THE EFFECT OF ATMOSPHERIC CORROSION ON ENVIRONMENTAL FATIGUE CRACK PROPAGATION AND ITS INHIBITION

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Abstract
Age-hardenable aluminum alloys used in aerospace structures are susceptible to environment assisted fatigue crack propagation (EFCP). There has been no controlled examination of thin film electrolyte, typically produced by atmospheric exposures, effects on EFCP or inhibition of such cracking. The goal of this research is to understand EFCP and inhibition for atmospheric conditions of important aerospace alloys: 7075-T651 (Al-Zn-Mg-Cu) and C47A-T8 (Al-Cu-Li). A candidate chromate (CrO$_4^{2-}$) replacement inhibitor, molybdate (MoO$_4^{2-}$), is examined. MoO$_4^{2-}$ effectively inhibits EFCP in 7075-T651 stressed during full immersion in chloride solution; as understood by hydrogen environment embrittlement and film stability where MoO$_4^{2-}$ promotes crack tip passivity, thus reducing H uptake. MoO$_4^{2-}$ inhibition is promoted by reduced loading frequency and stress intensity range and potentials at or anodic to free corrosion. The inhibiting effect of MoO$_4^{2-}$ parallels that of CrO$_4^{2-}$, but is shifted to lower frequencies suggesting the Mo-bearing passive film is less stable under crack tip deformation than the Cr-bearing. MoO$_4^{2-}$ can fully inhibit EFCP by reducing crack growth rate to that of ultra-high vacuum. For slightly anodic potentials, full crack arrest occurs. This research aims to improve fatigue life prediction for safe and economic operations of aircraft.

Introduction
Age-hardenable aluminum alloys such as AA7075 and C47A, which are Al-Zn-Mg-Cu and Al-Cu-Li alloys, are selected for military and commercial aerospace structures because of their corrosion resistance and high strength to weight ratio. One major form of degradation in these alloys is fatigue, damage that accumulates with loading to cause the structure to fail. This damage is enhanced by the environment in which the structure is stressed and is referred to as environment-assisted fatigue.

Aluminum alloys in aerospace structures are susceptible to environment assisted fatigue crack propagation (EFCP) by hydrogen environment embrittlement (HEE)[1][9]. EFCP damage in water vapor and aqueous chloride solutions is attributed to the interaction between irreversible plastic deformation, tensile stresses, and atomic hydrogen (H) produced by chemical or electrochemical reactions all highly localized at the crack tip. Basically, HEE is initiated when O$_2$ is depleted within the crack solution causing the crack tip to become anodic with respect to the external surface and crack wake. The anodic tip preferentially corrodes and dissolved Al (Al$^{3+}$) reacts with water molecules creating H ions and through a cathodic reaction at the crack tip they become H atoms.[10][11] The hydrogen atoms then enter the fatigue process zone (FPZ) ahead of the crack tip by diffusion through the lattice. Interactions between the H trapped in the FPZ and local tensile stresses and dislocation structure cause embrittlement, enhancing fatigue crack propagation rate (da/dN) relative to inert gas and vacuum.

Much of the prior research conducted on EFCP was performed under full immersion in aqueous chloride solutions[7][12][19] in uncontrolled laboratory-moist air[8][13][14][16][17][19][20], or pure water vapor[6][7][21][22]. EFCP in these environments depends not only on the mechanical driving force for cracking, quantified by stress intensity range ($\Delta K=K_{max}-K_{min}$) and maximum stress ($K_{max}$ or $R=K_{max}/K_{min}$); but also on an environmental/chemical driving force. For full immersion, the environmental driving force is: (a) loading frequency ($f$), (b) amount of H embrittling the alloy which is controlled by the overpotential at the crack tip (an electrochemical parameter which is a function of crack tip pH and crack tip potential (E)), and (c) passivity (creates a protective passive film which is a barrier to H adsorption). Although aluminum alloys develop a passive film in aqueous solution, chloride ions (Cl$^-$) weaken the native Al passive film (Al$_2$O$_3$) allowing atomic H to more readily enter the alloy for embrittlement. For water vapor, the chemical driving force is an environmental exposure parameter which is defined by the ratio pure water vapor pressure to loading frequency ($P_{H_2O}/f$)[6][23][27].

