

Fig. 5. Typical (311) surface

composed of steps; a typical micrograph is shown in Fig. 5.

Specimens made from the wide ribbon and annealed at 1250°C appeared more and more shiny as oxidation proceeded. X-ray back-reflection measurements indicated the entire surface was oriented with a (111) plane parallel to the surface. Microscopic examination revealed that the specimens were fairly large-grained of the order of millimeters in diameter. No striated grains were observed nor were any grains with the typical (311) appearance (Fig. 5) observed. The surfaces were marked with die scratches from drawing and

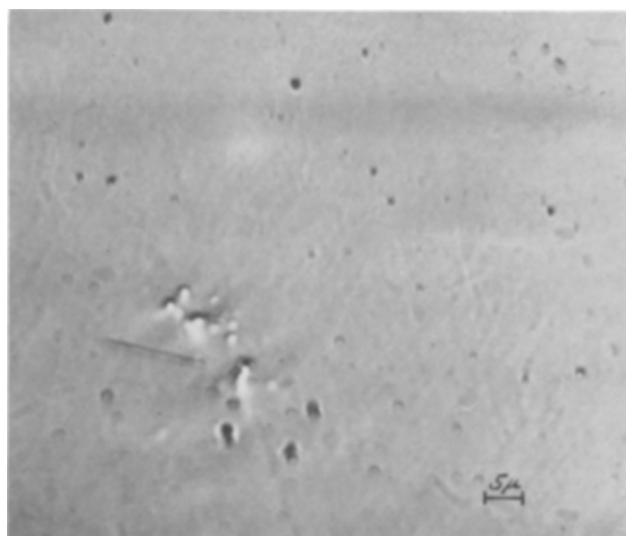


Fig. 6. Surface of wide ribbon after much oxidation

dimpled from rolling. As oxidation proceeded these markings were smoothed out. Figure 6 shows a heavily oxidized ribbon depicting the typical smooth surface dotted with small pips. It was not determined whether these pips were the result of dislocations as found on tantalum by Bakish (23), or whether they resulted from specks of dirt on the surface inhibiting the normal oxidation at that spot. It was noted, however, that the concentration of pips was much greater near places where the ribbons had been bent appreciably.

## The Oxide Films Formed on Copper Single Crystal Surfaces in Water

### II. Rate of Growth at Room Temperature

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#### ABSTRACT

Measurements utilizing polarized light were made of the increase in film thickness with time on {100}, {110}, {111}, and {311} surfaces of a copper single crystal immersed in water in equilibrium with atmospheres containing either oxygen or oxygen-helium mixtures containing 1, 10, or 20% oxygen. With the oxygen atmosphere a  $\text{Cu}_2\text{O}$  film rapidly reached a limiting thickness that remained constant for 1.5 to 2 hr after which time the formation of  $\text{CuO}$  was observed. Stirring increased the time required to observe the formation of  $\text{CuO}$ . Similar behavior was observed for 10% and 20% oxygen atmospheres; the limiting film thickness of  $\text{Cu}_2\text{O}$  and the time required to observe the formation of  $\text{CuO}$  increased with decreasing oxygen content in the atmosphere. When a 1% oxygen atmosphere was used, parabolic film growth was observed. In all cases the {111} plane exhibited the lowest growth rate.

The first paper in this series (1) described qualitative studies of the films formed on copper single crystal surfaces immersed in water containing oxygen. It was concerned with the chemical composition of the film, structural relationships between metal and oxide, and the morphology of the oxides. The work described here deals with experiments designed to learn something about the rate of film formation by measuring change in film thickness with time.

The polarizing spectrometer or, as it will be called throughout this paper, the ellipsometer was used to measure the thickness of the films formed on copper. With this instrument the thickness of oxide film growing on a metal surface is determined by reflecting polarized light from a polished metal surface and then measuring the change in ellipticity that this polarized light suffers as a result of its being reflected by the film-bearing metal surface. This

change is dependent on, among other things, the thickness of the film.<sup>1</sup>

One of the important advantages in using the ellipsometer to study film formation on metal surfaces immersed in a liquid is that it is possible to study the rate of formation while the process is actually going on without disturbing it. Further, the growth of films on selected areas of a specimen can be studied. This is especially valuable in this study which uses single crystal surfaces in that a number of crystallographic planes on a given specimen can be studied during a single experiment.

