Low Temperature Oxidation of Copper. I. Physical Mechanism[1a]

BY T. N. RHODIN, JR.[1b]

Introduction

The ambiguity of the experimental picture in the field of the oxidation of metal surfaces can be considerably diminished by a precise evaluation of the physical characteristics of some metal–oxygen systems. Some of the ambiguities have been caused by neglect of the following general factors: the extent and structure of the metal surface, the physical and compositional non-uniformity of the oxide film, and the lack of proper consideration for the boundary conditions imposed by the range of film thicknesses and temperatures considered. A low temperature oxidation study of single crystal copper surfaces is a promising system to study from this point of view. The thin films formed at low temperatures are essentially physically and mechanically homogeneous, and there exists considerable information on the semi-conductor properties of copper and its oxides.[1c] In addition, the structure and orientation characteristics of cuprous oxide films formed at low temperatures have been thoroughly investigated and defined.[2] It is very likely that an insight into the fundamental mechanism of oxidation under these more favorable conditions may well be extrapolated to higher temperatures with suitable modifications.

At low temperatures oxidation occurs rapidly at first but practically ceases in a relatively short time forming highly protective stable oxide films of thickness in the range 10–100 Å. The reactions rate is relatively insensitive to temperature and oxygen pressure, the latter over a wide range even for oxides which are deficit semi-conductors at high temperatures. At higher temperatures it has been demonstrated that oxidation mechanism involves the migration of electrons and cations to the reaction zone.[3] It has also been demonstrated that for copper oxide growth it is the copper ions that diffuse and not the oxide.[4] The transfer of metal ions actually occurs by the formation of vacant cationic sites at the oxide–oxygen interface, followed by their diffusion to the metal–oxide interface. An interpretation of low temperature oxide film formation consistent with these phenomena was

originated by Mott[5] and elaborated by Cabrera and Mott.[6] It depends on the hypothesis that a very strong electric field is set up through the oxide film between the metal and the oxygen absorbed at the gas interface which enables the metal ions to move through the oxide to the reaction zone without requiring very much kinetic energy. In order to evaluate their speculations, the authors have applied them to the anodic oxidation of aluminum with some success.

The task of a precise evaluation of the boundary conditions of temperature and of film thickness in which their treatment is valid and of making a systematic correlation with precise experimental data over an appreciable temperature range remained. Since this behavior is characteristic of many metals, the low temperature oxidation characteristics of single crystal faces of copper were systematically studied.

Procedure

The samples were single crystal plates of copper (0.5" × 0.75" × 0.01") sectioned from a large single crystal of copper. The metal was oxygen-free high-conductivity copper, vacuum cast to a purity of 99.995% with Fe and Al chief impurities. The single crystal section was reduced from a thickness of 0.125 in. to a final thickness of 0.010 in. by a long and careful succession of mechanical and electropolishing and hydrogen anneal treatments. X-Ray diffraction tests indicated a lattice distortion of 3 degrees or less and other studies indicate that the exposed surface atoms of the final sample are in the macroscopic surface of the plate.[7] All results of this report refer exclusively to oxidation of the cubic face of copper.

The effective surface areas on a molecular scale of the electropolished samples were determined from microadsorption isotherms of nitrogen and argon on the plates at 78.1°K. and 89.2°K. to be very close to that of the geometric or apparent surface area. That is to say, the roughness factor of the surfaces was close to unity or the metal surfaces were essentially planar on a molecular scale. This is a critical factor since rough, i. e., non-planar, surfaces show a considerable decrease in surface area and, of course, roughness upon oxidation.[8] Since it is impossible to obtain any reasonably accurate estimate of the average film thickness from over-all weight increments if the surface is initially very rough and/or the surface area is in doubt, it is most desirable to have planar metal surface of known surface area. The calculated film thickness was based on the average of the surface areas determined before and after oxidation.

The vacuum microbalance developed by Gulbransen is ideally suited to the study of reaction rates occurring on metal surfaces. The operation and construction of the instrument is adequately described elsewhere.[8,9] In brief, a thin plate of metal, 0.5 g. in weight, is suspended from one arm of a beam-type sensitive quartz microbalance enclosed in a gas container. Suffice it to say that the balance can be baked out at 300°, is capable of obtaining

(1a) Presented at the Oak Ridge Meeting of the American Physical Society, March, 1950.

