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Stress Corrosion Cracking of Titanium Alloys:

Potential Transients at Open Circuit During SCC and Pitting Corrosion, and Chloride Absorption During Formation of Ti O$_2$

T. R. Beck

Quarterly Progress Report No.
for Period of
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1.0   SUMMARY

Experiments were conducted to test aspects of the pitting corrosion model and the electrochemical mass-transport-kinetic model for SCC previously developed. The potential transient experiments in general raised more questions than they answered but several conclusions can be drawn. The potential in an active corrosion pit in titanium is much more negative than the pitting potential but the precise thermodynamic or kinetic significance of the potential is not known. The transient potentials observed in SCC were consistent with predictions of the mass-transport-kinetic model but the presence of an undefined cathodic reaction in the crack is indicated. Tagged chloride experiments indicate that chloride is not appreciably absorbed in growing TiO_2 films at current densities expected in a stress corrosion crack. This appears to eliminate absorption of chloride in the walls as a mechanism of anodic passivation in chloride solutions and focuses attention on electrochemical reactions near the crack tip.

2.0   INTRODUCTION

This report describes part of a study of stress corrosion cracking of titanium alloys initiated in July 1965 (1) and continued under NASA sponsorship beginning July 1966 (2). This is the fifth Quarterly Report in the series (3, 4, 5, 6) and covers the period July 1 through September 30, 1967.

Work described includes potential transient studies in pitting corrosion and stress corrosion cracking of titanium and absorption of tagged chloride in growing TiO_2 films. Other work in progress, which includes activation energy of SCC velocity, acoustic emission during SCC and further SCC experiments in methanol solutions will be described in the next Quarterly Report.

3.0   TECHNICAL DISCUSSION

3.1   Potential Transients at Open Circuit During SCC and Pitting Corrosion

Some analogies between potential transients at open circuit during SCC and pitting corrosion have been presented (6). The technique has been refined and further results have been obtained. A logarithmic time base produced with a silicon diode on the x-axis of the oscilloscope increased the amount of information per experiment. A graded photographic negative on the oscilloscope screen compensated for variable exposure resulting from the decreasing sweep speed across the screen. Up to five decades in time could thereby be photographed in a single experiment as shown in Fig. 1.

