The Role(s) of Substrate Alloy Heterogeneity in Underpaint Corrosion on Aluminum Alloys

D. A. Little and J. R. Scully

The overall goal of this project is to understand the effect of the microstructure and composition of the precipitation age hardened Al alloys on the mechanisms of under-paint corrosion. As well as to understand the role(s) of the microstructural heterogeneities of the substrate on the corrosion process under pristine coatings and those coatings with macroscopic defects such as scratches.

We seek to understand the roles of the composition, density, identity, and distribution of IMCs on the initiation and propagation of under-paint corrosion. A variety of methods will be utilized to study these local corrosion processes, including capillary electrochemical impedance spectroscopy (EIS), scanning kelvin probe (SKP), and confocal scanning laser microscopy (CSLM) for locally resolved spatial resolution studies. Tests over the propagation stage will be performed with both planar electrodes utilizing capillary EIS and engineered close-packed simple cubic multi-electrode arrays utilizing a multichannel microelectrode analyzer (MMA). These arrays can be used to study the initiation stage of under-paint corrosion because of the flexibility with controlling the composition and treatment of individual wires. Electrodes of Al2024 will be utilized with various thermal treatments (e.g. T3 and over-aged) to vary the amount of Cu in solid solution. Pretreatments will be used to maximize or minimize the extent of Cu on the surface. Major modes of under-paint corrosion on military aircraft such as scribe creep, filiform, and blister growth will be investigated.

It is well known from literature that the Cu and Fe containing microstructure of aluminum alloys leads to the formation of galvanic cells between intermetallic compounds (IMCs) and the matrix and Cu-replating[1-5]. These events govern the local breakdown of coatings. IMCs can serve as local anodic and cathodic sites as well as sources for Cu-replating. Additionally Cu-replating may originate from the matrix. Literature has shown that the composition of the aluminum alloy, particularly Cu and Fe, has a direct and dominant effect on the growth rate of filiform corrosion[6, 7]. The effect of Cu and Fe on the amount of filiform corrosion can be seen in Figure 1 from Alcoa[6, 7]. However, it is unclear whether the detrimental action of Cu and Fe in filiform corrosion occurs as a result of their presence in IMCs or Cu-replating. Moreover, it is unknown whether anodic IMCs, cathodic IMCs, or some combination are required for initiation.

Electrodes were prepared by mechanically polishing to 1200 grit with SiC paper and immersing in butanone for 30 sec. Three surface treatments were utilized for maximizing and minimizing the replated copper content for testing purposes: (1) a 40 min immersion in 1.5 g/L NaOH and rinsed with deionized water was used to etch and replate Cu on the surface (high surface Cu yield), (2) a 40 min immersion in 1.5 g/L NaOH, rinsed with deionized water, 30 sec immersion in 50 wt% HNO_3, and rinsed with deionized water was used to etch the surface then remove the IMCs from the surface (low surface Cu yield), and (3) no treatment of the surface[8].

Cyclic voltammetry (CV) was performed on 2024-T3 electrodes with these various pretreatments to qualitatively determine the initial amount of replated surface Cu prior to under-paint corrosion. Scanning auger microscopy (SAM) will be used to assay the surface composition of the electrodes including Cu-replating to compare with and quantify the CV results. These methods will be repeated after under-paint corrosion has taken place.

Humid air exposure studies were performed on scratched coated 2024-T3 planar electrodes. 2024-T3 panels (5 cm x 5 cm) with the pre-treatments mentioned were coated with an epoxy polyamide coating similar to aircraft primers. The average coating thickness is about 10 μm and ranges from 2 to 22 μm. Samples were scribed (4 cm long) using a sharp scalpel that penetrated the coating on the 2024-T3 panels. Drops of 16 wt% HCl were placed along the scratch for 30 sec then the excess acid was removed with Kimwipes®. These test coupons were then placed in humid air chambers at 40°C and 80% relative humidity (RH) as well as room temperature (~25°C) and ~85% RH. Variations in temperature at a given relative humidity (30°C and 50°C at 80% RH) will also be performed. Planar electrodes were monitored in-situ utilizing a digital camera. The rate of scribe-creep was monitored and ranked according to scribe-creep susceptibility for the different surface treatments. Initial results from the humidity exposure tests can be seen in Figure 2, which shows that the average scribe-creep length does not grow for pure aluminum over the length of the test. This figure also depicts that the surface treatment of 40 min NaOH and 30 sec HNO_3 has a slower scribe-creep growth rate than does the conditions with no surface treatment or the surface treatment of 40 min NaOH. The difference between no pretreatment and the NaOH pretreatment seems to be minor. In-situ images of the scribe-creep appearance, after periodic exposure times for the 40 min NaOH surface treatment, the most susceptible surface treatment, are shown in Figure 3. These experiments are aimed at determining the effect of the Cu content, replating Cu, and Cu-(Fe)-bearing IMCs on the rate of scribe-creep caused by under-paint corrosion. Experiments show that the specific alloy and pretreatment strongly influence scribe creep.

