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REACTIONS AND ELECTROCHEMICAL KINETICS OF
NEWLY-GENERATED METAL SURFACES

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Several types of experiments and theoretical analyses were conducted. An extensive series of experiments was carried out in which notched 0.040 cm diameter titanium wires were fractured in HCl and H₂SO₄ solutions to determine initial anodic passivation behavior. An anodic process caused passivation to begin at a time of 10⁻⁴ to 10⁻³ sec from fracture. A salt-film model of initial passivation was modeled for titanium and the results showed that such a salt film would have to form and redissolve in 10⁻⁵ to 10⁻³ sec. As this time period was smaller than the resolution of the titanium experiments, the model was tested for a slower system, iron in sulfuric acid. Agreement between the model and the iron experiments was reasonably good. Electrical properties of the salt film in a titanium pit in bromide solutions were studied. The film exhibited high-field conduction with an exchange current density, i₀, about 10⁹ greater than for titanium dioxide films. The apparent dielectric constant of the film varied from about 150 near the pitting potential down to about 5 at a potential of 8 V, indicating a change in composition from predominantly oxide to predominantly salt. The MTK model is in process of revision to include titanium dissolution and formation of a salt film at the crack tip, based on the above experiments. Passivation kinetics of new surfaces of aluminum and zirconium were also determined.

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FINAL SCIENTIFIC REPORT

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3935 Leary Way N.W.
Seattle, Washington 98107
3. TITLE: Reactions and Electrochemical Kinetics of Newly-Generated Metal Surfaces
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5. ABSTRACT:

Air Force flight vehicles must withstand increasingly complex environmental and operational regimes. Fundamental knowledge of the mechanisms of fatigue and fracture of flight structures is required. This research is related to the understanding of crack propagation, stress corrosion and corrosion fatigue in titanium and other metals.

An electrochemical mass transport kinetic (MTK) model was previously formulated by the author to quantitatively describe the electrochemical events in a crack. It turned out that the model was not completely accurate because initial reactions on a newly-generated surface of titanium such as at the crack tip were not understood at that time. All electrochemical studies reported in the literature were for aged surfaces of titanium which had an oxide skin. The present work was done to fulfill the requirement of the model for quantitative data on new titanium surfaces and to develop a general understanding of the kinetics of the repassivation process.

Several types of experiments and theoretical analyses were conducted. An extensive series of experiments was carried out in which notched 0.040 cm diameter titanium wires were fractured in HCl and H₂SO₄ solutions to determine initial anodic passivation behavior. An anodic process caused passivation to begin at a time of 10⁻⁴ to 10⁻³ sec from fracture. A salt-film model of initial passivation was modeled for titanium and the results showed that such a salt film would have to form and redissolve in 10⁻⁵ to 10⁻³ sec. As this time period was smaller than the resolution of the titanium experiments, the model was tested for a slower system, iron in sulfuric acid.

Agreement between the model and the iron experiments was reasonably good. Electrical properties of the salt film in a titanium pit in bromide solutions were studied. The film exhibited high-field conduction with an exchange current density, i_0 , about 10^9 greater than for titanium dioxide films. The apparent dielectric constant of the film varied from about 150 near the pitting potential down to about 5 at a potential of 8 V, indicating a change in composition from predominantly oxide to predominantly salt. The MTK model is in process of revision to include titanium dissolution and formation of a salt film at the crack tip, based on the above experiments. Passivation kinetics of new surfaces of aluminum and zirconium were also determined.

6. PROJECT SUMMARY:

Introduction

The plan and progress of the present research program is illustrated with the flow diagram in Fig. 1. The present research is part of a continuous effort on the part of the principal investigator, beginning in 1965, to unravel the mysteries of stress corrosion cracking of titanium. Specifically, the objective has been to develop a better understanding of the electrochemistry at the crack tip, where the decision is made at the atomic and molecular level whether the environment will promote or inhibit crack propagation.

Initial work, conducted at the Boeing Scientific Research Laboratories, determined the effect of electrochemical and other environmental conditions on crack growth rate (References 1, 2, and 3). Early it became evident that one would have to understand events at the crack tip, but no probes are small enough to measure potentials and concentrations at the atomic scale of a propagation crack. An alternate was to mathematically model the events in a crack and check calculated against experimental results. The principal investigator collaborated with Professor E. A. Grens and formulated a mass transport-kinetic (MTK) model for the electrochemistry in a titanium crack (Reference 4).

The model considered the two electrochemical reactions known to occur at that time on newly-generated surfaces of titanium:

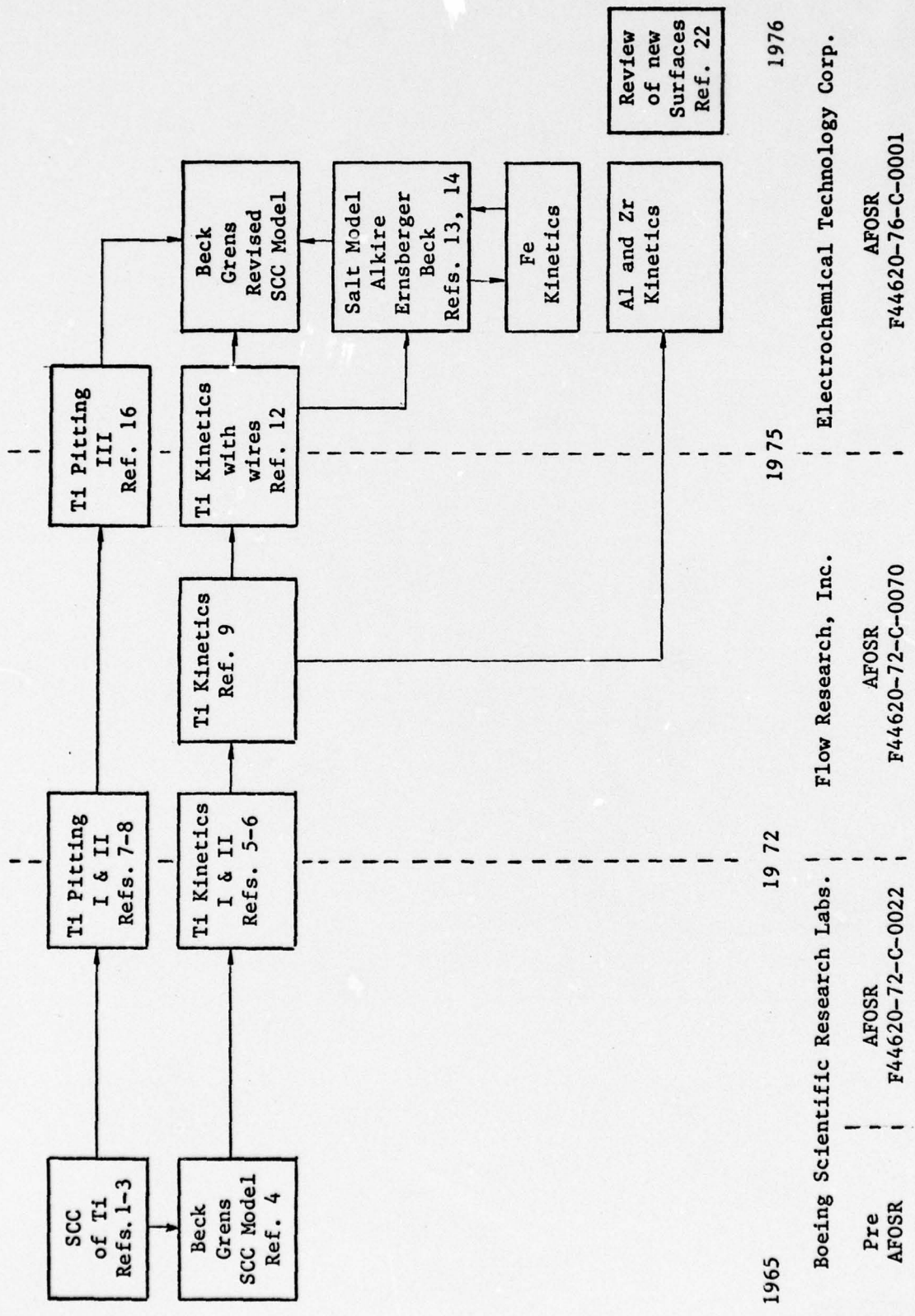


Fig. 1 Flow diagram relating work carried out on AFOSR funding.