3.1.1   Pitting Corrosion Transients

The initial plateau gives an IR-drop-free potential which is diagnostic in interpretation of electrochemical mechanism. The initial plateau potentials in pitting corrosion experiments with commercially pure titanium foil (3) in 0.6 molar chloride, bromide and iodide solutions are shown in Fig. 2. Several interesting features were found. The initial plateau was different for the three halides: -650 mv in chloride; -300 mv in bromide; and -30 mv in iodide. These compare to the standard reversible potentials for the three titanium tetrahalides (calculated from Latimer, 7) of: -630 mv, -760 mv and -810 mv, respectively. The chloride potential is near the reversible potential but the bromide and iodide potentials are considerably more positive. Surprisingly, the initial plateau in bromide solution was independent of
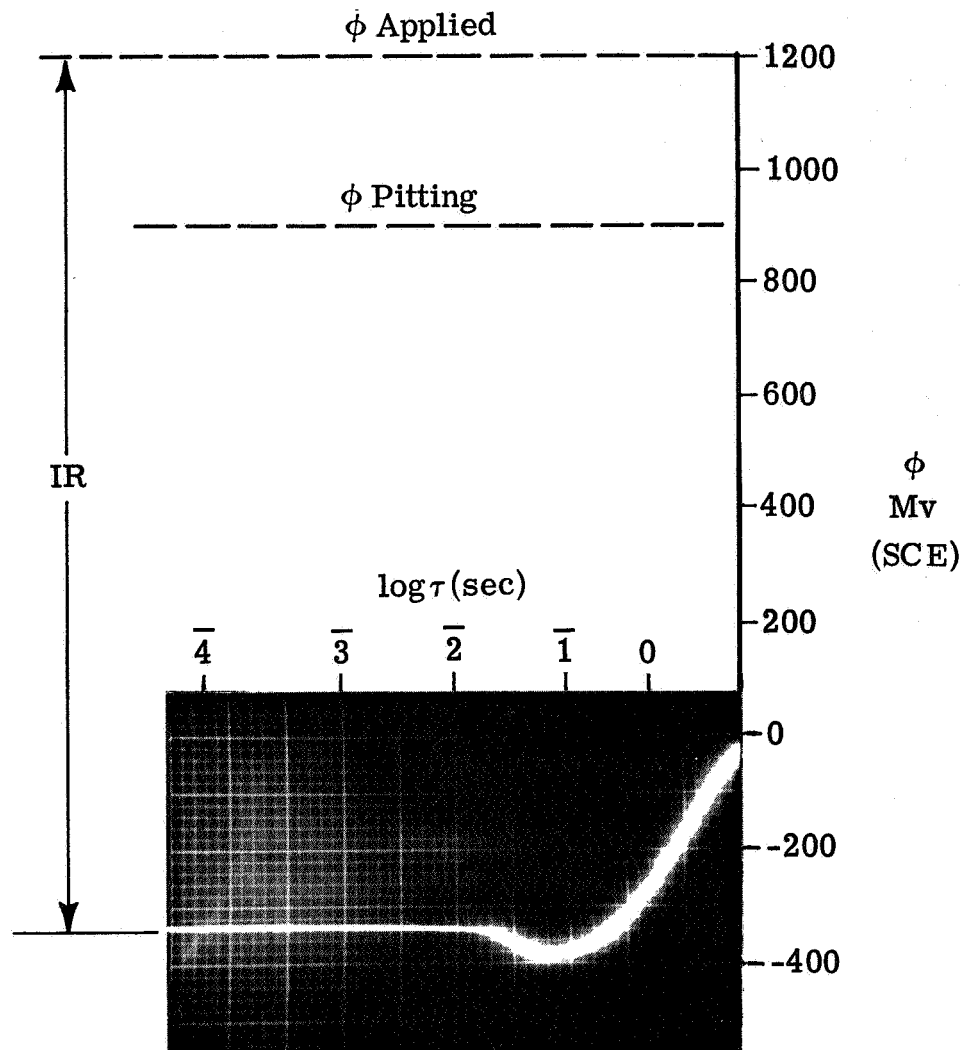
Fig. 1. Photograph of Potential Transient at Open Circuit During Pitting Corrosion of Titanium. (Approximately logarithmic time scale, Ti in 0.6 M KBr initially at +1200 mv.)
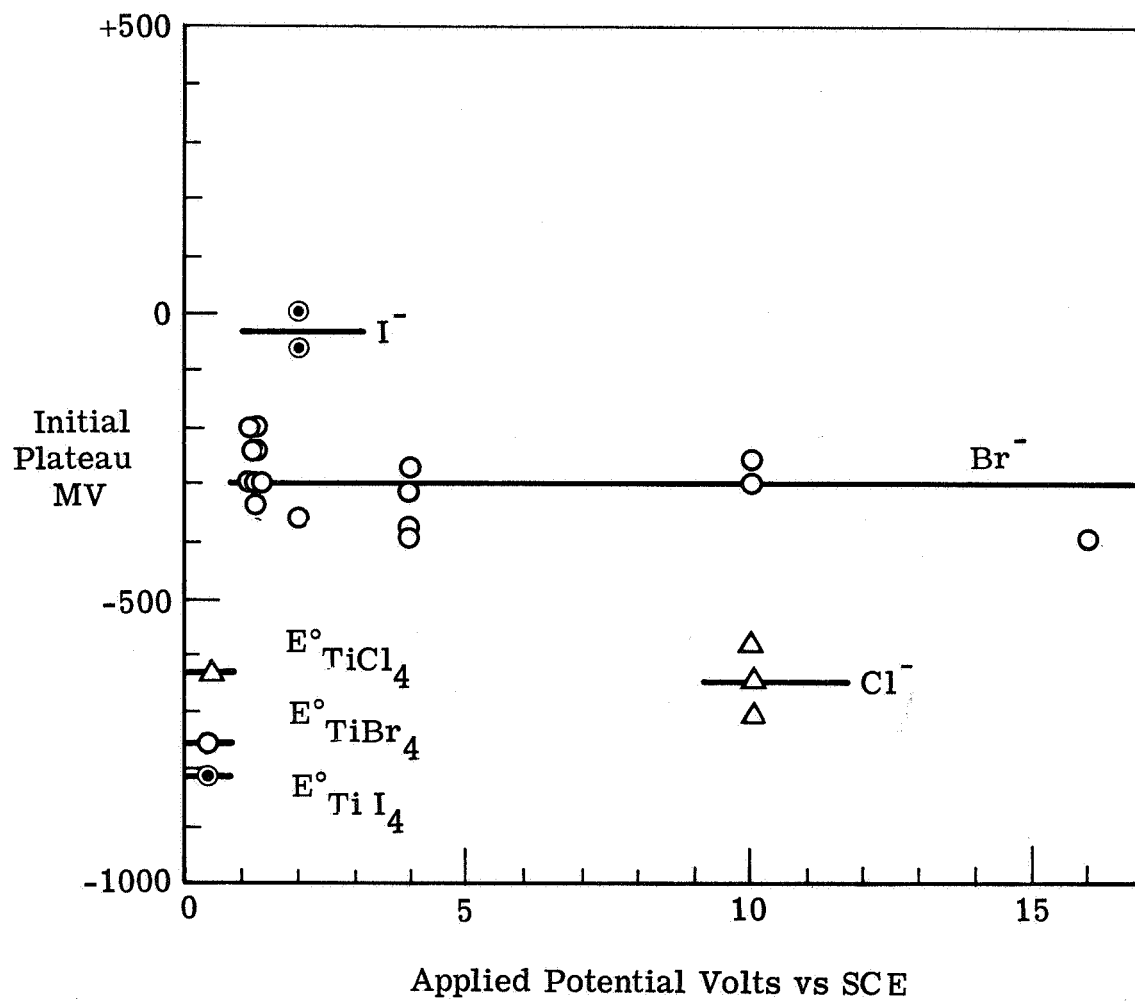
Fig. 2.   Initial Open-Circuit Potential During Pitting of
          Titanium in 0.6 M Halide Solutions.

the applied potential, within experimental error, from 1 volt to 16 volts. Pitting corrosion in bromide and iodide solutions generally produced a dip or minimum in the potential vs. log time curve as illustrated in Fig. 1. With chloride solution, however, the potential went in the positive direction in the five runs that were made.

