2017 Department of Defense – Allied Nations
Technical Corrosion Conference

Paper No. 2017-471006

THE EFFECT OF CORROSION INHIBITORS ON THE CORROSION FATIGUE OF A LEGACY AIRCRAFT ALUMINUM ALLOY

Sarah E. Galyon Dorman, SAFE Inc.

Keywords: Corrosion Fatigue, Chromate, Environmentally Assisted Cracking, Aluminum Alloys, Corrosion Fatigue Inhibition

ABSTRACT

The corrosion protection chromate provides to metallic structures has been well documented. To fully quantify chromate replacement coatings an understanding of the effects that chromate has on corrosion fatigue must be fully documented and understood. Researchers have shown that high levels of inhibitors (chromate, molybdate) added to full immersion corrosion fatigue tests on aluminum alloys slow the fatigue crack growth rate substantially. The limitation of this research was that the amount of inhibitor present in the environment was not related to leach rates of chromate from polymeric coatings used on commercial and military aircraft. For these inhibitors to slow fatigue crack propagation the inhibitors must become mobile from the polymer coating matrix.

In research funded by the Office of the Secretary of Defense's Office of Corrosion Policy and Oversight (OSD-CPO) work is ongoing to develop a better understanding how to better predict and prevent environmental effects on fatigue crack propagation. In this work it has been shown that chromate in levels related to coating leaching effects ($SrCrO_4$ = 0.5mM) can inhibit corrosion fatigue damage in full immersion sodium chloride (NaCl) solution at two different stress ratios (*R*), 0.65 and 0.02.

INTRODUCTION

As the United States Department of Defense (DoD) directs that the Air Force extend the service life of the aircraft fleets corrosion damage becomes a larger concern. At the same time that longer service is being demanded, the use of chromate is being limited due to personnel and environmental concerns. (1) Likewise corrosion prevention and control is frequently traded during the acquisition cycle for weapon system performance. As a result, the DoD remains entrenched in a find-and-fix corrosion management philosophy which is expensive and unsustainable. The DoD estimated that the annual cost of corrosion, the unintended material degradation due to the environment, to weapon systems and infrastructure in 2014 exceeded $18 billion, and that the number was likely to continue to rise. (2)

Chromates are used in a variety of corrosion prevention coatings including conversion coatings and primers. 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. (3-6) Other testing has shown effects of commercial chromate coating systems on corrosion fatigue damage under acidified salt spray. (7) While these laboratory tests can provide useful relative information they can have limited applicability to service environments. 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.

EXPERIMENTAL PROCEDURE

Inhibition of Corrosion Fatigue

To determine the effect chromate or the chromate replacement inhibitor molybdate, has on corrosion fatigue damage in DoD-relevant materials, a single edge notch (SENT) 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 fatigue tested using a computer-controlled servo-hydraulic test frame and the crack growth rate was measured using a direct current potential drop (DCPD) system. Testing was completed using a constant load (*K*-increasing) test profile where the maximum stress (σ_{max}) was 150 MPa, stress ratio (*R*) was 0.65 and the loading frequency was either 0.2Hz or 0.02 Hz. All testing was completed in full immersion 0.06M NaCl solution with corrosion inhibitors of strontium chromate ($SrCrO_4$) or calcium molybdate ($CaMoO_4$) added to the solution in the concentrations listed in Table 1.

Several studies have been completed on the effect of chromate as a general corrosion inhibitor and even on the effect of crack growth rate, however few researchers have examined the effect of chromate in levels based on leaching rates from coatings. (3-13) While there is variation in the data published on chromate leaching rates, it was found that the amounts were bound by the solubility limit of $SrCrO_4$ and the volume of the liquid present. Based on these results the upper and lower bounds for $SrCrO_4$ testing were selected to be 4.7mM and 0.5mM respectively. (8-15) The upper and lower bounds for $CaMoO_4$ were selected to be 0.05mM and 0.002mM (13-15). Table 1 shows the test matrix for inhibitor effects.

RESULTS

Based on the leaching rates noted previously, testing was completed with 4.7mM $SrCrO_4$, the maximum amount expected based on solubility, and 0.5mM $SrCrO_4$, amount based on expected leaching rates, using constant maximum stress, 150 MPa, testing at a frequency (*f*) of 0.2 Hz with an *R* of 0.65 in 500 mL of 0.06 M NaCl. Prior published work with lower concentrations of inhibitors had shown that lower frequency tests are needed to see inhibition effects; as such the test frequency of 0.2 Hz was selected. (3-6) Figure 2 shows a highlight of the effect of low levels of $SrCrO_4$, 0.5mM and 4.7mM, on fatigue crack growth rates as compared to 0.06M NaCl. For both concentrations of $SrCrO_4$ inhibition of the fatigue crack growth rates is seen below a ΔK of 5 MPa√m.