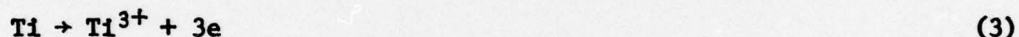


and



These reactions were coupled by mass balance to the ionic transport equations for H^+ , Na^+ and Cl^- ions in the solution in the crack. Although the model was in agreement with some of the stress corrosion data, it was deficient in some respects; in particular, it did not account for the large potential drop known to exist in the crack. Modeling results suggested that dissolution of titanium also occurred on the newly-generated metal surface at the crack tip.

Scraping and rapid-fracture experiments with titanium (References 5, 6) verified that dissolution did occur initially by the reaction:



This work was done in part under AFOSR funding.

At the same time, research on pitting was conducted (References 7, 8) because there are many apparent analogies between the electrochemistry of stress corrosion cracking and pitting. Moreover, the pitting phenomenon is simpler and easier to study in that metal stress is not a factor and it is less sensitive to metallurgical effects. This work (Reference 8) was done in part under AFOSR funding. An important finding was that a salt film, which plays a very important role in pitting behavior, exists at the base of a pit.

At this point the Boeing Scientific Research Laboratories were phased out and the principal investigator transferred activities to Flow Research, Inc. During the period at Flow Research, the main effort was on reactions and kinetics of newly-formed surfaces of titanium, determination of mass transport conditions related to formation of salt films, and determination of the electrical properties of the salt film on the pitting titanium surface.

The initial work at Flow Research was published in Reference 9. Fig. 2 shows the rapid passivation of titanium reported. The region of -0.8 slope between 10^{-1} and 10^2 sec is caused by high-field growth of oxide by reaction 1. The important question unanswered was what was happening at times less than 10^{-1} sec; this is the period important to the tip of a stress

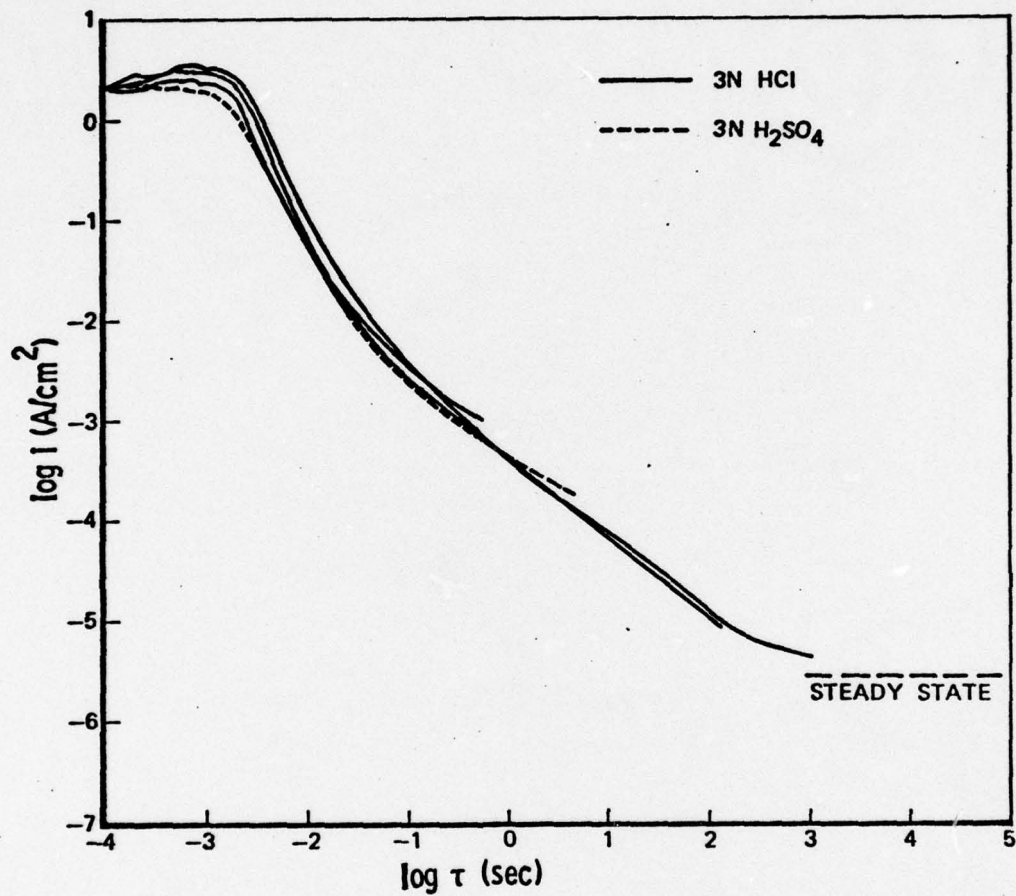


Fig. 2 Anodic current-density transients for newly-generated surfaces of titanium ($\phi = 0 \text{ V}_{\text{SCE}}$).

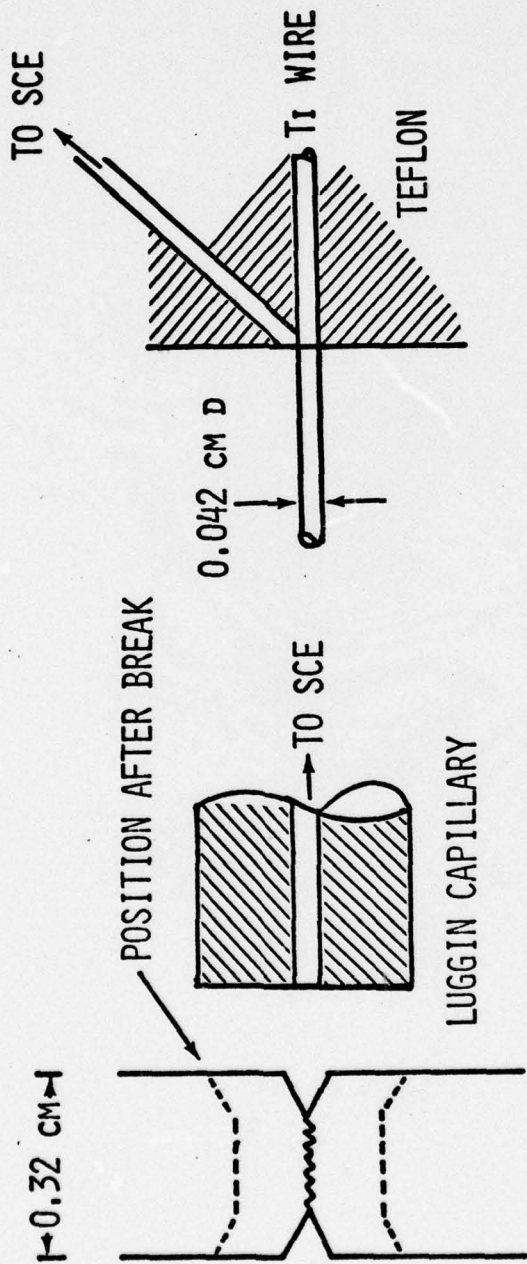


Fig. 3 Geometry of wire electrode compared to notched fracture specimen.

corrosion crack. Ellipsometry work at the Bureau of Standards (Reference 10) indicated that the first monolayer of oxide on titanium was not complete until about 6×10^{-2} sec from cessation of abrasion of a titanium surface. This result suggested that growth of some other resistance had to cause the steep negative slope in Fig. 2 at less than 10^{-2} sec. It was then postulated that precipitation of a salt film by saturating the solution next to the electrode with Ti^{3+} ions by reaction 3 might cause the initial steep decay of current. W. J. Müller (Reference 11) in the 1920's and 1930's, in work now largely neglected, reported on formation of salt films on iron, nickel and other metals.

High Current Density Experiments with Titanium

Experiments were devised to obtain a smaller resistance between the newly-generated metal surface and the tip of the Luggin capillary; this resistance limited the initial current density in Fig. 2. The effect of this resistance was to mask important kinetic information at times of less than 10^{-2} sec. The initial measured anodic current was, of course, the difference between currents for reactions 1 + 3 and reaction 2. A smaller wire electrode, illustrated in Fig. 3, was used to obtain smaller resistance and higher initial current density. The ohmic-limited current density can be approximated by hemispherical conduction to the new surface

$$i = \frac{\kappa \Delta E}{\sqrt{2r}} \quad (4)$$

in which κ is electrolyte conductivity, ΔE is the ohmic drop in the electrolyte, and r is the radius of the disk of new metal surface. It can be seen that, in principle, as high a current density as desired can be achieved, but there are practical limitations in obtaining small radii.