For in-service aircraft none of these simplified laboratory circumstances accurately describe atmospheric conditions[28]. The atmosphere is neither made up of pure water vapor nor contains the small number of contaminants found in laboratory air. Rather, atmospheric exposure involves a complex number of constituents that include: nitrogen dioxide...
(NO₂), sulfur dioxide (SO₂), oxygen (O₂), ozone (O₃), and sodium chloride (NaCl) to name a few. The presence of these contaminating constituents causes deliquescence (dissolution of a solid by absorbed water vapor) at P_H₂O lower than that expected for simple condensation of water vapor. This creates a contaminated water layer or thin film electrolyte which can accelerate corrosion and possibly EFCP [29]-[31]. Given this and the lack of EFCP experimentation under thin film electrolyte conditions, current life predictions made from EFCP experimentation may not be accurate.

Chromate (CrO₄²⁻) addition to bulk chloride solution effectively inhibits EFCP in AA7075 stressed under full immersion by reducing da/dN; but only below a critical da/dN (mm/cyc) at which point da/dN increases with increasing frequency (Hz) at a lower bound critical f (f_critLB) where inhibition is no longer observed and da/dN behavior returns to that of aqueous chloride solution. The proposed mechanism of CrO₄²⁻ inhibition is the film rupture-hydrogen embrittlement interaction [2]-[4][32]-[34], where a Cr-bearing passive film forms on the crack tip and is more resistant to mechanical deformation and Cl⁻ attack than the native passive film (Al₂O₃). This enhanced passive film reduces/prevents the production and uptake of embrittling H; thus decreasing EFCP. The passive film can be destabilized mechanically when deformation is sustained above a critical crack tip strain rate (ε_crit), a material-environment property. This destabilization of the Cr-bearing passive film causes inhibition to be compromised and H production/uptake to increase. Crack tip strain rate (ε_cyc) has been experimentally determined to depend proportionately on the loading conditions ΔK and f [4][57][58]. This mechanism explains the f-dependence as follows: The Cr-bearing crack tip film is a completely stable H-barrier at f lower than the f_critLB. Above f_critLB, ε_cyc is exceeded and the passive film is destabilized exposing the crack tip; but, complete loss of inhibition is not observed as the time between rupture events (related to f) is sufficient to allow for repassivation of the crack tip passive film providing partial inhibition. At f_critUB, the time between rupture events is short enough to prevent any significant repassivation; thus, full destabilization occurs causing complete loss of inhibition and the pure NaCl level of da/dN(2,3)

Although chromate is the preeminent inhibitor of corrosion and EFCP, much research has been conducted to find replacement inhibitors [33]-[52] because of toxicity concerns tied to application and removal of chromium-bearing coatings [53]. In identifying a suitable replacement, attention has focused on inhibition of localized corrosion, but not the ability to inhibit EFCP [39][48]. Research has shown chromate is capable of inhibiting EFCP [2][7] in addition to localized corrosion [54][56]. Therefore, disregard of replacement capability to inhibit EFCP may be deleterious once a crack is initiated in an airframe. For this reason, it is important to quantify chromate-replacement inhibitor capability to reduce EFCP kinetics.

