Galvanic Corrosion of Coated Al Alloy Panels with More Noble Fasteners

DISSERTATION

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By

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Abstract

A test sample incorporating a painted Al alloy panel, uncoated through-hole fasteners, and scribes has been shown to provide accelerated response during atmospheric corrosion testing in the field and in laboratory chambers. Several different aspects of this test sample and the behavior of different coating systems are investigated in this dissertation. The galvanic current between SS316 or Ti-6Al-4V fasteners and painted and scribed AA7075-T6 panels was examined during exposure in a salt fog chamber using a zero-resistance ammeter. The anodic current of the AA7075-T6 panel and the cathodic current of each of the four fasteners were monitored using different connection schemes. The anodic current of the panel depended on the number of fasteners connected. The total cathodic current of fasteners was approximately equal to the anodic current of the AA7075-T6 panel, which validates the accuracy of the current measurement. Furthermore, galvanic interaction between the fasteners was observed such that the cathodic current of other fasteners was decreased when a new fastener was added to the measurement. Scribes on a panel can interact with distant fasteners, not just the closest ones. The amount of corrosion as determined by charge and optical profilometry were close and indicated SS316 fasteners caused more corrosion attack than Ti-6Al-4V fasteners.
The galvanic current of an AA7075-T6 panel coupled with mixed SS316 and Ti-6Al-4V fasteners was monitored using a zero-resistance ammeter during 3 weeks exposure in an ASTM B117 chamber or immersed in 5 wt% NaCl solution. SS316 fasteners provided more cathodic current than Ti in both environments and the current in ASTM B117 was higher than in 5 wt% NaCl solution due to greater oxygen availability. The integral of the anodic current with time and optical profilometry (OP) analysis were used to assess the corrosion attack quantitatively for two different coating systems. An acceleration factor was defined to represent the extent of accelerated corrosion for galvanically-connected fasteners. The acceleration factors were in the range of 20-50 for panels with SS316 fasteners and two different coating systems, both with and without a topcoat. The effects of SS316 fasteners were similar for the different coating systems even though the attack morphology was very different.

The corrosion morphology and extent of attack of Al alloy panels with five different surface pretreatments prior to painting and scribing were compared after exposure to ASTM B117 with galvanic connection to uncoated stainless steel fasteners. The nature of the attack for samples with different surface pretreatment samples was found to exhibit two different trends: they either penetrated deeply into the substrate at the scribes or spread out under coatings. The galvanic currents between the coated Al alloy panel and the bare SS316 fasteners were monitored during 21 days exposure in an ASTM B117 chamber. The current trends measured for different surface pretreatment panels were consistent with Optical Profilometry (OP) results. However, the galvanic current and OP techniques both underestimated the extent of corrosion attack due to local H₂ evolution
and undercut attack, respectively. The results from both techniques were modified to compensate for these deficiencies. Acceleration factors associated with the galvanic interaction for the different surface pretreatment panels were determined.

Corrosion of different coated galvanic panels was quantified after exposure to ASTM B117 and a beach field site. Galvanic currents were continuously monitored between the panel and stainless steel fasteners in the field and in the laboratory chamber, exhibiting current transients and stable high value currents, respectively, associated with the two different environmental conditions. The morphology and quantification of corrosion were consistent with the galvanic current results. Acceleration factors were determined to describe the influence of either galvanic coupling or an environment to accelerate coating degradation relative to the condition of no galvanic coupling or of another environment. An acceleration factor for the oxygen reduction reaction was also determined by comparing cathodic currents of a bare SS316 fastener in the different environments. The acceleration factor for different environments can be regarded as a correlation factor between lab results and field applications.

Finally, electrochemical impedance spectroscopy (EIS) was used for over a hundred days exposure of coated Al alloys with different surface pretreatment in 5 wt% NaCl solution. The breakpoint frequency extracted from EIS spectra allows determination of small electrochemically active areas of coatings. It shifts from low to high values with increasing exposure time, due to the enlargement of active areas. A critical breakpoint frequency, in the range of $10^2$ to $10^3$ Hz, appeared after a certain exposure time corresponding to a drop of open circuit potential and $Z_{0.01\text{Hz}}$, indicating visual pits
initiation under the coating. The same chromate primer coated Al alloy with different surface pretreatments had an individual incubation period before reaching to the critical breakpoint frequency. The incubation time can be used as a criterion to evaluate the susceptibility to coating degradation during exposure. Localized corrosion attack was observed on stripped Al alloy after a long term EIS measurements. Optical profilometry analysis was also conducted to determine corroded areas of coatings that were a little larger than electrochemically active areas estimated by the breakpoint frequency method. The breakpoint frequency method is valid for a very small active area such as pit initiation, probably not able to quantify the large active area after pit propagation.
Dedication

Dedicated to my beloved parents and brother
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Chapter 1: Introduction

High strength aluminum alloys are widely used in structural aircraft applications because of the combination of good mechanical properties and light weight. However, during the exposure to corrosive environments, Al alloys are prone to localized corrosion such as pitting caused by different electrochemical properties between intermetallic compounds and the Al alloy substrate. Some intermetallic compounds are more cathodic relative to the Al matrix inducing anodic dissolution of Al matrix nearby and causing trenching. Other intermetallic compounds that are more anodic relative to the matrix may dissolve into the electrolyte and detach from the matrix. Therefore, aluminum alloys for aircraft applications are usually protected from the corrosion attack using multi-layered coating systems. The typical coating systems used on high strength Al alloys are consisted of a conversion coating layer, inhibitor primer, and organic topcoat. Chromate conversion coatings (CCC) are commonly used in the surface pretreatment of AA2024-T3 and AA7075-T6 due to their great resistance to localized corrosion and excellent paint adhesion. Different inhibitor primers, such as chromate epoxy primer, Mg-rich primer, Zn-rich primer and Pr-rich primer, are painted after the surface pretreatment to protect the substrate from localized corrosion by different
mechanisms. Then, the organic topcoat offers optical appearance and a protective barrier to environments such as UV, ozone, water penetration, and mechanical abrasion.

Because of the generally excellent corrosion resistant properties by multi-layered coating systems, coating manufacturers and scientists need to spend a very long time to observe degradation or failure of these coatings even when exposed to very aggressive environments, which makes comparison of different coating systems difficult. Therefore, it is necessary to design accelerated corrosion methods to rapidly assess different coating systems. The common accelerated tests are accomplished by using more aggressive environmental factors, such as pH, temperature, concentration of NaCl, relative humidity, water condensation, UV radiation and wet/dry cycled exposures. Coating degradation initiates from the intrinsic defects in the coating where water penetration and accumulation occur. Intrinsic defects include pores, contamination, and missing point during painting. However, this initiation still takes a long time due to the tiny size of the intrinsic defects. Therefore, artificial defects are usually made on the coatings to shorten the initiation time of degradation. NAVAIR (U.S. Navy Naval Air Systems Command) has developed a test sample design, which is galvanic coupling between noble metal fasteners and coated aluminum alloys with artificial scribes on the top surface. Such combination of galvanic corrosion, artificial defects, and aggressive environment acts as a highly accelerated exposure test where coating degradation occurs much faster.