Initial current densities of over 100 A/cm^2 were obtained by fracturing notched titanium wires in the new apparatus. Example current-time curves are compared to the Fig. 2 data in Fig. 4. An important observation was that the current decayed sooner for the higher initial anodic current density. This indicated that the current decay was caused by an anodic process (reaction 1 or 3). Preliminary data were presented at the NACE Corrosion Research Conference in 1974 (Reference 12). It was postulated at the time that formation of a $TiCl_3$ salt film caused the initial passivation.

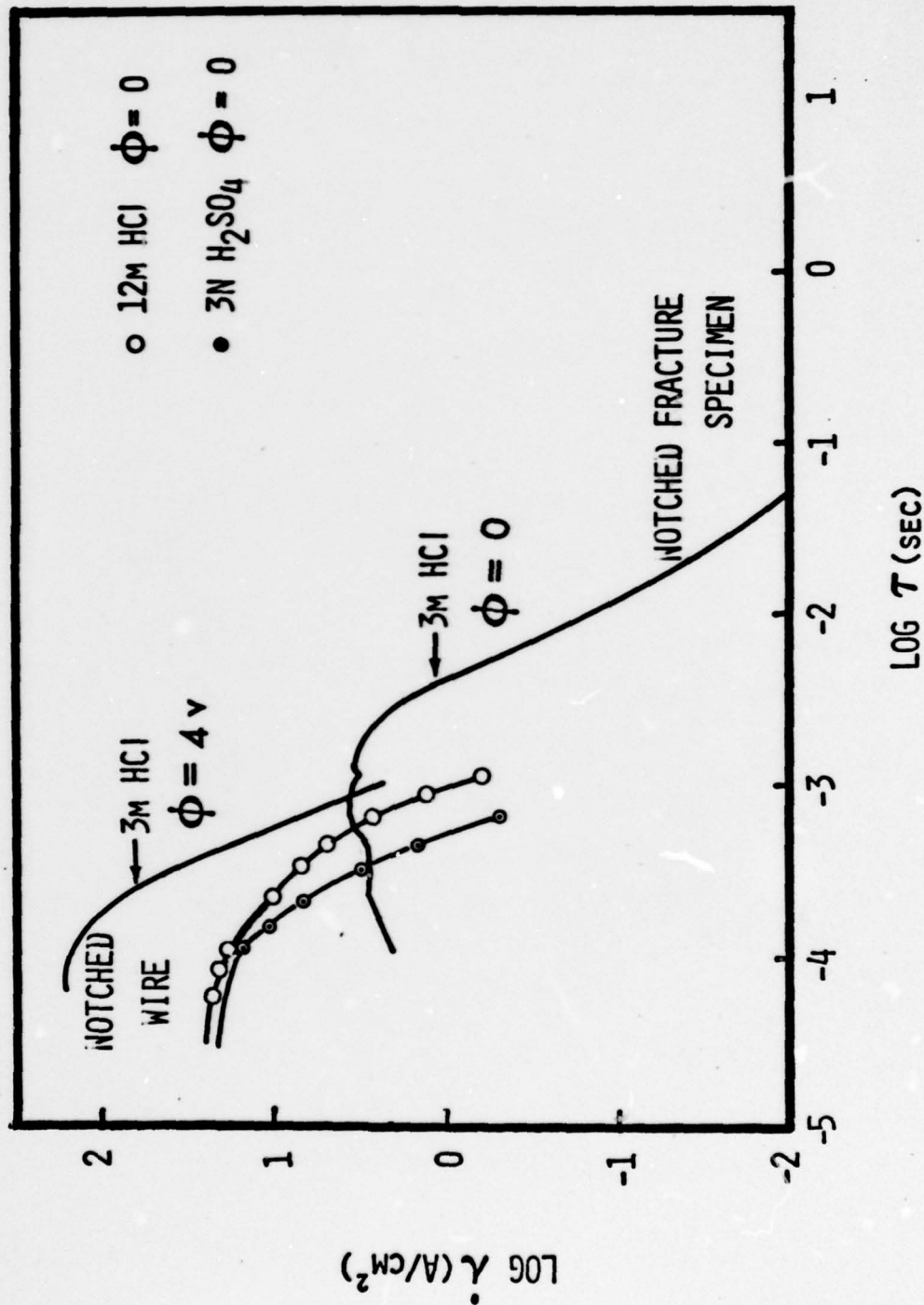


Fig. 4 High anodic-current-density transients for wire compared to data for notched fracture specimen (Fig. 2).

Model of Transient Salt Film

Now the problem was to determine if a salt film was indeed a feasible explanation of the initial passivation. The time scale of $<10^{-3}$ sec, the small amount of dissolution occurring, and the geometry of the system ruled out direct optical observations. Again, the mass-transport modeling approach was used. The principal investigator collaborated with Professor R. C. Alkire, Department of Chemical Engineering, University of Illinois, in developing a mathematical model. The programming and calculations were carried out by Professor Alkire and a student at Illinois. Preliminary results were presented at the Fall 1975 Electrochemical Society Meeting (Reference 13). The significant finding from these calculations was that if a salt film formed it would have a transient life between 10^{-5} and 10^{-3} sec. No feasible method was devised to check the model calculations with titanium experiments, so other metals having slower rates of passivation were sought.

Passivation and Depassivation of Iron

Iron in sulfuric acid was a suitable system to test the salt film model. High-purity, zone-refined iron* in the form of a rod was cast into epoxy resin to form a shielded electrode (Reference 11) or artificial pit. It was placed in sulfuric acid solutions in the anode-facing-up position and the potential was stepped from an active value near the mixed potential to a value in the passive region. Ferrous sulfate salt films were seen to form and disappear as they were succeeded by oxide after the potential step. Professor Alkire modified the mass transport model for iron parameters and found a reasonable agreement between calculated and measured times of appearance and disappearance of the salt film. The new results were presented at the Fall 1976 Electrochemical Society Meeting (Reference 14). It is planned to submit the manuscript to the Journal of the Electrochemical Society in December 1976. The modeling and the experimental results for iron demonstrated the feasibility of the transient salt film passivation process, but it remains to be proved for titanium.

Formation of a transient FeSO_4 film during passivation of iron in sulfuric acid has had only fleeting mention in the literature since the work of Müller (Reference 11). It was decided to explore this phenomenon in detail

*Courtesy of the Iron and Steel Institute

using a storage oscilloscope to freeze transient data. Previously, the principal investigator had reported on the importance of formation of salt films (References 15, 16) on metals but iron in sulfuric acid offered the intriguing, sequential, salt-film, oxide-film steps. It is tentatively planned to present this work at the Fourth International Symposium on Passivity in October 1977, but the salient points will be described here.

When the potential of a shielded iron electrode is increased linearly in sulfuric acid solution the current also increases linearly, as shown in Fig. 5. The current is limited by solution ohmic resistance. At a certain point on the curve the current suddenly drops to a low value coincident with visual appearance of a salt film that spreads over the surface. The higher the potential sweep speed, the higher the point at which the current drops. If the potential is stepped up from the mixed potential, the initial peak current falls on the dashed extension of the linear curve in Fig. 5.

The current decay after a potential step is illustrated in Fig. 6. The pattern of current decay is different below and above the Flade potential. Curve a), below the Flade potential, does not decay to as low a current density as curve b), above the Flade potential. The salt film persists for curve a) whereas it disappears at the point indicated on curve b). The minimum in curve a) corresponds to a visible change in morphology of the salt film. Flushing out the cavity with an eyedropper any place on curve a) reactivates the surface and gives a repeat current profile. Flushing out the pit on curve b) after the salt layer disappears does not reactivate the surface.

The time at which the current starts to decay in Fig. 6 is plotted versus initial current density in Fig. 7. The points fall on approximately a $-1/2$ power line according to Sand's equation, at applied potentials both below and above the Flade potential. The initial reaction is therefore dissolution and salt precipitation in both cases. Oxide passivation does not occur until after the salt film is laid down and decreases the dissolution rate. This is exactly the mechanism proposed for new surfaces of titanium (Reference 17) but which has eluded verification because of the rapidity with which it must occur on titanium.

