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Subject

**THE ROLE OF PASSIVE FILM GROWTH KINETICS AND PROPERTIES IN
STRESS CORROSION SUSCEPTIBILITY**

Submitted to the Office of Naval Research

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THE ROLE OF PASSIVE FILM GROWTH KINETICS AND PROPERTIES IN STRESS CORROSION SUSCEPTIBILITY

Submitted to the Office of Naval Research

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TABLE OF CONTENTS

	<u>Page</u>
I. Introduction	1
1. Repassivation Kinetics	2
Experimental.	3
Results and Discussion	4
Summary and Conclusions	9
2. Film Ductility	11
Experimental.	12
Results and Discussion	14
References	18
Figure Captions.	20
II. Tarnish Film Formation	
Introduction	32
Experimental	33
Results.	35
Discussion.	37
References.	43
Figure Captions	44

THE ROLE OF PASSIVE FILM GROWTH KINETICS AND PROPERTIES IN
STRESS CORROSION SUSCEPTIBILITY

ABSTRACT

The role of passivation kinetics, film ductility, and tarnish film formation in stress corrosion cracking were each examined in the following studies:

1) Repassivation kinetics of iron in solutions known to cause stress corrosion cracking of low carbon steels have been compared to that for those environments where cracking has not been observed. Ellipsometry measurements of film growth on iron have shown growth rates to be comparable in 4N NaNO_3 (a cracking solution) and 0.1N NaNO_2 (noncracking) when polarized to the same passive potential. However, at the corrosion potential for the respective solutions a protective passive film was grown in the nitrite solution whereas the films in nitrate solutions was non-protective and metal dissolution occurred. The rates found in the presence of chloride (a nonsusceptible anion for steel) in a borate buffer solution were dependent on potential. Below 0.200 v SHE the rates were comparable to those observed in the absence of Cl^- , above this potential a higher rate of formation of a non-protective film results which leads to extensive pitting rather than S.C.C. In a 5% NaOH solution (a S.C.C. susceptible anion) polarization to the passive region yielded rates higher than those observed in the other susceptible solution, nitrate. At open circuit the hydroxide solution does not produce a protective film.

2) A technique has been developed to measure film ductility directly. This technique couples an ellipsometer with a tensile machine. Thin films on Ta show a ductility of 3-4% in the presence and absence of F^- , an ion thought to decrease ductility.

3) Because copper in cupric acetate and sulfate solutions has tarnish film growth rates comparable to that found for brasses susceptible to S.C.C. it should under go cracking in such solutions if kinetics play a role. It was found that pure copper is susceptible to cracking in cupric acetate solution but not in cupric sulfate. Light, which retards film formation on copper, but not corrosion, prevents stress cracking in the cupric acetate solution. In the absence of stress, oxide forms all over the copper surface, while stress concentrates oxide formation at the grain boundaries. These experiments point to a brittle-film rupture mechanism of stress cracking.

THE ROLE OF PASSIVE FILM GROWTH KINETICS AND PROPERTIES IN
STRESS CORROSION SUSCEPTIBILITY

In the many studies of the complex phenomenon of stress corrosion cracking (1-5) a number of factors have been suggested as being of critical importance in determining if a given alloy in a given environment is susceptible to this type of failure. Among these are rupture of passive films (1), low stacking fault energy lattice (2), segregation of solute atoms (3), complex formation (4), electrochemical-mechanical interactions (5), short range order (6), precipitate effects (7) and many others. All of these factors can influence the cracking process in one or both of two ways:

1) They can affect the way in which the metal's lattice is altered by the application of stress.

2) They can affect the chemical (or electrochemical) interaction of the stress-affected metal structure with the environment. Scully in a recent paper (8) points out that kinetic studies of both of these necessary ingredients have been neglected. He suggests, using parts of a number of proposed mechanisms (especially those that require a passive film), that the first item is influenced both by structure (e.g., types of dislocation arrays), and composition (e.g., precipitates). Item 1 determines the speed at which slip steps emerge during plastic deformation to produce bare metal sites. The second item determines at what rate these bare sites re-passivate. Alloys where the rate of slip step emergence through an initially present passive film (bare surface production) exceeds the rate of their protection from the environment by re-passivation are the ones

susceptible to cracking. A great deal of attention has been placed on the first requirement. Its kinetic aspects have, however, been ignored (8). This is not surprising since it is difficult to measure, for example, the rate of production of bare slip steps on a surface. Techniques do exist, however, that measure the rate of repassivation of a metal surface. The optical technique of ellipsometry (9) has been so employed, but not in experiments directed at a study of stress corrosion. Moreover, passivation kinetics is a part of the stress corrosion process that is most likely affected by the nature of the environment. Such studies would thus promise to throw some light on the still largely unanswered question of why small changes in the environment greatly affect stress corrosion susceptibility.

This study, therefore, seeks to examine the effect that the kinetics of repassivation has on susceptibility. However, it seeks to go one step further by looking at the ductility of the passive film as well as its rate of formation. This is necessary because the possibility that rupture of the passive film by slip steps or metal movement in general may not occur if the film is sufficiently ductile. Such a suggestion was made by Vermilyea (10). Therefore, in addition to repassivation kinetic studies, the effect of metal composition and cracking environment on film ductility must also be studied.

Film formation kinetics may have another bearing on susceptibility that is unrelated to repassivation, the fracture of brittle films formed rapidly in grain boundaries. The last part of this report is concerned with this aspect.

1. Repassivation Kinetics

The approach in these experiments is to produce by cathodic reduction a bare metal surface, shift the potential into the passive region, and study the repassivation of the bare surface by a fast ellipsometric recording technique (11). This procedure thus studies a process that is

essentially equivalent to the repassivation of the bare surface produced by the emergence of bare slip steps on a stressed metal surface. In a system undergoing stress corrosion, the polarization necessary to repassivate is provided by the difference in potential between the newly produced bare surface and the remaining filmed surface. We polarize our bare surface by bringing it to potentials well into the passive region as well as to the corrosion potential exhibited by a given metal in the selected environment.

EXPERIMENTAL

These studies used a high purity polycrystalline iron obtained from the Battelle Memorial Institute which was refined by a floating zone technique. It has less than 10 ppm gaseous impurities and less than 130 ppm metallic impurities¹. The surface of the specimen was mechanically polished using 6 and 1/4 micron diamond abrasives followed by electropolishing in a 20:1 acetic acid/70% perchloric acid mixture at 17°C.

Several solutions were used in these studies, all prepared from CP Grade reagents and doubly distilled water.

- 1) Standard sodium tetraborate (0.0375M)/boric acid (0.05M) buffer solution (pH = 8.4).
- 2) 4N sodium nitrate.
- 3) 0.1N sodium nitrite.
- 4) 5% w/v sodium hydroxide.
- 5) 3.5% w/v sodium chloride, prepared in the stock borate solution.

¹Gaseous impurities (ppm): O₂ (vacuum fusion), 2.1; S (colorimetric), 4±3; C (combustion-conductometric, 3±3; N₂ (vacuum fusion), 0.5; H₂ (vacuum fusion), 0.3.
Major metallic impurities (ppm): Al, 15; Cr, 5; Co, 5; Cu, 7; Ni, 20; P, 9; Si, 10.

Solutions were usually deaerated with high purity helium except in those cases where the effect of oxygen was to be studied, in which case the solution in the cell was saturated with high purity air.

The potentiostatic ellipsometric technique described by Kruger (11) was used in these studies. The electronic circuitry and the electrolytic cell were the same as used in that previous investigation except that an auxiliary chamber was added to the gas bubbler so that measured volumes of other solutions could be rapidly introduced into the cell by the deaerating gas.

A typical experiment would involve the production by cathodic reduction of a bare metal surface in the environment being studied, followed by either anodic polarization to a potential in the passive region or by opening the electric circuit and allowing the potential to drift to the corrosion potential. In each case, the growth of oxide film was followed by the ellipsometer.

The oxide films thus generated were reduced either galvanostatically at a constant current of $-25 \mu\text{A}/\text{cm}^2$ or potentiostatically at a potential of -0.758 v SHE . The solution was then replaced, a bare metal surface again produced, and a new experimental run started.

RESULTS AND DISCUSSION

Four anions were chosen for this study of the role of environment on the initial rates of repassivation of bare surfaces. Low carbon steels have been found to be not susceptible to S.C.C. in two of these, chloride and nitrite, and to be susceptible in nitrate and hydroxide (1). It is especially useful to compare nitrite and nitrate because of their chemical similarities.

Chloride Environment

The chloride ions in these experiments were placed in a neutral buffered borate solution because past studies had characterized the passivation process in this solution in the absence of chloride, and by adding chloride to it we could observe the role of chloride as compared to past experience. Fig. 1 shows the growth process of the passive film was the same, regardless of whether or not chloride ions were present, so long as it occurred at potentials below that potential called E_a^2 by Nagayama and Cohen (12). At a pH of 8.4 in the solution used, E_a^2 was approximately +0.200 v (SHE). This is the potential they observed during the passivation of iron in the same solution used in these experiments, below which ferrous ions were observed in solution while above it no appreciable ferrous ion concentration could be detected. However, Fig. 1 also shows that when a film was grown in a chloride containing solution ($10^{-2}M$) at a potential above this value (+0.64 v SHE), it continued to grow at a much greater rate (initial rate = $3.78 \frac{nm}{sec^{1/2}}$) to much greater thicknesses than the limiting thickness observed when chloride was absent.

It is difficult to determine the rate law applicable during the initial stages of growth. Both a linear variation of thickness with time, t , and parabolic variation (thickness proportional to \sqrt{t}) can be fitted to the data (see Fig. 2). If the rate law is linear, diffusion is of no significance. If parabolic, diffusion is controlling. The resolution of this question may be of importance in determining susceptibility to stress corrosion once cracking has been initiated because a parabolic rate law may indicate that diffusion of oxidizing species may be rate limiting. In deep narrow cracks where diffusion is difficult, this may lower the rate of film repair.

As was demonstrated by the ellipsometric measurements in Fig. 1, passive film growth was perfectly normal, regardless of the presence of chloride ion, so long as the potential of growth remained below E_a^2 . All attempts to grow a passive film above E_a^2 in the presence of chloride ion were fruitless. Although the anodic current did drop slightly from its peak value of $4000 \mu\text{A}/\text{cm}^2$, probably due to the physical presence of oxide, no real degree of passivity could be observed.

Once formed in the presence of chloride ion, this film would continue to grow, and at a faster rate, even when the potential was lowered to values well below E_a^2 (+0.04 v SHE) and would not thin until the potential was lowered below -0.21 v (SHE). It thus appears that with chloride present, and at a potential above E_a^2 , the nature of the film is so altered that ferrous ions pass readily through the film and are deposited as an unprotective film in the manner described by Nagayama and Cohen (12) and Markovac and Cohen (13,14). Electron diffraction studies have further shown that chloride produces films which contain $\gamma\text{-FeOOH}$ as well as cubic oxide (15).