Table 1
Test matrix to determine the effect of chromate and molybdate in leached concentrations.

Inhibitor	Inhibitor Form	Environment	Amount (concentration in solution)
$SrCrO_4$ /$CaMoO_4$	Salt	Bulk Solution NaCl	<0.5/0.002mM
$SrCrO_4$ /$CaMoO_4$	Salt	Bulk Solution NaCl	>4.7/0.05mM

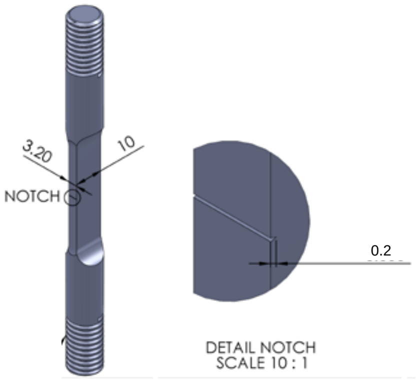


Figure 1
Single edge notch (SENT) specimens were made of 7xxx series aluminum alloy. All dimensions in millimeters.

The effect of stress ratio on inhibition of fatigue crack growth was also investigated. The same maximum stress of 150 MPa was used, with an *R* of 0.02. The stress ratio was selected such that crack was sometimes closed. The precracking protocol used was a *K*-shed from a K_{max} of 6.66 MPa√m to K_{max} of 2.0 MPa√m with an *R*=0.1. For this testing the original plan was to complete all testing at a frequency of 0.2 Hz as the largest effect of chromate had been noted at that frequency. Three tests were placed into the combined 0.5mM $SrCrO_4$ 0.06M NaCl solution and precracking started. Two of the tests failed to register any crack growth after 4 weeks of testing, at which point the DCPD lead wires failed, the third test failed in the threaded grip region after over 1,000,000 cycles with no crack growth noted. For the final successful test the sample was precracked in air and the inhibited solution added after the sample was precracked, the test was completed at a frequency of 1 Hz. Figure 3 shows the results of this test as compared to testing completed in 0.06M NaCl at an *R* of 0.65 and 0.02, frequency of 0.2 Hz. The comparison between the baseline 0.06M NaCl tests with different stress ratios does not show any signs of crack closure, only the effect of mean stress. When the 0.5mM $SrCrO_4$ is added, inhibition is observed to a ΔK of approximately 9 MPa√m.

Similar constant load fatigue testing was completed for 0.05mM $CaMoO_4$, the maximum amount expected based on solubility at a frequency of 0.2 Hz and an *R* of 0.65. The results of these tests are shown in Figure 4. The inhibitive effects of $CaMoO_4$ are only noted below a ΔK of 3 MPa√m and only for one test.

DISCUSSION AND CONCLUSIONS

Using inhibitor leaching estimations from chromate containing coatings, it was shown that strontium chromate added to a sodium chloride solution was able to slow fatigue crack growth, Figure 2 and Figure 3. Concentrations of $SrCrO_4$ (4.7mM and 0.5mM) based on leaching rates from polymer coatings have been shown to slow fatigue growth rates below a ΔK of 5 MPa√m in 0.06M NaCl full immersion under a constant σ_{max} of 150, stress ratio of 0.65 and a frequency of 0.2Hz, Figure 2. For the stress ratio of 0.02 the effect of low levels of $SrCrO_4$ is even more pronounced, having an effect to a ΔK of almost 10 MPa√m, Figure 3. This result is particularly critical as the DoD plans to remove chromate from corrosion protection systems. (1) The result showing that there is an effect of fatigue crack growth rates in the lower ΔK region could mean that the chromate effect is present in most damage tolerant models. Damage tolerant models use teardown and other damage data to estimate crack growth rates to set inspection intervals. The damage noted on aircraft likely below a ΔK of 12 MPa√m, meaning that a large portion of the crack life is spent in a ΔK range where chromate is effective at slowing fatigue crack growth. This means that if chromate is removed from the corrosion protection systems, the required damage inspection interval could be underestimated.

It was found that there is a gradient across the fracture surface for the samples exposed to $SrCrO_4$ which may explain the breakdown in inhibition as the crack length increases. Interestingly the 0.5mM $SrCrO_4$ test completed at a stress ratio of 0.02 has more chromate at the back of the crack than the 4.7mM test at a *R*=0.65, likely explaining the higher ΔK inhibition. Figure 5 shows the gradient variation and the locations of measurement.

