

Electrochemical Testing to Predict Corrosion Performance on Various Aluminum Alloys

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ABSTRACT

Previous research has shown that electrochemical techniques can be used to provide quantitative measures of corrosion performance for conversion coatings on aluminum alloy 2024-T3.¹ These techniques could replace the lengthy, costly neutral salt spray test with a few hours of electrochemical testing. This testing provides numerical and statistical comparisons of coatings, which is more robust than the subjective and qualitative analysis performed visually during salt spray testing. Consistent relationships are seen on two common aerospace aluminum alloys (2024 and 7075) coated with two different conversion coatings. Results show predictive correlations between salt spray testing and electrochemical testing. Improvements in corrosion resistance during salt spray had more negative open circuit potentials, lower polarization resistances, larger polarization resistance slopes, and lower corrosion rates measured via electrochemistry. We conclude that electrochemical testing could be an affordable, efficient, quantitative replacement for neutral salt spray testing.

Key words: chemical treatment, coating (process), coatings, corrosion control, electrochemistry, corrosion monitoring, surface finishing, test methods, thin films

INTRODUCTION

Corrosion Testing Background

The gold standard for corrosion testing any new material will always be exposure to the most aggressive environment it will experience in the field, to prove that it will hold up well during real use (often called a field test). Unfortunately, only doing field tests would waste years of time and resources on metals, coatings, and parts that will not be viable in the long term. The easy solution for this was to create a more aggressive environment that would product similar results to the field test in a much shorter period of time (an accelerated corrosion test). Longer term studies have often found poor

correlation between accelerated corrosion tests and field test, but the accelerated corrosion tests have been incorporated into many military specifications, mainly the ASTM B117 neutral salt fog test.¹⁰ The current use of the salt fog test is more aimed at process control. The military specifications require conformance testing materials with salt fog for 168 hours to ensure that the process is providing consistent corrosion resistance over various manufacturers of chemistry and contractors preparing parts. If the one-week test cannot be passed reproducibly, the chemistry and process cannot be used for military applications. Even with the accelerated corrosion test, new chemistries, products, and processes must be put on hold for at least a week to confirm performance. Electrochemical testing could provide results that are just as telling about process control in a fraction of the time as the current accelerated degradation tests. It will also require less material for the testing (salt spray requires five 3" x 10" panels, electrochemistry only needs one for 5 measurements) and less energy and supplies to run the test (salt spray has a large, heated chamber running 24/7, electrochemistry uses a small potentiostat and computer for ~5 hours).

Additionally, electrochemical testing will provide more useful data than salt spray testing. Electrochemistry has numerical results which can be analyzed statistically to rank and evaluate performance. Salt spray testing requires a human eye to determine the material failure, which will vary by personal opinion when assigning pits. Rankings and evaluations depend entirely on pit assignment, a qualitative measurement that varies from person to person. Moving away from subjective results will improve test reliability and possibly the predictive performance.

Two different aluminum alloys are examined with two different conversion coatings to provide support for the viability of replacing salt spray testing with electrochemical testing as a predictive indicator of process control and coating performance. Ideally, electrochemistry could be used as a predictor of long term field performance to cut out the accelerated degradation test entirely.

Aluminum Alloy Background

The aluminum alloys used in this study (2024-T3 and 7075-T6) are commonly found in aerospace applications due to their high strength to weight ratios.² These alloys create strong structural support components while decreasing the overall weight of the vehicle. Alloy 2024 is composed of mainly aluminum with other metals alloyed into it, the bulk of which is copper. Alloy 7075 is also composed of mainly aluminum with other alloying metals, the bulk of which is zinc, then magnesium, followed by copper. The alloyed metals tend to segregate out of the aluminum matrix while the metal is cooling, which leads to small islands of the alloyed metals in the aluminum matrix. These are commonly referred to as intermetallic particles (IMPs).^{3,4} When these IMPs are mainly composed of copper (as is the case for 2024), and when the metal surface is exposed to an electrolyte (such as mist when passing through clouds) a small galvanic cell forms between the IMP and the aluminum matrix.^{3,4}

This galvanic cell typically leads to corrosion and damage to the more active partner, the aluminum. Damage to the base material can lead to catastrophic failure in critical support structures. If the aluminum can be protected to prevent any damage, many lives could be saved. Decreased corrosion would also lead to fewer man hours spent repairing corrosion damage.