Molybdate (MoO₄²⁻) has shown promise in both inhibition of corrosion [35][38], [50][52] and, through limited literature, EFCP [45][47]. Because MoO₄²⁻, like CrO₄²⁻, is a reducible hexavalent anion which forms an insoluble oxide [35] and is the inhibitor whose properties are the most similar to chromate [38]; it is hypothesized that the chromate mechanism of EFCP inhibition will be applicable to molybdate. MoO₄²⁻ offers advantages over chromate in its capability to self-heal, or reduce localized corrosion and/or environmental contribution to da/dN by ionic release of the inhibiting species from a coating and subsequent delivery to a crack tip. Chromate inhibitors are not eligible for release from dissolution of a metallic coating because Cr does not dissolve into Cr⁶⁺, which forms the inhibiting anion chromate, until very high potentials. Molybdate offers enhanced self-healing ability because it can be utilized as a conversion coating [38] or be released by dissolution of a metallic coating [49]-[51]. Because prior research on inhibition of EFCP by molybdate is neither sufficiently quantitative nor covers a range of ε_cyc, research is required.

The objectives of this research are:
1) To extend the current understanding of EFCP driving forces for full immersion and water vapor to
characterize crack propagation kinetics for atmospheric exposure.

2) To assess the capacity of molybdate to inhibit EFCP under atmospheric conditions, and identify the controlling mechanism(s) and destabilization conditions. The aim is to examine the effects of loading variables $\Delta K$ and $f$ as well as $E$ on inhibition of EFCP in both full immersion and atmospheric conditions.

**Assessment of Molybdate Inhibition:**

**Experimental Procedure:**

Al-Zn-Mg-Cu alloy 7075 (Al-5.6Zn-2.5Mg-1.4Cu-0.2Cr-0.1Si-0.3Fe; wt.% in the peakaged T651 temper (24 h at 120°C) was obtained from the previous study of chromate inhibition of EFCP. Mechanical properties are: $\sigma_y$ of 469 MPa, $\sigma_u$ of 538 MPa, and $K_{IC}$ in the longitudinal-transverse direction (LT) of 29 MPa$\sqrt{m}$. Single edge micronotch (SEN) specimens were machined in LT orientation with a notch depth of 200 $\mu m$, width of 10.2 mm, and thickness of 2.5 mm. Fatigue experiments of constant $\Delta K$-varied frequency were performed using a computer controlled servo-hydraulic machine operated in load control with a constant amplitude sinusoidal waveform. The specimen was fully immersed in a Plexiglas cell filled with NaCl + Na$_2$MoO$_4$ solution. For high $R$ experiments, specimens were precracked in solution to a crack length of 0.5 mm at a high $K_{max}$ of 17 MPa$\sqrt{m}$. In the constant $\Delta K$-varied frequency experiment, each frequency was maintained over a crack length of 0.4-0.8 mm. Crack length was monitored continuously using the Direct Current Potential Difference (DCPD) method. $da/dN$ was determined by linear regression of the crack length versus load cycle relationship except when the open circuit potential changed dramatically during a segment as discussed in a subsequent section. The resolvable average crack length was 0.4 $\mu m$ for the 12 to 15,000 ampere current and 10$^5$ gain amplifier employed. For the majority of experiments, the specimen was freely corroding, with one exception: the constant $\Delta K$-decreasing $f$ experiment in 0.06M NaCl + 0.6M Na$_2$MoO$_4$ where -650 mV$_{SCE}$ and -850 mV$_{SCE}$ potentials were alternately applied with a potentiostat. Scanning Electron Microscopy (SEM) characterized crack surface morphology as a function of loading frequency and environment on specimens cleaned ultrasonically in acetone and methanol.

**Results:**

Figure 2 and Figure 3 show the $f$-dependence at a constant $\Delta K$ of 6 MPa$\sqrt{m}$ and two stress intensity ratios ($R = K_{MIN}/K_{MAX}$) in solutions of low Cl$^-$ and varying MoO$_4^{2-}$. The low Cl$^-$ content was selected based on chemical analysis of solutions extracted from aircraft lap joints which indicate low Cl$^-$ concentrations of ~0.02M [60]. Cl$^-$ concentration (0.6M NaCl-used in the chromate studies [2],[3] vs. 0.06M NaCl) did not affect the frequency dependence of EFCP as shown by comparison of ○ vs. ● in Figure 2a. This is most likely because the concentration of Cl$^-$ at the occluded crack tip is high and independent of the bulk solution composition [10],[11].

