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REACTIONS AND ELECTROCHEMICAL KINETICS OF NEWLY-
GENERATED METAL SURFACES

Theodore R. Beck

Flow Research, Incorporated

Prepared for:

Air Force Office of Scientific Research

July 1975

REACTIONS AND ELECTROCHEMICAL KINETICS

OF NEWLY-GENERATED METAL SURFACES

FINAL SCIENTIFIC REPORT

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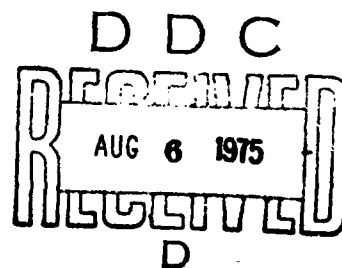
Theodore R. Beck

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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.

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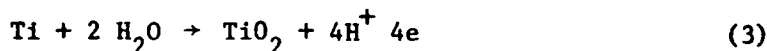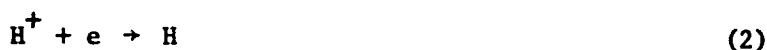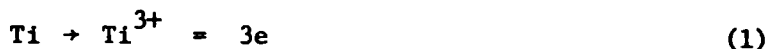DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE

20.

It turned out that the model was not completely accurate because initial re-
actions 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 under-
standing of the kinetics of the repassivation process.

Preliminary work had already shown that corrosion of the new metal surface is
important as well as the hydrogen ion reduction and formation of oxide that
were considered in the MTK model. All three reactions must be considered:

$$Ti \rightarrow Ti^{3+} = 3e \qquad (1)$$

$$H^+ + e \rightarrow H \qquad (2)$$

$$Ti + 2 H_2O \rightarrow TiO_2 + 4H^+ 4e \qquad (3)$$

The first phase of experimentation was to generate current-time curves for new
surfaces using 0.16 x 0.32 cm notched specimens and following the course of
current versus time from generation (approx. 10^{-4} sec. from fracture) to steady
state (approx. 10^4 sec.). The current density in this period decayed by a
factor of 10^6 so that special instrumentation had to be built.

It became evident that reactions 1 and 2 dominated initially, giving a mixed
potential at the surface. The measured initial anodic current of about $3A/cm^2$
was limited by iR drop in the electrolyte between the Luggin capillary and the
new surface, and was obviously smaller than the true anodic current density.
Because the initial reaction was considered to be important at the crack trip,
it was necessary to design an experiment with lower ohmic resistance between
the Luggin capillary and the specimen.

Notched 0.040 cm diameter wires were mounted in a Teflon holder with a Luggin
capillary tip that approached within one wire diameter of the notch. This
permitted initial current densities of over 10^2 A/cm^2. Now some interesting
new effects were observed. Passivation time was shorter at the higher initial
current density, showing that it was due to an anodic process. Higher HCl
concentration also caused a shorter passivation time, indicating a mass action
effect on precipitation of a salt layer.

A review of the literature showed that after the classic researches of W. J.
Müller in the 1920's and 30's on salt films in corrosion, the subject had been
largely neglected. Experiments were therefore conducted with copper and silver
at conditions at which salt films form but not oxides. Data were observed to
fit the Sand equation for unsteady-state mass transport using degrees of
supersaturation for the precipitating salt. Salt-film passivation times as
short as milliseconds were observed for high dissolution current densities,
directly analogous to experimental data for newly-generated titanium surfaces.

Studies were also made with pitting of titanium because in this case measure-
ments can be made of the properties of the salt film at steady state. Con-
ductivity and thickness were measured. An important observation made during
pitting is that the metal-to-salt-film interface appears to be close to the
equilibrium potential, even at high current density. It is proposed that a
similar situation occurs at a crack tip and that the increased free energy

20. Continued

there as a result of the stress intensity causes increased local activity and thus
the crack to propagate.

A more fundamental model for salt film formation on newly-generated titanium surfaces
is being formulated based on Fick's second law. When the salt film formation and
dissolution are completely worked out it is planned to revise the MTK model. Perhaps
then the electrochemistry of crack propagation in titanium will be understood.