In this dissertation, a literature review is presented in Chapter 2 comparing different accelerated corrosion testing methods in the lab, discussing galvanic corrosion issues in...
real applications, and introducing the coating failure mechanisms. Chapter 3 provides understanding of the accelerated corrosion mechanism on the coated galvanic panels designed by NAVAIR, which was previously published 16. In this chapter, the galvanic current is monitored flowing between the Al alloy panel and noble fasteners. The galvanic interaction exists between noble fasteners to reduce the current flowing from each fastener. After knowing the corrosion mechanism, Chapter 4 presents the quantification of galvanic attack and introduces the concept of acceleration factor on the galvanic panels, which was previously published 17. In this chapter, the galvanic attack is quantitatively determined by charge and optical profilometry. The acceleration factor is introduced to describe the influence of galvanic coupling between fastener and substrate to accelerate coating degradation relative to situation with no galvanic coupling. Then, Chapter 5 discusses the effect of surface pretreatment on galvanic attack after exposure to ASTM B117 for different periods of time, which was also previously published 18. Chapter 6 compares the galvanic attack between laboratory and field exposure and discusses the limitation of accelerated corrosion tests in the lab. Finally, Chapter 7 exhibits using the breakpoint frequency method to evaluate the protectiveness of different coatings. The limitation of breakpoint frequency method is also discussed in Chapter 7. Chapter 8 presents conclusions from the whole thesis and offers some topics for future work.
1.1 Reference


Chapter 2: Literature Review

2.1 Introduction

This chapter introduces the accelerated corrosion testing methods for the evaluation of coated metals, including standard accelerated corrosion tests, electrochemical accelerated tests, and galvanically accelerated tests. After that, it presents how the fundamental mechanism of galvanic corrosion has been used in lab and field application, such as cathodic protection, sacrificial anode coatings, and micro-galvanic interaction in Al alloys. The third part reviews coating failure mechanisms on metals, containing the aspects of wet adhesion, blistering, and cathodic delamination. At the end, some unresolved issues are raised on the galvanic corrosion of coated Al alloys and noble fasteners.

2.2 Accelerated Corrosion Testing Methods

2.2.1 Standard Accelerated Corrosion Tests

Many accelerated corrosion testing standards have been used to examine the corrosion resistance of coating systems, such as ASTM B117, ASTM G85-Prohesion, and ASTM G154. ASTM B117 involves a continuous 5% NaCl salt fog at 35 ± 2°C in 100% relative humidity. ASTM G85-Prohesion is a dilute electrolyte cyclic fog/dry test in which the specimens are exposed to 1 hour saline fog (NaCl 0.05 % and (NH₄)₂SO₄ 0.35%) at 25 °C and 1 hour dry off at 35 °C. ASTM G154 simulates the weathering
effects on coatings when exposed to sunlight and moisture in natural usage, containing 8 hours of UV exposure and then 4 hours of pure water condensation. In real environments, the coated metal surface is covered with an adsorbed moisture layer in equilibrium with humid air, droplets of spray, condensation, or precipitation. Such atmospheric environments can influence the kinetics of various forms of corrosion initiation and growth by changing local aggressiveness and the solution resistance between active anodes and cathodes. Field exposure provides realistic and accurate evaluations of degradation susceptibility of coatings. However, a long period of time is required to observe degradation or failure of commercial coating systems even in very aggressive environments such as beach exposure. Therefore, those standards have been generally considered as reasonable accelerated corrosion testing methods.

The accelerated corrosion standards described above have long been combined with Electrochemical Impedance Spectroscopy (EIS) to evaluate corrosion protective properties provided by coatings on metals. The low frequency impedance magnitude ($|Z|$) in EIS represents coating resistance and the coating capacitance can be determined at higher frequency in EIS results. Buchheit et al. developed a correlation between salt spray ASTM B117 exposure and EIS tests by comparing the corrosion resistance results of 33 inorganic conversion coatings applied on Al alloys in those two tests. It was found that the probability of a coating without a failure (pit number < 5) in 168 hours of ASTM B117 exposure increased as the coating impedance $R_c$ increased. Based on the correlation, threshold $R_c$ values for AA2024-T3 and AA7075-T6 of $2.5 \times 10^6 \ \Omega \text{cm}^2$ and $1.5 \times 10^7 \ \Omega \text{cm}^2$, respectively, were found. These two $R_c$ values were proposed to be
minimum values for which a given coating can be expected to survive in salt spray test for 168 hours. The combination of ASTM B117 exposure and EIS testing provides many advantages, including standardized protocols for coating assessments and semi-quantification of coating corrosion resistance.

Intrinsic defects in coatings are often the initiation sites for degradation. A very long period of time is needed for water penetration and accumulation at these tiny defects, which greatly delays the initiation of corrosion. So, in order to shorten or eliminate the initiation time, artificial defects have been made on coated metals for accelerated corrosion tests in previous studies \(^7\)-\(^{11}\). EIS measurements on samples with artificial defects were utilized by Yasuda et al. to characterize the effects of two different scribe types on corrosion of coated Al alloy panels in ASTM G85-Prohesion exposure \(^8\). One type of scribe, defined as V-shaped, was made by horizontal dragging of a cutter tip across the sample surface; the other type was made with a spinning cutter tip, defined as U-shaped, which produced wider scribes than the V-shaped type. Visual images of prohesion-exposed panels indicated that U-shaped scribes caused worse corrosion attack than V-shaped scribes, but the scribe depth in each type had little effect on corrosion attack. EIS measurements were carried out nearby the scribes after different periods of prohesion exposure. The results showed that the low frequency impedance for U-scribed panels dropped earlier than for V-scribed panels. Those data implied that the combination of aggressive environment and wider U-shaped scribes might be a new accelerated corrosion testing for coating performance assessments.
2.2.2 Electrochemical Accelerated Tests

Besides intensifying the conditions of service environments to accelerate corrosion, electrochemical methods can also be utilized to evaluate coating performance in a relatively short period $^{12-15}$. In electrochemical aspects, coatings protect metal substrates by limiting the interaction between anodic and cathodic sites at the metal/coating interface. Anodic and cathodic reactions occur easily in the presence of electrolyte accumulation at the metal/coating interface due to the low ohmic drop $^{16}$. During this process, corrosion products and hydroxyl ions are generated from anodic and cathodic reactions, respectively. Both are able to induce coating adhesion loss and further cause coating degradation or failure $^{16}$. Therefore, speeding up anodic and cathodic electron transfer reactions at the metal/coating interface could be a reasonable method for accelerating coating damages, which can be carried out by using an external power supply to generate or consume electrons on the samples, such as potentiostatic or galvanostatic measurements.

An electrochemically accelerated experiment utilized for coating performance assessment is the AC-DC-AC test $^{13,14,17}$. The first AC test, an EIS measurement, uses a very small amplitude current signal to slightly polarize the sample. Then the sample is subjected to a period of constant cathodic current, followed by a relaxation time that allows the test sample to reach a new steady state. Finally, another EIS measurement (the second AC test) is applied to monitor the coating resistance changes induced by the imposed constant cathodic current polarization. The test sequence is repeated until the loss of protective properties of the coating is observed by comparing the results of the
two AC measurements. Coating damage associated with the DC step is because of the production of hydroxide ions from the hydrogen evolution promoted by the cathodic current applied \(^1\). The lifetime of a waterborne acrylic coating was predicted by Bethencourt et al. using the AC-DC-AC method \(^1\). The coating resistance quickly dropped from initial value of \(2 \times 10^6 \, \Omega \text{cm}^2\) to \(4 \times 10^4 \, \Omega \text{cm}^2\) after just four cycles. So, the AC-DC-AC test cycle allows the coating performance assessments to be accelerated. However, a large cathodic current in DC step usually is not applied to coatings in the actual usage. Also it is quite difficult to apply cathodic current in natural environments where the sample surface is covered with an adsorbed moisture layer. There is no appropriate way to introduce the counter and reference electrodes into this very thin electrolyte layer. Therefore, the AC-DC-AC cycle can be only considered as a laboratory-accelerated corrosion test.

### 2.2.3 Galvanically Accelerated Tests

Current applied to accelerate coating degradation can also be carried out by coupling with noble metals based on galvanic corrosion potential series \(^1\). Two or multiple dissimilar metals that are in electrical contact and immersed in the same electrolyte will result in galvanic corrosion \(^1\). Each metal has its own corrosion potential (\(E_{\text{corr}}\)), and when two metals come into contact in the electrolyte, these coupling metals will share the same potential called the couple potential (\(E_{\text{couple}}\)), with an assumption that no ohmic drop exists between two metals. For the more active metal between the two, \(E_{\text{couple}}\) can be much higher than \(E_{\text{corr}}\) resulting in large anodic current flowing into the active metal and acceleration of the corrosion attack. A galvanic-accelerated corrosion method is quite
similar to AC-DC-AC tests by applying high current to rapidly corrode samples. However, the difference is that AC-DC-AC test uses an external power to provide current, while galvanic-accelerated corrosion methods offer current by the potential difference of dissimilar metals. The other difference is that the galvanic-accelerated method only polarizes the coated substrate anodically.