Coating System Background

The current best method for protecting the base aluminum alloy is using a 3-part coating stack-up. This consists of a base adhesion promoter/corrosion protector, a primer, and a top coat. In the past, the base coating was a hexavalent chromium containing oxide, which provided excellent corrosion resistance and adhesion to the primer. Hexavalent chromium was recently acknowledged as a respiratory carcinogen and an aquatic toxin. Europe has banned the use of all hexavalent chromium containing compounds since 2017, and the United States is following shortly behind. The currently leading replacement for hexavalent chromium is a trivalent process coating (TCP) patented by the Naval Air Systems Command (NAVAIR).⁵ Several companies licensed the patent to produce their own

variations of the TCP coating, with the same basic formulation involving chromium and zirconium salt solutions which spontaneously form metal oxide coatings on light metals during solution exposure.

The TCP coatings provide excellent coverage and protection on less heavily alloyed aluminums, like 6061 (which contains >95% by weight aluminum). The coating mechanism and formation changes with more highly alloyed aluminum, such as 7075 and 2024. Of these two alloys, the 2024 contains a significantly higher amount of copper (3.8-4.9% by weight) compared to the 7075 (1.2-2% by weight).^{3,4} In standard corrosion resistance testing, the 2024 aluminum alloys are much more prone to corrosion than the 7075 aluminum alloys due to the higher amount of copper.^{3,4} The oxide layer tends to be thicker, more uneven, and more prone to cracks and pinholes around the IMPs, especially those containing copper. This leads to less corrosion protection, which could cause more catastrophic failures of the coating stack-up down the line. Improvements on this base TCP coating must be made to boost the corrosion protection and prevent future catastrophic failures.

One such improvement involves using additives to improve the corrosion inhibition of the base coating, which can be done inside the TCP bath itself. One such corrosion inhibiting additive is called the extended protection additive (EPA), which is simply added into a TCP bath (run at 30% by volume dilution). The EPA goes in at 25% by volume dilution and the bath is run as normally recommended by the manufacturer. Improvements in corrosion inhibition were seen through salt spray performance and electrochemical analysis when using this additive on aluminum alloys 2024 and 7075.

EXPERIMENTAL PROCEDURE

Salt spray results were compiled over several months, while electrochemical experiments were compiled over several weeks. Six panels of each aluminum alloy were processed through each conversion coating at the same time, with five of the panels going into salt spray testing. The sixth panel was tested via electrochemistry.

Panels were allowed to cure overnight at room temperature in a room outside of the coating laboratory before any handling. Salt spray panels were coated with paraffin wax along the edges to prevent any edge effects from interfering with the corrosion resistance testing. The electrochemistry panel was not waxed. Panels began testing at least 24 hours post-coating to allow sufficient curing time.

Coating Process

Aluminum alloys were coated through the recommended process in the manufacturer's technical data sheet (TDS):

1. Clean for 6 minutes in Cleaner 1000 at 120°F, with air agitation
2. Rinse for 1 minute in tap water, followed by 1 minute in deionized (DI) water
3. Activate the metal surface for 1 minute in 50% by volume nitric acid at room temperature (RT), with air agitation
4. Rinse for 1 minute in tap water, followed by 1 minute in DI water
5. Coat in the conversion coating bath (either 30% by volume TCP or 30% by volume TCP with 25% by volume EPA) for 5 minutes at RT, with no agitation
6. Rinse for 30 second in DI water
7. Gentle compressed air to break off surface water, then allow to air dry
8. Cure in clean, ambient temperature air for at least 24 hours before salt spray or electrochemical testing

Test Protocol

After the cure time, panels were either placed into a salt spray chamber to run until failure per the MIL-DTL-5541 and MIL-DTL-81706 specifications (more than 5 pits on one panel or more than 15 pits total on 5 panels) or electrochemically tested.