In future work, a long focal length microscope and a capillary electrochemical microprobe will help to determine the sites of initiation and the propagation rates for under-paint corrosion in relation to the overall microstructure.

This research will establish the effect of the microstructure, composition, and surface treatments on under-paint corrosion utilizing an epoxy polyamide coating similar to aircraft primers. This will benefit the Air Force by determining the optimum conditions (composition, heat treatment, and surface treatment) to minimize the initiation and growth rate of under-paint corrosion on aerospace alloys.

This work is supported by AFOSR Grant F49620-96-1-0178 with Lt. Col. Paul Trulove as program director.

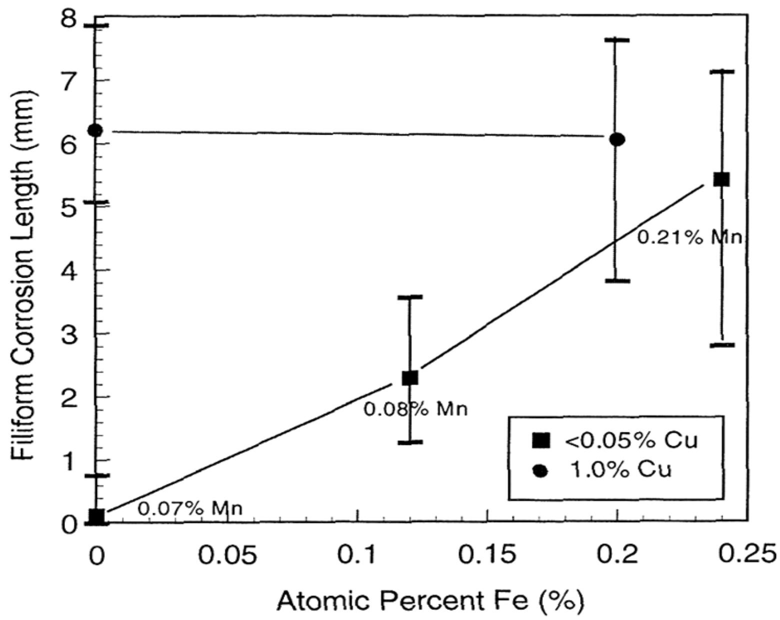

Figure 1. Filiform corrosion length on Al-Cu-Fe alloys as a function of Fe content subjected to humid air exposure after HCl dip[6, 7].

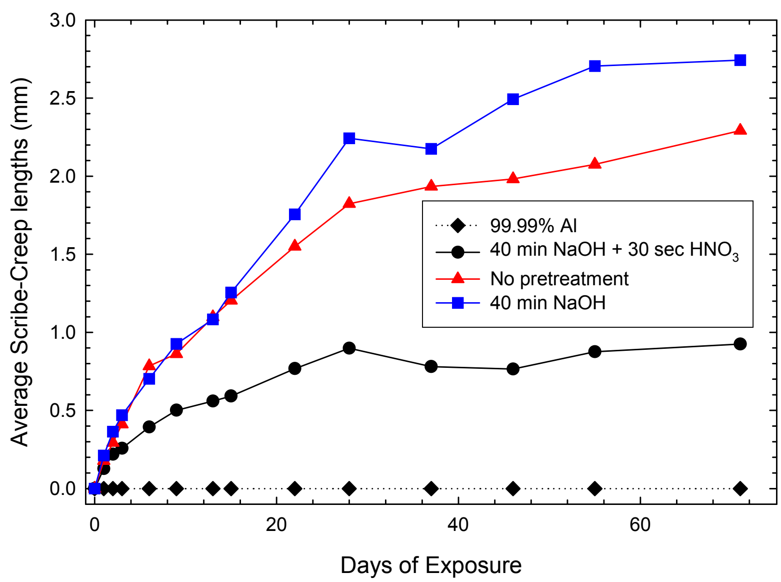

Figure 2. Average scribe-creep lengths for 99.99% Al, and 2024-T3 with various pretreatments exposed to 80% RH at 40°C.

