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**SIMULTANEOUS POTENTIOSTATIC-MICROSCOPIC
OBSERVATIONS OF THE
PASSIVATION OF IRON IN SULFURIC ACID**

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ABSTRACT

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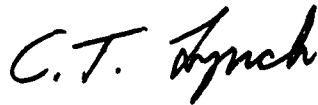
FOREWORD

This program was initiated under Project No. 7353, "Characterization of Solid Phase and Interphase Phenomena in Crystalline Substances", and Task No. 735302, "Correlation of Physical and Mechanical Properties of Metals and Ceramics", during the period February 1967 through February 1968.

This research was done in the Advanced Metallurgical Studies Branch of the Metals and Ceramics Division, AFML, Wright-Patterson Air Force Base, Ohio 45433. The principal investigators were Mr. Adolph Pigeaud and Dr. Harry B. Kirkpatrick.

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This technical report has been reviewed and is approved.



C. T. LYNCH, Chief
Advanced Metallurgical Studies Branch
Metals and Ceramics Division
Air Force Materials Laboratory

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SECTION I
INTRODUCTION

A number of authors, notably Muller (Reference 1), Bartlett and Stephenson (Reference 2), and Froment (Reference 3), have reported the formation of ferrous sulfate crystals on the surfaces of active iron electrodes in sulfuric acid when maintained at potentials in the range 250-500 mV normal hydrogen electrode (NHE), and when undergoing oscillatory behavior at potentials near the Flade potential. The present paper reports some optical effects observed on iron surfaces undergoing cyclic activation and passivation in 1N sulfuric acid which appear to be different from those previously reported and to have some interesting implications as to the initial stages of passive film formation.

SECTION II
EXPERIMENTAL PROCEDURES

For the purpose of making detailed correlations between microscopic observations and electrical behavior during the passivation process, it was decided to take advantage of the cycling between active and passive states which iron (and some other metals) exhibits when it is maintained at a constant potential in the vicinity of the Flade potential, i.e. about +500 mV relative to the NHE. Under potentiostatic conditions more or less irregular, oscillatory current fluctuations have been reported at this voltage which have been extensively studied, mainly by Franck (References 4,5,6). Steady, reproducible behavior, however, is difficult to attain at this electrochemical transition point because any, even momentary, large flow of ions due to an ongoing active process is apt to seriously disturb the diffusion layer. Rapid transport of products and reactants between the solution and the surface of the metal quickly gives rise to random concentration and density gradients with accompanying effects of thermal diffusion and bulk flow. Hence if the active state persists for more than just a few seconds, and particularly if the electrode surface is large and complex or oriented in a vertical plane, a number of simultaneous half-cell and diffusion layer reactions can occur. (In fact alternating events over electrode region which complement each other have been reported (Reference 3) and have been observed by the present authors even on a small horizontally oriented surface. In such cases the maximum current attained at each oscillation approaches the same value only one oscillation in two.) Thus, without great precaution, irregular current oscillations are usually the result. They are difficult to follow and are particularly annoying if one wishes to study the details of the short-lived, active-passive transitions by repeatedly and reproducibly going through the same cycle.

When, however, the potential is adjusted more and more toward the passive region, the oscillations can be made to cycle with a very short active period followed by rapid passivation. The passive state then lasts for a considerable time, long enough to allow any large concentration

differences to equalize by diffusion so that they do not affect succeeding cycles. The oscillations can then be made to repeat themselves quite precisely both in period and duration by using a small electrode and mounting it so that only a single, highly polished surface faces horizontally upward in the electrolyte. This geometry in conjunction with a quiescent state of the electrolyte avoids mixed potentials and localized currents due to edge effects, granularity of the surface, and unequal flow-off of reaction products. Under these conditions, the oscillations were sufficiently regular and reproducible that details could be observed repeatedly cycle after cycle.