(1b) Engineering Department E. I. du Pont de Nemours and Co.

(1c) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford University Press, New York, N. Y., 1940, p. 152 ff.

(2) R. F. Mehl, E. H. McCandeless and F. N. Rhines, *Nature*, **134**, 1009 (1934); *Discussions Fara. Soc., Crystal Growth*, **5**, 208 (1949).

(3) G. Wagner and K. Gruenewald, *Z. physik. Chem.*, **40B**, 455 (1938).

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

(5) N. F. Mott, *Trans. Faraday Soc.*, **43**, 429 (1947); *J. Chim. Phys.*, **44**, 172 (1947).

(6) N. Cabrera and N. F. Mott, *Reports Prog. Phys.*, **12**, 163 (1949).

(7) T. N. Rhodin, *J. Appl. Phys.*, communicated.

(8) T. N. Rhodin, THIS JOURNAL, communicated.

(9) E. A. Gulbransen, *Rev. Sci. Inst.*, **15**, 201 (1944).

vacuums of 10^{-7} mm. if necessary with suitable getters in the glass envelop, and has a sensitivity of a microgram per 0.1 mm. horizontal deflection of the beam. Since the deflection could be readily measured to 0.01 mm. with a filar micrometer eyepiece on a telescope mounted on a carefully adjusted Geneva cathetometer, the effective film thicknesses could be observed to better than a 0.1 Å. Oxidation rates were followed by successive observations of the beam deflections for different samples held at a given temperature at temperatures ranging from 78 to 353 °K. The pressure of oxygen gas was varied from 10^{-3} mm. to 10 cm. at each of various temperatures with no apparent effect on the rate isotherms or on the apparent effective limiting film thickness. Apparently in this pressure range the very small supply of oxygen adsorbed on the surface is adequate for the low temperature oxidation process.

Results

It is observed that at all temperatures up to and including room temperature the oxidation rate was very rapid in the first few seconds or minutes and then decreased sharply to a negligible value. This is indicated by the linear sections of the plots in Fig. 1 in which the effective film thickness of the oxide is plotted against time over 4.5 cycles on a logarithmic scale ranging from 10 seconds to 30 hours. Extrapolation of the
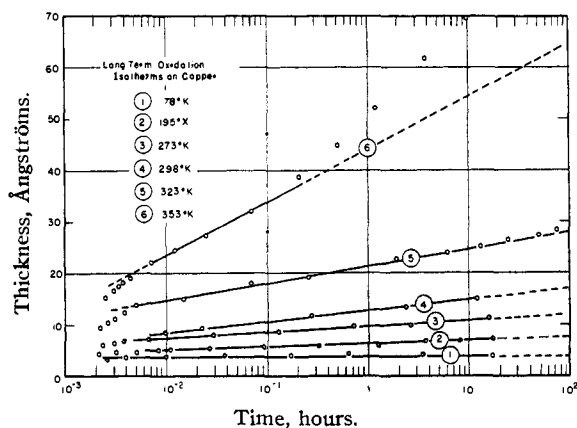

Fig. 1.

plots No. 1–5 is justified to 100 hours and yields significant values for dx/dt after that relatively long interval. It is also observed that a slight indication of the experimental points to deviate to higher values in plot No. 5 at 323° K. becomes clearly pronounced in plot No. 6 at 353° K. Replotting plot 6 in Fig. 2 clearly indicates that the logarithmic dependence of film thickness on time has changed to a cubic one defined by

$$x^3 = A_0 e^{-W_1/kT} t \qquad (1)$$

type of equation where A_0 is a temperature independent constant and W_1 is an energy of activation. The details of this relationship in the temperature range 100 to 250° has been observed by others.[10]

The oxidation isotherms 1–5 were found to agree reasonably well with Eq. (2) derived by

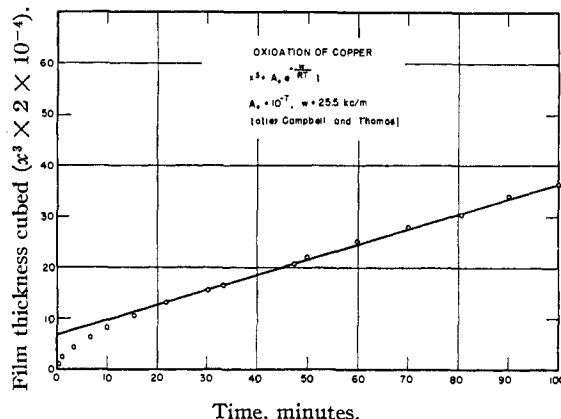(10) W. E. Campbell and U. B. Thomas. *Trans. Electrochem. Soc.*, **91**, 345 (1947).

