

# NATIONAL BUREAU OF STANDARDS REPORT

10 594

AD 725166

Technical Summary Report Number 2  
For the Period  
March 1, 1970 to February 28, 1971

Contract NAONR 18-69  
ONR Contract Authority Identification Number 036-082

## 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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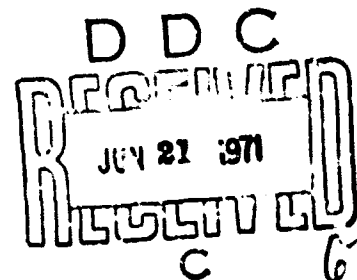


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ADDITIONAL INFO	
STATUS	WHITE SECTION
DATE	DIFF SECTION
UNANNOUNCED	
JUSTIFICATION	
BY	
OBTAINATION/AVAILABILITY CODE	
PCT.	AVAIL. and/or SPECIAL
A	

Unclassified

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

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

1. ORIGINATING ACTIVITY (Corporate author) National Bureau of Standards Washington, D. C. 20234		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE The Role of Passive Film Growth Kinetics and Properties in Stress Corrosion Susceptibility			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) TECHNICAL SUMMARY REPORT No. 2			
5. AUTHOR(S) (First name, middle initial, last name) Jerome Kruger John R. Ambrose Edward Escalante			
6. REPORT DATE		7a. TOTAL NO. OF PAGES 60	7b. NO. OF REFS 23
8a. CONTRACT OR GRANT NO NAONR 18-69, NR 036-082		9a. ORIGINATOR'S REPORT NUMBER(S) 3120448 - Technical Summary Report No. 2	
b. PROJECT NO 3120448			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES Details of illustrations in this document may be better studied on microfiche		12. SPONSORING MILITARY ACTIVITY Office of Naval Research	
13. ABSTRACT A new technique has been developed for studying the rate of repassivation of a stressed metal surface exposed by film rupture. This technique, which removes the film on a metal by abrasion and then follows film regrowth and metal dissolution by transient ellipsometry and current transients, was applied to low carbon steel in a nitrate solution where it stress cracks and a nitrite where it does not. The rate of repassivation was greater in the non-susceptible solution while the ratio of current going into film formation to that producing metal dissolution was less.  Another new technique was developed which measures the ductility of films on metal surfaces by determining by ellipsometry the amount of thinning the film undergoes upon straining the metal. The technique gives values for maximum ductility of the film rather than the fracture strain that other techniques give. Measurements were made on anodic films on Ta, Al and Al-4% Cu.			

DD FORM 1473

(PAGE 1)

S/N 0101-807-6801

Unclassified

Security Classification

~~Unclassified~~  
Security Classification

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Stress corrosion cracking						
Repassivation kinetics						
Film ductility						
Low carbon steel						
Aluminum						
Aluminum alloys						
Tantalum						
Ellipsometry						
Nitrates						
Nitrites						

# NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

3120448

May 13, 1971

NBS REPORT

10 594

Technical Summary Report Number 2  
For the Period  
March 1, 1970 to February 28, 1971

Contract NAONR 18-69  
ONR Contract Authority Identification Number NR 036-082

Subject

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

Submitted to the Office of Naval Research

by

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U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

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

Technical Summary Report Number 2 consists of two papers  
as follows

1. A NEW TECHNIQUE TO STUDY THE RELATIONSHIP OF REPASSIVATION KINETICS  
TO STRESS CORROSION.
2. A NEW TECHNIQUE FOR MEASURING THE DUCTILITY OF METAL OXIDE FILMS

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A NEW TECHNIQUE TO STUDY THE RELATIONSHIP OF REPASSIVATION  
KINETICS TO STRESS CORROSION

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ABSTRACT

Since the susceptibility of a material to stress corrosion cracking (S.C.C.) may be related to the rupture of a protective film and the repassivation rate of the material thus exposed, a technique has been developed which simulates film rupture by abrading off the surface oxide. During the subsequent repassivation of this exposed surface, this technique allows simultaneous determination of film growth kinetics by ellipsometry and current transients during that time interval following removal of the oxide film. The utility of the technique is demonstrated by comparing repassivation rates for a low carbon steel in a sodium nitrate solution in which the metal is susceptible to S.C.C. to those in a sodium nitrite solution, in which it is not. Results obtained using this method indicate that growth rate of the oxide is slower at elevated temperatures in the nitrate solution and is accompanied by substantial metal dissolution which may offer an explanation for the observed susceptibility of mild steels to S.C.C. in such environments.



A NEW TECHNIQUE TO STUDY THE RELATIONSHIP OF REPASSIVATION  
KINETICS TO STRESS CORROSION

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A number of studies<sup>(1,2,3,4)</sup> in recent years have pointed to the importance of the rate of repassivation to the mechanism of stress corrosion cracking (S.C.C.). The rationale of these studies is that, upon stressing, the film that exists on a metal in a given environment fractures and, unless its repair is sufficiently rapid, metal dissolution occurs at the film fracture site leading to crack initiation. Most of the studies directed at this problem have looked at straining electrodes measuring either current<sup>(2,3)</sup> or potential transients<sup>(4)</sup>. One problem with these techniques has been that it is difficult to determine which part of the parameter measured, especially the current, is involved in film repair and which part in metal dissolution — both anodic processes. Because of this, one cannot judge whether rapid initial current surges upon straining indicate rapid metal dissolution, rapid film repair, or some combination of both. It is only by looking at both processes, film growth and metal dissolution simultaneously, that we can sort out the role of repassivation on stress corrosion susceptibility.

This work describes an approach that has been developed to deal with this problem, using a technique that can measure the rate of film formation directly, ellipsometry, while simultaneously measuring the current involved in the overall anodic process. However, in order to measure the rate of film repair, it is first necessary to produce the bare surface that corresponds to that resulting from rupture of the

protective film. For some metals, e.g., steel, a bare surface can be produced by cathodic reduction of the film, for others, e.g. aluminum, this is not feasible for thermodynamic reasons. In past studies<sup>(5,6)</sup>, for those metals whose films are reducible, the rate of the repassivation process was measured ellipsometrically after cathodic reduction. The repassivation occurred in the presence of the reduction products, and the results obtained by jumping from a cathodic potential to the potential where cracking would occur may have been unrealistic with respect to simulating stress corrosion conditions. A way to overcome these problems is described in this paper. A technique has been developed that removes the protective film on metals by abrasion and then allows rapid ellipsometric measurements of repassivation to be made at any potential. This technique can be applied to both aqueous and gaseous systems since the repassivation kinetics determination does not depend on electrochemical measurements. It can thus study systems where S.C.C. takes place in gaseous atmospheres. It can also look at the role of films in affecting fatigue and corrosion fatigue.

This paper, in addition to describing the techniques developed, also illustrates their application to a preliminary study of the repassivation kinetics of the films formed on low carbon steel in nitrate solutions where it is susceptible to S.C.C. and nitrite solutions where it is not.

#### DESCRIPTION OF TECHNIQUE

The technique to be described here for studying repassivation kinetics has to accomplish three tasks: 1) film removal to simulate the surface produced when the natural film is ruptured, 2) potential control to simulate the potential existing at a surface under stress

corrosion conditions, and 3) measurement of film regrowth and current transients.

#### Film Removal

In order to remove the film and enable ellipsometric measurements to be made, two criteria had to be met. First, there was the requirement that a specularly reflecting metal surface, necessary for ellipsometry, be produced during film removal. This indicated that some type of mechanical polishing should be used and led to the use of a rotating wheel incorporating a fine abrasive which would remove the film while still preserving a surface finish sufficiently reflective to retain enough sensitivity for the ellipsometer to measure the formation of films of less than  $10\text{\AA}$  thickness. The second criterion requires that, upon removal of the surface layers on the metal, the surface be exposed to the environment and to the light beam of the ellipsometer sufficiently fast to measure the rate at which the repassivation takes place. This means that the rotating polishing wheel must be withdrawn from the specimen surface and from the path of the ellipsometer light beam at high speed.

The device developed for carrying out these objectives is shown in Figure 1 (a and b). It incorporates two fast rise-time solenoids (A and B), which allow measurement of growth kinetics within 10 msec of cessation of polishing. Solenoid A drives the polishing wheel (C) against the surface. This wheel is pulley driven by a DC motor (D) mounted on a movable plate (E). A microswitch (F) is required to shut off the retracting solenoid (B) when the polishing wheel clears the ellipsometer beam because allowing the solenoid to remain on for the whole retraction cycle will slam the movable plate E against the frame (G)

resulting in the transmittal of vibration to the cell (see Figure 2). This will mask out the growth process to be observed ellipsometrically.

The most difficult step in the entire film removal procedure is that of the polishing. Since the overall sensitivity to be obtained is directly related to the effective surface area undergoing polishing, it is critical that there be intimate contact between the polishing wheel and the specimen surface. Since it is difficult to align both the axes of the specimen and the polishing wheel so that the respective faces are perfectly parallel, some method of allowing the wheel to conform to the specimen surface during polishing had to be devised. Use of a flexible shaft on the wheel was found to be unsatisfactory. However, use of a compressable silicone foam rubber pad behind the abrasive material gives reasonably effective polishing.

One of the most difficult problems to overcome in the development of the technique is a satisfactory abrasive system (abrasive plus embedding medium). The use of a solid abrasive (diamond, alumina, etc.) embedded in a solid substrate had to be discarded since, as previously stated, it is necessary that the abrasive surface be flexible. An abrasive impregnated sheet material was found to be most effective. It has the disadvantage, however, of losing polishing efficiency after only a few cycles of abrasion. Thus far, a 40 micron alumina abrasive embedded in a Mylar plastic sheet has been found to be the most satisfactory. Studies are, however, continuing to develop more suitable abrasive systems.

#### Measurement of Repassivation and Current Transients

Because the initial phase of repassivation is completed in less than 50 milliseconds, ellipsometric measurements capable of such rapid response

are necessary. This required modification of the transient ellipsometry techniques described elsewhere<sup>(5,6)</sup>. A low impedance current-voltage converter was designed for use with the photomultiplier detection-system and yielded rise times on the order of 0.2 msec (Figure 3). Noise levels in the photometer system were lowered significantly by using a high intensity tungsten filament lamp and interference filter in place of the conventional mercury arc lamp. Overall sensitivity was markedly increased by use of the off-null ellipsometer technique<sup>(7,8)</sup>.

Both ellipsometric and current transients are monitored on a dual beam oscilloscope. Current is measured as a voltage drop through a precision resistor. The low input impedance of the oscilloscope does lead to error in the absolute measurement of current transients using such a technique. This will be replaced with a zero impedance current amplifier which is being developed for more accurate current measurement.

#### Potential Control

Since film rupture changes the potential<sup>(4)</sup> at the rupture sites while the rest of the surface is essentially at open circuit potential, it is necessary to keep the potential at the open circuit value during film removal. This simulates the situation at the tip of a crack for the surface looked at by the ellipsometer. A dual channel potentiostat of 20 milliseconds rise time was used, coupled to the electrodes shown in the cell in Figure 1b. By the use of the potentiostat we also are able to measure the current transient and thereby compare the total current involved during repassivation to the kinetics of film growth observed ellipsometrically.

## APPLICATION OF TECHNIQUE TO STUDY OF NITRATE CRACKING OF MILD STEEL

As an example of the utility of this technique in studying repassivation kinetics, studies were made on the relationship between rate of repassivation and stress corrosion susceptibility for a mild steel in a sodium nitrate solution, an environment which is known to produce cracking<sup>(9)</sup>.

Procedures

These studies were made at the predetermined open circuit potential of the material immersed in the environment in question since it was thought that any exposed bare metal would be immediately polarized to this value. Of course, any potential gradients resulting from those environmental variations caused by the restrictive geometry within a crack (pH lowering, anodic reaction products, deoxygenation, etc.) would lead to potentials negative to this value.

A polished specimen was placed in the cell and polarized to the open circuit potential using a potentiostat. After allowing the system to come to steady state, the surface was polished at 275 rpm until the anodic current level stabilized. The wheel was withdrawn and the transients recorded.

The specimens were cylindrical specimens 1.25 cm in diameter machined from stock AISI 1018 mild steel. No attempt was made to heat treat the specimens since it was thought that the presence of cold work in the material would simulate stress conditions at the tip of a stress corrosion crack.

Three solutions were used in this phase of the investigation:

- 1) a sodium tetraborate - boric acid buffer solution (14.003 g  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , 9.275 g  $\text{H}_3\text{BO}_3$ ; pH=8.4), 2) a 1.0N sodium nitrate

solution; 3) a 1.0N sodium nitrite solution. All solutions were aerated since we were attempting to reproduce cracking conditions within our environments.

#### Control Experiments

The buffered borate solution was used in control experiments for the following reasons: 1) much of our prior experience in oxidation kinetics of films on iron has been carried out in this solution, 2) at the cathodic reduction potentials used in this and previous studies, the reduction of oxide on iron occurs at essentially 100% current efficiency, and 3) due to the buffering action of the solution, and the thermodynamic stability of the solutes at this potential, once the oxide reduction products are removed by changing the solution, there should be no other build-up of reduction products to influence anodic reaction kinetics. Thus, the potential step method (moving from a cathodic potential where film is removed to an anodic potential where growth occurs) and the "at-potential" abrasion technique would be expected to give identical measurements of oxide growth kinetics in the borate. Figure 4 shows the oscilloscope traces obtained using the two methods for removing the oxide film; growth kinetics are seen to be the same for both procedures. However, this is clearly not the case for the associated current transients. Use of the abrasion technique results in a pronounced cathodic loop in the repassivation current. Such an effect clearly points out the disadvantage in using only current measurement to determine repassivation kinetics. All that can be seen is the total current supplied by the potentiostat to maintain the specimen potential at the set value. This current is not directly related to either the total anodic or cathodic reactions occurring during the transient, but rather to their difference. This is clearly shown in Figure 4

where film growth does occur during the cathodic loop as a result of an anodic reaction, the partial current of which is overshadowed by the cathodic reaction. By carrying out ellipsometric transient measurements, however, the film growth is directly measured.

The borate solution can also be used to calculate polishing efficiency. For example, if a series of repassivation studies in the nitrate solution are sandwiched between two growth studies in the borate control solution, which are determined to occur at equally high polishing efficiencies, then any uncertainty in the efficiency of abrasion during the given series of experiments is eliminated. In addition, the use of non-inert materials (cements, abrasive etc.) in the electrochemical cell can be evaluated using the borate control solution, since it is possible that they will affect observed growth kinetics.

#### Nitrite-Nitrate Experiments

To illustrate the applicability of the technique just described to an understanding of stress corrosion, it was used to look at the repassivation kinetics of low carbon steel in susceptible nitrate and non-susceptible nitrite solutions.

First, a comparison between the abrasion and the potential step technique was made for these solutions. Figure 5 shows such a comparison. It can be seen that when one removes the oxide film cathodically and steps the potential to the open circuit value, slower growing, thicker films are obtained than are formed when the oxide is abraded off at the open circuit potential. Using the potential step technique, where the rate of film growth and perhaps the nature of the film itself are influenced by the presence of cathodic reduction products at the specimen surface, the oxide film grows faster in the nitrite than in the nitrate solution, although the total coulombs passed



at any given time are identical. Using the abrasion technique, however, where such reduction product influence is eliminated, film growth in both systems is rapid, only the latter stages of growth being detected; films are thinner as well (Figure 6).

The fact that growth kinetics are affected by cathodic reduction products as shown by the potential step technique has significance. Repassivation occurring at the tip of a stress corrosion crack undoubtedly occurs in environments containing both anodic and cathodic reduction products (metal cations,  $H^+$  etc.). Thus, the potential step experiments can be worthwhile, providing that solution composition can be controlled and the oxide is reducible.

The temperature was then raised to 85°C where susceptibility in nitrate increases markedly<sup>(9)</sup>. Figure 7 shows the great difference in the repassivation kinetics using the abrasions technique that takes place at this temperature between the nitrate and the nitrite and the power of the technique in determining how much of the current goes into film growth and how much into metal dissolution. A comparison of repassivation kinetics for mild steel in the two solutions at their respective open circuit potentials reveals several important facts. 1) rate of film growth in the nitrite is higher; 2) although the initial charge passed is higher for the nitrite solution, the rate at which coulombs are passed decreases more rapidly than in nitrate solutions. The effect is explicitly displayed in Figure 8 where the charge to film thickness ratio is plotted against time. Although initially this ratio is the same for both solutions indicating a similarity in the first stage of film growth, the respective ratios change abruptly after about 20 milliseconds, indicating not only a more protective film has formed in the nitrite solution, but that a large portion of the coulombs passed

during repassivation transients in nitrate solution are going into metal dissolution. This point of ratio change may be quite significant in determining the susceptibility of a material to stress corrosion cracking.