In the present experiments the iron was of purity 99.95% and the electrolyte was 1.0 N reagent grade sulfuric acid. Figure 1 illustrates diagrammatically the experimental arrangement. The iron specimens were made by cutting short lengths from a rod having a cross-sectional area of 0.25 cm^2 , which was thus the area exposed to the electrolyte. The specimens were mounted in a tight Teflon holder so that one circular end was exposed, which was then carefully polished making sure that no crevasses occurred between the metal and Teflon holder. Crevasses would cause a small cathodically active ring to form around the electrode and large hydrogen bubbles would soon form and give rise to irregular behavior. The specimen was maintained at a potential of about +500 mV (NHE) by current supplied from a high-speed 'Wenking' potentiostat, Model 61 RH. The cell current fluctuations were recorded on one channel of an X-Y₁-Y₂ recorder. Two platinum helix counter electrodes were placed inside porous cups in order to minimize stirring effects from the evolution of hydrogen bubbles. A Luggin probe containing a saturated calomel electrode was situated in the vicinity of the metal surface in such a way as not to interfere with ion transport to and from the diffusion layer. The arrangement was such that the specimen surface could be observed with a low power binocular microscope and photographed with a conventional 35 mm single-lens reflex camera and electronic flash. While only one frame could be exposed per cycle, the regularity of the oscillations allowed

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photomicrographs to be taken in random sequence as long as each frame could be exactly keyed to some particular instant in the output current curve. This was done by having the electronic flash circuit trigger an event marking pulse on the second channel of the recorder.

SECTION III

RESULTS

The potential of the electrode was fixed to maintain a frequency of about one oscillation per minute at room temperature. Each oscillation lasted about ten seconds with a peak current density of about 800 ma/cm^2 . While, as stated above, the oscillations were regular and reproducible if conditions were carefully controlled, the regularity and frequency of the oscillations were found to be very much dependent on the orientation of the electrode surface. If the active surface is tipped only slightly out of the horizontal plane, the shape of the current output curve as well as the frequency may be drastically changed. In general the shape of the curves is as shown in Figure 2 - a very rapid increase of current to about 800 ma/cm^2 during activation, followed by a fast-slow-fast current decay over a period of some seconds until passivation is reestablished. When passive, the baseline current is about $0.01\text{-}0.1 \text{ ma/cm}^2$. It is the current decay during passivation which is orientation sensitive, the activation part not being visibly affected.

The iron surface was observed microscopically with 7X magnification during the oscillations. Under illumination with plane polarized light - the analyzer being crossed with respect to the polarizer to extinguish reflections from the shiny metal surface - there were no visible optical changes during the fast current jump accompanying spontaneous activation. However, during the current decay associated with the onset of passivation and commencing about two or three seconds after the current peak, a roughly circular zone of very greatly increased reflectance was seen to grow from the circumference to the specimen towards its center until the entire surface was covered at about the time the base-line current was reached. The reflective zone, or layer, then darkens uniformly until the extinguished condition is re-attained. At this point, if the analyzer is uncrossed, the electrode surface has its normal shiny, metallic appearance with no 'visible' trace of a surface film.

Figure 2 is a composite photograph showing the sequence of reflective layer growth and darkening at different points of a typical cycle. Light from the brightly reflecting zone is depolarized, in the sense that upon rotating the analyzer there is no change of intensity or point of extinction. The zone also has the appearance of possessing a domain structure, which is apparently unrelated to the metal surface grains because the domains change in size and shape from one cycle to the next. The reflecting layer, however, is evidently very thin inasmuch as some vague features of the metallic surface are discernible beneath it independent of which cycle we look at. Figure 3 shows the reflective layer at higher magnification in an intermediate stage of growth.