With the possible exception of the classic work of Tronstad and co-workers (3, 4) on iron and aluminum, the ellipsometer has not been employed in the study of film formation on immersed metal surfaces. Nothing appears to be available in the literature on the use of the ellipsometer to study the rate of film formation on copper immersed in high-purity water containing oxygen. A few electrometric measurements were made on this system by Davenport, Nole, and Robertson (5), but the thin films formed precluded any detailed analysis because of their method of measurement. Hence very little has been done for this system in spite of the fact that such a study would appear to be of utmost importance in serving as a starting point toward gaining a more fundamental understanding of the corrosion of copper in more complicated systems.

### Experimental Method

**Ellipsometry.**—A detailed description of the type of ellipsometer used and the method and theory employed to interpret the results obtained with it are given elsewhere (6). However, in order that certain points in what follows be clear, it is necessary to outline briefly the manner in which ellipsometric measurements were made.

It should be pointed out first that it is necessary to know the index of refraction of the material making up a film in order to determine its thickness with the ellipsometer. This quantity is a complex number for the oxides of copper and may vary depending on the manner in which the film was formed. In order to determine the refractive index, one has to calculate for the system under study values for the relative phase retardation,  $\Delta$ , and relative amplitude reduction,  $\tan \psi$ , for a number of film thicknesses using an assumed refractive index. Since this calculation is a long and tedious one, it has been programmed for an IBM 704 Digital Computer. One then compares the calculated curve with an experimental curve obtained by measuring  $\Delta$  and  $\tan \psi$  for different film thicknesses for the system under study where film growth is taking place. When a theoretical curve for a given refractive index corresponds to the experimental curve, the refractive index of the film material is taken as that of the matching theoretical curve. In order that an accurate determination of the refractive index of the oxide film be made, it is necessary to measure films whose thicknesses range as high as about 1000 Å. However, most of the films studied had thicknesses less than 150 Å;

therefore, the refractive index could not be determined accurately. For films below 100 Å, however, thickness values are rather insensitive to changes in the refractive index, and an accurate knowledge of it is not necessary to measure thickness to  $\pm 3$  Å or better (7). Another condition that must be met in order to measure film thickness, with the calculation as presently programmed for the computer, is that the film be composed of a single isotropic component. It is possible to consider two component films but this increases the complexity greatly.

As a check of the ellipsometric method of measuring film thickness, a few crude electrometric reduction measurements were made. These agreed within  $\pm 10$  Å in the 0–100 Å range. This agreement is satisfactory when account is taken of the fact that the crystal had to be removed from the reaction apparatus in order to make the electrometric reduction measurements. During this time changes in film thickness could occur.

**Reaction apparatus and procedure.**—The apparatus used to carry out the film formation studies under controlled conditions is shown in Fig. 1. The copper single crystals used were machined as cylinders with their axes in the  $\langle 110 \rangle$  direction. Using a crystal of this orientation, it was then possible to cut flat surfaces parallel to the  $\{111\}$ ,  $\{110\}$ ,  $\{100\}$ , and  $\{311\}$  crystallographic planes, these planes being parallel also to the cylinder's axis as shown in Fig. 1. The  $\{311\}$  plane was studied in addition to the low index planes because it has been found to be the slowest oxidizing plane in gaseous oxidation (8). With such a crystal sealed into this apparatus, the various crystallographic planes could be rotated into position by means of a magnet so that measurements could be made on them with the ellipsometer at various times during the oxidation process.

