CURRENT-LIMITED IMPOSED-POTENTIAL TECHNIQUE FOR INDUCING AND MONITORING METASTABLE PITTING EVENTS

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ABSTRACT

A technique has been developed to selectively induce metastable pitting while preventing the transition to stable pit growth. The current-limited imposed-potential (CLIP) technique limits available cathodic current to an initiated site using a resistor in series with the working electrode to form a voltage divider. Potentiodynamic CLIP testing yields a distribution of breakdown potentials from a single experiment. Potentiostatic CLIP testing yields induction time data, which can be used as input to a calculation of germination rate. Initial data indicate that a one-to-one correlation exists between electrochemical transients and observed pitting sites. The CLIP technique provides a consistent means of gathering quantitative potential and current transients associated with localized oxide breakdown.

INTRODUCTION

A statistical analysis of pitting requires the observation of a large number of initiation events. This can be accomplished by testing a large number of specimens (1,2) or by testing under experimental conditions suitable for inducing and monitoring pit initiation without allowing for pit stabilization (3-8). Monitoring of current during potentiostatic polarization can yield values for induction times and estimates of current flow during metastable pitting. Repetition of these techniques at many potentials yields relationships between germination rate and applied potential. The interrupted potential sweep method of Williams yields information on metastable pitting as a function of applied potential in a single experiment (9).

Independent of the technique used, two requirements have to be met to accurately record metastable pitting. Firstly, the experimental conditions must promote initiation but inhibit propagation. This is accomplished by lowering the driving force for stable pitting – i.e., lowering the aggressive ion content, increasing the presence of a passivating species, applying potentials below the stable pitting threshold, or a combination of these techniques. Secondly, the breakdown and repassivation signals (current or potential) must be discernable above the background levels. Often this is accomplished by setting an arbitrary threshold for distinguishing an event. A more correct approach is to reduce the exposed surface area to decrease the background passive current such that localized signals dominate the response of the system (10).

In our studies of pit initiation on Al thin films and high purity Al rod we have found that these techniques do not yield satisfactory results (11). As the quality of the oxide increases, it becomes more difficult to selectively initiate metastable events without allowing the events to stabilize and mask or obscure subsequent breakdown phenomena.
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In the extreme case, the driving force (i.e., applied potential) for initiation of an event may be greater than that required to sustain the event once initiated.

When only a single datum is extracted from a sample, much of the information concerning pit initiation sites is lost. In essence only the weakest link on the sample is examined and other more robust sites go undetected. While, in principle, reducing the test area should allow examination of the entire distribution of initiation sites, this approach would require one experiment per datum collected and could prove prohibitively expensive in terms of time and resources.

The current work seeks to develop an experimental methodology for promoting localized oxide breakdown but inhibiting stabilization of pits. As a consequence, the identification of individual oxide breakdown events is simplified and quantitative analysis of metastable pitting becomes more straightforward.

**EXPERIMENTAL**

**Materials**

E-beam evaporated Al on an Si/SiO₂ substrate was used in several scoping experiments and in the Cu-wire experiments (described below). The details of the preparation are given elsewhere (11,12). In summary, evaporated Al was deposited on Si/SiO₂ substrates to approximately 200 nm thickness and average grain size of 150 nm. The oxide was formed by a 600 s exposure of the Al surface to O₂ plasma. No further treatment of the sample surface was used.

The majority of the technique development was carried out on 99.999% Al rod. The samples were cut to approximately 9 mm thickness and hand polished to a 1 μm alumina finish. Ultrasonic cleaning was performed in three stages using the following media: Liquinox™ laboratory soap in deionized H₂O, acetone, then ethanol. Surfaces were dried with clean compressed air.

**Environment**

All experimentation was performed in aerated 0.05 M NaCl solution at 25°C. Reagent grade chemicals and 18 M-Ω deionized H₂O were used to prepare the test solution.