The initial plateau is either the potential of the base of the pits or it is an immediately established potential between the dissolution reaction in the pits and a reduction on the oxide-covered surface outside of the pits. It is not possible to definitely answer which it is yet, but further discussion is given below.

The apparent constancy of the initial plateau with applied potential, and therefore current density (3), suggests a reaction going at its reversible potential. This would require a very high exchange current density because the pitting corrosion current densities are in the range of 1 to 40 amp/cm^2 (3), but this is not unreasonable. Only the chloride, however, gave a potential near the standard potential for the formation of tetrahalide. Bromide and iodide gave potentials that were 450 mv and over 750 mv, respectively, more positive. If these are reversible potentials, there is a question of what the reaction is. However, if these are reversible potentials for titanium corrosion, they may relate to the anodic protection for SCC as will be described in section 3.3.

If the potential in bromide includes an activation overpotential there is a problem to explain the constancy of initial plateau potential with applied potential and the lack of change in the plateau to

10^{-2} seconds from open circuit. Constancy of a mixed potential would be similarly difficult to explain.

The dip in the transient potential curve is consistent with collapse of the concentration gradient in the diffusion layer with termination of reaction in the pits. The concentration polarization is: $\eta_c = 59/4 \log [C_{Ti\ X_4}/(C_{X^-})^4]$. When the current ceases, the concentration of the halide ion would increase at the electrode surface. It is difficult to explain, however, why the dip did not occur in chloride solutions.

The final increase in potential must be due to a cathodic reaction on the oxide-covered surface which provides current for repassivation of the pits. The only likely reactions with high enough potentials are reduction of the halogens which were oxidized from their respective ions. The brown color of iodine was observed forming on the titanium oxide surface.

Further work is planned to resolve more of the detailed electrochemistry of pitting corrosion of titanium as it appears relevant to SCC.

3.1.2 SCC Transients

A typical potential transient for open circuit in stress corrosion cracking has been shown (6). Further experiments were done with mill annealed Ti:8-1-1 that were epoxy coated to avoid any contribution of current from the surface of the specimens. After the initial plateau the potential always went negative towards the mixed potential for oxide formation and hydrogen ion reduction.

The rate of change of potential with log time as the potential approached the open circuit mixed potential is given in Fig. 3. The data for chloride, bromide and iodide solutions all fell on the same line, indicating the same process occurring. The zero intercept is at the open circuit mixed potential observed during SCC.

A plot of initial plateau versus applied potential is given in Fig. 4. It is seen that the initial plateau is only slightly below the applied potential up to an applied potential of +200 mv. At higher applied potentials the initial plateau becomes asymptotic to +200 mv. The value of the asymptote appears to be independent of whether bromide or iodide solutions were used and independent of pH of the bulk solution in the range of zero to 14.

As with the pitting corrosion transients, the initial plateau either represents the IR-free potential at the region of the crack tip or it represents a mixed potential that may be established on the walls of the crack. A tip potential of +200 mv near the crack tip appears to be unreasonably high if the kinetics of oxidation of newly generated plane surfaces of titanium (4,5) apply in a crack. The oxidation current density for an activation overvoltage of 1300 mv [200 mv − (−1100 mv reversible)], an exchange current density of 10^{-2} amp/cm^2 and a Tafel slope of 120 mv (4) would be about 10^9 amp/cm^2, an unreasonable value. The initial plateau is therefore assumed to be a mixed potential established on the walls of the crack.