FINAL SCIENTIFIC REPORT
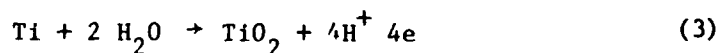
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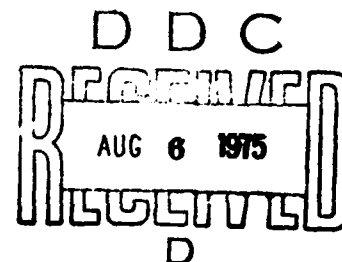
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3. TITLE: Reactions and Electrochemical Kinetics of Freshly Generated
    Metal Surfaces.

4. PERIOD COVERED: December 1, 1972 through June 30, 1975

5. ABSTRACT:

Air Force flight vehicles must withstand increasingly complex environ-
mental 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
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because initial reactions on a newly-generated surface of titanium such as
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studies reported in the literature were for aged surfaces of titanium which
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the model for quantitative data on new titanium surfaces and to develop a
general understanding of the kinetics of the repassivation process.

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surface is important as well as the hydrogen ion reduction and formation
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be considered:

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Studies were also made with pitting of titanium because in this case measurements can be made of the properties of the salt film at steady state. Conductivity and thickness were measured. An important observation made during pitting is that the metal-to-salt-film interface appears to be close to the equilibrium potential, even at high current density. It is proposed that a similar situation occurs at a crack tip and that the increase free energy there as a result of the stress intensity causes increased local activity and thus the crack to propagate.

A more fundamental model for salt film formation on newly-generated titanium surfaces is being formulated based on Fick's second law. When the salt film formation and dissolution are completely worked out, it is planned to revise the MTK model. Perhaps then the electrochemistry of crack propagation in titanium will be understood.

6. PROJECT SUMMARY:

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.

Titanium is a metal high on the electromotive series, and it should be very active. It is well known though that titanium is one of the more corrosion resistant metals owing to a spontaneously-formed protective oxide skin. But it has an Achilles heel. Titanium structures have failed catastrophically by stress corrosion cracking, crevice corrosion and pitting corrosion. What are the conditions under which the protective skin breaks down, or scratches heal, and how fast, and what are the mechanisms? These are the questions to which this program was addressed.

Specifically the objective was to develop a better understanding of the electrochemistry at a crack tip. The crack tip is the scene of the action where the decision is made on a molecular level whether the environment will cause a crack to propagate or stop. New metal surfaces are generated at the crack tip. Electrochemical properties of these surfaces are very different from aged surfaces that have been in contact with air and moisture and have a protective oxide film. Although the electrochemistry of steady-state, oxide-covered titanium has been extensively studied there was no information on the kinetics of reactions on newly generated surfaces of titanium at the time the present research was begun.

The technique used to generate a new surface was to snap a small double-notched specimen in two by suddenly applying a large load. The specimens were fractured in electrolyte solutions at various constant applied potentials and the current-time transients measured. By conducting fast-fracture experiments under a variety of conditions and conducting supporting experiments the mechanisms have been worked out (Papers No. 2, 3, 5 and 8 in the Bibliography).

The main reactions on a new titanium surface are:

$$Ti \rightarrow Ti^{3+} + 3e \tag{1}$$

$$H^{+} + e \rightarrow H \tag{2}$$

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^{+} + 4e \quad . \tag{3}$$
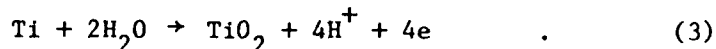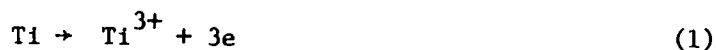
The proposed sequence of events, from the moment of formation of new surface and contact with the electrolyte, to steady-state passivity, is indicated in Fig. 1. It can be summarized as follows:

- Initial simultaneous anodic and cathodic current densities are large, driving the surface to a mixed potential little influenced by the applied potential. Cathodically generated hydrogen diffuses into the metal and solution. Anodically formed Ti^{3+} goes into solution.

