MEASUREMENT AND MODELING OF CRACK CONDITIONS DURING THE ENVIRONMENT-ASSISTED CRACKING OF AN AL-ZN-MG-CU ALLOY

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Abstract

Although it is well known that Al-Zn-Mg-Cu alloys are susceptible to intergranular environment-assisted cracking (EAC) in some temper conditions, the relative contribution of hydrogen embrittlement (HE) and anodic dissolution (AD) to the crack advance process remains uncertain. This work reports the results of combining experimental and modeling data of crack potentials to help elucidate the role of AD to the EAC process. Micro-reference electrodes were used to make in situ measurements of the crack potential during Stage II cracking of AA 7050. The crack tip potential was –0.85 ± 0.05 V\textsubscript{SCE}; near-tip potential gradients were large, ~ 1 V/cm. Modeled crack potential distributions were strongly dependent on the value of the crack tip opening and the presumed presence or absence of a resistive salt-film at the crack tip. Although quantitative assessment of the contribution of AD to crack propagation is confounded by a lack of knowledge of the tip dissolution area, AD cannot be excluded as playing a significant role in the crack advance process of AA 7050.
Introduction

High-strength Al-Zn-Mg-Cu alloys are susceptible to intergranular (IG) environment-assisted cracking (EAC) in aqueous chloride [1]. However, the relative contribution of hydrogen embrittlement (HE) and anodic dissolution (AD) to the crack tip damage process during aqueous cracking are not known [1-3]. Mechanistic understanding is lacking, in part because the crack’s tip geometry, chemical and electrochemical conditions are not well characterized.

The goal of this research was to characterize the crack potential for an EAC-susceptible 7000-series aluminum alloy (AA) and the associated crack tip geometry and environment to help elucidate the contribution of AD to the crack propagation process. This objective was addressed by measurement of the crack potential via in situ reference electrodes during crack growth tests acquired under mechanical and electrochemical control combined with modeling of the steady-state crack potential distribution.

A one-dimensional (1-D) model was developed to assess the influence of crack geometry and tip and wall dissolution rate. Comparison of model results to measured profiles allows a determination of the applicability of various modeling assumptions. In this work, the effects of assumed tip geometry and salt film properties are presented.

Metal salts have been implicated as playing a significant role in the localized corrosion and cracking in some alloy-environment systems. Modeling work of Simonen et. al. [4] predicted that a resistive NiCl_2 film forms at the tip of long cracks of Ni-base alloys at the EAC threshold stress intensity. Artificial pits were used to determine the conductivity (κ) of NiCl_2 films, κ = 1.8x10^{-4} 1/Ω-cm [5] and in a following study, the measured Ni-salt conductivity gave the best prediction of the Stage I crack growth rate-stress intensity dependence when compared to experimental observations [4]. Pitting of high-purity Al at an applied electrode potential (E_{App}) between ~0.70 and ~0.52 V_{SCE} was characterized by the formation of an aluminum oxychloride film (Al(OH)_2Cl and Al(OH)Cl_2) on the electrode surface [6, 7]. These transitory compounds were also reported by Foley [8] to exist in pits of Al. Beck [9, 10] noted that a high resistance, bi-layer salt film covered the electrode surface at high anodic potentials (> +4 V_{SCE}) in concentrated AlCl_3 solutions. The salt film was proposed to consist of anhydrous AlCl_3 next to the metal surface and an outer hydrated layer (AlCl_3⋅6H_2O), the total salt film thickness is estimated to be ~100 nm for an overpotential of 1 V and metal dissolution rate of 0.1 A/cm^2. Note that this dissolution rate would correspond to a crack growth rate of 3.3x10^{-5} mm/s. Beck [9] reported that although Al salt films may form at E_{App} < +4 V_{SCE} and low salt concentrations, they are not stable due to hydrogen bubble-induced mixing within the cavity. However, cracks have more restricted mass transport than pits and thus a tip film may be more stable at the lower current densities, E_{App}, or in less concentrated bulk solutions than observed for pits. In the present work, the effects of tip film conductivity and thickness on the E_{Crack} profile was examined.

Experimental

Material

Thick (152 mm) plate of Aluminum Association (AA) 7050 was provided by the Aluminum Company of America (Alcoa) and heat treatments were performed at the Alcoa Technical

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Overpotential is defined as the difference between the actual potential measured (or applied) and the reversible potential.
Center. The chemical composition was Al-6.09Zn-2.14Mg-2.19Cu-0.11Zr-0.05Si-0.09Fe (wt. %). Blanks were resolutionized for 2 hr at 466°C, cold water quenched, stretched to relieve residual stresses, heated for 4 hr at 121°C for microstructure stabilization, and subsequently aged 20 hr at 118°C plus 12 hr at 154°C. This heat treatment simulates the peak aged (T651) condition. Some material was aged using single-step, non-commercial heat treatments consisting of aging for 6 or 12 hr at 163°C after the stabilization treatment. Material aged 6 hr at 163 °C was similar to T651 in its mechanical and EAC behavior where as the 12 hr aging treatment at 163°C produced a material with mechanical and EAC properties between that of T651 and overaged, EAC-resistant T7451 [11].

The resulting microstructure was partially recrystallized, with an elongated grain structure of variable size but typically 100 µm (S) x 200 µm (T) x 600 µm (L) [11]. Mechanical properties for T651 material were: $\sigma_{YS} = 530$ MPa (S), Elongation = 8 % (S), $E = 66$ GPa and $K_{IC} = 21.5$ MPa$\sqrt{m}$ (S-L) [11].