**Low R:**

For low $R$ of 0.1, results in Figure 2 establish that addition of 0.6M Na$_2$MoO$_4$ causes $da/dN$ to decrease by an order of magnitude at the slowest loading frequency examined, 0.2 Hz, in 7075-T651. Inhibition is eliminated and $da/dN$ approaches that of pure NaCl by increasing frequency to $f_{critUB}$, near 25 Hz for 0.06M NaCl.
NaCl + 0.6M Na₂MoO₄. The frequency below which the inhibiting effect becomes frequency independent, was not observed. The minimum \( \frac{da}{dN} \) was 1.5x10⁻⁵ mm/cyc for 0.06M NaCl + 0.6M Na₂MoO₄ at 0.2Hz, while \( \frac{da}{dN} \) for vacuum is approximately 1x10⁻⁶ mm/cyc. Thus, MoO₄⁻² addition will reduce \( \frac{da}{dN} \) by at least an order of magnitude at low frequencies and a high molybdate to chloride ratio of 10, but does not completely eliminate EFCP.

Inhibition was also observed for a lower MoO₄⁻² concentration (0.1 M Na₂MoO₄ and molybdate to chloride ratio in the bulk solution of 1.7), but \( f_{\text{critUB}} \) was reduced to 3 Hz showing inhibition decreases as the concentration of Mo decreases in bulk solution, which is consistent with the chromate study²³. Chromate and molybdate results are compared in Figure 2b.

For high R of 0.65, molybdate effectively inhibits EFCP as seen in Figure 3. Addition of molybdate (0.6 M) to chloride solution decreased \( \frac{da}{dN} \) by over an order of magnitude as frequency decreased from 10 Hz to 0.02 Hz. The \( f_{\text{critUB}} \) is ~12 Hz and the \( f_{\text{critLB}} \) is below 0.05Hz. For 0.1 Hz in 0.06M NaCl + 0.6M Na₂MoO₄, \( \frac{da}{dN} \) changed mid-test from 8.1x10⁻⁵ mm/cyc to 3.3x10⁻⁵ mm/cyc at a crack length of ~1.25 mm, total time in solution of ~19 h, and ~1841 cyc into 0.1 Hz loading. This abrupt change in \( \frac{da}{dN} \) (Figure 4) is indicated by the arrow in Figure 3, and explained by a corresponding change in OCP. At 0.05Hz and below, a growth rate of ~1.8x10⁻⁵ mm/cyc, which is typical of ultra-high vacuum, was observed. These results indicate that molybdate at low frequencies is capable of producing complete inhibition or elimination of the environmental contribution to FCP. For frequencies higher than 1Hz, there was no observable affect of molybdate concentration on inhibition for the concentrations considered (0.03M and 0.6M Na₂MoO₄). This is in contrast to what is observed for low R molybdate (Figure 2) and chromate²³.

The open circuit potential versus time behavior for high R loading and no applied potential are shown in Figure 5 and Figure 6. For stressing in 0.06M NaCl, the OCP remained constant around -710 mVSCE throughout the entire 7 h loading (Figure 5a). For 0.06M NaCl + 0.6M Na₂MoO₄, two separate specimen were loaded over frequency ranges of 30 Hz to 0.5 Hz (Figure 5b) and 0.2 Hz to 0.02 Hz (Figure 6). For 30 Hz to 0.5 Hz, OCP fluctuated between -690 mVSCE and -710 mVSCE over the 15 h stressing duration. For 0.2 Hz to 0.02 Hz, a very definable increase in OCP occurred at ~19h.
slowly increased from -910 mV\text{SCE} towards -775 mV\text{SCE} over an 18 h time period and subsequently jumped to -600 mV\text{SCE} at 19 h. The potential then proceeded to decrease slightly and fluctuate between -645 mV\text{SCE} and -675 mV\text{SCE} throughout the remainder of testing. The OCP increase to -600 mV\text{SCE} at 19 h correlates directly to the change in da/dN at 0.1 Hz discussed previously, as indicated by the arrow in Figure 4b which represents the exact time the OCP increase occurred (19.2 h or ~1838 cyc into 0.1 Hz loading). Upon the OCP increase from -775 mV\text{SCE} to -600 mV\text{SCE} da/dN subsequently decreased from 8.1\times10^{-5} mm/cyc to 3.3\times10^{-5} mm/cyc; revealing a strong dependence of da/dN on potential.