- The titanium salt with the solution anion builds up to a critical supersaturation adjacent to the surface and precipitation is initiated. The flux of titanium salt back to the surface is determined by the Sand equation for unsteady-state diffusion. Growth of the resistive salt layer causes a type of passivation as described by W. J. Müller, in the 1920's and 30's, for more common metals.

- Water diffuses through the salt layer and nucleation of oxide patches begins on the metal surface as the corrosion rate is retarded by the salt layer. Two-dimensional nucleation and growth of the oxide patches occurs as described by Fleischmann and Thirsk kinetics. The growth rate at the edge of the patches is limited by diffusion of water through the salt layer.

- As the first layer of oxide is completed, the rate of formation of Ti^{3+} ion decreases further and the salt film dissolves. The oxide film thickens by high-field conduction. A steady state oxide film thickness is ultimately achieved at about 10^4 seconds from fracture.

Time (Sec) →

$O(10^{-3})$	$O(10^{-1})$	$O(\ \cdot\ )$
The reactions, 1. Ti → Ti^{3+} + 3e and 2. H^{+} + e → H occur at a high rate giving a mixed potential.	salt film dissolves	steady state oxide thickness achieved
salt precipitates slowing reactions 1. and 2. Water diffuses through the salt film giving 3. Ti + 2H$_2$O → TiO$_2$+4H^{+}+4e. oxide patches grow and merge	Oxide film grows by high-field conduction	

