Eq. (3.8.)

Determination of Diffusion Coefficient by the Galvanostatic Method

One electrochemical method known as galvanostatic intermittent transient technique (GITT) involves the imposition of a constant current I through the cell for a time interval τ . This technique is used to study the kinetics of electrodes in electrochemical cells and combines both transient (polarization) and steady-state (relaxation) measurements. It allows an extensive determination of the kinetic and the thermodynamic properties of A_yB as a function of stoichiometry.

The potential between the working electrode and the reference electrode, E , is measured as a function of time during the current pulse. The latter produces a constant flux of mobile species A across the electrode-electrolyte interface.

The following assumptions are made: (1) one deals with a single-phase diffusion process. (2) The variation of the molar volume of the electrode with composition can be neglected. (3) The diffusion in the solid electrode is the rate-determining process. (since the applied current is very small). (4) Diffusion obeys Fick's second law

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial X^2} \quad (3.9.)$$

where X is the distance into the solid from the electrode-electrolyte interface, C_A the local concentration and D the

diffusion coefficient.

Now the GITT method consists of alternating intervals of (1) Polarization: imposition of constant current and build-up of diffusion resistance. (2) Relaxation: interruption of the current and disappearance of the non-uniformity until steady state is reached. (see Fig. 7).

Cylindrical Diffusion Model^{37,38}

(1) Polarization interval; Diffusion obeys Fisk's second law

$$\frac{\partial C_A^I}{\partial t} = D \left(\frac{\partial^2 C_A^I}{\partial r^2} + \frac{1}{r} \frac{\partial C_A^I}{\partial r} \right) \quad (3.10.)$$

where C_A^I is the local concentration in polarization process, r the radial distance from center of the cylindrical sample electrode. The initial and boundary conditions for this model are

$$C_A^I = C_0 \quad 0 \leq r \leq a, \quad t = 0 \quad (3.11.)$$

$$\left. \frac{\partial C_A^I}{\partial r} \right|_{r=a} = \frac{I}{2\pi a l F D} \quad r = a, \quad 0 < t \leq t_1 \quad (3.12.)$$

where a is the radius of the electrode, C_0 the initial concentration of the electroactive species, l the total length of the wire. F the Faraday constant, t_1 the time period during polarization.

The solution of (Eq. 3.10.) is

Figure 7. Principle of the Galvanostatic Intermittent Transient Technique (GITT)

$$C_A^I(r,t) = C_0 + \frac{I}{\pi \ell F D} \left[\frac{Dt}{a^2} + \frac{r^2}{4a^2} - \frac{1}{8} - \sum_{n=1}^{\infty} \exp\left(-\frac{D\alpha_n^2 t}{a^2}\right) \frac{J_0(\alpha_n r/a)}{\alpha_n^2 J_0(\alpha_n)} \right] \quad (3.13.)$$

where α_n is the positive root of

$$J_1(\alpha) = 0 \quad (3.14.)$$

and the surface concentration is

$$C_s^I(a,t) = C_0 + \frac{I}{\pi \ell F D} \left[\frac{Dt}{a^2} + \frac{1}{8} - \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t/a^2)}{\alpha_n^2} \right] \quad (3.15.)$$

A solution useful for small values of time³⁷⁻³⁹, i.e., $t \ll a^2/D$, is

$$C_A^I(r,t) = C_0 + \frac{I}{\pi a \ell F D} \left[2 \sqrt{\frac{Dt}{r}} \operatorname{ierfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + \frac{Dt(a+3r)}{2\sqrt{a}r^3} i^2 \operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + \dots \right] \quad (3.16.)$$

and the simplest surface concentration is

$$C_s^I = C_0 + \frac{0.5642I}{\pi a \ell F} \sqrt{\frac{t}{D}} \quad (3.17.)$$

(2) Relaxation interval; Diffusion again obeys Fick's second law (see Eq.(3.10.)), but the initial and boundary conditions are

$$C_A^{II}(r,0) = C_A^I(r,t) \quad t=0, \quad 0 \leq r \leq a \quad (3.18.)$$

$$\left. \frac{\partial C_A^{II}}{\partial r} \right|_{r=a} = 0 \quad r=a, \quad 0 < t \leq t_2 \quad (3.19.)$$

where C_A^{II} is the local concentration during the relaxation process, and t_2 is the time period of relaxation.

The solution satisfying these I.C. and B.C. is

$$C_A^{II}(r,t) = C_0 + \frac{I}{\pi l F D} \left\{ \frac{Dt_1}{a^2} + \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2 J_0(\alpha_n)} \cdot \right. \\ \left. \cdot \exp(-D\alpha_n^2 t/a^2) J_0(\alpha_n r/a) [1 - \exp(-D\alpha_n^2 t_1/a^2)] \right\} \quad (3.20.)$$

and the surface concentration is

$$C_s^{II}(a,t) = C_0 + \frac{I}{\pi l F D} \left\{ \frac{Dt_1}{a^2} + \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t/a^2)}{\alpha_n^2} \cdot \right. \\ \left. \cdot [1 - \exp(-D\alpha_n^2 t_1/a^2)] \right\} \quad (3.21.)$$

