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An application of Differential Reflectometry to the study of Characteristics of Non-flow Corrosive Media on the Corrosion of Copper Metal

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ABSTRACT

The new technique of differential reflectometry was applied to study the characteristics of non-flow corrosive media on the corrosion of copper metal. Differential reflectometry is a form of modulation spectroscopy which measures the normalized difference in reflectivity between two samples, or two adjacent areas of the same sample.

In this study, following results have been found. (a) The exact thickness of cuprous oxide film can not be estimated from the intensity of the differential reflectivity at a given wavelength because optical constants for cuprous oxide have not been measured yet. However, it is suggested that the film formed during 69 h of polarization is within about 50 nm thick. (b) Cuprous oxide film grows substantially with time in the first about 45 h of polarization after which the growth is slower.

INTRODUCTION

It is well known that the technique of X-ray diffraction is capable of monitoring the layers of corrosion products forming on the surface of metals¹⁻⁴). But X-ray diffraction techniques, which probe as much as 1mm into the surface of a metal, will often not show an oxide layer on the outer 10 nm of the surface.

Differential reflectometry has been shown to be a powerful tool for investigating thin film corrosion products in the thickness range up

to about 5 nm⁵). In addition, the technique is able to identify the species of thin film corrosion products and to be performed in *si-tu*.

Thin film corrosion products such as oxides, hydroxides, chlorides, or something else of aluminum, copper, or silver can form insulating or rectifying contacts on electrical equipments. They are therefore of great concern in the field of electronic materials.

A differential reflectogram is obtained by scanning monochromatic light across a corroded and an uncorroded area of a metal at the same

time and measuring the normalized difference in reflectivity ($\Delta R/\bar{R}$) as a function of wave-

length(λ). Here, $\Delta R/\bar{R}$ is $\frac{R_2 - R_1}{(R_2 + R_1)/2}$ Where

R_1 and R_2 are reflectivities of a corroded and an uncorroded area of a metal, respectively.

A given corrosion product is characterized by specific peaks in a differential reflectogram which are due to electron transitions from one energy band to another, or other electron effects. Thus the features in a differential reflectogram can generally be related to calculated electron band diagrams.

The purpose of this work was to obtain information about the thickness of cuprous oxide film as a corrosion product of copper metal and to investigate the growth kinetics of cuprous oxide film on copper substrate.

Copper metal was chosen as the sample upon which the corrosion product film was formed, since copper has a fairly well-characterized corrosion product (cuprous oxide) which has a visible color. In addition, theoretical⁶⁾ and experimental⁷⁾ Pourbaix diagrams have been established and the electronic band structure of cuprous oxide is known⁸⁾

EXPERIMENTAL METHOD

A detailed description of the differential reflectometer has been given by Holbrook and Hummel⁹⁾. An improved version of this instrument was shown in Fig. 1.

Light coming from a monochromator is alternately scanned by a vibrating mirror across the corroded and protected areas. The total area scanned is about $2 \times 4 \text{ mm}^2$. The signal from a photomultiplier tube (PMT) which picks up the reflected light from the sample is electronically processed to obtain the normalized difference in reflectivity ($\Delta R/\bar{R}$). The average value of the

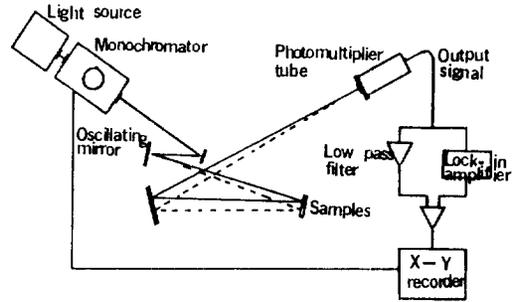


Fig. 1. Schematic diagram of the differential reflectometer.

two reflectivities, $\bar{R} = (R_1 + R_2)/2$, is held constant by a PMT high voltage servo. An X-Y recorder plots $\Delta R/\bar{R}$ automatically as a function of wave-length. A scan between 200 and 800 nm requires about one minute.

For the preparation of samples, copper discs were cut from a 15mm diameter bar of 99.99% pure copper and immersed in 20% HNO_3 (HNO_3 : E.P, Fisher chemicals) for 15 h.