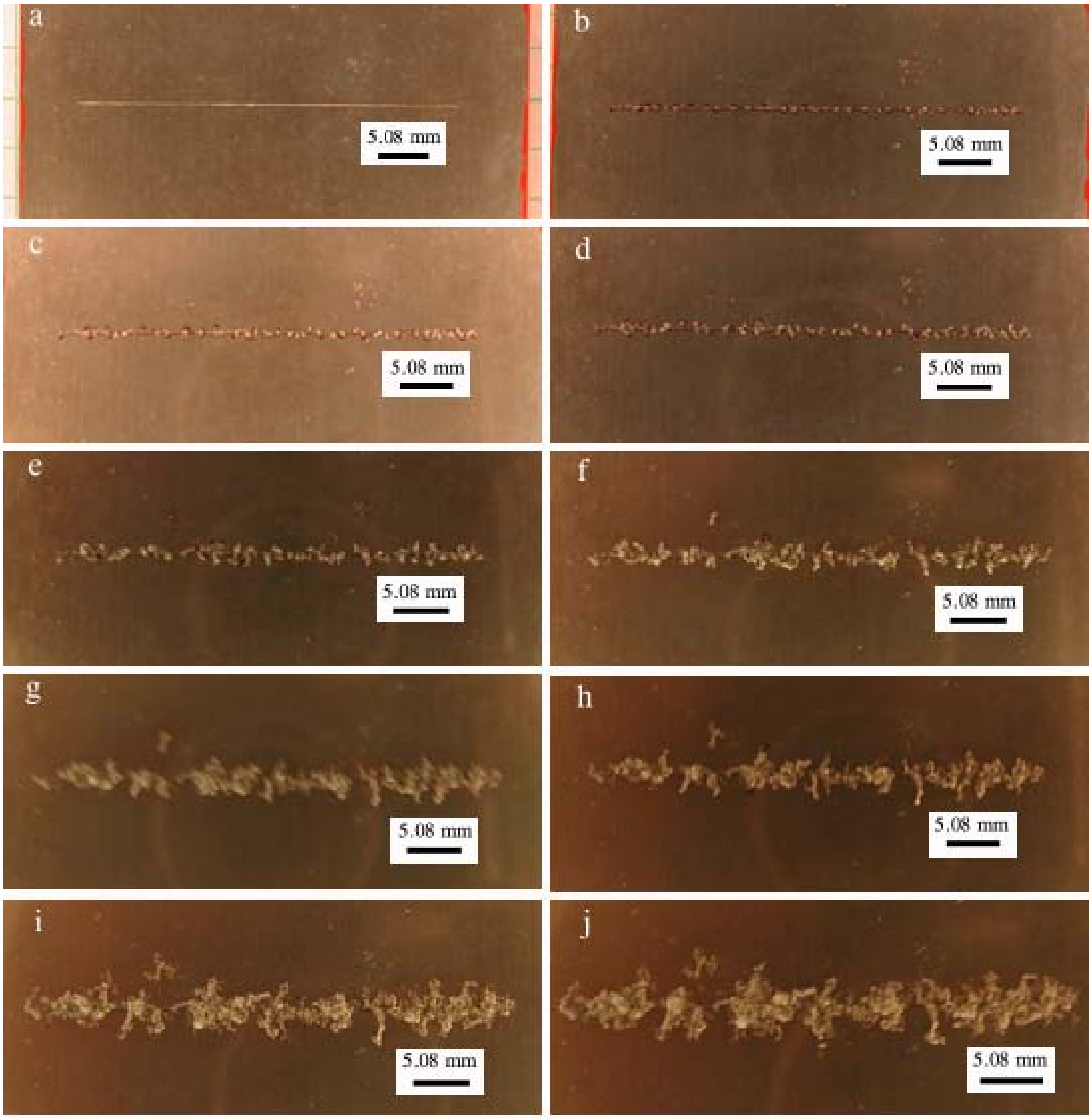

Figure 3. Scribe-creep on epoxy polyamide coated 2024-T3 with a surface pretreatment of 40 min NaOH. A scratch was put in the coating, drops of 16 wt% HCl were placed on the scribe mark for 30 sec, and then the excess acid was removed with a Kimwipe®. The panel was then placed in a chamber at 40°C and 80% RH. The micrographs show the scribe creep present on the panel after a) 0 days, b) 1 day, c) 2 days, d) 3 days, e) 6 days, f) 9 days, g) 13 days, h) 15 days, i) 22 days, j) 28 days of exposure.

<u>References</u>

1. Buchheit, R.G., Journal of Electrochemical Society, 1995. **142**: p. 3994.
2. Buchheit, R.G., et al., *Local Dissolution Phenomena Associated with S Phase (Al_2CuMg) Particles in Aluminum Alloy 2024-T3.* Journal of Electrochemical Society, 1997. **144**(8): p. 2621-2628.

3. Buchheit, R.G. and R.K. Boger. *Cu Redistribution and Surface Enrichment due to Dissolution of Al-Cu Alloys*. in *NACE Topical Research Symposium Proceedings*. March 2001: NACE.
4. Scully, J.R., et al., *Electrochemical Characteristics of the Al_2Cu, Al_3Ta and Al_3Zr Intermetallic Phases and Their Relevancy to the Localized Corrosion of Al Alloys.* Corrosion Science, 1993. **35**(1-4): p. 185-195.
5. Sieradski, K. and N. Dimitrov. *Evolution of Localized Corrosion in Al. Alloy 2024-T3*. in *NACE Topical Research Symposium Proceedings*. March 2001: NACE.
6. Vega, L.F., *Influence of Surface Treatments on Durability ofPainted Al Alloys*. 1997, SAE.
7. Vega, L.F., F. Bovard, and e. al. *Filiform Corrosion of Aluminum Alloys, Influence of Alloy Composition*. in *NACE Topical Research Symposium Proceedings*. March 2000: NACE.
8. Davenport, A.J. and B. Liu. *Copper Accumulation During Cleaning of Al-Cu Alloys*. in *Electrochemical Society Proceedings*. 2000: Electrochemical Society.