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AN ATTEMPT TO MEASURE THE DIFFUSION OF ALUMINUM INTO NATURAL ALUMINUM OXIDE

BY

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I. Introduction

A. Background and Theory

The goal of this research was to investigate the diffusion of aluminum ions in natural aluminum oxide grown under atmospheric conditions. The basis for the approach employed here had been developed earlier by J. H. Christian and H. L. Taylor.(1) However, these authors studied the diffusion of aluminum ions in an oxide grown in a pure oxygen atmosphere. They utilized a glass slide upon which aluminum metal was deposited in vacuo (10^{-11} Torr). Oxide was then allowed to grow on this metal by back-filling the vacuum with pure oxygen to a pressure of 40 to 50 m Torr while infrared lamps heated the aluminum metal substrate to 550° K. After again pumping to a low pressure, and with the substrate at room temperature, a second evaporation of aluminum was made which formed the other electrode. Connection was made to these electrodes by metal spring contacts. They determined the diffusion current by measuring the potential drop across a 100 ohm resistor in series with the electrodes.

According to Christian and Taylor(1) there exist four concentration gradients in such an aluminum - aluminum oxide - aluminum structure: an oxygen gradient and an aluminum gradient at each of the aluminum - aluminum oxide - interfaces. At the upper interface (see Figure 1, adapted from reference 1) both the aluminum and oxygen concentration

