The Effect of Corrosion Inhibitors on Environmental Fatigue Crack Growth in Al-Zn-Mg-Cu

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Abstract. Corrosion fatigue is an area of concern for the United States Air Force (USAF) and other Department of Defense (DoD) organizations. Often DoD corrosion prevention systems include chromate containing coatings, typically in the form of chromate conversion coatings and polymer primers. Chromate has been used successfully for many years within the DoD to prevent corrosion damage. However the environmental and personnel risks associated with chromate coatings have caused the USAF to pursue non-chromate containing corrosion prevention coatings [1]. To fully quantify chromate replacement coatings, an understanding of the effects that chromate has on corrosion fatigue crack growth rates must be fully characterized. Some researchers have shown that high levels of chromate added to 0.6 M NaCl full immersion corrosion fatigue tests on 7xxx series aluminum alloys slow the fatigue crack growth rate substantially [2,3]. The limitation of that research was that the amount of chromate present in the test solution environment was not connected to expected leach rates of chromate from polymeric coatings and a high solubility salt was used.

The majority of DoD assets are protected from corrosion by polymer coatings loaded with corrosion inhibitors. For these coatings to slow fatigue crack propagation the corrosion inhibitors must become mobile as a consequence of hydration of the polymer coating matrix. Based on this mechanism of corrosion inhibitor release, the examination of atmospheric corrosion fatigue becomes important to help understand how inhibitors work in real world situations with hydrated salt layers rather than only fully immersed solutions.

Introduction

As the USAF and DoD extend the life of current weapon systems, corrosion damage becomes a larger concern. At the same time the DoD has moved to phase out the use of chromates as a corrosion inhibitor due to the environmental and personnel risks [1]. Chromates are used in a variety of corrosion prevention coatings including conversion coatings and primers. Corrosion damage is of concern to the aircraft sustainment community for many structural integrity reasons (reduction in static strength and stability allowables, etc.), including situations in which corrosion damage may act as a stress raiser and initiate fatigue cracks. While it has been documented that high levels of chromate and a chromate replacement inhibitor, molybdate, added to a bulk solution can inhibit fatigue crack propagation, it has not been shown that these inhibitors leaching from a coating can do the same [2-5]. However, if chromate does provide protection that slows corrosion fatigue crack propagation, current systems have unaccounted for corrosion fatigue protection. If that protection is not documented, then the protection will be lost in replacement chromate-free systems. At the same time, chromate is considered the benchmark for all other corrosion inhibitors to meet, so an understanding of the protection current chromate coatings provides to corrosion fatigue is needed.

For current commercial coatings the loading amounts of inhibitors can vary, but are designed such that the coating is not depleted of inhibitor during a maintenance cycle, typically 6 to 8 years [6-8]. Organic coatings with inhibitors are understood to readily absorb water or other liquid environments through inherent defects in the coating resulting in interconnected pores which allows inhibitor pigments within the coating to dissolve and dissociate in electrolyte within the coating itself [7-10] . Typically pigments with low water solubility are selected for use in coatings so that (a) osmotic pressure-induced blisters are avoided, and (b) the inhibitor remains in the coating over long times rather than rapidly dissolving out when first in contact with corrosive environments [7,9]. Because of the low solubility, only low concentrations of inhibitors would be expected in the surrounding solution before precipitation of solids occurs. For the previously completed bulk solution corrosion fatigue testing (sample fully immersed), Na_2CrO_4 (solubility in water: 87.6 g/100mL) and Na_2MoO_4 (65.0g/100mL) were used as inhibitors; these salts have a much higher water solubility than coating pigments ($SrCrO_4$: 0.096g/100mL, $CaMoO_4$: 0.0011g/100mL) [7,9,11]. However the high solubility salts have advantages in studying corrosion fatigue inhibition in that the high solubility prevents precipitates that could cause crack closure, allowing for a better understanding of the crack tip passivation mechanism.