Spherical Diffusion Model^{37,38}

(1) Polarization interval; Diffusion obeys Fick's second law

$$\frac{\partial C_A^I}{\partial t} = D \left(\frac{\partial^2 C_A^I}{\partial r^2} + \frac{2}{r} \frac{\partial C_A^I}{\partial r} \right) \quad (3.22.)$$

where C_A^I is the local concentration during the polarization process, r is the radial distance from the center of the spherical sample electrode. The initial and boundary conditions for this model are

$$C_A^I = C_0 \quad 0 \leq r \leq a, \quad t=0 \quad (3.23.)$$

$$\left. \frac{\partial C_A^I}{\partial r} \right|_{r=a} = \frac{I}{4\pi a^2 F D} \quad r=a, \quad 0 < t \leq t_1 \quad (3.24.)$$

where a is the radius of the electrode, C_0 is the initial concentration of the electroactive species A. F and t_1 are as defined in the cylindrical diffusion model.

The solution of Eq.(3.22.) is

$$C_A^I(r,t) = C_0 + \frac{3I}{4\pi a F D} \frac{Dt}{a^2} + \frac{1}{6} \frac{r^2}{a^2} - \frac{1}{10} - \frac{2a}{3r} \sum_{n=1}^{\infty} \frac{\sin(\alpha_n r)}{\alpha_n^2 a^2 \sin(\alpha_n a)} \exp(-D\alpha_n^2 t) \quad (3.25.)$$

where $\alpha_n a$ is a positive root of

$$(\alpha_n r) \cot(\alpha_n r) = 1 \quad (3.26.)$$

and the surface concentration is

$$C_s^I(a,t) = C_0 + \frac{3I}{4\pi a F D} \frac{Dt}{a^2} + \frac{1}{15} - \frac{2}{3} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)}{\alpha_n^2 a^2} \quad (3.27.)$$

For very small values of time, i.e., $t \ll a^2/D$, a useful solution is (see Appendix)

$$C_A^I(r,t) = C_0 + \frac{I}{4\pi DrF} \left[-\operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + \exp\left(\frac{Dt}{a^2} - \frac{a-r}{a}\right) \cdot \operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) + \operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}}\right) - \exp\left(\frac{Dt}{a^2} - \frac{a+r}{a}\right) \operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) + \dots \right] \quad (3.28.)$$

In this case the surface concentration can be expressed as follows (see Appendix)

$$C_s^I(a,t) = C_0 + \frac{I}{2\pi a^2 F} \sqrt{\frac{t}{D\pi}} \quad (3.29.)$$

(2) Relaxation interval: Diffusion obeys Fick's second law (Eq. (3.22.)), and the initial and boundary conditions are

$$C_A^{II} = C_A^I(r, t_1) \quad t=0, \quad 0 \leq r \leq a \quad (3.30.)$$

$$\left. \frac{\partial C_A^{II}}{\partial r} \right|_{r=a} = 0 \quad r=a, \quad 0 \leq t \leq t_2 \quad (3.31.)$$

where C_A^{II} and t_2 are as defined in the cylindrical diffusion model. The solution satisfying these I.C. and B.C. is

$$C_A^{II}(r,t) = C_0 + \frac{3I}{4\pi aF} \left\{ \frac{Dt_1}{a^2} + \frac{2}{3} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)}{\alpha_n^2 a^2} \cdot \frac{\sin(\alpha_n r)}{\sin(\alpha_n a)} \left[1 - \exp(-D\alpha_n^2 t_1) \right] \right\} \quad (3.32.)$$

In this case the surface concentration is

$$C_s^{II}(a,t) = C_0 + \frac{3I}{4\pi aF} \left\{ \frac{Dt_1}{a^2} + \frac{2}{3} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)}{\alpha_n^2 a^2} \cdot \left[1 - \exp(-D\alpha_n^2 t_1) \right] \right\} \quad [3.33.]$$

Planar Diffusion Model^{4,37,38}

(1) Polarization interval; This diffusion also obeys Fick's law

$$\frac{\partial C_A^I}{\partial t} = D \frac{\partial^2 C_A^I}{\partial X^2} \quad [3.34.]$$

where X is the distance into the solid from the electrolyte/electrode interface. Under polarizing conditions, the initial and boundary conditions are

$$C_A^I = C_0 \quad 0 \leq X \leq a, \quad t=0 \quad [3.35.]$$

$$D \frac{\partial C_A^I}{\partial X} = \frac{I}{Z_A F S} \quad X=0, \quad 0 < t \leq t_1 \quad [3.36.]$$

$$\frac{\partial C_A^I}{\partial X} = 0 \quad X=a, \quad 0 < t \leq t_1 \quad [3.37.]$$

where S is the surface area common to both the electrolyte and the sample electrode, Z_A , F and t_1 are defined as above. The solution of Eq.[3.34.] satisfying Eq.[3.35.] to [3.37.] is

$$C_A^I(X,t) = C_0 + \frac{2It^{\frac{1}{2}}}{Z_A F S D^{\frac{1}{2}}} \sum_{n=0}^{\infty} \left[\text{ierfc} \frac{(2n+1)a-X}{2(Dt)^{\frac{1}{2}}} + \text{ierfc} \frac{2na+X}{2(Dt)^{\frac{1}{2}}} \right] \quad [3.38.]$$

and an equivalent form:

$$C_A^I(X,t) = C_0 + \frac{It}{Z_A F S a} + \frac{It}{Z_A F S D} \left[\frac{3(a-X) - a}{6a} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{a^2}\right) \cos \frac{n\pi(a-X)}{a} \right] \quad [3.39.]$$