An interesting and surprising property of the reflective layer is that it can be readily disrupted by squirting a jet of liquid from the surrounding solution at the electrode surface. The reflective layer is instantly washed away and the electrode surface returns to its fully active state allowing a current of 800 ma/cm^2 to flow. This level of activity can be maintained more or less indefinitely until the jet is stopped and the reflective layer has a chance to reform. The current then begins to decrease back to the passive level and, this being reached, the reflective layer gradually darkens to the extinguished condition typically of the passive state. As long as the transition of the brightly reflecting layer to the dark passive condition is incomplete the surface can be reactivated by a jet of solution. Although, to accomplish this becomes more and more difficult depending on how far the layer has faded. Once the transition is complete the surface film is in a very stable state and cannot be removed by a jet of solution or even by a dull glass rod scratched over the surface. Occasionally, when a jet of solution strikes the surface early in the passivation cycle, a thick, opaque layer of grayish, crystalline-looking material also precipitates on the surface and then slowly redissolves. While no analysis has been attempted, it is presumed that this material is the often mentioned ferrous sulfate heptahydrate. It has a strikingly different appearance from the bright layer precursor and the sporadic formation of it in no way correlates with the cycling of the active-passive transitions.

If, as has been most recently reported by Froment (Reference 3), the growing reflective layer too were a solid crystalline precipitate of ferrous sulfate on the electrode substrate, its mechanical strength and cohesiveness should be at least such that no sudden removal could be possible due to a slight disturbance of the diffusion layer. In the present case, however, the extreme sensitivity, both of the reflective layer and of the electrochemical activity, to fluid flow and electrode orientation suggested that the precursory process leading to passivation took place in the liquid phase rather than in any solid layer tightly bound to the metal surface.

While no distinct precipitate particles could be resolved in the bright zone, the depolarization of originally polarized light suggested the possible existence of colloidal particles in the layer. It is well known that such particles, if anisotropic, can scatter an incident plane-polarized beam in all directions as well as depolarize the scattered light. In order to test this hypothesis, a Zsigmondy slit-ultramicroscope was arranged as shown in Figure 4. Light from a zirconium arc lamp is passed through a negative lens and several slits to form a narrow parallel beam passing through the solution immediately above the electrode surface. The metal receives no light and so the necessity of using crossed polaroids to prevent strong reflection from the metal surface is avoided. When viewed from above through a microscope under high magnification (150 X) small glittering points of scattered light should be visible against a black background if colloidal particles are present. The iron electrode surface was viewed in this manner during active-passive cycling. While passive and during the current jump accompanying activation nothing could be seen in the ultramicroscope, but as the current decayed a wave of small, glittering points of light was actually observed to sweep across the surface in much the same fashion as the bright reflective layer in the previous experiment. The points of light were visible momentarily and then appeared to move downward out of the light beam towards the electrode surface. By comparison with measured asperities on the metal surface, the layer of illuminated particles was estimated to be about seven to ten microns

above the surface. The appearance of the light specks was peculiar however in that they did not seem to exhibit the customary Brownian motion of colloidal particles and had some tendency to arrange themselves in rows. This can perhaps be explained by the fact that each glittering speck of light was visible only a fraction of a second which made it difficult to follow the movement of any individual particle.

Unfortunately, it is not possible to illustrate these phenomena with photographs because of the low intensity of the scattered light. Even visual observation was not easy because of the transient nature of the effect and the critical geometrical factors. However, it does appear that colloidal particles definitely exist some distance from the surface and that the appearance of these particles in a laterally growing layer is directly related to the slow current changes of an active-passive transition.

SECTION IV

DISCUSSION

From these observations, at least under the conditions of these experiments, the sequence of events during an activation-passivation cycle can be summarized as follows:

1. Sudden spontaneous activation, accompanied by an abrupt increase in current density from about $0.01-0.1 \text{ ma/cm}^2$, the value when passive, to about 800 ma/cm^2 .
2. Relatively gradual decay of the current back to 0.1 ma/cm^2 , accompanied by inward radial growth of the reflective layer, the reflected light being depolarized, and formation of colloidal precipitate in the liquid adjacent to the metal surface. The colloid appears to migrate to the metal surface.
3. Fading of the reflective layer and stabilization of the passive film.