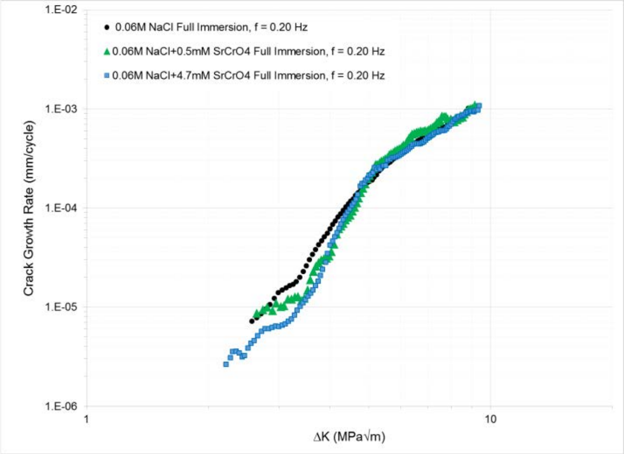


Figure 2
Effect of $SrCrO_4$ (0.5mM and 4.7mM) at a *f* of 0.2Hz, constant σ_{max} =150 MPa, *R* = 0.65 in 0.06M NaCl.

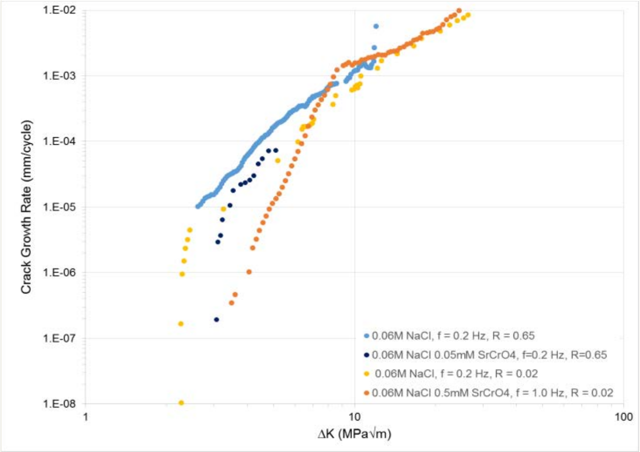


Figure 3
Inhibition effect of 0.5mM $SrCrO_4$ added to 0.06M NaCl on fatigue crack growth rates at a σ_{max}=150MPa, *R*=0.02 and 0.65. Baseline testing was completed at a *f* of 0.2Hz but due to crack arrest the testing with inhibitor at a *R*=0.2 was completed at 1 Hz. Even with the higher testing frequency the inhibitor shows effect up at a ΔK of 9 MPa√m.

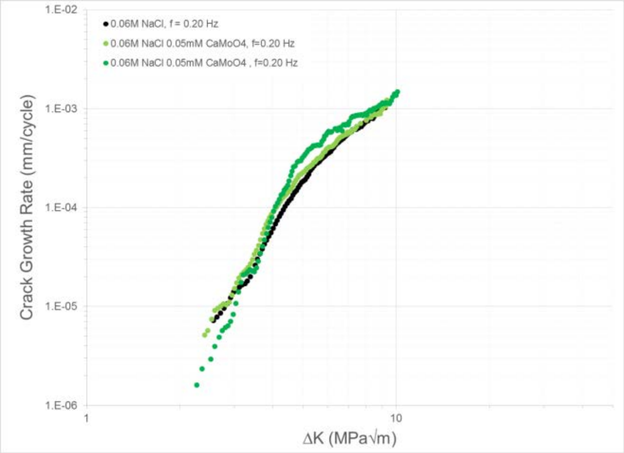


Figure 4
Effect of $CaMoO_4$ at a frequency of 0.2Hz, constant σ_{max} of 150 MPa, R of 0.65 in 0.06M NaCl.

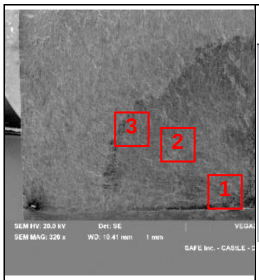
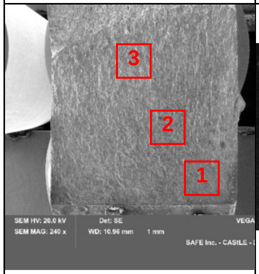
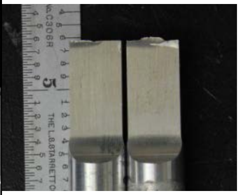
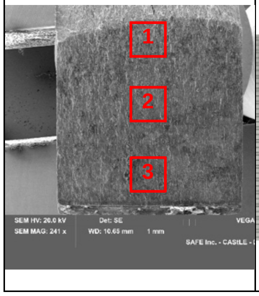
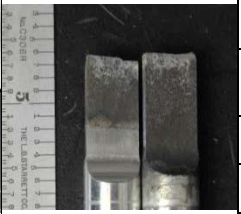
		**$SrCrO_4$=0.5mM, R=0.02, f=1 Hz**
		Chromium Concentration by Location
		1: 0.9 wt %
		2: 0.7 wt %
		3: 0.4 wt %
		**$SrCrO_4$=4.7mM, R=0.65, f=0.2 Hz**
		Chromium Concentration by Location
		1: 1.15 wt %
		2: 0.79 wt %
		3: 0.26 wt %
		**0.06M NaCl, R=0.65, f=0.2 Hz**
		Chromium Concentration by Location
		1: 0.14 wt%
		2: 0.18 wt %
		3: 0.14 wt %