Aqueous EAC Testing and Crack Potential Measurements

Wedge-open loaded (WOL) specimens (12.7 mm thickness x 52.3 mm width x 50.8 mm height), machined in the S-L orientation with the crack plane at the T/4 position in the plate, were anodized 48 hr at +0.30 V$_{SCE}$ in 0.5 M Na$_2$CrO$_4$, natural pH. Fracture specimens were clamped in a plastic chamber to expose the crack and notch to the 0.5 Na$_2$CrO$_4$ + 0.05 M NaCl, pH 9.2 test solution. Figure 1 illustrates the test apparatus. The fracture mechanics procedures are described in detail elsewhere [11, 12]. The low [Cl$^-$]/high [CrO$_4^{2-}$] electrolyte permitted application of a range of $E_{App}$ without initiation of stable pitting (pitting potential, $E_{Pit} \approx -0.230$ V$_{SCE}$ for AA 7050-T651) and limited crack wake corrosion which facilitated post-test fractography. The alkaline bulk solution was also desirable for studying changes in crack solution pH [13]. A 3-electrode configuration and potentiostat were used to control the potential of the grounded WOL specimen.

WOL specimens were corrosion fatigue pre-cracked (10 Hz, $K_{max} = 10$ MPa$\sqrt{m}$, $R = 0.3$) in the test solution at –0.675 V$_{SCE}$, then rapidly loaded to a fixed crack mouth opening displacement (CMOD) in a computer-controlled servohydraulic test frame. During EAC growth, initial and final stress intensities ($K$) were $\approx$ 14-15 and 9-12 MPa$\sqrt{m}$, respectively. Crack length was calculated via an elastic compliance solution [14, 15] and corrected to the optically measured initial and final crack length [11]. Crack growth rate was determined by linear regression of crack length vs. time data.

Just prior to fatigue pre-cracking, 1.0 mm (Microelectrodes Inc., NH, USA) or 1.6 mm (Diamond General Development Corp., MI, USA) diameter reference electrodes were inserted into holes in the reservoir. From pump

To reservoir

Micro-reference electrode

Controlling reference electrode

Plexiglass chamber

Apply CMOD

CMOD gauge

Figure 1: Schematic of aqueous EAC test-cell illustrating location of micro-reference electrodes for in situ crack potential measurements.
top face of the fracture specimen such that the electrode’s sensing interface coincided with the crack plane. Figure 1 illustrates the position of the reference electrode used to measure the crack electrode potential ($E_{\text{Crack}}$).

Reference electrode signals, shielded from ambient electromagnetic interference, were conditioned through a high input impedance (100 GΩ) operational amplifier and recorded with a computer controlled data acquisition system at a rate of up to 1 point/s.

**Crack Potential Modeling**

Measured crack potential profiles were modeled in 1-D in order to assess the parameters that most influence the crack potential distribution. Parameters examined included crack tip geometry, crack tip and flank current density, and solution conductivity, the latter being a function of the presumed presence or absence of a precipitated film at the tip.

**Model Outline.** The quasi steady-state potential distribution was estimated using Ohm’s Law which states that a potential change ($\Delta E$) results from the passage of current ($I$) through a medium of finite resistance ($R$),

$$\Delta E = I \cdot R .$$  \hspace{1cm} (1)

Strictly, this methodology is only valid under conditions of uniform solution concentration because of the non-linear dependence of the potential gradient to concentration gradients [16]. Justification for the applicability of Ohm’s Law for modeling the crack potential in this system is provided in the discussion section.

Figure 2 illustrates the procedure and details the nomenclature. The voltage change or IR-drop across the $j^{th}$ element ($\Delta E_j$) is a function of the current through the element ($I_j$) and its resistance ($R_j$),

$$R_j = \frac{\Delta r_j}{\kappa_j A_j} ,$$  \hspace{1cm} (2)

where $\Delta r_j$ is the element thickness along the length of the crack, $\kappa_j$ is the element conductivity and $A_j$ the average cross-sectional area of the element.

The crack is represented by a smooth-sided trapezoid of length $L$ from the tip to the base of the notch, the CMOD and the crack tip opening displacement (CTOD). The crack angle ($\theta$) is then,

$$\theta = \tan^{-1}\left(\frac{CMOD - CTOD}{2 \cdot L}\right) .$$  \hspace{1cm} (3)

The average cross-sectional area of the $j^{th}$ element is,

$$A_j = (CTOD + 2r_j \tan \theta) \cdot b ,$$  \hspace{1cm} (4)
Figure 2: Crack geometry and nomenclature used in 1-D model of crack potential profile, $E_{\text{Crack}}$. Note that if the tip corrosion height exceeds CTOD, it is considered to include the necessary near-tip portion of the wall.

where $r$ is the distance from the crack tip and $b$ is the crack thickness ($i.e.$, WOL specimen thickness).

Current results from ion transport via diffusion, migration and convection. For the purposes of this 1-D analysis, ion movement, and thus current, was assumed to only occur parallel to the crack length. The total steady-state current passing through element $j$ is the net anodic current originating at the crack tip ($I_{\text{Tip}}$) plus the sum of anodic currents from the crack walls for all elements from the tip to the $j^{th}$ element,

$$I_j = I_{\text{Tip}} + 2 \cdot \sum_{k=1}^{j-1} i_{\text{wall},k} \cdot A_{\text{wall},k} + (1/2) \cdot 2 \cdot i_{\text{wall},j-1} \cdot A_{\text{wall},j-1} + (1/2) \cdot 2 \cdot i_{\text{wall},j} \cdot A_{\text{wall},j},$$

(5)

where $i_{\text{wall},k}$ is the $k^{th}$-element wall current density and $A_{\text{wall},k}$ is half the total wall area of that element ($= \Delta r_k \cdot b$). The last two terms in equation (5) account for half of the wall current from the element $j$ as well as the preceding element, $j-1$.

