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GA-3349

A STUDY OF COPPER OXIDATION AND SOME IRRADIATION EFFECTS

Final Report

By
J. Martin Tobin

February 6, 1963

General Atomic Division
General Dynamics Corporation
San Diego, California

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DIVISION OF
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METALS, CERAMICS, AND MATERIALS

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by

J. Martin Tobin

* This research was carried on by General Atomic Division of General Dynamics Corporation, and was supported in part by the U.S. Atomic Energy Commission under Contract No. AT(04-3)-407.

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ABSTRACT

A new volumetric apparatus and a procedure for the study of the kinetics of oxidation of metals in a nuclear reactor are described. Measurements have been made on the initial stages of oxidation of 99.999% pure, polycrystalline copper wires at temperatures from 100° to 300°C. The oxygen gas was held at constant pressures during each isothermal oxidation. The pressures employed ranged from 50 to 200 mm Hg. A significant increase in logarithmic oxidation rate was observed in the presence of 2×10^6 r/hr of gamma irradiation in the temperature range 100° to 250°C.

The experimental data have been interpreted to be in support of the discontinuous oxidation theory of Bénard. Sharp transitions were observed in the kinetic rate laws. In general, a logarithmic rate region was observed which was both preceded and followed by regions of parabolic rate behavior. No cubic rate behavior was observed.

The effect of temperature on the parabolic rate constants was found to obey the Arrhenius equation. The activation energy was found to be from 0.73 to 0.82 ev. The logarithmic rate constants were found to be independent of temperature. The latter behavior is explained on the basis of the Bénard concept.

The effect of pressure was observed to be marked in the early part of the oxidation. Increased pressure of oxygen decreases the transition time and thickness where the change from parabolic to logarithmic rate behavior occurs.

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I. INTRODUCTION

To determine the physical mechanism or mechanisms of oxidation, it is necessary to measure the kinetics of oxidation and to obtain the rate law which applies to a particular metal at constant temperature, oxygen pressure, and surface condition. Since a single rate law may result from several possible mechanisms, a knowledge of the magnitude of the constants in the rate law, plus the temperature and oxygen-pressure dependence of the rate-equation constants, is also necessary.

Oxidation of copper metal has been intensively studied. The theory given by Wagner⁽¹⁾ has been supported by a large body of experimental evidence. For example, according to Pilling and Bedworth,⁽²⁾ the oxidation of copper at temperatures above 400°C follows a simple parabolic rate. The equation

$$W^2 = Kt \quad (1)$$

states that the square of the film thickness is proportional to time. Dunn⁽³⁾ showed that K varies with temperature according to the equation

$$K = K_0 e^{-Q/RT} \quad (2)$$

This indicates that a diffusion process with an activation energy Q governs the oxidation rate. The diffusing species in thick-film copper oxidation was identified as copper by Bardeen, Brattain, and Shockley.⁽⁴⁾ Vacant cation sites were assumed to diffuse in the opposite direction towards the metal. The Wagner theory predicts a rate dependence on the eighth root of the oxygen pressure, $p^{1/8}$. Wagner and Grunewald⁽⁵⁾ have shown a seventh-root pressure dependence, $p^{1/7}$. Jost⁽⁶⁾ and Wagner⁽⁵⁾ have expressed the parabolic oxidation rate in terms of transport number for the anions, cations, and electrons, and in terms of the specific electrical conductivity of the oxide film. The controlling oxidation-rate mechanism is assumed to be the diffusion of copper across the cuprous oxide film. A clear and detailed description of the Wagner theory of oxidation is given in a recent publication of Kubachewski and Hopkins.⁽⁷⁾

The physical mechanism of oxidation at lower temperatures is not yet firmly established. A transition from the Wagner mechanism to another low-temperature mechanism is a well-known fact. However, it is not

clear where the transition takes place in time, temperature, or film thickness; nor is it clear what rate equation describes the oxidation which occurs below the region where the Wagner theory can be applied. Campbell and Thomas⁽⁸⁾ suggest that a cubic rate law is satisfactory for copper between 100° and 256°C.

Lustman and Mehl⁽⁹⁾ found that a transition is generally observed between two logarithmic oxidation rate regions for copper at temperatures from 80° to 155°C. Their data show a definite increase in oxidation rate at long times, which was not noted by Campbell and Thomas.

At lower oxidation temperatures, from -195° to 50°C, Rhodin⁽¹⁰⁾ observed logarithmic oxidation rates which were preceded by a region having a slower oxidation rate. After the first minute of oxidation, there was a transition from the slower film growth rate to the logarithmic rate behavior. The transition (or critical) film thickness increased with temperature.

Knowledge of these influences suggests that the ambiguities observed in oxidation rates in the thin-film region are traceable to these effects. They are in general agreement with the discontinuous-film-growth concept of Bénard. ⁽¹¹⁾ It can be concluded that the comparison of rates of oxidation of copper in the thin-film region must be made with reproducible and well-defined surface conditions and chemical purities. This need was recognized in the work to be described.

Several excellent experiments have been performed in an attempt to resolve the ambiguities in the rates observed for the low-temperature oxidation of copper. The starting condition of the metal surface is difficult to reproduce. Consequently, the influence of epitaxy, microtopography, and crystal orientation was investigated by Gwathmey and Lawless⁽¹²⁾ and by Young, Cathcart, and Gwathmey. ⁽¹³⁾ Along with the surface condition of the metal, the chemical purity of the metal and of the oxygen have important effects on the oxidation rates.