For small values of time, i.e., $t \ll a^2/D$, $C_A^I(0,t)$ yields the expression known to electrochemists as the Sand equation⁴¹

$$C_s^I(t) - C_0 = 2It^{\frac{1}{2}} / Z_A F S (D\pi)^{\frac{1}{2}} \quad [3.40.]$$

In principle, Eq. [3.40.] may be used to evaluate the chemical diffusion coefficient D if the time variation of the surface concentration $C_s(t)$ is known. Unfortunately, the instantaneous value of the concentration at the electrolyte-electrode interface is usually not directly measurable. This difficulty can be avoided for the short-time case by differentiating Eq. [3.40] with respect to the square root of time and then expanding it by ∂E as follows

$$\frac{\partial E}{\partial t^{\frac{1}{2}}} = \frac{2 IV_m}{Z_A F S (D\pi)^{\frac{1}{2}}} \frac{\partial E}{\partial (\Delta X_A)} \quad [3.41.]$$

in which the surface concentration C_s is replaced by the change of stoichiometry ΔX_A through the relationship $C_A = (y + \Delta X_A)/V_m$ for a solid binary compound $A_{y+\Delta X_A}B$. Rearrangement of this expression yields

$$D = \frac{4}{\pi} \left(\frac{IV_m}{Z_A F S} \right)^2 \left[\frac{dE}{d(\Delta X_A)} / \frac{dE}{dt^{\frac{1}{2}}} \right]^2 \quad [3.42.]$$

The diffusion coefficient, D , can be determined from Eq. [3.42.] because all the quantities are either known or experimentally measurable. The quantity $dE/dt^{\frac{1}{2}}$ is directly obtained from the measurement of the potential as a function of time during the constant current pulse (polarization interval). The value of $dE/d(\Delta X_A)$ in the above expression is determined from the slope of the coulometric titration curve, which is obtained by plotting the steady-state equilibrium potential of the electrode

against the composition after each galvanostatic titration step.

(2) Relaxation interval; Diffusion obeys Fick's second law Eq. [3.34.], and the initial and boundary conditions are

$$C_A^{II} = C_A^I(X, t_1) \quad t=0, \quad 0 \leq X \leq a \quad (3.43.)$$

$$\left. \frac{\partial C_A^{II}}{\partial X} \right|_{X=0} = 0 \quad X=0, \quad 0 < t \leq t_2 \quad (3.44.)$$

$$\left. \frac{\partial C_A^{II}}{\partial X} \right|_{X=a} = 0 \quad X=a, \quad 0 < t \leq t_2 \quad (3.45.)$$

where C_A^{II} and t_2 are as defined in the cylindrical and spherical diffusion models. The solution satisfying these I.C. and B.C. is

$$C_A^{II}(X, t) = C_0 + \frac{It_1}{Z_{AFS}a} + \frac{It_1}{Z_{AFSD}} \left(\frac{1}{12} + \frac{2}{\pi^2} \cdot \sum_{n=1,3,\dots}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \cos \frac{n\pi X}{a} \right) \quad (3.46.)$$

and the surface concentration is

$$C_s^{II}(0, t) = C_0 + \frac{It_1}{Z_{AFS}a} + \frac{It_1}{Z_{AFSD}} \left(\frac{1}{12} + \frac{2}{\pi^2} \cdot \sum_{n=1,3,\dots}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \right) \quad (3.47.)$$

CHAPTER IV

EXPERIMENTAL CONSIDERATION

Preparation of the Binary Ca-Al and Zn-Al Alloys

Apparatus

A schematic of the experimental set-up is shown in Fig. 8 and 9.

A one-zone furnace (Lindberg Crucible Furnace, Model 56622, Scientific Products, McGraw Park, Ill.) was used; it has an 18-inch heating zone of diameter 10 cm and generates temperature up to 1473 K (1200°C). The temperature was controlled by a console with excess temperature protection (Lindberg Model 59344B, Scientific Products, McGraw Park, Ill.).

A 95×100 mm dia., 18-inch high quartz tube and cap with 103/60 pyrex joint was used as a container to provide an oxygen and moisture free surroundings for the preparation work.

A polyethylene glove-bag (Inflated size: 27"W × 17"L × 12"H, Thiokol/Ventron Division, Alfa Products, Danvers, Mass.) attached to the top of the quartz tube was utilized for oxygen and moisture free work in the quartz tube and for weighing the sample alloy.

A model O electrolytic oxygen analyzer (Type VAC Manufactures Engineering and Equipment Corp., Warrington, PA) provided an efficient and economical method for the measurement of trace oxygen in the outlet gaseous stream from the

Figure 9. Schematic of the Quartz-Tube System for Alloy Preparation

quartz tube system.

The inert gas supply into the system was pre-purified helium, further purified by passing the gas through reduction stage consisting of a fixed bed of copper shot heated in a cham-shell furnace to 773 K (500°C), to remove traces of oxygen.