**Cu-wire experiments**

Copper wire measuring 0.203 mm in diameter was inserted into a glass rod and sealed with epoxy. The end of the rod was polished with 600 grit SiC polishing paper to expose approximately 0.032 mm². An Al thin film electrode was mounted in a vertical flat cell using a knife-edge Teflon gasket to expose a 1 cm² area to the test environment. The cell was filled with 0.05 M NaCl and the Cu wire inserted into the top of the test cell. The Cu wire electrode was then connected externally to the Al film either through a direct short or through a 10 M-Ω resistor. An Ag/AgCl (+0.058 V_SCE) reference electrode was used to monitor the potential of the Al electrode as a function of time.
CLIP testing

Current-Limited Imposed-Potential (CLIP) testing was performed by exposing 0.8 mm² of the test material to solution using a glass capillary test cell. Silicone adhesive provided the seal between the capillary and the sample. The electronics for the CLIP experiment are divided into a control circuit and a monitoring circuit (Figure 1). The control circuit consists of a three-electrode arrangement: working electrode, Ag/AgCl reference electrode (+0.058 V SCE) and a platinized niobium counter electrode. A Princeton Applied Research model 283 potentiostat is used to bias the control circuit in either potentiostatic or potentiodynamic modes. The CLIP resistor (R(CLIP)) is inserted in series between the potentiostat and the working electrode. The guidelines for selecting the value of R(CLIP) will be discussed in the results and discussion section of this document. Resistances on the order of 50 MΩ to 200 MΩ were used in the present work. The monitoring circuit consists of two battery powered Keithly 614 electrometers connected to a Metrobyte DAS 1801-ST through Analog Devices model 5B41-02 voltage signal isolators (10 kHz bandwidth). One electrometer is used to monitor the potential of the sample versus the Ag/AgCl electrode and the other is used in ZRA mode to measure the current flowing through the counter electrode. Data acquisition rates were 100 Hz for the raw data and a rolling average was used to filter the data down to 5 Hz.

Prior to testing, samples were either monitored under free corrosion conditions or held potentiostatically at approximately -0.740 V SCE for up to 1200 s. For potentiostatic experiments (PS-CLIP) the applied potential was ramped from the initial value to the target value at 1 mV/s. For potentiodynamic experiments (PD-CLIP) the applied potential was ramped anodically from the initial potential at a ramp rate between 0.02 and 0.5 mV/s. The test was terminated when the background current rose to levels that obscured the signals from metastable pitting.

Traditional Potentiodynamic Testing

Potentiodynamic experiments were performed on 99.999% Al rod using the capillary cell described above. Samples were conditioned at -0.740 V SCE while the passive current stabilized. The applied potential was then ramped in the anodic direction at a sweep rate of 0.1667 mV/s. A pitting potential was determined for each curve by assessing the potential at which the current underwent a transition from passive to active behavior. Samples were examined using SEM to ensure that crevice corrosion had not occurred at the seal between the sample and capillary.

RESULTS AND DISCUSSION

Nano-engineered 10 μm diameter Cu islands deposited on an Al substrate have been shown to induce both localized dissolution at the Al-Cu interface and metastable pitting in the Al matrix away from the Cu islands when exposed to 0.05 M NaCl (11). Additionally, monitoring of the open circuit potential revealed numerous potential fluctuations having a sharp negative transient followed by a gradual decay. It was unclear if the potential fluctuations were caused by metastable pitting or by degradation at the Al-Cu interface. The Cu-wire experiments in the present work were designed to determine if the galvanic driving force from an Al-Cu couple could induce metastable
pitting in the Al and if corresponding fluctuations in the open circuit data would be detectable.

Figure 2.a shows the response of an Al thin film externally shorted to a Cu wire. The potential of the sample shows a gradual negative drift until the Cu wire is connected at approximately 640 s. At that time the Al is polarized above its pitting potential and a pit initiates. When repassivation occurs, the potential climbs until another pit is initiated and the process repeats. Examination of this sample revealed pitting and sustained attack in the form of filiform corrosion. The difference between the Cu-wire experiment and the previously reported data from Al with Cu islands is the available cathodic current from the Cu. The Cu-wire has approximately 3200 times the area of a 10 μm Cu island. The smaller the Cu electrode, the earlier the pit becomes cathodically limited and switches off.