Thus the development of the passive oxide film is preceded by the precipitation of a precursor substance in the liquid along the iron surface. This substance migrates to the electrode surface and the final form of the passive film is then developed.

As mentioned previously, a thick, opaque layer of grayish crystalline material is sometimes suddenly precipitated when the surface is activated by a jet of liquid, or it may gradually accumulate in clumps when the cell is operated for long periods. This apparently is the ferrous sulfate described by Muller, Bartlett and Stephenson, and Froment as forming on active electrodes. It is entirely different in appearance from the bright, reflective passivation precursor layer and its sporadic formation is not correlated with the regular active-passive cycles. Salt precipitation of this type was not observed when the iron electrode was cycled in 1N perchloric acid, presumably because of the greater solubility of

$\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (e.g. 97.8 g/100 ml H_2O as against 15.65 g/100 ml for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.) On the other hand reflective layer formation during passivation took place identical to that in sulfuric acid. Thus precipitation of iron salts does not seem to be essential to passivation.

Other than ferrous sulfate, the most likely chemical species to precipitate would be a hydroxide or hydrous oxide of iron, such as colloidal ferrous hydroxide. Ferric hydroxide might also form if there is dissolved oxygen in the electrolyte. Belyi, Dolgaya, and Pamfilov have reported the formation of colloidal precipitates about 0.005 to 0.001 mm from the cathode surface during the electrolysis of silver nitrate and nickel sulfate solutions (Reference 8). They apparently attribute this effect to the formation of nickel hydroxide and silver oxide due to local pH increases.

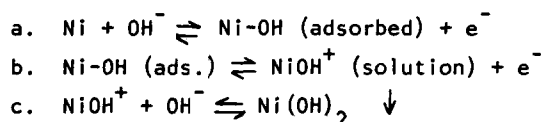
Since ferrous hydroxide is fairly soluble (solubility = 0.00067 g/100 ml of cold H_2O ; $K_{\text{SP}} = 1.64 \times 10^{-14}$) and since the present work was carried out in 1N sulfuric acid, a large local increase of pH along the electrode surface would be necessary to permit formation of the hydroxide. Franck and Fitzhugh have derived a kinetic model for periodic electrode processes based on fluctuations in hydrogen ion concentration in the vicinity of the electrode surface and in the fraction of surface covered by passive oxide film (Reference 6). They give as a first approximation, assuming current due entirely to H^+ - ion transport and a linear concentration profile within the diffusion layer, the following expression for the time rate of change of H^+ -ion concentration on the electrode surface:

$$\frac{d[\text{H}^+]}{dt} = - \frac{2}{F\delta} I_p \quad (1)$$

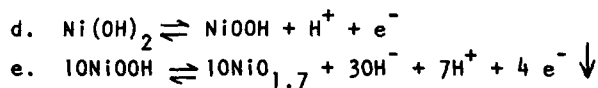
where $[\text{H}^+]$ = hydrogen ion concentration; t = time; F = the Faraday constant; δ = the diffusion layer thickness; and I_p = the total current density. In the present work, the reflective layer was first observed at the edge of the specimen about three seconds after activation, during which time the current density decreased from about 800 ma/cm^2 to 600 . The colloidal particles appeared to form about 0.010 mm above the specimen

surface. Taking the average current density in Equation 1 as 700 ma/cm^2 and δ as 0.001 cm , we obtain, as a rough estimate, an initial rate of decrease of H^+ -ion concentration of 0.014 equivalents per cubic centimeter per second, or $14 \text{ moles}\cdot\text{liter}^{-1}\cdot\text{sec}^{-1}$. Crude though this estimate may be, it clearly indicates an enormous initial increase of pH along the electrode surface, more than enough to precipitate ferrous hydroxide and to cause charge reversal on the colloidal particles. The latter point is discussed subsequently.