Ti^{2+} TiCl$_3$ H$_2$O
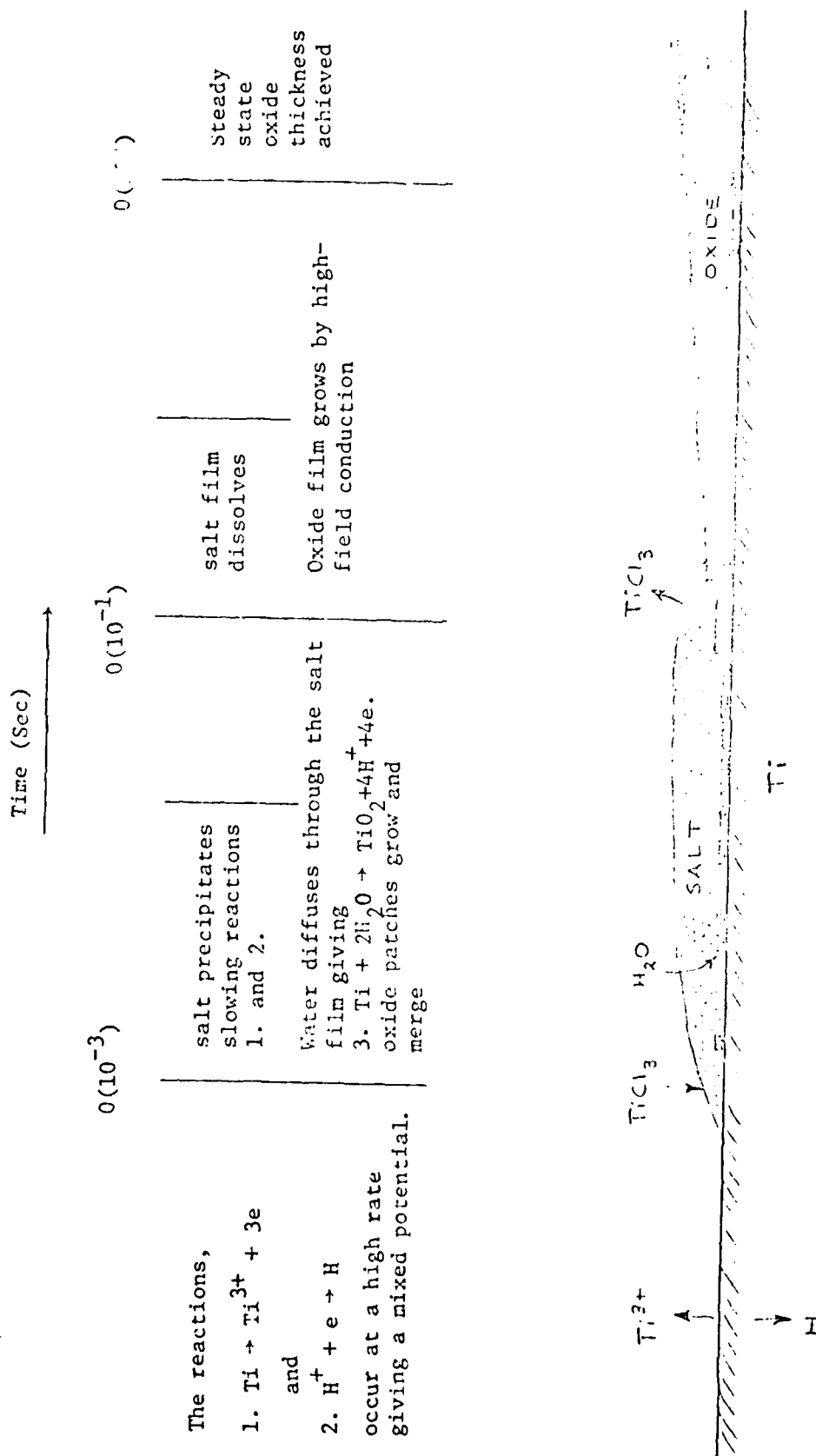
SALT

TiCl$_3$

OXIDE

Ti

I

Fig. 1. Time sequence of events after exposure of new titanium surface to HCl electrolyte.

This sequence of events is so fast and the mixed-potential current densities so high that it is difficult to get direct experimental verification of the transient salt film on titanium. Three approaches were used to test the validity of the concept of a transient salt film:

1. Transient rapid-dissolution experiments were conducted with copper and silver at conditions in which salts can form but not oxides (Papers No. 4 and 7). Experiments reported by W. J. Müller were repeated with higher current densities and shorter times to salt-film passivation. Data were observed to fit the Sand equation for unsteady-state mass transport with a degree of supersaturation of the precipitating salt. Salt-film passivation times as short as milliseconds were observed for high dissolution current densities, directly analogous to experimental data for newly-generated titanium surfaces.

2. Experiments were conducted using artificial pits in titanium in which an oxide-salt film exists at steady state, at the base of the pit (Papers No. 1 and 6). Application of step potentials and measurement of current transients gave information on conductivity and thickness of the film.

3. Mathematical modelling of the transient mass transport conditions for rapidly dissolving titanium is being conducted as a joint effort with Prof. R. C. Alkire of the University of Illinois (Paper No. 8).

Bibliography

(Papers Presented and Published as a Result of this Contract Work)

* 1. "One-Dimensional Pits in Titanium," presented at Electrochemical Society, Miami Beach, Florida, October, 1972; published in J. Electrochem. Soc. <u>120</u>, 1310 (1973).

* 2. "Electrochemistry of Freshly-Generated Titanium Surfaces, II," Electrochimica Acta, <u>18</u>, 815 (1973).

* 3. "Electrochemical Reactions on Newly-Generated Titanium Surfaces," Presented at NACE, Anaheim, Calif., March, 1973; published in Corrosion, <u>30</u>, 408 (1974).

4. "Formation and Properties of Salt Films during Corrosion of Metals," presented at Electrochemical Society, Boston, Mass., October, 1973. (Extended Abstract in Appendix A).

5. "High-Current-Density Anodic Transients for Newly-Generated Titanium Surfaces," presented at NACE, Chicago, Ill., March, 1974 (Extended Abstract in Appendix B, to be submitted to Corrosion.)

6. "Electrical Transient Studies with One-Dimensional Pits in Titanium," presented at Gordon Conference on Corrosion, Colby College, NH, July, 1974 (work in progress, to be submitted to J. Electrochem. Soc.).

7. "Salt Films and Their Influence on the Corrosion of Metals," presented at NACE, Toronto, Canada, April, 1975. (Extended Abstract in Appendix C, to be submitted to Corrosion.)