Introducing a 10 M-Ω resistor between the Al and the Cu resulted in a succession of clearly defined potential fluctuations (Figure 2.b) which continued until the external connection between Al and Cu was broken (t=600 s). Optical examination of the surface following testing revealed only the presence of small pits (less than 5 μm diameter) and no indication of sustained corrosion at any given site. The 10 M-Ω resistor limits the cathodic current to the anodic sites and effectively switches off pits before they can stabilize.

The Cu-wire experiment does not provide a well-controlled means of studying metastable pitting because polarization of the Al depends on the behavior of the Cu in the test environment. Additionally, if the breakdown potential of the Al falls above the open circuit potential of the Cu, then this experiment is incapable of inducing breakdown in the Al oxide. The remedy is to replace the Cu cathode with electronic instrumentation. The result is the basic framework for the Current-Limited Imposed-Potential (CLIP) technique (Figure 1).

An example of the type of signals observed during a CLIP test is given in Figure 3. These data are from a potentiostatic CLIP test performed on 99.999% Al with RCLIP set to 200 M-Ω (see Figure 1) and the target potential set to -0.650 V SCE. The system response is represented schematically in Figure 4. In this figure the sample impedance is modeled simply as a combination of resistors representing the passive oxide (ROX) and an active pit (RPIT). When passive, only ROX is present. If ROX >> RCLIP, then the applied potential will be divided across these resistances such that the majority of the potential drop occurs across ROX and the potential of the sample will approach the applied potential (Figure 4.a). When the sample becomes active, RPIT is in parallel with ROX and since RPIT << ROX, the sample impedance can be approximated by RPIT. Since RCLIP >> RPIT, active behavior will result in the applied potential being divided with the majority of the potential drop across RCLIP (Figure 4.b). Hence, the potential of the sample becomes independent of the control circuit and the only available cathodic current is that supported by reactions on the sample surface. The effect of this voltage divider circuit manifests itself in the data as oscillations between passive and active behavior (Figure 3).

A technique related to the CLIP test was presented by Sikora et al., where a bias potential was imposed between two identical electrodes in a zero-resistance ammeter based noise experiment (13). The authors pointed out several advantages of this biasing technique including: the ability to localize more of the metastable events to a preferred
electrode, a means of driving the sample potential away from open circuit and into regimes more conducive to metastable pitting and finally an improvement in current sensing capability. The similarity to the CLIP test is apparent if the CLIP experiment is performed with identical working and counter electrodes and $R_{\text{CLIP}}$ is set to 0 $\Omega$. However, the full-blown CLIP test encompasses the advantages of the biased noise experiment with at least two key improvements. The CLIP experiment biases the sample with respect to a reference electrode rather than tying the sample potential to the behavior of the counter electrode, thus allowing for greater control and reproducibility. Additionally, the CLIP experiment is tunable to the extent that proper choice of sample area and CLIP resistor allows the user to define the allowable available cathodic current to an initiation site.

The limitation of the CLIP experiment stems from the requirement that:

$$R_{\text{OX}} \gg R_{\text{CLIP}} \gg R_{\text{PIT}}.$$ 

Since $R_{\text{PIT}}$ may vary as a function of material and environment, and since this value may not be accessible, it is convenient to choose an arbitrarily large $R_{\text{CLIP}}$. In the scoping experiments we have performed with aluminum, we have achieved good results with $R_{\text{CLIP}}$ values ranging as low as 1 M-$\Omega$ and as high as 200 M-$\Omega$. In general, the higher the value of $R_{\text{CLIP}}$, the faster the pitting event is switched off with less current flow and less material dissolution. Once $R_{\text{CLIP}}$ is defined, the sample area must be chosen to yield a sufficiently high $R_{\text{OX}}$ ($R_{\text{OX}} = r_{\text{OX}} / A$). As the passive current density of the sample decreases, larger areas can be used with acceptable CLIP behavior. However, in general, minimizing the area yields better results. Good behavior has been observed when using areas on the order of 0.2 to 1 mm$^2$. Larger areas can result in undesirable voltage drop (10 mV or more) across $R_{\text{CLIP}}$ even when the sample is in a passive state. The drawback to smaller samples is that less material is being interrogated in each experiment. If an oxide under study has good average properties but fails at sparsely distributed sites, then reducing the area decreases the odds of encountering a representative weak link or can yield a skewed subset of the actual flaw distribution.