Based on the galvanic corrosion mechanism, a coated galvanic test panel has been designed and utilized by NAVAIR to rapidly evaluated corrosion protective properties of different coatings. This sample incorporates a painted Al alloy panel with uncoated through-hole noble bolts and artificial defects in the coating under the bolts, as shown in Figure 2.1. The different corrosion extent of galvanic panels and non-galvanic panels after 567 hours of exposure to ASTM B117 indicates that noble material bolts offer large cathodic current to drive severe attack around artificial defects. Also, the accelerated response of different material bolts showed that SS316 bolts caused the worst corrosion attack comparing with Ti-6-4 and Al alloy bolts. Al alloy bolts resulted in much less attack, which was similar to the attack around artificial defects with no bolts. The Ti-6-4 fastener exhibits more positive corrosion potential than the SS316 fastener. However, the SS316 fastener provides larger cathodic current than the Ti-6-4 fastener in the cathodic polarization curves. As a result the SS316 fastener provides driving more severe galvanic attack even though it has a less positive corrosion potential. The galvanic series just provides the tendency of corrosion in the thermodynamic aspect, instead of the quantification of galvanic attack. So, more concern is paid on the galvanic current measurements in this dissertation. This sample configuration was modified in a
subsequent study\textsuperscript{21}, in which the panel and bolts were electrically isolated by applying several layers of plastic tape and copper wires were connected to the panel and each bolt. Such modification allows the measurement of galvanic current between panel and bolts during the exposure in ASTM B117.

2.3 Galvanic Corrosion Issues in Real Applications

Besides corrosion acceleration, galvanic coupling is important in many different applications such as cathodic protection, sacrificial anode coating, micro-galvanic interaction in Al alloys, and structural panels coupled with uncoated fasteners. Those applications are based on the fundamental understanding of the mechanism of galvanic corrosion. Coated Al panels coupled with uncoated noble fasteners will be thoroughly discussed in chapters 3 to 6. So the topic is not introduced in this chapter.

2.3.1 Cathodic Protection

In the galvanic coupling of two dissimilar metals, corrosion attack of the active metal is accelerated, which has been explained above, while the noble metal is protected because the couple potential is lower than its corrosion potential. This lower potential results in a reduced rate of corrosion of the more noble metal, which is the basis for cathodic protection. Cathodic protection is widely used on carbon steels in conditions of intermediate aggressiveness. These applications include buried pipelines, off-shore oil drilling platforms, seagoing ship hulls, and water tanks\textsuperscript{22-29}. Cathodic protection can be achieved by either sacrificial anode protection or impressed cathodic current.

Figure 2.2 shows the schematic circuit of cathodic protection by impressed current. The inert anode is the most important component in cathodic protection. An ideal anode
should have good electrical properties, low rate of consumption, low anode polarization, capability of forming different shapes, and low cost \(^{24}\). However, no single material can easily meet all the requirements. The commonly used anodes for different applications are mild steels, ferrosilicon, graphite, lead alloys, magnetite, and platinized titanium. There are many advantages of impressed current cathodic protection system such as large driving potential, higher current output, flexibility of current output control, applicability in almost any resistivity soil environment, and applicability for protecting larger pipelines. However, the disadvantages are the higher installation and maintenance costs. Also impressed current system requires constant supervision to make sure the system is working \(^{24}\).

The polarization curves in Figure 2.3 provide a quantitative assessment of the reduction of corrosion rate caused by impressed cathodic current protection, which is for steel in acid environments \(^{18}\). The corrosion rate of Fe before cathodic protection is about \(10^{3} \mu\text{A/cm}^{2}\). Cathodic polarization of 120 mV will decrease the corrosion rate by three orders of magnitude, to \(1 \mu\text{A/cm}^{2}\), if the Tafel slope is 40 mV/dec. In this case, the required impressed current density, \(i_{\text{app}}\), is about \(1.5*10^{2} \text{ A/cm}^{2}\), which means 1 m\(^2\) of exposed area would need 150 A for protection. Coatings are usually utilized to reduce the exposed area and thus decrease the impressed current requirements; however they are not resistant to strong acid solutions. Therefore, the impressed cathodic current protection is not practical for aggressive acid environments with large corrosion rates. The situation is totally different for a neutral aerated seawater environment. Figure 2.4 illustrates the more practical use case for cathodic protection of steel in neutral aerated water \(^{18}\).
corrosion rate before protection is about 100 µA/cm², which is controlled by the diffusion rate of dissolved oxygen in the electrolyte. The same cathodic polarization of 120 mV decreases the corrosion rate to 0.1 µA/cm² in this case. Now the required impressed cathodic current is a maximum of 100 µA/cm², because the kinetics of cathodic reaction is limited by diffusion of dissolved oxygen. This small applied current can be reduced in the presence of coatings, which are quite stable in the neutral seawater.

A metal structure can also be cathodically protected by electrically connecting to a sacrificial anode that has a more negative corrosion potential. Aluminum, zinc, and magnesium alloys are more active materials than carbon steels, which are the structural metals for pipelines, off-shore structures, ship hulks, etc. Therefore, when coupled with the steel pipelines in soil, these active metals are preferentially dissolved instead of the pipelines. Figure 2.5 shows an example of buried steel pipeline protected by a magnesium sacrificial anode. The sacrificial anodes must be replaced periodically due to consumption. Figure 2.6 illustrates a schematic polarization diagram for galvanic couple between a sacrificial anode of \( E_{\text{corr(a)}} \) and the cathodically protected structure of \( E_{\text{corr(c)}} \). These two materials are polarized to the coupled potential, which provides cathodic protection in a different way comparing with an impressed current in Figure 2.3 and Figure 2.4. At the coupled potential, the corrosion rate of the structure is decreased from \( I_{\text{corr}} \) to \( I_{\text{corr(sc)}} \).  

### 2.3.2 Sacrificial Anode Coating

The fundamental understanding of the sacrificial anode protection is also utilized in coating applications, such as Mg-rich primers (MRPs) on Al alloy and Zn-rich primers
(ZRPs) on steels. The protective modes of MRPs and ZRPs include cathodic protection driven by the more active Mg and Zn particles compared to the substrate and a barrier-type protection due to the insulation of the substrate from the environment. In this review, the focus is on the MRPs instead of ZRPs. The deep understanding of MRPs on Al alloy substrates has been characterized using open circuit potential, potentiodynamic measurement, EIS, scanning vibrating electrode technique, and Scanning Kelvin Probe.

Battocchi et al. found a two-stage mechanism of the sacrificial protection provided by MRPs to an Al alloy substrate. In the first stage, magnesium particles decrease the corrosion potential of the Al substrate below the pitting potential by cathodic polarization. Hydrogen evolution and possible oxygen reduction reactions can increase the local pH above the threshold for magnesium oxide precipitation, which results in an oxide layer, further inhibiting corrosion by a barrier mechanism. However, this two-stage mechanism overlooked the susceptibility of Al alloy substrate to basic corrosion (corrosion in high pH environments), which needs to be considered during cathodic protection. The local high pH causes the protective Al oxide film to become soluble and induces Al corrosion even under cathodic polarization. Maier and Frankel found pitting corrosion on bare AA2024-T3 sheet when coupled to an equal area MRP-coated sheet after exposure to dilute Harrison’s solution (0.35 wt% (NH₄)₂SO₄ and 0.05 wt% NaCl) for 3 hours. No pitting corrosion was found on the bare AA2024-T3 sheet after increasing the coated/bare area ratio to 6.4, which indicating that the ability of MRPs to protect the Al alloy substrate depends on the coated/bare area ratio.
Recent studies about MRPs on Al alloys have been concentrated on the different corrosion performance under field exposure and in ASTM B117 environment \(^{39}\). MRP-coated Al alloy performed very well during beach exposure, but it failed within a short period of time in ASTM B117 environment by blister formation \(^{39}\). A thin and porous magnesium hydroxide layer was detected in the primer after exposure to the salt spray environment. A thick and dense magnesium carbonate layer was formed during outdoor exposure indicating that it inhibits both anodic and cathodic corrosion and prevents blister formation. Magnesium carbonate formation is caused by the higher \(\text{CO}_2\) concentration in field exposure than in the salt spray chamber \(^{39}\). Carbonate formation is preferred to hydroxide due to its lower solubility product. However, other scientists suggested that \(\text{CO}_2\) from the atmosphere stabilizes the pH of electrolyte in a range where Al alloys are passive and prevents blister formation \(^{39}\).