8. "The Occurance of Salt Films During Initial Stages of Titanium Corrosion," T. R. Beck, D. Ernsberger and R. Alkire, to be presented at Electrochemical Society, Dallas, Texas, October, 1975. (Extended Abstract in Appendix D, to be submitted to J. Electrochem. Soc.)

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Abstract No. 99

FORMATION AND PROPERTIES OF SALT FILMS
DURING CORROSION OF METALS

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When metals anodically dissolve at a high rate or in restricted geometry the electrolyte adjacent to the surface may become saturated and metal salt films form. Practical conditions in which salt films can form are electrochemical machining, pitting and crevice corrosion, and stress corrosion cracking.

Applying a constant current to an initially film-free plane metal surface should give precipitation of a salt film when

$$i\tau^{1/2} = \tfrac{1}{2}zF(C_s-C_b)(D \cdot \tau)^{1/2} , \qquad (1)$$

where τ = time from application of constant current density, i, C_s is the saturation concentration, C_b is the bulk concentration, and D is the diffusivity of the metal salt. The equation assumes that the electrolyte is stagnant, there is an excess of supporting electrolyte, and there is no supersaturation, complexing, or common-ion effect. At the steady state,

$$i_L = \frac{zFD(C_s-C_b)}{\delta} , \qquad (2)$$

where δ is the effective diffusion-layer thickness.

At steady state the salt film will reach a thickness determined by its conductivity, the potential applied and the mass-transport limiting current density. A step potential change, up or down, will therefore give a current transient associated with thickening or thinning of the film. Conductivity and thickness of the film can be calculated from such experiments.

Experiments were conducted with a number of metals including silver, copper, titanium and aluminum in nitric, sulfuric and hydrogen-halide acids. Starting with a film-free silver or copper surface a supersaturation by about a factor of ten appeared to occur before salt layer formation. Salt film conductivities determined from transient experiments at the limiting current density were several orders of magnitude greater than available published values for bulk or single-crystal salts. The data indicated high-field conduction at high current densities through the films. Calculated film thicknesses were on the order of tens of Angstroms as for barrier oxide layers.

Salt-layer conductivity can be related to the pre-exponential and exponential constants in the high-field conduction equation by taking the low field limit of the hyperbolic-sine torm as in electrode kinetics. Thus the conductivity,

$$\kappa = 2 \, i_o \beta \, , \qquad (3)$$

where i_o is the exchange current density and β is the exponential constant in the high-field conduction equation. Calculated conductivities from the transient experiments for several salts were on the order of 10^{-8} ohm^{-1} cm^{-1}, and values of ε would be expected to be similar to those for oxides or about 5×10^{-6} cm/v for an ion-hopping mechanism. Thus, values of i_o are on the order of 10^{-3} A/cm^2 and both high-field and low-field conduction should be observable experimentally.

ACKNOWLEDGMENT

Extended Abstract

High Current-Density Anodic Transients for Newly-
Generated Titanium Surfaces

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In previous work, initial current density to titanium surfaces newly
generated by fast fracture under potentiostatic conditions was found to be
limited by electrolyte ohmic drop. Little difference was observed in
current density transients between hydrochloric and sulfuric acid electro-
lytes, whereas stress corrosion cracking of titanium is promoted by
chloride and inhibited by sulfate. The presently reported set of experiments
was aimed at determining if differences in the transients in different
electrolytes could be observed with greater initial current densities
obtained with smaller cross-section specimens and close Luggin-capillary
to electrode spacing.

Initial anodic current densities of over 100 A/cm^2 were obtained by
fracturing notched titanium wires in the new apparatus. The higher initial
anodic current densities caused a more rapid decay of current density
indicating that the initial passivation was due to an anodic process. The
current density also decayed more rapidly in concentrated (12N) HCl and in
3N H_2SO_4 than in 3 N HCl. This is interpreted as due to more rapid
precipitation of salt films by lower solubility of the Ti^{3+} salt. The
initial passivation is quantitatively consistent with precipitation of
the salt in accordance with the Sand equation for unsteady-state diffusion.