The disc was then mechanically polished through $1 \mu\text{m}$ diamond paste using standard metallographic techniques. After that, the disc was divided into two parts which were electrically insulated from each other with Microflex (Trademark of Michigan Chrome and Chemical Co., Detroit, Michigan.) and then fabricated for a disc electrode (Fig. 2). For the formation of cuprous oxide film as a corrosion product, one part of the disc electrode was held at the protective potential (-600 mV , SCE¹⁰⁾) and the

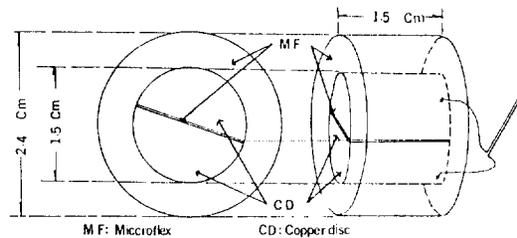


Fig. 2. Schematic representation of the disc electrode used in this work.

other part held at the corrosion potential (-200 mV, SCE) in the corrosive media. The corrosive media were buffered solutions of pH 9.2 and were stationary in the corrosion cell.

They consisted of 143 ml 0.7M H_3BO_3 (H_3BO_3 : E.P. Fisher Chemicals) mixed with 117 ml 0.5 M NaOH (NaOH: E.P. Fisher Chemicals), diluted to 2000 ml solutions with triple distilled water. The solutions were deaerated with nitrogen for at least 1½ h prior to any given experiment. No adjustment in solution pH was made. Fig. 3 shows the corrosion cell designed for the in situ examination of thin film corrosion products.

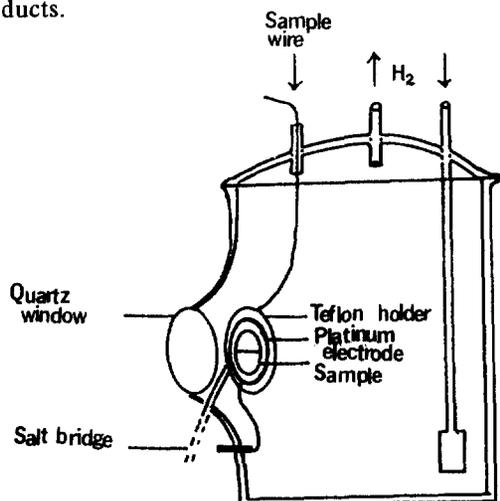


Fig. 3. Schematic diagram of the corrosion cell used for in situ experiments.

It consists of a quartz window for the light beam and a Teflon (Trademark of E.I. DuPont de Nemours and Co., Inc) sample holder to keep the sample rigidly fixed at the focal point of the oscillating mirror. The auxiliary or platinum electrode is in the form of a ring around the sample in order to avoid interference with the light path.

The materials which are in contact with the corrosive media solutions other than the sample are made of quartz, Pyrex (Trademark of Corning Glass Works), Tygon (Trademark of Norton

Co.) and Teflon. The cell was mounted in a thermostatically controlled water bath kept at 20°C ($\pm 0.2^\circ C$).

A potentiostat (RDE 3 type, Pine Instrument Co., U.S.A.) maintained a constant potential difference between the sample electrode and the reference electrode (Saturated Calomel Electrode).

EXPERIMENTAL RESULTS AND DISCUSSION

The Pourbaix diagram (Fig. 4) for copper presents that at least three solid species are stable depending upon potential and pH: copper, cuprous oxide and cupric oxide. The corrosion product for copper such as cuprous oxide or cupric oxide can therefore be obtained separately using the Pourbaix diagram. Fig. 5 shows structures of differential reflectograms obtained by holding copper potentiostatically for various time (0-69 h) in the cuprous oxide region of the Pourbaix diagram. Some experimental evidences^{7,11} have pointed out that cuprous oxide co-exists with cupric hydroxide in a certain region of the Pourbaix diagram. The solubility of cupric hydroxide in water is, however, larger than that of cuprous oxide and cupric hydroxide is also less stable thermodynamically than cuprous oxide.⁶

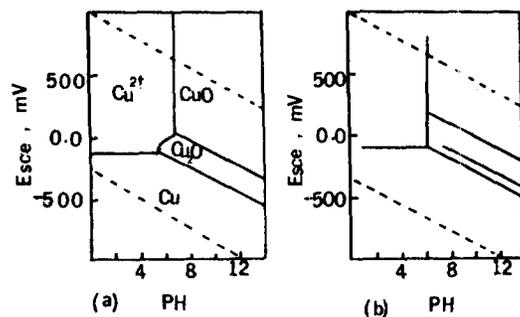


Fig. 4. Theoretical (a) and experimental (b) Pourbaix diagrams for copper in chloride-free solution.