High R, Alternating Potential: Due to the direct correlation between da/dN and the OCP increase, the effect of applied potential on da/dN was investigated at a $\Delta K$ of 6 MPa√m and R of 0.65 in pure low-chloride solution (a) and 0.06 M NaCl + 0.6M Na$_2$MoO$_4$ (b). The arrows indicate the time at which the frequency changed. The frequency was changed from high to low f over a range of 20Hz to 0.2Hz for a) and 30Hz to 0.5Hz for b).

Figure 5: Open circuit potential as a function of loading time for 7075-T651 loaded at $\Delta K$ of 6 MPa√m and R of 0.65 in pure low-chloride solution (a) and 0.06 M NaCl + 0.6M Na$_2$MoO$_4$ (b). The arrows indicate the time at which the frequency changed. The frequency was changed from high to low f over a range of 20Hz to 0.2Hz for a) and 30Hz to 0.5Hz for b).

Figure 6: Open circuit potential as a function of loading time for 7075-T651 loaded at $\Delta K$ of 6 MPa√m and R of 0.65 for 0.06M NaCl + 0.6M Na$_2$MoO$_4$. a) is loaded under ultra-low frequencies of 0.2 Hz to 0.02 Hz and had a total time in solution of over 600 hours. The black arrows indicate the times at which the frequency was shifted. b) is the 0.1 Hz regime of a) and shows that the quick increase in potential occurs at a time of about 19 h.

High R, Alternating Potential: Due to the direct correlation between da/dN and the OCP increase, the effect of applied potential on da/dN was investigated at a $\Delta K$ of 6 MPa√m and R of 0.65 and found to be considerable. Figure 8 shows da/dN vs. f results obtained for two polarizations: 850 mV\text{SCE} and -650 mV\text{SCE}. With the exception of one segment, the specimen was cathodically polarized when held at -850 mV\text{SCE} and anodically polarized when held at -650 mV\text{SCE}. For the 0.02 Hz, -850 mV\text{SCE} segment; polarization was initially anodic. This had no effect on da/dN in this segment.
Inhibition was observed at both potentials, but -650 mV<sub>SCE</sub> exhibited a larger inhibiting capacity (#1, 7 and 9; in Figure 8). At a loading frequency of 20 Hz, a frequency above ə<sub>critLB</sub>, no effect of applied potential was detected and da/dN was comparable to pure chloride. At 0.02 Hz, below ə<sub>critLB</sub>, -650 mV<sub>SCE</sub> caused complete crack arrest and -850 mV<sub>SCE</sub> had stable da/dN of 3.7x10<sup>-5</sup> mm/cyc, which is lower than pure Cl<sup>-</sup> but higher than 0.06M NaCl + 0.6M Na<sub>2</sub>MoO<sub>4</sub> at OCP. Upon arrest at 0.02 Hz and -650 mV<sub>SCE</sub>, when the potential or frequency was changed (-850 mV<sub>SCE</sub> at 0.02 Hz from point 1 to 2, or 0.5 Hz at -625 mV<sub>SCE</sub> from point 7 to 8 on Figure 8) crack growth resumed and achieve a steady state value after 2.5-3.5 d. At 0.5 Hz and -650 mV<sub>SCE</sub>, sub-vacuum level da/dN was detected, implying ə<sub>critLB</sub> increased from 0.02 Hz to above 0.5 Hz. While potential affects the degree of molybdate inhibition, results in Figure 8 establish that the influence is second-order to the fundamental relationship between inhibited da/dN and ə, which is not affected by applied potential.