The sequence of events now proposed for the newly-formed titanium surface may be summarized as follows:

1. Rapid anodic dissolution occurs, supersaturating the solution adjacent to the metal surface.

2. At a critical supersaturation a salt film precipitates from solution forming a relatively high resistance layer and decreasing the current density; at about 10^{-3} sec.

3. Water diffuses through the salt layer to form oxide on the surface providing a further passivation at about 10^{-1} sec.

4. With decreased anodic current density the salt film dissolves and the oxide layer thickens.

5. Finally, the surface reaches steady state passivity at about 10^4 sec.

Differences in stress corrosion cracking behavior are apparently attributable to differences in properties of titanium chloride and sulfate salt films.

SALT FILMS AND THEIR INFLUENCE

ON THE CORROSION OF METALS

T. R. Beck

Flow Research, Inc., 1819 S. Central Ave., Kent, WA 98031

The existence of salt films in certain corrosion processes has been mentioned in relatively few papers in the literature and is generally ignored in electrochemical and corrosion tests. Yet, salt films appear to play an important role in pitting and stress corrosion cracking. Formation of salt films on anodically-dissolving, shielded-metal, electrodes was demonstrated by W. J. Müller in the 1920's. Salt films on iron, copper and other metals were found to cause a partial passivation. The time to reach this state varied as about the $-\frac{1}{2}$ power of the current density prior to passivation. He also correctly showed that with convection there is a current density below which the salt passivation does not occur. It is possible to predict now, based on Fick's second law for unsteady mass transport and correlations for steady-state mass transport, when salt films should form. The $-\frac{1}{2}$ power observed by Müller is in accord with Sand's equation, a one-dimensional, integral form of Fick's second law.

Salt films may be expected to form in the restricted geometries of corrosion pits. Films are observed during pitting of titanium in bromide solutions. By electrical transient experiments the thickness and conductivity of the films can be estimated. Analysis of the data indicates that the film is a mixed bromide-oxide, increasing in the ratio of the salt at high applied potentials. In the region of the pitting potential the film appears to be largely oxide. Previously published photomicrographs of the metal morphology appear to be in accord with changes in the film composition. Modelling of the salt-film behavior will be discussed.

THE OCCURRENCE OF SALT FILMS DURING INITIAL
STAGES OF TITANIUM CORROSION

Theodore R. Beck
Electrochemical Technology Corp., Seattle, Wash.
and
Daniel Ernsberger and Richard Alkire
Department of Chemical Engineering, University
of Illinois, Urbana, Ill.

Experiments have been conducted (1) in which new surfaces of titanium are produced in aqueous solutions under potentiostatic conditions. A very rapid decay of anodic current density results through passivation processes. A large fraction of the initial anodic current density can be attributed to the corrosion reaction producing Ti^{3+} ion. Thus, primary passivation by formation of a salt film has been proposed. Experimental verification is difficult because an oxide film quickly follows the suspected salt film.

A mathematical model of the diffusion-limited dissolution process has been developed in order to evaluate the sequence of events hypothesized above. In the paragraphs which follow, the salient features of the model will be described without recourse to excessive details of equations.

The diffusion of $TiCl_3$ in the electrolyte is assumed to obey Fick's law

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial y^2} \tag{1}$$

The equation is integrated with side conditions which correspond to the foregoing hypothesis of salt film formation during early stages of oxidation. Immediately following exposure of fresh metal surface to the electrolyte, anodic dissolution occurs under constant current conditions,

$$c(y,o) = 0 \quad ; \quad c(\sim,t) = 0 \quad ; \quad \frac{\partial c}{\partial y}(o,t) = -\frac{i_a}{nFD} . \tag{2}$$

The solution of eqs. (1) and (2), given in ref. (2), will be denoted for convenience as $C_I(y,t)$ since it represents the timewise concentration distribution during Stage I.

Eventually the concentration near the dissolving surface exceeds saturation by an amount sufficient to initiate precipitation of a salt film onto the anodic surface. After salt film formation, the concentration at the film-electrolyte interface remains constant at the saturation concentration. The side conditions for Stage II, which begins at $t = t^*$, are therefore

$$c(y,t^*) = C_I(y,t^*) \quad ; \quad c(\infty,t) = 0 \quad ; \quad c(o,t) = C_{sat} \qquad (3)$$

The solutions of eqs. (1) and (3), as $C_{II}(y,t)$, represents the concentration distribution during Stage II.