The analysis of the copper used in the crystal (99.99+ % copper), the method of preparation used to render the crystal surface smooth and strain-free, and the manner in which high-purity water was introduced into the lubricated joint-free apparatus are described in the first paper of this series (1). Lubricated stopcocks were used to introduce purified

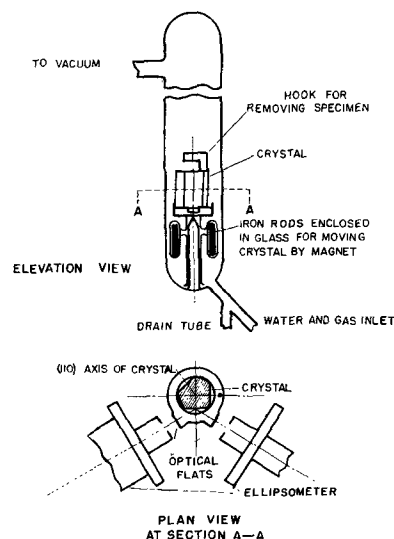


Fig. 1. Apparatus for studying the formation of films on a copper single crystal immersed in water.

<sup>1</sup> The thickness measured by the ellipsometer is that thickness one would observe if one redistributed the material making up the film so as to form a uniform layer (2).

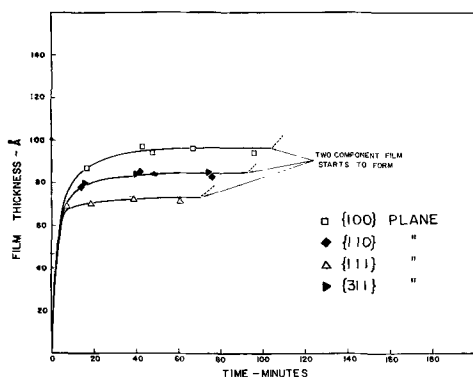


Fig. 2. Growth of oxide film on copper in unstirred water in equilibrium with 1 atm of  $O_2$ .

gases, but these were separated from the system by traps containing copper turnings. Satisfactory reproducibility was obtained only after distilling in water a number of times to wash the crystal and apparatus. After each washing the apparatus was baked out over night, and annealed in purified hydrogen at  $500^\circ\text{C}$ . The rate of oxidation was checked each time while the crystal was immersed during a wash, the water being drained out before the oxide got thicker than  $50\text{\AA}$ . When the values obtained matched those obtained previously, a complete run was made. The optical parameters of the unfiled copper surface in water, on which all of the data on the film surface were based, were determined by measurements on the copper surface in vacuum immediately after annealing in hydrogen. Thus values for the unfiled copper surface in water then could be calculated from these vacuum values.

### Results

The results obtained when a copper crystal was immersed in unstirred water in equilibrium with 1 atm of oxygen are shown in Fig. 2. Very rapid oxidation took place initially, followed by a leveling off at  $65\text{--}95\text{\AA}$ . This leveling off indicated that some type of logarithmic law governed the process. Further it was found that the  $\{111\}$  face exhibited a smaller limiting film thickness than the other three faces studied. This oxidation behavior was similar to that observed by Rhodin (9) for copper single crystal surfaces oxidized at room temperature in gaseous oxygen except that the limiting thickness was greater for oxidation in water.

Another very important feature noted for oxidation under these conditions was that  $\Delta$  reaches a minimum after from 90 to 120 min and then begins to increase. This is shown in Fig. 3, where instead of film thickness,  $\Delta$  is plotted *vs.* time because the thickness cannot be determined after  $\Delta$  reaches the minimum shown in Fig. 3. It can be seen that the greatest change in  $\Delta$  occurs for the  $\{100\}$  and the  $\{111\}$  faces. This change in optical parameters was probably associated with the formation of a new component or layer in the oxide film. Evidence from the x-ray results described in the first paper of this series (1) would indicate that this is most probably  $\text{CuO}$ . The reasonableness of this assumption, *i.e.*, that a new component starts to form, is made clear by Fig. 4. In this figure are plotted the two optical

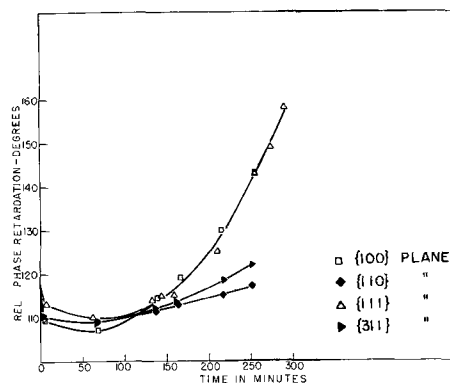


Fig. 3. Change in relative phase retardation for film growing on copper in unstirred water in equilibrium with 1 atm of  $O_2$ .