#### RELEVANCE TO MECHANISM OF STRESS CORROSION

The technique described in this work clearly demonstrates the difference in behavior between the repassivation kinetics of steel in a nitrate solution where it is susceptible to S.C.C. and in nitrite where it is not. By means of this technique it is possible to show not only that the rate of repassivation in nitrite is greater but that a larger proportion of the anodic current passed after film rupture goes to metal dissolution in the nitrate under susceptible conditions. Thus, by means of this technique it is possible now to assess correctly the importance of repassivation kinetics on stress corrosion susceptibility. It, of course, has to be strongly emphasized that film repair is only one element, among many, in determining susceptibility. It is, however, one that strongly depends on environment. All other factors being equal, this technique now allows one to assess quickly the effect of new and unknown environments on the important factor of repassivation kinetics—while also measuring its effect on metal dissolution kinetics. Once fully developed to its greatest potential, it could prove to be both a most valuable analytical tool for evaluating whether a given alloy has a good possibility of suffering S.C.C. in a given environment as well as contributing towards our understanding of the mechanism of stress corrosion.

#### ACKNOWLEDGMENTS

We are grateful to John L. Pararas for his basic design of the polishing apparatus, to Louis Marzetta for his design and construction of the current-voltage converter photometer system, and to G. M.

Ugiansky for his helpful discussions and suggestions. We are most grateful to the Office of Naval Research who supported the work under contract NAONR 18-69.

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## FIGURES

- FIGURE 1a POLISHING APPARATUS USED TO REMOVE SURFACE OXIDE FOR STUDIES OF REPASSIVATION KINETICS. THE DRAWING IS A SCHEMATIC REPRESENTATION OF THE ASSEMBLY.
- FIGURE 1b ELECTROCHEMICAL CELL USED IN THE STUDY OF REPASSIVATION KINETICS. THE DRAWING IS SCHEMATIC AND SHOWS THE POSITIONING OF SPECIMEN AND POLISHING WHEEL ASSEMBLY.
- FIGURE 2 PHOTOGRAPH OF THE ASSEMBLED ELECTROCHEMICAL CELL-ABRASION APPARATUS USED IN REPASSIVATION KINETIC STUDIES.
- FIGURE 3 CIRCUIT DIAGRAM FOR THE FAST RESPONSE, LOW IMPEDENCE CURRENT-VOLTAGE CONVERTER PHOTOMETER USED IN THE ELLIPSO-METRIC MEASUREMENTS. RISE TIME OF THE INSTRUMENT: 0.2 MSEC.
- FIGURE 4 COMPARISON OF REPASSIVATION KINETICS FOR MILD STEEL IN THE SODIUM TETRABORATE-BORIC ACID BUFFER SOLUTION AT 1.042V (SHE). OSCILLOSCOPE TRACE A SHOWS ELLIPSOMETRICALLY MEASURED FILM GROWTH (TOP TRACE) AND ASSOCIATED CURRENT TRANSIENT (BOTTOM) AFTER CATHODIC REDUCTION OF OXIDE FILM AT -1.000V NHE. TRACE B SHOWS REPASSIVATION BEHAVIOR WHEN OXIDE REMOVED BY ABRASION AT 1.042 V NHE.
- FIGURE 5 COMPARISON OF REPASSIVATION RATES FOR MILD STEEL IN SODIUM NITRITE AND SODIUM NITRATE SOLUTION AT 0.024V NHE AT ROOM TEMPERATURE USING THE POTENTIAL STEP METHOD. COULOMBS PASSED (HEAVY LINE) AND FILM THICKNESS (LIGHT LINE) ARE PLOTTED AGAINST TIME. REDUCTION POTENTIAL IS -1.000V NHE.
- FIGURE 6 COMPARISON OF REPASSIVATION RATES FOR MILD STEEL IN SODIUM NITRITE AND SODIUM NITRATE SOLUTION AT ROOM TEMPERATURE

USING THE ABRASION METHOD. COULOMBS PASSED (HEAVY LINE) AND FILM THICKNESS (LIGHT LINE) ARE PLOTTED AGAINST TIME.

FIGURE 7 COMPARISON OF REPASSIVATION RATES FOR MILD STEEL IN SODIUM NITRITE AND SODIUM NITRATE SOLUTION AT 85°C. OPEN CIRCUIT POTENTIALS ARE -0.110 AND -0.310V NHE RESPECTIVELY. COULOMBS PASSED (HEAVY LINE) AND FILM THICKNESS (LIGHT LINE) ARE PLOTTED AGAINST TIME.

FIGURE 8 COMPARISON OF THE CHARGE TO THICKNESS RATIOS REPASSIVATION OF MILD STEEL IN SODIUM NITRITE AND SODIUM NITRATE SOLUTIONS AS PLOTTED AGAINST TIME. CONDITIONS ARE SAME AS IN FIGURE 7.