The rate of salt formation by anodic dissolution, $R_1(t)$ is found from Faraday's Law; the rate of salt transfer between film and electrolyte is proportional to $\partial C_{II}(o,t)/\partial y$ and, for convenience, will be denoted $R_2(t)$. The film thickness, d, is therefore,

$$d(t) \sim \int_{t^*}^{t} (R_1 + R_2) \, dt \qquad (4)$$

It was found that d(t) passes through a maximum. During the early part of Stage II, the supersaturated solution causes precipitation and film growth; during latter stages, the flux $R_2(t)$ reverses sign and film dissolution occurs. Eventually, dissolution is complete and the salt film disappears.

The foregoing model permits detailed estimates of the timewise sequence of events during precipitation, growth and redissolution of the proposed salt film. In particular the model can predict the moment of precipitation, the maximum film thickness and the moment of complete dissolution. Calculations require specification of several parameters which have been measured or estimated from auxiliary considerations. Chief among these are the value of the dissolution rate during Stage I, the degree of supersaturation prior to precipitation and the timewise variation of current during the initial portion of Stage II. Calculated results based on reasonable estimates of these parameters are compared with the interpretation of experimental results reported above.

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1. T. R. Beck, Corrosion, 30, 408 (1974).

2. H. S. Carslaw and J. C. Yeager, "Conduction of Heat in Solids," 2nd Ed., Oxford University Press, 1959.

7.   PAPERS PRESENTED, SYMPOSIA, SEMINARS, HONORS, ETC.:   (During period of
     AFOSR funding, December 1971 - June 1975)

Organized the 6th Annual Pauling Award Meeting of Puget Sound and
Oregon Sections, ACS at Pacific Science Center, Seattle, December 4, 1971.

Completed term as Chairman of Puget Sound Section, ACS, December 31,
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Organized Symposium, "Electrochemical Contributions to Environmental
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Assumed office of Vice-President, The Electrochemical Society, May 12,
1972.

Continued as Editor, Corrosion Division of the Journal of The Electro-
chemical Society, to June, 1975.

Presented paper, "Pitting of Titanium" at AFOSR Electrocochemical
Contractors Meeting, Air Force Academy, Colorado, June 28, 1972.

ECS Vice-Presidential and Presidential visits to 18 Local Sections -
presented technical talk and Soceity news, October, 1972 through May, 1976.

Introduced Acheson Medallist Prof. Charles W. Tobias at Award Banquet,
ECS, Miami Beach, October 10, 1972.

Presented paper, "One-Dimensional Pits in Titanium," Electrochemical
Society, Miami Beach, October 12, 1972.

Appointed Research Professor, Dept. of Chemical Engineering, University
of Washington, Seattle, October, 1972.

Appointed Chairman, Long-Range Planning Committee, Puget Sound Section,
American Chemical Society, 1972 - 1973.

Presented paper, "Electrochemical Reactions on Newly-Generated Titanium
Surfaces," National Association of Corrosion Engineers, Corrosion Research
Conference, Anaheim, Calif., March 19, 1973.

Presented seminar, "Pitting of Titanium," University of California at
Los Angeles, March 20, 1973.

Appointed Consultant to lithium-sulfur battery development in Chemical Engineering Dept., Argonne National Laboratories, May, 1973.

Presented symposium Keynote paper, "Electrochemical Engineering and Industry," Electrochemical Society, Chicago, May 14, 1973.

Presented paper, "Formation and Properties of Salt Films During Corrosion of Metals," Electrochemical Society, Boston, Mass., October 11, 1973.

Presented seminar, "Surface Stress of Solid Metal Electrodes," Dept. of Chemical Engineering, University of Washington, October 29, 1973.

Presented seminar, "Pitting Corrosion of Titanium," Dept. of Metallurgy, University of British Columbia, Vancouver, November 20, 1973.