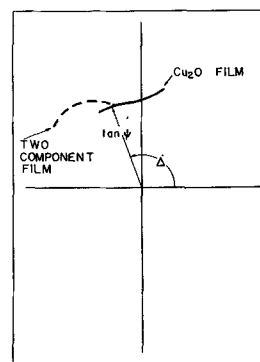


Fig. 4. A comparison between the polar plot of relative phase retardation,  $\Delta$ , and relative amplitude reduction,  $\tan \psi$ , calculated for a  $\text{Cu}_2\text{O}$  film growing on copper and obtained experimentally for a film starting out as  $\text{Cu}_2\text{O}$  and then starting to form a second component.

parameters,  $\Delta$  and  $\tan \psi$ , determined by the ellipsometer for films of different thicknesses both for the all- $\text{Cu}_2\text{O}$  film, and for the two-layer film found experimentally. If the  $\text{Cu}_2\text{O}$  film had continued to thicken, the optical parameters would have moved to the right on the solid curve. Instead, after a film of  $65\text{--}95\text{\AA}$  had formed on the copper surface after 90 to 120 min, the parameters suddenly followed the dashed curve. It is also known from previous work on the system that the introduction of  $\text{CO}_2$  will convert the  $\text{CuO}$  to  $\text{Cu}_2\text{O}$ . When this was done, after the parameters measured were those found on the two component curve, subsequent measurements of  $\Delta$  and  $\tan \psi$  always lay on the solid curve, that calculated for a film made up of  $\text{Cu}_2\text{O}$  only. If the sudden change in optical parameters was associated with changes in structure or the introduction of strain, as is sometimes the case, it is highly unlikely that introduction of  $\text{CO}_2$  would have brought the values of the optical parameters back to the curve calculated for  $\text{Cu}_2\text{O}$ . Hence it seems reasonable to say that the sudden change in the optical parameters was associated with formation of  $\text{CuO}$ . Since the  $\text{CuO}$  was formed as a second component, the method described for studying the rate of its formation could not be used because calculations have not been made for films containing two components.

One observation made when a crystal was removed after being immersed for 18 hr should be mentioned. The  $\text{CuO}$  formed was loosely held and could be par-

tially wiped off. Beneath it a film was observed showing interference colors, presumably  $\text{Cu}_2\text{O}$ . These interference colors indicated thicknesses greater than the limiting thickness of the  $\text{Cu}_2\text{O}$ , 65-95Å, observed before the formation of  $\text{CuO}$ . Thus it appeared that, as the  $\text{CuO}$  formed, the  $\text{Cu}_2\text{O}$  layer underneath was also increasing in thickness. Therefore, since both  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  were growing simultaneously and at different rates, the values of  $\Delta$  plotted in Fig. 3 were related in a complicated manner to the thickness of the combined film. Hence one cannot say from looking at this plot that the {100} and {111} planes have thicker films on them than the {311} and {110}.

As a valuable aid in understanding the process just described wherein  $\text{CuO}$  starts to form after 1.5 to 2 hr, spectrochemical analyses of the water in which the copper crystal was immersed were made after given times of exposure. It was found that the concentration of copper was extremely low, no concentration higher than 0.05 mg/l being observed. Further it was found for the case where oxidation was carried out with the water in equilibrium with 1 atm of pure oxygen that before the formation of  $\text{CuO}$  the concentration of copper was found to be less than 0.02 mg/l. After  $\text{CuO}$  began to form the concentration was 0.04 mg/l. This concentration of copper agrees quite well with the concentration that one would calculate from the solubility product of  $\text{CuO}$ . Hence it would appear that the  $\text{CuO}$  precipitates out on the  $\text{Cu}_2\text{O}$ -copper surface when the concentration of cupric ions reaches the proper level.