With the exception of the results of Lustman and Mehl, ⁽⁹⁾ the experimental data from a particular isothermal oxidation have been fitted to a single equation, which is used to find the single rate law applicable at that temperature. This has been possible at temperatures above 600°C, but not at lower temperatures, evidently largely as a result of the poorly defined boundary conditions of film thickness and time at the start of the experiment. By means of several integrated forms of the parabolic law with either a virtual thickness or a virtual time or both, the range of application of parabolic rate laws has been extended down to 300°C. The vertex of the parabola becomes translocated and a better fit is obtained except in the vicinity of the origin of the curve. The

parabolic equation can be expressed as

$$(\Delta W)^2 = k_1 t + C .$$

The generalized parabolic law is given by

$$(\Delta W)^2 + k_2 (\Delta W) = k_3 t ,$$

which involves the possibility that two different processes can be rate-governing during the progress of oxidation. The interface term $k_2(\Delta W)$ would be rate-determining during the initial stages of oxidation.⁽⁷⁾

When the inverse differential oxidation rate, dt/dW , is plotted against the film thickness, W , as suggested by Campbell and Thomas,⁽⁸⁾ a straight line is obtained if, and only if, a parabolic-rate kinetic behavior occurs in the time and thickness interval being studied, since

$$\frac{dt}{dW} = kW + C . \quad (3)$$

A sharp curvature is observed if the rate law is cubic, since

$$\frac{dt}{dW} = kW^2 + C , \quad (4)$$

which is a parabolic curve. If the rate is linear, the differential rate and the inverse differential rate are both constant. A straight line of zero slope, in the suggested plot, indicates a linear law, since

$$\frac{dt}{dW} = C ; \quad \frac{dt}{d^2W} = 0 . \quad (5)$$

The data of a true cubic rate will give a straight line when dt/dW is plotted against W^2 ; and when d^2t/dW^2 is plotted against W , the line will have zero slope.

The logarithmic rate law is fundamentally different from the three laws just described, which are power functions of the film thickness, W . The exponential relationship is expressed in the form of the logarithmic equation

$$\Delta W = k \log (at + b) . \quad (6)$$

Because of the usefulness of these equations in determining the general rate law independently of the boundary conditions, they can be used to analyze oxidation isotherms to find transitions in kinetic rates during the growth of the oxide film. Since a transition temperature has not been found, it is likely that transition (critical) film thicknesses may be found. Ranges of critical film thickness are implicit in many thin-film oxidation theories, and explicit in some. The experiments and apparatus described in the Appendix of this report were devised to obtain this information.

II. EFFECTS OF TEMPERATURE

The effects of temperature were found to be the most interesting. Parabolic and logarithmic rates were observed for each oxidation isotherm obtained at temperatures from 100° to 300°C. Rate transitions from (1) parabolic to slower parabolic, (2) parabolic to faster logarithmic, and (3) logarithmic to slower parabolic are evident from the plots of inverse oxidation rate (dt/dW) versus time or film thickness. This method of analysis is described in Section I.

The thin-film cuprous oxide density and the real surface area were not measured; therefore, the data are expressed in terms of the total weight of oxygen consumed divided by the apparent surface area. Conversion factors can be applied for rough comparison of these data with the results of other investigators. Using the bulk cuprous oxide density of 5.8 g/cm³ and the apparent surface area, the following conversion factor will further aid in the comparison of present data with those reported by Lustman and Mehl:⁽⁹⁾

$$\frac{1 \mu\text{g O}_2}{2 \text{ cm}} = 154 \text{ \AA apparent thickness} . \quad (7)$$

Since the "real" area is known to be greater by a factor of 1.8 for a typical sample, another conversion factor can be given:

$$\frac{1 \mu\text{g O}_2}{2 \text{ cm}} = 85.5 \text{ \AA "real" thickness} . \quad (8)$$

Using oxidation temperatures of 100°, 150°, 200°, 250°, and 300°C, the effects of temperature were studied at 50-mm oxygen pressure. At 100°C, the oxidation rate begins with a fast parabolic rate, as indicated in Fig. 1. (It must be noted that a large value of dt/dW is a small value of dW/dt .) When the film thickness reaches 0.7 $\mu\text{g O}_2/\text{cm}^2$, the mechanism evidently changes and the oxidation rate is parabolic, but of a higher inverse rate constant and slower. Data from the same oxidation isotherm are plotted against time in Fig. 2, but cover a ten-times-longer oxidation. Another sharp discontinuity in the oxidation rate is seen at 1.69 $\mu\text{g O}_2/\text{cm}^2$, followed by a faster oxidation rate. The observation of faster oxidation rates following a slower rate was first made by Lustman and Mehl.⁽⁹⁾

Fig. 1 -- Inverse differential oxidation rates for copper at 100°C and 50-mm oxygen pressure as a function of oxygen consumed

Fig. 2 -- Inverse differential oxidation rates for copper at 100°C and 50-mm oxygen pressure as a function of time

Similar plots (Figs. 3 and 4) of inverse-rate data for the 150°C oxidation isotherm show a parabolic rate behavior to 1.51 $\mu\text{g O}_2/\text{cm}^2$ film thickness, where, abruptly, a transition to a logarithmic rate occurs. The logarithmic rate constant is approximately the same as that which is found for the 100°C oxidation isotherm, indicating a temperature independence of the rate-controlling mechanism. The transition film thickness is also approximately the same as that which is observed at 100°C; therefore, the faster logarithmic rate region is identified with the number III, and the preceding parabolic region is given the number II in Figs. 1 through 4.