Kinetics of reactivation of the oxide-passivated surface of iron was also investigated. Just below the Flade potential the current density jumped

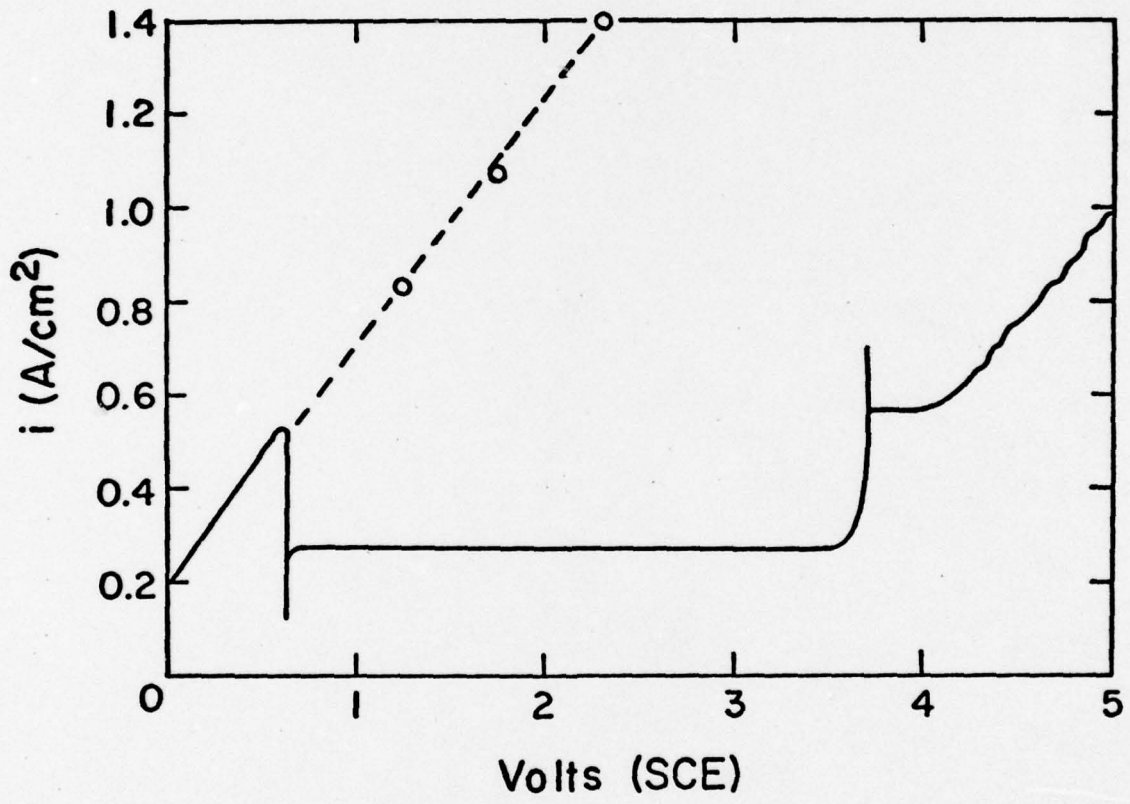


Fig. 5 Polarization curve for iron.

up to the ohmic limit given in Fig. 5 and subsequently decayed according to curve a) in Fig. 6. The depassivation occurred in a few milliseconds and appeared to be kinetically similar to the inverse process of nucleation and growth of oxide patches (Reference 18).

Salt Film Properties in Titanium Pit

Evidence accumulated that a $TiCl_3$ film may play an important role at the tip of a stress corrosion crack. Such a film could continuously form in a saturated $TiCl_3$ solution at a crack tip and redissolve downstream on the crack walls where the solution is less concentrated. Formation and dissolution of a salt film in the fast-fracture kinetics experiments was too rapid to measure the properties, so other experiments were sought.

Pitting of titanium occurs at a quasi-steady state, and electrical transient techniques could be used to probe the properties of the salt film in the pit. It was already known from previous work that the current density in an artificial pit was limited by mass transport but that most of the potential drop occurs across a barrier salt film at the metal surface (Reference 8). By using step potentials and currents and AC signals the properties of the barrier film were probed. Titanium forms 4-valent species when it pits.

Superposition of a sine or triangular wave potential on the steady state value gave a Lissajous figure for current, with frequency-dependent shape, as shown in Figure 8. At low frequency, ≤ 0.1 Hz, the current was constant and equal to the mass-transport limited value. The amount of current to change the barrier film thickness was negligible compared to the steady state current in this case. At high frequency, > 1 kHz, a slanting line, characteristic of a resistive film, was obtained. In this case the cycle is completed before the barrier film appreciably changes in thickness. At intermediate frequencies a loop formed due to change in barrier film thickness and resistance in the cycle.

At high frequencies and wide potential spans the current-potential line became curved like an exponential function. The salt film appeared to conduct by the high-field mechanism. In addition there was a series ohmic resistance in the solution in the pit. The current for this set of series resistances is therefore

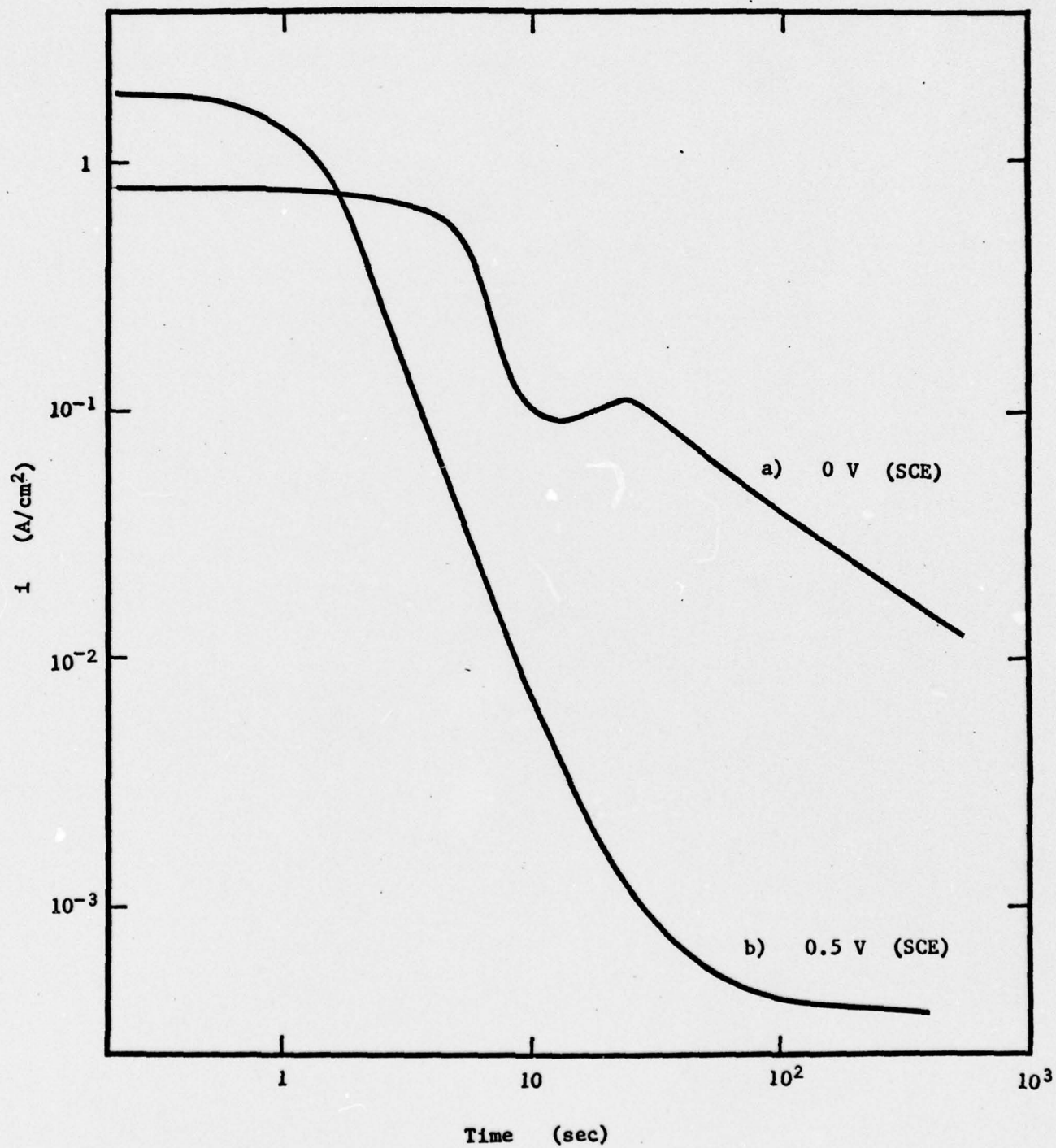


Fig. 6 Current decay curves for iron in 3N H₂SO₄.