Going from these experiments where stagnant water was in equilibrium with 1 atm of oxygen to the case where the water was stirred by bubbling in oxygen at different rates, the same behavior was observed except for one significant difference. The time necessary for the first traces of  $\text{CuO}$  to appear increased with an increase in stirring rate. Table I illustrates this. The stirring rates were not sufficiently accurately maintained to allow one to draw any quantitative conclusions, and the manner of stirring was not conducive to reproducibility. Qualitatively, however, there was a definite relationship between stirring rate and time required for the formation of  $\text{CuO}$  to commence.

*Oxygen-helium mixtures in equilibrium with pure water.*—The next series of experiments was carried out with the copper crystal immersed in water in equilibrium with oxygen at partial pressures less than 1 atm. In all of these experiments the total pressure was brought up to 1 atm by the addition of helium. Figure 5 shows the progress of oxidation under stagnant conditions in an atmosphere containing 1% oxygen. The curves are not plotted for longer times than those shown in Fig. 5 because a

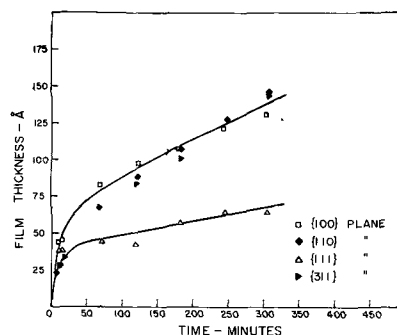


Fig. 5. Growth of an oxide film on copper in unstirred water in equilibrium with 1 atm of a helium-1% oxygen mixture.

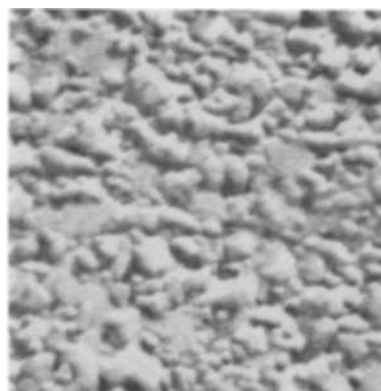


Fig. 6. Electron micrograph of {100} surface of copper oxidized in water in equilibrium with a helium-1% oxygen atmosphere for 18 hr. Direct carbon replica, preshadowed with palladium. 40,000X (All magnifications are before reduction for publication.)

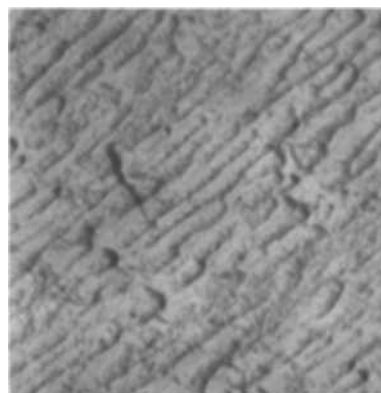


Fig. 7. Electron micrograph of {110} surface of copper oxidized in water in equilibrium with a helium-1% oxygen atmosphere for 18 hr. Direct carbon replica, preshadowed with palladium. 40,000X

gradual change in refractive index took place. Thus, after a film of about 160Å or more was formed, thickness measurements became uncertain. Quite thick films, 1000Å or more, were formed after a period of 18 hr. Electron micrographs of replicas of the four crystal surfaces studied are shown in Fig. 6, 7, 8, and 9. They show that the films formed were not uniform in thickness and that the oxide morphology depended on the crystallographic orientation of the metal surface on which they were growing. This nonuniformity may not be the case, however, for very thin films.