How do these results fit in with the fact that, in general, iron and low carbon steels are not susceptible to S.C.C. in chloride environments (1)? Above E_a^2 the presence of chloride increases markedly the rate of film formation on a bare surface. If such a bare surface were produced by a rupture of the passive film under stress, these exposed sites, because of their small area, may be polarized to values of potential above E_a^2 . The film formed under these circumstances is unprotective, and rapid dissolution would lead to pitting. Cracking probably does not occur because both the rate of dissolution and film growth are such that pits, or lines of pits

(postage stamp effect), too wide to act as effective stress raisers or notches, are formed. If, on the other hand, polarization is not sufficient to raise the potential above E_a^2 , the rate of formation is comparable to the borate solution, which has not been shown to cause cracking. It is necessary to compare now this rate of repassivation with a system where S.C.C. is known to occur as is done in the next section.

NITRATE/NITRITE ENVIRONMENTS

There is one great experimental difficulty in studying repassivation of bare iron in nitrate solutions, where steel undergoes S.C.C., and in nitrite, where it does not.

It is virtually impossible to produce a bare metal surface on iron in these solutions using conventional cathodic reduction techniques. This is due to competing solution reduction processes occurring at the specimen surface (nitrate \rightarrow nitrite \rightarrow ammonium ion) which proceed at essentially 100% current efficiency, thereby preventing oxide reduction.

Several alternative techniques to in situ reduction were tried. First, we produced a bare metal surface in the borate solution. Then 3 cm³ of the 4N sodium nitrate solution was flushed into the cell and the electrical circuit opened. The potential dropped rapidly to -0.458 v (SHE) as a mixture of surface roughening and film growth occurred. Significantly more film grew in the presence of nitrate ion (10A) but surface roughening was greater, indicating that films at the corrosion potential in nitrate solutions are not protective. Attempts to reduce the oxide film, even in these dilute concentrations of nitrate ion, by galvanostatic reduction

($-25 \frac{\mu\text{A}}{\text{cm}^2}$) (Fig. 4) and potentiostatic reduction (0.758 v SHE) resulted in only about 1/3 the film being removed. Since this technique only allowed us to investigate film growth kinetics in extremely dilute solutions of these ions, nowhere near the concentrations known to produce stress corrosion cracking, we decided to try another approach. Here, after producing a bare metal surface in the borate solution, and while under a cathodic potential of -0.758 v SHE and an inert helium atmosphere, this solution was replaced by either a 4N NaNO_3 or an 0.1N NaNO_2 solution, both standard cracking solutions. Oxide film was then grown either by opening the circuit or by anodic polarization. Although the cell was not airtight, and apparently about 5\AA of film was present on the surface prior to the growth experiments, several observations were quite clear. The presence of oxygen in the solution did not affect the rate of film growth to any great extent; films were slightly thicker. Thus, limiting thickness for a film grown at -0.108 v SHE on iron in 0.1N NaNO_3 was 18.9\AA in aerated solution and 17.0\AA in deaerated solutions. Films grown in NaNO_3 at open circuit (~ -0.308 v) were fairly thin as stated before and surface roughening occurred, indicating that they were not particularly protective. However, films grown at open circuit (-0.108 v) in NaNO_2 were thicker ($\sim 19\text{\AA}$) and surface roughening was minimal. Rates of growth in borate with and without chloride, nitrate, and nitrite at an applied anodic potential of -0.108 v SHE showed them to be comparable, with films in nitrite growing slightly faster. Here also, the data would fit either a linear or a parabolic rate law (Fig. 5,6).

SODIUM HYDROXIDE ENVIRONMENT

Open circuit growth experiments were impossible in 5% NaOH due to severe metal roughening. This was to be expected since this is a corrosion area as predicted by the Pourbaix Diagram for Iron where formation of soluble HFeO_2^- occurs.

Polarizing iron to a potential within the passive region (-0.108 v) in NaOH showed rate of growth of oxide to be much more rapid than the other solutions studied, probably due to the higher overpotential used (Fig. 7).

If the crack tip is not polarized to anodic potentials in the passive region, film repassivation kinetics would not play a role in the mechanism of S.C.C. in this solution. However, if it polarized into the passive region, these preliminary experiments show a rate higher than that observed for the other solutions studied.

SUMMARY AND CONCLUSIONS

In Table 1, we have tabulated both linear and parabolic rate constants for the initial stages of repassivation of iron in the solutions studied.

Table 1

Solution	v SHE Potential,	K_t linear, $\frac{\text{nm}}{\text{sec}}$	$K\sqrt{t}$ Parabolic, $\frac{\text{nm}}{\text{sec}^{1/2}}$
$\text{Na}_2\text{B}_4\text{O}_7/\text{H}_3\text{BO}_3$	-0.35	0.31	0.87
NaNO_2	-0.35	0.35	1.04
$\text{Cl}^-/\text{borate}$	-0.35	0.31	0.87
$\text{Cl}^-/\text{borate}$	+0.64	2.55	3.78
NaNO_3	-0.35	0.28	0.85
NaOH	-0.35	0.69	1.56

Comparing data for those environments known to cause stress-corrosion cracking in low carbon steels - ie hydroxide and nitrate - to that for nitrite and chloride, we have no clear cut trend upon which to base an explanation for the observed behavior of low carbon steel. We do know that when iron is polarized above a certain potential in chloride solutions it does pit, and, when pitting, produces a non-protective type of film. Thus, rate of repassivation probably has no real significance for iron in a chloride environment at sufficiently noble potentials.

There is no marked distinction in repassivation behavior to separate film growth kinetics in nitrate from nitrite and borate solutions. However, we cannot ignore the possibility that differences may exist if we were able to start with a bare metal substrate before initiating film growth in either nitrate or nitrite solutions. We are now developing a new technique which would allow us to generate a bare metal surface in such redox environments, not only on iron, but on other stress corrosion susceptible alloys having films that are difficult to reduce. Furthermore, once growth studies have been well characterized using pure iron, we will then proceed to a low carbon steel which may also lead to results which would differentiate between nitrate and nitrite solutions. These experiments may thus allow us to examine more realistically the role of repassivation kinetics.

2. Film Ductility

These studies are concerned with a second aspect of films that may have some bearing on susceptibility to S.C.C. — the ductility of the film. There have been a number of studies of the deformation of films, mainly on rather thick anodic films (16,17). Recently Bubar and Vermilyea (18,19) have looked at thin passive films on a number of metals. They found, using an electrochemical technique, that of the metals studied, tantalum had the highest relative ductility. This study combines their electrochemical technique with the optical measurements of ellipsometry. By so doing, we can concentrate directly on the thinning of a passive film during stressing and thereby measure its deformation throughout the entire straining process and not just determine, as the electrochemical technique does, the elongation that coincides with the onset of its fracture. As Vermilyea and Bubar have pointed out, there can exist localized variations in elongation that may cause film breakage at overall strains that are lower than that necessary to break the film under non-localized elongation. This will give low film ductilities. The direct ellipsometric measurement avoids this problem by simply measuring the reduction in film thickness upon stressing with no dependence on a knowledge of specimen elongation. In order to carry out such measurements we have constructed an ellipsometer that is coupled with a tensile machine in such a way that we can measure changes in film thickness on an immersed surface that is subjected to an applied tensile stress at selected potentials controlled by a potentiostat. In this way the relative ductilities of films as affected by environment can be measured because the ellipso-

metric technique can sensitively detect thickness differences that correspond to fractions of a monolayer.

The preliminary experiments described here are concerned with films on tantalum. It was chosen as a good metal to use to develop the technique for examining effects of environment because of the high ductility of tantalum oxide films as found by Vermilyea and Bubar (16).

EXPERIMENTAL

Materials

Tantalum sheet of 99.95% purity in a cold rolled condition was used in these experiments. Specimens were machined from this sheet so that the stress was applied in the long transverse direction. Specimens were 70 mm long, 9.5 mm wide, and 0.5 mm thick with a 6.35 mm reduced section near the center.

The medium used in all experiments was a combination 0.075N $\text{Na}_2\text{B}_4\text{O}_7$ 0.05N H_3BO_3 solution having a pH of 8.4. In some experiments where the effect of fluoride ion was studied, NaF was added to the borate solution to bring the concentration to 0.1N NaF. Reagent grade chemicals were used throughout.

Surface Preparation

The specimen was mechanically polished through 600 grit cloth. It was then chemically polished in a mixture of sulfuric acid, nitric acid, and hydrofluoric acid in a volume ratio of 5:2:2, followed by a hydrofluoric acid rinse, a water rinse, and finally dried in warm air. In the experiments where the fluoride ion was not wanted, the specimen was boiled in distilled water for one minute in order to leach out the fluoride from the oxide before drying as suggested by Young (20).

Apparatus

Fig. 7 shows a photograph of the apparatus that allows one to make film thickness measurements on a metal surface while it is being stressed in an aqueous solution at a controlled potential or current. The apparatus consists of the conventional ellipsometer components attached to the center post of a tensile testing machine in such a way that it is possible to position a tensile specimen for observation with the ellipsometer. This tensile specimen is surrounded by a reaction cell (Fig. 8) which consists of a glass cylinder having windows at the proper angle for making ellipsometric readings. A platinum screen counter electrode and a reference electrode stopcock bridge for controlling the specimen potential is incorporated in the reaction cell. The cell is also provided with teflon fittings which allows the gripping of the specimen for controlling applied stress without introducing unwanted galvanic couples. The valves shown are for the introduction and removal of a solution. Once placed in the reaction cell, a preload of 5% of the yield strength was applied to the specimen to maintain mechanical stability during alignment and subsequent oxide growth steps.

Procedure

The general procedure was to grow an oxide film to some thickness on the specimen by bringing its anodic potential to a value in the passive region, then lowering the potential to some value (still passive) but corresponding to a thickness less than that originally grown. Since no dissolution takes place at the lower potential, the film remains at its originally grown thickness. The potential is lowered and measurements are made of any reduction in film thickness that may occur during straining.

If the potential were maintained at a value corresponding to the original thickness, the oxide upon thinning would regrow to its original thickness to maintain the steady state field appropriate to the potential at which the surface is held, but by lowering the potential below that at which the film was originally grown, no regrowth takes place until the film is thinned below the value of thickness appropriate for the lower potential. In this way thinning can be observed with the ellipsometer without the complications of regrowth. At the point in the straining process at which rupture takes place, no further thinning is observed by the ellipsometer but instead the cracks in the film are repaired. Film elongation can then be estimated from either the % elongation observed at the time of rupture (no further thinning) or by calculating the elongation of the film based on the thickness measured when rupture occurred. For the flat surface used, this can be calculated from the ratio of the final to the initial thickness.