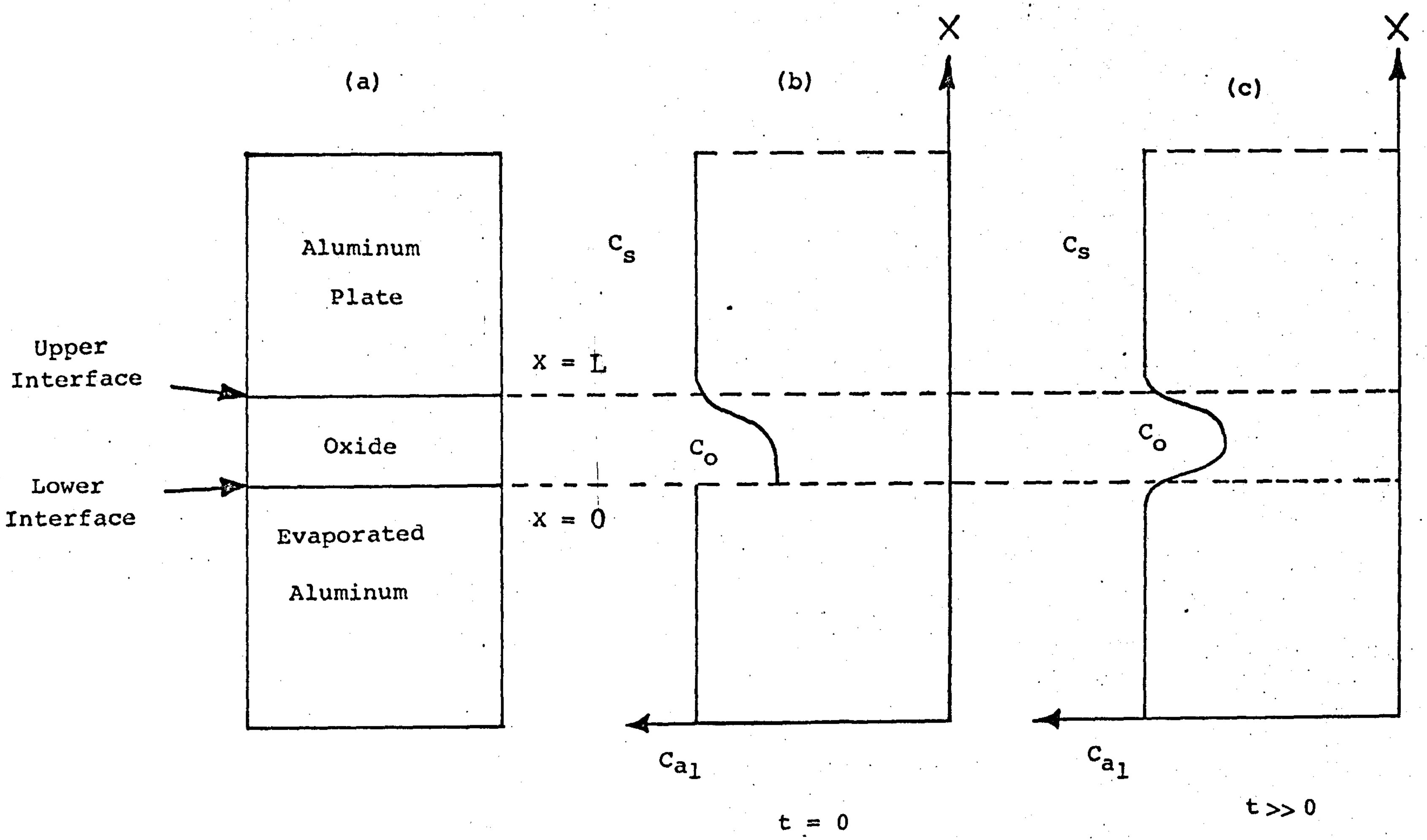


FIGURE 1 - Specimen cross section and concentration distribution profile.

gradients are stable because the reaction rate for thermally grown oxide approaches zero rather quickly. If, now, a layer of aluminum metal is deposited forming a lower interface, an abrupt concentration change exists temporarily for both oxygen and aluminum at this second interface. Figure (1b) illustrates the concentration distribution of aluminum in this aluminum - aluminum oxide - aluminum structure.

It has been shown by Barrer(2) and Smithells(3) that no measurable oxygen diffusion through aluminum is possible because oxygen is insoluble in aluminum. Consideration of the atomic radii of Al° and O° (neutral species) which are 1.4 Å and 0.6 Å, respectively, and of the ionic radii ($Al^{3+} = 0.5$ Å and $O^{2-} = 1.3$ Å) reveals a possible explanation of this fact. When neutral aluminum reacts with the oxide lattice, aluminum ions are formed, and these ions can diffuse much more readily than the oxygen ions because of their smaller radius. Because of this only diffusion of aluminum ions need be considered. Due to the abrupt aluminum concentration change at the lower interface ($X = 0$), gradient induced diffusion should occur if left unimpeded (see Figure 1c). Thus, since ions are diffusing into the oxide, a current is produced which characterizes the magnitude of the diffusion process.

If the two aluminum electrodes are connected by a low resistance circuit, an electron current is established in this circuit which balances the movement of the ions; i.e., any charge attempting to accumulate on the electrodes flows through the external circuit. Thus, with no charge accumulation at the evaporated aluminum interface, the ionic diffusion proceeds unimpeded by an electric field and should be a function of concentration only.

Assuming the oxide layer is to be an isotropic medium, diffusion through this medium should follow Fick's 1st law,(4)

$$\bar{J} = -D \text{ grad } C \qquad (1)$$