Table I. Effect of stirring on time required for the start of  $\text{CuO}$  formation

Oxygen flow rate, ml/min	Time, min
0.0	120
0.17	237
0.47	292





Fig. 8. Electron micrograph of {111} surface of copper oxidized in water in equilibrium with a helium-1% oxygen atmosphere for 18 hr. Direct carbon replica, preshadowed with palladium. 40,000X



Fig. 9. Electron micrograph of {311} surface of copper oxidized in water in equilibrium with a helium-1% oxygen atmosphere for 18 hr. Direct carbon replica, preshadowed with palladium. 40,000X

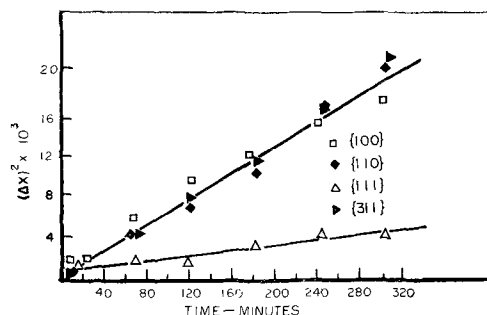


Fig. 10. Parabolic plot for growth of an oxide film on copper in unstirred water in equilibrium with 1 atm of a helium-1% oxygen mixture.

It can be seen from Fig. 5 that the results obtained here differed markedly from the pure oxygen atmosphere case. First, the film thicknesses exhibited were greater than in the pure oxygen case, and second, as Fig. 10 shows, the rate appeared to obey a parabolic law.

The fact that a parabolic rate law appears to be observed poses the question as to whether, at these low concentrations of oxygen, diffusion of oxygen in the solution was the rate-controlling step or whether diffusion in the film was important. It is difficult, however, to explain such a marked difference in the rate between the {111}, which had a parabolic rate constant of  $0.13 \text{ Å}^2/\text{min}$ , and the other

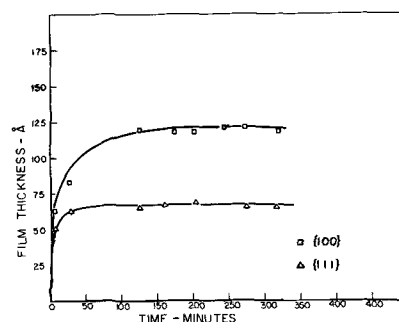


Fig. 11. Growth of an oxide film on copper in unstirred water in equilibrium with 1 atm of a helium-10% oxygen mixture.

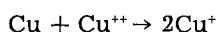
orientations, which had essentially equivalent rate constants whose average was  $0.63 \text{ Å}^2/\text{min}$ , if diffusion of oxygen in solution were rate controlling. Further, stirring did not appear to affect appreciably the rate but tended to make the behavior less parabolic, indicating that greater accessibility of oxygen made the process tend to approach a logarithmic behavior. Figure 11 would indicate that this is so. Here the oxidation occurred in water in equilibrium with an atmosphere of 10%  $\text{O}_2$ . Only the results for the {111} and {100} planes are plotted since the {110} and {311} gave results similar to that for the {100}. For the 10% oxygen atmosphere the rate of  $\text{Cu}_2\text{O}$  formation was greater than that for the stagnant 100%  $\text{O}_2$  case; thicker films of  $\text{Cu}_2\text{O}$  were formed, but less than in the 1% case. Moreover the behavior was logarithmic in nature rather than parabolic as was the case for a 1% oxygen atmosphere. The film thickness for this 10% case lay intermediate between the 100% oxygen and the 1% oxygen. The rate, however, of cupric ion formation was also important. It was increased and hence the rate of  $\text{Cu}_2\text{O}$  formation was still further inhibited. By allowing the crystal to stand in contact with the water and the 10% oxygen atmosphere for two days,  $\text{CuO}$  was observed to form in the same fashion as in the 100% oxygen case. After the thickness had leveled off to a constant value, the formation of  $\text{CuO}$  could be brought about immediately by replacing the 10% oxygen atmosphere with pure oxygen.

When the water was in equilibrium with a 20% oxygen atmosphere, the behavior approached that of a 100% oxygen atmosphere in an even more pronounced fashion than for the 10% case, and  $\text{CuO}$  appearance was observed after about 4 hr.