Figure 5
Macro surface pictures and SEM micrographs of the 0.5 mM SrCrO4 test completed at a R=0.02, f=1 Hz, 4.7mM $SrCrO_4$ test completed at a R=0.65, f=0.2 Hz, 0.06M NaCl test completed at an R=0.65, f=0.2 Hz. The chromium content is listed by location of measurement.

The corrosion inhibiting pigment $CaMoO_4$was able to inhibit fatigue crack growth rates below a ΔK of 3 MPa√m at a R of 0.65 and a frequency of 0.2 Hz, Figure 4. This result suggests that while there is some inhibition from a possible chromate replacement coating, the effect on fatigue crack growth rate cannot be inferred from high solubility salts with the same anion.

ACKNOWLEDGEMENTS

This work was funded under USAFA Broad Agency Announcements (FA7000-11-2-0011; FA7000-14-2-0013) by the United States Office of the Secretary of Defense Corrosion Policy and Oversight Office under the Technical Corrosion Collaboration (TCC).

The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies and endorsements, either expressed or implied of US Air Force Academy or the US Government. This material is declared a work of the United States Government and is not subject to copyright protection in the United States.

REFERENCES

1 Young, Jr., John J., Undersecretary of Defense, (2009) “Limiting the Use of Hexavalent Chromium,” *Memorandum for Secretaries of the Military Departments*.

2 Hertzberg, E.F. et al, *Estimated Impact of Corrosion on Cost and Availability of DoD Weapon Systems: FY2016* Report SAL4IT2 2016, Tysons Corner, VA.

3 Gasem, Z. and Gangloff, R.P., (2001) “Rate-Limiting Processes in Environmental Fatigue Crack Propagation in 7000-series Aluminum Alloys”, in *Chemisty and Electrochemistry of Corrosion and Stress Corrosion Cracking*, p. 501-521. R.H. Jones, Editor. TMS-AIME: Warrendale, PA.

4 Warner, J.S. (2010) “The Inhibition of Environmental Fatigue Crack Propagation in Age-Hardenable Aluminum Alloys.” *PhD Dissertation,* University of Virginia, Charlottesville, VA.

5 Warner, J.S., Kim, S. and Gangloff, R.P., (2009) *International Journal of Fatigue* vol. 31, p. 1952-1965

6 Lui, X.F., Huang, S.J. and Gu, H.C. (2003) *Corrosion Science* vol. 45 n.9, pp.1921-1938.

7 Wanhill, R.J.H., De Luccia, J.J. and Russo, M.T. (1989) *The Fatigue in Aircraft Corrosion Testing (FACT) Programme* AGARD Report 713 (AGARD-R-713).

8 Sinko, J. (2001) “Challenges of chromate inhibitor pigments replacement in organic coatings”. *Progress in Organic Coatings* vol. 42**,** p.267-282.

9 Sinko, J. (2009) “Pigment grade corrosion inhibitors: a review of chemistry and relevant concepts”. *DoD Corrosion Conference*, Washington D.C.

10 Petry, L., Dante, J.F. (1999) “Analysis of isocyanate-free topcoats by electrochemical impedance spectroscopy”, *Evaluation Report No. 99-71*, AFRL/MLSA.

11 Office of the Inspector General Department of Defense, (1996) “Air Force Aircraft Painting and Corrosion Control,” *Report Number 96-062*.

12 Scholes, F.H. et al, (2006) “Chromate leaching from inhibited primers Part I. Characterization of leaching,”.*Progress in Organic Coatings*, vol.56**,** p.23-32.

13 Funke, W. (1983) “Towards Environmentally acceptable corrosion protection by organic coatings”,

Journal of Coating Technology vol. 55, p 705

14 W.M. Haynes, Ed, (2011) *The Handbook of Chemistry and Physics*, 92nd Ed, New York, New York.

15 Galyon Dorman, S.E., et al, (2016) *Managing Environmental Impacts of Time-Cycle Dependent Structural Integrity of High Performance DoD Alloys*, SAFE Inc., SAFE-RTP-16-045.