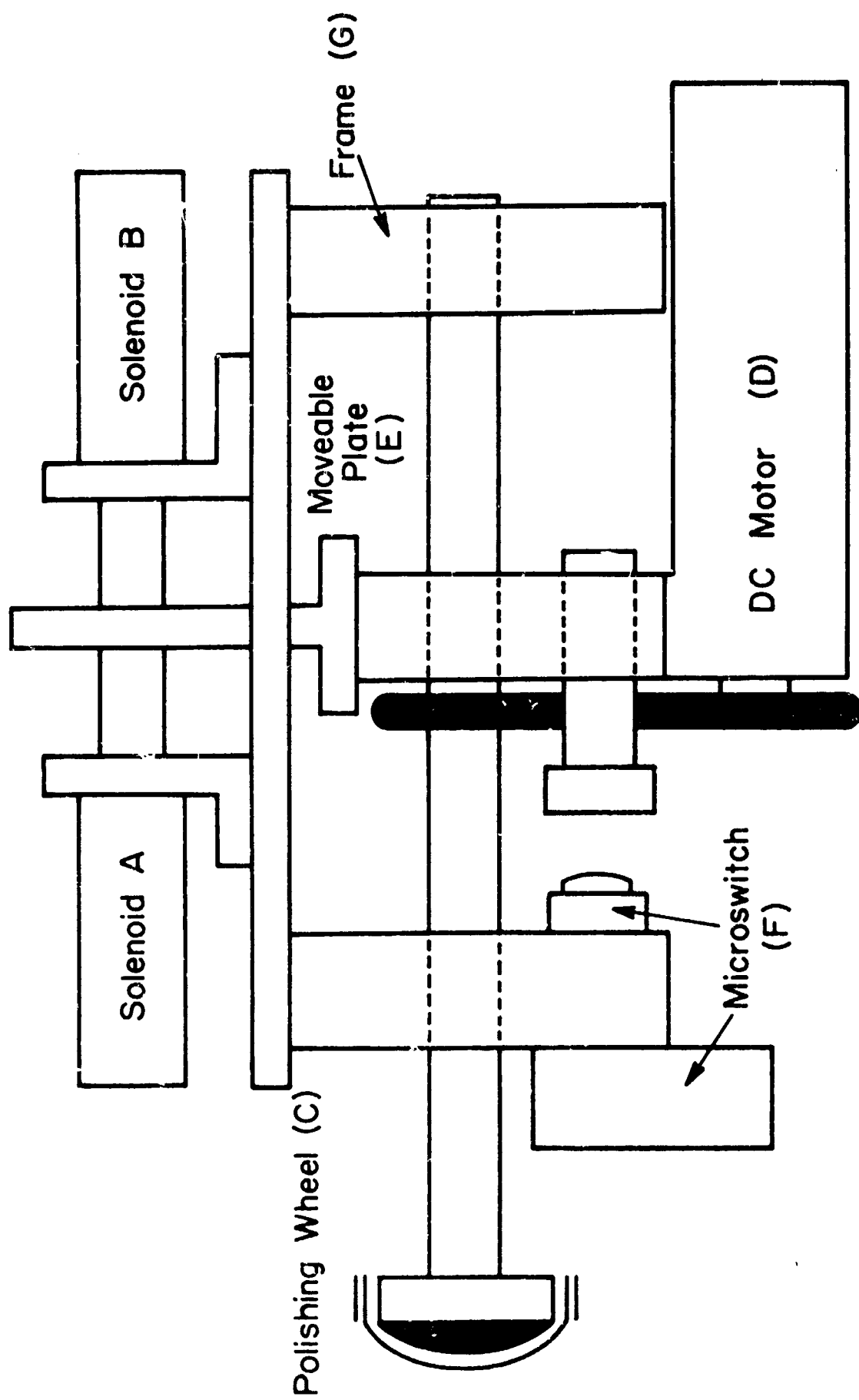


FIG 1a

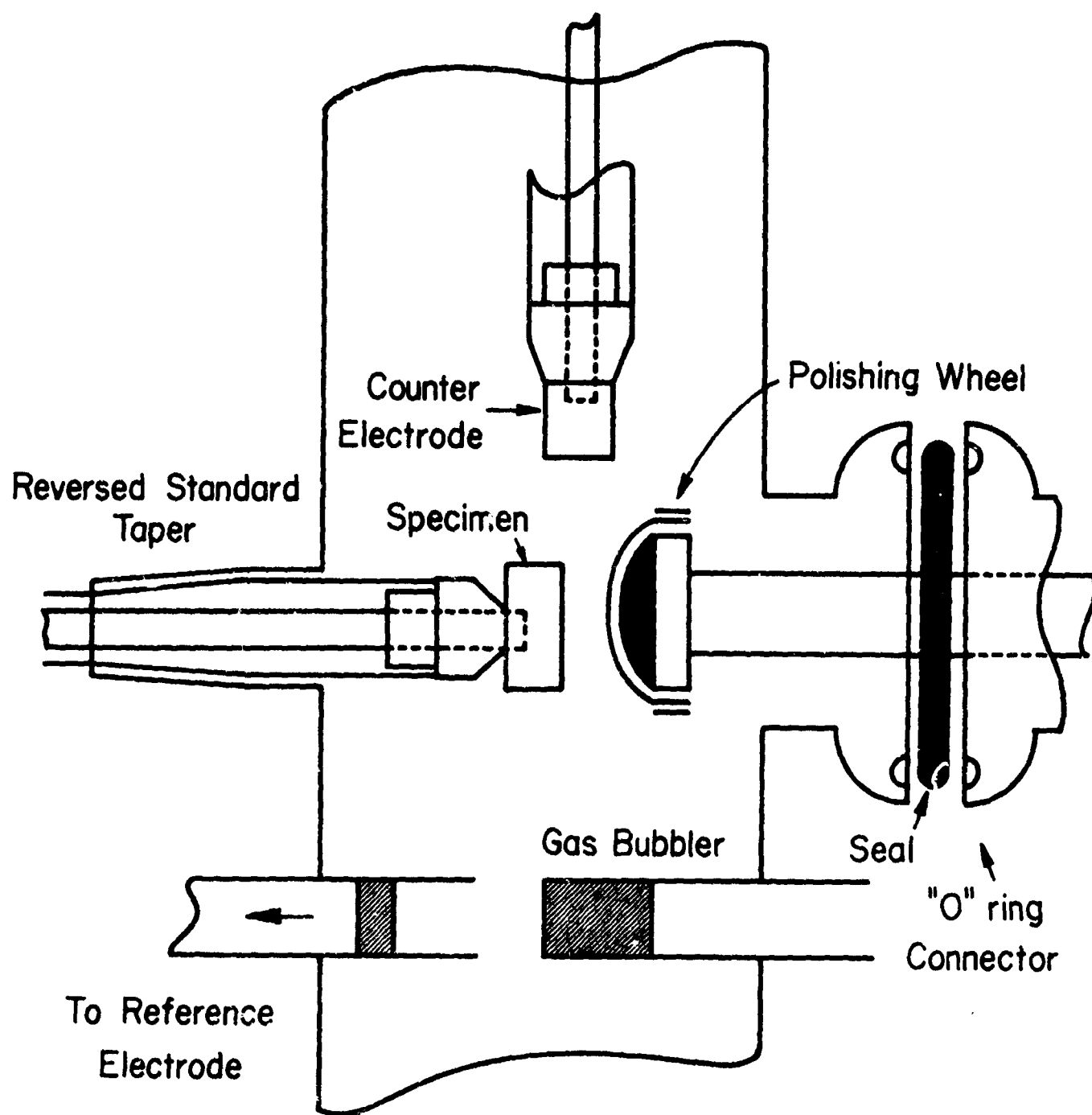


Fig 1b



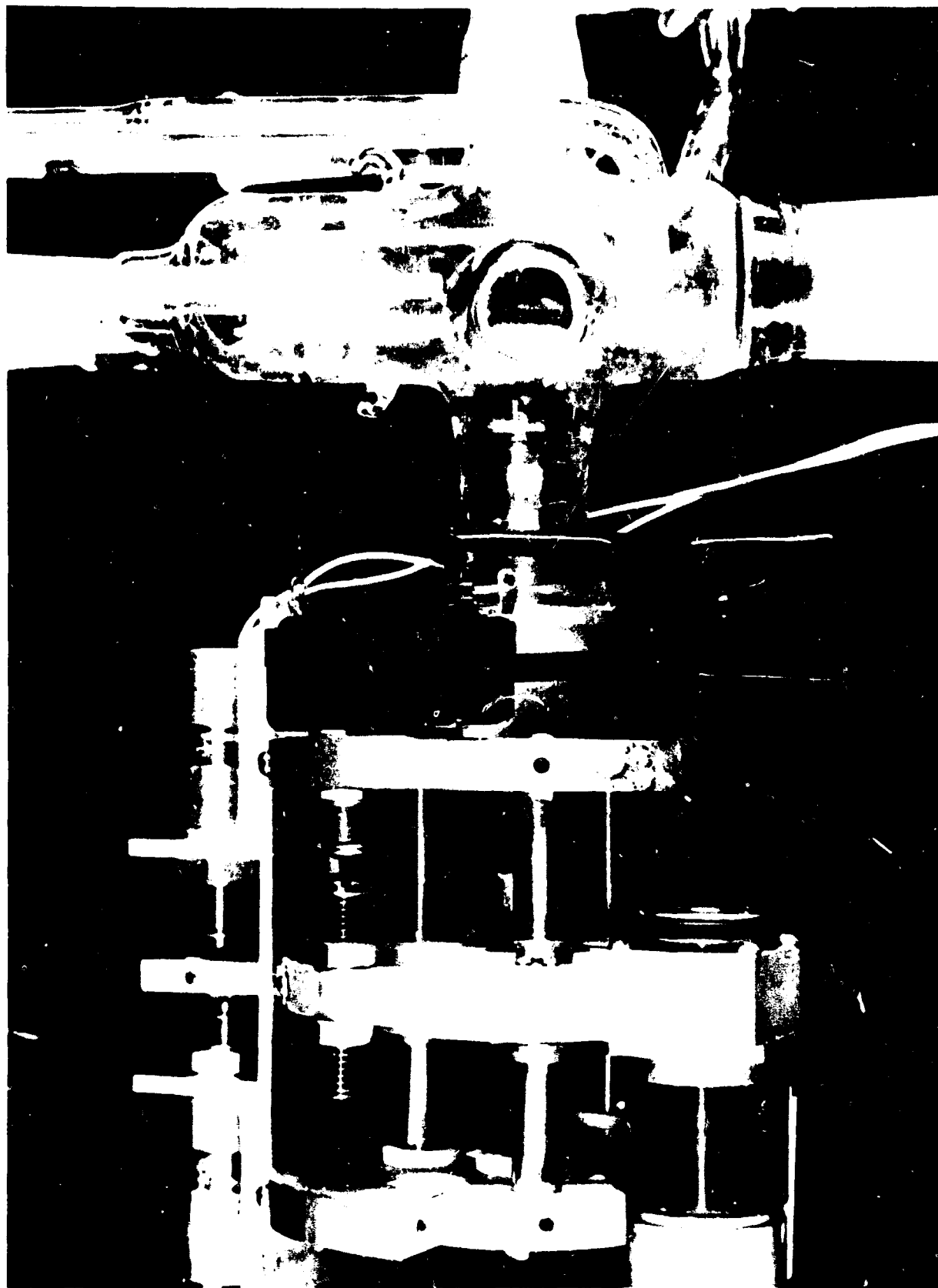


Fig 2

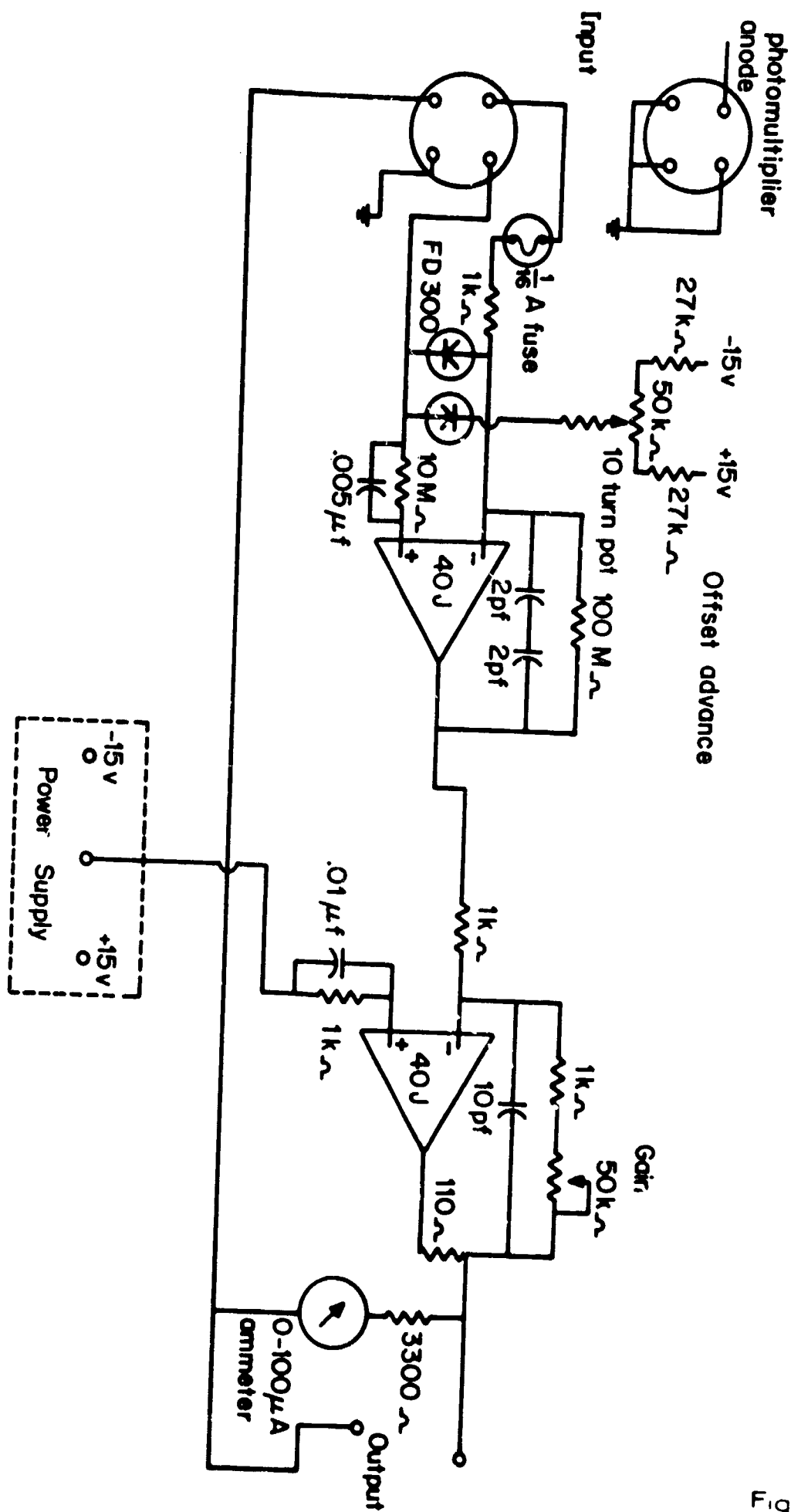
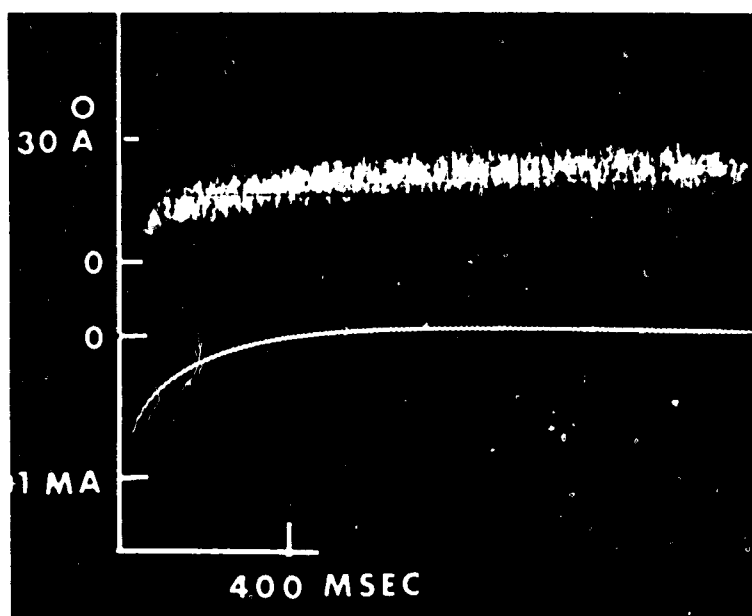