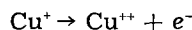
### Discussion

The oxidation of copper in oxygenated water produces two oxides, and the factors that control which of these oxides is the thermodynamically stable phase have a major influence on the rate observed and the type of rate law followed. Those factors as pointed out in the first paper of this series are the partial pressure of oxygen and the pH.  $\text{Cu}_2\text{O}$  is always formed next to the copper surface, but whether or not this thin film continues to grow as  $\text{Cu}_2\text{O}$  depends on the oxygen concentration and on the pH of the solution. (The pH was altered by the introduction of  $\text{CO}_2$ .) Considering first the situation when the oxygen concentration was high, it was

found that the  $\text{Cu}_2\text{O}$  film after a rapid initial logarithmic buildup ceased to grow appreciably and reached a limiting thickness. It appears that the limiting thickness of the initial  $\text{Cu}_2\text{O}$  film resulted from the competing reactions



and



The value of the limiting thickness probably depended on the ability of electrons and ions to get through the oxide film and react at the surface. At thicknesses below the limiting thickness enough electrons were available to reduce  $\text{Cu}^{++}$  to  $\text{Cu}^+$ , and the film increased in thickness. At greater thicknesses, the cuprous ions were oxidized to cupric, and these went into solution until the solubility product constant for  $\text{CuO}$  was exceeded. Once this happened,  $\text{CuO}$  precipitated out onto the surface. This then limited the oxygen available to the surface, and conditions became favorable for cuprous oxide to continue to grow underneath this  $\text{CuO}$  film. This is just what was observed. When the solution was stirred, the time for  $\text{CuO}$  to form was increased. This appears to be due to the fact that the cupric ions were simply carried away from the surface by stirring, and precipitation could occur in the body of the liquid, thus increasing the time required before enough  $\text{CuO}$  was precipitated at the surface to affect the oxidation process.

The fact that the initial buildup of  $\text{Cu}_2\text{O}$  was logarithmic is not too informative because almost any process which tends to come to a standstill would conform approximately to a logarithmic "law" (10). Because of the subsequent formation of  $\text{CuO}$ , it appears that such a relationship is not necessarily the result of a single uniform process. Consequently no rate constant has been derived. The theories of either Cabrera and Mott (11) or Uhlig (12), both of which predict logarithmic behavior for very thin films at low temperatures, may be applicable if a single process is operative. Studies on the effect of temperature would perhaps decide between the two theories since the Cabrera and Mott theory predicts that the rate constant is temperature independent while Uhlig's does not. Or perhaps, more likely, an entirely new theory is necessary for film growth in contact with a liquid where the dielectric constant of the liquid, electrochemical potentials between various crystal faces, adsorption of ions from solution, and other factors must all influence the oxidation process.

When the oxygen concentration was low, it was found that  $\text{Cu}_2\text{O}$  was the stable phase. Its films grew to greater thicknesses than those formed when the oxygen concentration was high because there was less tendency for the cuprous ions formed to oxidize to the more soluble cupric. Stirring did not increase this rate of  $\text{Cu}_2\text{O}$  formation in the 1% oxygen atmosphere experiment because oxygen accessibility was increased and the equilibrium shifted toward  $\text{CuO}$ . This is further emphasized when the oxygen concentration was increased by using a 10% oxygen atmosphere because the rate of  $\text{Cu}_2\text{O}$  formation became logarithmic again and  $\text{CuO}$  was eventually

formed. Here, however, the limiting thickness of  $\text{Cu}_2\text{O}$  was higher than in the case where 100% oxygen atmosphere was in equilibrium with the solution.

For both high and low oxygen concentrations, the {111} crystallographic plane exhibited the smallest rate of oxidation. This fact may be related to Tragert and Robertson's observation (13) that the {111} plane of copper exhibited the most noble electrochemical potential of all of the low index planes studied.