where $\bar{J}$ is the instantaneous net flux of diffusing ions and C is the ionic concentration. D is the diffusion coefficient or diffusivity. Since matter is conserved at each point, the time rate of change of the concentration of ions is given by Fick's 2nd law,

$$\frac{\partial c}{\partial t} = \text{div } (D \text{ grad } C). \qquad (2)$$

If the direction of motion of the diffusing ions is assumed to be the x-direction, these equations simplify to

$$J = -D_x \frac{\partial c}{\partial x} \qquad (3)$$

and

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} (D_x \frac{\partial c}{\partial x}). \qquad (4)$$

Furthermore, if D is independent of composition and, therefore, position in the medium, equation (4) can be written

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \qquad (5)$$

If J and C have the units of $g/(cm^2\text{-sec})$ and g/cm^3, respectively, then the units of D are cm^2/sec. Thus, $\partial c/\partial t$ is the rate of change of concentration with time from which diffusion arises.

The solution to Fick's 2nd law under the initial and boundary conditions depicted in Figure (1) is

$$C(x,t) = C_o + \left\{(C_s-C_o)/2\right\} \left\{1 + \text{erf}\left[(x/2)\ (D_x t)^{1/2}\right]\right\}.^{(1)} \qquad (6)$$

where C = concentration, C_o = initial concentration of aluminum in aluminum oxide, C_s = concentration of aluminum in the upper aluminum electrode, x = distance, t = time, D_x = diffusion coefficient in the x-direction (assumed constant). It is shown in the appendix that this solution leads to the following expression for the diffusion current if the two electrodes are shorted together:

$$I_{sc} = (1/2)\ AQ\ (C_s-C_o)\ (D_x/\pi)^{1/2}\ t^{-1/2}, \qquad (7)$$

Where I_{sc} = ionic current, Q = charge of aluminum ion, and A = active area of the cell. From this equation, it is seen that a plot of I_{sc} vs $t^{-1/2}$ yields a straight line. Since this is a linear equation of form $I_{sc} = Kt^{-1/2}$, where $K = (1/2)\ QA\ (C_s-C_o)\ (D_x/\pi)^{1/2}$ and Q, A, (C_s-C_o) are constant, D_x can be determined from the slope. Using this theory, Christian and Taylor determined D_x to be 5.8×10^{-19} cm²/sec. The diffusion currents they measured ranged from 0.10 to 0.30 μa at 25 seconds and decreased to zero in 400 seconds or less.