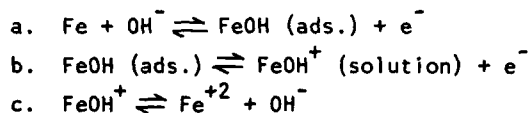
Passivation thus appears to take place via the precipitation of colloidal ferrous hydroxide which migrates to the metal surface and is transformed into the final passive oxide film. Bockris, Reddy, and Rao have suggested a similar dissolution-precipitation mechanism for the passivation of nickel in $\text{H}_2\text{SO}_4\text{-K}_2\text{SO}_4$ solution (Reference 9). According to their mechanism the passive film on nickel is established by the following sequence of reactions:



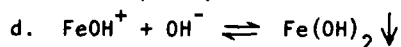
The nickel hydroxide (precursor) layer on the electrode is then oxidized to a nonstoichiometric oxide film (the passive layer) by a mechanism established by Briggs, Stott, and Wynne Jones (Reference 10):



Bockris, Reddy, and Rao also point out that the mechanism for the anodic dissolution of iron is similar to that for nickel, i.e.:

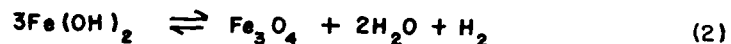


In this sequence, reaction b is the rate-determining step. At sufficiently high pH's, the hydroxide would precipitate as in the case of nickel:



The precipitation of the hydroxide in the form of a colloidal dispersion offers a clue as to the reason for its rapid migration to the electrode surface, a point not otherwise immediately apparent. Because of their high specific surface, particles of colloidal size tend to become electrically charged due to adsorption of ions from the electrolyte. Thus in mildly acid solution both ferrous and ferric hydroxide sols are positively charged due to hydrogen ion adsorption (Reference 11). However, Hazel and Ayers have shown by electrophoresis measurements that at pH values above 8.6 the charge is reversed on ferric hydroxide (or hydrous ferric oxide) particles and they become negatively charged by hydroxyl ion adsorption (Reference 12). While similar measurements do not seem to have been carried out for ferrous hydroxide, Weiser states that it behaves toward electrolytes like ferric oxide sol (Reference 13). Therefore, it is reasonable to suppose that at sufficiently high pH it is negatively charged and moves to the anode by electrophoresis.

While the structural chemistry of freshly precipitated $\text{Fe}(\text{OH})_2$ is exceedingly complex, it does have a strong tendency to transform into iron oxides, either by oxidation or decomposition. Thus Ephraim mentions (without giving a reference) that white ferrous hydroxide decomposes even in absence of air (Reference 14):



Weiser (Reference 13) refers to the work of Huttig and Moldner as reporting that thermal dehydration of ferrous hydroxide yields hydrogen, probably by this same reaction. Weiser also describes the results of Baudisch and Welo who observed that, when oxygen is admitted, the freshly precipitated hydroxide undergoes the following reactions:

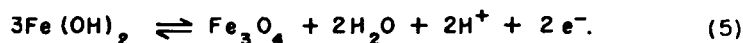


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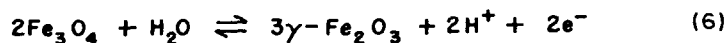


On the other hand when the hydroxide is aged four days in neutral solution in the absence of air, a mixture of α - Fe_2O_3 with a small amount of γ - Fe_2O_3 is formed on oxidation.

The first reaction above leads naturally to the type of layer postulated by Vetter (Reference 15) and by Lange and Gohr (Reference 16) to account for the Flade potential. Thus



Oxidation of the outer portion of the Fe_3O_4 layer could then follow according to Vetter (Reference 17):



In order to account for the present results, it is proposed that the passivation of iron under these conditions takes place by a dissolution-precipitation mechanism involving the following reactions:

- (a) $\text{Fe} + \text{OH}^- \rightleftharpoons \text{FeOH}(\text{adsorbed}) + \text{e}^-$
- (b) $\text{FeOH} \rightleftharpoons \text{FeOH}^+(\text{solution}) + \text{e}^-$
- (c) $\text{FeOH}^+ + \text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2$ (negatively charged colloid)
- (d) $3\text{Fe}(\text{OH})_2 \rightleftharpoons \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$
- (e) $2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons 3\gamma\text{-Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}^-$

While such a mechanism is consistent with the ideas of Bockris and Vetter and with the chemistry of ferrous hydroxide, certain difficulties exist with respect to the physical properties of the reflective precursor layer. It has the seemingly contradictory properties of being very labile and sensitive to fluid flow and yet to impose a high resistance to ionic conduction, since the current decreases rapidly as the layer spreads across the surface. It might be argued that the reflective layer and colloidal particle formation are merely coincidental to the true passivation process and are not causally related to it. However there is no apparent reason why the tightly bound $\gamma\text{-Fe}_2\text{O}_3$ or chemisorbed oxygen layers postulated by the usual passivation theories should be so easily washed away and activity

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restored. One possible explanation might be that if reaction (d) is rapid, the Fe(OH)_2 is immediately converted to a coherent layer of Fe_3O_4 which may act to reduce the current but be rapidly soluble in a jet of fresh acid. Foley, Kruger, and Bechtoldt have reported the presence of Fe_3O_4 in pre-passive films (Reference 18).

SECTION V
CONCLUSIONS

1. Cyclic active-passive transitions of iron in 1N sulfuric acid have been observed microscopically with vertically incident, plane-polarized light and by means of slit ultramicroscopy.

2. During the onset of passivation a brightly reflecting passivation precursor layer was observed to grow across the surface, the reflected light being depolarized. When viewed ultramicroscopically, the layer was seen to consist of colloidal particles which appeared to migrate to the electrode surface.

3. Clumps of dull, grayish crystals resembling the ferrous sulfate crystals described in the literature were observed to form sporadically during the experiments but their occurrence was unrelated to the regular active-passive cycles. Such crystals were not observed in perchloric acid.

4. In order to account for the observations a dissolution-precipitation mechanism, involving the precipitation of negatively charged colloidal ferrous hydroxide, is suggested.