Fig 3

A



B

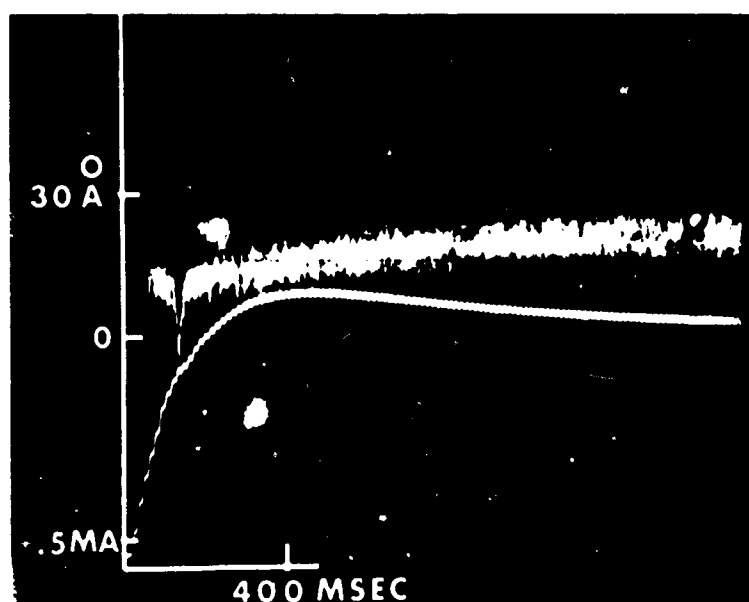


Fig 4

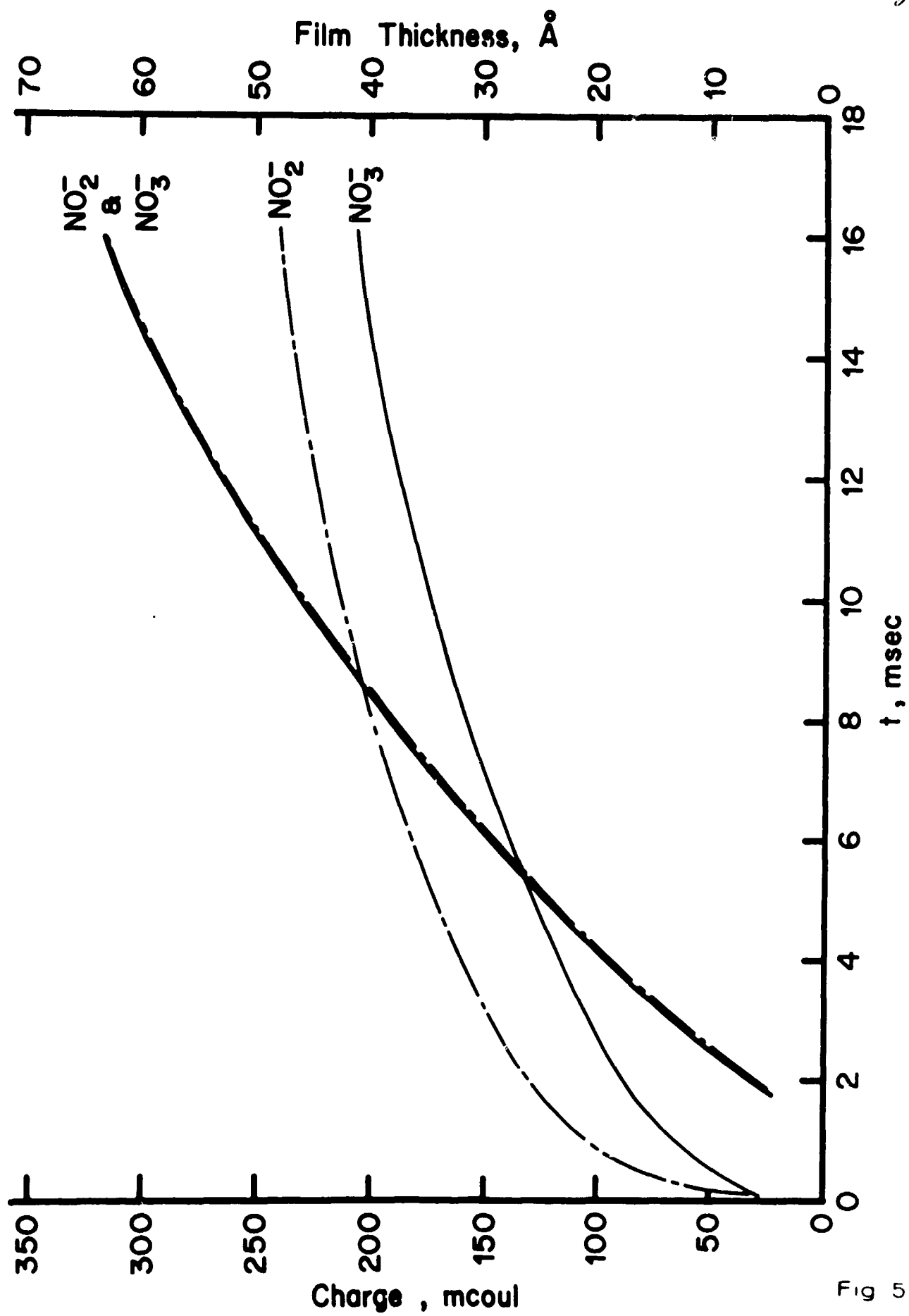


Fig 5

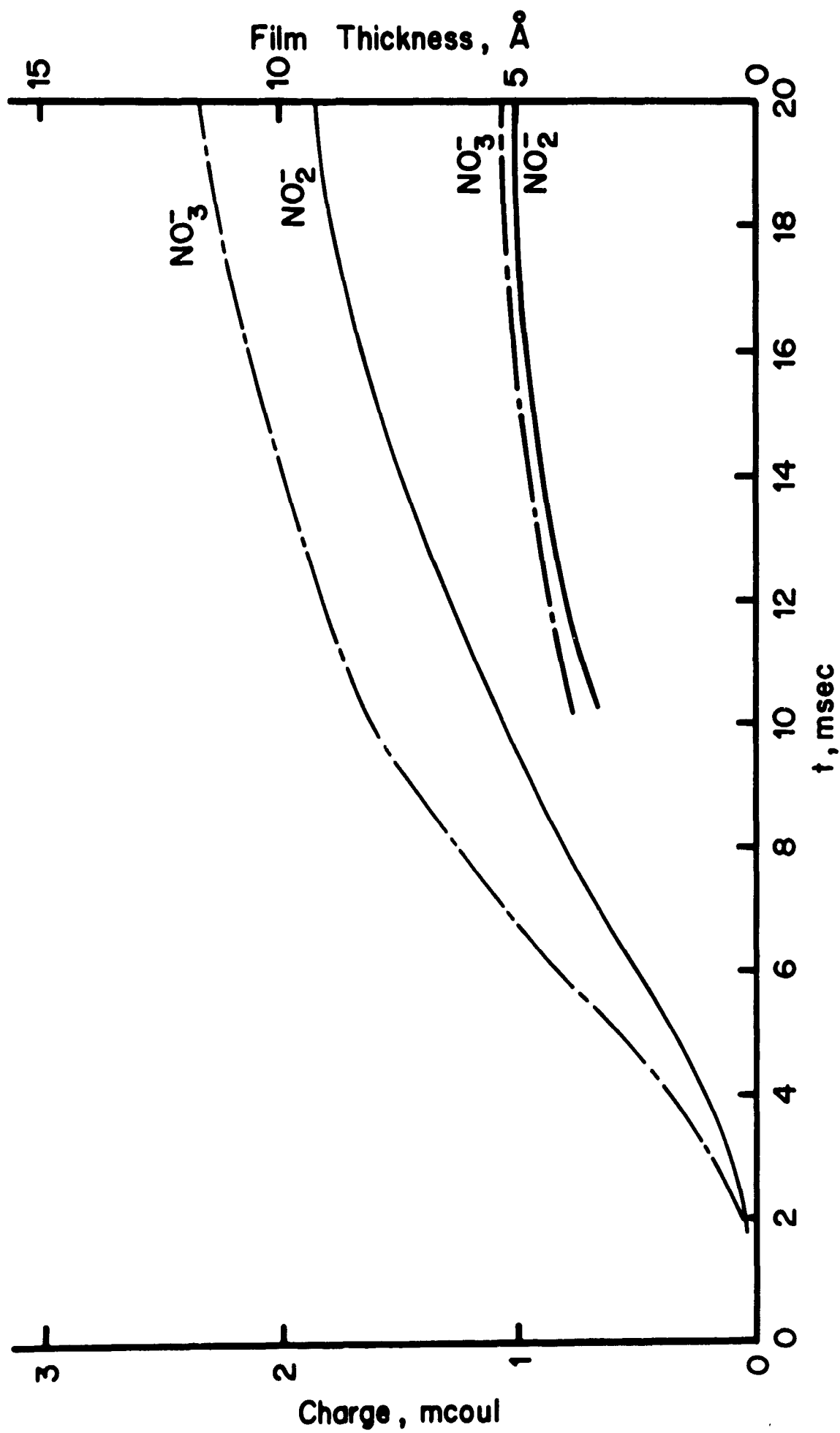


Fig 6

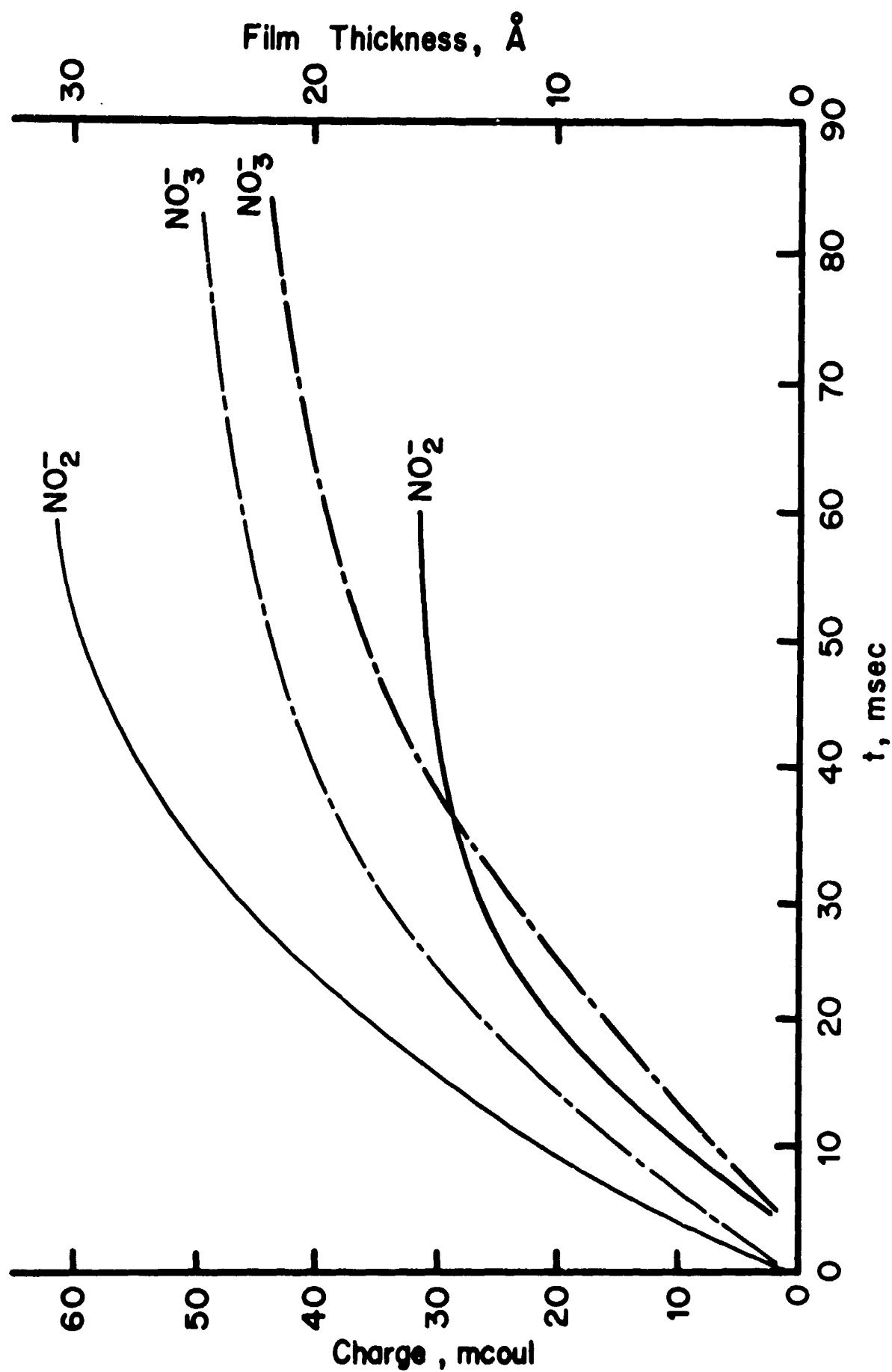


Fig 7

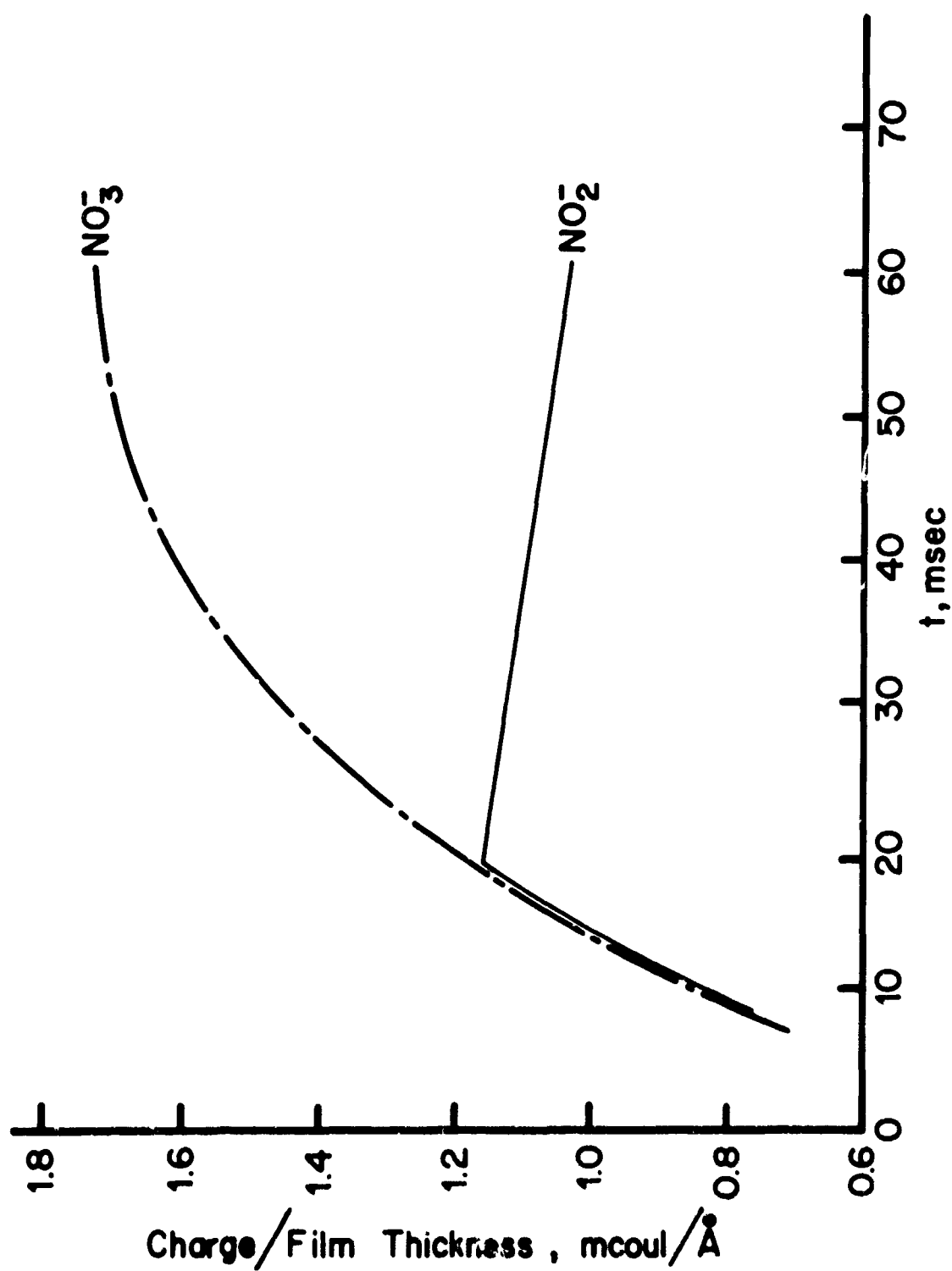


Fig 8

## A NEW TECHNIQUE FOR MEASURING THE DUCTILITY OF METAL OXIDE FILMS

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## ABSTRACT

A technique has been developed which directly measures the maximum ductility ( $D_{\max}$ ) of an oxide on a metal in an aqueous environment. Furthermore, initiation of oxide film rupture which occurs before  $D_{\max}$  is reached is measured as a function of strain while the metal is under potentiostatic control. These measurements have been made on tantalum, aluminum, and a 4% copper in aluminum alloy. The trend observed is that as the impurity content of the metal increases, the ductility of its oxide increases. The results are discussed in terms of values reported in the literature using different techniques.



## A NEW TECHNIQUE FOR MEASURING THE DUCTILITY OF METAL OXIDE FILMS

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Whenever a metal undergoes stress, the oxide film that is normally present on this metal in most environments also undergoes stress. The mechanical properties of this oxide film have both an influence on the mechanical properties of the metal<sup>(1)</sup> and, perhaps more importantly, may affect the susceptibility of the metal to stress corrosion cracking and corrosion fatigue. This is so because if this protective film fractures readily, i.e., has low ductility, bare metal will be exposed to an environment that promotes surface attack which may lead to failure.

Because of the importance of these considerations there have been in recent years a number of studies of the mechanical properties of oxide (especially aluminum oxide) films<sup>(2-6)</sup>. A variety of techniques have been employed to measure the fracture strain, characteristics of fracture, and the stress strain curves of the detached films. The techniques employed can be grouped into three types as follows:

1) Stress strain curves of separated and adhering films. For studies of detached films, the film is usually separated by dissolution of the substrate. The separated film is then placed in a tensile machine and a stress strain curve is determined. Examples of work employing this technique are the work of Bradburst and Leach<sup>(2)</sup> and Grosskreutz<sup>(4)</sup>. Leach and Neufeld<sup>(1)</sup> have also studied adhering films by measuring the effect of anodizing on the stress strain curves of fine wires.

2) Microscopic studies of fracture characteristics. An early example of this approach is the work Edeleanu and Law<sup>(6)</sup> who by means of a microscope measured the number of cracks per unit length as a function of percent permanent strain. Other more recent examples per- to crack spacing and morphology are those of Grosskreutz<sup>(7)</sup> and Block<sup>(5)</sup>.

3) Electrical or electrochemical detection of fracture. By straining an oxide covered specimen in an electrolytic solution provided with suitable electrodes, the point in the straining process at which fracture of the film occurs can be determined. Bradhurst and Leach<sup>(2)</sup> measured this point by determining the capacitance or resistance of the film on an anodized metal surface by means of an A.C. bridge. The capacitance gives a measure of the thickness of the oxide provided the oxide is undamaged. When fracture occurs, the values of capacitance and resistance become those for the metal with a thin natural film (10-20Å). These workers also used a change in the open circuit electrode potential as an indicator of fracture, a sudden change occurring at cracking. Finally, a number of studies<sup>(2,3,4)</sup> have employed current measurements to detect fracture. In this technique the potential is kept constant and a surge in current, because of the reduced resistance of the fractured film, signals the formation of cracks. In order to ensure that current changes are entirely due to cracking rather than thinning, Bubar and Vermilyea<sup>(3)</sup> carried out their straining at a lower potential than the one at which the film was grown. This is necessary because when straining at the potential at which the film was grown, thinning would cause an increase in the field across the film (since the potential is constant) and the current would increase without it being necessarily due to fracture.

Only the third group of techniques measures the ductility or, more precisely, the fracture strain of an adhering oxide film. Such a measurement is probably the most relevant one in the above catalogue of film mechanical property measurements related to the initiation of stress corrosion. All of the techniques in the third group measure the strain of the specimen bearing the film. The fracture strain of film is signalled by an abrupt change in current, potential, or capacitance.

Unlike these techniques, the technique described in this paper makes measurements of the adhering film itself, determines its reduction of thickness during straining and can thereby determine the film's ductility independently of the strain of the metal substrate. Information of this sort is necessary because the local variations in strain on a film adhering to a polycrystalline substrate can be very great and may not bear much relationship to the overall macrostrain of the metal specimen being studied. For example, Bubar and Vermilyea<sup>(3)</sup> by looking at the interference colors of anodic films on various grains of tantalum found certain grains whose films had thinned 50% before fracture, while current measurements using percent elongation of wires as a measure of fracture strain gave values of less than 10%. The technique described in this paper measures the thinning of a film on a metal specimen being strained by means of the optical technique of ellipsometry<sup>(8)</sup>. The ellipsometric measurements are made while the specimen is immersed in an electrolytic solution under potentiostatic or galvanostatic control so that it is possible to compare the measurements obtained by ellipsometry to those

obtained by current or potential measurements. Special care is devoted to measuring extremely small current surges to be certain that the fracture strain of the most vulnerable part of the film is detected.

#### DESCRIPTION OF TECHNIQUE

##### Apparatus

To measure the thinning of an adhering oxide film upon straining, an apparatus was developed that consists of a tensile machine provided with a means for making ellipsometric measurements on a tensile specimen whose potential in solution is maintained potentiostatically. As Figure 1 shows, the ellipsometer is firmly mounted on the movable cross head of the tensile machine so that as elongation progresses the ellipsometer makes measurements on the same area of the specimen at an angle of incidence of  $72-74^\circ$  to the specimen surface. Ellipsometric nulls are detected by means of a photomultiplier tube. The specimen itself is held by stainless steel grips arranged in such a way that they are never in contact with the experimental solution. The grips are attached to the tensile machine by tight fitting pins which reduce twisting to a minimum. The specimen is surrounded by the glass cell shown in Figure 2. The cell is held in place by the upper grip. Two optically flat windows are incorporated in the cell to provide for ellipsometric measurements. To maintain the potential by means of a potentiostat, reference and counter electrodes are provided. The reference electrode shown in Figure 2 is connected to the solution through a stopcock bridge, and a fine mesh platinum screen serves as a counter electrode.

### Specimen

Specimens are made from sheet material giving the flat surface necessary for ellipsometric measurements. Straining of the specimen is restricted to the area that the ellipsometer sees by reducing the cross section of the specimen at that point. The dimensions of a typical specimen are given in Figure 3. The surface of the specimens is mechanically polished to a flat mirror finish. Prior to conducting film ductility measurements, stress strain curves are always carried out for the material being studied. It is especially important to have the stress strain behavior of the specimen carefully characterized in order to relate the mechanical properties of the film properly to those of the substrate.

The stress strain curves are determined on carefully cleaned and degreased specimens. Stress measurements are made by recording the load on the specimen as indicated by a calibrated diaphragm type load cell. Elongation is measured using a strain gage mounted at the reduced section of the specimen with the strain reading taken from a digital strain indicator or from a recorder. The strain gage is bonded to the clean metal surface using a fast setting epoxy adhesive.

### Procedure for Film Ductility Measurements

After surface preparation and mechanical characterization, the specimen is mounted in the cell as shown in Figure 2. A solution is introduced and the specimen anodically polarized to form a film under low preload conditions. Just before measurements are started, the applied potential is lowered by approximately 20%. This is done because it assures that the film will decrease in thickness as the specimen is elongated so that any change in film thickness can be measured with the

ellipsometer. If the potential were to be maintained at its original value, any thinning would increase the field across the film and cause rapid thickening until the field reached its original value before straining. Thus, detection of thinning would be very difficult to measure. The potential is, however, maintained at as high a value as possible consistent with preventing film regrowth because the chances of detecting film rupture are increased by doing so, since the current surge upon film fracture is proportional to the potential.

The specimen is stressed in small increments of strain with film thickness measurements made at each increment. The current is monitored by recording the voltage drop across a resistance in the circuit. Current changes as small as 0.035  $\mu\text{A}$  can be detected. The experiment is continued until the film thickness measurement show a cessation of thinning at which point the ellipsometric parameters either cease to change or change their direction and become erratic. Figure 4 shows a typical run. The current measurements shown in this figure indicate fracture well before the ellipsometric measurements indicate the cessation of thinning.

It was necessary to determine whether stress affects the optical constants of the substrate and thereby introduces errors in the determination of oxide film thinning with strain. To determine whether this posed a problem, specimens of the metals whose films were to be studied, having very thin air-formed oxide films, were strained and ellipsometric measurements made as a function of strain. It was found that there were no significant changes in the substrate optical constants upon straining. Thus, the changes observed upon straining specimens with anodic films formed in aqueous environments, as

described in the next section, were due to changes in the film's thickness and not to changes in substrate optical constants. Only when extremely thin films are studied do the possibilities of very small changes in substrate constants introduce uncertainties in film measurements.

On the basis of the ellipsometric readings we can calculate the ductility of the anodic film in the area of the specimen being examined. Thus, % ductility =  $\frac{\Delta t}{t_0} \times 100$ , where  $\Delta t$  is the thickness change upon straining to the point where thinning ceases or the ellipsometric parameter change and become erratic, and  $t_0$  is the film thickness as measured by the ellipsometer before straining. On the basis of the current measurement we determine at what average strain the anodic film ruptures sufficiently so that it can be detected by a current surge. The word "average" strain is used because it is based on the overall elongation of the specimen.

#### APPLICATION OF TECHNIQUE

The technique just described was applied to measurements of the ductility of anodic films on Ta, Al and an Al alloy.

##### Tantalum

Tantalum was chosen for the initial trials of the technique because the ductility of its oxide has been measured and reported to be very high<sup>(3)</sup>. It thus provided us with a system where large changes could be easily detected. The tantalum, in the form of 0.5 mm thick sheet, had a purity of 99.95% and was used without any further heat treatment. After mechanically polishing its surface to a mirror finish, the specimen was chemically polished in a solution containing

5 parts sulfuric acid, 2 parts nitric acid, and 2 parts hydrofluoric acid for 30 seconds followed by rinsing and drying.

Two sets of experiments were carried out. The first set was on films formed in a solution 0.035 molar in sodium tetraborate decahydrate and 0.05 molar in boric acid, the second set was in the same solution but which also was 0.1 molar in sodium fluoride. Without fluoride the ductility of the anodic film was found to be 3.6% for a film 60Å thick as shown in Figure 5. Film thickness was determined using a refractive index for the oxide of 2.2, a solution refractive index of 1.335, and a substrate refractive index of 3.30-2.30i<sup>(9)</sup>. All ellipsometric experiments were carried out using 5461Å light and an angle of incidence of 72.5°-73.5°. Current measurements indicated fracture at 0.3% average strain.

Fluoride was added to the stock borate solution because it has been reported to affect the cohesion of the film<sup>(10)</sup>. With fluoride the ductility of the film increased to 4.5% as illustrated in Figure 6.