The oxidation rate at 200°C is rapid. Figures 5 and 6 show a logarithmic rate behavior in the film-thickness region below 6 $\mu\text{g O}_2/\text{cm}^2$. This is identified as the same region III as is observed at 100° and 150°C. At 6 $\mu\text{g O}_2/\text{cm}^2$ a transition occurs from logarithmic to parabolic rate behavior. The rate of oxidation is slower in the new region, which is given the number IV in Fig. 5.

The oxidation proceeds so rapidly at 250° and 300°C that the average film thickness is greater than 6 $\mu\text{g O}_2/\text{cm}^2$ before the first experimental datum point can be obtained. This may be the reason why the plots in Figs. 7 and 8 for these two oxidation isotherms only show parabolic (region IV) rate behavior. Since the lines on the graphs do not pass through the origin, the use of boundary conditions is required to express the data in an integrated parabolic oxidation equation. These boundary conditions are not arbitrary, but rather are obtained by requiring the oxidation rates in transition regions to be equal at a particular time or film thickness. Such kinetic behavior is frequently observed when a series of more than one interdependent reaction competes for the available reactant. (14) The reaction then will proceed at the rate of the slower reaction. The boundary conditions therefore have probable physical significance. The mechanism change at the parabolic to logarithmic (paralog) transition probably involves a lateral growth of oxide film. The mechanism change at the logarithmic to parabolic transition probably occurs as the lateral, discontinuous growth of the oxide nuclei ceases, and a uniform, continuous increase in film thickness resumes.

The simplest temperature relationship observed was the temperature independence of the logarithmic (region III) rate constants. A table summarizing the temperature dependence of the rate constants is given in Section VI.

The parabolic rate constants for regions II and IV follow the same temperature dependence and probably result from the same physical mechanism. The equation expressing the temperature dependence is

$$\frac{2}{k} = \frac{2}{k_0} e^{-Q/RT} \quad (9)$$

Fig. 3 -- Inverse differential oxidation rates for copper at 150°C and 50-mm oxygen pressure as a function of oxygen consumed

Fig. 4 -- Inverse differential oxidation rates for copper at 150°C and 50-mm oxygen pressure as a function of time

Fig. 5--Inverse differential oxidation rates for copper at 200°C and 50-mm oxygen pressure as a function of oxygen consumed

Fig. 6--Inverse differential oxidation rates for copper at 200°C and 50-mm oxygen pressure as a function of time

Fig. 7 -- Inverse differential oxidation rates for copper at 250°C and 50-mm oxygen pressure as a function of oxygen consumed

Fig. 8 -- Inverse differential oxidation rates for copper at 300°C and 50-mm oxygen pressure as a function of oxygen consumed

The temperature dependence of the parabolic rate (regions II and IV) constants is evident in Fig. 9. The activation energy, Q , for the mechanism is between 0.73 and 0.82 ev (16.8 to 19 kg cal/mole), in rough agreement with the 20.1 kg cal/mole value reported by Valensi for copper oxidation from 300° to 550°C. (15) There is a possibility that the parabolic rate just described can be found at temperatures up to 550°C.

The region I parabolic rate at 100°C was not observed at the other temperatures. Since region I was not observed at 150°C, the activation energy may be less than 0.43 ev.

Fig. 9 -- Temperature dependence of parabolic rate constants ($2/k$)

III. EFFECTS OF IRRADIATION

Radiation may influence the oxidation rates of copper by its effects upon:

1. The metal. The dislocation, interstitial, and vacancy defects produced in the metal primarily by fast neutrons can be expected to alter the thin-film oxidation rates. High-energy gamma radiation may cause photoemission of electrons and an increased thin-film oxidation rate.
2. The oxide film. Ionizing radiation may cause ionization of adsorbed oxygen atoms and "F" center formation. Also, fast neutrons may increase the number of vacancies and thereby increase the diffusion rates of the copper cations. A parabolic rate increase at higher temperatures should be expected in the latter case.
3. The oxygen gas. Ionization of the oxygen gas may be expected to increase the number of ions adsorbed at the oxide surface, and to increase oxidation rates which are not controlled by cation diffusion processes.

Early attempts to study the effects of fast-neutron irradiation at 10^{12} nv on the parabolic-oxidation 300°C isotherms showed no measurable effects. The oxidation isotherms for different conditions of irradiation are plotted in Figs. 10 and 11, with the curves superimposed upon each other. Irradiating the capsule during the entire oxidation and pulsing the reactor (at the times indicated) to a peak power of 800 Mw for 15 msec had no measurable effect on the oxidation rate.