Procedures

(1) Calibrate the chromel/alumel thermocouple (Aero-Park, style T-91, Aero Research Instrument Div., Franklin Park, Ill.) contained in an alumina sheath, using an ice bath as a reference junction, by checking the melting points of pure aluminum shot (Alfa Division/Ventron Corp., Danvers, Mass.) and of pure zinc by the cooling curve method⁴² under pre-purified helium.

(2) Check the oxygen content of the gaseous stream existing from the copper reduction furnace.

(3) Weigh a sample of granular CaAl_2 alloy (provided by Argonne National Laboratory, ANL, Argonne, Ill.) and a quantity of pure granular zinc (~ 20 mesh, 99.8% purity, J.T. Baker Chemical Co., Phillipsburg, N.J.) in the helium-filled glove-bag. (Before weighing, the glove-bag was purged by helium five times.)

(4) Mix CaAl_2 or zinc with aluminum shot or wire in the glove-bag in stoichiometric quantities to make $\text{CaAl}_{7\frac{1}{3}}$ or $\text{Zn}_{0.491}\text{Al}_{0.509}$ alloys.

(5) Place the mixed sample in an alumina crucible (5.5 cm O.D., 9.3 cm high) and cover with a small alumina

crucible. (5.6 cm I.D.)

(6) Move the sample-containing crucible into the quartz tube through the glove-bag and purge this tube by helium five times after evacuating the tube and bag by the small vacuum pump in the oxygen analyzer.

(7) Heat the furnace up to 1403 K(1100°C) (for $\text{CaAl}_{7\frac{1}{3}}$ preparation) or 953 K(680°C) (for $\text{Zn}_{0.491}\text{Al}_{0.509}$), for three hours.

(8) Stop the heating and wait till the system cools down to room temperature.

(9) Move the alloy-containing alumina crucible to a helium-filled glove-bag to check the formation of the alloy and remove it for analysis.

Emf Measurements By GITT Method

Experiments were performed using an electrochemical cell consisting of three electrodes, namely, working electrode(WE), counter electrode(CE), and reference electrode (RE) immersed in a molten chloride electrolyte, as follows:

Apparatus

A schematic of the experimental set-up is shown in Fig. 10. a one-zone furnace was used as above.

A Galvanostat/Potentiostat (Princeton Applied Research Co., Model 371, Princeton, N.J.) was used to pass a small

Figure 10. Schematic of the Experimental Set-Up for Emf Measurements

constant current through the cell shown above. The applied current was controlled by a fixed applied potential at the current-control resistor. (Leed's & Northrup Co., Catalog No. 4754, North Wale, PA).

The gas supply to the cell was pre-purified nitrogen, further purified by passing the gas through a fixed bed of copper shot heated in a cham-shell furnace to 773 K(500°C), to remove traces of oxygen.

Cell Configuration

The cell electrolyte was made up of ZnCl_2 and KCl (Analytic Reagent, Mallinckrodt Inc., St. Louis, Missouri), was contained in a 69 mm dia., 148 mm high, 500 c.c. volume cylindrical alumina crucible (Coors Porcelain Co., Model CN-500, Golden, Colorado). The alumina crucible was covered with an aluminum plate. A schematic of the cell is shown in Fig. 11.

The reference electrode and counter electrode of zinc were made by Baker Chemical (~ 20 mesh, 99.8% purity, J.T. Baker Chemical Co., Phillipsburg, N.J.). The working electrode of 2 mm dia. pure aluminum wire, supplied by Alfa Products (Thiokol/Ventron Division, Danvers, Mass.), was placed inside a 10 cm long, 0.64 cm dia. tantalum tube. The tube was closed by two plugs, a plug of 12 mm niobium web (porosity 96.5%) followed by a tantalum frit, similar to that used in Qafisheh's work¹⁴. The tantalum tube was then screwed onto a 40 cm long, 0.64 cm dia. tantalum rod.

A chromel/alumel thermocouple was used as above. The

Figure 11. Cell Configuration for Emf Measurements

potential was recorded vs. time using a strip chart recorder (Model SR-204, Schlumberger Product Corp., St. Joseph, MI) of input impedance 10^7 ohms; it was also independently monitored on a digital multimeter (DMM, Model 4200, Dana Laboratories Inc., Irvine, CA) of input impedance 1,000 milliohms.

Procedure

(1) Four hundred grams of $\text{ZnCl}_2\text{-KCl}$ (eut.) (eut. melting point 501 K, 46 mol.% (31.9 wt.%) KCl)^{42,43} was heated in the alumina crucible at about 633 K (360°C) for 10 hours during the purging of nitrogen. This molten electrolyte was clear and colorless. The molten salt electrolyte was purified by electrolysis at 523 K (250°C) for 10 hours with an impressed potential of 2 volts between graphite electrodes to ensure virtually complete elimination of hydrogen chloride. The electrolysis also served to coagulate a finely divided black substance which always appeared when the salts were first melted²⁶.

(2) The granular zinc, which served as the reference and counter electrode, and an aluminum wire, which served as the working electrode, were dipped 3 cm into the bath.

(3) The potential between the reference electrode and the counter electrode was checked to be approximately 0 mV (± 0.1 mV) by using the digital multimeter (DMM).

(4) Next, Galvanostat/Potentiostat provided a constant current pulse of 5 μA for 30 to 70 minutes.