Fractography:
Figure 7 shows fatigue crack surface morphology formed by loading at a Δ<sub>K</sub> of 6 MPa√m and R of 0.65. In humid air, investigated by Ro et al. [23],[25],[27], and exhibit complex facet crystallography parallel to the low index planes of {110} and {100} and high index {hkl} planes. Due to the similar morphology, it is expected that the surfaces shown in Figure 7 present complex facet crystallography. In addition, these morphologies are consistent with those seen for the same material loaded under R of 0.1 in pure chloride solutions [21].

At 0.02 Hz, where vacuum level crack growth rates were detected, crack morphology is transgranular and lacking {111} slip band cracking morphology; as
shown in Figure 9 b and c. The morphology consists of two distinct features not consistent with the possible low/high index plane cracking seen at higher frequencies (Figure 7). This unique crack surface morphology was seen at frequencies of 0.1 Hz and below. The lack of slip band cracking is expected because under these loading conditions in ultra high vacuum (UHV, fatigued at ΔK of 5.5 MPa√m, f of 20 Hz, R of 0.65, and pressure of 0.3 μPa) the crack surface morphology shows the same lack of {111} slip band cracking (Figure 9d). However, detail in morphology between UHV and 0.02 Hz is very different.

Discussion:

The results of the present study establish that molybdate effectively inhibits EFCP in precipitation hardened 7075-T651 stressed under full immersion in chloride solutions, comparable to chromate inhibition [2],[3]. This conclusion is supported by the direct comparison in Figure 2b and results in Figure 2a and Figure 3. The degree of EFCP rate inhibition depends on the important variables: f, by inference ΔK, and E.

Strength of MoO$_4^{2-}$ Inhibition:

As with CrO$_4^{2-}$, the inhibiting strength of MoO$_4^{2-}$ at low R decreases with increasing frequency until inhibition is lost at an $f_{\text{crit UB}}$. Following the argument for chromate inhibition [2],[3], this frequency dependence suggests molybdate creates a Mo-bearing passive film on the crack tip surface which prevents production and uptake of embrittling H. MoO$_4^{2-}$ also replaces some Cl$^-$ in the crack tip effectively lowering the H$^+$ activity and decreasing the acidity of the crack tip solution. When this passive film is completely destabilized at a $\varepsilon_{\text{crit}}$ inhibition of EFCP is lost.

The $f_{\text{crit UB}}$ increases 10-fold as the molybdate to chloride ratio increases from 2 to 10 (Figure 2a). This indicates the passive film is stable to higher $\varepsilon_{\text{tip}}$ with increasing MoO$_4^{2-}$, as seen in Figure 1 for chromate [2],[3]. The low R $f_{\text{crit UB}}$ for 0.6M Na$_2$MoO$_4$ (25 Hz) is less than that of 0.5M Na$_2$CrO$_4$ (60 Hz) suggesting that the passive film of molybdate is more prone to mechanical destabilization than the chromate passive film.

For high R, Figure 3, the two MoO$_4^{2-}$ concentrations produced a similar degree of da/dN reduction and identical $f_{\text{crit UB}}$ (15 Hz). This concentration independence is in contrast to chromate inhibition [2],[3] and the low R molybdate results (Figure 2). From an electrochemical perspective, a critical MoO$_4^{2-}$ inhibitor concentration exists above which passivity is sufficient to prevent significant localized corrosion on boldly exposed AA2024 when submersed in aqueous chloride solution [50],[51]. Such a critical MoO$_4^{2-}$ concentration may also exist for EFCP. As the critical inhibitor concentration is a material property, an R effect on bulk inhibitor concentration to reach a supersaturated critical crack tip concentration may be due to the average fatigue crack opening over a single load cycle being larger for higher R at the same crack length and ΔK.