The fact that tantalum is a body centered-cubic metal complicates the interpretation of the data. Body centered-cubic materials form Luder's bands when strained beyond the elastic region. This band is initially a line of high local strain. As elongation proceeds the line broadens into a band within which the metal is deforming. Once the band has traversed the surface, the ellipsometry is not affected by this anisotropic strain, because it measures ductility by determining the change in film thickness. However, determining when the first crack forms as a function of strain can be in considerable error because of these high local strains.



On the stress-strain curve for tantalum as shown in Figure 5 initial film fracture occurs by the time that the Luder's band begins to form, or soon after, as indicated by the arrow which shows the point at which the first current surge was observed. On the other hand, the film continues to deform in a ductile manner beyond the elastic limit until a crack saturation limit is reached in the region beyond the arrow on the stress-strain curve. At this point the ellipsometer detects cessation of thinning. The results for tantalum are summarized and compared to literature values in Table 1.

#### Aluminum

Aluminum in two forms was studied, (1) 99.99% aluminum rolled into 1.6 mm sheet from which specimens were machined and then annealed, and (2) commercially pure aluminum (99.0%)\* (known as 1100-0 aluminum) sheet as received. The initial anodizing process was carried outside of the cell where the solution could be adequately stirred to reduce local heating effects. The solution used was 0.42 molar in boric acid and .004 molar in sodium tetraborate decahydrate and had a pH of 7.5. The film thickness was calculated using an index of refraction for the oxide of 1.66, 1.0-6.7i for the substrate and 1.33 for the solution<sup>(11)</sup>. The final stage of anodizing was performed in the cell to a film thickness of 1200Å<sup>o</sup> with the tensile specimen under a low preload condition. It was found that long term film growth (~ 24 hours) produced a "better" film in the sense that after several hours of growth the anodic current was lower and more stable than that which existed in the first hour of growth. In the first few hours of growth, current bursts occurred for no

\*99.0% Al minimum, 1% Si + Fe, .05 - 0.2% Cu, 0.05 Mn, 0.1 Zn

obvious reason. These were indistinguishable from current bursts caused by strain. It is believed that though the film grew to the desired thickness in a matter of minutes, subsequent anodizing repaired imperfections that developed during growth. In aluminum for example, these imperfections perhaps are in the form of vertical pores like those that form in sulfate solutions<sup>(12)</sup>. Long term anodizing may fill in these pores and form a more uniform oxide. The film on Ta did not exhibit current instability, but became stable in minutes.

We found that the oxide on pure aluminum exhibited no measurable ductility as observed with the ellipsometer; that is, no thinning was observed. Our sensitivity for the 1200Å<sup>0</sup> films studied was approximately .08%. Apparently massive rupturing manifested itself in the film growth shown in Figure 8. This perhaps suggests that for pure aluminum the oxide regrowing in the cracks was more voluminous than the ruptured oxide resulting in film thickening. The current measurement did not indicate cracking until 0.012% elongation had taken place. It thus appears that our current measurements were not sensitive enough to detect the earliest cracks. Indeed, as we developed and improved our capability to measure the current burst we found cracks occurring earlier and earlier in the straining sequence. The stress-strain curve for pure aluminum (Figure 9) illustrates where cracking is detected. It is in this area that massive deformation begins.

When more impurities are present in the aluminum, as in the commercially pure aluminum, the ductility of the oxide increases. The ductility of this aluminum oxide is a  $0.4\% \pm 0.2$  as measured with the ellipsometer. Figure 10 illustrates the film thinning plot obtained. In this case thinning progresses smoothly until

the crack saturation point is reached and thinning ceases. The point at which cracking is detected by current measurements is  $0.05\% \pm 0.03$  average strain. Figure 11 clearly shows that this initial oxide rupture occurred well below the yield strength of the metal substrate.

#### Al - 4% Cu Alloy

Because the addition of copper to aluminum increases its susceptibility to stress corrosion<sup>(13)</sup>, the film on an Al - 4% Cu alloy was measured and compared to the values obtained for the films on the non-susceptible pure aluminum and commercially pure aluminum to see if film ductility had any bearing on S.C.C. The aluminum copper alloy was prepared from 99.99% copper and aluminum. The resulting material was rolled into 1.6 mm sheet machined into specimens. The specimens were then solution heat treated and aged at 190°C for 19 hours. Anodic films of 1200Å thickness were formed on the specimen in the same manner as for the aluminum.

The addition of 4% Cu to pure aluminum not only increased its strength but also resulted in an increase in the ductility of its oxide. The amount of change in oxide thickness for the alloy is measured at  $0.5\% \pm 0.2$  thinning. Film thinning is uniform as seen in Figure 12 until maximum thinning is reached where the slope changes. The first cracks in the oxide as detected by current surges formed below the yield strength at an average strain of  $0.1\% \pm .05$ . This is shown on the stress-strain curve given in Figure 13. Thus, for the aluminum specimens studied as the impurity content of the metal increased its oxide ductility increased. The results for aluminum and the aluminum alloy are summarized and compared to values in the literature in Table 2.

## DISCUSSION

This study has considered the feasibility of the application of ellipsometry to the measurement of the ductility of an adhering oxide film. Results were obtained that are in reasonable agreement with those determined by other techniques. One problem with the optical technique is that unless one is looking at a film of good ductility such as that on tantalum, only films of the order of  $500\text{--}1000\text{\AA}$  can be measured. This is so because for ductilities of less than 1%, one has to measure thickness changes of less than  $1\text{\AA}$  for films of less than  $100\text{\AA}$  thickness. While ellipsometry is capable of measuring such thickness changes under ideal conditions, it cannot measure a specimen being stressed in a solution with the great sensitivity required for thin films, because slight changes in orientation, changes in optical constants of the film and or the metal, introduce uncertainties of sufficient magnitude to make detection of  $1\text{\AA}$  changes highly subject to error. With thicker films, measurements on substrates indicate that the larger changes can be detected with sufficient sensitivity.

Another problem that the ellipsometer shares with other techniques is that it only makes a determination of the ductility averaged over that part of the surface the ellipsometer looks at ( $>0.25\text{ cm}^2$ ). Because of variations in film thickness from one grain to another and variations in microstrain it is possible to obtain different values from the same specimen.

The ellipsometer offers, however, a real advantage in overcoming this problem because it actually looks at the thinning of the film on the metal and does not have to rely on a measurement of the elongation of the metal to determine the ductility of the film. When one relies only on

the specimen elongation, highly localized strains tend to give low values with regard to the ductility of the oxide at other sites.

The ellipsometer can attack this problem because it is able to confine its ductility measurements to a small area. Thus, by working with large grains or single crystal specimens it can examine in detail the ductility as a function of stress direction and orientation of substrate. The complications of any anisotropies of strain or film fractures occurring at edges of specimens or at grips etc. which are signalled, for example, by current surges would be eliminated. Since Logan<sup>(14)</sup> has shown that crystallographic orientation has some influence of stress corrosion susceptibility, the ellipsometric ductility technique will next be applied in this study to such single crystal studies.

Being thus able to examine small localized areas of the film, what does the ellipsometric technique actually determine about the film's mechanical properties and, disregarding anisotropy, are these properties the same as those determined by other techniques? To explore these questions we must look at Tables 1 and 2 and compare three groups of measurements; 1) the percent decrease in thickness an adhering oxide film undergoes upon straining until thinning ceases as determined ellipsometrically; 2) the macroscopic strain at which fracture occurs, the fracture strain,  $\epsilon_f$ , as signalled by current measurements and 3) measurements similar to (2) from other studies in the literature. In examining the values in groups (2) and (3) we find that our values, all at or below the yield point, are considerably lower than those in the literature and that the values in the literature are not always in good agreement. Two possible reasons can be suggested for our values being lower than those in the literature. The first may be due to differences in the way the strain measurements are made. This study took

special care to measure strain accurately using sensitive strain gages to calibrate the tensile machine. When these procedures are not followed, extension of grips, of cements etc. can introduce errors as high as two orders of magnitude. The studies described in the literature do not indicate whether such precautions were taken.

The other possible source of error may lie in the current measurements. Before refining our current measuring techniques to measure fractions of microamps, we could only detect current surges well after fracture had supposedly occurred. Figure 4 shows how these current surges build up to microamp values presumably by the introduction of many microcracks until a large surge (beyond a microamp) is finally observed. Which current surge signals initial fracture? We chose the earliest surge we could detect at a sensitivity of better than  $0.04 \mu\text{A}$ . Even this may not be sufficient to detect the first crack as our results on pure aluminum suggest. Perhaps the current measurements made in the other studies were not sufficiently sensitive to detect the early surges.

While one of the above considerations may account for the differences between our values of  $\epsilon_f$  and those in the literature, they do not explain the disparity between our values determined by current surges and those obtained ellipsometrically. This may be accounted for by assuming that after the initial fracture of the oxide film, the remaining segments, because they still adhere to the substrate, continue to thin. Grosskreutz<sup>(4)</sup> has pointed out that while the stress may be reduced to zero at the crack it builds asymptotically

with distance from the crack back to a stress level equal to local fracture stress levels at some given defect. Thus, as thinning of the oxide segments continues, new cracks are produced accompanied by new current surges as Figure 4 indeed shows. These segments can continue to strain and fracture until further straining produces only a widening of cracks. This occurs at the point where the crack density reaches its saturation value (no new cracks are formed). Such a phenomenon was observed by Edeleanu and Law<sup>(6)</sup> and Grosskreutz<sup>(4)</sup>. The latter has proposed a model which allows the prediction of the crack spacing at which further cracking does not occur. It thus appears that the ellipsometric measurement, rather than determining the point of initial fracture, determines an overall point in the process where film thinning ceases and crack widening occurs.

The ramifications of these considerations are that our sensitive current measurements are probably determining an upper limit for  $\epsilon_f$ , the fracture strain, while the ellipsometer is determining,  $D_{max}$ , the maximum ductility of the film, the point during straining at which thinning, or "necking down" ceases and the cracks widen. We cannot judge whether the fracture values are either  $\epsilon_f$  or  $D_{max}$ . We can only speculate that if their current sensitivity is low, probably  $D_{max}$  is being determined (The reasonable agreement between our ellipsometric values and those of Grosskreutz may indicate this). If the strain measurements are at fault,  $\epsilon_f$  was determined but its value was too high. If neither current or strain measurements are at fault the differences in environments and alloys can certainly always be responsible for the different values.

Having considered the significance of the results from the standpoint of evaluating the ellipsometric ductility measurements, it is worthwhile to discuss briefly their relevance to stress corrosion. The results with tantalum indicate a highly ductile film (as compared to most metals studied) and there are no instances in the literature to our knowledge of tantalum's susceptibility to stress corrosion cracking. This would indicate the greater the ductility of the film the less the susceptibility. The results for aluminum, however, indicate the opposite. The most susceptible alloy the Al - 4% Cu, has the greatest ductility while pure Al which is not known to be susceptible has the lowest ductility. This may not rule out a relationship between film ductility and susceptibility for two reasons. First, our measurements were made on 1200Å films. The properties of the thinner natural films which may play a role in determining susceptibility may be entirely different. Secondly, assuming that we can extrapolate the thick film results to thinner films, the films on more susceptible alloys may be more ductile thereby offering fewer sites where cracks in the metal can initiate than the less susceptible metals. Those metals bearing very little films suffer a multitude of attack sites and the corrosion current is not concentrated so that general corrosion occurs rather than the highly localized attack that leads to stress corrosion. The very brittle film may thus fail to provide a satisfactory initiation site.



## ACKNOWLEDGMENTS

The authors wish to express their appreciation to R. Bloss, B.W. Christ, J. Yahalom for many helpful discussions, to D. P. Fickle who made or obtained the specimen material, and to C. H. Brady who prepared the specimens. We are also most grateful for the support of this work by the Office of Naval Research Contract Number NAONR 18-69.

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TABLE 1

## Ductility of Ta Oxide Film

	Metal			
	Yield % Point %	Elongation % Ellipsometer 60Å	Elongation % Current 60Å	Elongation % Vermilyea 50-90Å
Oxide without Fluoride		3.62	0.3	1.5-4.0
Oxide with Fluoride	0.18	4.45	—	—

TABLE 2

## Ductility of Al Oxide Film

	Metal			
	Yield Point %	% Elongation Ellipsometer 1200 Å	% Elongation Current 1200 Å	% Elongation (Grosskreutz) 1500 Å
Oxide on 99.99% Al	.01	0.0	0.012	0.23
Oxide on 1100-.0 Al	0.1	0.37	0.050	0.5
4% Cu in Al	0.25	0.517	0.095	0.3
				(2024-T4)

## FIGURES

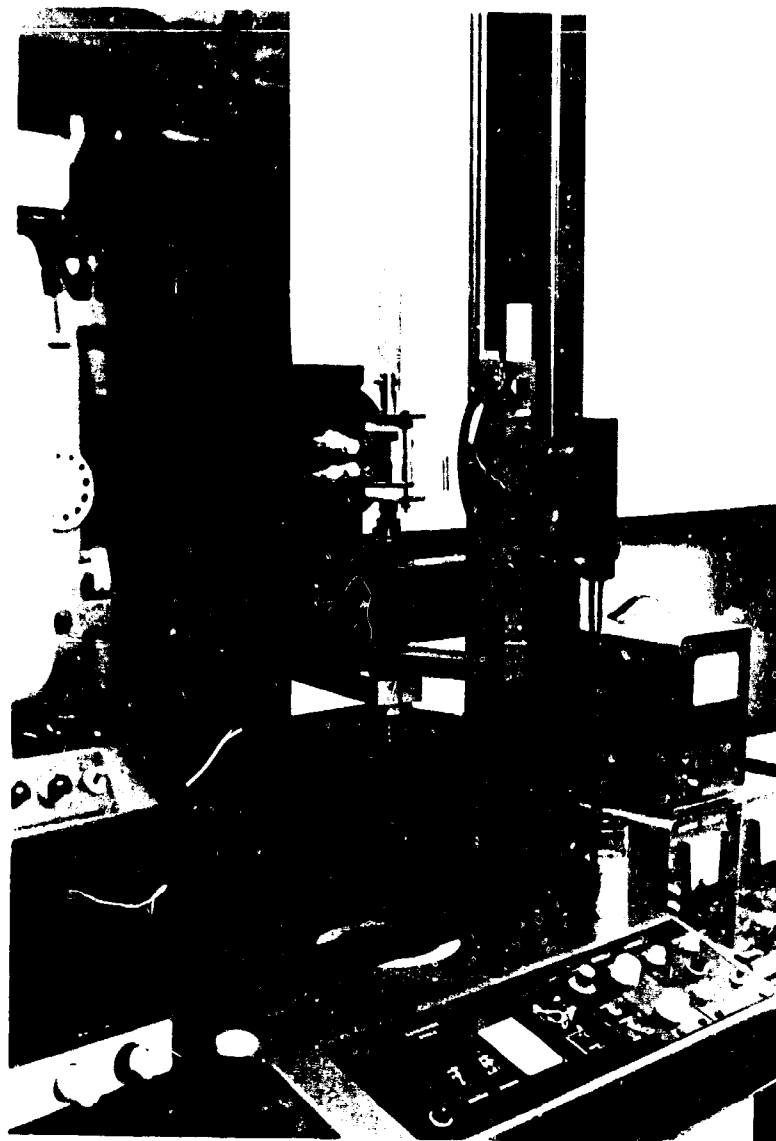
- FIGURE 1 ELLIPSOMETER COUPLED WITH TENSILE MACHINE FOR IN SITU STUDIES OF FILM DUCTILITY.
- FIGURE 2 SPECIMEN CELL DETAIL FOR APPARATUS SHOWN IN FIGURE 1.
- FIGURE 3 SPECIMEN DIMENSIONS USED IN STUDY.
- FIGURE 4 TYPICAL THICKNESS — CURRENT VERSUS STRAIN DATA AS OBTAINED FROM A 1200Å<sup>0</sup> OXIDE FILM ON 4% COPPER IN ALUMINUM ALLOY IN A SOLUTION CONTAINING 0.004 SODIUM TETRABORATE DECAHYDRATE AND 0.42 MOLAR BORIC ACID.
- FIGURE 5 TANTALUM STRESS-STRAIN CURVE WITH ARROW INDICATING POINT AT WHICH CURRENT SURGE WAS FIRST DETECTED.
- FIGURE 6 REDUCTION IN THICKNESS OF OXIDE ON TANTALUM AS A FUNCTION OF CROSSHEAD DISPLACEMENT FOR A 60Å<sup>0</sup> FILM FORMED IN A SOLUTION CONTAINING 0.035 MOLAR SODIUM TETRABORATE DECAHYDRATE AND 0.05 MOLAR BORIC ACID.
- FIGURE 7 REDUCTION IN THICKNESS OF OXIDE ON TANTALUM AS A FUNCTION OF CROSSHEAD DISPLACEMENT FOR A 60Å<sup>0</sup> FILM FORMED IN A SOLUTION CONTAINING 0.035 MOLAR SODIUM TETRABORATE DECAHYDRATE, 0.05 MOLAR BORIC ACID AND 0.1 MOLAR SODIUM FLUORIDE.
- FIGURE 8 CHANGE IN THICKNESS OF OXIDE ON 99.99% PURE ALUMINUM AS A FUNCTION OF CROSSHEAD DISPLACEMENT FOR A 1200Å<sup>0</sup> FILM FORMED IN A SOLUTION CONTAINING 0.004 MOLAR SODIUM TETRABORATE DECAHYDRATE AND 0.42 MOLAR BORIC ACID.
- FIGURE 9 99.99% PURE ALUMINUM STRESS-STRAIN CURVE WITH ARROW INDICATING POINT AT WHICH CURRENT SURGE WAS FIRST DETECTED.
- FIGURE 10 REDUCTION IN THICKNESS OF OXIDE ON COMMERCIAL PURE (99.0%) ALUMINUM AS A FUNCTION OF CROSSHEAD DISPLACEMENT

FOR A 1200Å<sup>°</sup> FILM FORMED IN A SOLUTION CONTAINING 0.004 MOLAR SODIUM TETRABORATE DECAHYDRATE AND 0.42 MOLAR BORIC ACID.