In the above theory, diffusion resulting from a concentration gradient is the only mechanism considered. Should chemical reactions occur at the interface (as might be the case where absorbed oxygen and water vapor are present), one would not expect the theory to adequately describe the situation.

II. Experimental Methods

A. Materials

The material used in this study was aluminum sheet, 1/16" thick, for the upper electrode, and foil, 0.004" thick, for evaporation to form the lower electrode. The purity of each was 99.99 percent.

B. Equipment and Procedure

Figure 2 shows the arrangement used for evaporating aluminum onto the natural oxide on the lower side of the aluminum plate. A Lucite disk fastened to the lower side of this plate served to support and insulate wires used to make connection to the evaporated films. These electrode wires (0.010 inch diameter gold) were embedded in the Lucite disk, and their exposed ends were covered with silver paint to facilitate contact with the films. Thus, simultaneous connection was made to a wire and to the aluminum oxide when a film was evaporated.

Eastman 910 epoxy was used throughout the experiments to anchor the wires and to fasten the Lucite plate edge to the aluminum sheet. It was found earlier that a microscopic chasm existed between the Lucite and the aluminum sheet. This amounted to a small step which the evaporated aluminum could not bridge to make contact with the wire. Hence, the 910 epoxy was used to fill in this gap.

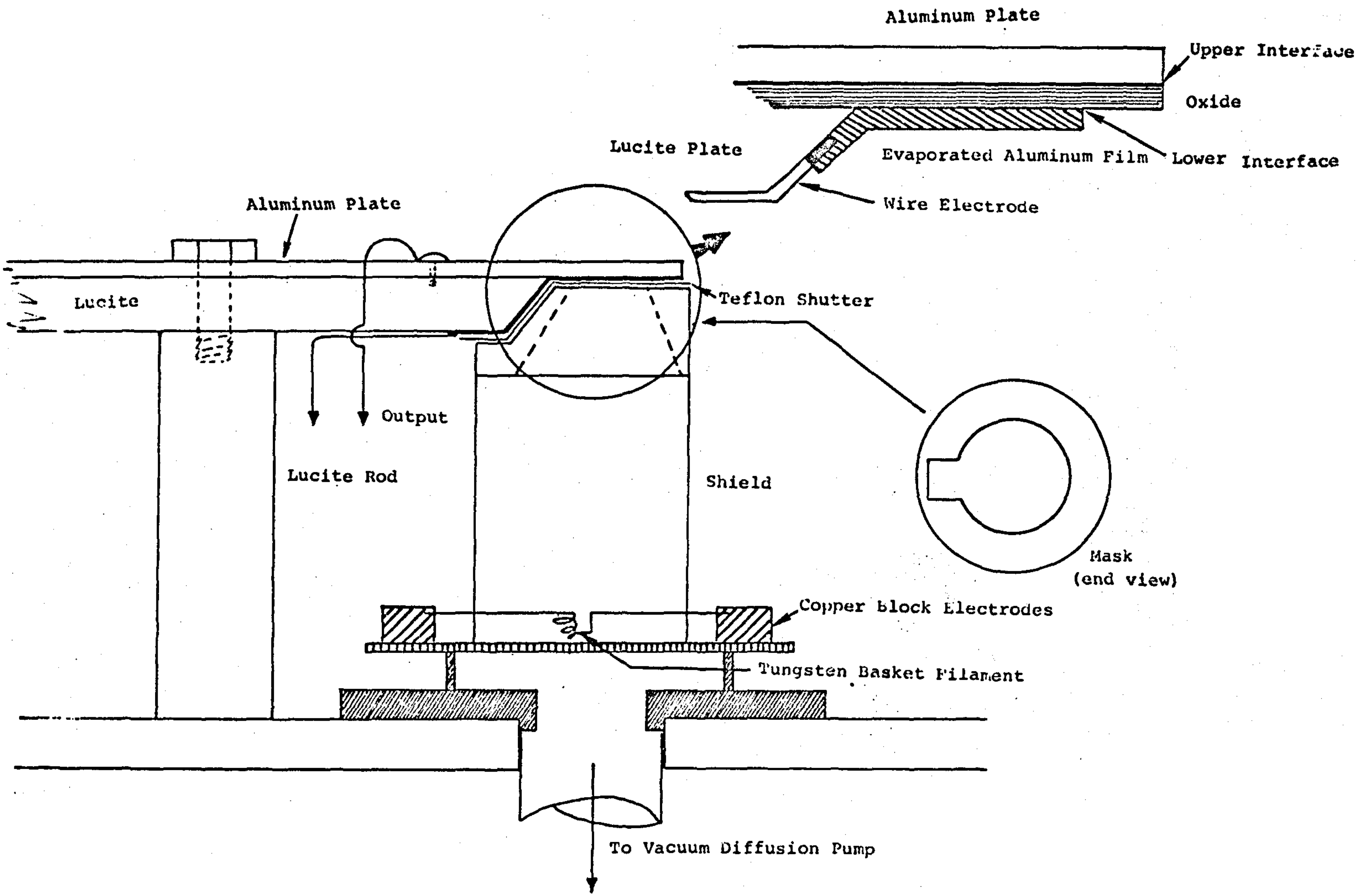