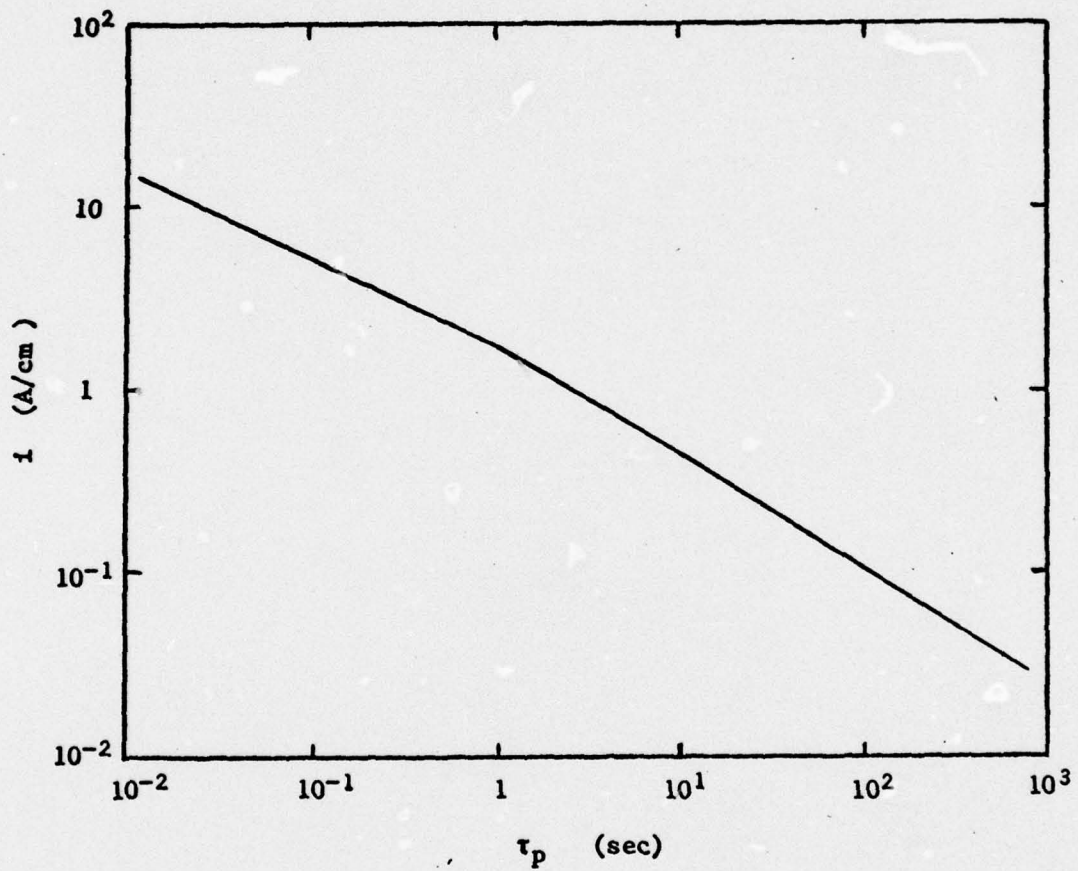


Fig. 7 Salt passivation time as a function of current density for iron in 3N H₂SO₄.

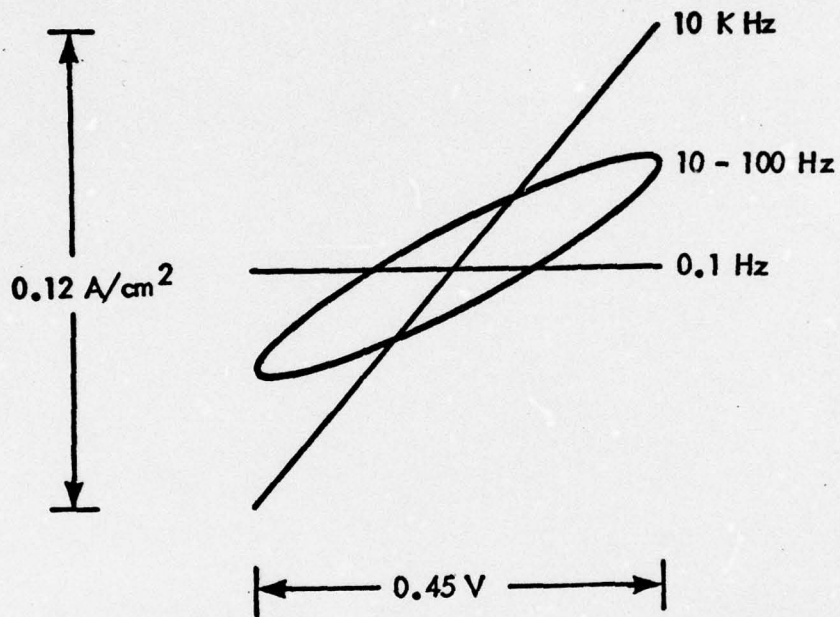


Fig. 8 Lissajous figures for titanium pit.

$$i = i_0 \exp \left[\frac{\beta(\phi - \phi_0 - iR_0)}{t} \right] \quad (5)$$

in which

i_0 = exchange current density for the film, A/cm²

β = high-field constant, cm/V

ϕ = applied potential, V

ϕ_0 = equilibrium potential for film reaction, V

R_0 = ohmic resistance of solution, ohm cm²

t = film thickness, cm

At an applied potential, ϕ_1 , the pitting reaction proceeds at a mass-transport limited current density, i_L , and a film thickness, t_1 . If the potential is stepped to ϕ_2 , the current density immediately changes according to equation (1) for initial thickness, t_1 . The current density then decays back to the initial mass-transport limited value, i_L , as the thickness changes to t_2 . From the peak current densities, the parameters i_0 , t_1/β , and R_0 can be determined as a function of i_L and ϕ_1 .

A typical plot of initial peak current density as a function of ϕ_2 is given in Fig. 9. The magnitude of the exchange current density from these experiments was about 10^{-4} A/cm, a factor of about 10^9 greater than for titanium dioxide. This large difference in exchange current density accounts for an active pitting surface to exist side by side with a passive oxide surface. The value of t_1/β was found to be linear with potential,

$$t_1/\beta = 0.13 (\phi - \phi_0) . \quad (6)$$

It was not possible to evaluate β from these experiments but β was presumed to have a constant value close to that of TiO₂. Therefore, equation (6) indicates that the salt film thickness increases linearly with applied voltage, as do oxide films.