FIGURE 11 COMMERCIALLY PURE (99.0%) ALUMINUM STRESS-STRAIN CURVE WITH ARROW INDICATING POINT AT WHICH CURRENT SURGE WAS FIRST DETECTED.

FIGURE 12 REDUCTION IN THICKNESS OF OXIDE ON 4% COPPER IN ALUMINUM ALLOY AS A FUNCTION OF CROSSHEAD DISPLACEMENT FOR A 1200Å<sup>°</sup> FILM FORMED IN A SOLUTION CONTAINING 0.004 MOLAR SODIUM TETRABORATE DECAHYDRATE AND 0.42 MOLAR BORIC ACID.

FIGURE 13 4% COPPER IN ALUMINUM ALLOY STRESS-STRAIN CURVE WITH ARROW INDICATING POINT AT WHICH CURRENT SURGE WAS FIRST DETECTED.



NOT REPRODUCIBLE

Fig. 1

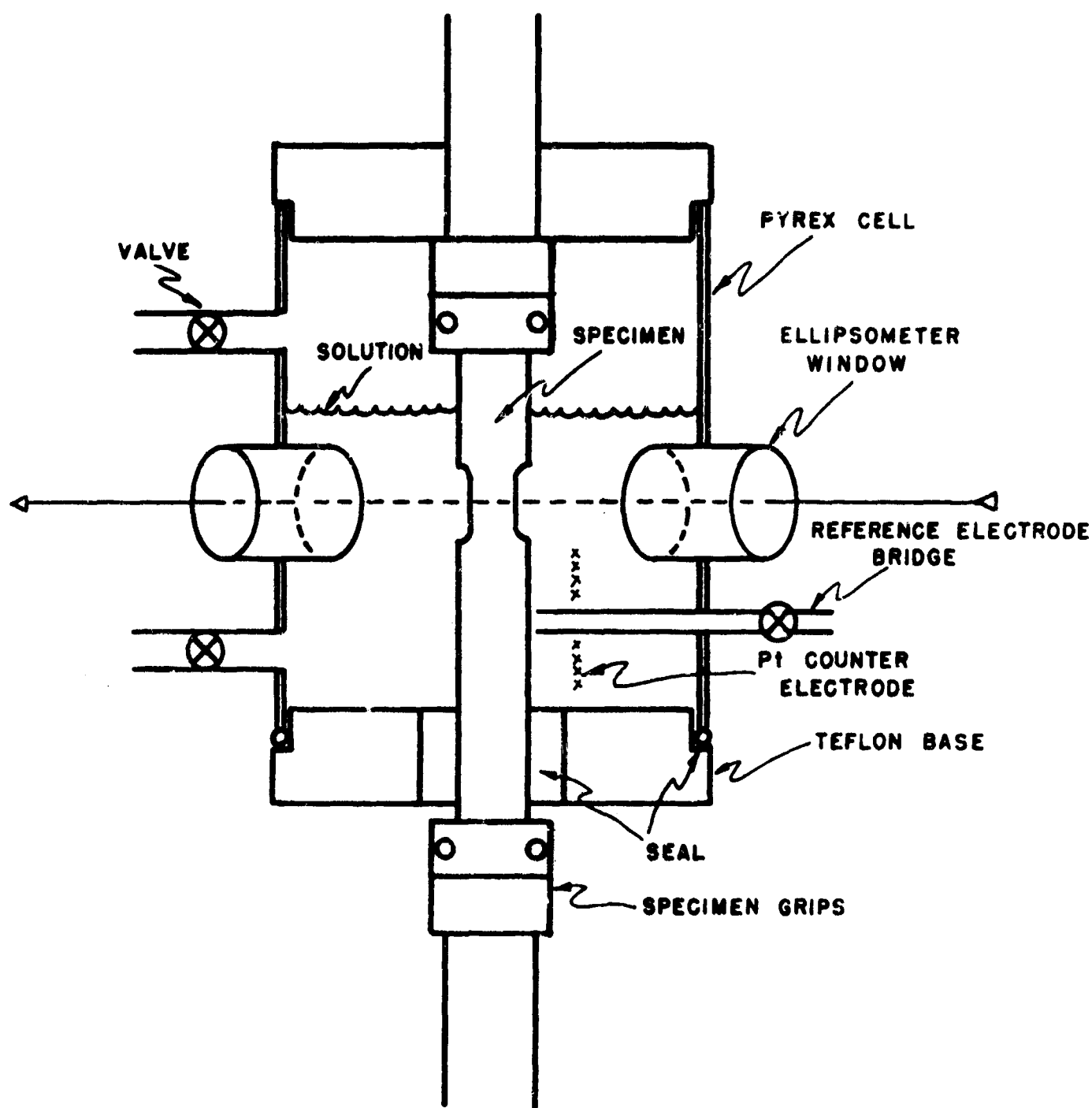


Fig. 2



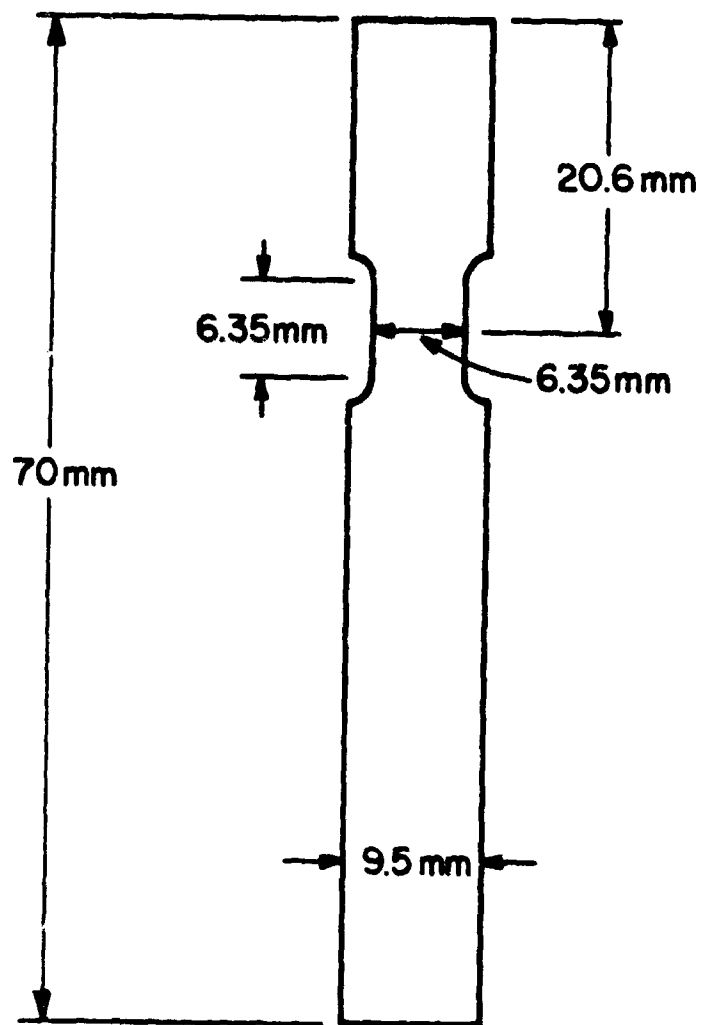


Fig. 3

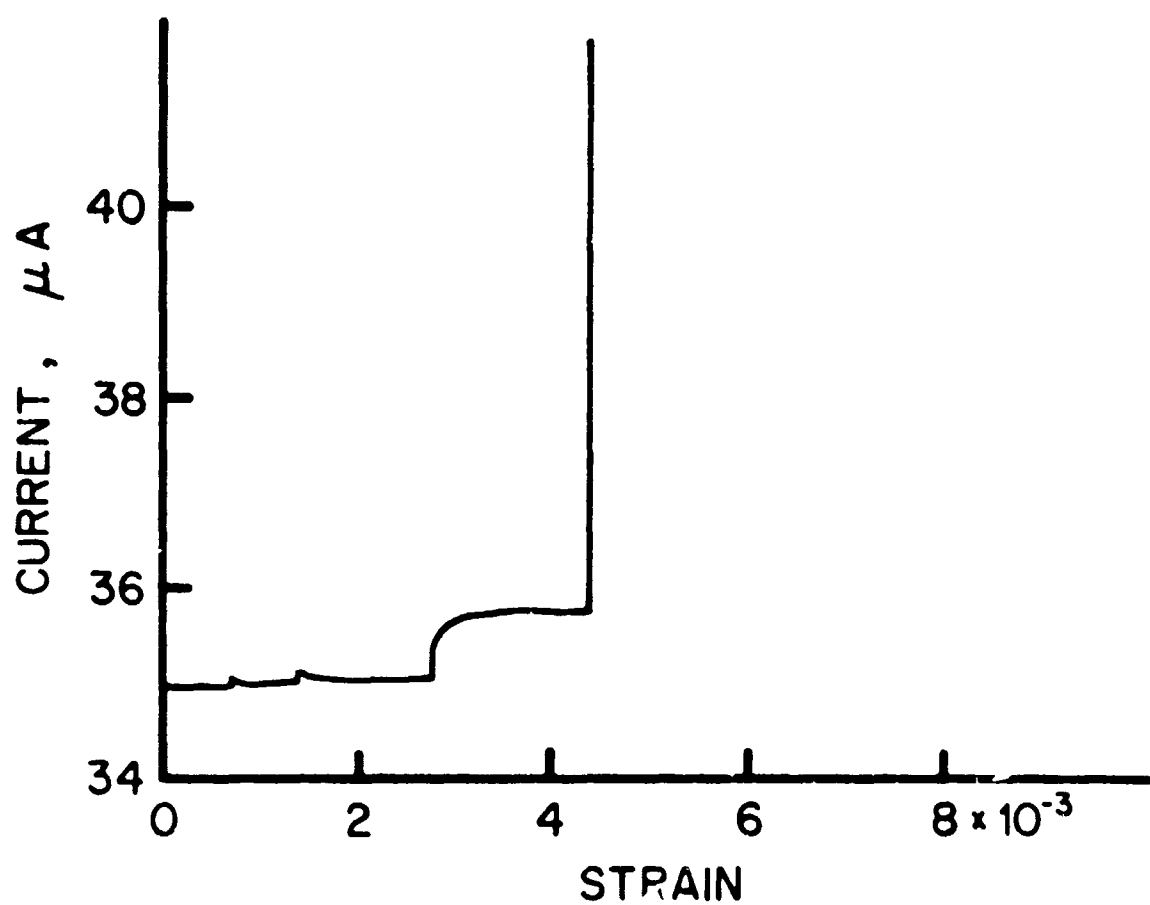
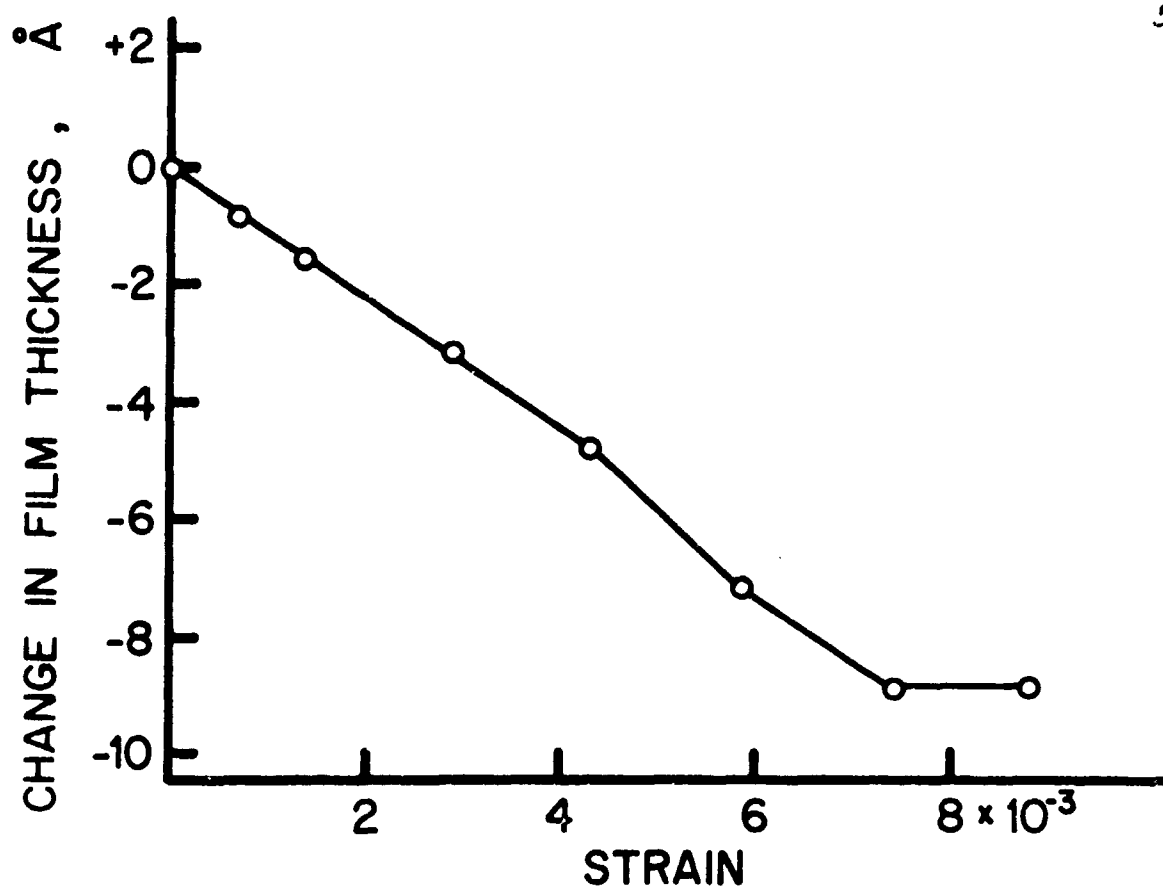
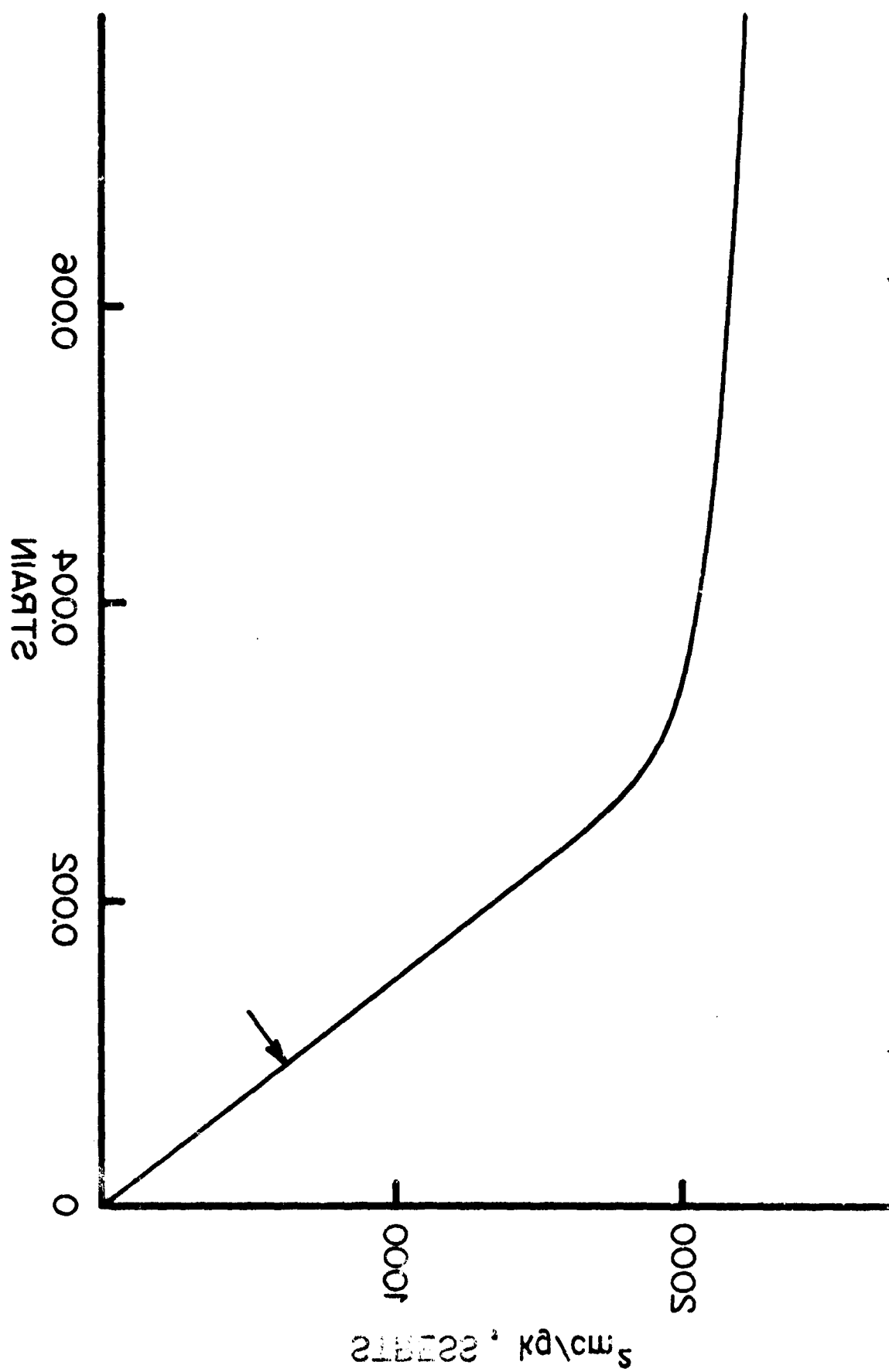