### 2.3.3 Micro-galvanic Interaction in Al Alloys

To obtain desirable mechanical properties of high strength Al alloys, heterogeneous microstructures are intentionally developed in Al alloys. The dominant feature of heterogeneous microstructures is the distribution of intermetallic particles. These particles have very different electrochemical characteristics from each other and the matrix. They can be either anodic or cathodic compared to the matrix, resulting in localized corrosion by micro-galvanic interaction between particles and Al matrix \(^{40-44}\). The electrochemical properties of intermetallic compounds synthesized in the bulk form have previously been studied to understand the role of micro-galvanic interactions in corrosion of Al alloys \(^{44-51}\). Liao and Wei \(^{52}\) used a zero resistance ammeter to study the
galvanic couple of Al and two separate model alloys (an Al-Fe alloy and an Al-Fe-Cu-Mn alloy). The significant galvanic currents between Al and the model alloys provided a clear mechanism of particle-Al interaction inducing pitting corrosion. Over the past decade, a micro-capillary electrochemical cell has been utilized for performing the electrochemical characterizations of intermetallic particles on the micrometer scale in bulk Al alloys \(^{42, 53-58}\). These approaches provide a basic ranking of corrosion susceptibility of different intermetallic compounds. For instance, it has been noted that Al\(_2\)CuMg (S-phase) is more prone to corrosion attack than Al\(_2\)Cu and Al\(_7\)Cu\(_2\)Fe \(^{42, 46}\).

Buchheit et al. \(^{47}\) used scanning electron microscopy to characterize the size of second-phase particles in AA2024-T3. They found that approximately 60% of intermetallic particles larger than 0.5 um were Al\(_2\)CuMg (S-phase). This particle is electrochemically more active than the matrix due to the lower open circuit potential (OCP), causing anodic polarization of Al\(_2\)CuMg by the surrounding Al matrix \(^{43, 44, 46, 47}\). The phase is subject to dealloying under strong anodic polarization, leaving behind porous Cu-rich particles during exposure to aggressive environments. Small 10 - 100 nm diameter metallic Cu clusters become detached from the alloy surface and can be carried away from the particle by moving electrolyte or growing hydrous corrosion product. Then pits form at the site of the detached Cu-rich clusters. This nonfaradaic detachment process electrically isolates the clusters from the matrix. These electrically isolated Cu clusters can be physically detached from the surface, dissolve in the solution and then reduced back on the surface at other locations, which behave as local cathodic sites, stimulating secondary pitting. Large porous Cu-rich remnants coarsen to decrease the
surface energy and reverse the galvanic relationship with surrounding Al matrix because the potential of the particle increases after dealloying. Such reversion of the galvanic relationship induces pitting corrosion in the Al matrix at the periphery of noble Cu-rich remnants. In other words, Al$_2$CuMg phase in AA2024-T3 serves as a local anodic site with respect to Al matrix initially and turns to be cathodic after the selective dissolution in the particle.

There are many other intermetallic particles such as Al-Cu and Al-Cu-Fe-Mn, which are noble with respect to the Al matrix and strongly interact with their surroundings. Trenching, a localized galvanic attack occurring at the interface between noble particle and the matrix, has been discussed extensively in the literature\textsuperscript{40-42, 59-62}. However, the actual mechanism behind trenching is not just simple galvanic coupling causing anodic dissolution at the interface between cathodic intermetallic particles and the matrix. Local high pH due to the oxygen reduction reaction is also capable of attacking the passive film on the matrix\textsuperscript{41,63,64}.

### 2.4 Coating Failure Mechanism

#### 2.4.1 Wet Adhesion

A very important factor to evaluate the protection of coatings is the adhesion to the metal surface, including dry and wet adhesion. Wet adhesion turns to be of great interest to scientists and coating engineers, since most aggressive applications of coatings are either immersed in water or exposed to wet conditions such as humid air, droplets of spray, and condensed water\textsuperscript{65-67}. Unfortunately, no organic coatings can behave as a perfect barrier to completely block water transport through them, because their free
volume and defects offer possible paths for water penetration $^{68,69}$. Funke $^{70}$ proposed that hydrogen bonding and polar interactions between the metal substrate and polymer chains is one possible adhesion mechanism. Linossier et al. $^{71}$ indicated that typical binding energy between metal substrate and polymer is around 25 kJ/mol, which is lower than the substrate-water binding energy of about 40-65 kJ/mol. In other words, the presence of water at metal/polymer interface can cause coating displacement via rupturing of the bond connections between polymer and metal substrate. So wet adhesion was defined by the extent of adhesion in the presence of water $^{67}$, which is more significant than dry adhesion for coating assessments and is the initiation of coating degradation.

Wet adhesion is also influenced by the intrinsic properties of organic coatings including the glass transition temperature (T$_g$), structure of the polymer, and water uptake. Polymers have very different behaviors as the temperature changes from below T$_g$ to above T$_g$. In the temperature above T$_g$, chain mobility in the polymer greatly increases, leading to higher free volumes. This provides more paths for water to transport through the coating to attack the substrate. Therefore, to increase the barrier property and avoid wet de-adhesion of the coating, the service temperature has to be lower than the T$_g$ of the primer to inhibit high chain mobility $^{70}$. Besides temperature, crosslinking and entanglement are also capable of decreasing chain mobility. Walker $^{72}$ stated that coatings with high extent of crosslinking can maintain the amount of original dry adhesion even after water contact. This result can also be explained by the fact that crosslinking decreases the solubility and permeation of water $^{73}$. 

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As mentioned previously, wet adhesion is a quite valuable parameter in evaluating adhesive strength of coatings. Water penetration and corrosion processes at the metal/coating interface can cause adhesion loss and eventually coating failure. So, wet adhesion measurement is very important in coating applications. Nevertheless, the test of wet adhesion is more difficult than dry adhesion. The tape test is a simple method for measuring adhesion, which is following the ASTM D3359-09 Standard Test Method for Measuring Adhesion. In this test, an adhesive tape is placed after immersion on the top of coating and peeled off. Funke indicated that few sites of detached coating from the substrate and failure proceeding along the tape/coating interface indicated “good” wet adhesion. Another wet adhesion measurement technique is a pull-off test, where a dolly is stabilized on the top of coating by a high strength adhesive epoxy and then tensile stress is utilized to detach it, providing the adhesion strength. The shortcomings for these two techniques are that the results do not quantitatively represent adhesion force and the results depend on the person doing the testing.

2.4.2 Blister

The initial coating degradation is mainly determined by the visual observation of blisters, which can be defined as a portion of adhesion loss of coating. Several different mechanisms exist to explain the formation of blisters such as volume expansion because of swelling, gas formation at the metal/coating interface and osmotic pressure. Funke proposed osmotic pressure as the main driving force for blistering. Osmotic pressure is driven by the activity gradient of water from the metal/coating interface to the external bulk electrolyte. Contaminants are inevitable at the metal/coating interface,
which can be residual salts and hydrophilic solvents remaining from surface treatments and the paint curing process \textsuperscript{77}. When coated metals are used in solution for a certain period of time, water can eventually penetrate through the polymer to the substrate, especially at the locations of contaminants. Then a water activity gradient will be formed between contaminated locations at the metal/coating interface and the bulk solution near the coating, resulting in osmotic blistering. Van der Meer-Lerk and Heertjes \textsuperscript{78, 79} proposed that the osmotic pressure can increase up to hundreds of atmospheres, which is much higher than the critical pressure a polymer film can stand without disbondment. Thus, during blister initiation, adhesion loss near the blister is a result of high osmotic pressures. Leidheiser \textsuperscript{76} reported a very interesting blister occurrence in a coated ship that sailed from the Atlantic Ocean to the Great Lakes. A handprint was accidentally left on the ship before it was coated. There was no blistering occurring during the trip in the ocean, since the high salt concentration in the ocean didn’t drive much osmotic pressure in the coating. However, when the ship sailed through the fresh water lake, the large water activity difference between metal/coating and coating/water interface caused a handprint shaped blister on the ship.