FIGURE 2 - Experimental arrangement for evaporation.

The procedure for evaporation was follows: About 0.15 gm of aluminum foil was placed in the basket filament, and the system was evacuated to 10^{-4} Torr. Then a D.C. voltage was applied to the filament for 15 seconds during which time it reached white heat. This insured the melting of the foil and some evaporation before the shutter was opened. The shutter was then opened to allow aluminum to be deposited on the oxide. Some times the shutter was closed immediately after the film was formed which generally took less than 15 seconds. Other times it was left open for a full 15 seconds and then closed. When the shutter was opened for 15 seconds the resulting deposited film was approximately 2 microns thick. Each time after the shutter was closed the filament voltage was removed. A D.C. current was used to heat the filament to prevent A.C. pick-up by the voltmeter. This pick-up was very noticeable at times since the output voltage of the system was in the order of microvolts.

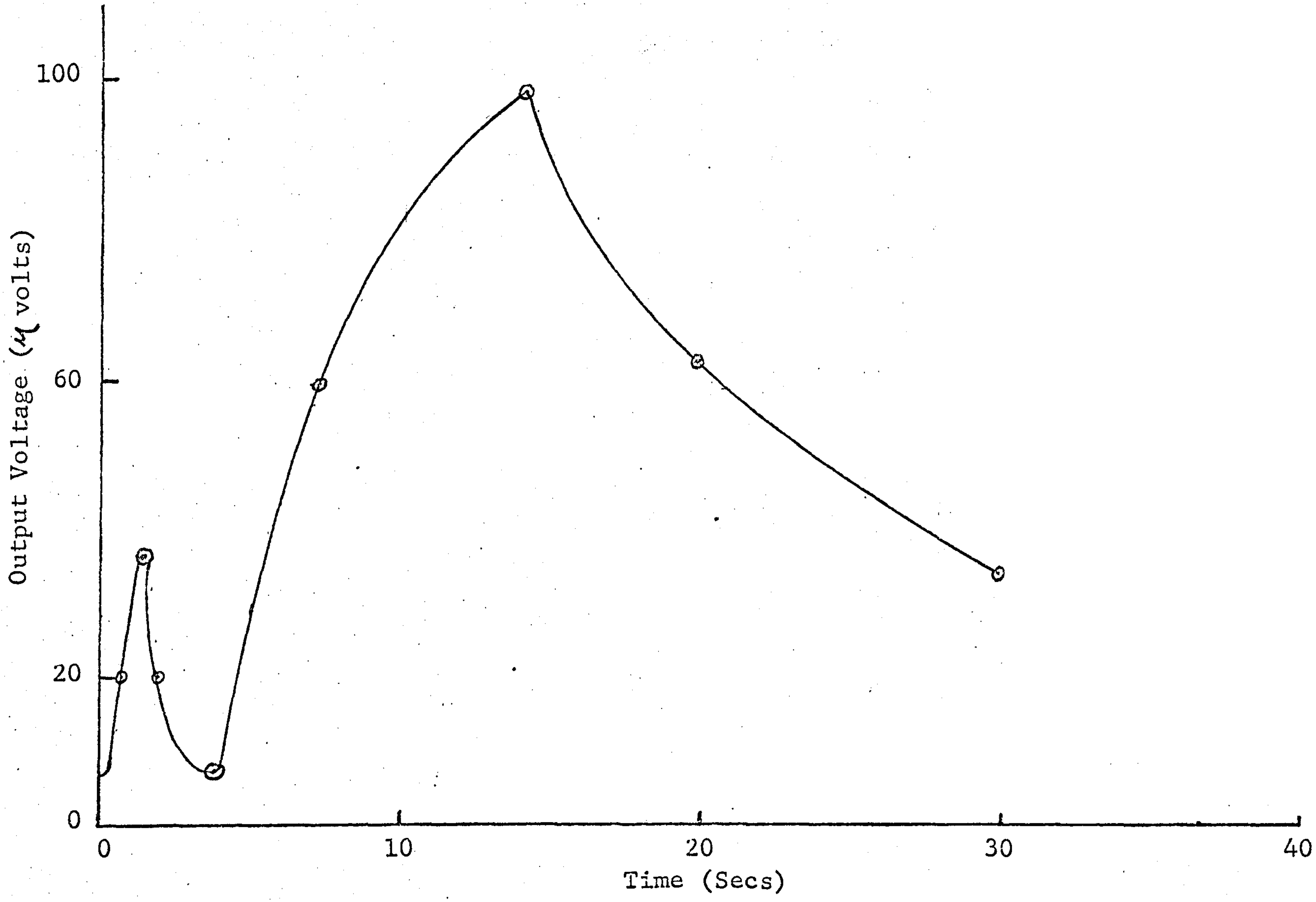
In order to detect the diffusion current, the voltage drop across a 100 ohm resistor connecting the electrodes was observed. The voltmeter used to measure this potential drop was a Keithley nanovoltmeter, model 148. The output of the voltmeter was recorded on a model G-14 Varian strip chart recorder running at a speed of 12 inches per minute. Hence, an output voltage, proportional to diffusion current, could be determined as a function of time.