It is therefore reasonable to assume that in this experiment, which used polarizing times of several hours, any cupric hydroxide might have been dissolved. Thus, Fig. 5 depicts evidently differential reflectivities caused by formation of cuprous oxide with increasing polarization time.

Immediately after immersion of the sample into the solutions, the differential reflectogram shows a flat spectrum with no evidence of structure (Fig. 5-a). During the first 3 h of polarization, the curve decreases slightly with decreasing wavelength without displaying any major structure (Fig. 5-b). It is suggested that this type of reflectogram is caused by the formation of cupric hydroxide. Akimov et al.¹¹⁾ observed a similar decrease in reflectivity using electroreflectance measurements and attributed this to a co-existence of cuprous oxide and cupric hydroxide. After about 6 h, some structural characteristics for cuprous oxide begin to appear (Fig. 5-c). The amplitudes of the peaks increase with polarization time, and the curves more nearly approach those known for cuprous oxide (Fig. 5-c~g). The features in differential reflectograms (Fig. 5-a~d) are similar to Shanley's results¹²⁾ for cuprous oxide which were identified using optical techniques.

As shown in Hummel's study¹³⁾, any experimentally observed peaks in differential reflectograms of corrosion product films are caused by electron interband transitions and amplitudes of the peaks increase with growth of corrosion product films. Thus, Fig. 5 indicates that cuprous oxide film grows with increasing polarization time. It is worthwhile to know whether or not the thickness of a corrosion product film can be estimated from the intensity of the peak in a differential reflectogram.

There are three distinct ranges relating film thickness to differential reflectivity. In the first

range, where the film is up to approximately 50 nm thick, the structure in a differential reflectogram is constant and unique for each kind of film. In this case, the film thickness can be calculated using the differential reflectivity obtained experimentally and following equations^{14,15)}.

$$\Delta R/\bar{R} = \frac{R_1 - R_2}{(R_1 + R_2)/2} \quad \text{----- (1)}$$

$$R_1 = \frac{(n_2 - n_0)^2 + k_2^2}{(n_2 + n_0)^2 + k_2^2} \quad \text{----- (2)}$$

where n_0 is the index of refraction of the medium surrounding the sample, which here is 1.33¹⁶⁾. n_2 and k_2 are indices of refraction and adsorption of the sample, respectively.

$$R_2 = \frac{(g_1^2 + h_1^2)e^{-2\alpha} + (g_2^2 + h_2^2)e^{2\alpha} + A\cos 2r + B\sin 2r}{e^{2\alpha} + (g_1^2 + h_1^2)(g_2^2 + h_2^2)e^{-2\alpha} + C\cos 2r + D\sin 2r} \quad \text{----- (3)}$$

where

$$A = 2(g_1g_2 + h_1h_2), \quad B = 2(g_1h_2 - g_2h_1)$$

$$C = 2(g_1g_2 - h_1h_2), \quad D = 2(g_1h_2 + g_2h_1)$$

$$g_1 = \frac{n_0^2 - n_1^2 - k_1^2}{(n_0 + n_1)^2 + k_1^2}, \quad g_2 = \frac{n_1^2 - n_2^2 + k_1^2 - k_2^2}{(n_1 + n_2)^2 + (k_1 + k_2)^2}$$

$$h_1 = \frac{2n_0k_1}{(n_0 + n_1)^2 + k_1^2}, \quad h_2 = \frac{2(n_1k_2 - n_2k_1)}{(n_1 + n_2)^2 + (k_1 + k_2)^2}$$

$$\alpha = \frac{2\pi k_1 d}{\lambda} \text{ [radians]} \quad \gamma = \frac{2\pi n_1 d}{\lambda} \text{ [radians]}$$