2.4.3 Cathodic Delamination

Steels are normally coated before use. The coated metal can be exposed to electrolyte in the presence of defects in the coating, through which it is easy for ions to transport to the metal/coating interface. Figure 2.7 is a schematic of the cathodic delamination mechanism. The coated area that has lost adhesion is defined as the delaminated area. Cathodic delamination drives organic coating separating from the substrate by the
galvanic coupling between the defect (anode) and the delamination front nearby the intact area (cathode) \(^{80-82}\). It is not a typical galvanic coupling of dissimilar metals electrically contact in the same electrolyte. This case is the same metal in two different electrochemical states. The delaminated area has more positive electrochemical potential due to abundant oxygen supply that leads to reduction reactions. The defect area has oxide layers on the surface that normally exhibit more negative potentials when exposed to the aggressive electrolyte \(^{80}\). It should be noted that oxidation occurs in the defect area, while only reduction takes place at the delamination front. The potential distribution as a function of distance to a 0.5 M KCl filled defect on steels was measured by Leng et al. \(^{80}\), as shown in Figure 2.8, which proves the galvanic coupling between defects and delaminated areas. The oxygen reduction reaction at the delamination front consumes the electrons provided from active dissolution of metal at the defect, generating hydroxide ion, which attacks the metal/coating bonds and leads to delamination propagation from the defect. From this point, three main steps for adhesion loss by cathodic delamination are (a) cation transport along the interface, (b) oxygen reduction at delamination front and (c) disbondment by the products of oxygen reduction reaction.

Cation transport builds up the ionic connection in cathodic delamination \(^{81}\). Deflorian and Rossi \(^{83}\) found that cathodic delamination is negligible in distilled water. Anions do not have significant influences on the delamination rate \(^{81}\). This point is also supported by Stratmann et al. \(^{84}\) who used Auger electron spectroscopy in the delaminated area to show a low Cl\(^-\) signal but strong Na\(^+\) signal for experiments in NaCl solution. Moreover, experiments with different cations (LiCl, NaCl, KCl and CsCl) indicate that the cation
type has a significant influence in the delamination kinetics [85]. The delamination front is shifted to intact area with increasing corrosion time and the delamination rate can be deduced from Figure 2.8. The delamination distance is proportional to the square root of time \(^{80,84}\). This was also confirmed by other authors \(^{83}\).

Oxygen reduction also plays an important role in the cathodic delamination process. The partial pressure of oxygen affects the potential of the local cathode at the delamination front. The potential of the delamination front would decrease to the similar potential as that in the defect area if oxygen was replaced by argon atmosphere \(^{82}\). Similar points have been made by other authors in other anaerobic atmospheres \(^{85,86}\). Furthermore, the oxygen reduction reaction helps cation migration from the defect area to the delamination front because of negative charge (OH\(^{-}\)) accumulation. It was proposed that the metal/coating interface degradation is due to hydroxyl ions produced by the oxygen reduction reaction at the delamination front \(^{85,87}\). However, Leng et al. \(^{82}\) compared the delamination kinetics in deaerated 1 M NaOH solution and in 1 M NaCl solution, and found very low delamination rate occurring in 1M NaOH deareated solution. This implied that OH\(^{-}\) is not the only reason for degrading the bond. Some other species must exist to induce bond degradation. Besides OH\(^{-}\), there are also many other species during the oxygen reduction reaction, such as O\(^{2-}\), and H\(_2\)O\(_2\). It is still not well-known how these species affect the bond between metal and coating.

### 2.5 Unresolved Issues

Although many studies have long been done on rapid assessments of different coatings, many important issues remained unknown at the start of this dissertation. For
many coated metals that were exposed to the standard salt spray or natural environments, previous scientists mainly used visual images as evidence to evaluate the coating performance, or mass loss method to obtain the extent of corrosion attack. EIS technique was also used to analyze corrosion resistant properties of coatings. Those methods have shortcomings in that they are qualitative or ex-situ. It is very difficult to quantify the corrosion attack on the coated metals in-situ during the salt spray test or field exposure, because there is no bulk electrolyte phase to establish the three electrodes system. A special sample design in Figure 2.1 introduces two almost coplanar electrodes on which ionic connection can be built up even in a fog environment, allowing the galvanic current measurements when coated metals were exposed to ASTM B117 or in the field 19, 20. The noble fasteners provide considerable cathodic current, accelerating corrosion attack around the artificial defects. Since cathodic current on the noble fasteners is much higher than that of the substrate under the coating, most of corrosion attack is caused by cathodic current on fasteners. Thus, based on Faraday’s law, the galvanic current changing as a function with time can be used to quantify the extent of corrosion attack. This sample design allows quantification of the corrosion attack under coatings during the exposure to ASTM B117. However, due to the artificial defects in this design, information of water uptake and the initiation of coating degradation cannot be obtained. Although there are many intrinsic defects left in the coating during the fabricating process, these intrinsic defects have totally different behavior than artificial defects. So, a similar sample design without artificial defects is worthy of study. More importantly, there are some remaining questions unanswered in the work of this design. (1) How do the artificial defects
propagate? (2) What is the propagation rate of artificial defects? (3) Does this galvanic panel have different response to the lab and field exposure? (4) How and when do the intrinsic defects become visual corrosion sites? (5) Can we optimize the galvanic sample design for lifetime prediction?

In addition, the mechanism of artificial defect propagation on coated Al alloys when exposed to ASTM B117 and in the field is not clear. Leidheiser \textsuperscript{86} stated that a conductive oxide is a requirement for cathodic delamination. Since oxides on Al substrate are insulating, cathodic delamination might not be the mechanism of defect propagation on coated Al alloys. For that reason, many questions arise, such as: how does disbondment between Al substrate and coatings happen? How do cations and anions transport under the coatings? Where is the local anode and cathode? How does the defect front move? Mechanical delamination could happen at the Al substrate/coating interface due to the generation of corrosion products, which may provide a lifting force to peel the coating from the substrate. Filiform corrosion may also occur on coated Al alloys with artificial defects, which has totally different mechanism compared to delamination. The most common corrosion type on coated Al alloys is blistering. But how the blister propagates is still unknown. As discussed previously, Al oxide layer is an insulator, which greatly inhibits the oxygen reduction reaction, thus not much hydroxyl ion is generated at the blister front to weaken the bonding between substrate and coating. There must be some other locations in the coated Al alloys for cathodic reaction to occur, or some other explanations for blister growth. Furthermore, in the galvanic panel \textsuperscript{19, 20}, the oxygen reduction reaction can occur on the surface of SS316 fasteners. Is there any possibility for
OH\textsuperscript{−} generated on fasteners to migrate to the defect areas and cause coating degradation? If this happens, it would be of interest to know how this process might change if SS316 fasteners were replaced by Ti alloy fasteners or other metal fasteners. These questions are still unknown and worthy of study.
Figure 2.1. Schematic of galvanic panel for accelerated corrosion tests \textsuperscript{20}.
Figure 2.2. Cathodic protection by impressed current $^{18}$. 

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$^{18}$ Reference or note number.
Figure 2.3. Cathodic protection by impressed current density, $i_{\text{app}}$, in an acid solution.\textsuperscript{18}
Figure 2.4. Cathodic protection by impressed current density, $i_{app}$ for steel in neutral water $^{18}$. 
Figure 2.5. Cathodic protection with sacrificial anode.\textsuperscript{18}
Figure 2.6. Schematic polarization diagram for sacrificial anode coupled to a cathodically protected metal structure\textsuperscript{18}. 
Figure 2.7. Schematic of the cathodic delamination mechanism.
Figure 2.8. Potential distribution as a function of distance to a 0.5M KCl filled defect on steels$^{80}$. 
2.6 Reference


Chapter 3: Galvanic Test Panels for Accelerated Corrosion Testing of Coated Al Alloys: Measurement of Galvanic Interaction

3.1 Introduction

Multilayer coating systems are commonly applied on metals for corrosion protection. A typical coating system consists of a surface treatment, conversion coating, primer and topcoat. The surface treatment is applied to aluminum alloy substrates (AA2024-T3 or AA7075-T6) to provide a quite smooth surface morphology for conversion coating adhesion. Chromate conversion coating (CCC) formed by immersion of aluminum alloys in an acidic solution of chromate and fluoride have been used for many years to inhibit corrosion. Chromate ions in conversion coating increase the pitting potential of aluminum alloys in chloride solution and decrease the pit initiation and growth rate.