RESULTS AND DISCUSSION

The purpose of these preliminary experiments is mainly to develop the technique for ductility measurements. Two sets of experiments were carried out. The first set was done in the absence of fluoride, the second in the presence of fluoride. Without fluoride, the oxide film began to rupture at an elongation of 7.1% (Fig. 9). With fluoride in the system oxide rupture started at a 6.6% elongation (Fig. 10). The two figures show both the elongation at the point in the deformation process at which rupture takes place and the extent of thinning that occurs when this point is reached. Table 2 shows the ductility of the film that one would calculate on the

basis of these two different criteria. It should also be taken into consideration that tantalum is a body centered cubic metal which deforms discontinuously forming Luder's bands. Therefore, though we can measure the film thickness in the slip band, we have not measured the corresponding amount of strain in the same region. The values that we get for the overall elongation may be considerably different from that existing at the part of the surface we are looking at with the ellipsometer. Moreover, the overall elongation used to arrive at the value in the second column of Table 2 may be much lower than the localized elongation in the Luder's bands where film rupture finally takes place. Thus, the value for the ductility of the film on this basis may be too low. Bubar and Vermilyea estimating the thickness of films by means of interference colors found elongations of 50% for the films on some grains while on the basis of overall elongation their values were comparable to those we show in column 2. Our generally lower values in column 1 based on the thinning of films are average values of a number of grains and because of the direct measurement probably the most reliable values in this study. They are fairly close to that determined by Bubar and Vermilyea in their second paper in which they report approximately 3% elongation using a borate solution (19). They indicated that their values were probably too low because of possible problems with enhanced localized deformation. However, the direct ellipsometric measurements do not depend on specimen elongation measurements and the low values may be realistic.

The effect of fluoride on the film's ductility is rather small and of the order of the experimental error ($\pm 1\%$). Thus, fluoride which has been

found to affect the adhesion of Ta_2O_5 films does not appear to have any appreciable affect on its ductility. A further refinement of the technique should easily increase its sensitivity and it will be possible to determine whether the slight lowering of ductility by fluoride is real. These experiments do, however, demonstrate that direct measurements of film ductility is possible and show promise for exploring the role of ductility in stress corrosion cracking.

Table 2
Ductility of Oxide Film

	% Reduction In Thickness Before Rupture	% Elongation Before Rupture
oxide without fluoride	3.62	7.1
oxide with fluoride	4.45	6.6

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FIGURE CAPTIONS

- FIGURE 1. The effect of potential on film growth in the absence and presence of chloride ion ($10^{-2}M$) in boric acid-sodium tetraborate buffer solution (pH = 8.4). Potentials were above E_a^2 (+0.64 v SHE) and below E_a^2 (-0.11 v SHE). Film thickness was measured by ellipsometry.
- FIGURE 2. Plot of film thickness vs. linear time (— ● — ●) and square root of time (— ⊙ —) for potentiostatic growth at +0.64 v SHE in $10^{-2}M$ sodium chloride/boric acid-sodium tetraborate buffer solution (pH = 8.4). These plots are compared to plots of thickness vs. linear time (--- Δ ---) and square root of time (--- ⊖ ---) for growth in the standard boric acid-sodium tetraborate buffer solution.
- FIGURE 3. Effect of the presence of nitrite or nitrate ions on the galvanostatic reduction of the passive film on iron at $-25 \mu A/cm^2$ in boric acid/sodium tetraborate buffer solution (pH = 8.4). Plot of film thickness and potential vs time for unaltered buffer solution (solid line) and buffer solution with 0.15N $NaNO_3$ (dashed line).
- FIGURE 4. Plot of film thickness vs. linear time (— ● — ●) and square root of time (— ⊙ —) for potentiostatic growth at -0.110 v SHE in 0.1N $NaNO_2$. These plots are compared to plots of thickness vs. linear time (--- Δ ---) and square root of time (--- ⊖ ---) for growth in the standard boric acid-sodium tetraborate buffer solution.

FIGURE 5. Plot of film thickness vs. linear time (— ● — ●) and square root of time (— ⊙ —) for potentiostatic growth at -0.110 v SHE in $4N$ $NaNO_3$. These plots are compared to plots of thickness vs. linear time (--- Δ ---) and square root of time (--- ⊖ ---) for growth in the standard boric acid-sodium tetraborate buffer solution.

FIGURE 6. Plot of film thickness vs. linear time (— ● — ●) and square root of time (— ⊙ —) for potentiostatic growth at -0.110 v SHE in 5% w/v $NaOH$. These plots are compared to plots of thickness vs. linear time (--- Δ ---) and square root of time (--- ⊖ ---) for growth in the standard boric acid-sodium tetraborate buffer solution.

FIGURE 7. Ellipsometer coupled with tensile machine for in situ studies of film ductility.

FIGURE 8. Reaction cell for the apparatus shown in Fig. 7.

FIGURE 9. a) Thickness of oxide film on tantalum as a function of potential in $0.075N$ NaB_4O_7 - $0.15N$ H_3BO_3 solution.
b) Reduction in thickness of oxide on tantalum as a function of elongation. Potential held at 2300 mv (S.C.E.)

FIGURE 10. a) Thickness of oxide film on tantalum as a function of potential in $0.075N$ NaB_4O_7 - $0.15N$ H_3BO_3 - $0.1N$ NaF solution.
b) Reduction in thickness of oxide on tantalum as a function of elongation. Potential held at 1500 mv (S.C.E.)