Fig. 2.

Cabrera and Mott for the formation of very thin films.

$$dx/dt = A \exp(x_1/x - W/kT) \qquad (2)$$

where x is the film thickness at time, t; k the Boltzman constant; T, the absolute temperature. The definition of the other terms can be best interpreted by referring to the diagram of the potential energy of a metal ion at the metal-oxide interface schematically indicated in Fig. 3. It is obvious that a metal ion at a lattice site
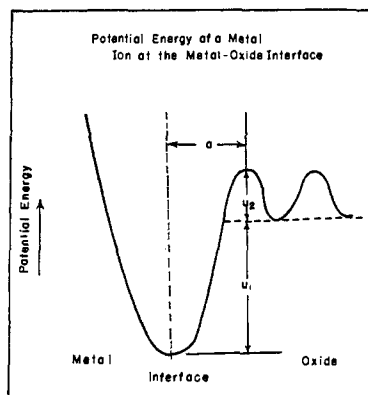

Fig. 3.

n the interface must have an energy, W, to move a distance, a, to a vacant position in the oxide, where

$$W = U_1 + U_2 \qquad (3)$$

U_1 is the difference in potential energy for a metal ion at a lattice position in the metal and a metal ion dissolved in the oxide and U_2 is the energy of activation for diffusion of the metal ion through the oxide. The term x_1 is a critical oxide film thickness defined in terms of V, the electric contact potential difference existing through the oxide caused by a redistribution of electrons between the metal, the oxide and the adsorbed oxygen, and n, the charge per ion.

$$x_1 = na V/kT \qquad (4)$$

The derivation of Eq. (2) is based on the assumption that the motion of cations is overwhelmingly

in one direction. There is no continual exchange of ions back and forth across the metal–oxide interface. The cations that have the energy, W, to escape are pulled through the oxide by a relatively strong field and almost inevitably combine with the oxide ions already waiting their arrival at the oxygen–oxide interface. This condition holds only when the actual film thickness is less than the critical value, x_1. The values of the latter are, in turn, very much smaller than the film thickness at which space charge effects caused by unequal diffusion of electrons and cations become important. The term, A, is a proportionality constant that can be calculated from fundamental values characteristic of the metal and the oxide which for the copper–cuprous oxide system can be expressed

$$A = 10^{12} \times \frac{1}{a^2} \times \frac{M}{2\rho N} = 10^4 \text{ cm./sec.} \quad (5)$$

where the first term is the mean frequency of vibration of the metal ions at the interface position, the second term corresponds to their concentration per unit of interface area (N) and the last term is the volume of oxide formed per metal ion in terms of N, Avogadro number and ρ and M, the density and molecular weight of cuprous oxide, respectively.

The comparison between theory and experiment for isotherms 1–5 was made by integrating Eq. (2). This is done as follows: let $u = A e^{-W/kT}$ and replace the variable x by x'.