A major effort was expended on trying to determine the actual salt film thickness as a function of potential by integration of current density pulse at a step potential. It turned out, however, that a very complex sequence of events occurs which has not been completely unraveled yet. The idea was that the integral

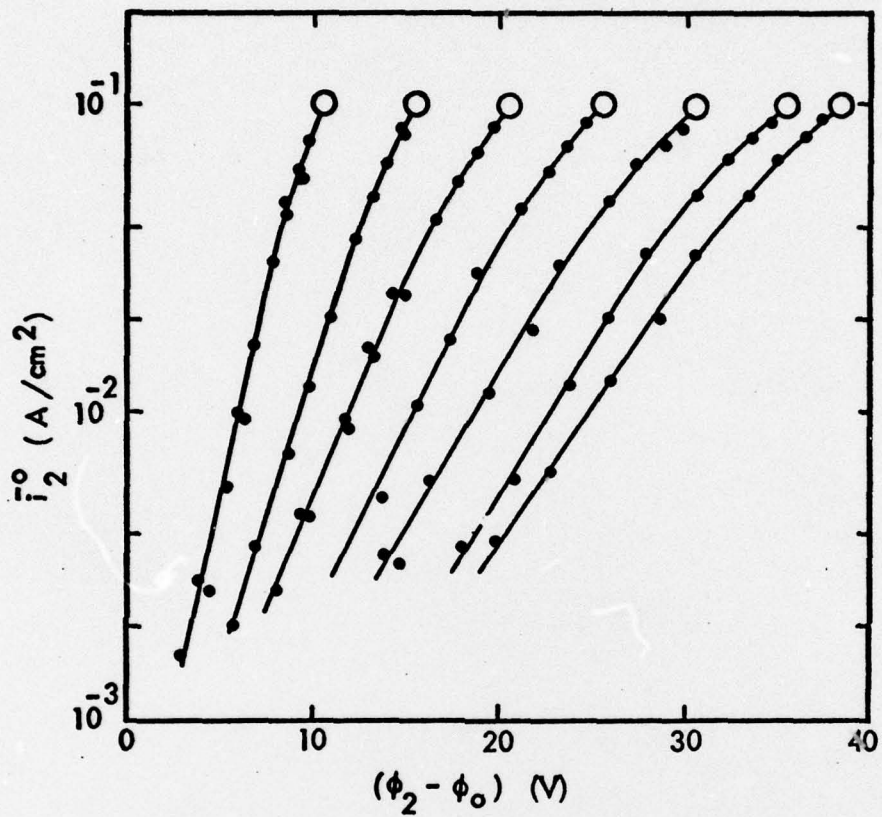


Fig. 9 Initial peak current at a large step potential for titanium pitting in bromide solution at various steady potentials.

$$\Delta Q = \int_0^{\infty} (i - i_L) d\tau \quad (6A)$$

would be the charge required to change the film thickness from t_1 to t_2 . The incremental charge is related to the incremental thickness by

$$\Delta Q = \frac{(t_1 - t_2)zF\rho}{M} \quad (7)$$

in which ρ is the film density and M is its molecular weight. Unfortunately there is evidence that i_L may not be constant during the transient, and the salt film may change in composition, thus changing M .

Another set of experiments that yielded important information about the salt film properties was potential decay on open circuit. As shown in Reference 8, the potential decays linearly with log time. This may be explained by discharge of the capacitance across the salt film through the high-field resistance of the salt film. This model leads to

$$-\frac{d\phi}{d \ln \tau} = (t_1/\beta) \quad (8)$$

from which it was determined that $t_1/\beta = 0.11 (\phi_1 - \phi_0)$. This is close to the relationship found for the step-potential experiments, indicating that model is substantially correct. By employing the equation for capacitance of a parallel-plate capacitor it can be shown that

$$\kappa = \frac{i_1 \tau_1 \beta}{(0.0885 \times 10^{-12})} \quad (9)$$

in which

κ = dielectric constant

i_1 = initial current density, A/cm²

τ_1 = extrapolated intercept time at which potential starts to decay, sec (see Fig. 9, Reference 8)

Assuming β is constant at 6×10^{-6} cm/V for TiO₂ (Reference 19) gives values of dielectric constant shown in Fig. 10.

At low applied potentials near the pitting potential +0.9 V(SCE), the calculated dielectric constant from equation (9) approaches the values for TiO₂. At potentials between 6 and 8 V(SCE) the dielectric constant

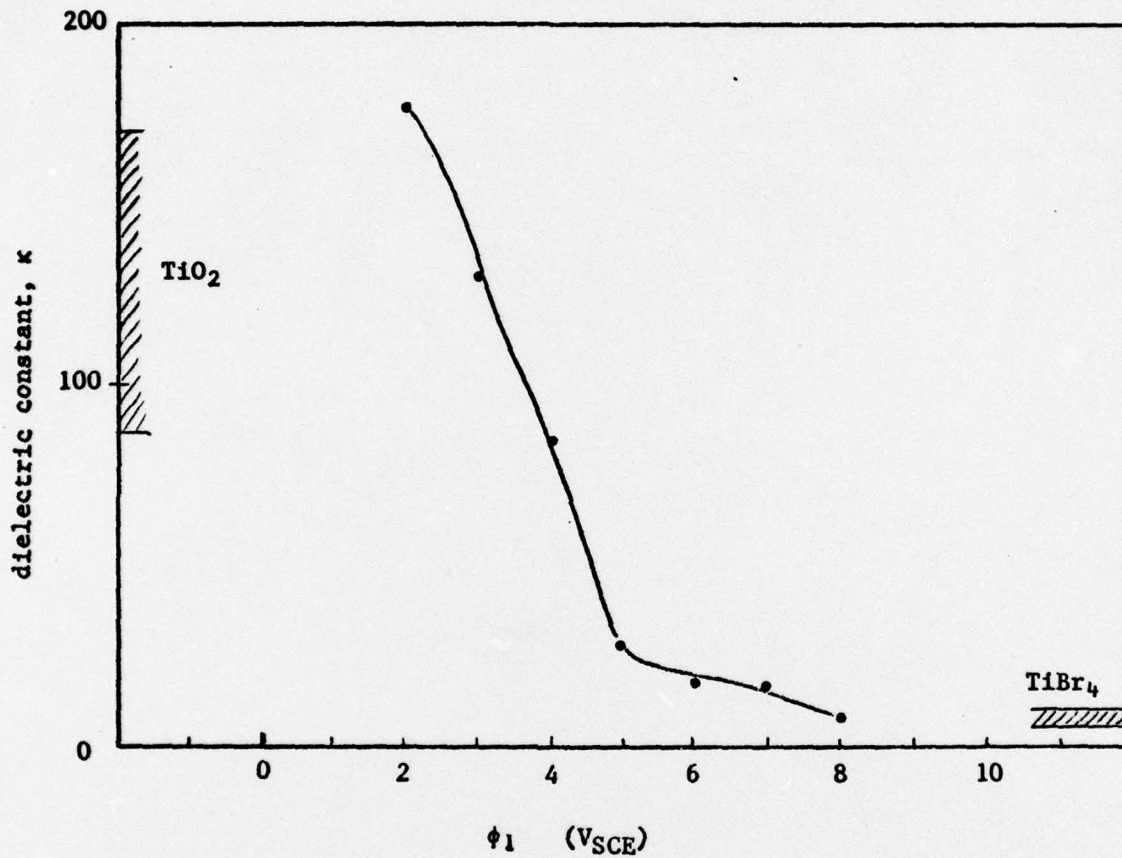


Fig. 10 Dielectric constant of pitting film for titanium in bromide solution.

asymptotically approaches the estimated value for TiBr_4 . No value of κ for TiBr_4 was found in the literature but a range is indicated for similar salts. These data suggest that the salt film is an oxyhalide which changes composition with thickness. This interpretation is in agreement with visual observations of the pit. Above 6V there is a transparent orange film on the metal surface the color of TiBr_4 . Below 6V the film becomes cloudy and white, becoming increasingly white as 2V is approached. White is the color of TiO_2 .

Assuming that the dielectric constant from equation (9) is an additive function of the mole fraction of TiBr_4 and TiO_2 gives

$$x_s = \frac{\kappa_o - \kappa}{\kappa_o - \kappa_s} \quad (10)$$

in which

$$\begin{aligned} x_s &= \text{mole fraction salt (TiBr}_4\text{)} \\ \kappa_o &= \text{dielectric constant of TiO}_2 \sim 150 \\ \kappa_s &= \text{dielectric constant of TiBr}_4 \sim 5 \end{aligned}$$

It can be seen from Fig. 10 that x_s varies from zero to one as the potential is changed from 2 to 8V.

A possible explanation of the change in composition of the film is that water diffuses into the films and reacts at the metal-film interface to form an oxybromide. The thinner the film, the greater the oxide fraction. The flux of water would be

$$i_w = \frac{zFD_w C_w^o}{t} \quad (11)$$

in which D_w is the diffusivity of water in the film and C_w^o is the concentration of water on the solution side of the film. It is assumed that the water reacts completely at the metal-salt interface. The fraction of oxide is then

$$\frac{i_w}{i_L} = \frac{zFD_w C_w^o}{ti_L} \quad (12)$$

The thickness, t , increases with potential by

$$t = 0.13(\phi - \phi_o)\beta \quad (6)$$

so that the fraction oxide increases as the potential is decreased.