The primer also includes corrosion inhibitors to assist in offering the function of corrosion prevention. Finally, the topcoat provides acceptable optical and physical appearance and a protective barrier to environments (UV, ozone, sunlight, water, mechanical abrasion, etc.).

Due to high corrosion resistance provided by good coating systems, such as chromate-containing systems, a long period is needed to obtain degradation or failure even during exposure to aggressive environments like immersion in high concentration NaCl solution, ASTM B117, wet/dry cyclic tests or beach exposure. This makes
comparison of different coating systems difficult. In most coating assessment tests, the sample design uses artificial scribes through the coating to the metal substrate \(^2, 6-12\). However, as much as 2000 hours exposure is needed to qualitatively differentiate the protection of high performance coatings in salt spray or room temperature immersion \(^13\). Exposure tests in neutral salt spray for scribed coated panels commonly last 3000 hours \(^14\). Therefore, a scribed panel sample design is not efficient and rapid for assessing coatings.

A new test sample design providing accelerated response during atmospheric corrosion tests was recently reported \(^15\). It incorporates a painted Al alloy panel, uncoated through-hole noble fasteners, and scribes. The introduction of noble fasteners in such sample design activates galvanic corrosion and provides cathodic current to drive severe corrosion attack at scribes after only 567 h exposure to ASTM B117. Morphology and corroded volume data were provided \(^15\), but details of the galvanic corrosion between the fasteners and the panel and between individual fasteners, and how to optimize the sample design are unknown.

Structural aircraft components normally are made of painted aluminum alloys. Due to the difficulties of welding high strength aluminum alloys \(^16\), those components are joined together by fasteners, which is quite similar to the accelerated corrosion test panel design studied here. Fasteners in the aircraft industry are made of stainless steels, titanium alloy, carbon steel and aluminum alloy. The major benefit of using stainless steel fastener is that it normally requires no protective coating and has wider service temperature \(^17\). Stainless steels and Ti alloy fasteners are much more noble than aluminum alloy components, can be uncoated, and are not electrically isolated from
aluminum components. Ionic connection between uncoated fasteners and substrate metal under the coating can be provided by humid air, condensation or rainwater. As a result, galvanic interactions between fasteners and aluminum components can be a real failure mechanism in aircraft applications.

In this chapter, galvanic couplings are studied in an accelerated corrosion test panel consisting of fasteners in AA7075-T6 panel in the galvanic corrosion and the material loss at scribed areas is assessed using charge and optical profilometry analysis.

3.2 Experimental

The test sample configuration consisted of a 150 x 75 x 6.5 mm AA7075-T6 panel with SS316 or Ti-6Al-4V hexagonal fasteners (head width 8 mm). The panels were given a chromate conversion coating and then painted with a chromate epoxy primer (PPG CA7233, which is a MIL-PRF-23377 Type I, Class C coating). A flat grey polyurethane topcoat (PPG CA9311/F36375, which is a MIL-PRFL-85285D Type IV, Class H coating) was used to paint half of the panels, and they were then cut into two halves (primer-only side and primer + topcoat side). Before coating, eight holes were drilled through a whole panel, four holes on each half panel as shown in Figure 3.1a. The holes were not painted internally. SS316 or Ti-6Al-4V fasteners were attached by nuts on the back side, torqued to 100 oz-in (0.7 N-m). To isolate the fasteners electrically and thereby allow galvanic current measurements, each fastener was coated with 3M scotch plastic tape as shown in Figure 3.1a. In the standard sample configuration, the coating was scribed through to the substrate to form an “X” at the bottom two holes. A numbering scheme was used to identify the four fasteners: #1 and #3 were inserted in the top unscribed holes and #2 and
#4 were inserted in the bottom scribed holes. The length from the end of scribes to the edge of the washers was about 10 mm. For some experiments, a scribe was only created at the #4 fastener. Insulated copper wires were connected to each fastener and the AA7075-T6 panel for electrical connection. Electrical continuity between the wires and the components as well as the isolation of each component was checked with a meter. Even the fasteners located at the scribed holes were isolated from the metal panel. The assembled sample was then embedded in epoxy with only the top surface of the panel and 4 fasteners exposed.

Galvanic current measurements were made during exposure in an ASTM B117 chamber, in which the mist was generated from 5 wt% NaCl solution. The sample was placed in the chamber tilted at an angle of 20° with the unscribed holes at the top. The copper wires were extended outside of the chamber and connected to a potentiostat, as shown in Figure 3.1b.

Galvanic current measurements between the AA7075-T6 panel and fasteners were performed using a Gamry Instruments Reference 600 potentiostat acting as a Zero Resistance Ammeter (ZRA). A specific notation was used to indicate the details of the galvanic coupling current. The current was measured between materials on the left and right of “/” with materials on the same side of “/” physically contacted to each other. For example, I\textsubscript{p2} represents the coupling current between the panel and #2 fastener. I\textsubscript{p24} is the coupling current between the panel and the combined #2 and #4 fasteners. In this case, the #2 and #4 fasteners were physically contacted to each other before connection to the ZRA. I\textsubscript{p24} represents the galvanic current between the #4 fastener and the combined #2
fastener and panel. In this case, the #2 fastener was physically contacted to the panel and then connected to the #4 fastener through the ZRA. For the period between galvanic current measurements, exposure to ASTM B117 continued with the panel and all fasteners connected together. The experiments were not replicated owing to the length of time required for each measurement.

After exposure tests, samples were immersed in concentrated nitric acid to remove coating and corrosion product. Weight change was monitored after every 10 minutes immersion in nitric acid. This process was terminated when the weight loss was less than 0.01 gram between two consecutive weight measurements. Topographic analysis of the scribed areas on the stripped panels was then performed using an optical profilometer (OP, Veeco Contour GT-K)\(^{18}\). The topographic image generated by OP can be analyzed by a software package (Visio64TM v5.30 from Bruker) to determine the volume of a scribe below the level of the uncorroded areas. However, the scribe volume after exposure is not the corroded volume as the measured value has to be corrected for the original scribe volume. The original scribe volume was estimated by analyzing “control scribes” that were not exposed to corrosive conditions and found to have a volume of about 0.8 mm\(^3\) from the repeated analysis of 2 different scribes. Therefore, 0.8 mm\(^3\) was subtracted from each of the scribe volumes reported. Analysis of each scribe was repeated 5 times, and the results varied slightly for each analysis owing to differences in determination of the level of the uncorroded areas. Average volumes and deviation from those repeated analyses are reported below.
3.3 Results

Galvanic current was measured using a series of connection of different fasteners and panels. The anodic current of the panel was assessed for different fastener combinations to see how the fasteners affect the panel anodic current and the role played by scribes. The cathodic current of a given fastener was also determined with various combinations of the other fasteners connected to the panel to see how that coupling changes the cathodic current. In a real application, all 4 fasteners are connected to the panel. The last condition measured was for all other fasteners connected to the panel.