Presented paper, "High Current Density Anodic Transients for Newly-Generated Titanium Surfaces," NACE Corrosion Research Conference, Chicago, Illinois, March 5, 1974.

Presented paper, "Electrical Transient Studies with One-Dimensional Pits in Titanium," Gordon Research Conference on Corrosion, Colby College, N.H., July 22 - 26, 1974.

Attended EPRI Workshop in Methods for Prediction of Optimum Battery Performance, Palo Alto, Calif., October 24 - 25, 1974, presented a discussion on battery economics.

Presented papers, "Effect of Potential on Surface Stress of Platinum," and "Hydrodynamic Effects on Pitting Corrosion of Titanium," American Institute of Chemical Engineers, Washington, D.C., December 1 - 5, 1974.

Presented invited paper, "Salt Films and Their Influence on the Corrosion of Metals," NACE Corrosion Research Conference, Toronto, Canada, April 16, 1975.

Appointed to Board of Directors, Seattle Youth Symphony Orchestra, April, 1975.

Presented paper, "Electrocapillary Curves for Gold," Electrochemical Society, Toronto, Canada, May 12, 1975.

Assumed office of President, The Electrochemical Society, Inc., May 17, 1975.

8. TOTAL PUBLICATIONS SINCE START OF CONTRACT:

1) M. J. Blackburn, J. A. Feeney, and T. R. Beck, "Stress Corrosion Cracking of Titanium Alloys," Advances in Corrosion Science and Technology, Vol. 3, Fontana and Staehle, Eds., Plenum Press, New York, 1973.

2) T. R. Beck, "A Review: Pitting Attack of Titanium Alloys," Symposium Volume, the U. R. Evans International Conference on Localized Corrosion, December 6 - 10, 1971, Williamsburg, Virginia, R. W. Staehle, Ed., NACE, 1973.

3) T. R. Beck, et al., Eds., "Electrochemical Contribution to Environmental Protection," Symposium Volume, Electrochemical Society, 1972.

4) T. R. Beck, "Electrochemistry of Freshly-Generated Titanium Surfaces, I. Scraped Rotating-Fisk Experiments," Electrochimica Acta, 18, 807, 1973.

5) T. R. Beck, "Electrochemistry of Freshly-Generated Titanium Surfaces, II. Rapid Fracture Experiments," Electrochimica Acta, 18, 815, 1973.

6) T. R. Beck, "Charles W. Tobias: Acheson Medalist," Journal of the Electrochemical Society, 120, 63C, 1973.

7) T. R. Beck, "Electrochemical Engineering and Industry," Extended Abstracts, p. 551, Vol. 73-1, Spring Meeting, Chicago, Illinois, May 13 - 18, 1973, The Electrochemical Society.

8) T. R. Beck, "Pitting of Titanium, I. Titanium Foil Experiments," Journal of the Electrochemical Society, 120, 1310, 1973.

9) T. R. Beck, "Pitting of Titanium, II. One-Dimension Pit Experiments," Journal of the Electrochemical Society, 120, 1317, 1973.

10) T. R. Beck, "Formation and Properties of Salt Films During Corrosion of Metals," Extended Abstracts, p. 249, Vol. 73-2, Fall Meeting, Boston, Mass., October 7 - 11, 1973, The Electrochemical Society.

11) T. R. Beck, "Reactions and Kinetics of Newly-Generated Titanium Surface and Relevance to Stress Corrosion Cracking," Corrosion, 30, 408, 1974.

12) T. R. Beck, "Industrial Electrochemical Processes," in Techniques of Electrochemistry, Vol. III, E. B. Yeager and A. J. Salkind, Eds., John Wiley, New York, in press.

13) T. R. Beck and K. Beach, "Measurement of Changes in Surface Stress of Electrodes," in Electrocatalysis Symposium Volume, M. W. Breiter, Ed., The Electrochemical Society, Princeton, N.J., 1974.

14) K. F. Lin and T. R. Beck, "Electrocapillary Curves for Gold," Extended Abstracts, Spring Meeting, Toronto, Canada, May 11 - 16, 1975, The Electrochemical Society.