The single boundary condition imposed was that the potential at the crack mouth was fixed at $E_{\text{App}}$ consistent with the experimental condition, in this work $-0.495 \text{ V}_{\text{SCE}}$. The average electrode potential at the $j^{th}$ element is then $E_{\text{App}}$ minus the sum of the potential drops across each element from the crack mouth to the $j^{th}$ element. The crack tip current was iterated such that $E_{\text{Tip}}$ was consistent with observed values ($-0.80$ to $-0.90 \text{ V}_{\text{SCE}}$).

Faraday’s Law was used to determine the crack growth rate due to Al dissolution, $da/dt_{\text{diss}}$,

$$\left(\frac{da}{dt}\right)_{\text{diss}} = \frac{i_{\text{Tip}} M}{z F \rho},$$

(6)

where $M$ is the atomic weight of Al ($26.98 \text{ g/mole}$), $z$ is the valence ($3 \text{ eq./mole}$), $F$ is Faraday’s constant ($96500 \text{ C/eq.}$) and $\rho$ is density of Al ($2.7 \text{ g/cm}^3$). A corrosion front height of 1 $\mu$m (multiplied by the crack thickness, $b$) was used to calculate the crack tip current density ($i_{\text{Tip}}$) subsequently used in equation (6).
Crack Geometry. Two significantly different crack tip topologies were examined for their influence of the crack potential distribution: blunt vs. sharp.

**Blunt Crack Tip Geometry** - A relatively open or blunt crack tip geometry was determined for the present experimental condition from the work of Dean and Hutchinson [17] on the elastic-plastic analysis of quasi-static cracks. Based on the assumption that the change in the mechanical driving force with crack extension is negligible, as in, for example, dissolution-based crack growth [4, 18], then the crack opening \( \delta \) at distance \( r \) from the crack tip is,

\[
\delta = \frac{\beta \sigma_0 r}{E} \ln \left( \frac{eR}{r} \right).
\] (7)

Here, \( \beta \) is a constant approximately equal to 5, \( \sigma_0 \) is the yield stress, \( E \) the elastic modulus, \( e \) is the natural logarithm base (2.7183) and \( R \) is a parameter that scales approximately with the plastic zone size [18],

\[
R = c \left( \frac{K}{\sigma_0} \right)^2,
\] (8)

where \( c \) is another constant (~ 0.28) and \( K \) is the stress intensity.

Dean and Hutchinson [17] used finite element analysis to calculate the \( \delta \) vs. \( r \) relationship in plane strain Mode I loading of an elastic-perfectly plastic material (work hardening exponent, \( n = \infty \)) and two cases involving non-linear work hardening materials (\( n = 3 \) and 10). Poisson’s ratio was 0.3 in all cases.

The following mechanical properties were applied to the results of Dean and Hutchinson [17] for all three cases of work hardening: \( \sigma_0 = 530 \) MPa, \( E = 66 \) GPa, \( K = 14 \) MPa \( \sqrt{m} \). Because aluminum alloys have \( n \sim 5 \) [19], and there were relatively small differences in the \( \delta-r \) curves for the \( n = 3 \) and \( n = 10 \) case, the results for the former condition were used to determine \( \delta \) over the first 32.5 \( \mu m \) from the crack tip. A smooth-sided trapezoid was used to represent the remainder of the crack opening as a function of distance from the crack tip.

**Sharp Crack Tip Geometry** - Evidence exists to suggest that intergranular EA cracks may not be well represented by the type of analysis presented above. Somerday et al. [20] report that IG EAC cracks in \( \beta \)-Ti exhibited crack surface opening displacement (CSOD) of 300 nm at \( r = 3 \) \( \mu m \) as opposed to CSOD ~ 1.25 \( \mu m \) for a transgranular crack at the same \( K \) level. Deshais and Newcomb [21] examined cracks within AA 7010 (Al-6.15Zn-2.34Mg-1.59Cu) in a transmission electron microscope. Their non-stressed TEM foils had 50 nm wide corrosion fronts that were restricted to the grain boundary precipitate free zone.

In the present work, cracks with very sharp tips were modeled as smooth-sided trapezoids with a CTOD of either 50 or 250 nm.

**Model Parameters.** The values used to model the E\(_{\text{Crack}}\) profile were based primarily on experimentally determined values. As mentioned above, the crack mouth potential, taken to the base of the machined notch, was fixed at \( E_{\text{App}} = -0.495 \) V\(_{\text{SCE}}\). Crack wall current density (i\(_{\text{wall}}\)) was either zero or 5 \( \mu A/cm^2 \) (determined for AA 7050 in quiescent CrO\(_4^{2-}/Cl^-\) solution using standard electrochemical techniques [22]) and was not varied as a function of position within the crack.
The bulk test solution conductivity was 0.0614 1/Ω-cm; simulated, concentrated (but not saturated) crack solutions [23, 24] had \( \kappa = 0.08 \) to 0.16 1/Ω-cm. The conductivity of wetted Al-OH-Cl-Cr precipitates prepared from saturated solutions was 0.07 to 0.14 1/Ω-cm. Conductivity was measured with a YSI Model 32 Conductance Meter and a calibrated, temperature-compensated YSI electrode #3440. To probe the influence of a highly resistive tip film on the \( E_{\text{Crack}} \) profile, 20 nm, 1, 10 and 100 μm thick films of low conductivity (\( \kappa = 0.01 \) and \( 10^{-4} \) 1/Ω-cm) were modeled as existing at the tip. The range of conductivity examined, \( \kappa = 10^{-4} \) to 0.1, was chosen such that the range of conditions from resistive metal salts such as NiCl\(_2\) [4] to conductive aqueous solutions was considered.