It was then decided to shield the capsule with 0.040-in. -thick cadmium and study the effect of intensely ionizing gamma radiation in the thin-film region at lower temperatures. The fluxes measured in the capsule at the position of the copper sample by means of neutron monitors of gold and cadmium-covered gold and by means of a cobalt-glass gamma-radiation monitor were as follows:

$$\begin{aligned}\text{gamma radiation} &= 1.8 \times 10^6 \text{ r/hr,} \\ \text{thermal-neutron flux} &= 3.16 \times 10^{10} \text{ nv,} \\ \text{fast-neutron flux} &= 1.91 \times 10^8 \text{ nv.}\end{aligned}$$

Fig. 10--Effect of irradiation on copper oxidation isotherms at 300°C and 50-mm oxygen pressure as a function of time

Fig. 11--Effect of irradiation on copper oxidation isotherms at 300°C and 50-mm oxygen pressure as a function of the square root of time

With the above radiation conditions existing during only part of the oxidation, as shown in Figs. 12 through 21, no effect was observed with the oxide film at $6 \mu\text{g O}_2/\text{cm}^2$ or at greater thickness before the sample was subjected to the gamma radiation. However, isotherms at 250° and 200°C gave indication of an increased amount of oxidation and an increased rate of oxidation early in the oxidation. The 150°C isotherms clearly indicate an effect from 2 to $4.5 \mu\text{g O}_2/\text{cm}^2$ film thickness, shown in Fig. 17, and an effect from 5.5 to $6.5 \mu\text{g O}_2/\text{cm}^2$ film thickness, shown in Fig. 18. However, when the gamma radiation was present from the beginning of an oxidation (see Fig. 19), no effect can be seen until a film thickness of $1.5 \mu\text{g O}_2/\text{cm}^2$ is reached. Figure 22 is an interesting graph of inverse oxidation rate plotted against time for a 150°C oxidation at 50-mm O_2 pressure. In this case, the irradiation was started after the oxidation had reached the logarithmic (region III) film thickness. A transient effect of rate acceleration (negative slope) occurs for 500 sec, followed by a logarithmic rate of the same rate constant. The resulting oxide has the same color as the oxide formed under identical conditions but without radiation, but the quartz containing the copper becomes quite dark in color. The 100°C oxidation isotherm shown in Fig. 21 indicates a rate increase of $\sim 13\%$ in region III.

It is concluded that the effect of the gamma radiation is seen only in the logarithmic (region III) rate. The effect saturates in approximately 500 sec. Since the rate constant is identical after the transient, it is concluded that the radiation has not changed the mechanism responsible for the logarithmic oxidation rate behavior, but has apparently altered at least one of the possible intensive factors in the mechanism: i. e., an increase in the equilibrium vacancy concentration in the oxide, an increase in the electrostatic potential existing across the oxide, an increase in photoemission of electrons, etc. A tentative explanation is given in Section V.

Fig. 12 -- Effect of part-time irradiation on copper oxidation isotherms at 250°C and 50-mm oxygen pressure as a function of time

Fig. 13 -- Effect of full-time irradiation on copper oxidation isotherms at 250°C and 50-mm oxygen pressure as a function of time

Fig. 14--Effect of part-time irradiation on copper oxidation isotherms at 250°C and 50-mm oxygen pressure as a function of the square root of time

Fig. 15--Effect of full-time irradiation on copper oxidation isotherms at 250°C and 50-mm oxygen pressure as a function of the square root of time

Fig. 16 -- Effect of part-time irradiation on copper oxidation isotherms at 200°C and 50-mm oxygen pressure as a function of time

Fig. 17 -- Effect of full-time irradiation on copper oxidation isotherms at 200°C and 50-mm oxygen pressure as a function of time

Fig. 18--Effect of irradiation on copper oxidation isotherms at 150°C and 50-mm oxygen pressure as a function of time

Fig. 19--Effect of part-time irradiation on copper oxidation isotherms at 150°C and 50-mm oxygen pressure as a function of time

Fig. 20 -- Effect of full-time irradiation on copper oxidation isotherms at 150°C and 50-mm oxygen pressure as a function of time

Fig. 21 -- Effect of full-time irradiation on copper oxidation isotherms at 100°C and 50-mm oxygen pressure as a function of time

Fig. 22 -- Effect of irradiation on copper oxidation rate at 50-mm oxygen pressure as a function of time

IV. EFFECTS OF PRESSURE

With the volumetric apparatus, it is difficult to attain a uniform oxidation of a bundle of wires at pressures lower than 50 mm Hg. Oxidation isotherms at 150°C were obtained at 50, 100, and 200 mm Hg oxygen pressures. A comparison of the inverse oxidation rates plotted against time in Fig. 23 shows a remarkable pressure effect. The increased oxygen pressures decrease the time and film thickness when the transition from the parabolic to the logarithmic rate behavior occurs. This takes place without alteration of the slope of the inverse rate in the logarithmic region.

As the curves in Fig. 24 illustrate, the combined effects of gamma radiation and increase in oxygen pressure to 100 mm Hg increase the oxidation rate by 32% over the unirradiated oxidation rate at 50 mm Hg oxygen pressure.

Fig. 23 -- Effect of oxygen pressure on copper oxidation isotherms at 150°C

Fig. 24 -- Effect of gamma radiation ($2 \times 10^6 \text{ r/hr}$) and oxygen pressure on oxidation rate at 150°C

V. DISCUSSION

The interpretation of the mechanisms of thin-film oxidation is considered by Kubachewski and Hopkins⁽¹⁶⁾ to be much less certain than that of the thick-film oxidations or scale formations. An important assumption on which the present thin-film oxidation theories are based is the uniform thickness growth or the linear proportion between the film thickness and the total amount of oxidation. The work of Bénard⁽¹¹⁾ and others⁽¹⁶⁾ give much experimental evidence of discontinuous growth, lateral growth, nucleation of oxide nuclei, and epitaxy effects. These conditions are difficult to treat theoretically.