Equations (6) and (12) may be combined to give

$$\frac{i_w}{i_L} = \frac{zFD_w C_w^O}{0.13(\phi - \phi_o)\beta i_L} \quad (13)$$

It may be assumed that the pitting potential occurs at a particular ratio of i_w/i_L at which the surface is essentially oxide covered. Assuming that value of $i_w/i_L = 1$ gives

$$\phi_p = \phi_o + \frac{zFD_w C_w^O}{0.13\beta i_L} \quad (14)$$

The value of ϕ_p is about 1.5 volts positive to ϕ_o , $z = 4$, $C_w^O \approx 55 \times 10^{-3}$ mole/cm³, $\beta \approx 6 \times 10^{-6}$ cm/V, and the pitting current density is of order 10^{-1} A/cm², giving $D_w \approx 5 \times 10^{-12}$ cm²/sec. This is the right order of magnitude for diffusivity of water in salts. We thus have a new mass-transport model for the pitting potential.

Passivation of Aluminum and Zirconium

One of the objectives of this program was to determine the passivation behavior for new surfaces of a number of metals and relate to known physical properties. Two other metals that have similar behavior to titanium are aluminum and zirconium. It was hoped to study tantalum but specimens of it were too ductile to get a clean fracture as obtained for titanium and zirconium. Pure aluminum was also too ductile, but material produced from sintered aluminum powder (SAP) was sufficiently brittle to give a clean fracture.

Current-time data for aluminum, titanium and zirconium are given in Fig. 11. Titanium and zirconium were nearly identical in behavior; aluminum was more active.

The growth of an oxide film by high-field conduction can be described by

$$\frac{dt}{d\tau} = A(1 - i_c) \quad (15)$$

in which

$$A = \frac{M_o}{zF\rho_o} \quad (16)$$

and

$$i = i_o \exp \left[\frac{\beta \Delta \phi}{t} \right] \quad (17)$$

If it is assumed that the corrosion current density can be neglected (i.e., $i \gg i_c$) equations (15) and (17) reduce to

$$dT = \left(\frac{A i_o}{\beta \Delta \phi} \right) d\tau = - \frac{dI}{I^2 (\ln I)^2} \quad (18)$$

in which $I = i/i_o$. Equation (18) has a solution shown in Fig. 12, computed from tabled Exponential Integral E_2 (Reference 20).

The nondimensional solution in Fig. 12 can be put into dimensional form for various metals if the properties of their oxides are known, M_o , z , ρ_o , i_o and β . Values of the parameters for aluminum, titanium and zirconium are given in Table 1. Values of i_o and β were from Johansen et al. (Reference 19), and M_o and ρ_o are handbook values. Values of $\Delta \phi$ were based on an applied potential of zero volts (SCE) and equilibrium oxide potentials (Reference 21) for titanium and zirconium at pH zero and aluminum at pH 7. The dashed lines for the model equation are seen to agree quite well with the experimental data for all three metals in the region of the -0.8 slope in Fig. 11.

The departure of the experimental data from the model equation at the long-time end of the curves is due to approach to the steady-state corrosion current density, i_c . The deviation of the experimental data at the short-time end may be due to several causes. The data for aluminum and titanium can each be fit to the model for another decade smaller in time if it is assumed that high-field conduction starts at a time of 3×10^{-2} sec from fracture rather than at fracture. That is not an unreasonable assumption because it takes time to form the first monolayer or more of oxide before the high-field condition is applicable. A part of the initial current is also for dissolution of the active new surface. The initial external current density is limited by ohmic drop between the new metal surface and the Luggin capillary. The actual initial anodic current density is, of course,

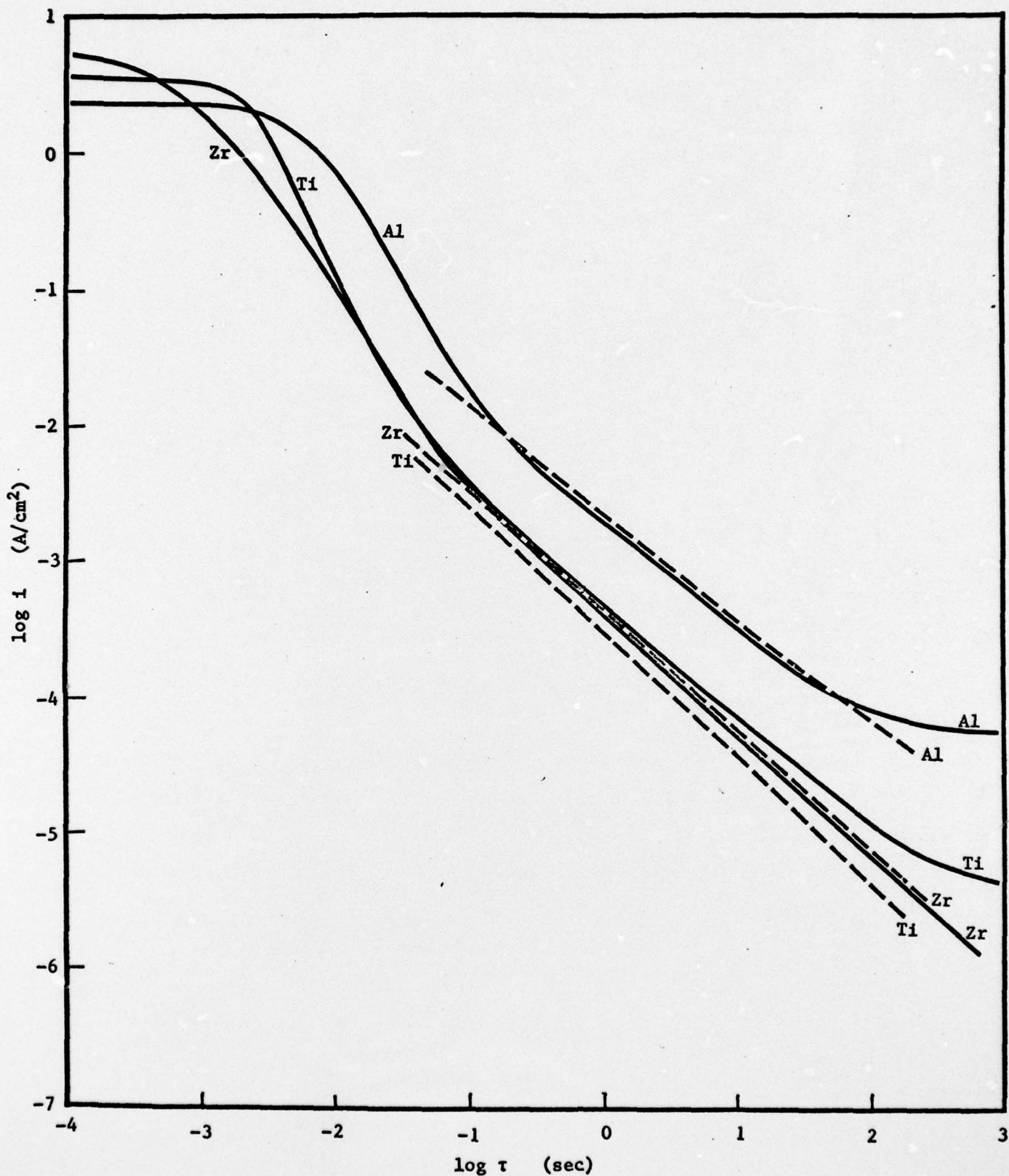


Fig. 11 Anodic current density transients for newly-generated surfaces of aluminum, titanium, and zirconium compared to theory (Al in N Na₂SO₄, Ti and Zr in 3N HCl).