Salt Spray Testing

The neutral salt spray (NSS) was performed per ASTM B117⁶, MIL-DTL-5541⁷, and MIL-DTL-81706⁸ specifications: 4-6% by weight sodium chloride solution at pH 6.5-7.2. The chamber is maintained at 33-37°C and disperses 1-2 mL of fog per hour. The test is typically run for 168 hours for conformance testing and 336 hours for qualification testing for new products⁸. The salt solution collected from the chamber is analyzed for pH and concentration daily (minus weekends and holidays) with the chamber open for less than hour. Panels were placed at ~6° from vertical inside the chamber. The tests for this study were run until failure (from 168 hours up to 1,800 hours, which is equivalent to 2.5 months).

Electrochemical Testing

Electrochemical testing was performed in a typical single-compartment, three-electrode cell, where the working electrode is the conversion coated aluminum alloy, the counter electrode is a carbon rod, and the reference electrode is a saturated calomel electrode (SCE). All electrodes were electrically connected through the electrolyte, which is a 10% by volume Harrison's solution, composed of 0.35% by weight ammonium sulfate and 0.05% by weight sodium chloride. Measurements were performed in a Faraday cage to prevent noise interference. A detailed setup picture (Figure 1) highlights the different components of the electrochemical experiment. This experiment is simple to setup and run, with each panel yielding 5 runs performed over a week with variations in the time of day to account for any environmental fluctuations during the runs.