$$ut = \int_0^x e^{-x_1/x'} dx' \quad (6)$$

substituting $y' = x'/x_1$ and $y = x/x_1$

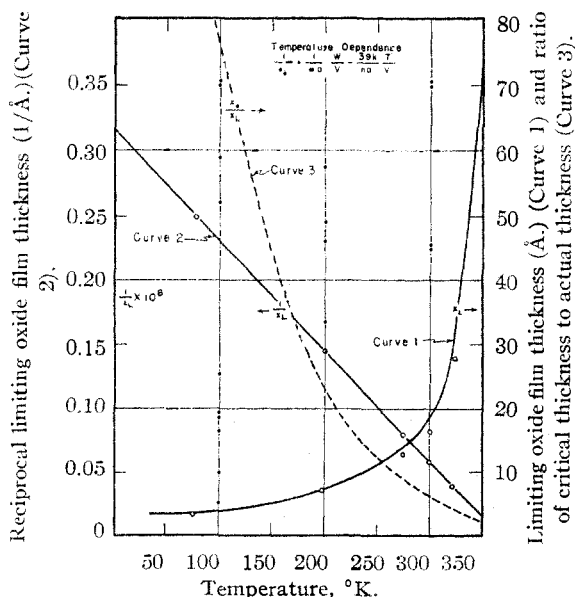$$ut = x_1 \int_0^{\frac{x}{x_1}} e^{-1/y'} dy' \quad (7)$$

and replacing y' with $1/z$

$$ut = x_1 \int_{\frac{x_1}{x}}^{\infty} \frac{e^{-z}}{z^3} dz \quad (8)$$

integrating by parts

$$ut = xe^{-x_1/x} - x_1 E_i (x_1/x) \quad (9)$$

where

$$E_i(x_1/x) = \int_{\frac{x_1}{x}}^{\infty} \frac{e^{-z}}{z} dz = \text{logarithmic integral } (-x_1/x) \quad (10)$$

It is desirable to evaluate (W) the energy of activation from the experimental data since reliable values are not as yet independently available. This must be done in order to evaluate the factor (u) prior to obtaining values of (t) and (x) from Eq. (9). This is done by defining an effective limiting film thickness (x_L) as that value of the film thickness when $dx/dt \lesssim$ one atom layer per day (or 10^{-13} cm./sec.). This characteristic value for x_L is unique for each temperature and from the nature of the rate curves especially at the lowest temperatures one sees has a general significance. Substituting the corresponding values of (dx/dt) and of A in Eq. (2)

$$\exp(x_1/x_L - W/kT) = 10^{-17} \quad (11)$$

Substituting $x_1 = naV/kT$ and rearranging

$$\frac{1}{x_L} = \frac{1}{na}\frac{W}{V} - \frac{39k}{na}\frac{T}{V} \quad (12)$$

The value of (n) is unity and (a) may be replaced by the length of the lattice edge of the cuprous oxide unit cell (4.3 Å.). Plotting $1/x_L$ against T yields a straight line, from which the values of (V) and (W) can be calculated from the slope and the intercept. The values of (x_L) and its reciprocal $(1/x_L)$ have been plotted (curves 1 and 2, respectively) against the absolute temperature in Fig. 4. The latter plot is linear and yields values of 0.83 v. (V) and 1.13 eV. (W). In the former case the experimental points for x_L fall reasonably well on curve 1 predicted by Eq. (12).
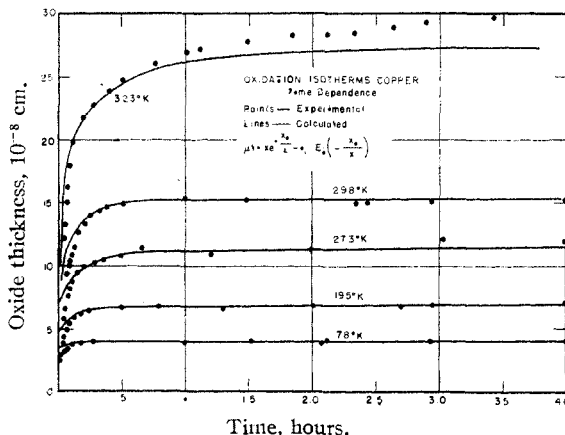

Fig. 4.

Fig. 5.

The value obtained for (V) is reasonably close to that of the contact potential between copper and cuprous oxide (0.7 v.) and the constancy of the energy term (W) with temperature suggests that a single mechanism governs the process in the temperature range considered. Finally, substituting suitable values for (V), (W), etc., in Eq. (2) the dependence of (t) upon (x) for a range of thicknesses and temperatures may be calculated. The isotherms so obtained are plotted as solid lines in Fig. 5 and are found to predict the trend of experimental points adequately.

