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Strips of copper foil were plated with a thin deposit of radioactive copper and the specimens then oxidized in air at 800°, 900°, 1000°C. From the distribution of radioactive copper in the oxide diffusion coefficients, D, for cuprous ion in cuprous oxide were calculated. Over the temperature range D was found to be $0.0358 \exp(-37,000/RT)$ cm^2 sec.$^{-1}$. The activation energy for the oxidation of copper is 39 ± 2 kcal./mole, so that these measurements provide further evidence that diffusion of Cu$^+$ in Cu$_2$O is the rate-determining step in the oxidation.

BARDEEN, Brattain, and Shockley[1] have recently determined the distribution, after oxidation in air at 1000°C, of radioactive copper deposited in a thin layer on a copper blank. The results were interpreted in terms of Wagner's[2] theory of oxidation. We have made more extensive measurements of the same kind over a range of temperatures, and from our data have derived values for the diffusion coefficient of Cu$^+$ in Cu$_2$O under the conditions of the oxidation process.

EXPERIMENTAL PROCEDURE

Copper 64, a β-emitter of 12.8-hours half-life, was prepared by a d, p reaction with copper 63. We are indebted to Dr. D. B .Cowie and Dr. M. A. Tuve of the Carnegie Institution of Washington for their kind cooperation in supplying this material. After separation from the cyclotron target, the copper was precipitated as thiocyanate, ignited to CuO, and made up into a cyanide plating solution.[3] The copper was plated at 6 volts and a current density of 4 ma/cm^2 on both sides of a strip of copper foil $2 \times 7.5 \times 0.005$ cm. The calculated thickness of the deposit of copper was around 10^{-5} cm. The total count, measured with a Victoreen VG-10 Geiger counter and a Herbach and Rademann GL532B scaling circuit, was 3000 to 4000 counts per minute.

After weighing, the strips were suspended in air in a furnace for times varying from 0.50 to 2.00 minutes. The temperature was controlled manually within ± 5°C. Oxidations were made at 800°, 900°, and 1000°C. The time required for the thin strip to reach the furnace temperature uniformly was calculated on the assumption that the slow step in the heating is conduction of heat from the surface to the interior. This time was of the order of 4×10^{-2} second.

After oxidation, the strip was reweighed, the calculated thickness of the oxide being 1 to 2×10^{-3} cm. One side of the active area was coated with Glyptal, and the strip was dried in an oven at 100°C. The exposed active area was etched in 1:3 hydrochloric acid to remove successive layers of the oxide. Four etchings were made. The copper in the solutions was precipitated as CuCNS, which was filtered off on filter paper, dried, and counted on the filter paper. The precipitate was then dissolved and analyzed colorimetrically for copper. The total copper found by analysis was generally a few percent

TABLE I. Typical data showing the distribution of radioactivity in the different layers of Cu$_2$O. Layers are numbered beginning at the oxide-gas interface. Count is corrected for background.

800° Layer No.	% total thickness	% total count	900° Layer No.	% total thickness	% total count	1000° Layer No.	% total thickness	% total count
1	32	50	1	17	27	1	25	43
2	28	34	2	19	26	2	24	35
3	32	13	3	27	20	3	24	15
4	8	3	4	37	27	4	27	7
Total thickness: 1.12 ×10^{-3} cm			Total thickness: 2.19 ×10^{-3} cm			Total thickness: 2.12 ×10^{-3} cm		
Total time: 120 sec.			Total time: 120 sec.			Total time: 30 sec.		
1	33	55	1	21	34	1	34	58
2	43	35	2	24	38	2	33	32
3	24	10	3	26	20	3	22	7
4	—	—	4	29	8	4	11	3
Total thickness: 0.91 ×10^{-3} cm			Total thickness: 2.36 ×10^{-3} cm			Total thickness: 2.15 ×10^{-3} cm		
Total time: 120 sec.			Total time: 120 sec.			Total time: 30 sec.		

[1] J. Bardeen, W. H. Brattain, and W. Shockley, J. Chem. Phys. **14**, 714 (1946).

[2] C. Wagner and K. Grunewald, Zeits. f. physik. Chemie **B40**, 455 (1938).

[3] H. J. Creighton and W. A. Koehler, *Principles and Applications of Electrochemistry* (John Wiley and Sons, Inc., New York, 1935), Vol. II, p. 117.

TABLE II. Values of the diffusion coefficient computed from the data of Table I by the use of Eq. (2).

| 800°C		900°C		1000°C	
Layer No.	$D \times 10^{10}$	Layer No.	$D \times 10^{10}$	Layer No.	$D \times 10^{10}$
1	11.8	1	48.5	1	145
2	9.5	2	49.6	2	120
3	9.4	3	65.2	3	122
1	6.6	1	52.9	1	137
2	7.4	2	40.3	2	128
1	10.7	3	38.2	3	130
2	8.4			*1	(145)
1	11.4			*2	(123)
2	9.1			*3	(115)
Average: 9.4±1.3		Average: 49.1±6.8		Average: 130±7	

* Data of Bardeen et al.

higher than that calculated from the weight gain on oxidation, indicating, perhaps, a slight attack on the underlying copper during etching.