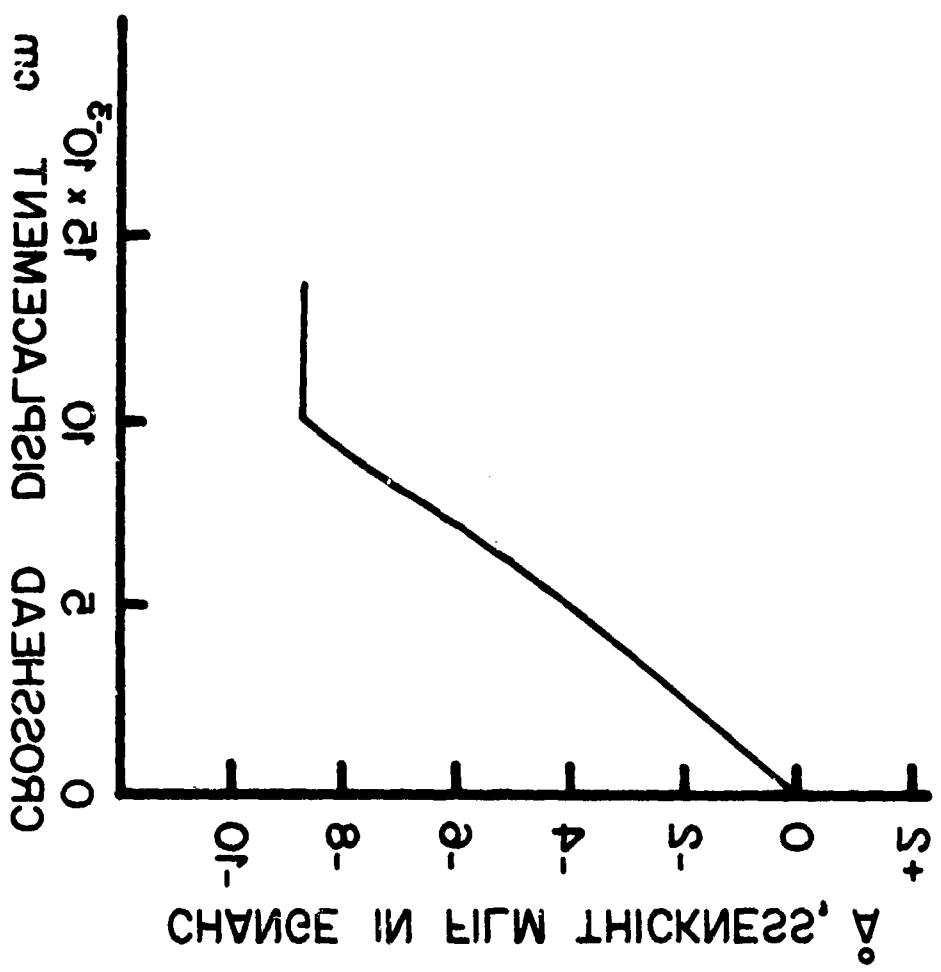
Fig. 4

Fig 12

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Fig. 11

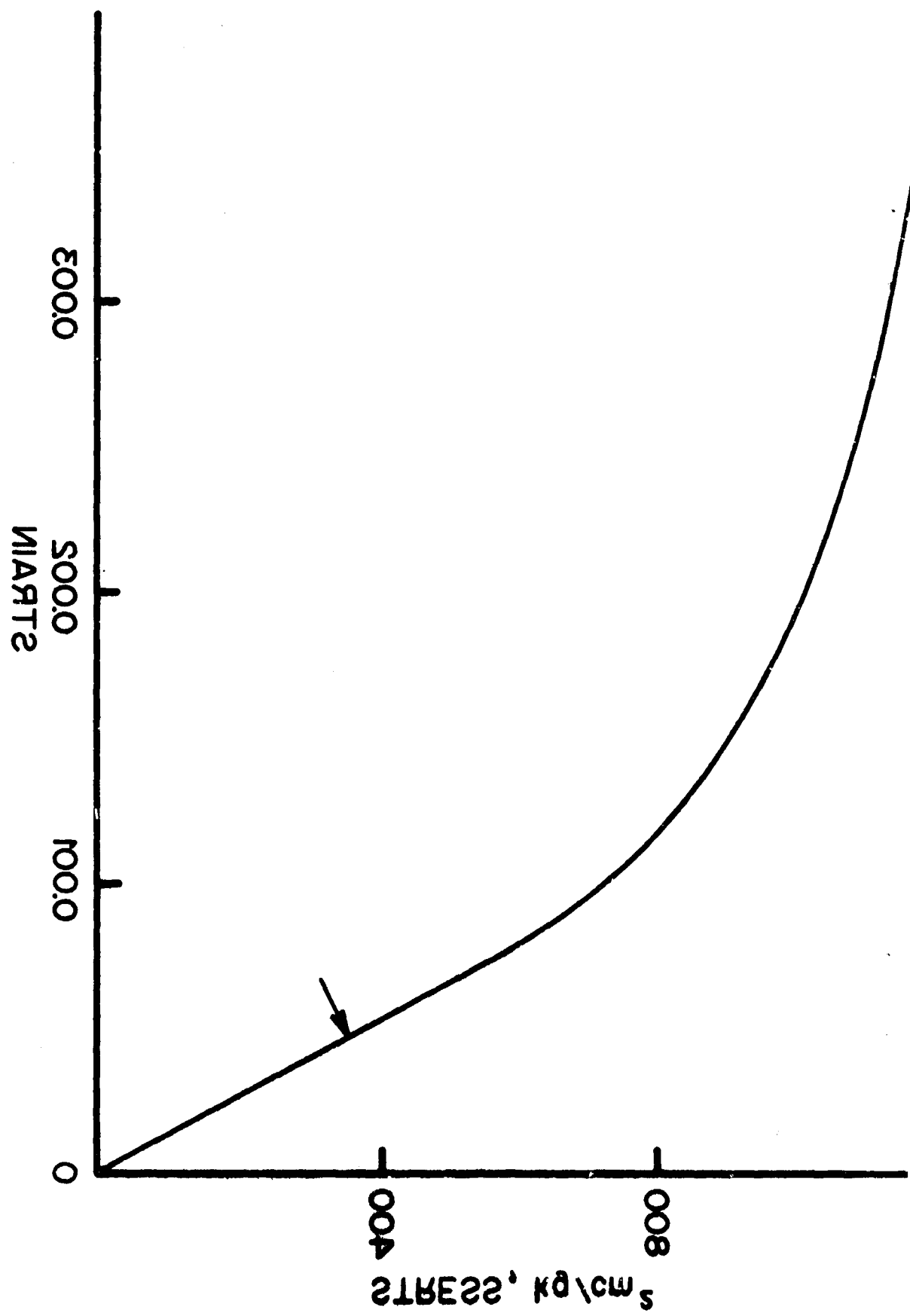
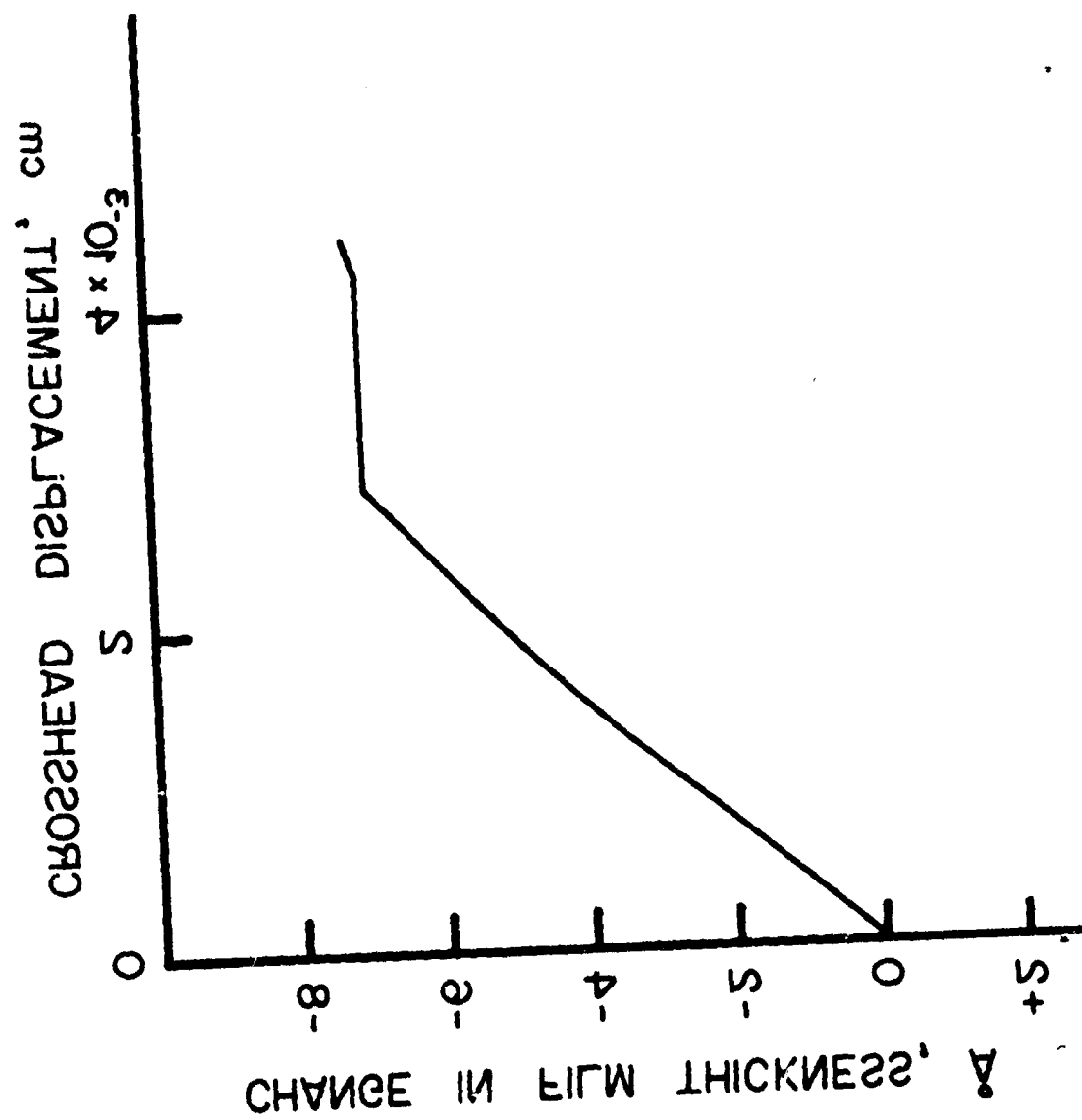
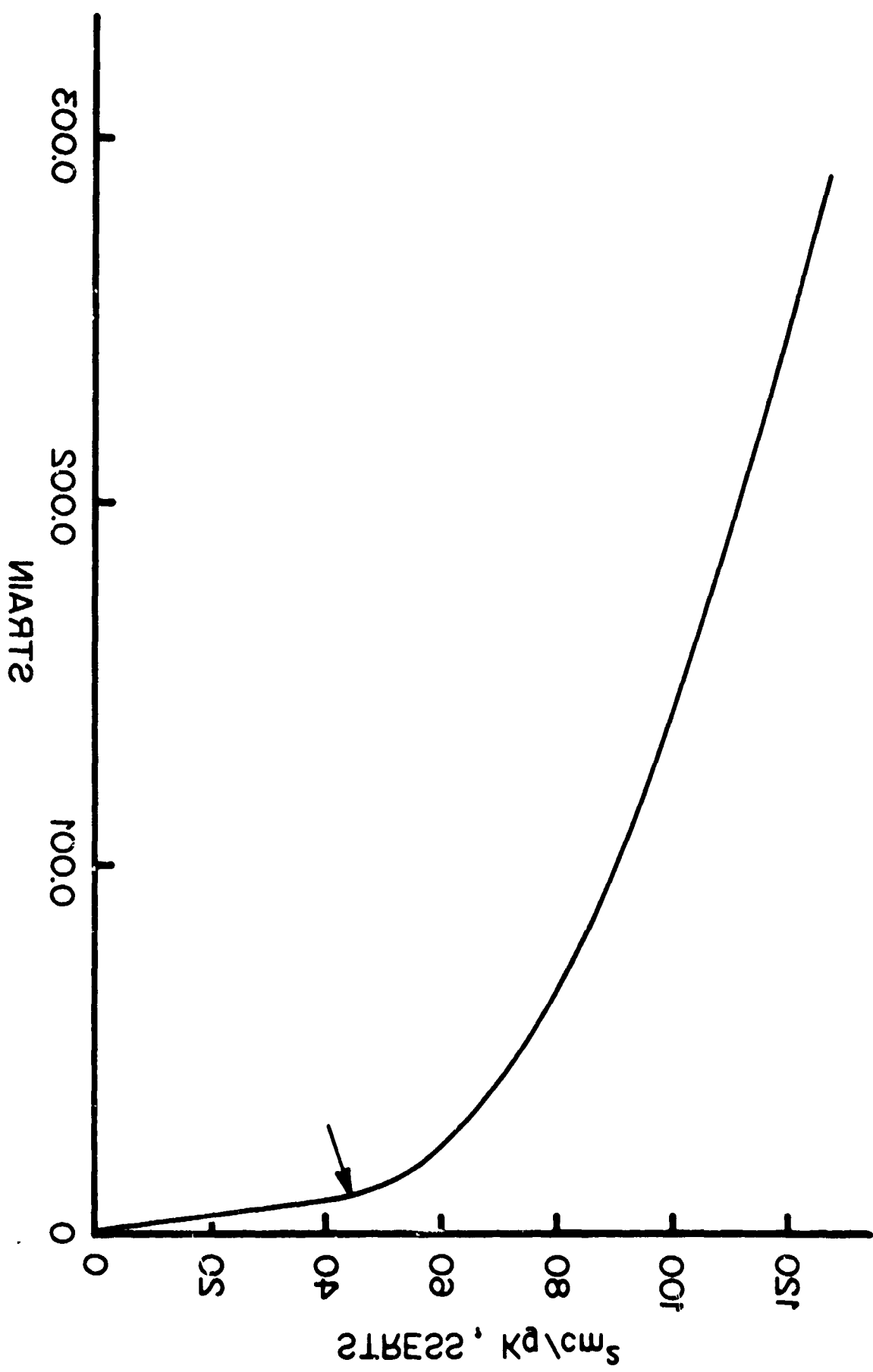
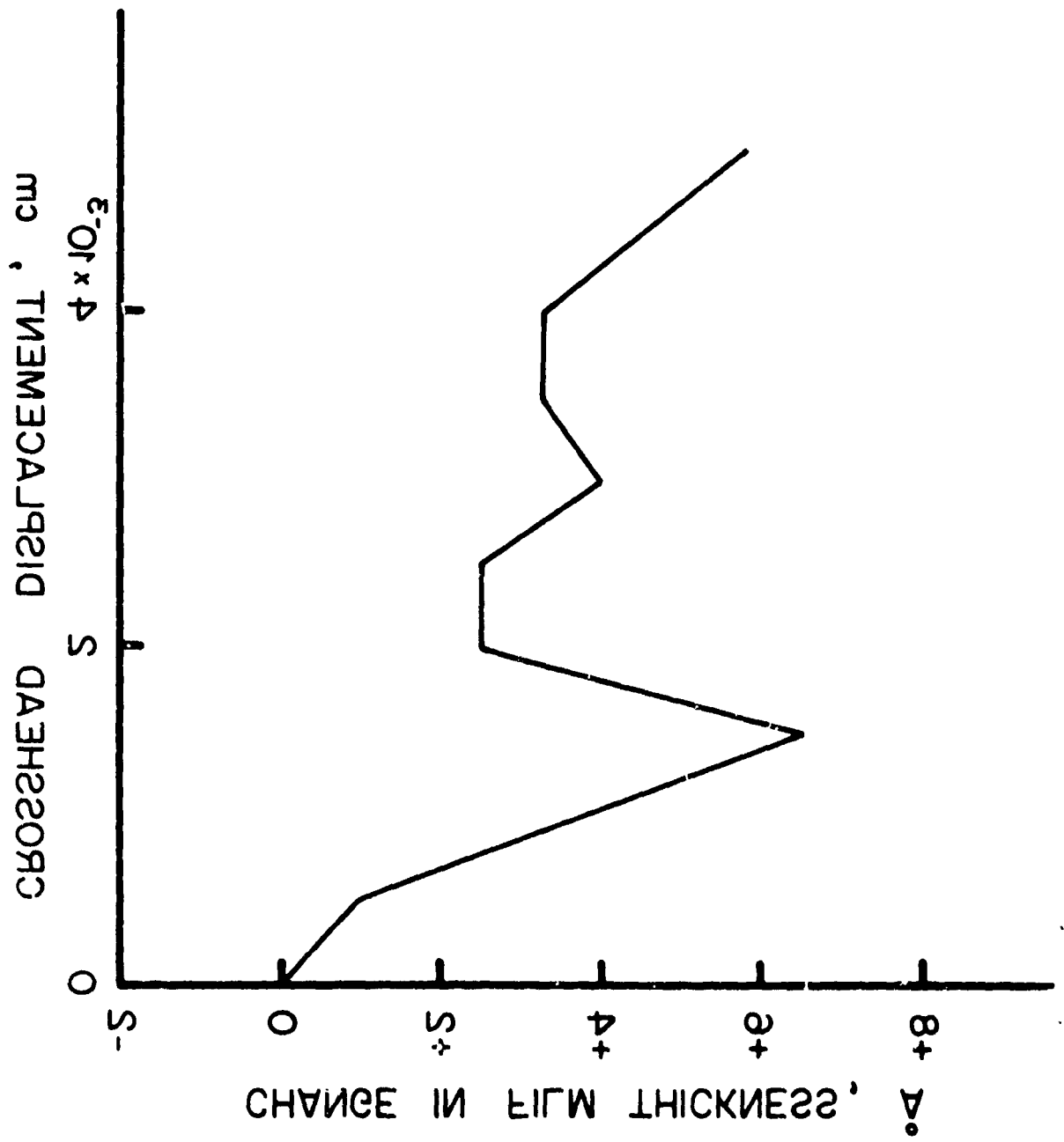