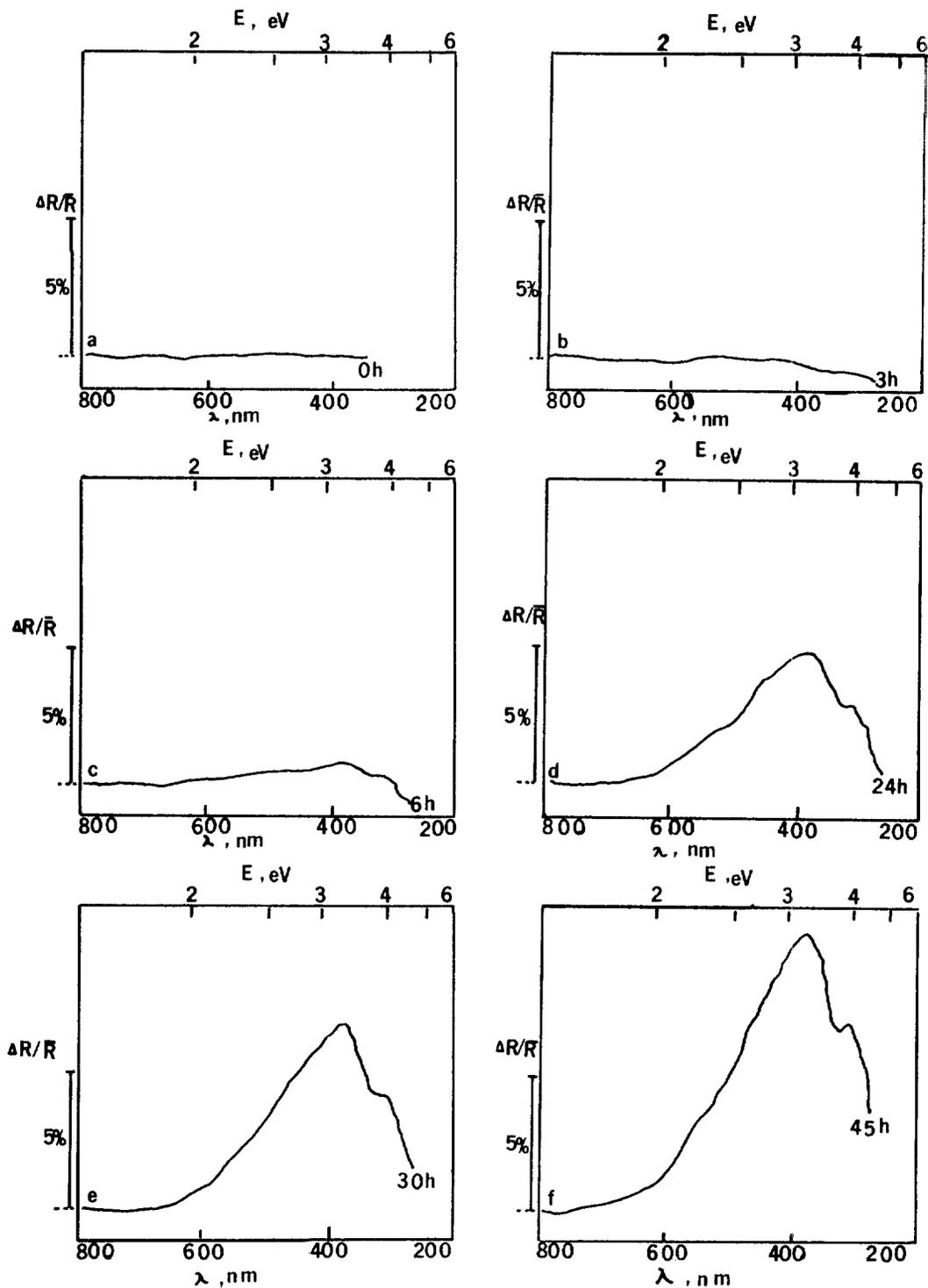


Fig. 5. Differential reflectograms of copper held potentiostatically at -200mV(SCE) , $\text{pH } 9.2$ and 20°C for various times.