(5) The current was shut off the emf between working

electrode and reference electrode was recorded or observed while a steady-state value was obtained, for a total of 1 to 2 hour(s).

(6) The emf between working electrode and reference electrode was recorded vs. time at temperature between 569.5 K(296.5°C) and 649.5 K(376.5°C) using a strip chart recorder, and was independently monitored on the digital multimeter (DMM).

(7) Repeat steps (4) and (5) five times.

CHAPTER V

RESULTS AND DISCUSSION

Results of Alloy Preparation

It was found that in the preparation of Zn-Al as well as Ca-Al alloys, aluminum oxidation prevented proper alloying. (the latter was obviously already sensitive to oxidation of the calcium) Therefore the oxygen impurity in the inert gas stream was reduced by leading gas over heated copper shot, by which means oxygen content could be decreased by about 70% of original value which was typically 6ppm.

Since air leakage at the junction between the glove-bag and the quartz tube could not be avoided completely, a thin layer of white-colored aluminum oxide (melting point about 2000 K) formed on the surface of the aluminum wire. The sample, therefore, did not melt homogeneously and mix sufficiently at the operation temperature to form the required alloys.

The material used for the glove-bag (polyethene) was not suitable for high operation temperature since it became soft in the hot gas stream existing from the quartz-tube system; this probably caused the leakage problem. Therefore, aluminum oxidation could not be avoided by the present experimental set-up. It is likely that the Zn-Al alloy may also contain aluminum oxide.

Results of Emf Measurements by GITT Method

The application of a two-suffix Margules equation,

Eq.(3.5.), is shown in Fig. 12. $A(T)$, the empirical constants derived from Eq.(3.5.), are listed in Table 10. $A(T)$ listed in Table 10 shows a tendency of increasing with increasing operation temperature.

It can be seen from Fig. 13 that the steady-state potential is a function of composition for various operation temperature.

The typical transient potential response obtained means of GITT are shown in Fig. 14 to Fig. 17. At small time but larger than 2 minutes, the potential varies linearly with the square root of time as expected from Eq. (3.41.) since the surface diffusion on the wire can be considered as a planar diffusion. Therefore, we utilize Eq.(3.42.) to calculate the diffusion coefficient of zinc in aluminum. Below 2 minutes other effects may cause a deviation from Eq.(3.41.). This could be due to a surface

Table 10. Variation with Temperature of Empirical Constant $A(T)$ in the Two-Suffix Margules Equation for the Binary Solid Solution, Zn-Al

T, K(°C)		A(T), kJ/g-mol
569.5	(296.5)	10.23
599.5	(326.5)	10.34
628.5	(355.5)	10.71
649.5	(376.5)	10.96

Figure 12. Applicability of a Two-Suffix Margules Equation to Zn-Al Binary Alloys

Figure 13. Concentration Dependence of Steady-State Emf in Zn-Al Solid Solution

Figure 14. Time Dependence of Transient (Polarization) Emf Using GITT at 569.5 K (296.5°C)

Figure 15. Time Dependence of Transient (Polarization) Emf Using GITT at 599.5 K (326.5°C)

Figure 16. Time Dependence of Transient (Polarization) Emf Using GITT at 628.5 K (355.5°C)

Figure 17. Time Dependence of Transient (Polarization) Emf Using GITT at 649.5 K (376.5°C)

oxide layer beginning to form on the surface of the working electrode, or a non-uniformity current distribution to the cell at the starting time.

According to Eq.(3.42.) the diffusion coefficient D can be determined from the slope $dE/dt^{\frac{1}{2}}$ and the factor $dE/d(\Delta x_A)$. These two quantities are not affected by the potential drop, IR_b , in the bulk electrolyte between the working electrode and reference electrode. Therefore, ohmic effects in the electrolyte at the interface are totally eliminated when using this simplified form of GITT method.

Fig. 18 shows the diffusion coefficient data obtained by the GITT method as a function of composition for different temperature. These data are larger than those in the work by Gödeny³³ (see Fig. 5), but are in quite good quantitative agreement with the investigation by Hässner, et al.³⁵.

Hässner et al.³⁵ investigated the ratio of D_{eff}/D_v , where D_{eff} is the diffusion coefficient of Zn^{65} in the $\text{Al-Al}_2\text{O}_3$ (13 wt.%) system and D_v is the diffusion of Zn^{65} in the pure aluminum. This ratio is about 10^5 at 373 K (100°C) but 5 at 873 K (600°C) (see Fig. 19). Based on this result, our data would probably be affected by the concentration of aluminum oxide formed in the working electrode.

Hence the factors causing fairly high values of the diffusion coefficient may be ascribed to the following:

- (1) The experimental error.
- (2) The aluminum oxide concentration in solid.

Figure 18. Concentration Dependence of the Diffusion Coefficient of Zinc in Zn-Al Solid Solution

Figure 19. The Variation of the Ratio of D_{eff} / D_v with Operation Temperature (T_m is the Melting Point of Pure Aluminum) (Ref. 35)

electrode. According to the investigation by Hässner et al.³⁵, the lower operation temperature the higher ratio of D_{eff}/D_v .