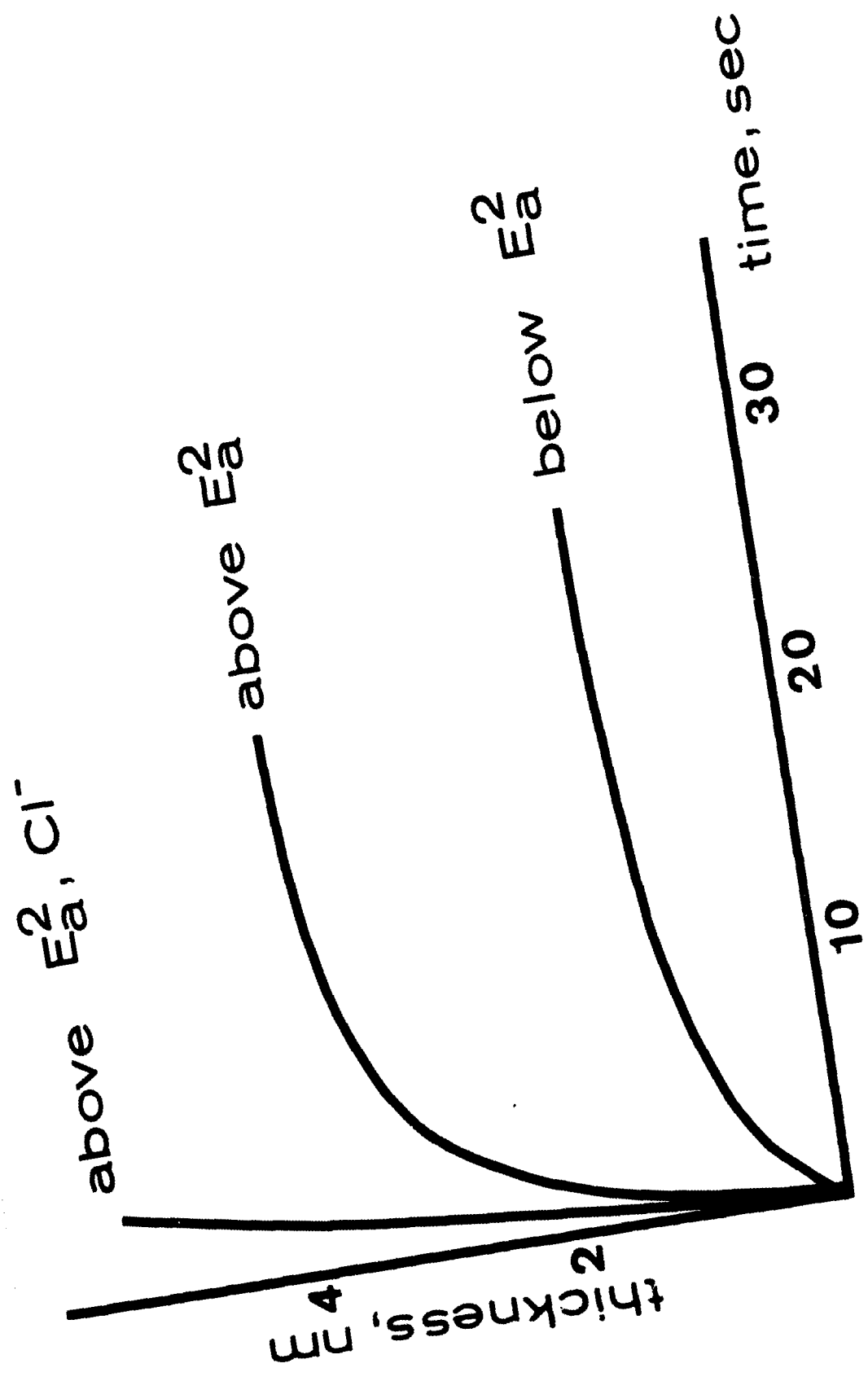


FIGURE 1

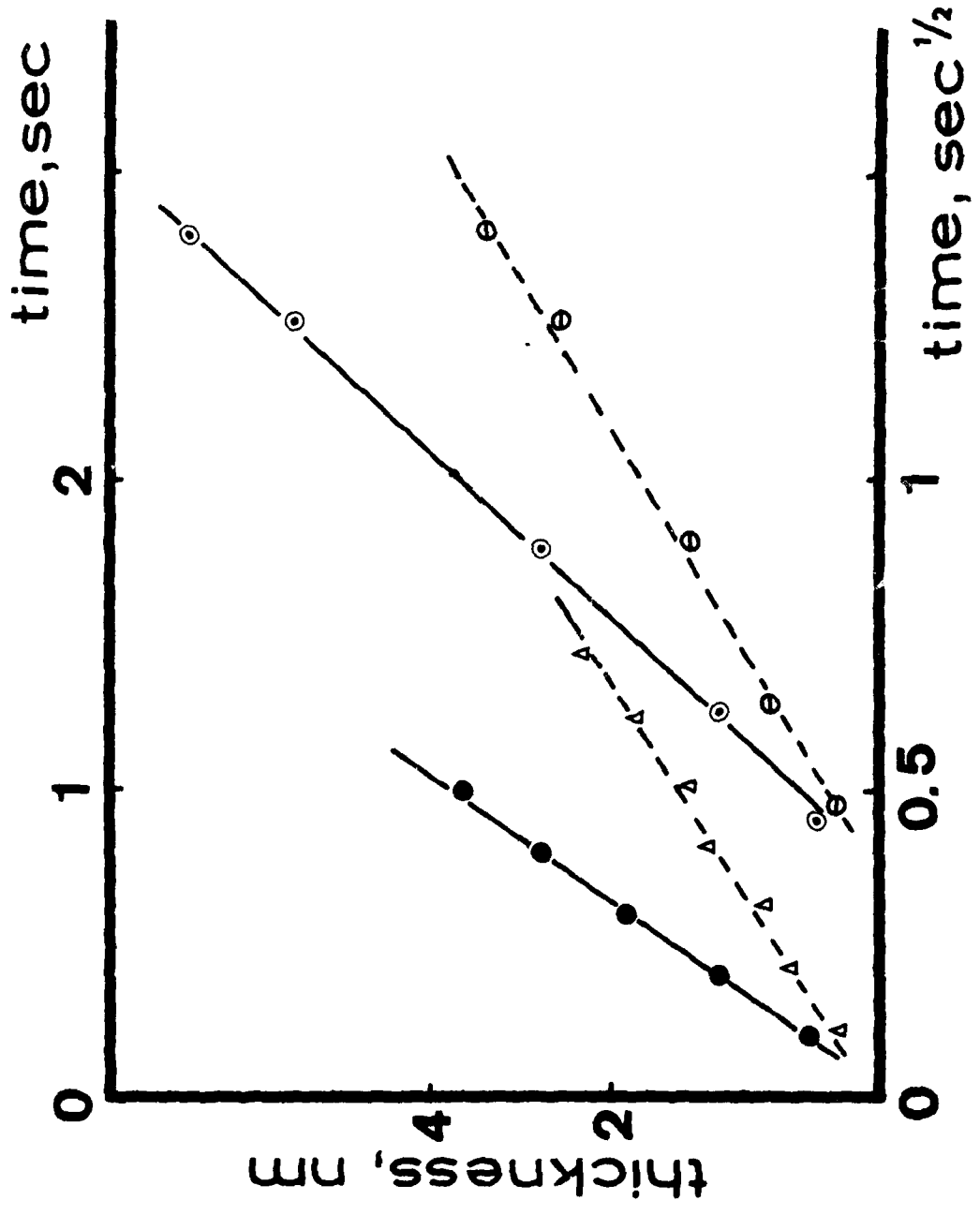


FIGURE 2

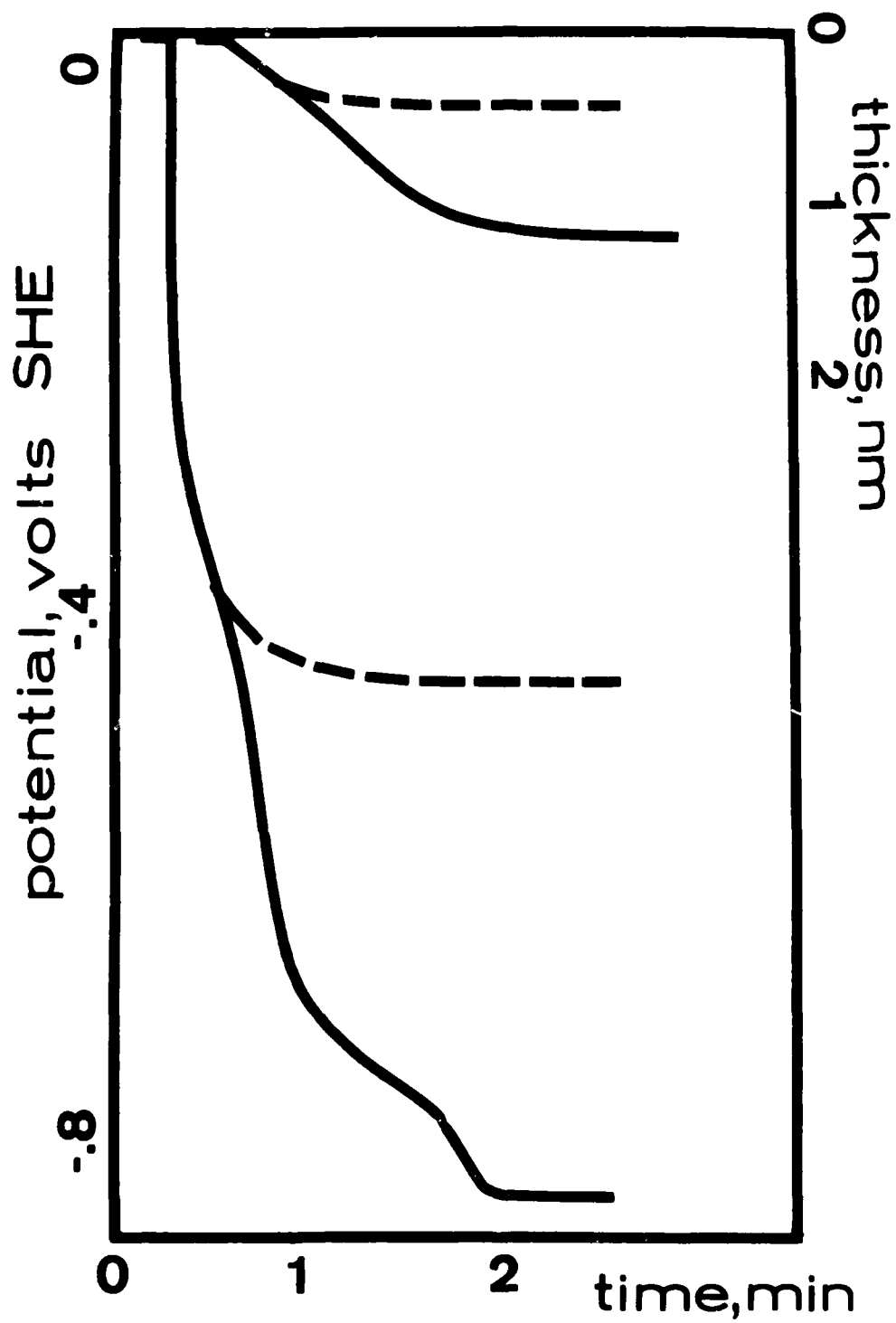