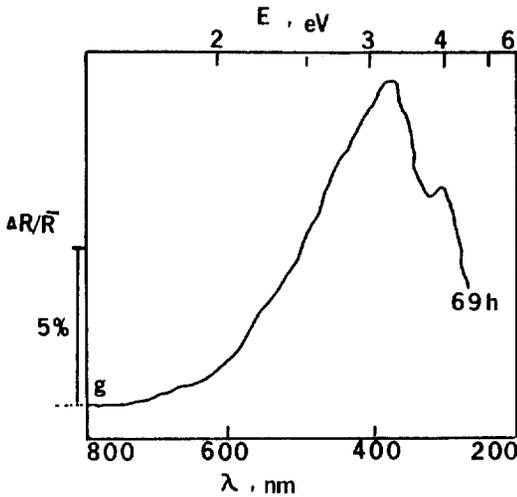


Fig. 5. Differential reflectograms of copper held potentiostatically at -200mV (SCE), pH 9.2 and 20°C for various times (continued)

where n_1 , k_1 and d are indices of refraction, adsorption and thickness of the corrosion product film, respectively.

In the second range, extending from 50nm to a thickness of about 750nm, interference effects which occur when the film thickness is of the same order of magnitude as the wavelength of the incoming light dominate the spectra. In this case, interference peaks occur in the differential reflectogram. If only one interference peak, which is a one oscillation-type, exists in the differential reflectogram, it is also possible to estimate the greater film thickness by applying the equation(4)¹⁷⁾.

$$d = \frac{\lambda_1}{5n_1} \text{----- (4)}$$

where λ_1 is the position of the longest wavelength peak at which interference starts to occur.

For the case in which the reflectogram exhibits three or more interference peaks, the thickness may be found from the equation(5)¹⁷⁾.

$$d = (n_1/2)(\lambda_a - \lambda_b) / (\lambda_a - \lambda_b) \text{----- (5)}$$

In equation (5) λ_a is the position of a given peak and λ_b is the position of the second peak from λ_a .

Finally, in the third range, where the film thickness is greater than 750nm, the differential reflectogram will again be unique for each corrosion product. However, peak intensities will be unaffected by increasing film thickness. In this case, the film thickness can usually be analyzed by X-ray techniques.

In Fig. 5, the structures of differential reflectograms are constant and unique for each time of polarization. The emergence of a new peak after 24 h of polarization can be clearly identified, by reviewing Urban's publication¹⁷⁾, as being caused not by interference effects but by the growth of cuprous oxide film. The film thickness of cuprous oxide can therefore be calculated by applying equations (1)~(3).

However, optical constants for cuprous oxide have not been measured yet. Only those for copper metal^{18,19)} and cupric oxide²⁰⁾ have been measured. For this reason, it is impossible to estimate the exact film thickness of cuprous oxide, while it can be suggested from the consideration discussed above that the film is within about 50nm thick even during 69 h of polarization.

In order to investigate the growth kinetics of cuprous oxide film on copper substrate, the differential reflectivity for the wavelength of 380nm (which positions main peaks in Fig. 5) is plotted as a function of polarization time in Fig. 6. It can be seen in the figure that a considerable change in slope of the curve at about 45 h of polarization. The slope of the curve during the first 45 h of polarization becomes somewhat larger than that of the curve appeared after the time. It can be also known by extrapo-

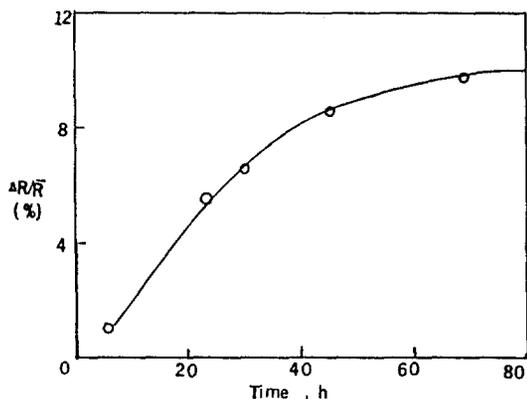


Fig. 6. Differential reflectivity for the wavelength of 380nm versus polarization time.

lating the curve that, after 69 h of polarization, the differential reflectivity is approaching 10% of the steady value. These results indicate that cuprous oxide film grows substantially with time in the first about 45 h of polarization after which the growth is slower.

CONCLUSION

In the application of the technique of differential reflectometry to this study, it is found that structures in differential reflectograms for cuprous oxide film are constant and unique. But the thickness of cuprous oxide film can not be estimated exactly because optical constants for cuprous oxide have not been measured yet. However, it is suggested that the film formed during 69 h of polarization is within about 50nm thick.

The technique is also capable of investigating the growth kinetics of cuprous oxide film. It shows that cuprous oxide film grows substantially with time in the first about 45 h of polarization after which the growth is slower.

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