If the area interrogated by the CLIP test contains a distribution of flaws that are potential sites for initiation, then the distribution may be uncovered from a single experiment. For example, potentiodynamic CLIP testing of 99.999% Al disks was performed in 0.05 M NaCl with $R_{\text{CLIP}}$ set to 100 M-$\Omega$ and the exposed area restricted to 0.8 mm$^2$. The results of ramping the applied potential at 0.02 mV/s are shown in Figure 5. As the applied potential increases, many distinct fluctuations in the measured potential and current are recorded corresponding to oxide breakdown and repassivation. Eventually the measured potential becomes erratic and does not recover to the level of the applied potential. This effect is caused by changes in the resistivity of the oxide ($R_{\text{OX}}$) as metastable pitting occurs. Once $R_{\text{OX}}$ becomes close in value to $R_{\text{CLIP}}$, the CLIP test will no longer maintain the desired potential across the oxide. As suggested above, this effect could be minimized or at least delayed by using a smaller area working electrode.

Oxide breakdown events occur over a range of potentials during the PD-CLIP experiment (Figure 5). It is not clear if these potentials relate to pitting potentials as determined by a standard potentiodynamic experiment, or if these potentials are merely artifacts of pit induction time superimposed on the slow CLIP ramp rate (0.02 mV/s).
For comparison, 10 traditional potentiodynamic polarization experiments were performed on 99.999% Al at a ramp rate of 0.1667 mV/s in 0.05 M NaCl using the same capillary test cell. The pitting potentials extracted from these experiments are overlaid on the measured potential vs. time trace from the CLIP experiment (Figure 5). Clearly, breakdowns in both experiments occur within the same potential band. For further comparison, cumulative distribution plots were constructed from the potentiodynamic data and from PD-CLIP data (Figure 6). The distribution of breakdown potentials from the 10 potential scans is bounded by two PD-CLIP experiments. Currently, the similarity in results is regarded as a promising indication that the data are related; however, further testing will be necessary to accurately describe the nature of relationship.

Potentiostatic CLIP (PS-CLIP) tests were performed at $-0.650 \text{ V}_{\text{SCE}}$ and at $-0.575 \text{ V}_{\text{SCE}}$ (Figure 7) in order to determine if the CLIP test was sensitive to effects of applied potential on induction time. The raw data qualitatively show a decrease in induction time (more pits per unit time) as the hold potential is increased. Figure 7.c shows an induction time distribution for each potential based on the same number of metastable events. Figure 7.d is a plot of the negative log of the survival probability at each potential; the slope in these data is a measure of germination rate (2,8). All of these data formats suggest that increasing applied potential results in increased germination rate. The measured potential during periods of passive behavior in the potentiostatic testing tended to drift over a range of tens of millivolts. This drift can complicate analysis and is due to changes in the voltage divider circuit caused by changes in the average working electrode impedance. In the future, efforts will be made to minimize the drift through fine-tuning sample surface area and the value of $R_{\text{CLIP}}$.

In order to accurately interpret the distributions of data generated by the CLIP experiments it is necessary to link the transients in the electrochemical data to physical phenomena and to understand interaction effects (if any) between subsequent events. The first issue to resolve is whether or not there is a one-to-one correlation between electrochemical transients and metastable pits or whether one site may generate multiple transient signals. One approach to resolving this question is to study a system with a robust oxide, induce a small number of events and then count the pitted sites on the sample post-test. Figure 8 shows the data and resulting optical image from a PD-CLIP experiment performed on an Al thin film in 0.05 M NaCl with $R_{\text{CLIP}} = 50 \text{ M}\Omega$. The applied potential was ramped anodically from the sample open circuit potential at $+0.5 \text{ mV/s}$. The number of electrochemical transients is the same as the number of pitting sites revealed using optical microscopy. This experiment suggests a one-to-one correlation. Future work will be performed to determine if this relationship holds in other systems. Interaction effects will be studied by using a segmented electrode, which should allow the approximate position of metastable pits to be known in addition to when they occur and their associated potentials and currents.