It is felt that the fit for the rising portions of the oxidation rate curves is the most critical test since the curves rise very rapidly to an apparent limiting value. That this effect is a real one has been substantiated by comparing theory and experiment for oxidation isotherms for extended periods up to a months duration described in a subsequent paper.[11] In all cases the experimentally determined values of the effective limiting oxide film thickness were predicted by Eq. (2) to within $\pm 10\%$ in the temperature range 78–300° K. The experimental values of x_L for a long-term isotherm were determined with a reproducibility of the same amount. This increased error was occasioned by difficulties of accurate long term temperature control.

Allan and Mitchell[12] have also made some studies of the low temperature oxidation of copper surfaces. They find the oxygen uptake to depend on the temperature and the structural properties of the surfaces in a manner which is in fair agreement with the results of this study. More precise comparison is invalidated by the difficulties of evaluating the true surface area and crystallography of the metal atoms exposed in their evaporated metal surfaces.

Discussion

The good agreement over the greatest range of thicknesses and temperatures considered between the experimental data and the values predicted by Eq. (9) are taken to suggest the possible validity of the Cabrera and Mott hypothesis under the aforementioned conditions. The fact that smooth oxidation curves are predicted even when the average oxide film thickness is as small as a single monolayer must be considered as but an approximate description of the surface; parts of which are covered with patches whose thickness varies in units of oxide monolayer and parts of which are, of course, bare of oxide. It can be shown that the Mott and Cabrera function is a satisfactory approximation for such a system. The prediction of correct values for the effective limiting film thickness (x_L) listed in Table I and plotted as a function of temperature in Fig. 4 provides additional evidence.

(11) T. N. Rhodin, This Journal, communicated.
(12) Allan and Mitchell, *Faraday Soc. Symp. on Catalysis*, p. 7815, 1950.

TABLE I

T, °K.	x_L (calcd.) Å.	x_L (expt.), Å.	dx/dt Å./hr.	t, hr.
78	4.0	4.0	0.10	1
195	7.2	7.5	.12	6
273	13	12	.13	12
298	17	16	.20	20
323	32	28	.25	74
353	70	200	.30	10³

Evidence for the validity of the analysis is also indicated by the rapid breakdown of Eq. (9) at temperatures above 300° K. Inspection of the dependence of (x_1/x_L) upon temperature plotted as curve 3 in Fig. 4 indicates that it is in this temperature range that the actual film thickness values are approaching those of x_1, the oxide film thickness above which the cationic mobility no longer is exponentially dependent on the field. Hence the beginning of deviations of the data for the isotherm at 323° K. and the clear-cut discrepancy observed for the isotherm at 353° K. are to be expected and indirectly indicate the validity of the analysis. It is also interesting to note that the data at 353° K. satisfy a cubic rate law defined by Eq. (1) and illustrated in Fig. 2 which yield a rate constant in good agreement with similar oxidation data obtained by Campbell and Thomas.[10] They used an electrometric method to follow the oxidation rates at temperatures from 100 to 250°.

Some critical remarks as to the limitations of the hypothesis are pertinent at this point. Inspection of Fig. 5 shows that for a small interval at the beginning of the run, the film is not thickening as rapidly as predicted. If this is a real effect it may indicate that the somewhat idealized conditions assumed by Cabrera and Mott are not satisfied in the first stage of oxidation. On the other hand, although the response time of the balance is about 10 seconds, it may possibly be an error in defining the experimental zero point of the reaction. Another point of question is the assumption in Eqs. (4) and (5) that (a) and (N) may be replaced by the lattice constant value of cuprous oxide and by the squared reciprocal of this lattice constant, respectively. At any rate they are the best values available and since the logarithm is used in both cases, it is only critical that the order of magnitude be correct. In addition, it would be desirable to use values of the activation energy term (W) independently obtained to test rigorously Eq. (9). It may be recalled that (W) is the sum of two energies; that of cation diffusion in the oxide (U_2) and that of the heat of solution (U_1) of the cation in the oxide. Although precise values for the energy of diffusion of Cu^+ ions in Cu_2O are not available, approximate values for Cu^+ diffusion in similar silver salts vary from 0.1 to 0.2 eV.[13] The difference of approximately 1.0

(13) R. M. Barrer, "Diffusion in and Through Solids," Cambridge University Press, New York, N. Y., 1941, p. 274.