The average crack mouth opening displacement (CMOD) is proportional to (1+R)/(1-R). As R decreases to decrease CMOD, replenishment of the crack tip solution is increased by convective mixing and possible turbulent mixing [61]. Therefore, the crack tip solution is closer in concentration to the bulk and ion migration plays a larger role in transport of Cl$^-$ and MoO$_4^{2-}$ to the crack tip. The ionic mobility of Cl$^-$ is two-times greater than that of MoO$_4^{2-}$, allowing the crack tip to become more concentrated in Cl$^-$ and the

Figure 9: SEM images of the crack surface morphology of 7075-T651 stressed in 0.06M NaCl + 0.6M Na$_2$MoO$_4$ loaded under a ΔK of 6 MPa√m, R of 0.65, and frequency of 0.02 Hz (b and c). b) and c) shows the two different types of morphology observed at 0.02 Hz where the vacuum level crack growth rates were obtained. d) is the crack surface morphology of 7075-T651 when stressed in an UHV environment under the same loading conditions as b and c. For all images freely corroding conditions were observed and the crack growth direction is from bottom to top.
molybdate to chloride ratio to decrease. Therefore, a smaller R yields more Cl\(^-\) and less MoO\(_2\)\(^2-\) than higher R for the same bulk concentration. Furthermore, it has been shown\(^{[50],[51]}\) that the critical inhibitor concentration increases as Cl\(^-\) concentration increases. Ignoring the effects of ion mobility and assuming perfect convective mixing, a larger CMOD in a load cycle for the same ΔK will increase the volume of solution interacting with the same crack surface area\(^{[61]}\). This allows for an increase in the number of inhibiting ions present per unit crack surface. The three above considerations combine to give a possible explanation as to how higher R could promote passivity and enhance inhibition for a solution with reduced-bulk inhibitor concentration.

An \(f_{critLB}\) was observed only under high R, da/dN at this \(f_{critLB}\) corresponds to that in UHV (1.8x10\(^{-5}\) mm/cyc). This indicates the \(\Delta t_{eq}\) at which the passive film is completely stable and unruptured at all times, allowing fatigue damage to proceed by mechanical fatigue only. The fractographs in Figure 9 show the fully inhibited molybdate fracture surface differs from that produced in UHV, implying a passive film on the crack surface may affect dislocation motion and slip while leaving da/dN unaffected. This is supported by Grinberg\(^{[62]}\) who showed the absence of an oxide or chemisorbed film on the crack surface in vacuum changes the dislocation behavior with respect to moist air in the regions near the crack, but this would be an unlikely cause for a decrease in da/dN. Therefore, it is possible an Al\(_x\)Mo\(_y\)O\(_z\) passive film, when completely stable and a perfect barrier to H uptake, causes a change in the dislocation behavior but not da/dN. Complete inhibition was not observed for the low R loading case, where \(f_{critLB}\) must be below the slowest frequency examined (0.2 Hz in Figure 2). The previous discussion of the effect of R on crack chemistry suggests that \(f_{critLB}\) should decrease with decreasing R; a value below 0.05 Hz is expected for loading at R of 0.1.

**Effect of Potential:**

Results from this study show molybdate inhibition depends on applied potential (Figure 8). This phenomenon can be explained by the film rupture model and consideration of the Al and Mo Pourbaix diagram\(^{[63]}\). For Al, the Al\(_2\)O\(_3\) phase is stable over a range of potential and pH which fully encompasses the experimental conditions; therefore, analysis will focus on the Mo Pourbaix regions of stability. The thermodynamically stable phase in the bulk applied potential range of this study (-650 mV\(_{SCE}\) to -850 mV\(_{SCE}\)) is MoO\(_2\). For bulk solution conditions (pH of 8-10) and -650 mV\(_{SCE}\), the stable species bridge MoO\(_2\) and MoO\(_2\)\(^2-\) stability, while for -850 mV\(_{SCE}\) the stable species is clearly MoO\(_2\). This does not coincide with the results in Figure 8 where the greatest inhibition was for a -650 mV\(_{SCE}\) polarization.