**SUMMARY**

Through the use of a voltage divider circuit based on an external resistor, the CLIP experiment is able to selectively induce localized breakdown events while limiting the current available for growth. The ability of the CLIP circuit to switch off corrosion allows many initiation sites to be studied on a single electrode. Testing of an Al thin film electrode indicates a one-to-one correlation between electrochemical data and metastable
pits. Statistical analysis of breakdown potentials from PD-CLIP testing on aluminum disks shows good correlation to pitting potentials determined from more traditional potentiodynamic polarization testing. Induction time data from PS-CLIP data indicate a decrease in average induction time (thus increase in germination rate) as the applied potential is increased. These results demonstrate the applicability of CLIP testing to the study of localized corrosion initiation in both thin film and bulk materials. The CLIP technique has the ability to collect distributions of data from a single experiment, allows for selectively activating weak links on a sample surface and provides both potential and current signatures related to localized breakdown and repassivation.

ACKNOWLEDGEMENTS

Michael Martinez for performed the experiments described in this paper and aided in the design and development of the capillary based test cell for exposing small areas of the working electrode. Charles Barbour developed the techniques necessary for evaporation of the aluminum thin film specimens and formation of the aluminum oxides.

This work was supported by the United States Department of Energy under Contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

Technique development was funded by Sandia Labs MS&T Research Foundations. Work related to fabrication of Al and Al-Cu thin film specimens was funded by the office of Basic Energy Sciences.

REFERENCES

Figure 1. Schematic representation of the CLIP experiment. The control circuit is based on a standard 3-electrode cell and potentiostat with the addition of the CLIP resistor in series between the potentiostat and the working electrode. The separate monitoring circuit is necessary in order to track the actual potential of the sample. Battery powered electrometers and signal isolation are necessary to prevent ground loop effects.

Figure 2. Cu wire externally connected to an Al thin film through (a) a direct short and (b) a 10M-Ω resistor. Samples were exposed to aerated 0.050 M NaCl.

Figure 3. 99.999% Al in aerated 0.05M NaCl. Potentiostatic CLIP test with R-CLIP set to 200M-Ω and E-applied set to −0.650 V_{SCE}. (a) potential, (b) current.
Breakdown Potential (V-SCE)

0.0 0.5 0.6 0.65 0.7

% of Population

0 20 40 60 80 100

Figure 6. Cumulative distributions.

CLIP experiment (solid line), and potential response during PD- and potential response during PD-

Figure 5. 99.999% Al tested in 0.05 M.

Ignited and the AC component of the response is not shown.

(a) Active behavior. Causitive behavior at the solution interface has been potential drop across the various elements is distributed during (a) passive and potential.

Figure 4. Schematic representation of the CLIP circuit showing how the
Figure 7. Evaporated Al film with plasma grown oxide. PS-CLIP tests in 0.05M NaCl performed with R-CLIP = 200 M-Ω. (a) $I$ vs. $t$ for sample held at $-0.650\text{V}_{\text{SCE}}$, (b) $I$ vs. $t$ for sample held at $-0.575\text{V}_{\text{SCE}}$, (c) Cumulative distributions based on first 18 events at each potential, (d) $-\ln (1-P(t))$ based on 18 events. Germination rate of metastable pits scales with applied potential.

Figure 8. Evaporated Al film with plasma grown oxide in 0.05 M NaCl solution. PD-CLIP test performed with R-CLIP = 50 M-Ω and $dV/dt = 0.5$ mV/s. Three electrochemical transients (a) correspond to three metastable pits observed with optical microscopy (b).