Experimental Procedure

To determine the effect chromate has on corrosion fatigue damage in DoD-relevant materials, a single edge notch specimen, shown in Figure 1, was used for all fatigue testing. The samples were made from a peak-aged, legacy age-hardenable Al-Zn-Mg-Cu aluminum alloy and temper (7075-T651). The sample was loaded into a computer-controlled servohydraulic test frame and crack growth was measured using a direct current potential drop (dcPD) system. The test load was controlled to provide a constant ΔK of 6 MPa√m with a stress ratio (R) of 0.65. The loading frequency (f) was varied from 0.02 to 20 Hz in a bulk 0.06 M NaCl environment.

For the inhibitor leaching studies, Luna Innovations developed four different epoxy coatings containing different loading amounts of $SrCrO_4$ (either 12 or 17 weight %) [12]. Leaching studies were completed by exposing the free-standing films in 100 mL of DI water for 2 and 4 days. The leached liquid samples were then examined using UV-Vis Spectroscopy using standards serially diluted from a 1000 ppm CrO_4^{2-} purchased standard solution to determine the amount of CrO_4^{2-} present. The leaching data from the free films was extrapolated from the standards by the WinUV software on the Varian Cary Series spectroscope[13].

Results

Inhibitor Leaching. All of the prior corrosion fatigue work with aluminum alloys was completed using inhibitors added to a bulk NaCl solution or deliquesced onto the surface of a sample rather than the migration of inhibitors from polymer matrix coatings [2-5]. The inhibitors used for most of these fatigue studies were high rather than low solubility inhibitors, the latter of which are typically used in military aviation corrosion prevention coatings [2-5]. This difference may be of importance as the leaching of inhibitors is purposely controlled in organic coatings via salt solubility in order to make the life of the coating acceptable. That said, inhibitor leaching would be the source of any inhibitor that could slow fatigue crack propagation. All of these variables make understanding the leaching rate of known coatings and inhibitors critical to designing appropriate fatigue test criteria. An understanding of the chromate leaching rate from coatings and how chloride concentration and pH could change the amount of chromate present in a solution was needed. To answer these questions literature reviews of chromate leaching rates and inhibitor pigment solubility effects were performed, along with in-house leaching studies.