Additional model parameters include: \( L = 1.7 \) cm, \( b = 1.27 \) cm, CMOD = 110 μm. Element thickness (\( \Delta r \)) was 5 μm except when a 20 nm or 1 μm thick crack tip film was incorporated into the model in which case \( \Delta r \) was reduced to 20 nm or 1 μm, respectively, for the first element.

### Results

**Aqueous Crack Growth Behavior of EAC-Susceptible AA 7050**

Environmental crack growth was produced in AA 7050 stressed at fixed CMOD in aqueous chromate-chloride test solution. Key observations, presented in detail elsewhere [11-13], are provided for clarity. Slow rate incubation crack growth (1-10x10\(^{-7}\) mm/s) usually preceded accelerated steady state Stage II crack propagation (1-9x10\(^{-5}\) mm/s) at \( E_{\text{App}} \geq -0.495 \) V\(_{\text{SCE}}\). Crack growth kinetics given are for AA 7050-T651. Material aged 6 hr at 163 °C exhibited similar EAC-behavior at the T651 temper whereas 12 hr/163 °C aged material displayed improved resistance to crack propagation. For example, at \( E_{\text{App}} = -0.445 \) V\(_{\text{SCE}}\), steady state \( da/dt \) was \( \sim 5 \) to 10x10\(^{-5}\) mm/s for the T651 and 6 hr/163 °C aged material and approximately 10 to 20x slower for the 12 hr/163 °C specimen (\( \sim 4 \times 10^{-6} \) mm/s) [11].

Small gas bubbles, likely H\(_2\), emanated from crack wakes during fast-rate EAC, as reported previously [25]. Bubbles were not observed during the slow growth rate incubation period.

EAC in AA 7050-T651 was always intergranular for the S-L crack orientation. In addition to fracture surface analysis by SEM, metallographic cross-sections revealed that EAC growth occurred along high-angle grain boundaries, predominantly between unrecrystallized grains [11, 13]. There was no difference in the crack path for slow-rate and fast-rate cracking at the various levels of \( E_{\text{App}} \).

**Crack Potential Measurements**

The crack electrode potential during EAC in aqueous chromate-chloride solution varied from the external applied value, \( E_{\text{App}} \). Figure 3 shows in situ reference electrode measurements of the crack potential for three separate fracture tests conducted with EAC-susceptible AA 7050 cracking at \( E_{\text{App}} \sim -0.50 \) V\(_{\text{SCE}}\). When the reference electrode was very near the crack tip (< 0.5 mm) the measured potential was –0.90 to -0.80 V\(_{\text{SCE}}\); approximately 0.35 V of IR-drop was observed at the tip. As the crack propagated away from the in situ reference probe, crack wake polarization was observed (i.e., \( E_{\text{Crack}} \) approached \( E_{\text{App}} \)). Figure 3 indicates that the majority of
Figure 3: Crack potential as function of distance from the crack tip for three different EAC tests. $E_{\text{tip}}$ was $-0.90$ to $-0.80$ V$_{\text{SCE}}$. Note the steep potential gradient ($\sim 1$ V/cm) localized near the crack tip region, most potential drop occurred over the first 3 mm from the crack tip whereas crack flanks were almost completely polarized to $E_{\text{App}}$. Inset: Crack potential as function of time at the beginning of an EAC test. Note the change in $E_{\text{Crack}}$ at $t < 0$ hr when fatigue crack ($E_{\text{App}} = -0.675$ V$_{\text{SCE}}$) intersects probe hole where in situ reference electrode was located. $E_{\text{Crack}}$ increases with time as the crack grows and tip moves away from stationary reference probe, at $t = 9$ hr, the probe is $\sim 0.7$ mm from the tip. At the beginning of the EAC test, repeated crack tip activation and repassivation occurred; during this period slower $da/dt$ ($2.0 \times 10^{-5}$ mm/s) was observed, higher rate $da/dt$ ($5.4 \times 10^{-5}$ mm/s) was established at 14 hours. AA 7050 aging condition and $E_{\text{App}}$ are shown in the legend, 0.5 M Na$_2$CrO$_4$ + 0.05 M NaCl, pH 9.2 or 6.8, $K = 10$ to 14 MPa $\sqrt{m}$.

the IR-drop was limited to within 3 mm of the crack tip resulting in a potential gradient $\sim 1$ V/cm or greater near the tip.
Figure 3 also demonstrates that active crack potentials develop during establishment of the steady-state crack growth. For the specimen aged 6 hr at 163°C (—), repeated activation and repassivation of the crack tip region near the reference is indicated by the long duration potential transients during the early portion of the test (see Figure 3 inset). During the first five hours of this test, slower crack growth ($2 \times 10^{-5}$ mm/s) was observed. Faster crack growth ($5.4 \times 10^{-5}$ mm/s), fully established at approximately 14 hours, coincided with the development of continuously active crack tip potentials (i.e., crack tip polarization and repassivation events were not observed after higher rate crack propagation was established). By that point, the crack tip was ~0.7 mm from the in situ reference probe.