III Results and Discussion

In the first few runs it was obvious that an aluminum film had been deposited for a voltage "spike" was noted on the recorder when the evaporated film made contact between the oxide and the electrode wire. (This spike, indicating a film was complete, is indicated in Figure 3.) This produced a system consisting of gold wire, silver paint, aluminum film, oxide and aluminum plate, all in series. Verification of contact between the wire and the film was obtained by utilizing an ohmmeter to check continuity of the system after each run. The resistance of the oxide layer was usually 3 ohms.

Voltages up to 100 microvolts were observed and these voltages subsequently decayed as seen in Figure 3. Investigation of the decay of these voltages indicated that they did not vary as $t^{-1/2}$ as reported by Christian and Taylor. Furthermore, they were of opposite polarity to that expected for diffusion of aluminum ions.(5)

This led to a study of possible thermal emf's as a source of these potentials. In this investigation the same arrangement was employed except that the plate was inverted, and a previously deposited film was heated by an infrared lamp. Insulated thermocouples were attached to the aluminum plate directly underneath the film and to the film itself. The film was then heated. The voltage output and temperature is shown in Figure 4. As can be seen, the voltage is dependent on the difference in temperature between the film



<u>Figure 3</u> - Plot of typical output voltage vs. time with Au wire.

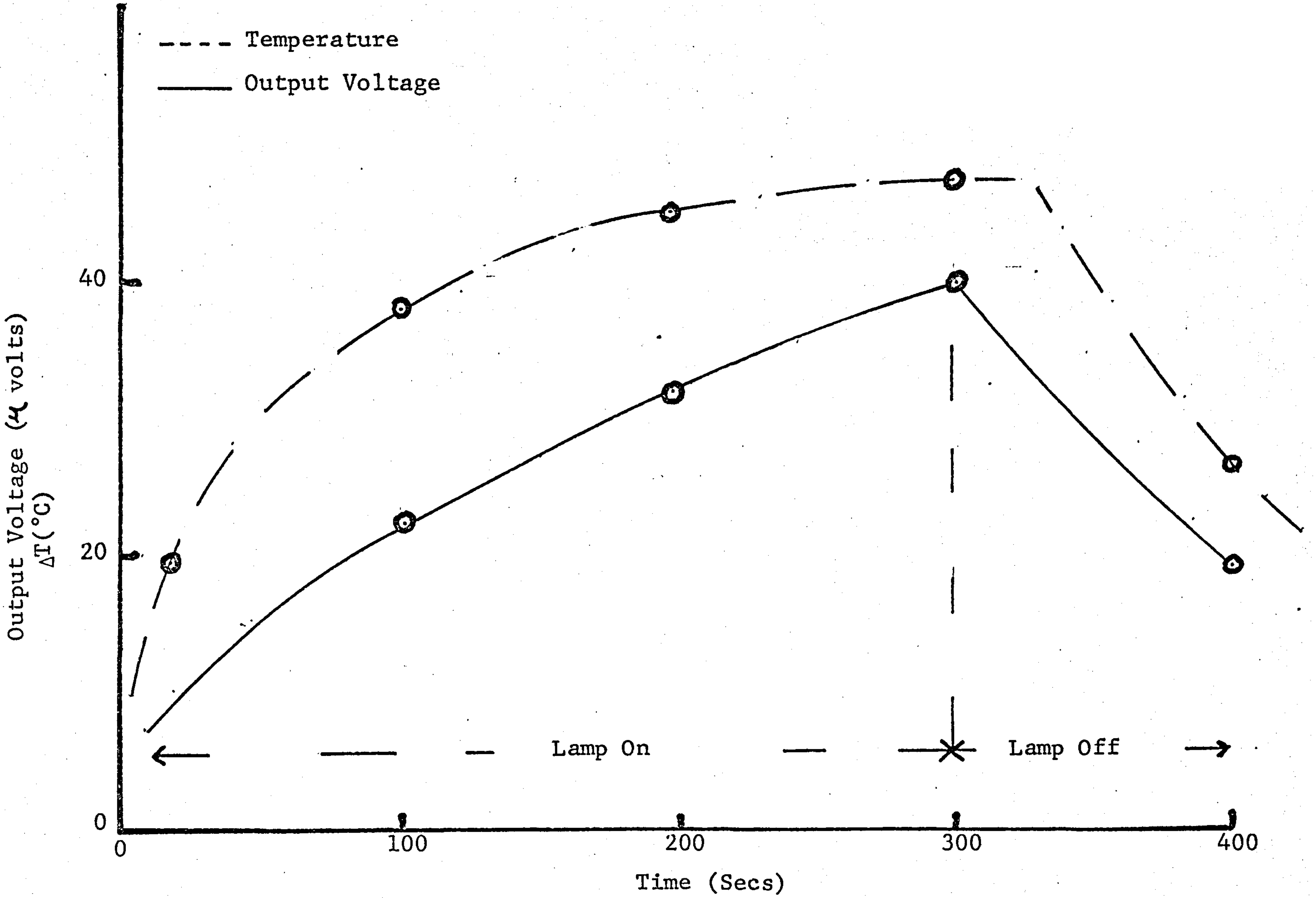


Figure 4 - Plot of output voltage and temperature vs. time while heating with infrared lamp (with Au wire).