Fig. 20 shows the temperature dependence of the diffusion coefficient of zinc in aluminum for various stoichiometries. From this figure, there is a tendency for the temperature coefficient to decrease with increasing molar fraction of zinc in this aluminum-rich solid solution. This may also be expressed as a decrease of activation energy with increase of the concentration of zinc in solid-phase alloy. (see Table 11).

Table 11. Variation with Concentration of the Activation Energy for Binary Solid Solution, Zn-Al

Case	$x_{\text{Zn}} \cdot 10^{-5}$	$E_a^*, \text{kJ/g-mol}$
1	0.65	58.21
2	1.30	51.01
3	2.65	36.68
4	4.00	26.91
5	5.30	23.88
6	6.60	20.69

*

$$\frac{d(\ln D)}{d(1/T)} = - \frac{E_a}{R}$$

where E_a is activation energy and R is the gas constant.

Figure 20. Temperature Dependence of the Diffusion Coefficient of Zinc in Zn-Al Solid Solution

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The activity and diffusion coefficient of zinc in aluminum have been measured over a temperature range of 569.5 to 649.5 K, by means of a coulometric titration technique. This technique is convenient and appears to give accurate results for single-phase diffusion.

2. The activity coefficient of zinc in aluminum solid solution was expressed by a two-suffix Margules equation:

$$RT \ln \gamma_{\text{Zn}} = A(1 - x_{\text{Zn}})^2 \quad (6.1.)$$

where A depends on the operation temperature.

3. Aluminum oxidation could not be avoided by the present experimental set-up.

4. Since the diffusion coefficient of zinc in aluminum (e.g. 8×10^{-10} cm²/sec at 628.5 K) was higher than that of zinc in pure aluminum (literature value³³ 10^{-11} cm²/sec at 623 K), it may be concluded that the aluminum oxide concentration in the working electrode was relatively high. (ref. to Fig. 19 of Hässner's work³⁵).

5. The activation energy of diffusion of zinc in aluminum-rich solid-phase alloy was expressed by the equation:

$$D = A \cdot \exp(-E_a/RT), \text{ cm}^2/\text{sec} \quad (6.2.)$$

where A is the pre-exponential factor and has the same units as the diffusion coefficient.

Recommendations

1. It is recommended to use an inert-atmosphere glove box to eliminate the aluminum oxidation problem.

2. Mathematical modelling of two-phase diffusion and comparison with experimental data is necessary to interpret the behavior over a wider range of zinc concentration.

3. Experimental work using different aluminum electrode shapes is desirable for comparison of various diffusion models introduced above.

4. Because the required time for coulometric titration and diffusion from pure metal to two-phase alloy is extremely long, preparation of sample alloys is still necessary in order to study thermodynamic and kinetic properties behavior in the range of the two-phase alloys.

$RT \ln \gamma_{Zn} = A(1-x_{Zn})^2$			
$X: (1-x_{Zn})^2$	$Y: RT \ln \gamma_{Zn}$	Y_{pred}	$S.D. = \frac{\sum (Y - Y_{pred})^2}{n-1}$
T = 649.5 K	0.999986676	11.13	10.95561232
	0.999973353	11.03	10.95546635
	0.999946707	10.96	10.95517442
	0.999920061	10.91	10.95488250
	0.999893416	10.88	10.95457058
	0.999866771	10.82	10.95429867
T = 628.5 K	0.999986104	10.84	10.70558452
	0.999973078	10.76	10.70544507
	0.999947024	10.71	10.70516614
	0.999920918	10.73	10.70488665
	0.999894919	10.59	10.70460832
	0.999868367	10.60	10.70432941
T = 599.5 K	0.999986904	10.51	10.34224125
	0.999973809	10.35	10.34210582
	0.999947619	10.34	10.34183495
	0.999921429	10.25	10.34156408
	0.999895240	10.36	10.34129323
	0.999864686	10.24	10.34097723
T = 569.5 K	0.999987133	10.31	10.22721742
	0.999974266	10.30	10.22703582
	0.999948532	10.30	10.22682263
	0.999922797	10.13	10.22655945
	0.999897066	10.11	10.22629627
	0.999871333	10.21	10.22603309

$$\sum X^2 = 5.999174006$$

$$\sum XY = 65.72550038$$

$$\text{Slope} = \sum XY / \sum X^2 = A$$

$$= 10.95575829$$

$$S.D. = 0.012320788$$

$$\sum X^2 = 5.999181858$$

$$\sum XY = 64.22564094$$

$$\text{Slope} = 10.70573329$$

$$S.D. = 9.1435002-3$$

$$\sum X^2 = 5.999179412$$

$$\sum XY = 62.04577380$$

$$\text{Slope} = 10.34237670$$

$$S.D. = 7.4278016-3$$

$$\sum X^2 = 5.999202294$$

$$\sum XY = 61.35593575$$

$$\text{Slope} = 10.22734902$$

$$S.D. = 8.1259940-3$$

Spherical Diffusion for Small Value of Time in Polarization Interval

The Fick's second law is followed:

$$\frac{\partial C_A}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_A}{\partial r} \right)$$

or,

(A.1.)