FIGURE 3

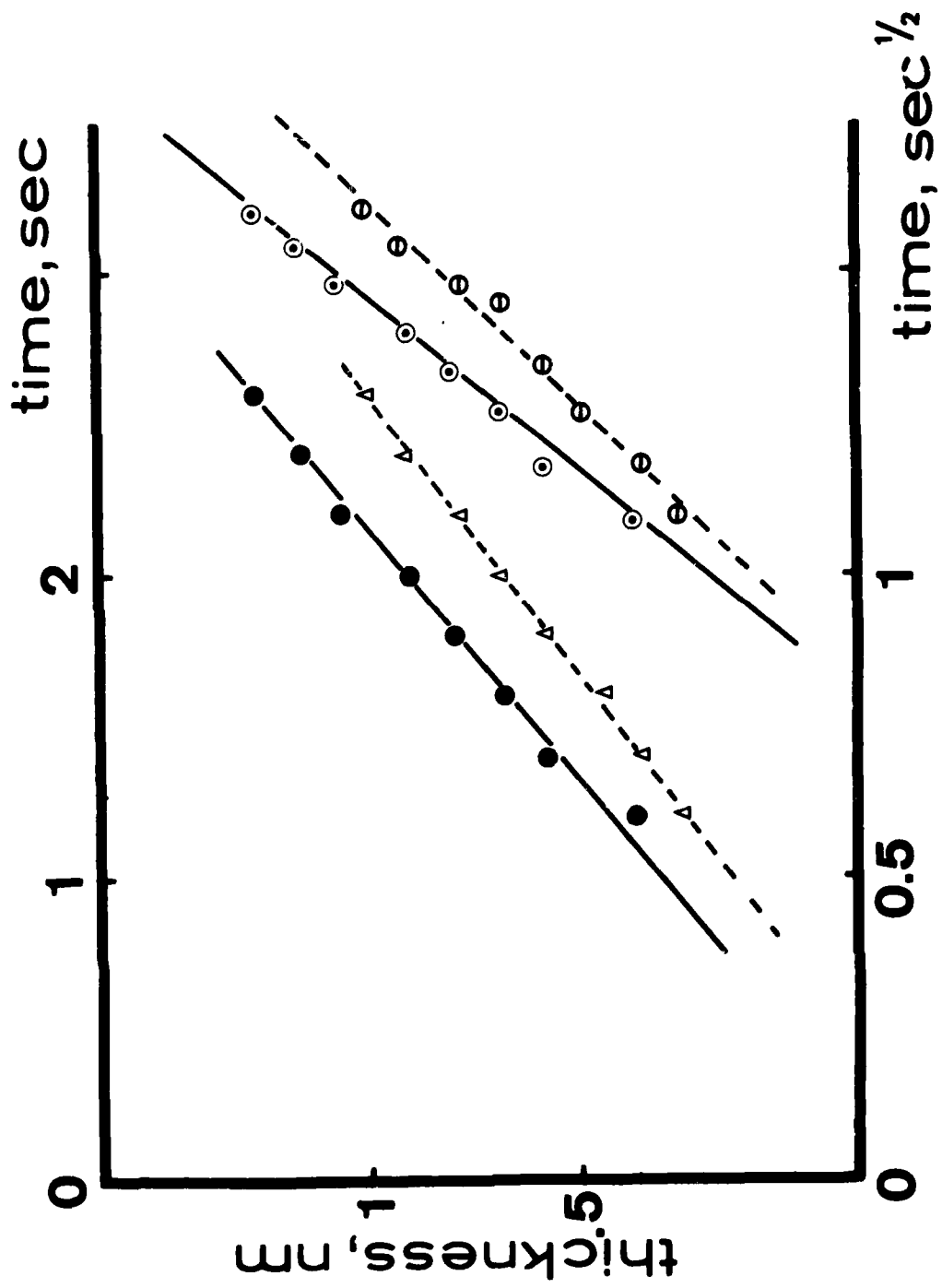


FIGURE 4

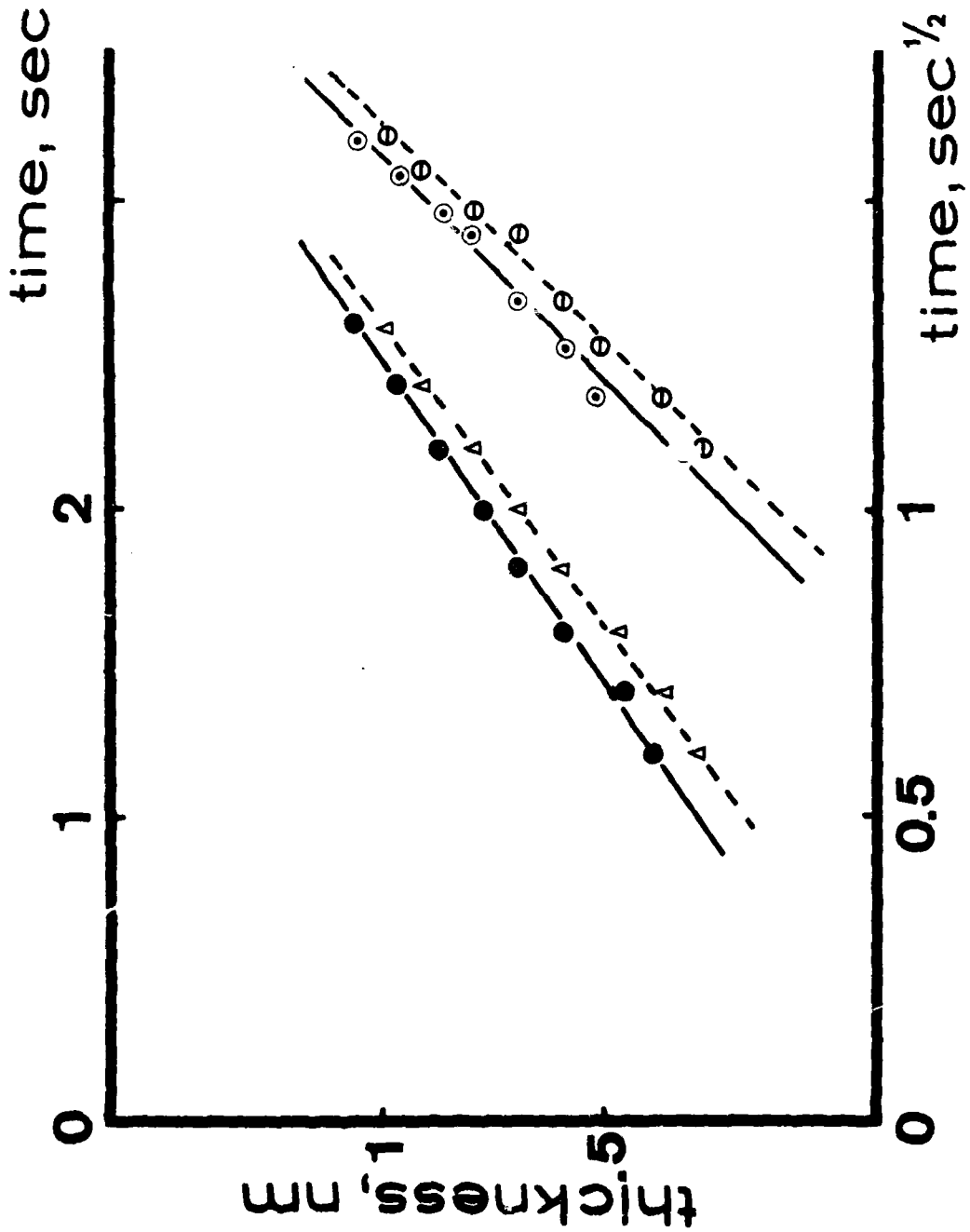
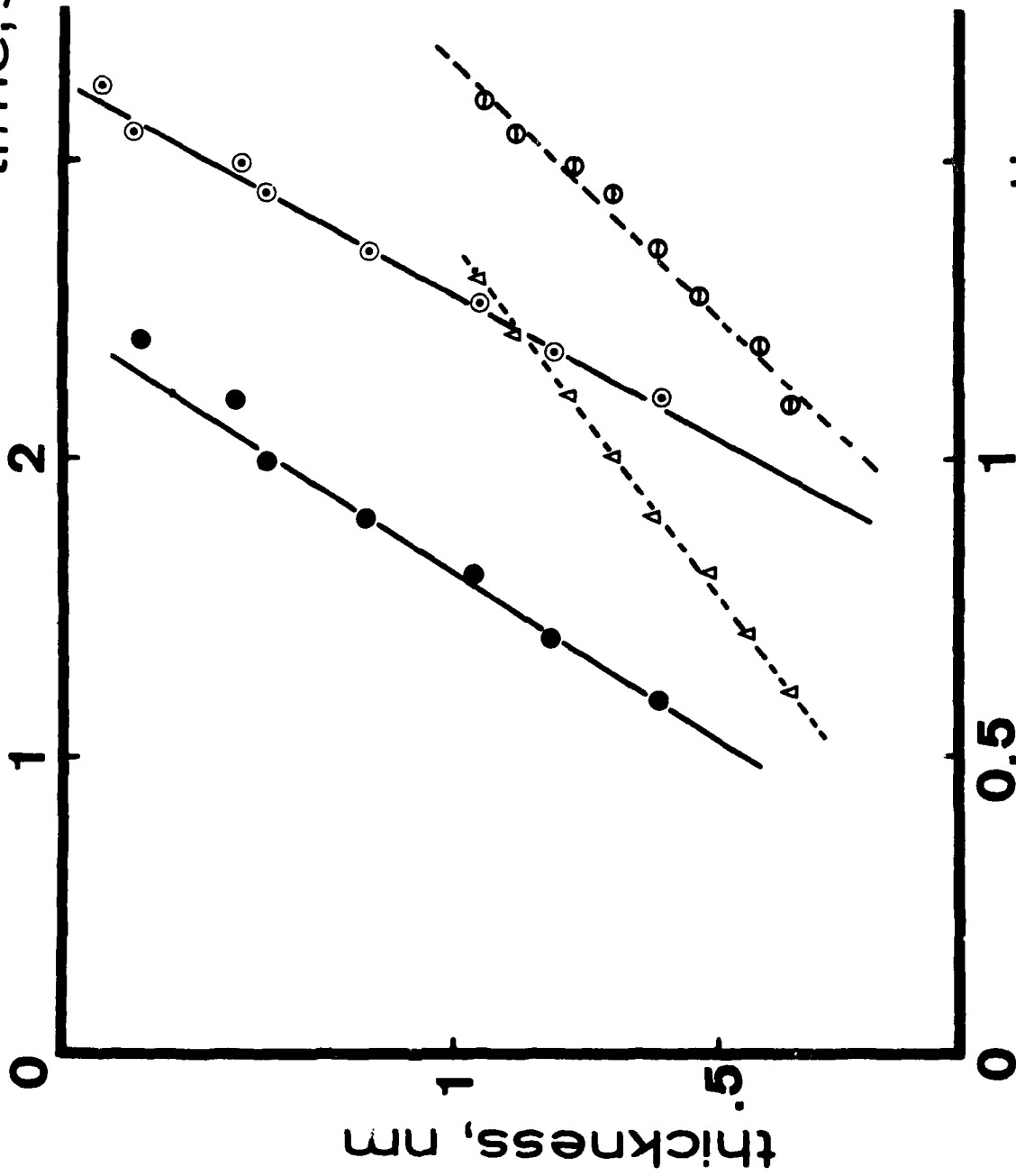