A mixed potential established in the monolayer zone of the crack appears to be consistent with the results of calculations for the
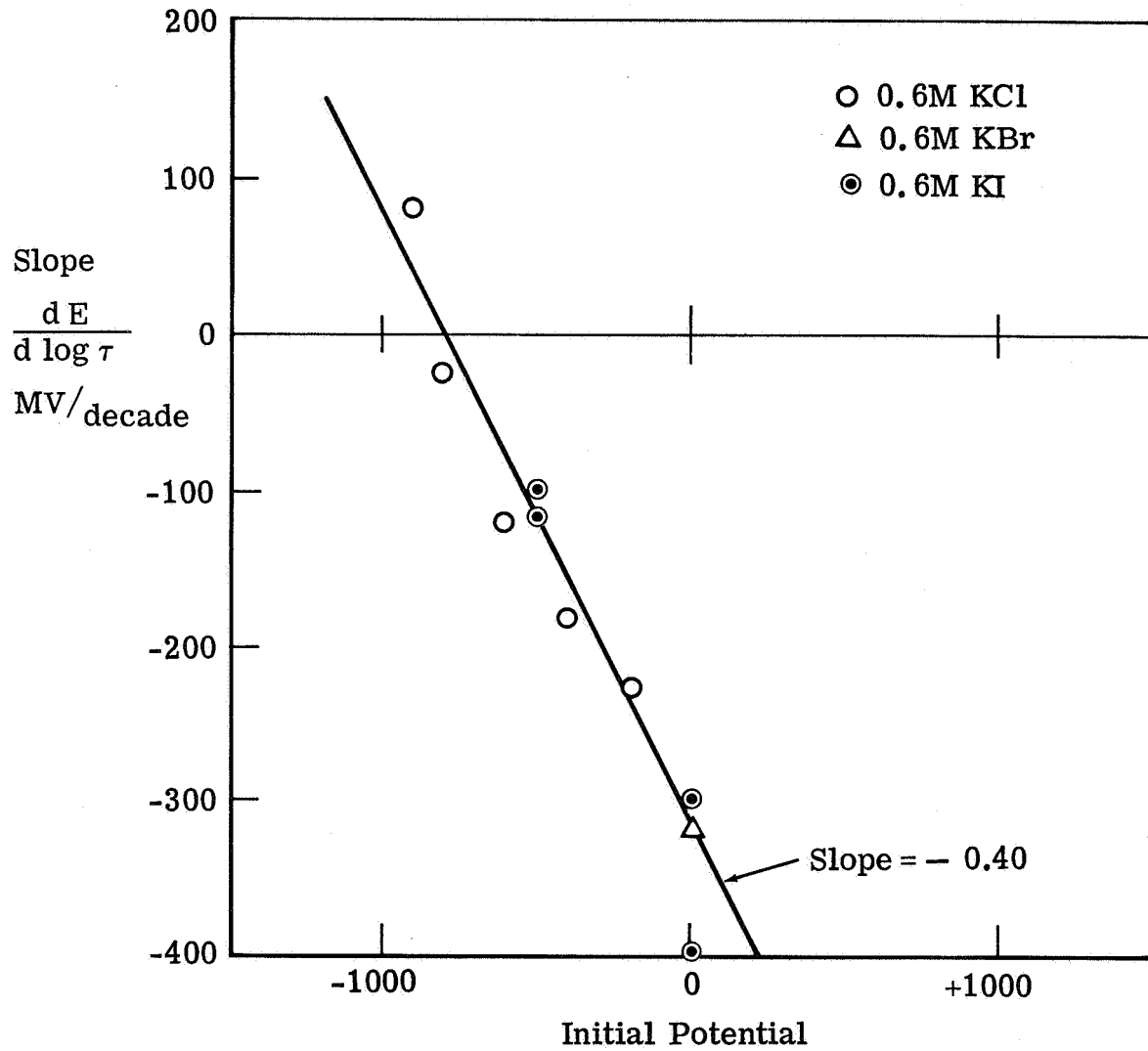
Fig. 3. Slope of Potential versus Log Time Plot on Open
Circuit of a stress Corrosion Crack as a Function
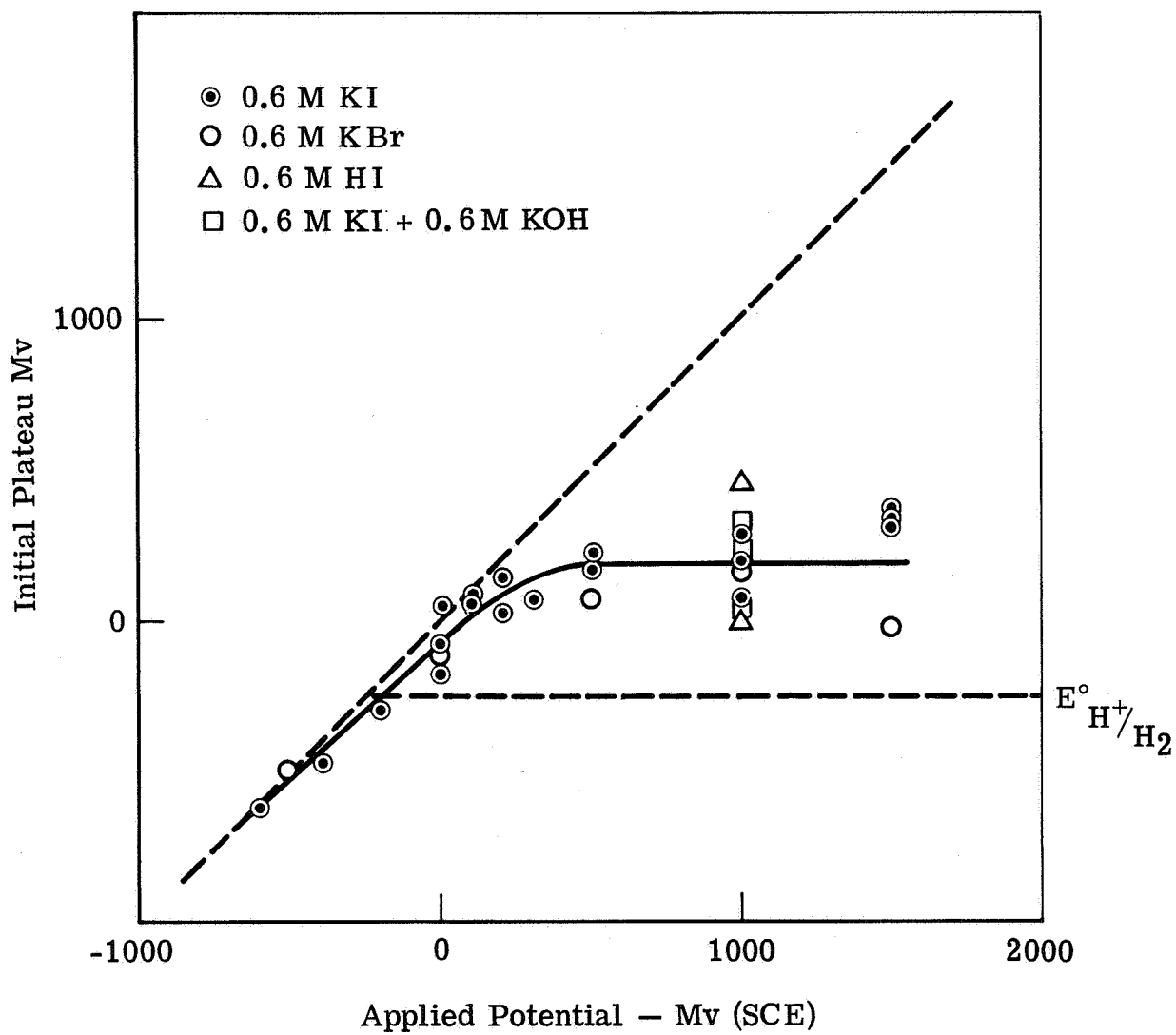of Applied Potential.