This points out that electrochemical considerations may be of great importance in determining the order of increasing rate of oxidation for the various crystal planes. While the {111} is the slowest for oxidation in water, it is, next to the {100}, the fastest in gaseous oxidation at temperatures from 70° to 178°C (8). The fact that {111} exhibits both the slowest oxidizing rate and the most noble potential may be due to the fact that of all the planes in the F.C.C. system it has the highest work function, i.e., it gives up its electrons least easily. Another important factor, however, in determining order of rate of oxidation among crystallographic planes is the physical nature of the oxide formed (degree of preferred orientation, imperfections, morphology, etc.). As the earlier study of this system (1) showed, the {100} has the most poorly oriented oxide film and would tend to oxidize faster. However, a great deal more has to be learned before any really definite reasons for the order in rate of oxidation between the various orientations can be given.

Besides the differences of rate of oxide formation between the different planes, work by a number of investigators (14-16) points to differences observed on the same crystal face where impurities, dislocations, and other imperfection may play a great role. Figures 6, 7, 8, and 9 illustrate the noncontinuous nature of the oxides formed and their dependence on crystallographic orientation. A study of these considerations will be the next step in the investigation.

#### Acknowledgment

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1961 JOURNAL.

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## Use of Polarization Methods in the Determination of the Rate of Corrosion of Aluminum Alloys in Anaerobic Media

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### ABSTRACT

Tafel-type cathodic polarization curves were obtained for aluminum alloys corroding in anaerobic acid and food media. The overvoltage-intercept method was found to give corrosion currents equivalent to the measured rates of hydrogen evolution. Tafel-type anodic polarization curves could not be obtained. Anodic polarization curves calculated from cathodic polarization data in the vicinity of the corrosion potential gave Tafel slopes which were identical to the cathodic Tafel slope, within 20%, in each individual case. On using suitable values for the Tafel slopes in the Stern and Geary equation, the polarization resistance method likewise gave corrosion currents in good agreement with measured rates of hydrogen evolution.

This investigation arose from the need for a sensitive method of determining the instantaneous corrosion rate of aluminum in anaerobic media under conditions where it is not possible to measure such quantities as weight loss and hydrogen evolution. The use of polarization methods in determining the corrosion rate of iron and steel has been demonstrated (1-3). The purpose of this investigation was to determine the applicability of such methods to the corrosion of aluminum.

In a study of the corrosion of iron in a variety of deaerated acid media it has been found that there exists a pH range for each acid studied wherein the corrosion potential varies by approximately 0.059 v for each unit pH range (1, 4-6). In effect the corrosion potential of an iron electrode behaves in a manner analogous to the reversible hydrogen electrode.

Stern (1) has reported that the cathodic polarization curve for iron in deaerated acid media exhibits Tafel-type behavior and has derived a relationship between corrosion rate, corrosion potential and hydrogen overvoltage. Utilizing these principles, Kaesche and Hackerman (2) graphically determined corrosion rates for iron in 1N HCl from cathodic polarization measurements. This graphical method is referred to in this paper as the overvoltage-intercept method.

Polarization data obtained in the region of the corrosion potential have also been used to determine corrosion rates. Skold and Larson (7) have demonstrated that for iron and steel in media of varying

corrosiveness the polarization potential is a straight line function of the applied anodic or cathodic currents at low current density. Since the slope,  $\Delta E/\Delta I$ , has units of resistance, this term has been conveniently called the polarization resistance (8). A plot of corrosion rates vs. polarization resistances on logarithmic scales yields a straight line with a slope of minus one.

Stern and Geary (9), in a discussion of the shape of polarization curves for corroding systems controlled by activation polarization, showed that a linear relationship is expected in the region where the polarized potential is close to the corrosion potential. The following equation was derived:

$$\frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.3 (I_{\text{corr}}) (\beta_a + \beta_c)} \quad [1]$$

where  $\Delta E/\Delta I$  is the polarization resistance,  $\beta_c$  and  $\beta_a$  are the slopes of the logarithmic local cathodic and anodic polarization curves, and  $I_{\text{corr}}$  is the corrosion current, equivalent to the rate of corrosion by Faraday's law. Stern has described the polarization resistance method in detail, discussing its advantages and limitations (8).

Each of these two methods has its advantages and limitations, and both will find their areas of application. The polarization resistance method has the advantages of greater general applicability and greater ease of use. Successful use of the polarization resistance method depends on proper evaluation of the beta constants in the Stern and Geary equation,