Table I gives the measured leaching rates converted into mol/L of CrO_4^{2-} to allow comparison with published results. Based on the leaching results, Film 1 was selected for fatigue crack growth testing given the high leaching rate and relatively high CrO_4^{2-} remaining in the film, both desired for fatigue testing. Table II shows the expected leaching concentrations of CrO_4^{2-} based on the film leaching rates from Table I for the different test geometries used in the program. Figure 1 shows the single edge notch (SEN) sample and three different test configurations. The Bulk Testing label refers to a standard test cell filled with 500 mL of solution with a SEN sample primed on all four sides (Coating Surface Area: 7.92 cm^2) which mimics areas of standing water. The Restricted Volume refers to a very small cell containing approximately 0.5 mL of solution covering a 2 cm high portion of the flat on the SEN sample (Coating Surface Area: 5.28 cm^2) which mimic areas such as lap joints and other occluded regions of aircraft. The Coating Surface Area to Volume ratio for the reduced volume cell was determined using aircraft components from the USAF. Thin Film refers to salt deliquesced to form a 100 μm thickness film (8×10^{-5} L) onto the four flat surfaces of the SEN sample (Coating Surface Area: 7.92 cm^2). The Thin Film environment is used to mimic how atmospheric corrosion is understood to occur on aircraft structure rather than a large pool of liquid around the sample [14-16].
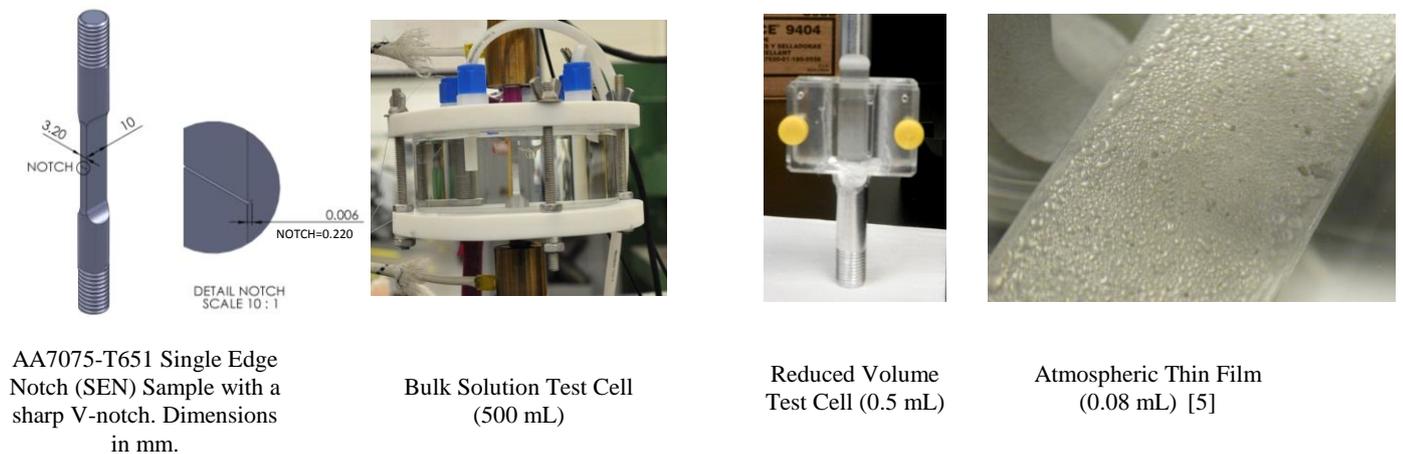

| AA7075-T651 Single Edge Notch (SEN) Sample with a sharp V-notch. Dimensions in mm. | Bulk Solution Test Cell (500 mL) | Reduced Volume Test Cell (0.5 mL) | Atmospheric Thin Film (0.08 mL) [5] |

Figure 1: Sample Volumes used for Concentration Calculations

Table I: Leaching results for $SrCrO_4$ primer films with 29 cm^2 surface area leached into 100 mL DI water converted into millimol/L (mM) CrO_4^{2-}. [12]

Film Number	Concentration (mM) 2 Days	Concentration (mM) 4 Days
1	0.4	0.6
2	0.3	0.4
3	0.7	0.8
4	0.4	0.5

The leach rates from the model films were compared to that expected from published CrO_4^{-2} leach rates [7-9]. To make the comparison, the published leaching data were converted to molarity using the geometries and volumes of the Luna film leaching experiments and the testing geometries reviewed above. The Luna films were able to leach about 6-20 times more chromate into solution than the commercial epoxy primer. This result suggests that the Luna film is likely more porous than the commercial primer as the loaded salt was the same ($SrCrO_4$). A 12-17% loading amount is on the low end for chromate, so that is unlikely to be the cause of the leaching differences [6,7].

A summary of the published chromate leaching data follows. The overall leaching rates varied by about 16 times between the high and low leaching coatings [7-9]. The loading amount of chromate for all of the coatings can vary, however, as the porosity of the film can also greatly affect the

leaching rates. Therefore it is unclear what causes the variation in leaching amounts [6,7]. There is no significant difference in leaching rates with the variation of low (below 0.1 M NaCl) chloride content. However higher chloride content (0.85 M) makes a large difference, nearly doubling the amount of CrO_4^{2-} leached from the coating. This result suggests there could be a threshold of chloride content over which the chloride is detrimental to the polymer matrix allowing for more inhibitor release [6,7]. The published data also suggests that the change in pH does not cause large changes in the amount of chromate leached. There is some suggestion that more acidic environments cause more leaching for that coating, but the change in the amount of chromate leached is about the same as the scatter with NaCl concentration changes, which is less than the leaching amount variation from one epoxy primer to the next.