The crack potential profiles for the three tests shown in Figure 3 exhibit considerable scatter despite similar $E_{\text{App}}$ amongst the tests. The local potential varied even within a single test in which steady-state cracking was well established. This phenomenon can be seen in the data for the T651 specimen (○) just before and after the in situ probe was 2 mm from the crack tip. With increasing distance from the crack tip, $E_{\text{Crack}}$ decreased 60 mV from $-0.60$ V$_{\text{SCE}}$ and subsequently increased again to $-0.60$ V$_{\text{SCE}}$ at $r \sim 2.5$ mm. Such transient phenomena were not included in the modeling work.

Crack Potential Profile Modeling

One-dimensional modeling reveals that the parameters that most influence the crack potential distribution are: (1) crack tip geometry, and (2) the presence of a resistive crack tip film, whereas the contribution of the crack wall current to the IR-drop is relatively minor.

Crack Tip Geometry – Blunt vs. Sharp. Figure 4 shows the calculated crack opening displacement ($\delta$) as a function of distance from the crack tip ($r$) for AA 7050. For the blunt crack, the results for $r \leq 32.5$ µm are based on the finite element analysis of Dean and Hutchinson [17] for quasi-static crack growth under conditions of small scale yielding with the mechanical properties given above. Sharp cracks with CTOD = 50 or 250 nm are shown for comparison.

Calculated crack potential profiles for blunt and sharp cracks are shown in Figure 5. For a constant tip dissolution rate ($I_{\text{Tip}}$), the blunt crack potential profile appears shallow in comparison to the sharp tip scenarios and total IR-drop at the tip was ~50% of that for the 50 nm CTOD case. Comparison with the experimental data shown in Figure 3 indicates that the blunt $E_{\text{Crack}}$ profile model data do not qualitatively reproduce the experimental results, particularly the steep potential gradient near the tip.

In contrast to the blunt crack condition, model $E_{\text{Crack}}$ profiles for sharp cracks (CTOD = 50 and 250 nm) appear to well represent the experimental data, closely reproducing the large near-tip potential gradient. With constant $\kappa$ equal to that of the bulk solution and $I_{\text{Tip}} = 0.21$ A/cm$^2$ (assuming a corrosion front height of 1 µm), 0.355 and 0.322 V of IR-drop was generated for CTOD = 50 and 250 nm, respectively. This corrosion rate translates to $da/dt_{\text{diss}} = 7.2 \times 10^{-5}$ mm/s, consistent with the observed $da/dt$ for material aged to the T651 temper or 6 hr at 163 °C at $E_{\text{App}} = -0.495$ V$_{\text{SCE}}$ (2 to $8 \times 10^{-5}$ mm/s). The applicability of a 1 µm high corrosion front is discussed below.

Crack Flank Current. The passive current density of AA 7050 in the CrO$_4^{2-}$-inhibited bulk environment was 5 µA/cm$^2$ and was independent of potential in the range of interest (free corrosion potential = -0.80 V$_{\text{SCE}}$ and $E_{\text{App}} < E_{\text{Pit}}$). The influence of the wall dissolution current
on the $E_{\text{Crack}}$ is shown in Figure 5 for the case where CTOD = 50 nm. The crack wall current increased the IR-drop by $\sim 10\%$ (i.e., IR-drop to the crack tip increased 47 mV for $\sim 0.40$ V total IR-drop). Passive dissolution of the crack walls does not appear to be a major contributor to IR-drop within the crack. However, for completeness, all subsequent modeling results presented in this work include constant $i_{\text{wall}} = 5$ µA/cm$^2$ along the length of the crack.

**Crack Tip Film or Precipitate.** Figure 6 summarizes the $E_{\text{Crack}}$ profile for a sharp crack (CTOD = 250 nm) with tip films of different thickness and specific resistance. If a thick (10 or 100 µm), low conductance ($\kappa = 0.01$ or $10^{-4}$ 1/Ω-cm) crack tip film is included in the model, the $E_{\text{Crack}}$ profile was very poorly represented. If such a thick, low conductivity film were present at the tip essentially all of the IR-drop would occur across the film and very little along the length of the crack. Experimental results shown in Figure 3, however, indicate that the potential change within the crack occurs on a millimeter length scale and were not limited to the first 10 or 100 µm from the tip. As such, these results suggest that a thick, resistive film was probably not present within the AA 7050 EA cracks.

In contrast to thick films, a very thin, highly resistive film cannot be excluded as existing at the tip. For a 20 nm thick layer of $\kappa = 10^{-4}$ 1/Ω-cm at the tip, there was little change in $E_{\text{Crack}}$ in comparison to the non-filmed case. Obviously, the additional resistance provided by the thin film is small relative to that along the entire length of the crack.
Figure 5. Calculated $E_{\text{Crack}}$ profile for different crack tip geometry and wall current density ($i_{\text{wall}}$) for constant solution $\kappa$ and $I_{\text{Tip}}$. Inset summarizes $E_{\text{Tip}}$ for different model conditions. A blunt crack does not produce a large potential gradient near tip. Although there was only small a difference in the overall potential profile for the two sharp tip scenarios the IR-drop was 45 mV greater for the tighter tip, all else being equal. Incorporation of $i_{\text{wall}} = 5 \, \mu\text{A/cm}^2$ into model increases IR-drop by approximately 10% in comparison to the case wherein the crack walls are completely passive. Model conditions: $E_{\text{App}} = -0.495 \, \text{V SCE}$, $I_{\text{Tip}} = 2.66 \times 10^{-5} \, \text{A}$, $\kappa = 0.0614 \, 1/\Omega\cdot\text{cm}$ and $i_{\text{wall}} = 0 \, \text{A/cm}^2$ unless otherwise noted.