$$\frac{\partial C_A}{\partial t} = D \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right)$$

when passing constant current I at the sample electrode,
the initial (I.C.) and boundary (B.C.) conditions are

$$\text{I.C.} \quad C_A = C_0 \quad t=0, \quad 0 \leq r \leq a \quad (\text{A.2.})$$

$$\text{B.C.} \quad C_A = \text{finite} \quad r=0, \quad t>0 \quad (\text{A.3.})$$

$$\left. \frac{\partial C_A}{\partial r} \right|_{r=a} = \frac{I}{4\pi a^2 F D} \quad r=a, \quad t>0 \quad (\text{A.4.})$$

Let $u = (C_A - C_0)r$, then Eq.(A.1.) - (A.4.) become

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2} \quad (\text{A.5.})$$

$$\text{I.C.} \quad u=0, \quad t=0, \quad 0 \leq r \leq a \quad (\text{A.6.})$$

$$\text{B.C.} \quad u=0, \quad r=0, \quad t>0 \quad (\text{A.7.})$$

$$\left(\frac{1}{r} \frac{\partial u}{\partial r} - \frac{u}{r^2} \right)_{r=a} = \frac{I}{4\pi a^2 FD} \quad (A.8.)$$

Take the Laplace transforms of Eq.(A.5.) to Eq.(A.8.)

$$sU - u(r,0) = D \frac{d^2 U}{dr^2} \quad (A.9.)$$

Since $u(r,0) = 0$, and (A.6.)

$$U=0, \quad r=0 \quad (A.10.)$$

$$\left(\frac{1}{r} \frac{\partial U}{\partial r} - \frac{U}{r^2} \right)_{r=a} = \frac{1}{s} \frac{I}{4\pi a^2 FD} \quad (A.11.)$$

the solution of Eq.(A.9.) is

$$U = k_1 \exp\left(\sqrt{\frac{s}{D}} r\right) + k_2 \exp\left(-\sqrt{\frac{s}{D}} r\right) \quad (A.12.)$$

where k_1 and k_2 are arbitrary constants

From Eq.(A.10.)

$$U(0) = k_1 + k_2 = 0 \quad (A.13.)$$

$$\text{we have } k_1 = -k_2 \quad (A.14.)$$

$$\text{and } U = k_1 \left(\exp\left(\sqrt{\frac{s}{D}} r\right) - \exp\left(-\sqrt{\frac{s}{D}} r\right) \right) \quad (A.15.)$$

$$\frac{\partial U}{\partial r} = k_1 \sqrt{\frac{s}{D}} \left(\exp\left(\sqrt{\frac{s}{D}} r\right) + \exp\left(-\sqrt{\frac{s}{D}} r\right) \right) \quad (A.16.)$$

Substitute Eq.(A.14.), (A.15.) into Eq.(A.11.)

$$\frac{k_1}{a} \sqrt{\frac{s}{D}} \left(\exp\left(\sqrt{\frac{s}{D}} a\right) + \exp\left(-\sqrt{\frac{s}{D}} a\right) \right) - \frac{k_1}{a^2} \exp\left(\sqrt{\frac{s}{D}} a\right) - \exp\left(-\sqrt{\frac{s}{D}} a\right) = \frac{1}{s} \frac{I}{4\pi a^2 F D} = \frac{K}{s} \quad (A.17.)$$

Here

$$K = \frac{I}{4\pi a^2 F D} \quad (A.18.)$$

$$k_1 = K \frac{1}{s \left\{ \frac{1}{a} \sqrt{\frac{s}{D}} \left(\exp\left(\sqrt{\frac{s}{D}} a\right) + \exp\left(-\sqrt{\frac{s}{D}} a\right) \right) - \frac{1}{a^2} \left(\exp\left(\sqrt{\frac{s}{D}} a\right) - \exp\left(-\sqrt{\frac{s}{D}} a\right) \right) \right\}} \quad (A.19.)$$

$$U = K a \frac{\exp\left(\sqrt{\frac{s}{D}} r\right) - \exp\left(-\sqrt{\frac{s}{D}} r\right)}{s \left\{ \sqrt{\frac{s}{D}} \left(\exp\left(\sqrt{\frac{s}{D}} a\right) + \exp\left(-\sqrt{\frac{s}{D}} a\right) \right) - \frac{1}{a} \left(\exp\left(\sqrt{\frac{s}{D}} a\right) - \exp\left(-\sqrt{\frac{s}{D}} a\right) \right) \right\}} \quad (A.20.)$$

or,

$$U = K a \frac{\exp\left(-\sqrt{\frac{s}{D}} (a-r)\right) \left(1 - \exp\left(-2\sqrt{\frac{s}{D}} r\right) \right)}{s \left\{ \sqrt{\frac{s}{D}} \left(1 + \exp\left(-2\sqrt{\frac{s}{D}} a\right) \right) - \frac{1}{a} \left(1 - \exp\left(-2\sqrt{\frac{s}{D}} a\right) \right) \right\}} \quad (A.21.)$$

or,

$$U = Ka \frac{\exp\left[-\sqrt{\frac{s}{D}}(a-r)\right]}{s\left(\sqrt{\frac{s}{D}} - \frac{1}{a}\right)} \left[1 - \exp(-2\sqrt{\frac{s}{D}}r)\right] \cdot \left[1 - \frac{\sqrt{\frac{s}{D}} + \frac{1}{a}}{\sqrt{\frac{s}{D}} - \frac{1}{a}} \exp(-2\sqrt{\frac{s}{D}}a) + \dots\right] \quad (A.22.)$$

or,

$$U = Ka \frac{\exp\left[-\sqrt{\frac{s}{D}}(a-r)\right] - \exp\left[-\sqrt{\frac{s}{D}}(a+r)\right]}{s\left(\sqrt{\frac{s}{D}} - \frac{1}{a}\right)} - \frac{Ka}{s\left(\sqrt{\frac{s}{D}} - \frac{1}{a}\right)} \cdot \left\{\exp\left[-\sqrt{\frac{s}{D}}(3a-r)\right] - \exp\left[-\sqrt{\frac{s}{D}}(3a+r)\right] + \dots\right\} \quad (A.23.)$$