FIGURE 5

time, sec



time, sec^{1/2}

FIGURE 6



FIGURE 7

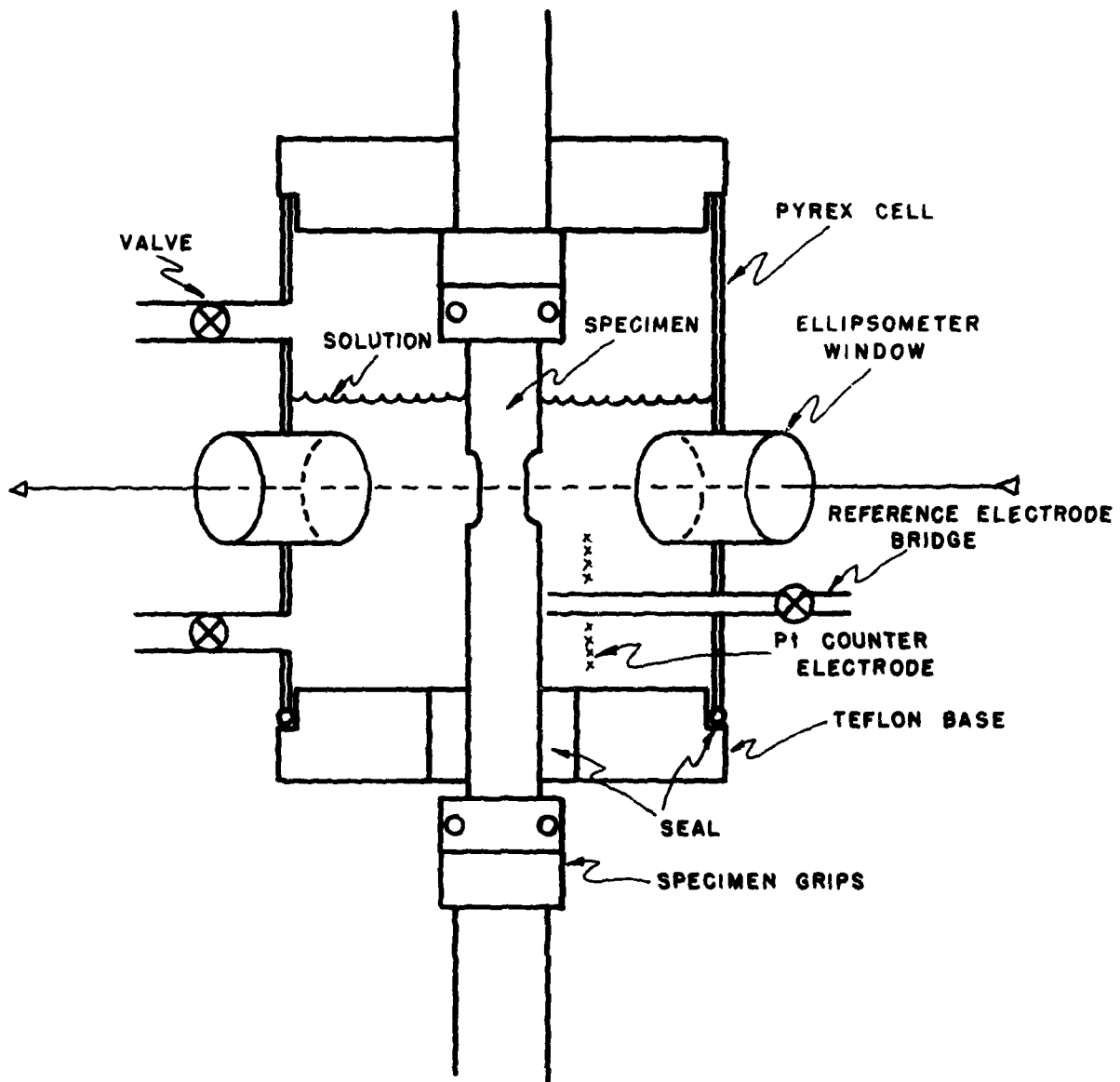


FIGURE 8

WITHOUT FLUORIDE

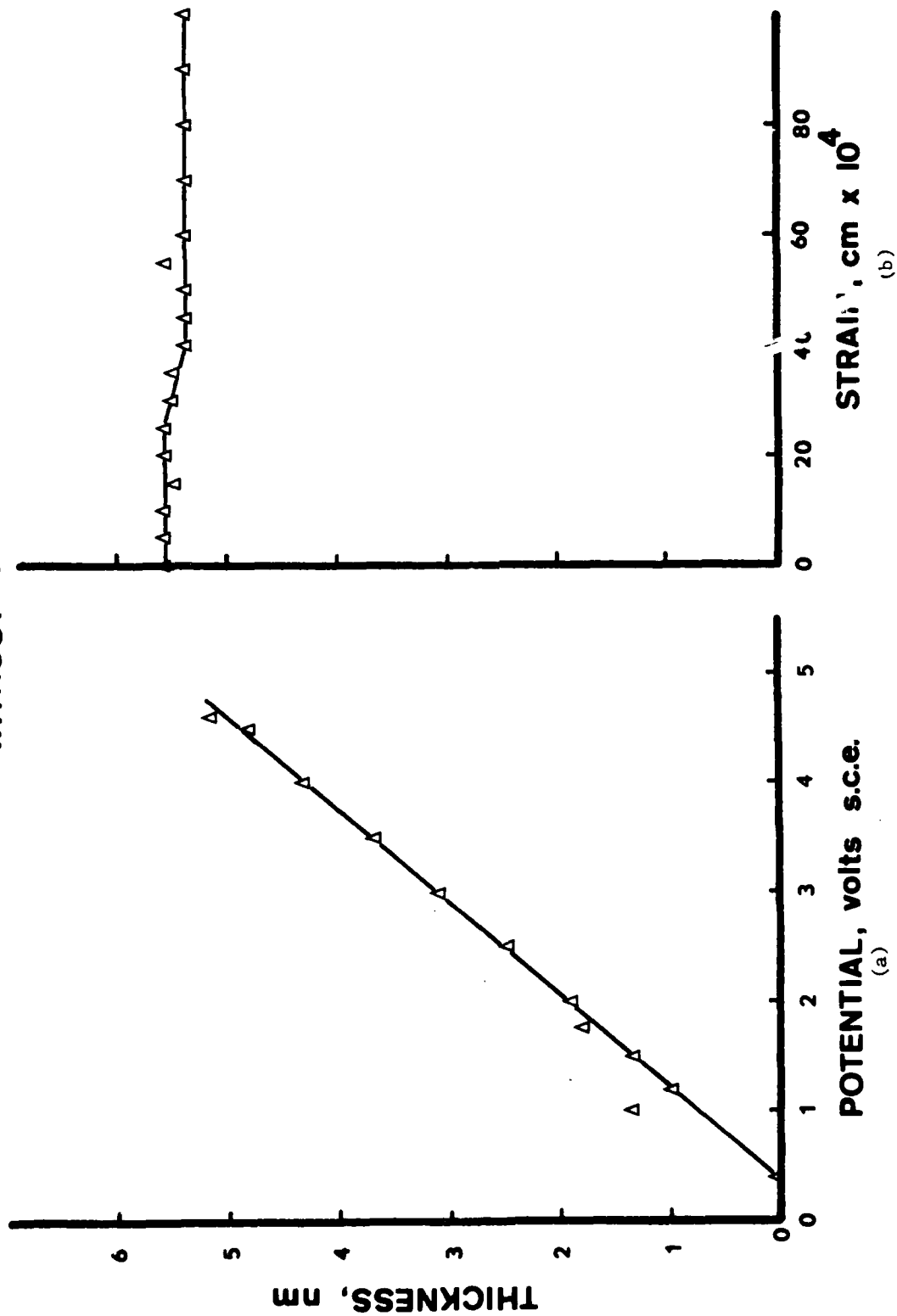


FIGURE 9

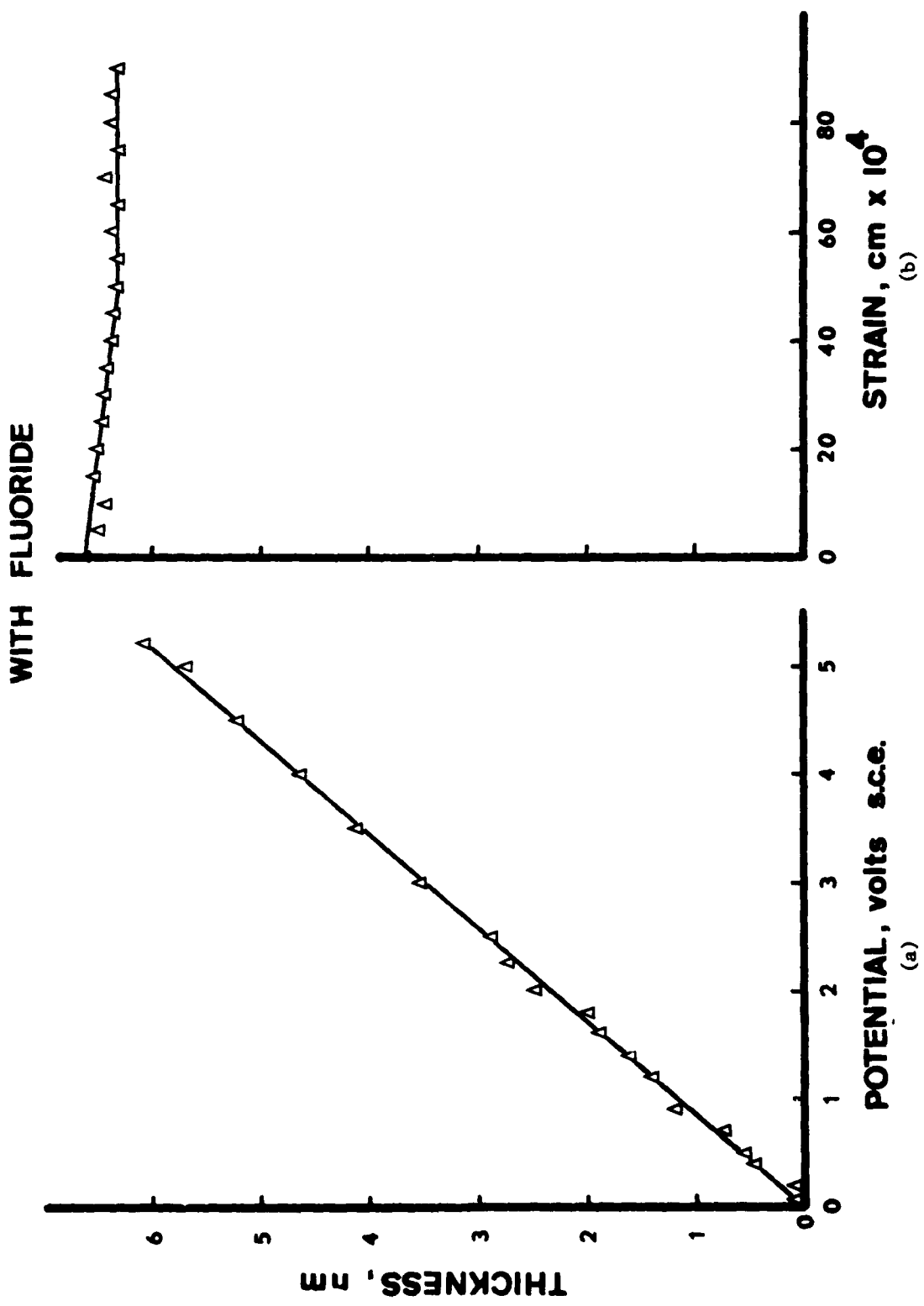


FIGURE 10

To be Submitted to Journal of the Electrochemical Society

Stress Corrosion Cracking of Pure Copper
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Washington, D. C. 20234

A recent study by Green, Mengelberg, and Yolken (1) has shown that the rate of formation of a tarnish film on copper and copper-zinc alloys in tarnishing ammoniacal solutions increases with the percentage of zinc. It is also known that the rate of cracking of α -brass in these ammoniacal environments increases significantly with increasing zinc content (2). One theory of stress corrosion cracking (SCC), the "brittle film" model of Forty and Humble (3), predicts that the rate of tarnish film formation determines the rate of cracking. The study by Green et al showed that pure copper, which is non-susceptible, does have a low rate of film formation in the tarnishing solution they used. If the "brittle-film" model's predictions are valid, pure copper should crack in an environment that produces a similar film to that in the ammonia tarnishing solutions provided the rate is comparable to that observed for the susceptible α -brasses. Such an environment is the cupric ion solutions (mostly cupric acetate and cupric sulfate) studied by Miller and co-workers (4-6). These solutions produce epitaxial Cu_2O films on copper that are similar to those that form in ammonia solutions on α -brass. They also grow on pure copper at a rate that is comparable to a susceptible brass (90 Cu - 10 Zn). Thus the "brittle-film" model would predict that pure copper should crack in Miller's solutions. This study will determine if such cracking can be observed.

If cracking of pure copper does occur in Miller's solutions, however, it is still necessary to establish whether it is "true SCC". Recently there have been two directly contradictory papers, one by Pugh, Montague, and Westwood (7) indicating that pure copper can undergo intergranular stress corrosion cracking, the other by Uhlig and Duquette (8) indicating that what was observed by Pugh et al was not SCC but instead a weakening by deep intergranular corrosion. Both of these studies used a 15N NH₄OH solution preconcentrated with 2.5 g/l of copper powder. However, Pugh et al indicate that this solution did not produce a tarnish film. Uhlig and Duquette did observe a "dark surface oxide film." This uncertainty about tarnishing makes it difficult to ascertain whether pure copper would indeed undergo stress corrosion cracking under conditions where a tarnish film exists.

Besides determining whether pure copper fails under conditions of rapid tarnishing, this study seeks to resolve the question of whether this film formation is an integral part of the failure process or whether simple intergranular weakening is involved.

EXPERIMENTAL

All experiments were carried out either in 0.4N cupric sulfate or 0.05N cupric acetate using reagent grade chemicals and deionized, double distilled water. The specimens were stressed in a constant load lever system. Since surface cleanliness has a strong influence on the rate of oxide growth on a single crystal (9), initial experiments were carried out using the careful surface preparation described by Miller et al (10). It was found, however, that the results were not significantly affected as long as a surface was prepared that was free of any adsorbed organic contaminants.

The following surface preparation procedure was adopted: Shortly before an experiment, the specimens were immersed in a 2:1 solution of nitric acid in water for 15 seconds, then rinsed in flowing distilled water for 30 seconds. The specimens were then dried in a stream of warm air and installed in the testing cell. At this point the oxide forming solution was introduced into the cell. After one minute the load was applied to the specimen.

The following materials were studied:

1) 99.9% copper wire - The first experiments carried out in the copper system were done using electrolytic copper having a diameter of 0.254 mm. The tensile load applied was approximately 220 meganewtons/meter or just slightly more than the yield strength of the material, thus, causing some plastic deformation to occur. The copper wire was tested in both solutions.

2) Large grain 99.999% copper - Continuous cast copper rods of 99.999% purity were machined to make flat tensile specimens 10 mm wide at their reduced section, 0.71 mm thick, and 19 mm long. These specimens had relatively large grains ranging from an average of one mm to seven mm in diameter. This material was tested only in the cupric acetate solution.