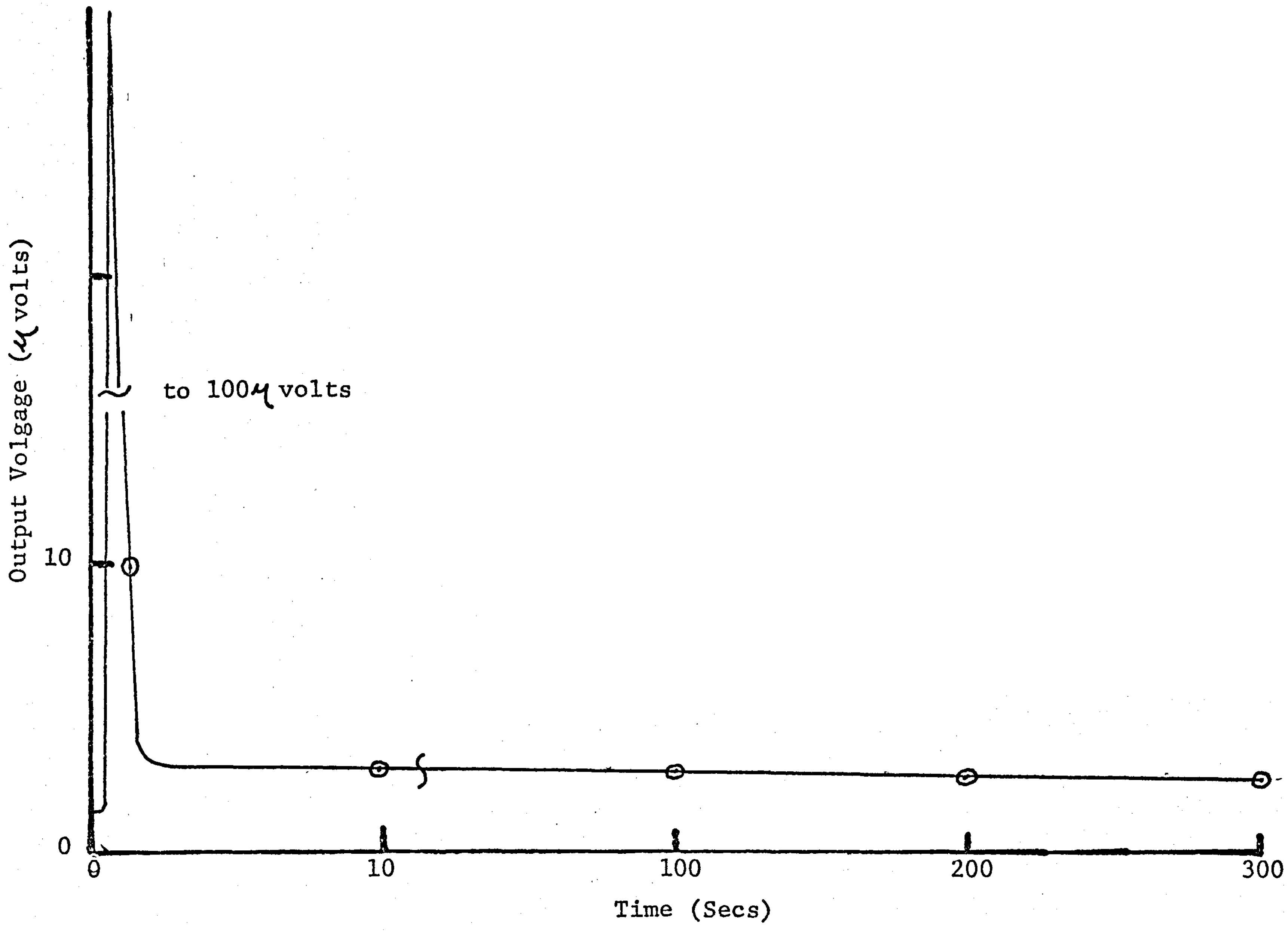
and plate. This also correlates with Figure 3 except for the initial "spike". Suspecting thermal emf's, the junction of the gold, silver, and aluminum film was heated, and the same variation of output voltage versus temperature was observed. It was obvious by this time that the thermal emf's caused by the different metal junctions were overshadowing any diffusion current that might be present.

This led to replacing the gold wire with aluminum wire and eliminating the silver paint in order to reduce the thermal emf's. Figure 5 illustrates the results of one of three reproducible experiments performed after these changes were made. These are as follows:

1. The polarity of the spike is opposite to that expected from the diffusion of aluminum ions moving into the oxide.

2. After the initial spike, the magnitude of the potential is about 3 microvolts which was shown to be a thermal emf probably resulting from impure aluminum wire used. Christian and Taylor observed 25 microvolts after 25 seconds and a minimum of 3 microvolts after 2.5 minutes. In the present experiment the area of deposited aluminum was about three times that used by Christian and Taylor. Since the diffusion current is directly proportional to area, output voltages due to diffusions should have been at least three times larger than theirs. This was never observed.

3. The initial pulse or spike reveals several points. First, its leading edge indicates the time at which system continuity occurs. Second, the time duration of the spike and its decay time is much too small to result from the diffusion of aluminum ions. Such decay times should be in the



<u>Figure 5</u> - Output voltage vs. time (aluminum wire)

order of minutes. Thus, this width and decay time do not indicate diffusion of the type found by Christian and Taylor. Instead it suggests the following possibilities:

a) Earlier work indicated that after system continuity was complete, any disturbance - such as opening the circuit - created voltage spikes. This may have been an experimental effect due to electromagnetic pick-up from the surrounding equipment.

b) The energ~~e~~y of the striking aluminum atoms may be quite high, thus causing a thermal emf between the deposited aluminum film and the oxide.

c) The most likely answer lies in the oxide itself. It is known that H_2O in the form of $Al_2O_3 \cdot H_2O$ or as vapor absorbed by the oxide is present since the oxide was exposed to the atmosphere.(6) It is then highly possible that some form of chemical reaction occurs between the water and the aluminum atoms. If this is true, then the first few layers of deposited aluminum react with the water forming another oxide layer and hence blocking the diffusion of aluminum ions into the original oxide.

In summary, it is concluded from the above results that no appreciable diffusion of aluminum ions occurs in natural aluminum oxide. This conclusion is based on the fact that the approximate 3μv potential shown in Figure 5 had the opposite polarity from that expected for the diffusion of aluminum ions and that it was again observed when the film was heated after deposition. Therefore, if diffusion existed, the diffusion current did not exceed 5×10^{-9} amperes. This lack of diffusion probably results from the chemical reaction of the ions with water or other impurities (i.e. oxygen) in the oxide to form more oxide at the interface. The trapping of the ions in imperfections in the oxide is also a possible explanation for the absence of diffusion.