The anodic current of the panel when connected with different fastener combinations after exposure for only 30 min in the ASTM B117 environment is shown in Figure 3.2. The coupling current between the panel and #2 fastener, \( I_{p/2} \), was monitored at first. \( I_{p/2} \) reached a stable value of about 61 \( \mu \)A at 3500 s. The #4 fastener was then connected to the #2 fastener and the anodic current of the panel, \( I_{p/24} \), increased to 122 \( \mu \)A because of the increase in the cathode/anode area ratio. However, when the #1 fastener was added to #2 and #4 fasteners, the current, \( I_{p/241} \), was essentially unchanged. The anodic current of panel increased again when #3 fastener was connected to other fasteners; the current \( I_{p/2413} \) was equal to 143 \( \mu \)A. This current reflects the full current that the AA7075-T6 panel would receive in a real application with all fasteners connected to the panel. The current decreased at each step when disconnecting the #2, #4 and #3 fasteners sequentially such that \( I_{p/2413} > I_{p/413} > I_{p/13} > I_{p/1} \) as shown in Table 3.1. At the end, the galvanic current between the panel and the #1 fastener was only 20 nA, which is close to zero and explains why the anodic current of panel barely changed when #1 fastener was
added to the #2 and #4 fasteners. After 4 h of exposure, the galvanic current between the panel and each fastener was measured, as shown in Figure 3.3. It can be seen that the currents between the panel and fasteners at scribes, $I_{p/2}$ (49 $\mu$A) and $I_{p/4}$ (61 $\mu$A) were larger than the current between the panel and fasteners at holes without scribes, $I_{p/1}$ (16 nA) and $I_{p/3}$ (27 $\mu$A).

Figure 3.4 shows the anodic current of the panel with different fasteners attached after exposure in ASTM B117 environment for 2 days. The anodic current of the panel increased as the fasteners were attached and decreased when fasteners were disconnected. The current from fastener #1, about 72 $\mu$A, was still smaller than the others, but was much larger than after 4 h. Furthermore, the current of the two fasteners at scribes ($I_{p/24} = 156 \, \mu$A) was larger than that of fasteners at holes without scribes ($I_{p/13} = 127 \, \mu$A) due to potential drop. Figure 3.5 displays coupling current between the panel and each fastener after exposure for 2 days. The currents $I_{p/2}$ and $I_{p/4}$ were larger than $I_{p/1}$ and $I_{p/3}$, which is consistent with the results of 4 hours. It is interesting that the sum of the individual currents of the #1 and #3 fasteners ($I_{p/1} + I_{p/3} = 153 \, \mu$A) is higher than the current measured when #1 and #3 fasteners were attached ($I_{p/13} = 127 \, \mu$A). Similarly, the sum of the individual currents of the #2 and #4 fasteners ($I_{p/1} + I_{p/3} = 188 \, \mu$A) is higher than the current measured when #2 and #4 fasteners were attached ($I_{p/24} = 156 \, \mu$A). As will be described below, this difference is because of galvanic interaction between the fasteners.

Further experiments were performed to figure out whether and how fasteners affect each other. Galvanic current between the panel and #4 fastener $I_{p/4}$ was found to be about 83 $\mu$A after exposure in B117 for 7 days, as shown in Figure 3.6. The #2 fastener was
then physically connected to the panel, which caused the cathodic current of #4 fastener, $I_{p2/4}$, to decrease to about 71 $\mu$A. Then the #2 fastener was replaced in turn by #3 and #1 fasteners to determine the cathodic current of #4 fastener, $I_{p3/4} = 74$ $\mu$A and $I_{p1/4} = 75$ $\mu$A. All of the current values to fastener #4 decreased when another fastener was connected to the panel. When #1, #2 and #3 fasteners were all physically connected to the panel, the cathodic current of #4 fastener, $I_{p123/4}$, reached its lowest value of 65 $\mu$A. These results show the fasteners interact galvanically to alter the current flowing to each individual fastener. Such relationship was observed subsequently after 9 and 13 days exposure.

Figure 3.7 displays the anodic current of the panel to different fasteners after exposure in ASTM B117 environment for 9 days. As previously, the current increased and decreased as fasteners were attached and disconnected, due to the change of cathode to anode area ratio. Figure 3.8 shows the cathodic current of each fastener individually for different connections after exposure for 9 days. In Figure 3.8a, the current between the panel and #1 fastener $I_{p/1}$ was measured at first; then #3 fastener was attached to the panel to measure $I_{p3/1}$; then #4 fastener also was attached to measure $I_{p34/1}$; and finally all the other fasteners were attached to measure $I_{p234/1}$. The cathodic current of #1 fastener decreased when other fasteners were connected to the panel, and the same was found for the other fasteners as shown in Figure 3.8b, c and d. So, each of the fasteners were influenced by each of the other fasteners. Similar results were found after exposure for 13 days, as shown in Figure 3.9.

Figure 3.10 shows the anodic current change of the panel as a function of exposure time in ASTM B117 environment. The anodic current of panel $I_{p/1234}$ with all fasteners
attached increased during the first two days and then slightly decreased. That could be because of corrosion product generated on the scribes, which reduced the exposed substrate area or increased the resistance. The current of scribed fasteners (#2 and #4) is higher than that of unscribed ones (#1 and #3), due to larger ohmic potential drop for #1 and #3 fasteners.

The sample configuration shown in Figure 3.1 was used for all of the experiments discussed above, with scribes at #2 and #4 fasteners. Experiments were also performed on a panel with a scribe only at the #4 fastener and no scribe at the #1, #2, and #3 fasteners. Figure 3.11 show the current of the #1 fastener $I_{p/1}$, which was farthest from the scribe, and the current of the number 4 fastener, $I_{p/4}$, which was on the scribe, at different times to 10 days. $I_{p/1}$ was very small and much lower than $I_{p/4}$ at all times. $I_{p/1}$ was less than 0.05 $\mu$A up to day 4, increased to a maximum value of about 11 $\mu$A at day 8, and then decreased somewhat at longer times. Meanwhile, $I_{p/4}$ reached a maximum value of over 60 $\mu$A at day 2 and then decreased a little to about 50 uA, but these values are much larger than $I_{p/1}$.

To assess the contribution of #1 fastener at day 8, the cathodic current of each fastener with all fasteners attached was measured, as shown in Figure 3.12a. The anodic current of the panel with different fasteners attached was also monitored, as shown in Figure 3.12b. With all fasteners attached to the panel, the cathodic current of #1 fastener, $I_{p234/1}$, was only 5.8 $\mu$A. This value is lower than $I_{p/1}$ because of the interaction of the other fasteners, which is consistent with previous results. Current $I_{p234/1}$ is also much less than cathodic current of other fasteners $I_{p134/2}$, $I_{p124/3}$ and $I_{p123/4}$, because the ohmic
resistance between the scribe and fasteners is largest for this relatively distant fastener. Figure 3.12b also supports this point. The anodic current of the panel \(I_{p/234}\) was about 116 \(\mu\)A without #1 fastener attached and after #1 fastener was connected to the panel, the anodic current, \(I_{p/1234}\), only increased to 118 \(\mu\)A. So the contribution of the #1 fastener is negligible, only 2.2 \(\mu\)A. Figure 3.13 shows that fastener #1 of this sample was rusty at day 4. This was not observed for the sample configuration with scribes at both #2 and #4 fasteners. The low cathodic current at this fastener resulted in less cathodic protection and the fastener corroded.

The results described above were all for chromated primer panels in which all fasteners were SS316 during exposure to ASTM B117. Measurements were also made on panels with Ti-6Al-4V fasteners. Figure 3.14 displays cathodic current of each fastener on chromate primer panel (Figure 3.14a to d) and topcoated panel (Figure 3.14e to h) after 3 weeks exposure to ASTM B117. The black and red curves are for SS316 and Ti-6Al-4V, respectively. It can be seen that current of SS316 fastener at each position is higher than Ti-6Al-4V fasteners.

Figure 3.15 displays anodic current curves of chromate primer panel (Figure 3.15a) and topcoat panel (Figure 3.15b). There was very little difference between the primed-only and topcoated samples as the topcoat has essentially no effect on the galvanic interaction of the fasteners and through-scribe. However, the anodic current of the panel connected to SS316 fasteners is much larger than that connected to Ti-6Al-4V fasteners, indicating SS316 fasteners are better than Ti-6Al-4V fasteners for accelerating corrosion attack and rapid assessment of coating system. Optical profilometry was used to assess
the scribes after the exposure tests and removal of the coatings. Figure 3.16 shows the morphology of scribes on chromate prime panel connected with SS316 fasteners (Figure 3.16a, b), Ti-6Al-4V fasteners (Figure 3.16c, d) and no fasteners (Figure 3.16e, f). In these pictures, the most severe corrosion attack occurred on scribes connected with SS316 fasteners. Some visible corrosion attack appeared on scribes connected with Ti-6Al-4V fasteners. However, it is hard to see any obvious corrosion attack on scribes with no fasteners. The lines that are visible might have been caused by the scribing process. This trend is in good agreement with the current results in Figure 3.15. Similar morphology results of scribes were found on the topcoated panel, as shown in Figure 3.17.