Another means of examining the feasibility of crack tip film thickness and conductivity is to compare experimental and model crack potentials at a constant position within the crack. Figure 7 summarizes $E_{\text{Crack}}$ at $r = 1 \, \text{mm}$ for the model cases (Figure 6) and the experimental data (Figure 5). It is clear from Figure 7 that if a very resistive film ($\kappa = 10^{-4} \, 1/\Omega\cdot\text{cm}$) were present at the tip, it would necessarily be very thin. On the other hand, a substantially less resistive film $\sim 10 \, \mu\text{m}$ thick cannot be excluded based on the 1-D modeling results presented here.

Discussion

Crack Potential Measurements

The crack electrode potential during EAC of AA 7050 in aqueous chromate-chloride solution varied from the external applied value (Figure 3), particularly during high rate $da/dt$. The steep
crack potential gradient measured with the in situ reference electrode indicates ion movement within the crack: cations are driven out of the crack while anions are attracted to the tip. In addition, the fact that there is a net current (and hence IR-drop) within the crack indicates that the anodic reaction at the tip is not balanced by local cathodic reactions. Anode and cathode are separated in this system.

The variability in crack wake potential profile during steady state da/dt shown in Figure 3 is likely related to: (1) metastable localized corrosion events near the in situ electrode, (2) changes in crack resistance due to H₂ gas bubble formation and emission [11, 25], and/or (3) corrosion product accumulation and possible re-dissolution.

**Crack Potential Modeling**

**Model Limitations.** Ion movement results from solution potential and chemical concentration gradients, ignoring convection, a valid assumption for stress corrosion cracks [26]. The model developed for this work assumes that the ion movement and, therefore, crack current are

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Figure 6: Calculated $E_{\text{Crack}}$ profile for a sharp crack with tip surface film of varying thickness and conductivity. Model conditions that generally reproduce the potential profile observed experimentally include (1) no film (i.e., constant $\kappa$), (2) a very thin film (20 nm) of $\kappa \leq 10^{-4}$ $\Omega$-cm, and (3) a 1 to 100 µm film of $\kappa = 0.01$ $\Omega$-cm. A thick, highly resistive film ($10^{-4}$ $\Omega$-cm) does not duplicate the observed potential profile because the majority of the potential drop occurs across the film as opposed to along the length of the crack. Model conditions: $E_{\text{App}} = -0.495$ V SCE, $E_{\text{Tip}} = -0.90$ V SCE, CTOD = 250 nm, $i_{\text{wall}} = 5$ µA/cm² and $\kappa = 0.0614$ $\Omega$-cm except for noted tip films.
Figure 7: Crack potential at r = 1 mm for model results (Figure 6) and experimental data (Figure 3). In addition to the constant $\kappa$ case, incorporation of a thin 20 nm film of $\kappa = 10^{-4}$ $1/\Omega$-cm or a thicker (1 to 10 $\mu$m) film of $\kappa = 0.01$ $1/\Omega$-cm predicts $E_{\text{Crack}}$ at 1 mm within the observed range. A thick (1 to 100 $\mu$m), highly resistive tip film ($10^{-4}$ $1/\Omega$-cm) does not reproduce experimentally measured potentials at this position. Model conditions: CTOD = 250 nm, $E_{\text{App}} = -0.495$ V SCE, $E_{\text{Tip}} = -0.90$ V SCE and $\kappa = 0.0614$ $1/\Omega$-cm at all positions within crack except for noted tip films.

dominated by migration as opposed to diffusion. In other words, it is assumed that the potential gradient dominates any concentration gradients effects in terms of the relative contribution to steady-state ion flux. The non-linear dependence of the electrode potential on the concentration and the concentration gradient of all solution species [16] make such an assumption necessary for the simplified $E_{\text{Crack}}$ model used in this work. Stewart [27] suggested that the following criteria are necessary to satisfy the assumption that the solution potential is independent of concentration and concentration gradients:

1. There is no diffusional potential. This condition is met if the diffusivity is constant for all anions and cations.
2. The electrical flux must not depend on chemistry or position. This condition can be met if the tip and/or wall fluxes are constant.
3. Conductivity must be a constant and cannot vary with position. This condition can be met if there is a strong supporting electrolyte.

Obviously, the actual case does not strictly satisfy all of the above criteria. Concentration gradients do exist in a real crack [24], hydrogen ions have higher mobility than other species and the conductivity is not constant throughout the crack. However, the bulk solution (0.5 M Na$_2$CrO$_4$ + 0.05 M NaCl) is relatively concentrated and acts as a large supporting electrolyte. In addition, the difference in conductivity between the crack tip region and mouth is small, at
most a factor of $\sim 3x$ based on measurements of the bulk and simulated crack tip solution conductivity. Finally, the model implements constant crack tip and wall currents.

The 1-D model necessarily assumes that the (ionic) current is parallel to the crack length at all positions within the crack. In other words, ion flow out the side of the crack is assumed negligible. This assumption does not strictly apply for the experimental work in which crack sides were not masked to prevent transverse ion movement. If appreciable current flows perpendicular to the crack front the anodic tip current would be underestimated by the 1-D model implemented in this work.