Table II: Expected leaching results for $SrCrO_4$ primer films converted to the test three geometries. All concentrations are in terms of mol/L (M) CrO_4^{2-}.
*above the $SrCrO_4$ solubility limit of 0.0047 M CrO_4^{2-} [11]

Film Number	Expected Concentration (M) Bulk Solution (500mL) 4 Days	Expected Concentration (M) Restricted Volume (0.5 mL) 4 Days	Expected Concentration (M) Thin Film (0.08 mL) 4 Days
1	3.21×10^{-5}	0.021*	0.201*
2	2.41×10^{-5}	0.016*	0.151*
3	4.28×10^{-5}	0.029*	0.268*
4	2.95×10^{-5}	0.020*	0.184*

Similar leaching studies were completed on molybdate (a chromate replacement) primers. The University of Southern Mississippi (USM) developed three $CaMoO_4$ containing primers [17]. Each primer had a different loading amount of MoO_4^{2-} (20.8%, 28.7%, 36.9% weight percent). USM coated and scribed AA 7075 panels (Surface Area: 6.45 cm^2) prior to completing leaching experiments in 100 mL DI water. The leaching results appear in Table III along with the concentrations expected for the three test conditions. Table III shows that the higher the loading amount of MoO_4^{2-}, the lower the leaching amount. This result is unexpected, and the mechanism behind this result is currently not understood. It was originally thought the solubility limit between the $CaMoO_4$ and solution was being exceeded, but that is not the case as the leaching values are always below the solubility limit of 0.05mM [11]. Also, as the inductively coupled plasma mass spectrometry (ICP-MS) is capable of detecting 1 part per billion, it is unlikely the molybdate leaching from the coating was being incorrectly measured. The explanation for these results remains to be determined.

Table III: Leaching results for the $CaMoO_4$ coatings developed by USM [17].
*above solubility $CaMoO_4$ limit of 0.055mM [11]

Loading Amount	Leaching Concentration (100mL) 4 Days	Expected Concentration (M) Bulk Solution (500mL) 4 Days	Expected Concentration (M) Restricted Volume (0.5 mL) 4 Days	Expected Concentration (M) Thin Film (0.08 mL) 4 Days
20.8% MolyWhite	1.8×10^{-6}	4.3×10^{-7}	2.9×10^{-4}*	0.003*
28.7% MolyWhite	4.1×10^{-7}	1.0×10^{-7}	6.7×10^{-5}*	6.0×10^{-4}*
36.9% MolyWhite	4.7×10^{-7}	1.1×10^{-7}	7.7×10^{-5}	7.0×10^{-4}*

Fatigue Testing. Based on the leaching results presented, the maximum amount of $SrCrO_4$ in solution would be 4.7mM (the solubility limit), however for the bulk solution (500 mL) only 0.05 mM would be expected based on the highest leaching rate for the chromate coatings in literature [7-9,11]. For $CaMoO_4$ the maximum concentration of inhibitor in solution would be 0.05mM and for the bulk solution test only 0.002mM would be expected from the leaching tests [11]. However, it was noted for the Reduced Volume and Thin Film cases the solubility limit for both $SrCrO_4$ and

$CaMoO_4$ could be reached causing precipitation of solids in and about the crack which could cause crack closure. The test plan in Table IV is being executed to determine the effect of the corrosion inhibitors chromate and molybdate, in amounts that could be leached from a coating, on fatigue crack growth rates. Another theory being tested is that the low solubility inhibitors could inhibit fatigue crack propagation by forming solids within the crack and causing crack closure.

Table IV: Proposed test matrix to determine the effect of chromate and molybdate in leached concentrations.