Fig. 10

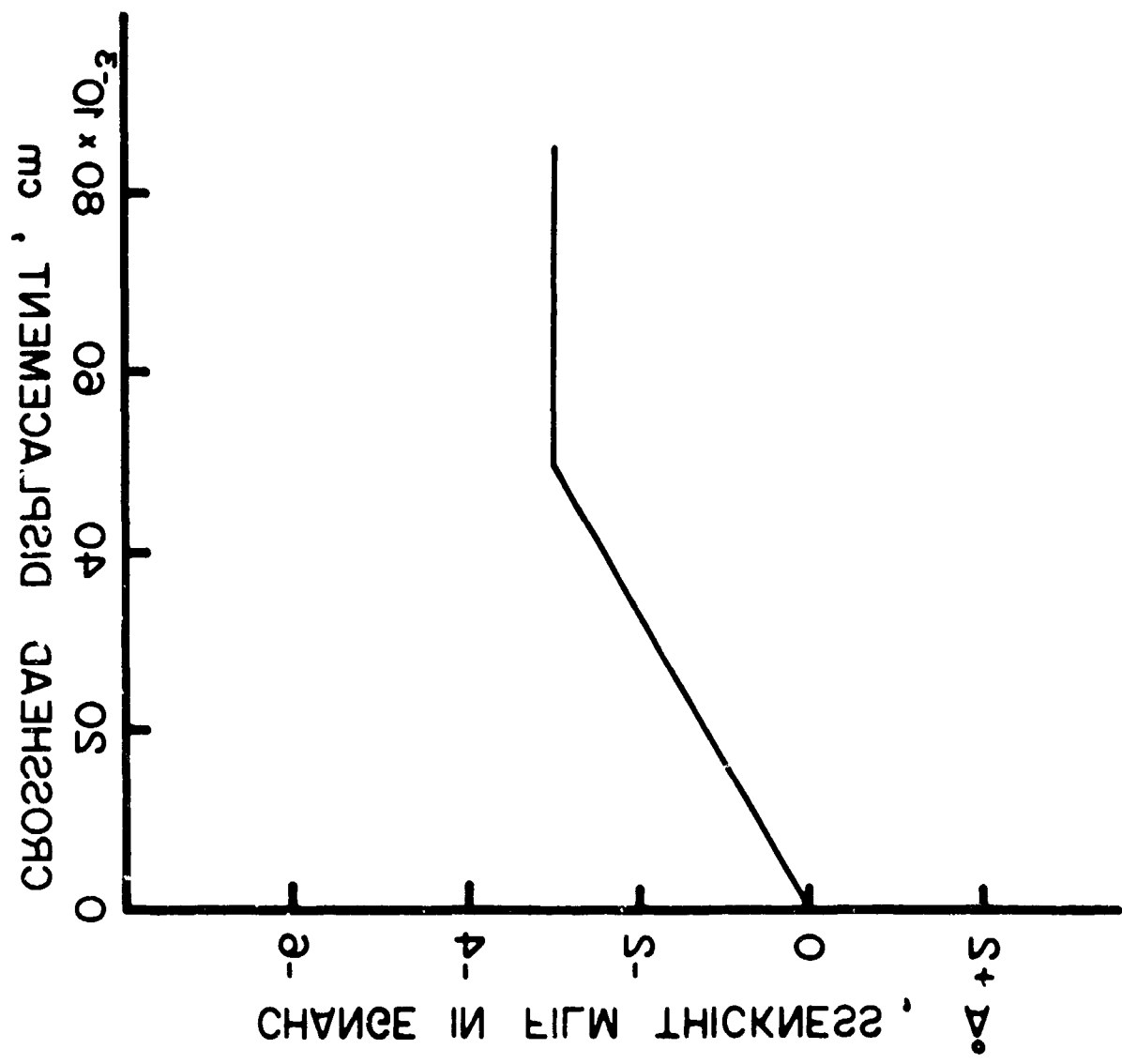




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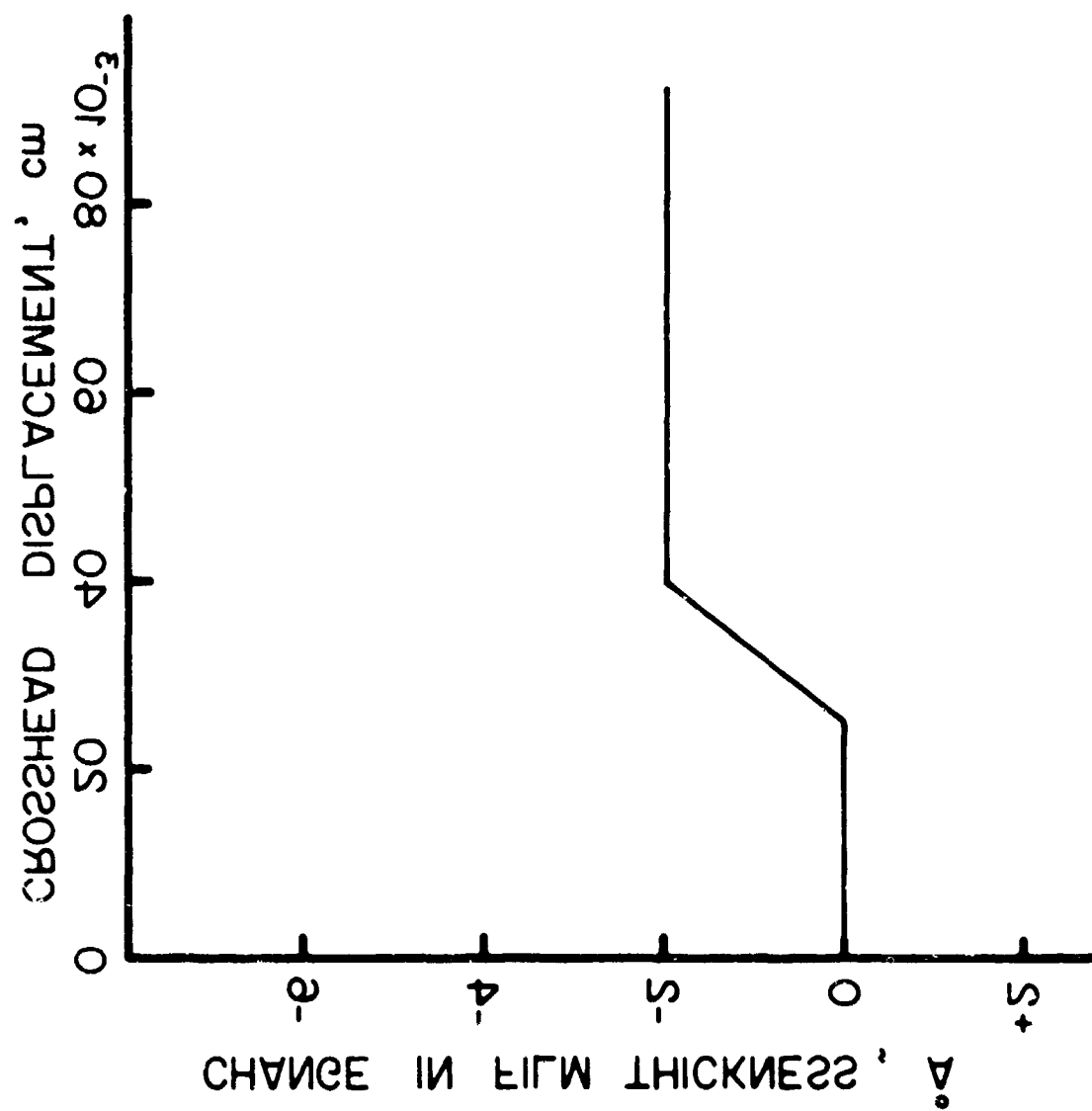






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Fig. 2



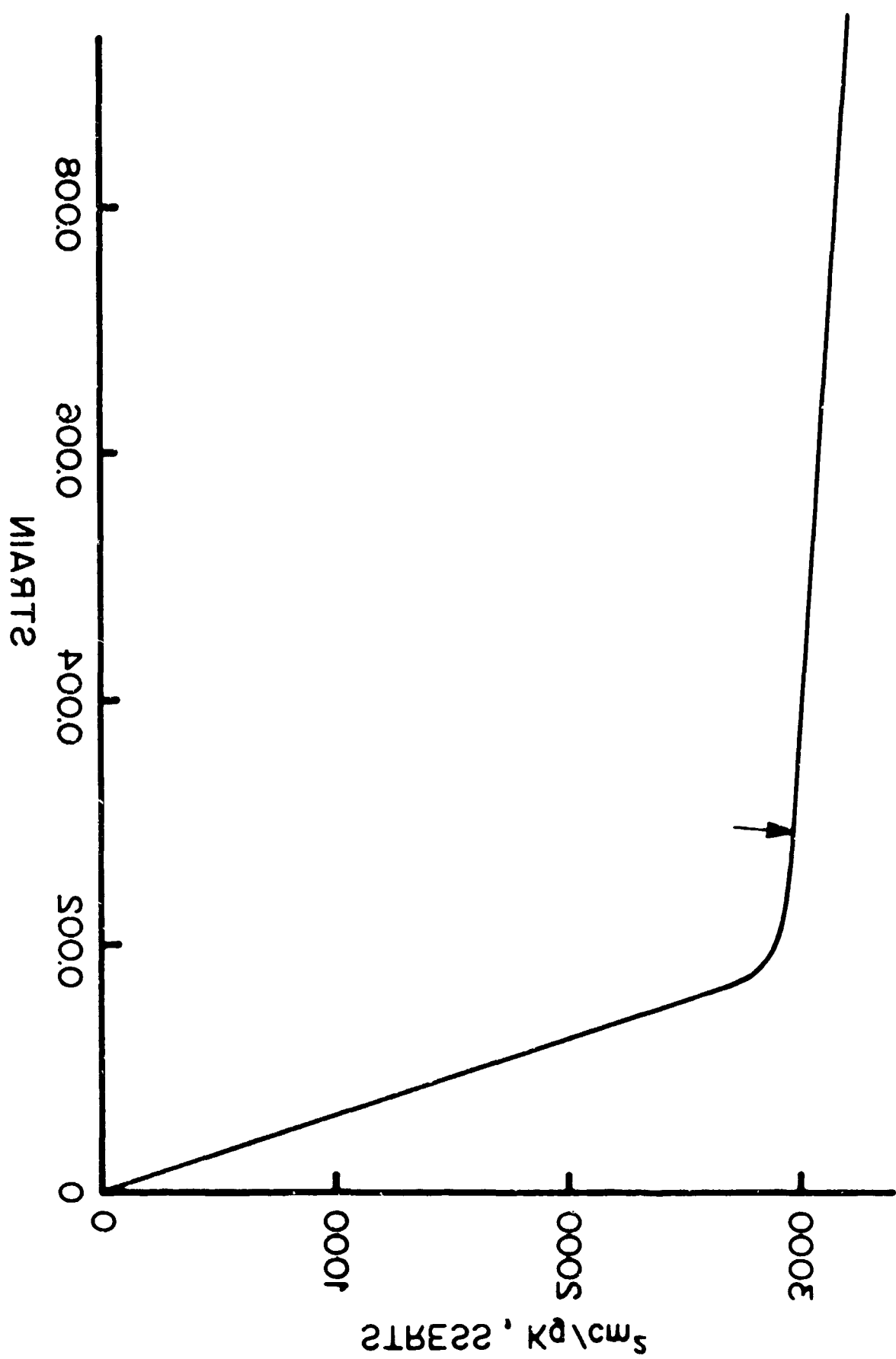


Fig. 2