**Solution Conductivity and Crack Wall Current.** Potential gradients facilitate steady-state concentration gradients. The crack solution chemistry within Al alloys becomes acidic (pH $\sim 3$) and concentrated in alloy dissolution products and anions from the bulk solution [13, 23, 28-32]. However, accounting for the increase in solution conductivity did not have a strong effect on the modeled crack tip current. This is a direct result of the bulk test solution being a strong supporting electrolyte. The bulk electrolyte and relatively concentrated crack solution have similar conductivity ($\kappa = 0.061$ and $0.08$ to $0.16$ $1/\Omega$-cm, respectively). Because IR-drop scales with $I_{\text{Tip}}/\kappa$ (Eq. 1, 2 and 5), for a constant $E_{\text{Tip}}$, the increase in $I_{\text{Tip}}$ is at most be $2.7x$ assuming the crack were uniformly filled with solution of $\kappa = 0.16$ vs. $0.061$ $1/\Omega$-cm. The exception may be the presence of a resistive film at the tip.

Crack wall passive dissolution currents contribute approximately 10% of the IR-drop observed in the corrosion-inhibited system (Figure 5). Although not insignificant, passive dissolution of the crack walls was not a major contributor to potential drop within the crack. The latter appears to be dominated by the crack tip geometry.

**Significance of Crack Potential Modeling.** One-dimensional modeling revealed that the parameters that most influence the crack potential distribution are: (1) crack tip geometry, and (2) the presence of a resistive crack tip film.

Comparison of the crack potential profile for a blunt crack tip geometry (Figure 5) with the experimental data shown in Figure 3 indicates that a blunt crack does not closely reproduce the experimental results. These results suggest that IG EAC cracks in AA 7050 are likely sharper than predicted by elastic-plastic analysis. This interpretation is consistent with the observations of Somerday et. al. [20] who examined the crack surface opening displacement (CSOD) of a $\beta$-Ti alloy while under load in a scanning electron microscope. They reported that where as transgranular fatigue cracks attained blunt-like crack tip morphology similar to that predicted via continuum elastic-plastic analysis with small scale yielding, intergranular EA cracks were much sharper. For an IG crack, the CSOD was $\sim 300$ nm at $r = 3$ mm [20]. In addition, Deshais and Newcomb [21] reported that IG EAC cracks of AA 7010 had $\sim 50$ nm wide corrosion fronts. The corrosion was restricted to the grain boundary precipitate free zone. Unfortunately, the exact nature of $\delta$ vs. $r$ is unknown because the loading condition during the cracking growth portion of the study was not replicated in the foil during the TEM investigation (i.e., TEM foils were not stressed in situ). The results of the 1-D crack potential modeling suggest that IG EA cracks in AA 7050 may also be significantly sharper than predicted via elastic-plastic analysis.

The choice of the crack tip corrosion area deserves discussion. Is a tip corrosion area of 1 $\mu$m (multiplied by the crack thickness, $b$) realistic? It is not unreasonable. Consider the case of a sharp crack with CTOD = 250 nm. Then 375 nm of wall on either side of the tip would also have to be considered to be corroding at the rate predicted by the $E_{\text{Crack}}$ model results (i.e., $I_{\text{Tip}}$ ~
0.1 A/cm²). Recall that observed crack growth rates were 2 to 8\times10^{-5} \text{ mm/s} at \text{ -0.495 V SCE} \text{ [11, 13]. Assuming a crack growth rate} = \text{5x10^{-5} mm/s, the amount of penetration or blunting of the near-tip wall would be 250 nm in the time it took the crack to advance 375 nm after which the wall is assumed to repassivate. Unclear is whether \sim 250 nm of near-tip wall corrosion would be sufficient to cause crack arrest due to blunting. If the dissolution zone is approximately 1 \mu m high, then the E_{Crack} modeling work suggests that anodic dissolution dominates crack growth.

Deshais and Newcomb [21] reported that cracks grown in NaCl solution in a similar Al alloy had \sim 50 nm high corrosion fronts. These authors also suggest that corrosion of as little as a 200 nm wide resulted in blunting and no crack growth. The problem, of course, is that if the corrosion front height is taken to be 50 nm, based on I_{tip} required to generate the observed \sim 0.35 V of IR-drop, calculated \text{da/dt}_{diss} is 20 to 40x greater than actual crack growth. This interpretation would imply that the effective crack resistance is 20 to 40x greater than calculated for a smooth-sided, wedge-shaped crack filled with a conductive electrolyte.

Flank surface roughness, hydrogen bubbles and corrosion product build-up could all contribute to increasing the crack solution resistance. Although not highly bifurcated, the IG crack path is tortuous [11]. An irregular crack path would essentially increase the distance over which the ions travel for the same “crack length”. Therefore, a smaller current would be required to develop an equivalent IR-drop in a tortuous crack in comparison to one with smooth walls. Hydrogen bubbles and solid corrosion products may also increase the crack resistance by providing local regions of high resistance, physically restricting portions of the crack to ion movement. The relative contribution of these factors to the overall resistance is uncertain, but it is not clear that collectively they could account for a 20 to 40 fold increase in crack resistance.

The 1-D model results presented in Figure 5 and 6 indicate that there are a host of crack geometry-environment combinations that generally provide good agreement with observed potential distribution. One such set of conditions is illustrated in Figure 8 where the experimental E_{Crack} profiles shown in Figure 3 are bounded if a 2 mm region adjacent to a sharp tip (CTOD = 250 \mu m) is presumed to contain a solution or precipitate of \kappa = 0.03 or 0.1 1/\Omega-cm. Such a scenario may represent the situation in which precipitated aluminum oxychloride and/or hydroxide forms over a significant distance back from the crack tip. Chloride and Cr^{6+}-bearing aluminum hydroxides at \text{pH} \sim 3 had conductivity’s ranging from 0.07 to 0.16 1/\Omega-cm. Given the very restricted crack geometry and sharp tip suggested by the steep potential gradient, it is possible that the near-tip solution is saturated in Al reaction products.