Transition (or critical) film thicknesses are given for many proposed theories of thin-film oxidation which give limits of application for the proposed mechanism. A number of examples are given by Cabrera and Mott⁽¹⁷⁾. They have presented the most fruitful theoretical model for the explanation of thin-film oxidation, based on the hypothesis of a strong electric field. Development of the logarithmic rate equations which are considered valid for the first stage of oxidation are due to Cabrera and Mott⁽¹⁷⁾ and Hauffe and Ilschner.⁽¹⁸⁾

The theories developed by Mott, Hauffe, and Ilschner are also based on continuous film growth and ionic mobility. It is expected that the logarithmic rate constant will be temperature-dependent. However, the experimental evidence obtained with the analysis above indicates a temperature independence. It is therefore concluded that the mechanism of the logarithmic rate behavior reported here is not the mechanism of the Mott-Hauffe-Ilschner models, since the true film thickness is probably excessive.

Another interpretation can be made using the concept of discontinuous film growth attributed to Bénard.⁽¹¹⁾ Three stages of growth are recognized, namely, the formation of (1) the invisible film, (2) the oxide nuclei, and (3) the continuous film. At the beginning, the metal is covered by a film, the thickness of which increases up to a critical value of several tens of Angstrom units. Then continued oxidation leads to the formation of islands of oxide nuclei, the average number of which corresponds, for a given crystallographic orientation, temperature, and oxygen pressure, to an equilibrium determined by the rate of surface diffusion of the metal and oxygen. The nuclei then grow laterally till they cover the surface. Subsequently, oxidation will be continuous, i. e., will increase the film thickness.

The results of the present work will now be interpreted in accordance with this model. Duplicate oxidations were performed using a thermostatic hot-oil bath in order to determine the color changes associated with the various rate regions observed. Oxidations at 300° and 250°C were rapid and the colors changed continually during the oxidation in region IV, where a parabolic rate behavior is found. At 200° , 150° , and 100° , it was observed that the copper oxidized with no observable color change, until the transition from region II to region III, when a red color developed uniformly and intensified during the region III logarithmic oxidation with no change of color (i. e., no blues, greens, yellows, etc., were observed as in the case of the higher temperatures). These oxidations were performed at 50 mm Hg oxygen pressure.

The first stage in oxidation is the development of the adsorbed monolayer, which is very rapid at the temperatures used, and is present on the reproducibly clean copper surface before the oxygen is admitted to the copper. This is an invisible layer.

The second stage corresponds to the invisible layer formation up to approximately 100-Å average thickness. The rate of oxygen consumption will be described by a logarithmic rate law and the oxide growth is continuous.

A parabolic rate law can be observed on a polycrystalline metal surface, as pointed out by Gulbransen,⁽¹⁹⁾ even if the thickness is not uniform or if the oxide nuclei grow in height but not in area. No color is observed, according to Bénard⁽¹¹⁾ and the observations noted above.

The third stage is the lateral growth of oxide nuclei. This corresponds to the logarithmic region (III) oxidation described above. During the logarithmic oxidation, the red color was observed to intensify, but not to change hue. The explanation is that the optically red nuclei are growing to cover the transparent layer below.

The fourth stage begins when the lateral growth covers the surface and an increase in thickness is observed. The thickness-dependent, parabolic region (IV) corresponds to this stage. Color changes are observed in region IV and are associated with continuous film-thickness growth.

The four above hypothetical stages can be used to obtain a model for a theoretical treatment of the logarithmic oxidation rate. If the oxide nuclei grow laterally, and the oxygen atoms diffuse rapidly across the transparent substrate layer, then a time-dependent logarithmic rate law and a temperature-dependent rate constant can be developed.

Additional data pertaining to the mechanisms involved in these stages of oxidation are presented in Ref. 20. Of particular interest to the present discussion is a suggestion that the islands of oxide form because of lattice defects, such as dislocation pipes, which allow enhanced diffusion of the copper ions at these sites.

Many questions have arisen which may be the subject of further investigation. Examples of possible further work are

1. The development of a comprehensive theory of oxidation which may result in a better understanding of the experimentally observed information. Present theories are satisfactory in treating various mechanisms, but not the interdependence of the mechanisms.
2. Experimental investigation at lower pressures, after a modification of the apparatus to allow a greater mean free path for the oxygen.
3. Experimental investigation of region I and the associated parabolic-parabolic transition by the use of lower pressures and temperatures and greater copper surface area.
4. Experimental investigation to find a parabolic-parabolic transition in the neighborhood of 550°C , and investigation of the role of oxidation of cuprous to cupric oxide in the oxidation process.

VI. SUMMARY

1. A new volumetric apparatus and a procedure for the study of the kinetics of oxidation of metals in a nuclear reactor are described. The pressure of the oxygen remains constant during oxidation. The differential rate of oxidation is obtained directly. The same apparatus has been used to measure the Langmuir adsorption isotherms to determine the real surface area of a typical sample.

2. A procedure for preparing polycrystalline copper wires has been employed which can be used to obtain copper oxidation rates reproducible to $\pm 1\%$ in small groups of samples.