APPENDIX I

Shown below is the derivation of equation 7 developed by Christian and Taylor using Fick's 1st law assuming their solution of (equation 6) Fick's 2nd law:

Now,

$$C(x,t) = C_o + \left\{\frac{(C_s - C_o)}{2}\right\}\left\{1 + \text{erf}\left[\left(\frac{x}{2}\right)(D_x t)^{1/2}\right]\right\} \qquad (1)$$

$$C(x,t) = C_o + \left\{\frac{(C_s - C_o)}{2}\right\}\left\{1 + \text{erf}\left[\left(\frac{x}{2}\right)\left(D_x t\right)^{1/2}\right]\right\}$$

$$\text{Where erf } Y = \frac{2}{\sqrt{\pi}}\int_0^Y e^{-x^2}\,dx = \frac{2Y}{\sqrt{\pi}}\left(1 - \frac{Y^2}{3} + \frac{Y^4}{10} - \frac{Y^6}{42} + \dots\right) \qquad (2)$$

$$C(x,t) = C_o + \left\{\frac{(C_s - C_o)}{2}\right\}\left\{1 + \frac{2}{\sqrt{\pi}}\left[\frac{x}{2}(D_x t)^{-1/2}\right] - \frac{2}{3\sqrt{\pi}}\left[\frac{x}{2}(D_x t)^{-1/2}\right]^3\right\} + \dots$$

$$C(x,t) = C_o + \frac{(C_s - C_o)}{2}\left[1 + \left(\frac{x}{\sqrt{\pi}}(D_x t)^{-1/2}\right) - \left(\frac{x^3}{12\sqrt{\pi}}(D_x t)^{-3/2}\right) + \dots\right]$$

$$\text{and } \frac{\partial C(x,t)}{\partial x} = \frac{C_s - C_o}{2}\left[\frac{(D_x t)^{-1/2}}{\sqrt{\pi}} - \frac{3x^2}{12\sqrt{\pi}}(D_x t)^{-3/2} + \dots\right]$$

$$\frac{\partial C(x,t)}{\partial x} = \frac{C_s - C_o}{2}\left[\frac{1}{(\pi D_x t)^{1/2}} - \frac{3x^2}{12\,(\pi D_x^3 t^3)^{1/2}} + \dots\right]$$

Using Fick's first law,

$$J\ (x,t) = Q\ D_x\ \frac{\partial c\ (x,t)}{\partial x}$$

we get

$$J\ (x,t) = Q\ D_x \left(\frac{C_s - C_o}{2}\right)\left[\frac{1}{(\pi D_x t)^{1/2}} - \frac{3x^2}{12(\pi D_x^3\ t^3)^{1/2}} + \cdots\right]$$

Evaluating this at x = o, the interface current density becomes

$$J\ (o,t) = Q\ D_x\ \frac{(C_s - C_o)}{2}\left[(\pi D_x t)^{-1/2}\right]$$

$$J\ (o,t) = Q\ D_x^{1/2}\ \ \pi^{-1/2}\ \frac{(C_s - C_o)}{2}\ (t)^{-1/2}$$

$$J\ (o,t) = Q\left(\frac{D_x}{\pi}\right)^{1/2}\left(1/2\right)(C_s - C_o)\ t^{-1/2}$$

Since I = JA the magnitude of the observed current is

$$I = \frac{Q}{2}\ A\ (C_s - C_o)\left(\frac{D_x}{\pi}\right)^{1/2}\ (t)^{-1/2}$$

BIBLIOGRAPHY

1. J. H. Christian, H. L. Taylor, J. of Applied Physics, 38, #10, p 3843, September, 1967.

2. R. M. Barrer, Diffusion in and Through Solids, (Cambridge University Press, Cambridge, England, 1951).

3. C. J. Smithells, Metals Reference Book (Butterworths Scientific Publications Ltd., London, 1962), Vol. II, 3rd Edition.

4. W. Jost, Diffusion In Solids, Liquids, and Gases, (Academic Press Inc., New York, 1963).

5. F. C. Collins, T. Nakayama, J. of The Electrochemical Society, 114, #2, p 167, February, 1967, Part I.

6. Hogues et al, Qual. Analysis and Chemical Equilibrium, (Holt, Rinehart, and Winston, Inc., 5th Edition, New York).

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