RESULTS AND DISCUSSION

Typical data from the experiments are tabulated in Table I. In order to evaluate diffusion coefficients from these data, the solution of the diffusion equation for diffusion into a semi-infinite solid from an instantaneous plane source was employed.[4] This has the form

$$C = \frac{Q}{(\pi Dt)^{\frac{1}{2}}} \exp(-x^2/4Dt), \qquad (1)$$
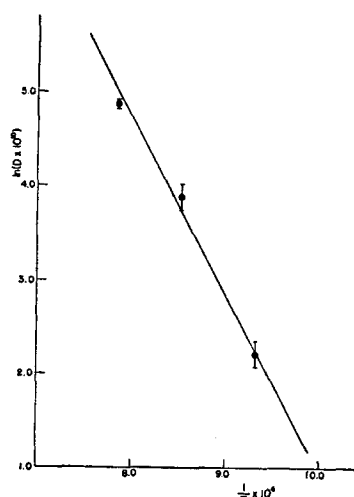
FIG. 1. Variation of D with temperature.

[4] R. M. Barrer, *Diffusion in and through Solids* (Cambridge University Press, Teddington, England, 1941), p. 43 ff.

where C is the concentration of radioactive copper at the point x, Q is the total quantity of radioactive copper, D is the diffusion coefficient, t is the time of the diffusion, and the origin is at the oxide-gas interface.

The use of Eq. (1) is equivalent to the physical assumption that the distribution of the radioactive copper throughout the oxide will be essentially the same as would be obtained if an equivalent amount of radioactive cuprous oxide were deposited on top of a cuprous oxide strip and this specimen maintained at temperature for a time equal to that in the oxidation experiments. This assumption seems reasonable in view of the fact that the thickness of radioactive copper originally deposited on the strip is very much less than the thickness of oxide finally obtained; as a result, the thickness corresponding to the original active deposit is oxidized in a time which is (roughly) less than one-thousandth of the total time of oxidation. Hence, it seems that the great part of the diffusion of the radioactive Cu^+ must be from an active layer of oxide into another layer of oxide. The approximation of the semi-infinite solid is supported by the observed approach of the activity in the layer adjacent to the metal interface to a low value. It is true, of course, that the cuprous oxide which is being studied is not ordinary equilibrium Cu_2O, so that the diffusion coefficient is not necessarily that for equilibrium Cu_2O, but rather that for the particular slab of Cu_2O formed on oxidation.

Equation (1) can be brought into convenient form for calculation by dividing through by Q and integrating from a to b to give the fraction of activity between a and b. The result is

$$\int_a^b \frac{C}{Q} dx = f_{ab} = H\left(\frac{b}{2(Dt)^{\frac{1}{2}}}\right) - H\left(\frac{a}{2(Dt)^{\frac{1}{2}}}\right), \quad (2)$$

where f_{ab} is the fraction of activity between a and b, and $H(t)$ is the error function. Since f_{ab}, a, b, and t are known, D can be calculated.

Table II shows the values of D at the three temperatures and the average values. The value of D has also been computed from the data of Bardeen, Brattain, and Shockley. This value is within 2 percent of our value at 1000°C. Although the values of D vary from layer to layer, there is not a very marked dependence on layer number.

In Fig. 1, the logarithm of D is plotted against $1/T$, and a straight line has been drawn through the points. From the slope of the line an activation energy of 37 kcal. is obtained for the diffusion.

This energy of activation for the diffusion agrees within experimental error with the energy of activation of the oxidation reaction. The data of Pilling and Bedworth[5] yield an energy of activation of 40 kcal.[6] between 800 and 1000°C. The weight gain data from the present experiment correspond to an energy of activation of 38 ± 3 kcal. These activation energies provide additional evidence that diffusion of copper in cuprous oxide is the rate determining step in the oxidation reaction.

The Eyring equation[7] for the diffusion constant is

$$D = d^2 \frac{kT}{h} \exp(\Delta S^{\neq}/R) \exp(-\Delta H^{\neq}/RT). \quad (3)$$

The value of the frequency factor calculated

from Fig. 1 is 0.0358 cm² sec.⁻¹. If the observed energy of activation is set equal to $\Delta H^{\neq}$, and d is taken as the equilibrium separation of the Cu⁺ ions in Cu_2O (3.01×10^{-8} cm), the entropy of activation, $\Delta S^{\neq}$, from Eq. (3), is 0.8 e.u.

The value of D at 1000°C can be calculated from the theoretical expressions

$$v = \sigma\tau/en, \quad (4)$$

$$eD = vkT. \quad (5)$$

Here v is the mobility of the Cu⁺ ion, σ is the electrical conductivity of Cu_2O, τ is the transport number of the Cu⁺ ions, n is the number of copper ions per cc in Cu_2O. The experimental values of these quantities are[8] $\sigma = 4.8$ ohm⁻¹ cm⁻¹, $\tau = 4\times10^{-4}$, $n = 5.05\times10^{22}$/cc. This calculation yields a value for D at 1000°C of 260×10^{-10} cm² sec.⁻¹, as compared with our average value of 130×10^{-10} cm² sec.⁻¹. This difference might be ascribed to the fact that Eq. (5) is derived for a condition of no net flow of current, while the apparent diffusion coefficient is measured during growth of the oxide film.

ACKNOWLEDGMENT

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[7] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 539.

[8] C. Wagner, Zeits. f. physik Chemie B21, 25 (1933).