3. The differential oxidation rates of 99.999% pure, polycrystalline copper wires were studied at temperatures of 100° , 150° , 200° , 250° , and 300°C .

4. The differential oxidation rate generally showed a discontinuous growth of thin-film oxides, since the inverse rate was found to have sharp discontinuities at critical times and apparent thickness. The inverse rate was found to be directly proportional to the apparent film thickness at all five temperatures, but was interrupted by a thickness-independent region of film growth. In the latter region, the inverse rate is directly proportional to total elapsed time. The thickness-dependent regions are identified as the parabolic rate regions (I, II, and IV), and the time-dependent region is identified as the logarithmic rate region (III).

5. Rate transitions from parabolic to faster logarithmic, logarithmic to slower parabolic, and parabolic to slower parabolic were observed. These transitions were at approximately the same estimated apparent film thickness at all temperatures.

6. The logarithmic rate constant was found to be nearly constant at 100° , 150° , and 200°C . The temperature independence of this constant is not in accord with theory presented by Cabrera and Mott. (17)

7. The parabolic rate constants which were found for regions II and IV at the five temperatures are related by the Arrhenius temperature-dependence law. These constants are given in Table 1.

Table 1

PARABOLIC RATE CONSTANTS

Temp. (°C)	Region	$\frac{2}{k}$ ($W^2 = 2t/k$) ($\mu g^2 O_2/cm^4 - sec$)
100	II	1.15×10^{-4}
150	II	2.4×10^{-3}
200	IV	0.20
250	IV	0.89
300	IV	3.7

The activation energy is calculated to be from 0.73 to 0.82 ev. It is assumed that region IV corresponds to the diffusion-controlled thickness-dependent parabolic rate described by Valensi⁽¹⁵⁾ for copper oxidation at temperatures from 300° to 550°C with an activation energy of 0.86 ev. Region II is tentatively identified with the same mechanism.

8. The gamma radiation produced no observed effects in the parabolic rate regions. However, in the logarithmic rate region its effect is pronounced. By means of reactor transients it was found that the gamma-radiation effect saturated in approximately 500 sec. The continued oxidation, in the presence of radiation, was found to have the same logarithmic rate constant but with a 12% increase in oxidation rate.

9. The pre-irradiation of copper to 1×10^{19} nvt (>1 Mev) fast-neutron exposure caused no observable change in the oxidation behavior at 200°C and 50 mm Hg oxygen pressure. The effect of pre-irradiation was not intensively studied.

VII. ACKNOWLEDGMENTS

The author wishes to acknowledge the encouragement and help of Dr. M. T. Simnad and Dr. W. Wallace. The work was made much easier by the assistance of Mr. B. Hightower, who supplied the differential-pressure null-point device which was so important in this investigation, Dr. D. Stoneburner, who supplied the low-current electronic relay used in this work, Mr. W. Tozer, and Mr. J. Shoptaugh.

APPENDIX

APPARATUS AND PROCEDURE

Several very sensitive methods of measuring oxidation-reaction kinetics have been developed. Most of these involve measurement of the oxide-film thickness or weight. A very sensitive method was used by Lustman and Mehl⁽⁹⁾ to measure film thickness optically. However, since the optical-path length between the operator and the core of the nuclear reactor used in the experiments described here was 36 ft, their method could not be used. The electrometric method of Miley⁽²¹⁾ and of Campbell and Thomas,⁽²²⁾ which is applicable to remote operation, may be subject to extraneous radiolysis effects in the aqueous solution and cannot furnish data by continuous readings. Still another technique, the use of continuously recording quartz-fibre microbalances which can measure the increase in weight of the oxidizing copper by remote control, was abandoned in early experiments because this method indicated a sensitivity to vibration and electrostatic effects.

For their low-temperature copper-oxidation studies, Campbell and Thomas⁽⁸⁾ measured the amount of oxygen consumed in a constant volume by means of the change in pressure. This is a manometric method which can indicate a great oxygen-pressure drop during oxidation. With oxygen at 100-mm pressure and $180 \mu\text{g}/\text{cm}^3$ density, a sample-bulb volume of 17 cm^3 and a copper surface area of 50 cm^2 , resulting in an oxide-film formation of $30 \mu\text{g}/\text{cm}^2$, can decrease the oxygen pressure by 50%. Since the pressure effect is of interest in the present experiments and since Lustman and Mehl⁽⁹⁾ found a strong oxygen-pressure dependence in the film region of less than $200 \text{ \AA}$, a volumetric system was considered preferable for use in a nuclear-reactor experiment.

APPARATUS

A new volumetric method and apparatus were developed to measure the oxygen consumed by copper with less than 0.5% increase in the total pressure during oxidation of copper for one day. This system is similar in principle to systems for measuring isothermal gas adsorption in order to measure real surface area. In fact, the surface area of one 420-m-long (0.003-in. -diameter) copper-wire sample was measured at liquid-nitrogen temperature. With the assumption that the oxygen chemisorption rate

changes discontinuously when a monatomic layer is adsorbed and each atom occupies $25 \text{ \AA}^2$ surface area, the ratio of real to apparent surface area is 1.8 to 1. The method of preparing the copper before oxidation is described later in this Appendix.