3) Small grain high purity copper - Some 99.999% Cu with large grains was reduced 50% in cross section by rolling. Specimens 6.3 mm wide, 0.36 mm thick and 25 mm long were cut out from the resulting sheet. These specimens were then recrystallized in hydrogen by heating to 700°C for 5 minutes then quickly cooling to room temperature at 300°C/minute. The resulting grain size was of the order of 0.1 mm diameter.

Surface preparation of this material was more critical because it was to be examined by electron microscopy. It was, therefore, electro-polished, then carefully rinsed in distilled water before testing in the cupric acetate. Two separate sets of experiments were done with this material. One set was the tarnishing of the material in an unstressed condition, and the other set was the tarnishing of the material under stress.

4) Brass - A few experiments were carried out on 70-30 brass containing less than 0.8% lead. 25 mm specimens were cut from a 38 mm diameter tube having a wall thickness of 1.7 mm. One quadrant of the tube was cut out so that the specimen resembled a "U". Load was applied across the U-bend through the center until some plastic deformation occurred. The only surface preparation done was to abrade the surface circumferentially using 320 grit paper. Brass was tested in both the cupric sulfate and the cupric acetate solutions.

RESULTS

Morphology of attack and susceptibility

The lower purity copper described above and the 70-30 brass were exposed to the 0.05N cupric acetate and the 0.4N cupric sulfate solutions under tensile loads exceeding the yield strength of the material. No cracking was ever observed at these loads when the specimens were not immersed in the cupric ion solutions. Failure of the 99.9% copper was observed for times as short as 18 hours in the acetate solution. Fig. 1a shows that the cracks formed were always found to occur in oxide film

growing into the metal. This micrograph looks similar to those found by Forty and Humble (3) in α -brass in ammonium hydroxide - copper sulfate solutions.

The 99.9% copper did not fail in the cupric sulfate solution. The micrographic examination indicated that oxidation was more general over the whole surface with pitting but no evidence of cracking as shown in Fig. 1b.

The large grain high purity copper failed in as short a time as 88 hours in the acetate solution. Practically all cracks found were initiated at grain boundaries or at surface imperfections within the grain as shown in Fig. 2a and 2b. The longer time to failure may possibly be due to the fewer grain boundaries at the surface as a result of the large grain size. As figure 2a shows for a large-grained specimen, crack initiation would usually occur in a grain boundary normal to the stress direction, but, because the boundary did not continue in this direction, the crack would leave the boundary.

Because we were interested in locating the initiation site of the crack, the fine grain size material was made. This made it easier to locate a grain boundary at the high magnification used with the electron microscope. The grain boundaries of the unstressed and stressed material were examined. Figure 3a showing the unstressed boundaries, revealed no unusual features other than the many oxide crystallites which formed on the grains, whereas the stressed material showed fissures at the boundary after one hour in the acetate solution and had less extensive oxidation in the grain interiors as seen in 3b. In general, the grain boundaries with fissures were perpendicular to the applied stress.

The 70-30 brass did not fail for times as long as seven days in either solution, and as Fig. 4 shows, the morphology of attack was quite different. This attack was intergranular and involved an actual loosening of surface grains in the acetate solution. In the sulfate solution most of the attack occurred on the compression side while the tension side was relatively uncorroded.

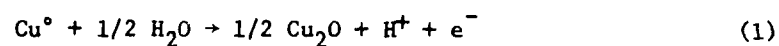
Effect of Illumination

Because it is known that illumination affects oxide growth on copper (11), the effect of light on the failure of copper in 0.05N cupric acetate solution was examined. Two experiments were run in parallel. In one, the copper wire was exposed to the solution under load and illuminated on two sides by 150 watt high intensity incandescent lamps. The other was carried out in an identical manner, but light was excluded. No failure was observed for illuminated specimens for periods as long as five days. The ones kept in the dark always failed in less than 24 hrs.

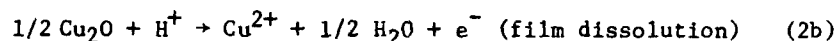
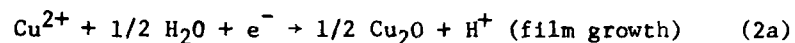
DISCUSSION

It was found that both 99.9% and 99.999% purity copper will crack in an environment where the rate of tarnish film formation is comparable or greater than the rate of tarnish for susceptible brasses. The results also indicate that cracking occurs in the oxide that forms by growth into the grain boundaries. Before considering the question of the mechanism of the failure and whether we are looking at intergranular weakening or SCC, it is useful to discuss the meanings of the phenomena observed in connection with the formation of the oxide film. In order to do this it is necessary to look at the electrochemical theory of copper corrosion as worked out by

Ives and Rawson (12). They propose that the copper-cuprous oxide-solution system can be divided into three zones: zone 1 is made up of a compact, adherent film of Cu_2O and the copper substrate; zone 2 is a porous film of Cu_2O and; zone 3 is the aqueous solution containing oxygen. Each of these zones has associated with it half-cell reactions. The half-cell reaction for zone 1 is the film growth process:



where at 25°C $E_1 = 0.471 - 0.0592 \text{ pH}$. Both film growth and film dissolution occur in zone 2 and are regarded by Ives and Rawson as constituting a hypothetical redox electrode. These reactions are:



where at 25°C $E_2 = 0.203 + .0592 \text{ pH} + 0.0592 \log [\text{Cu}^{2+}]$

Finally, the half-cell reaction at zone 3 is:

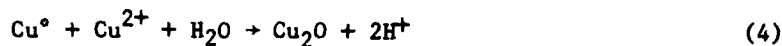


The whole system of electrode reactions can be regarded as two cells coupled to each other, reactions 1 and 2a an anodic and cathodic reaction involving film growth and reactions 2b and 3 anodic and cathodic reactions involving film dissolution.

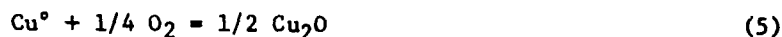
We can now apply this set of half-cell reactions to four situations pertinent to the results obtained:

1) Film Formation in The Absence of Light and Stress - Our results show film growth over the entire surface. The film growth observed is simply a combination of reactions (1) and (2a) as pointed out by Porterfield

and Miller (6)



or if all four reactions of Ives and Rawson are used



Both Porterfield and Miller; and Green et al (1) require a porous film to provide access of Cu^{++} or O_2 to the copper substrate. If there is a compact film at the substrate (zone 1) and it is sufficiently thin, rapid solid state diffusion through it may be a possibility.

2) Film Formation With Stress Applied in The Absence of Light - Our results show enhanced film growth at the grain boundaries normal to the direction of stress and diminished film growth elsewhere. If the film formed at the grain boundaries is brittle it would fracture, allowing access of more oxygen and cupric ions to bare copper. These bare copper sites would be very small, and, the current density would be very high so that reaction (1) would be polarized to a greater extent than in the absence of stress. By looking at Fig. 5 we can explain qualitatively why stress results in the growth of Cu_2O at those grain boundaries normal to the direction of stress and diminished growth or dissolution occurs elsewhere on the surface. Fig. 5a gives a schematic polarization diagram that reasonably represents the conditions existing when the specimen is not under stress. Here, since growth of Cu_2O over the entire specimen is observed, the corrosion current involved in growth, i_{growth}^{1-3} , predominates and is larger than i_{diss}^{2-3} , the current involved in dissolution of oxide. The growth resulting from reaction 2a is, judging from the diagram, of not too great a significance. When stress is applied, very small areas of metallic copper are exposed by rupture of the Cu_2O film at the grain boundary, and reaction 1, because it involves metallic copper,

is polarized to higher potentials than with no stress. This occurs because the current density at the bare sites must be high as a result of the small areas involved as compared to the large uncracked cathodic areas. The result is shown in Fig. 5b where the current for growth at the grain boundaries, i_{growth}^{1-3} , is much larger than that taking place elsewhere on the surface. However, the current for dissolution, i_{diss}^{2-3} , is now considerably larger than the current involved for growth elsewhere on the surface. It is thus reasonable to expect enhanced growth at the grain boundaries and enhanced dissolution on the rest of the surface when stress is applied. This is probably what happened in the experiments of Pugh et al (7) with all the tarnishing occurring at the grain boundaries and none detectable elsewhere.

3) The Role of Illumination - Ives and Rawson (11) have shown that illumination results in enhanced corrosion of copper with greater concentrations of Cu^{2+} ions being found in the corroding media. Duwell (13) also found an enhancement of corrosion rate in light. Kruger and Calvert (14) showed that the effect of the light was to cause a dissolution of a Cu_2O film present on the surface. This means that reaction 2b predominates. Also, Duwell's work suggests the reverse of reaction 1, the production of metallic copper, can also occur. Thus, it appears that light retards or stops the growth of the Cu_2O that forms in the grain boundaries and, in by doing so, retards or stops the cracking process.

4) The Role of The Anion - Our results show that the cracking observed when cupric acetate is used is not found when sulfate is substituted. Miller and co-workers (10) found that they could separate two general types

of oxide topographies, one relatively smooth, and the other composed of polyhedra. The smoother topographies are formed in acetate and formate solutions, the other in sulfate and perchlorate. They were able to show that these changes were probably due to the fact that in the sulfate and perchlorate solution, a decrease in pH occurred during the film formation process, whereas the acetate and formate ions acted as buffers and prevented any significant lowering of pH. When the pH is lowered, the dissolution reaction 2b predominates, and oxide formation is retarded or stopped. This lowering of pH with its attendant oxide dissolution would be especially pronounced in restricted geometries such as cracks (15). Elsewhere on the surface, oxide film formation can, and does, take place. But as Miller has shown, there are sites (between polyhedra of Cu_2O) where very little film forms.

From chemical and electrochemical considerations we can conclude that failure results under those circumstances which promote oxide formation at grain boundaries. This oxide formation in a sense results in a dissolution of copper from the grain boundary but it is not the same as simple dissolution without formation of oxide. Such dissolution (probably enhanced) can occur when copper is illuminated or when sulfate ions are present. If intergranular weakening by dissolution at the grain boundaries were involved, sulfate which lowers the pH in cracks would enhance the opportunity for failure. It does not. However, because oxide formation is retarded or stopped in the grain boundaries, no cracking results. Thus, intergranular weakening by simple metal dissolution is ruled out as an explanation for the cracking observed for copper in cupric acetate solutions. It would appear that the brittle film theory of Forty and Humble (3) better fits the

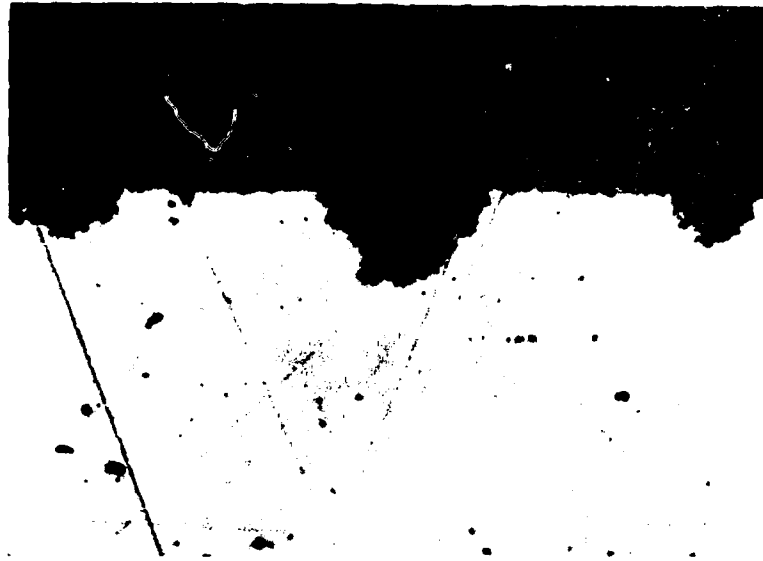
results. It also seems reasonable that the complex relationships between the mechanical properties of the film, as affected by the metal and the environment, and the rate of film formation in the grain boundaries play a role. An explanation of the failure to crack brass in the cupric acetate solutions will depend on a better future understanding of these relationships.