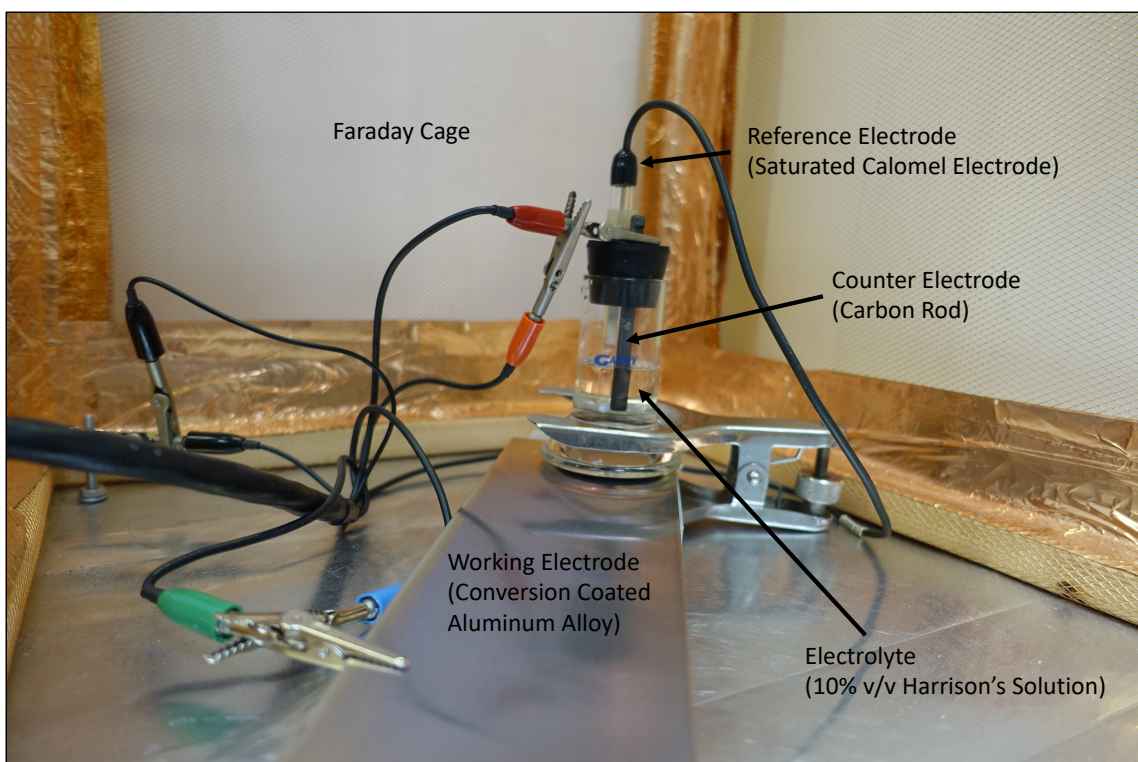


Figure 1: Electrochemical cell setup.

Three different electrochemical techniques were used: open circuit potential (OCP), polarization resistance, and Tafel analysis. During the test process, the OCP is run initially to stabilize the double layer interface between the conversion coated metal surface and the electrolyte. Then a polarization resistance measurement is performed, which provides an idea of how much current flow is resisted by the conversion coated metal. Then a Tafel analysis is performed, probing the resistance to cathodic and anodic corrosion (due to oxygen reduction and aluminum oxidation respectively).

Prior to immersion, the working electrode is set up with the electrochemical cell and a Viton o-ring (providing 8.3 in² exposed surface area). The cell is filled with DI water and soaked for 5 minutes to ensure equivalent coating hydration between different runs and coatings. Then the electrolyte is naturally aerated (by shaking the storage bottle for ~15 seconds) and ~50 mL is poured into the electrochemical cell. The counter and reference electrodes are immersed in the electrolyte. Then all electrodes are connected to the potentiostat.

Open Circuit Potential

The OCP measurement is run for 30 minutes while the electrodes are all immersed in the electrolyte. No external potential is applied to the system. The potential occurring between the reference electrode and working electrode is monitored during the run to see how the electrolyte moves and reorients during the stabilization time. This reorientation of electrolyte ions and water molecules leads to changes in potential. The reorientation is due to any naturally occurring charge on the metal surface. When comparing different metals and different coating systems, the more negative the OCP, the more corrosion resistant the system.

Polarization Resistance

Polarization resistance applies a potential starting 20 mV below the stabilized OCP, scans the potential more positive slowly (0.125 mV/s), and ends 20 mV above the OCP. During this scanning potential (applied between the reference and working electrodes), the resulting current is measured between the counter and working electrodes. The lower the slope of the best fit line to this curve, the more resistant to polarization and thus more corrosion resistant the coating. This relationship is defined via the Stern-Geary equation.⁹

Tafel Analysis

Tafel analysis involves a method similar to the polarization resistance, where the potential is scanned from a point negative of the OCP to a point positive of the OCP. This analysis is much more aggressive and damaging to the coating and base metal. It starts at a potential 300 mV below the stabilized OCP, scanning more positive quickly (5 mV/s), and ending 300 mV above the OCP. This allows a visualization of the cathodic corrosion (at the negative potentials, due to oxygen reduction at the surface) and the anodic corrosion (at the positive potentials, due to base aluminum oxidation). The region around the OCP is fit with two lines, with cathodic and anodic slopes which are used to determine a corrosion rate from their point of intersection, also using the Stern-Geary equation to determine the corrosion current. This corrosion current is used to determine a corrosion rate, per ASTM G102¹¹:

$$\text{Corrosion rate} = (I_{\text{corrosion}} * K * EW) / dA$$

Where the corrosion rate is in milli-inches per year, $I_{\text{corrosion}}$ is the corrosion current, K is the corrosion rate constant [1.288E5 milli-inches(amp-cm-year)], EW is the equivalent weight (8.83 grams/equivalent used for both 2024 and 7075), d is the density in grams/cm³ (2.73 g/cm³ used for both 2024 and 7075), and A is the sample area in cm² (13.12 cm² for all measurements).

The equivalent weight and density should have been modified for the two different alloys, leading to some unexpected relationships between the performance of the two different alloys.