The important element in the volumetric apparatus is the differential-pressure null-point device illustrated in Fig. 25. It consists of two 9-in.-diameter dessicator lids joined at their ground-glass surfaces, and separated by a diaphragm made of thin rubber. A platinum-foil contact cemented to the center of the diaphragm was conducted out of the device through the flat ground-glass joint, where a permanent seal was made of black wax. A platinum wire with a round turn on its end was used to contact the metal foil at the null position. This wire was conducted through a hole drilled into the center of one dessicator lid. The seal to the wire was also made with black wax. A low-current device was used to detect the making and breaking of the contact. Its circuit diagram is shown in Fig. 26.

Three important advantages, some of which cannot be obtained with mercury or oil differential manometers, are obtained with this device:

1. High sensitivity. The null point is detectable within 0.002 mm Hg differential pressure at total pressures from nearly 0.005 to 760 mm Hg, providing, however, that the null point is approached from the normal, open-contact condition.
2. Very low hysteresis. The difference between the differential pressure required to make contact and that required to break contact is approximately 0.020 mm Hg at 50-mm total pressure.
3. Null-point indication. The device is basically a single-point differential-pressure indicator which can be set for zero differential pressure with an alarm. This system need not be read, but can be listened to.

The disadvantages of the device are:

1. Permeability and gas solubility in the rubber. Both of these difficulties were overcome by introducing changes in procedure during many oxidation runs until a reproducible oxidation behavior was obtained using a routine, written procedure. The problem of oxygen permeation through the diaphragm was eliminated by periodically adjusting the null differential pressure across the membrane at the set point to zero. The oxygen pressure was maintained at 50 mm at all times. None of the data reported here were obtained during these preliminary developmental oxidations.

Fig. 25--Differential-pressure device used for indicating a null
differential oxygen pressure

2. Long-time drift. Periodic adjustments of the differential-pressure (ΔP) device null point were necessary because of the tendency of the wire to creep through the wax seal.
3. Rupture. The ΔP device ruptured several times because leaking or breaking of the system suddenly exposed the rubber to 1 atm of differential pressure. An all-metal device with a micrometric adjustment of the contact gap has been built recently which does not rupture when subjected to implosion.

Figure 27 shows the volumetric system, including the coupling of the ΔP device. Two nearly identical gas systems were built, so that one could act as a transient-temperature ballast for the other. As Fig. 27 shows, most of the apparatus can be installed on a rack which is placed on the floor near the reactor pool. The copper-sample ampule is sealed into a bulb and lowered into a conduit which leads into a thermostatic irradiation capsule. This capsule contains a vacuum-jacketed, 6 in. by 3 in. diameter aluminum block (see Fig. 28). The essential features of the block are the two air-filled aluminum insertion conduits terminating in holes drilled into the aluminum block, which permit insertion or removal of the two sample bulbs without the breaking of vacuum seals. The block is thermostatically controlled to $\pm 1/8^\circ\text{C}$ variation with time and $\pm 1/4^\circ\text{C}$ variation over a 4-in. length of the drilled sample holes. The temperature transients and power requirements were considerably reduced by evacuating the insulating space between the block and the vacuum jacket. Two 20-ft lengths of 1/4-in. diameter aluminum tubing were sleeved and welded together to make each of the two 40-ft-long flexible leads. These two tubes are the only connections required to the volumetric system. The quartz bulb which contains the copper and the empty quartz bulb are connected through aluminum tubing to opposite sides of the ΔP device. A set of four gas burettes is connected to the sample-bulb side of the ΔP device, while the dummy, or ballast, burettes are connected to the other side. The total adjustable volume of the gas burettes is 48 cm^3 .

PROCEDURE

Copper Preparation

The volumetric oxidation apparatus requires copper samples of a large surface area in order to attain the required sensitivity. At 100°C , a copper surface area of 776 cm^2 is needed to measure an $8\text{-}\text{\AA}$ change in "real" film thickness during the initial rapid oxidation. Hundreds of copper samples, from 55.4 to 776 cm^2 in apparent surface area, were oxidized.

I	CONSTANT-TEMPERATURE THERMOSTAT	VII	OIL ABSOLUTE MANOMETER
II	NULL-POINT DEVICE	VIII	MERCURY ABSOLUTE MANOMETER
III	AUDIBLE ALARM	IX	M ^c LEOD GAUGE
IV	2.85-MM BURETTE	X	MERCURY DIFFUSION PUMP
V	5.5-MM BURETTE	XI	ASSAYED OXYGEN
VI	9.2-MM BURETTE	XII	METAL OXIDATION SIDE OF SYSTEM
		XIII	BALLAST SIDE OF SYSTEM

Fig.27--Schematic diagram of the volumetric system, showing connections to the ΔP device, the irradiation capsule, and the gas-handling systems

Fig. 28-- Thermostatic irradiation capsule with vacuum-jacketed, 6 in. by 6 in. diam, cylindrical aluminum block. The two aluminum conduits for the copper sample and ballast bulbs are welded to the block so that the copper samples can be changed without breaking vacuum seals