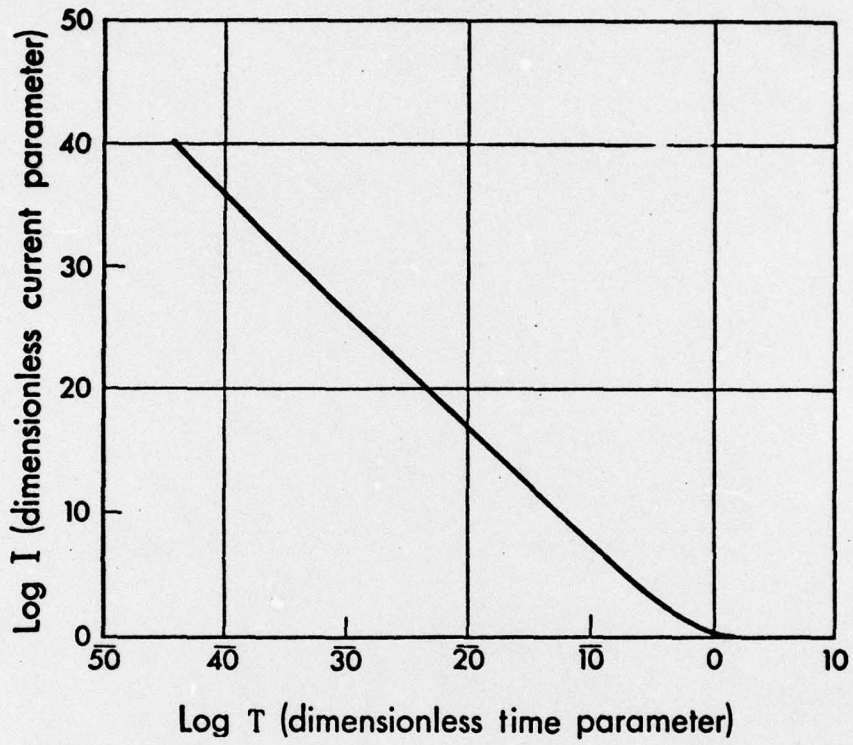


Fig. 12 Plot of dimensionless current and time parameters for formation of anodic oxide film by high-field mechanism.

larger than the measured value because hydrogen ion reduction also occurs at a high rate.

	Aluminum Al ₂ O ₃	Titanium TiO ₂	Zirconium ZrO ₂
z	6	4	4
M _o , gm/mole	101.94	79.9	123.22
ρ _o , gm/cm ³	3.9	4.26	5.6
A × 10 ⁵ , cm ³ /C	4.51	4.86	5.7
i _o , A/cm ²	2 × 10 ⁻⁶	2 × 10 ⁻¹³	2.9 × 10 ⁻¹¹
β × 10 ⁶ , cm/V	2.9	6	4.6
Δφ, V	2.14	1.2	1.7
$\left(\frac{\beta \Delta \phi}{A i_o}\right)$, sec	6.9 × 10 ⁴	7.4 × 10 ¹¹	4.6 × 10 ⁹

Table 1. Parameter values for metal oxides

Electrochemical Mass-Transport-Kinetic Model for Stress Corrosion Cracking of Titanium

The principal investigator is collaborating with Professor E. A. Grens to refine the previously published model (Reference 4). The main changes are inclusion of corrosion of titanium to form Ti³⁺ ions, transport of Ti³⁺, allowance for formation of a TiCl₃ salt film at the crack tip and a finite radius tip region. Ideas and data developed in the kinetics work with titanium, pitting of titanium and modeling of salt film formation and dissolution are incorporated. Inclusion of these changes has complicated the model and required considerable debugging. Coordination has been by telephone and two trips to Berkeley. This work will be completed after the end of the contract but AFOSR support will be acknowledged.

Review of Methods to Produce New Metal Surfaces

By invitation, a review paper was prepared on methods of producing new metal surfaces and studying their electrochemistry. The paper was presented at the 1976 NACE Meeting in Houston (Reference 22) and will appear in a symposium volume

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14. R. C. Alkire, D. W. Ernsberger and T. R. Beck, "The Occurance of Salt Films During Initial Stages of Corrosion," Extended Abstract No. 93, Fall Meeting, The Electrochemical Society, Las Vegas, Nevada, October 17-22, 1976.
15. T. R. Beck, "Formation and Properties of Salt Films During Corrosion of Metals," Extended Abstract No. 99, Fall Meeting, The Electrochemical Society, Boston, Massachusetts, October 7-11, 1973.
16. T. R. Beck, "Salt Films and Their Influence on the Corrosion of Metals," NACE Corrosion Research Conference, Toronto, Canada, April 1975.
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22. T. R. Beck, "Techniques for Studying Initial Film Formation on Newly-Generated Surfaces of Passive Metals," Symposium on Electrochemical Techniques for Corrosion, NACE, Houston, Texas, March 1976; to be published in a symposium volume.
7. PAPERS PRESENTED, SYMPOSIA, HONORS, ETC.: July 1975 - September 1976
Served as President of The Electrochemical Society, May 17, 1975 - May 8, 1976.

ECS Presidential visits to four Local Sections - presented technical talk and Society news.

Continued as consultant to lithium-sulfur battery development in Chemical Engineering Division, Argonne National Laboratories.

Continued as member of Board of Directors of Seattle Youth Symphony Orchestra and of the North Cascades Conservation Council.

Participated in AFOSR-AFML Workshop on Corrosion Prevention, Dayton, Ohio, September 17-18, 1975.

Presented paper, "The Occurance of Salt Films During Initial Stages of Titanium Corrosion," T. R. Beck, D. Ernsberger and R. C. Alkire, Electrochemical Society, Dallas, Texas, October 7, 1975.

Presented seminar, "Energy Use and Efficiency of Industrial Electrochemical Processes," Brookhaven National Laboratory, January 13, 1976.

Appointed consultant to National Science Foundation, February 1976 - reviewed electrochemistry proposals.

Presented paper, "Techniques for Studying Initial Film Formation on Newly Generated Surfaces of Passive Metals," NACE, Houston, Texas, March 23, 1976.

Presented paper, "Effect of Hydrodynamics on Pitting," NACE, Houston, Texas, March 23, 1976.

Represented The Electrochemical Society in the Ceremonial Session of the Centennial Celebration of The American Chemical Society, New York, April 5, 1976.

Received scroll for serving as a Divisional Editor of the Journal of The Electrochemical Society, May 4, 1976.

Continued as Research Professor, Department of Chemical Engineering, University of Washington, graduated first PhD student, July 1976.

Presented paper, "Energy Use and Energy Efficiency in Industrial Electrolytic Processes," Workshop on Energy Conservation, Argonne National Laboratory, August 10-12, 1976.

Received invitation to present a paper at the Fourth International Symposium on Passivity to be held at Airlie, Virginia, October 17-21, 1977.

8. PUBLICATIONS: (Submitted or published, July 1975 - September 1976 and in preparation)

Submitted or Published

- 1) K. F. Lin and T. R. Beck, "Surface Stress Curves for Gold," J. Electrochem. Soc., 123, 1145 (1976).
- 2) T. R. Beck, "Energy Use and Efficiency in Industrial Electrochemical Processes," in Proceedings of Workshop on Energy Conservation in Industrial Electrochemical Processes, Argonne National Laboratory, August 10-12, 1976.
- 3) T. R. Beck, "Effect of Hydrodynamics on Pitting," Corrosion Journal, NACE, to appear December 1976 or January 1977.
- 4) T. R. Beck, "A Review of Techniques for Studying Initial Film Formation on Newly Generated Surfaces of Passive Metals," to appear in symposium volume on Electrochemical Techniques for Corrosion, R. Baboian, Ed., NACE, Houston, Texas (about December 1976).
- 5) K. F. Lin and T. R. Beck, "Surface Stress Curves for Platinum," submitted to Journal of The Electrochemical Society.

In Preparation

- 6) R. C. Alkire, D. Ernsberger and T. R. Beck, "The Occurance of Salt Films During Initial Stages of Corrosion," to be submitted to The Journal of The Electrochemical Society, about December 1976.
- 7) T. R. Beck, "Pitting of Titanium, III. Electrical Properties of the Barrier Film," to be submitted to the Journal of The Electrochemical Society, about January 1977.
- 8) T. R. Beck, "Initial Passivation of New Titanium Surfaces," to be submitted to Corrosion Journal, about January 1977.
- 9) T. R. Beck and E. A. Grens, "An Electrochemical Mass Transport-Kinetic Model for Stress Corrosion Cracking of Titanium, II.," to be submitted to the Journal of The Electrochemical Society, about March 1977.
- 10) T. R. Beck, "Formation of a Salt Film During Passivation and Depassivation of Iron in H_2SO_4 ," (tentative title of paper for Fourth Symposium on Passivity, Airlie, Virginia, October 17-21, 1977).