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FIGURE CAPTIONS

- 1a) 99.9% copper specimen with cracks in oxide. Stressed in .05N cupric acetate. 1200X.
- b) 99.9% copper specimen showing general corrosion and pitting. Stressed in 0.4N cupric sulfate. 600X.
- 2a) 99.999% copper specimen (large grain) showing cracks initiated at grain boundary. Stressed in 0.05N cupric acetate. 65X.
- b) 99.999% copper specimen (large grain) showing crack initiated within grain at surface imperfection. Stressed in 0.05N cupric acetate. 65X.
- 3a) 99.999% copper specimen (small grain) showing featureless grain boundary and many crystallites in the grain. In 0.05N cupric acetate unstressed. 15,000X.
- b) 99.999% copper specimen (small grain) showing fissures in the grain boundary with fewer crystallites in the grain. Stressed in 0.05N cupric acetate. 15,000X.
- 4. 70-30 brass specimen showing intergranular attack. Stressed in 0.05N cupric acetate. 120X.
- 5a) Schematic polarization diagram of unstressed copper.
- b) Schematic polarization diagram of stressed copper.



(a)



(b)

FIGURE 1

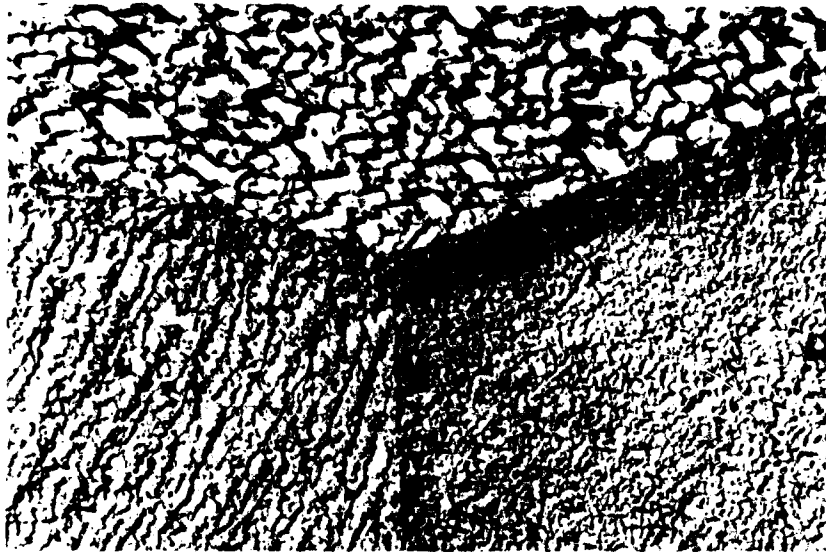


(a)

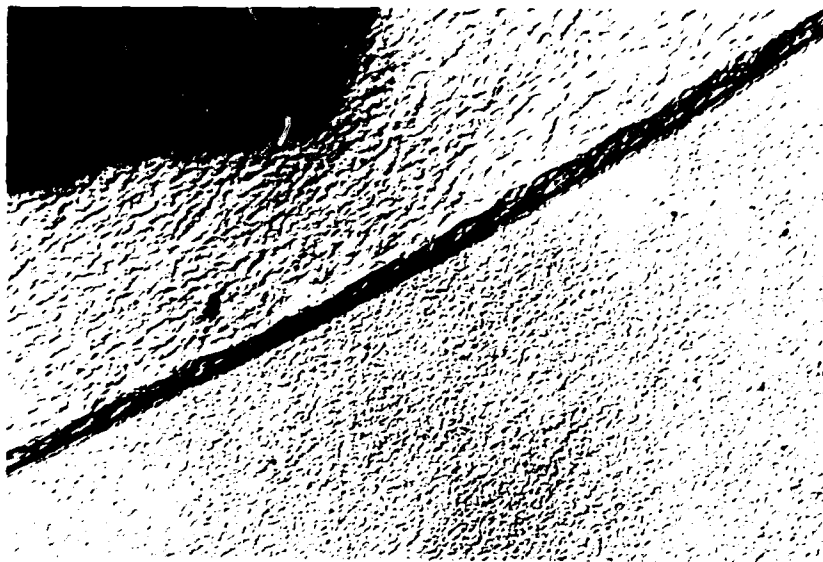


(b)

FIGURE 2



(a)

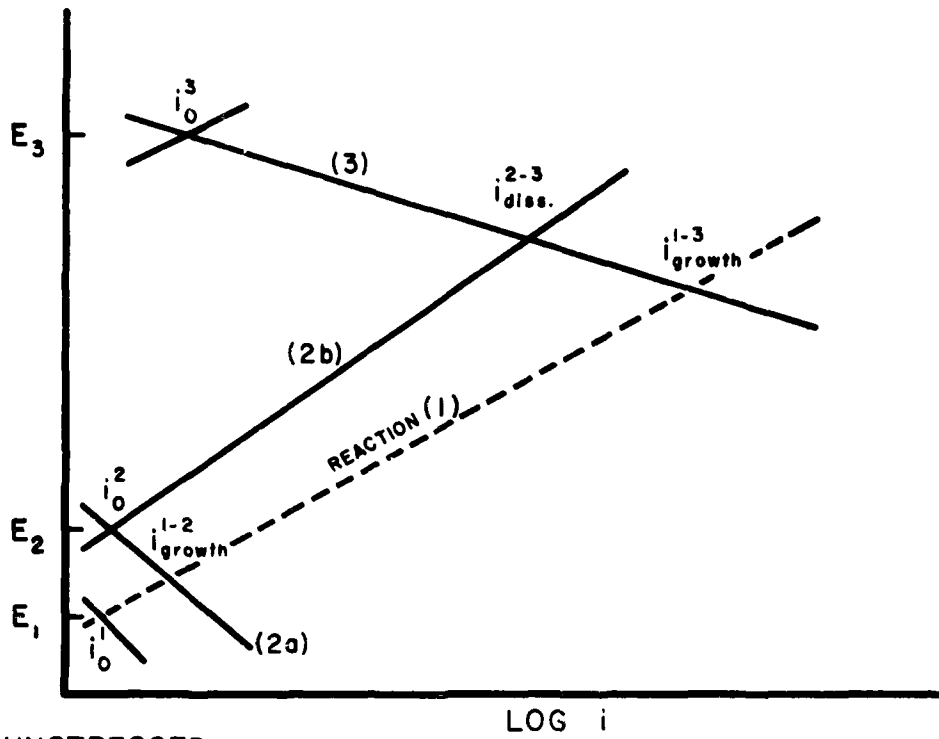


(b)

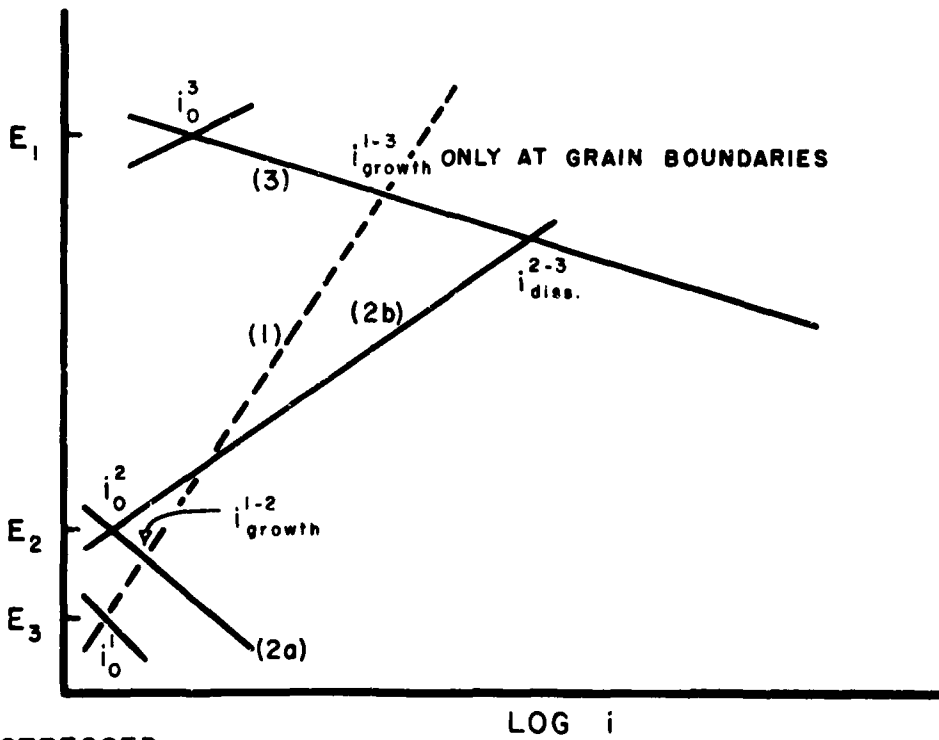
FIGURE 3



FIGURE 4



a) UNSTRESSED



b) STRESSED

FIGURE 5

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

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13. ABSTRACT The role of passivation kinetics, film ductility, and tarnish film formation in stress corrosion cracking were each examined in the following studies: 1) Ellipsometry measurements of film growth kinetics on iron have been made for two anions whose solution cause stress cracking of steel (nitrate and hydroxide) and two that do not (chloride and nitrite). 2) A technique has been developed to measure film ductility directly. This technique couples an ellipsometer with a tensile machine. Thin films on Ta show a ductility of 3-4% in the presence and absence of F ⁻ , an ion thought to decrease ductility. 3) Pure copper forms tarnish films in cupric acetate and sulfate solutions. It is susceptible to stress corrosion cracking in cupric acetate solution. In the absence of stress, oxide forms all over the copper surface, while stress concentrates oxide formation at the grain boundaries. These experiments point to a brittle-film rupture mechanism of stress cracking.			