The earlier use of copper single crystals having been abandoned as impractical, copper wires with a 0.003-in. (75- μ) diameter of 99.999% purity were obtained from the Sigmund Cohn Company. Spans of this copper wire were carefully measured and folded into loosely packed bundles 2 to 3 in. in length, and the bundles were placed and stored in clean quartz or glass vessels. All subsequent handling of the wires was done with clean tongs. Since the purity of the wire was apparently measured before the drawing process, the wire was heavily etched in a cleaning procedure to remove surface layers. First, wires in groups were rinsed several times in distilled water, acetone, and benzene, and then were dried. To saponify greases, oils, and epidermis tissue deposited because of handling, the wires were boiled for 2 hr in 10% NaOH solution. They were then rinsed in running water and stored under 5% HCl solution to neutralize the tenacious NaOH and remove a tarnish film. A rinse in running distilled water removed most of the HCl solution, but in 2 hr of exposure to the water a slight tarnish film reappeared. Water was removed by several rinses in acetone followed by benzene. The dried wires were then inserted into evacuable, breakseal quartz ampules. Next, the wires, in groups of seven, were simultaneously reduced and annealed, each wire in its previously cleaned quartz ampule. The air was evacuated and flushed from the ampules by three changes of hydrogen gas at 1-atm pressure. A tube furnace was then placed around the samples, and heating was started while the samples were under an atmosphere of hydrogen. When the samples reached 300°C, the reduction of the copper had ceased. Three changes of hydrogen gas were used to remove the moisture condensed on the cool glass near the furnace, which otherwise would have prevented the complete reduction of the copper.

Heating was continued with the copper under hydrogen till the temperature reached 950°C. Then the quartz ampules containing the copper were continuously evacuated overnight at 950°C. The pressure at the end of the anneal was approximately 10^{-5} mm Hg. The furnace was then removed and the samples were cooled. Next, the quartz ampules were sealed with a torch, with only the annealed quartz below the deposit of evaporated copper film being heated. The quartz envelope kept the copper surfaces reproducibly clean till the seal was broken.

One group of samples prepared in this manner gave reproducible oxidation curves to within $\pm 1\%$ accuracy. Smooth and bright copper surfaces were obtained which showed thermal etching at the grain boundaries with grain growth to 1.5 times the wire diameter. The wires did not become welded together. The real surface area (on a typical sample) was measured as 1.8 times the apparent surface area obtained from measurements of length and diameter.

Oxidation-data Collection

A copper-wire sample, sealed in its ampule, is illustrated in Fig. 29. The ampule was sealed into the sample bulb and lowered into the irradiation capsule inside the air-filled conduit. The aluminum tubing was connected, and the system was evacuated to less than 10^{-6} mm Hg pressure as indicated on a McLeod gauge. The oxygen was admitted from the assayed reagent-gas flask to increase the pressure in the entire system to 50 mm Hg, the usual oxidation pressure. Typical results of mass-spectrometric analysis of the oxygen indicate that

The ΔP device was connected by opening the stopcocks in a manner which would not force the metal foil against its contact and would avoid recalibration of the null point. The volumetric system was then isolated from the gas-handling system.

Fig. 29--Copper sample in quartz ampule

A long and careful check of the differential-pressure drift before the sample breakseal was broken was necessary for each oxidation in order to detect leakage or outgassing effects. When a stable condition was reached, the quartz breakseal was broken by shaking the aluminum tubing leading down into the capsule. The time of breaking the seal was accurately noted, since the ampule was void of gas ($<10^{-6}$ mm Hg pressure) before sealing. The sudden withdrawal of oxygen from the system was made apparent in a fraction of a second when the ΔP device sounded an alarm. At this moment, an electrical chronometer was started. The oxidation data were later corrected for the void volume in the ampule.

The mercury was quickly raised to a height sufficient to re-establish the differential pressure at approximately 100 μ higher pressure on the copper

side of the system. Each time the pressure fell to 2μ from the null point, the alarm would sound. The time and burette height were recorded, and the mercury in the burette was raised until contact was broken in the ΔP device, stopping the alarm. The height of the mercury was then fixed at a constant increment over the previous setting. The pressure increase was always greatest at this time, but was less than 0.5% of the total pressure. When the small volume of oxygen gas was consumed, the alarm again sounded and the cycle was repeated. By using fixed volume increments, the progress of the oxidation was apparent from the increasing time interval. The oxidation in a parabolic region was evident from the regular increase in time increment with volume increment. The differential rate was later calculated from the time intervals. The elapsed time was read directly from the chronometer, and the total oxygen consumed was indicated by the burette-height readings. The oxygen-gas density was calculated from the temperature and pressure, then compared with the weight of the oxide film after the oxidation was completed.

Oxidation in the absence of radiation was studied in the same apparatus, the capsule being moved away from the reactor core and placed behind a lead shield. Oxidation during full-time irradiation was performed with the capsule located on a reactor core operating at full 250-kw power. When it was certain that the null point did not drift, the ampule was broken. Since the operation of the TRIGA Mark I reactor was placed at our disposal, irradiation was often started with an oxidation in progress. A sharper increase from zero to steady, full-intensity irradiation in less than 25 sec was then obtained by moving the capsule to the operating core. Still sharper transients were obtained by pulsing the reactor to a peak of 800 Mw for 15 msec, a unique capability of the TRIGA reactor.

This volumetric oxidation system is usefully limited to gas pressures of 10 mm or greater. The large area of the copper surfaces in a small volume places the surfaces in close proximity. A short mean free path for the gas molecules is essential in obtaining a uniform oxidation throughout the wire bundle as indicated by uniform temper colors observed after oxidation.

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