As noted above, Al pits at high potentials become saturated in dissolution products [6-8, 33]. Evidence suggests that the crack tip solution is concentrated and may also become saturated in dissolution products. Cooper \text{et. al.} observed \sim 1 \text{ mole/L Al}^{3+} near the tip of AA 7050-T651 undergoing high-rate EAC in chromate-chloride solution [24]. Nguyen and coworkers also reported a concentrated crack tip environment for a similar alloy cracking at anodic potentials in NaCl solution [28]. Newman developed a 1-D model similar to the one described here for assessing the crack potential and derived an analytical equation for the concentration of metal ions at the tip (C_{Tip}) of a smooth-sided, wedge-shaped crack [34],
Figure 8: Experimental and calculated $E_{\text{crack}}$ profiles. Model results are for a sharp crack of constant $\kappa$ or a crack containing a 2 mm long region extending back from the tip of either $\kappa = 0.10$ or $0.03 \, \Omega\cdot\text{cm}^{-1}$. Both of the latter conditions may represent an Al-OH-Cl-Cr precipitate containing excess water. These two cases bound the experimental data at most positions within the crack. Calculated crack growth rate due to Al dissolution is comparable to observed $\text{da/dt}$ for a 1 µm corrosion front height. Model conditions: CTOD = 250 nm, $E_{\text{App}} = -0.495 \, V_{\text{SCE}}$, $E_{\text{CT}} = -0.90 \, V_{\text{SCE}}$, $i_{\text{wall}} = 5 \, \mu\text{A/cm}^2$, and $\kappa = 0.0614 \, \Omega\cdot\text{cm}^{-1}$ except where noted.

Modeling cannot completely discern the crack conditions. However, it can provide insight into the likely nature of the crack tip geometry and allow the exclusion of some film thickness-resistance combinations on the basis that they do not replicate measured potential profiles.
Hydrogen Embrittlement vs. Anodic Dissolution. Controversy over the crack tip damage mechanism of Al-Zn-Mg-Cu alloys persists despite extensive investigation [1, 36]. Hydrogen is likely responsible for cracking in humid air where dissolution can be excluded based on the absence of a condensed water layer necessary for electrochemical reactions [37]. Substantial evidence exists implicating HE as the dominant process in the aqueous EAC of these alloys [1, 36]. The Stage II crack path is similar under humid air and aqueous conditions [11]. In addition, crack growth kinetics in hot, humid air (60 °C, 90 % relative humidity) and chromate-chloride solution at $E_{\text{App}} = -0.495 \ V_{\text{SCE}}$ (at room temperature) are comparable for AA 7050-T651 [37]. For the measured crack tip potential and pH, the overpotential for the hydrogen evolution reaction is approximately -0.40 V. Obviously, there is a significant driving force for the production of atomic hydrogen. H-uptake during EAC of AA 7050-T651 in chromate-chloride solution was reported, including a positive correlation between crack wake H concentration and crack growth rate [11, 13]. However, dissolution cannot be ruled out as playing a significant role in the EAC process. At the very least, dissolution is responsible for generation of the critical crack tip chemistry. Furthermore, the crack tip current appears to be substantial. Even with very sharp tip geometry, crack potential modeling suggests that the tip dissolution rate is $\sim 0.1 \ A/cm^2$, equivalent to $\frac{d\sigma}{dt\text{diss}} \sim 3 \times 10^{-5} \ mm/s$. Thus, the observed crack growth rates for AA 7050-T651 (2 to $8 \times 10^{-5} \ mm/s$ at $E_{\text{App}} = -0.495 \ V_{\text{SCE}}$) could be justified on the basis of dissolution alone. Nonetheless, the evidence for hydrogen effects from companion [11, 13, 37] and other studies [2, 38] is compelling. It would thus appear that for AA 7050 in chromate-chloride solution, anodic dissolution and hydrogen embrittlement both contribute to crack propagation, although the relative contributions cannot be unequivocally determined. Based upon this work, the contributions of AD and HE appear to be on the same order of magnitude.

Conclusions

1. A large potential gradient ($\sim 1 \ V/cm$) exists near the tip of AA 7050 environment-assisted cracks. Tip potentials were $-0.90$ to $-0.80 \ V_{\text{SCE}}$ when $E_{\text{App}} = -0.495 \ V_{\text{SCE}}$.

2. Intergranular environment-assisted cracks in Al-Zn-Mg-Cu alloys are likely very sharp (CTOD $\sim 250 \ nm$); blunt cracks of the form predicted via continuum mechanics with small scale yielding do not generate sufficient IR-drop nor reproduce the observed $E_{\text{Crack}}$ distribution, particularly the steep potential gradient near the tip.

3. A highly resistive crack tip film is not necessarily required to achieve experimentally observed IR-drop; a tight, sharp crack can generate a steep potential gradient and significant IR-drop. However, unless a large crack tip corrosion area is assumed to exist, calculated crack growth rates based on Al dissolution significantly overestimated observed $d\sigma/dt$. The effective crack resistance may be greater than suggested by a smooth-sided crack filled with conductive electrolyte.

4. Very thin ($\sim 20 \ nm$), highly resistive films ($\kappa \sim 10^{-4} \ 1/\Omega$-$cm$) or thicker (1 to $10 \ \mu m$) moderately resistive films ($\kappa \sim 10^{-2} \ 1/\Omega$-$cm$) cannot be excluded as possibly existing at the crack tip of this alloy.

5. Anodic dissolution contributes significantly to the Stage II crack growth of AA 7050 in aqueous chloride solution.
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