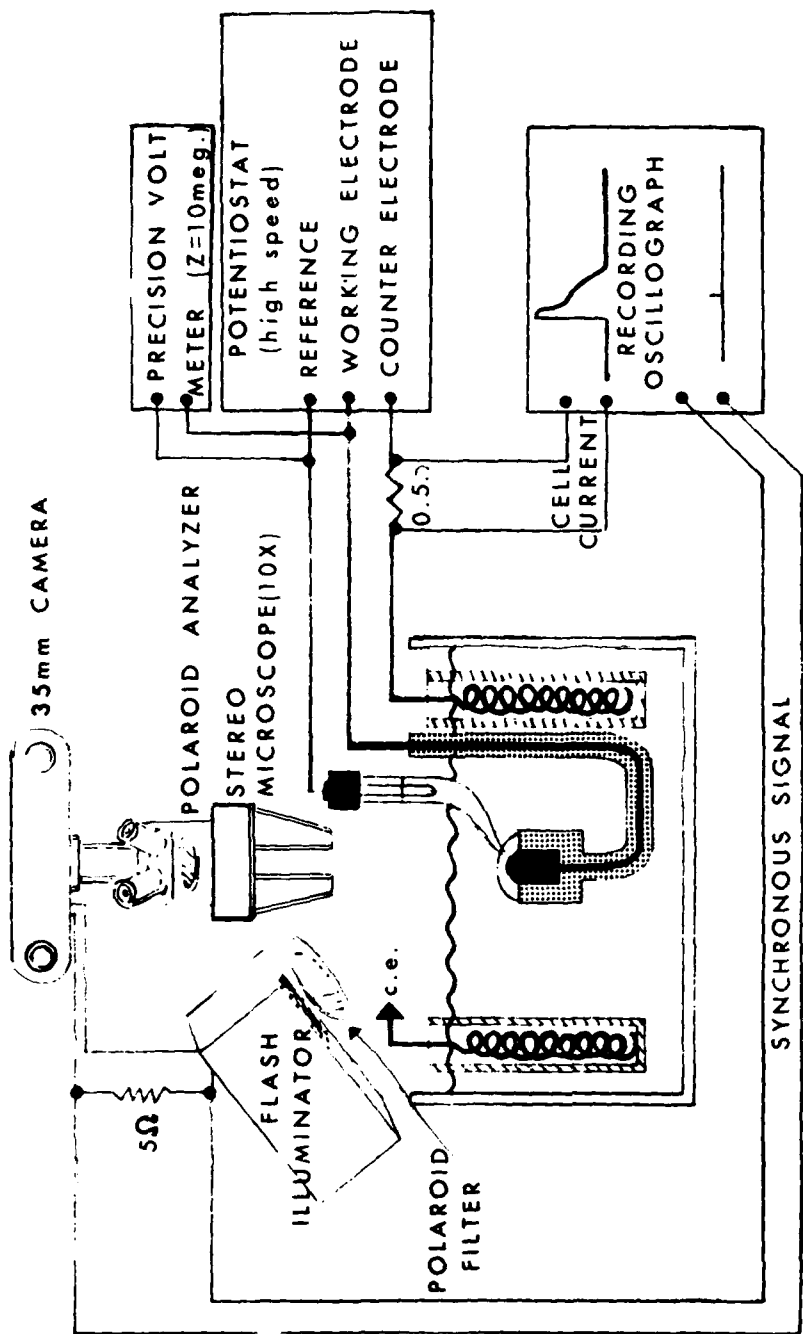


Figure 1. Diagrammatic Illustration of Microscope Arrangement (In later experiments vertically incident light was used.)