Inhibitor	Inhibitor Form	Environment	Amount (Concentration in Solution or wt % in Coating)
Na_2CrO_4/Na_2MoO_4	Salt	Bulk Solution NaCl	<0.05/0.002mM
$SrCrO_4/CaMoO_4$	Salt	Bulk Solution NaCl	<0.05/0.002mM
$SrCrO_4/CaMoO_4$	Salt	Bulk Solution NaCl	>4.7/0.05mM
$SrCrO_4/CaMoO_4$	Primer	Reduced Volume NaCl (<0.5mL)	17%/28%
$SrCrO_4/CaMoO_4$	Primer	Atmospheric	17%/28%
$SrCrO_4/CaMoO_4$	Primer	Bulk Solution NaCl	17%/28%

Testing was completed using inhibitor pigments that would be found in commercial molybdate coatings, calcium molybdate ($CaMoO_4$). All testing was completed at a constant ΔK=6 MPa$\sqrt{m}$, R=0.65 in a bulk (500 mL) 0.06 M NaCl solution. The results for this test are shown in Figure 2. The starting concentration of $CaMoO_4$ was 0.002 mM (gray star) which is below the solubility limit; the concentration was then increased to 0.01 mM $CaMoO_4$ (white star). For these concentrations the solubility limit would be expected to have been exceeded in the crack. The crack growth rates for the two concentrations of $CaMoO_4$ are in line with the pure 0.06 M NaCl showing no inhibition with the low concentrations of calcium molybdate added to a bulk solution and no inhibition due to crack closure. All other data in Figure 3 are from other published work [4,5].
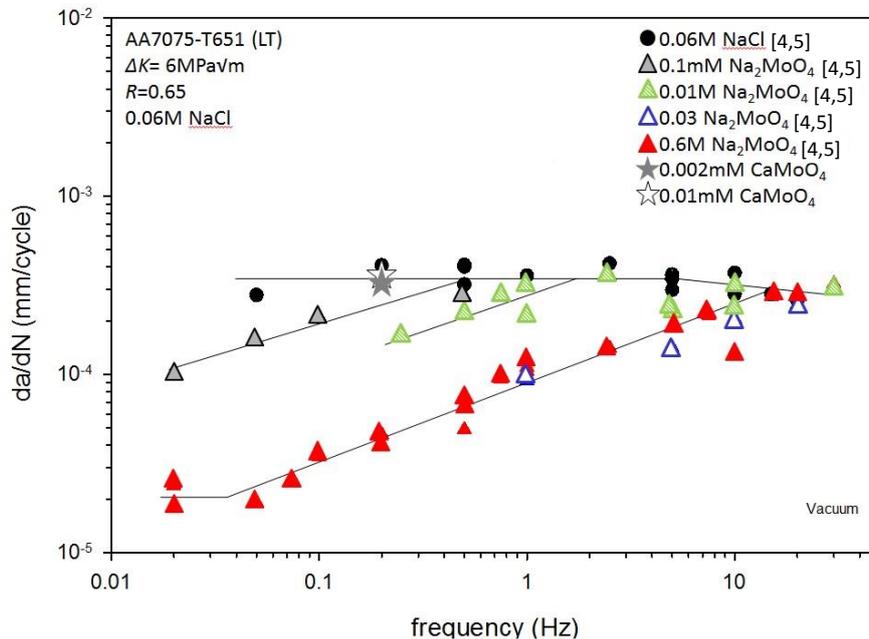

Figure 2: Crack growth rate data for low concentrations of low solubility corrosion fatigue inhibitor $CaMoO_4$ [4,5].

Conclusions

Low solubility corrosion inhibition pigments ($CaMoO_4$) have not shown the ability to reduce fatigue crack growth rates in bulk 0.06 M NaCl solutions whether through passive film formation or crack closure. It is currently unknown if moving toward slower frequencies or lower ΔK values would allow for inhibition at these low molybdate concentrations. The effect of chromate on small-scale fatigue damage can be characterized for the different primer types. The analysis of surface area-to-volume for leaching suggests that a thin salt film may be more applicable than full immersion testing for aircraft applications, particularly lap joints.

Acknowledgements

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