eV. is the energy required per mole to move a metal ion in a lattice site of the metal crystal at the metal–oxide interface to a vacant site in the cuprous oxide lattice, indicated in Fig. 3. Since the work of removing an ion depends on the crystal face from which it is taken, U_1 might be expected to vary several 0.1 eV. with crystallographic direction. Since diffusion is isotropic in a cubic crystal, variations in U_1 would be directly reflected in W and could be evaluated from the temperature dependence of the variation of effective limiting oxide film thickness with the exposed crystallographic face of the metal. Using the experimental method previously described, the investigation should also yield correlation of contact potential with crystallographic direction for copper–cuprous oxide. This correlation has been evaluated and is reported in a separate paper.[11]

In conclusion some cautionary remarks should be included. Although an expression of the form of Eq. (2) is in good agreement with the low temperature oxidation data on copper, the physical significance of the two parameters, W and especially V, remains somewhat speculative. The general validity of Eq. (2) should be evaluated by studying low temperature gas-oxidation of more metals systematically; some of which form excess semi-conductors (Zn), as well as others forming oxides with no appreciable semi-conductor properties (Al). Furthermore, unless there exist compensating factors hitherto undefined, the Cabrera and Mott hypothesis is based on somewhat idealized surface considerations, seldom, if ever, encountered. As applications of their theoretical treatment accumulate, modifications of Eq. (2) will probably be required to account for structural and other characteristics specific to a given metal–oxide system. Finally, the difficulties in the experimental and theoretical definition of electric contact potential differences in metal–oxide-adsorbed gas systems complicate the independent verification of the values of the parameter, V, derived from their rate analysis.

Summary

The validity of Mott's hypothesis was evaluated by a low temperature study of the oxidation of the cubic face of single crystals of copper in the temperature range 78 to 335° K. By use of a sensitive quartz vacuum microbalance, actual surface areas were determined from microadsorption isotherms and the growth of very thin oxide films were followed with an accuracy of 2%. The rate equation derived from Mott and Cabrera's hypothesis was found to be valid with some limitations for film thicknesses in the range of 5–50 Å. and temperatures from 78 to 300° K.

$$dx/dt = A \exp(x_1/x - W/kT)$$

where x is film thickness at time, t; x_1 is a critical film thickness; W is the energy of activation and A is a temperature independent constant. According to their hypothesis the value of the field accelerating the motion of metal ions through the oxide was found to vary from 10^7 to 10^6 v./cm., the contact potential between copper–cuprous oxide to be 0.83 v. for the (100) face, and the energy of activation for oxidation to be 1.2 eV. Some critical remarks pertinent to the limitations of the hypothesis are included.

The Association of Cerous Ion with Sulfite, Phosphate and Pyrophosphate Ions[1]

BY STANLEY W. MAYER AND S. DAVID SCHWARTZ

Introduction

Measurements of the association between polyvalent cations and inorganic oxygen acids have been made by several investigators.[2,3,4,5] The ion exchange measurements of ion-pair formation between cerous ion and three oxygen acids are reported in this paper.

Experimental

Materials.—Dowex 50[6] resin, 100–200 mesh, was used as the cation exchanger throughout these measurements. The resin was thoroughly washed with 6 N HCl, and water. It was then neutralized with sodium hydroxide solution, washed and briefly dried in air.

The purified mixture of Ce^{141}–Ce^{144} fission products, obtained from the Oak Ridge National Laboratory, contained less than 1% of radiochemical impurities.

The water for solutions was boiled to remove carbon dioxide and oxygen. All sodium salts were of reagent grade.

Procedure.—The method was similar to that heretofore employed.[6,7] All equilibrations were carried out at 25 ± 0.5°.

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Atlantic City Meeting, September, 1949.

(2) C. W. Davies, J. Chem. Soc., 2093 (1938); 349 (1939).

(3) B. B. Owen and R. W. Gurry, THIS JOURNAL, 60, 3074 (1938).

(4) R. E. Connick and W. H. McVey, ibid., 71, 3182 (1949).

(5) R. E. Connick and S. W. Mayer, ibid., submitted for publication.

(6) W. C. Bauman and J. Eichhorn, ibid., 69, 2830 (1947).

(7) E. R. Tompkins and S. W. Mayer, ibid., 69, 2859 (1947).