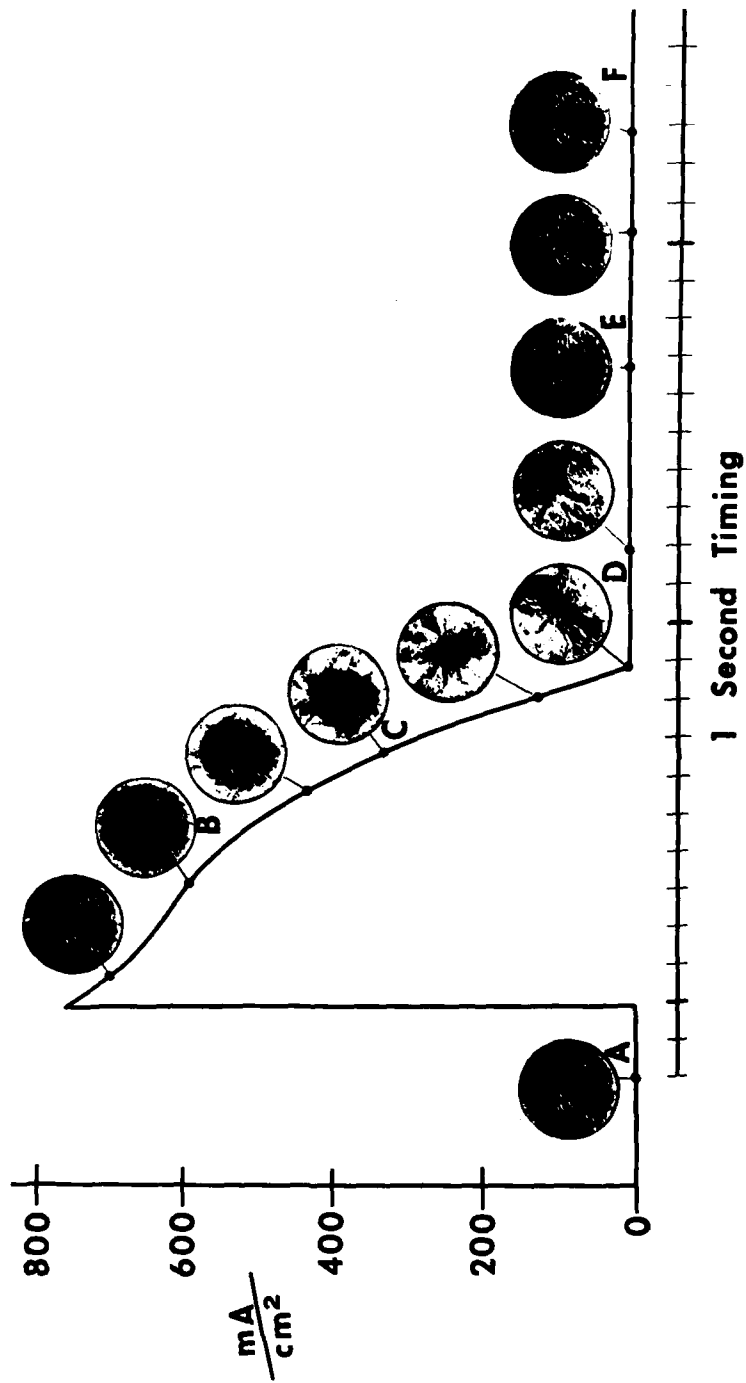


Figure 2. Typical Activation-Passivation Cycle, Showing Stages in Development of Reflective Layer



Figure 3. Enlarged Photomicrograph of Reflective Layer in Intermediate Stage of Growth (Fifth print from Figure 2)

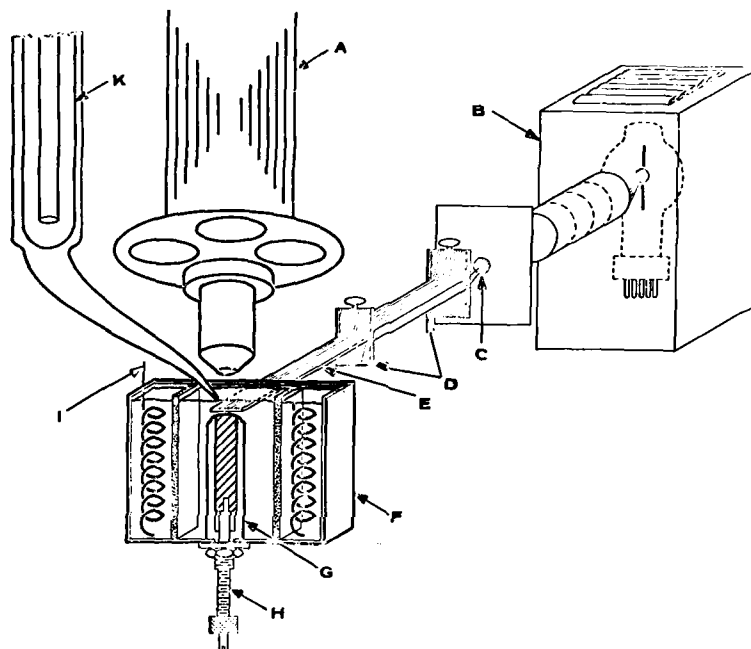


Figure 4. Diagrammatic Illustration of Ultramicroscope Arrangement:
 a) Light Microscope (150 X magnification); b) Zirconium-arc
 Light Source (300 watt); c) Double Concave Lens ($f = -8.5$ mm);
 d) Two Slit Systems (1 mm and 0.5 mm); e) High Intensity
 Parallel Light Beam (8 x 0.5 mm); f) 10 mm Light Path Cell
 with Optical Grade Windows and Porous Partitions added; g)
 Teflon Electrode Holder Incorporating Advancing Mechanism
 (active iron surface polished and slightly beveled); h)
 Working Electrode Connection to Potentiostat; i) Platinum
 Counter Electrodes; k) Calomel Reference Electrode Inside
 Luggin Probe.

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