Fig. 4. Initial Open Circuit Potential During SCC of Ti:8-1-1
in 0.6 M Halide Solutions.

electrochemical mass-transport-kinetic model (6,8). Only a small part of the IR drop in a crack would disappear immediately — that in the outer portion of the crack. The major part of the IR drop, in the monolayer zone near δ^p, would not disappear if a cathodic reaction could occur in this zone giving a mixed potential.

The question of which cathodic reactions occur to give the mixed potential remains to be completely resolved. The presence of a cathodic reaction in the monolayer zone will allow the crack to continue to propagate after the circuit is opened. The velocity should therefore change continuously from that at the original applied potential to that of the steady-state mixed potential for SCC on open circuit (about -800 mv). The average hydrogen ion reduction current density in the monolayer zone can be calculated from the equation:

$$I = \bar{i} \, \delta$$

For a velocity of 10^{-2} cm/sec, the M-T-K model gave a tip current, $I^p \approx 7 \times 10^{-6}$ amp/cm, and a value of $\delta \simeq 7 \times 10^{-5}$ cm (6). The average hydrogen ion reduction current density to provide the tip current would therefore be $\sim 10^{-1}$ amp/cm^2. The M-T-K model (6) gave a value $\sim 10^{-2}$ amp/cm^2, which is within an order of magnitude of this value. If the crack velocity continued on open circuit and the potential decreases only a small amount, oxidation of titanium must also continue by means of a cathodic reaction that proceeds at up to +200 mv, requiring an additional current.

The independence of +200 mv plateau on pH of the bulk solution indicates that the reduction reaction is either pH independent or that it occurs deep enough in the crack that the solution is always acid regardless of the solution pH outside of the crack. Possible reduction reactions for the various species that may be present are given in Table I. (Electrochemical reactions with aluminum, molybdenum, vanadium and other trace elements in the titanium alloy are not included but it remains to be demonstrated that they play no role.) The only reactions that appear to meet the various selection criteria are reduction of titanium ions. The presence of titanium ions in solution has been ignored in the M-T-K model but the formulation and results would not be seriously changed if some formed in solution in parallel with formation of TiO_2. According to the Pourbaix diagram for titanium (9), Ti^{+3} and TiO^{++} ions are the stable species in acid solution at high potential. The fact that titanium passivates in strong acid indicates that TiO_2 is kinetically favored over Ti^{+3} and TiO^{++} in spite of the thermodynamics, but the presence of these titanium ions should be expected.

The +200 mv plateau was observed independent of whether bromide or iodide solutions were used. The bromine/bromide and iodine/iodide reversible potentials are 550 mv apart so these reactions are not very probable.

Hydrogen ion reduction, although thermodynamically possible at +200 mv if the hydrogen activity in the metal surface is 10^{-7} atm, does not appear feasible kinetically. Using the approximate kinetic data

Reaction	$E°$	$200-E°$	$\underline{n}$	C_1/C_2*
pH independent				
$I_2 + 2e \rightarrow 2I^-$	+300	-100	2	
$Br_2 + 2e \rightarrow 2Br^-$	+850	-650	2	
$Ti^{+3} + e \rightarrow Ti^{++}$	-610	810	1	$\dfrac{C_{Ti^{+3}}}{C_{Ti^{++}}} \approx 10^{14}$
pH dependent				
$H^+ + e \rightarrow H$	-240	440	1	$(P_H \approx 10^{-7}$ atm H$)$
$O_2 + 2H^+ + 2e \rightarrow H_2O_2$	+440	-240	2	$\dfrac{C_{O_2}}{C_{H_2O_2}} \approx 10^{-8}$
$TiO^{++} + 2H^+ + e \rightarrow Ti^{+3} + H_2O$	+100	100	1	$\dfrac{C_{TiO^{++}}}{C_{Ti^{+3}}} \approx 10^{2}$

*NOTE: Calculated from the Nernst equation:

$$E - E° = \frac{59}{n} \log (C_1/C_2)$$

assuming H^+ at unit activity.