It is well established that when a specimen is polarized anodically (-650 mV\(_{SCE}\)) the crack tip E and pH decrease, while when polarized cathodically (-850 mV\(_{SCE}\)) the E and pH increase. For Al alloys in aqueous chloride solutions, the degree of crack tip pH and E deviation from bulk depends on crack tip dissolution rate\(^{[10],[11]}\). The film rupture model suggests the crack tip dissolution rate will increase with increasing \(f\) above the \(f_{critLB}\); thus, da/dN will increase as crack tip dissolution increases. Therefore, for slower da/dN the E and pH are much closer to bulk. The Mo Pourbaix diagram\(^{[63]}\) shows the crack tip E and pH deviations are more likely to be within the MoO\(_2\) stability regime for -650 mV\(_{SCE}\). Furthermore, stress to fracture a passive film increases with anodic polarization\(^{[64]}\), suggesting \(f_{critLB}\) should be higher for anodic polarization than cathodic polarization. It is expected, the influence of applied potential on inhibition will increase with increasing R because as a higher concentration of MoO\(_2\)\(^2-\) in the crack tip solution increases the stability region of MoO\(_2\)\(^{[63]}\).

No effect of potential was observed at high \(f\) (20 Hz which is above the upper bound of ~12 Hz). When loading at 20 Hz, the film rupture model suggests inhibition does not occur because the passive film is mechanically destabilized and there is not sufficient time to repassivate.

**Conclusions:**

- MoO\(_2\)\(^2-\) effectively inhibits EFCP in 7075-T651 stressed during full immersion in chloride solution, as understood by hydrogen environment embrittlement where ionic addition promotes crack tip passivity for reduced H production and uptake.
- MoO\(_2\)\(^2-\) inhibition of EFCP in aqueous chloride strongly depends on crack tip strain rate (\(f\) and ΔK) and applied potential.
- For low R, the inhibiting effect of MoO\(_2\)\(^2-\) parallels that of CrO\(_2\)\(^2-\), but molybdate effectiveness is shifted to a lower frequency regime suggesting the Mo-bearing passive film is less stable with regard to localized crack tip deformation.
- For high R under freely corrosion, MoO\(_2\)\(^2-\) fully inhibits EFCP in 7075-T651; with reduced da/dN typical of UHV. This suggests an Al\(_x\)Mo\(_y\)O\(_z\) passive film on the crack surface is a near-perfect barrier to H.
- Under full inhibition, the crack surface morphology is not consistent with that typical of vacuum or pure NaCl, suggesting the crack tip passive film affects dislocation motion and slip.
- The passive film is more resistant to mechanical deformation when formed under anodic conditions.
Future Work:
Thin film electrolytes more realistically describe the environmental conditions for in-service aircraft under atmospheric exposure. To date no quantitative research has been conducted on the effect thin film electrolytes have on EFCP and its inhibition. Thus, the following question arises:

III. How do atmospheric corrosion conditions affect EFCP and its inhibition compared to full immersion and water vapor?

Future work on this research project will answer this question by addressing the following two objectives:

IIIa. As stated previously for both full immersion and water vapor, a parameter which quantifies the environmental/chemical driving force has been identified and correlated to da/dN. For metals in an atmosphere with contaminants at a water vapor pressure below the deliquescent point, p_{H2O}/f would be the controlling parameter. But for p_{H2O} at or above the deliquescent point, a thin film electrolyte will develop of a thickness and resistivity that will control the degree of polarization on the crack tip. Therefore, it can be hypothesized that the environmental driving force is a combination of E and f. This research aims to characterize da/dN as a function of E and f for atmospheric exposure conditions for C47A-T8.

IIIb. The ability of MoO_4^{2-} to inhibit EFCP and transport from a coating site to the crack tip under atmospheric conditions will be examined by quantifying the effect of E and f on inhibition when a thin film electrolyte is present for C47A-T8.

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