Take the first term in the RHS of Eq. [A.18.] and invert the LaPlace transform. Then

$$u = Ka \left[-a \cdot \operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + a \cdot \exp\left(-\frac{a-r}{a} + \frac{Dt}{a^2}\right) \cdot \operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) - \frac{Ka^2}{D} \left\{ -a \cdot \operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}}\right) + a \cdot \exp\left(-\frac{a+r}{a} + \frac{Dt}{a^2}\right) \cdot \operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) \right\} \right] \quad (A.24.)$$

and

$$C_A - C_0 = \frac{Ka^2}{r} \left\{ -\operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + \exp\left(-\frac{a-r}{a} + \frac{Dt}{a^2}\right) \cdot \operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) \right\} - \frac{Ka^2}{r} \left\{ -\operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}}\right) + \exp\left(-\frac{a+r}{a} + \frac{Dt}{a^2}\right) \cdot \operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) \right\} \quad (A.25.)$$

or

$$\begin{aligned}
C_A = C_0 + \frac{I}{4\pi DrF} & \left[-\operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}}\right) + \exp\left(-\frac{a-r}{a} + \frac{\sqrt{Dt}}{a^2}\right) \cdot \right. \\
& \cdot \operatorname{erfc}\left(\frac{a-r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) + \operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}}\right) + \exp\left(-\frac{a+r}{a} + \frac{\sqrt{Dt}}{a^2}\right) \cdot \\
& \left. \cdot \operatorname{erfc}\left(\frac{a+r}{2\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) \right] \quad (A.26.)
\end{aligned}$$

At $r = a$, the surface concentration

$$\begin{aligned}
C_s - C_0 = Ka & \left[-1 + \exp\left(\frac{Dt}{a^2}\right) \operatorname{erfc}\left(-\frac{\sqrt{Dt}}{a}\right) \right] - Ka \cdot \\
& \cdot \left[-\operatorname{erfc}\left(\frac{a}{\sqrt{Dt}}\right) + \exp\left(-2 + \frac{Dt}{a^2}\right) \operatorname{erfc}\left(\frac{a}{\sqrt{Dt}} - \frac{\sqrt{Dt}}{a}\right) \right] \quad (A.27.)
\end{aligned}$$

The first term in the RHS of Eq.(A.21.) is

$$C_s - C_0 = Ka \left[-1 + \exp\left(\frac{Dt}{a^2}\right) \operatorname{erfc}\left(-\frac{\sqrt{Dt}}{a}\right) \right] \quad (A.28.)$$

In such a situation it is preferable to substitute the asymptotic expansions

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3 \cdot 1!} + \frac{x^5}{5 \cdot 3!} - \frac{x^7}{7 \cdot 5!} + \dots \right) \quad (A.29.)$$

$$\operatorname{erfc}(-x) = 1 + \frac{2}{\sqrt{\pi}} \left(x - \frac{x^3}{3 \cdot 1!} + \frac{x^5}{5 \cdot 3!} - \frac{x^7}{7 \cdot 5!} + \dots \right) \quad (A.30.)$$

and

$$\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad (A.31.)$$

One find that Eq.(A.22.) yields

$$C_s - C_0 = Ka \left\{ -1 + \left[1 + \frac{Dt}{a^2} + \left(\frac{Dt}{a^2} \right)^2 / 2! + \left(\frac{Dt}{a^2} \right)^3 / 3! + \dots \right] \right. \\ \left. \left\{ 1 + \frac{2}{\sqrt{\pi}} \left[\frac{\sqrt{Dt}}{a} - \left(\frac{\sqrt{Dt}}{a} \right)^3 / (3 \cdot 1!) + \left(\frac{\sqrt{Dt}}{a} \right)^5 / (5 \cdot 3!) + \dots \right] \right\} \right\} \quad (A.32.)$$

or,

$$C_s - C_0 = Ka \left\{ \frac{2}{\sqrt{\pi}} \frac{\sqrt{Dt}}{a} + \frac{Dt}{a^2} + \frac{2}{\sqrt{\pi}} \left(\frac{\sqrt{Dt}}{a} \right)^3 \left(1 - \frac{1}{3 \cdot 1!} \right) \right. \\ \left. + \dots \right\} \quad (A.33.)$$

Since $\frac{\sqrt{Dt}}{a}$ is very small, we take the first term in the RHS of Eq.(A.33.)

$$C_s - C_0 = 2K \sqrt{\frac{Dt}{\pi}} = \frac{I}{2\pi a^2 F} \sqrt{\frac{t}{D\pi}} \quad (A.34.)$$

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