Table I — Possible Cathodic Reactions in a SCC Crack and their Reversible Potentials and Reactant Concentration Ratios at +200 mv.

for hydrogen ion reduction on bare metal (5) gives a current density of $\sim 10^{-7}$ amp/cm^2 at +200 mv. This is far too small for hydrogen ion reduction to play a significant role.

Reduction of dissolved oxygen, while also thermodynamically feasible is also limited by kinetics (5) and by mass transport. The mass transport limiting-current density is (1):

$$I = \frac{z F D \gamma \ C^{\circ}_{O_2}}{\ell n \ (\ell / \delta)}$$

Assuming $z = 4$, $D \simeq 10^{-5}$ cm^2/sec, $\gamma = 0.05$ radians, $C^{\circ}_{O_2} = 1.26 \times 10^{-6}$ mole/cm^3 (saturation in H_2O at 1 atm is 0.0283 cm^3 (STP)/cm^3 H_2O @ 25°C), $\delta = 10^{-4}$ cm and $\ell = 10^{-1}$ cm; gives $I = 3.7 \times 10^{-8}$ amp/cm. Again this is too small to be significant.

Further work must be done to determine if dissolved titanium ions are present at sufficient concentration to support the current required for continued crack propagation on open circuit.

3.2 Chloride Absorption During Formation of TiO_2 Film

One of the mechanisms proposed for the anodic protection of titanium alloys against SCC in chloride solutions was that at high anodic potentials chloride would be absorbed in the forming oxide on the walls of a crack and not reach the crack tip (1). This hypothesis was tested experimentally by breaking notched mill-annealed, Ti:8-1-1 rods in tagged chloride (Cl-36) solutions and anodizing at various constant current values. In all runs (in which the current density was varied from 1.6×10^{-4} to 6.7×10^{-2} amp/cm^2) the coulombic efficiency for

chloride absorption was less than 0.3%. It is concluded that chloride absorption in the walls of the crack is not a likely mechanism of anodic passivation. A detailed description of the experiments follows.

The mill-annealed Ti:8-1-1 rods were 5/16 inches in diameter and six inches long. Each had a machined 60° notch 1/32 inch deep at the midsection, leaving a net diameter of 1/4 inch (net area of 0.32 cm^2). The rods were rinsed in kerosene and acetone after machining. They were then anodized to about 70 volts in order to minimize current to the old surface during the experiments. Some of the rods were additionally coated with eopxy resin to increase their electrical resistance, the resin being scored at the notch to facilitate its fracture.

A Teflon cell was used to contain the electrolyte at the midsection of the specimens. A platinum counter electrode was used. A saturated calomel reference electrode connected through a salt bridge containing non-radioactive salt solution was used to monitor potential The specimen and counter electrode were switched to a 100-volt power supply within a fraction of a second after the break. Series resistors of selected values were used to maintain an approximately constant current during each test.

The electrolyte was neutral 0.0038 molar sodium chloride made by neutralizing and diluting a 0.3 M HCl colution containing 99$^+$ % of the chloride as Cl-36. The HCl colution was obtained from Nuclear Science and Engineering Corporation, Pittsburgh. Cl-36 is a 0.77 Mev β-emitter with a half-life of 3.1 x 10^5 years. In one group of experiments, non-radioactive sodium chloride was added to increase the total chloride

concentration by a factor of ten for the same radioactive chloride concentration. This was done to avoid a mass-transport limitation during anodizing.

The specimens were pulled to rapid fracture in the Instron tensile machine at a cross head velocity of 0.5 cm/min. The anodizing current was switched on manually at fracture. Current and potential were recorded on a two-pen strip chart recorder. The anodizing current was adjusted so that, although the current was varied over four-hundred fold, the total coulombic quantity was the same order of magnitude in all of the experiments.

At the termination of current, the upper half of the specimen was removed from the tensile machine and rinsed; the time required was about 5 seconds. The first four specimens were rinsed with acetone only, the last three with distilled water then acetone, and air dried. The epoxy coating, if used, was then stripped off and the fracture surface was placed in the counter.

Counting was done with a Geiger tube and Tracerlab scaler. A lead shield was arranged so that only the new fracture surface was exposed to the Geiger tube, which was approximately 3/8 inch from the fracture surface. 30-minute count periods were used. The system was calibrated by placing one drop ($\sim 1/23$ cm^3) of the 0.0038 M active salt solution on a fracture face, evaporating the water and making a count. The calibration gave 21,600 counts/min compared to 194,000 disintegrations/min theoretical; the difference being due to geometrical and instrument factors. The conversion factor to coulombic charge is:

$$f = \frac{(0.0038 \text{ mole/liter})(1/23 \text{ cm}^3)(96,500 \text{ coul/mole})}{(10^3 \text{ cm}^3/\text{liter})(21,600 \text{ CPM})}$$

$$= 7.4 \times 10^{-7} \text{ coul/CPM}$$

The conversion factor for the solution containing 9:1 non-radioactive to radioactive chloride is 10-fold larger.

Data from the seven experiments run are given in Table II. The coulombic efficiency for absorption of chloride ion is:

$$\varepsilon = \frac{(\text{CPM})f}{Q}$$

where Q is the coulombic charge passed per fracture face. In all runs, with the exception of #1 which was conducted potentiostatically and had an inaccurate measure of total charge passed, the coulombic efficiency was less than 0.3%. The coulombic efficiencies are plotted in Fig. 5. The calculated steady-state mass-transport limiting current density for the two solutions is also plotted, showing that limiting mass transport should not have biased the results. The mass-transport limiting current efficiency was calculated from the equation:

$$\varepsilon = \frac{zFDC^\circ}{\delta i}$$

where $z = 1$, $F = 96,500$ coul/equiv, $D \approx 10^{-5}$ cm^2/sec, $\delta \approx 0.05$ cm, $C^\circ =$ bulk concentration in mole/cm^3 and $i =$ current density in amp/cm^2.

The thickness of oxide attained in the experiments can be calculated from the equation

$$t = \frac{QM_o}{\rho z F}$$

Table II — Coulombic Efficiency of Chloride Absorption

Run	I(ma)	τ(sec)	Q ($\frac{1}{2}I\tau$) (Coul/face x 10^3)	CPM (counts/min)	Coulombic Efficiency ε x 10^2
$1^{(a,b)}$	–	–	~ 1.8	9.1-14.2	0.37-0.58
$2^{(b)}$	1.0	66	33	88.9	0.20
$3^{(b)}$	0.10	318	16	47.0	0.20
$4^{(b)}$	10	7-12	35-60	122.4	0.15-0.26
$5^{(c)}$	10	10	50	3.4-11.6	0.05-0.17
$6^{(c)}$	42	2.3	48	9.1	0.14
$7^{(c)}$	1.0	61	30	2.0-9.3	0.05-0.23

NOTES:

(a) Experiment done potentiostatically at -500 mv. All other experiments at constant current.

(b) Specimen rinsed with acetone within approximately 5 seconds after termination of current.

(c) Epoxy-coated specimens. These specimens rinsed with distilled water, then acetone, within approximately 5 seconds after termination of current.
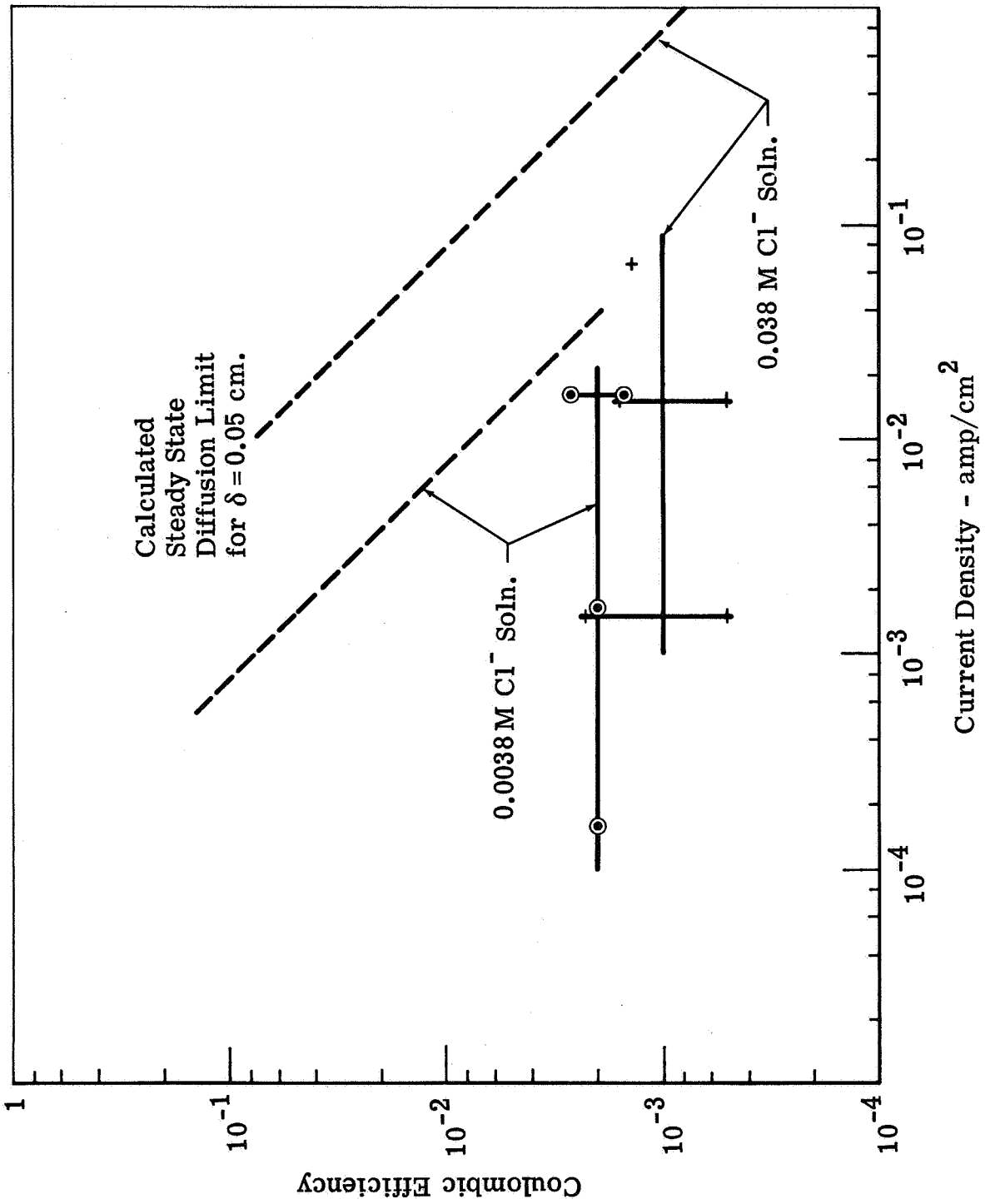
Fig. 5. Coulombic Efficiency of Chloride Absorption.

The value of $\frac{M_o}{\rho zF}$ is 4.85 x 10^{-5} cm^3/coul for rutile (1). For a charge density of 16 to 60 x 10^{-3} coulombs per 0.32 cm^2 face the thickness range was 240 to 910 A°. It is not likely that much of the chloride would be leached out of this thickness film during rinsing. The effect of other variables such as pH and temperature were not investigated because absorption of chloride in the oxide was small and does not appear to be an important factor in SCC of titanium.

3.3 Theory

3.3.1 Mass-Transport-Kinetic Model

Displacement of adsorbed halide ion or titanium halide on bare metal by oxide in the monolayer zone was added to the mass-transport-kinetic model to comply to the observed effect of concentration on velocity (6). With recycling of halide near the crack tip the calculated velocities increased several fold. In order to get the velocities again consistent with experimental potential-velocity-current data the tip potential was made more negative than the mixed potential for formation of TiO$_2$ in acid solution and hydrogen ion discharge. This increased the rate of hydrogen ion discharge in the monolayer zone and decreased the hydrogen halide acid concentration. Need for this computational change implies that the tip potential is a mixed potential determined by hydrogen ion reduction and an oxidation reaction more negative than the reaction of titanium with water to give TiO$_2$. This reaction could be formation of Ti^{++} (standard reversible potential of -1870 mv versus SCE compared to -1120 mv for TiO$_2$ in acid solution) or charging of the electrical double layer with halide ions.

3.3.2 Anodic Passivity in Chloride and Bromide Solutions

It has been proposed (1) that the anodic passivity observed in chloride and bromide solutions is due to these anions not reaching the crack tip because they are reacted and removed on the walls of the crack. The Cl-36 experiments reported herein indicate that absorption in oxide on the walls is negligible.

It has been proposed that if the passivation is due to formation of covalent tetrahalide in the monolayer zone, the lack of anodic passivity in iodide solutions may be due to rapid hydrolysis of titanium tetraiodide and regeneration of iodide ions (1). A necessary consequence of this hypothesis is that the passivity in chloride and bromide solutions should be sensitive to temperature because the hydrolysis rate constant should be strongly temperature dependent. A group of experiments in chloride and bromide solutions (3) gave little dependence of SCC strength on temperature. The hydrolysis of titanium tetrahalide in solution in the crack does not therefore appear to be important.

The initial plateau potentials observed on open circuiting the pitting reaction may be relevant to the anodic passivation in SCC. If these initial plateau potentials are the potentials for formation of titanium tetrahalides, they are in the right order to explain passivation in chloride solution, partial passivation in bromide solution and lack of passivation in iodide solution. Chloride solutions gave the most negative potential (-650 mv). The M-T-K model shows that there is little potential drop in the outer part of the crack so that potentials

more positive than this can easily be achieved in the monolayer zone, and $TiCl_4$ could be formed. If hydrolysis is slow in solution it could occur well outside of the monolayer zone and therefore the temperature influence would be small. This mechanism should, however, produce a decreasing velocity as the anodic protection zone is approached but this has not been observed (6). It is apparent that more refined kinetic experiments should be run with newly fractured titanium surfaces in halide solutions, to get a better understanding of the electrochemistry on the monolayer zone.

4.0   CONCLUSIONS

The following conclusions are based on the work accomplished in the period of July 1 through September 30, 1967.

1. In the pitting corrosion of titanium, the potential in the pits is considerably more negative than the pitting potential; the difference attributed to IR drop in the electrolyte diffusion layer.

2. Potential transients observed on open circuiting a propagating stress corrosion crack are consistent with predictions of the mass-transport-kinetic model.

3. Experiments on growth of TiO_2 on newly generated metal surface in solutions of tagged chloride indicate that chloride is not appreciably absorbed in a range of current densities expected in a stress corrosion crack, eliminating absorption of chloride in the crack walls as a mechanism of anodic passivation of SCC.

5.0   FUTURE WORK

The following items of work are planned for the immediate future:

1.   Resolve the problem of chloride analysis of titanium.

2.   Refine and extend kinetic studies to a wider range of halide con-
     centrations and to other alloys.

3.   Investigate metallurgical and mechanical parameters further and
     develop more quantitative relationships.

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