### 3.4 Discussion

From a galvanic corrosion perspective, exposure to ASTM B117 is quite different from full immersion in solution. In ASTM B117 some time is needed to form a layer of electrolyte on a sample that is sufficient to allow the ionic contact needed for galvanic corrosion, while immediate ionic connection occurs during immersion in solution. In the present work, the #2 and #4 fasteners were inserted into scribed holes whereas the #1 and #3 fasteners were in unscribed holes. This means it was easier for the #2 and #4 fasteners to form an ionic connection with scribes than the #1 and #3 fasteners. The results show that a thick and conductive electrolyte layer does not form during the early stages of exposure in a salt spray chamber. As a result, the ohmic resistance is larger for fasteners away from scribes than for those right on top of the scribes. After 4 h, the current of the #1 fastener, \( I_{p/1} \), was only about 16 nA as shown in Figure 3.3, which is close to zero and
reflects the absence of ionic connection between #1 fastener and the scribes. In contrast, a much larger current of about 27 μA was measured for the #3 fastener, \( I_{p3} \), even though it was also inserted in an unscribed hole. Because of the sample tilt in the salt spray chamber, coalesced electrolyte drops from the #3 fastener slid down toward the #4 scribe. In contrast, the drops from the #1 scribe seemed to miss the #2 scribe so no ionic pathway existed at the beginning of exposure. However, after 2 days exposure in ASTM B117 an ionic connection between #1 fastener and scribes was formed as indicated by the large increase in the current from #1 fastener to about 72 μA.

In an engineering application with all fasteners attached to the panel, the cathodic current from each fastener would be \( I_{p234/1} \), \( I_{p134/2} \), \( I_{p124/3} \) and \( I_{p123/4} \), respectively. The total cathodic current is therefore the sum of those 4 currents, which is about 243 μA after 9 days exposure as shown in Figure 3.8. Meanwhile, the anodic current of the panel, \( I_{p2341} \), was about 240 μA. These two values are approximately equal, which is reasonable because total cathodic current should be equal to total anodic current in galvanic corrosion. However, the sum of \( I_{p1} \), \( I_{p2} \), \( I_{p3} \) and \( I_{p4} \) is about 335 μA, which is much higher than the anodic current \( I_{p2341} \), 240 μA, because the individual currents do not include the interaction of the other fasteners. This relationship of total cathodic current equal to total anodic current was also found in other connection situations. For instance, when only #1, #2 and #4 fasteners were attached to the panel, the total cathodic current, \( I_{p24/1} + I_{p14/2} + I_{p12/4} = 203 \) μA, was close to the anodic current of the panel, \( I_{p124} = 198 \) μA. When only #1, #3 and #4 fasteners were attached to the panel, the total cathodic current \( I_{p34/1} + I_{p14/3} + I_{p13/4} = 189 \) μA was close to the anodic current \( I_{p134} = 188 \) μA.

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Turning back to the results at the early stages of exposure shown in Figure 3.2 and Figure 3.3, the anodic current of the panel $I_{p/1234} = 143 \, \mu A$ was close to the cathodic current summation of each individual fastener, $I_{p/1} + I_{p/2} + I_{p/3} + I_{p/4} = 137 \, \mu A$. This indicates that fasteners did not influence each other at the beginning of exposure, and that there was no ionic connection among the scribes and all fasteners in this case. Figure 3.18a shows a schematic representation of the surface electrolyte layer situation at the very beginning of exposure, with separated thin electrolyte layer regions around each fastener. There is no interaction between fasteners because of a lack of ionic connection between them. In this case, the anodic current of the panel $I_{p/1234}$ should be equal to the sum $I_{p/1} + I_{p/2} + I_{p/3} + I_{p/4}$. However, after exposure for 2 days, a large area of ionic interaction connected all of the scribes and fasteners, as shown in Figure 3.18b. In this case, the anodic current of the panel $I_{p/1234}$ should equal the sum of $I_{p234/1} + I_{p134/2} + I_{p123/4} + I_{p124/3}$, and not $I_{p/1} + I_{p/2} + I_{p/3} + I_{p/4}$. So, the sum of $I_{p234/1}$ and $I_{p134/2}$ is higher than $I_{p/1234}$ in most cases because of the galvanic interaction of fasteners, as shown in Figure 3.10. However, $I_{p/1234}$ is close to the sum of $I_{p24}$ and $I_{p13}$ at 30 min exposure because of the lack of ionic connection among fasteners at the beginning of exposure. It should be noted that the ionic connection could be through a defective and saturated paint region rather than just through the electrolyte layer on the surface.

It is possible to assess the extent of corrosion attack around a scribed area using different approaches. In the present work, two methods were used to calculate the effective mass loss, galvanic charge and OP analysis of the scribed area. From Faraday’s law, the integral of anodic current over time can be used to determine an effective mass.
loss that reflects the extent of corrosion attack. OP can also be used to determine an effective mass loss from the volume of the scribed area after removing corrosion products as described in the experimental section. The mass loss calculated by charge and OP are shown in Figure 3.19 for the different cases after exposure to ASTM B117 for 3 weeks. The values for each case are approximately equal, which certifies the accuracy of the calculations. Also, the differences in the cases for the SS316, Ti-6Al-4V, and no fasteners are made clear in this figure.

The potential difference between anode and cathode is the driving force for galvanic corrosion. However, kinetic factors are equally important. SS316 fasteners offer much larger cathodic current than Ti-6Al-4V fasteners, as shown in Figure 3.14, resulting in more corrosion attack on scribed areas, even though potential difference of SS316 and AA7075 is close to that of Ti-6Al-4V and aluminum alloys\textsuperscript{19}. Cathodic polarization curves for samples immersed in solution also show that the current of a SS316 fastener is higher than a Ti-6Al-4V fastener\textsuperscript{15}. Mass loss of scribed areas from optical profilometry was also reported\textsuperscript{15}. However the panel had mixed SS316 and Ti-6Al-4V fasteners, which is different from this study. These studies together show that galvanic corrosion is a good accelerated method to rapidly evaluate different coating system. Furthermore, galvanic coupling with SS316 fasteners is a more accelerated corrosion method than coupling Ti alloy fasteners.

The coating system in this work included a conversion chromate coating and chromate primer with/without a topcoat. The important role of conversion chromate coating and chromated primer is to release soluble hexavalent chromium, which can
migrate to defects or corrosion sites and inhibit further damage \(^3, 4, 20-22\). The topcoat is used for UV protection \(^23, 24\) and barrier properties \(^25\). It might be expected that the topcoat should slow down the corrosion process. However, the topcoat, as a barrier, blocked the release of soluble chromate from conversion coating resulting in wider corrosion attack areas at scribes than on a primed sample with no topcoat, as shown in Figure 3.20. The topcoat covered most of the conversion coating and primer, blocking release of chromate. The only region where the chromate-containing conversion coating and primer were exposed was at the scribes, which are quite small. As a result, only a small amount of chromate can be released from topcoated samples. However, it should be noted that UV exposure was not included in the test protocol, so the benefit of a UV-resistant topcoat in a real application environment was not realized in this work.

3.5 Conclusion

To understand galvanic mechanism of fasteners with an accelerated corrosion test panel for coated Al alloy, anodic current of the panel and cathodic current of each fastener at different attached condition during exposure in ASTM B117 were investigated. Also, mass loss by charge and optical profilometry analysis was calculated to quantitatively to characterize the corrosion extent of scribed areas. Specific conclusions are as following:

- Galvanic interaction of fasteners with an AA7075-T6 panel indicates that anodic current of the panel increases with the addition of attached fasteners and decreases when fasteners are disconnected because of the cathode/anode area ratio.
• Interaction of fasteners with each other shows that cathodic current of each fastener decreases when other fasteners are attached to the panel and the decrease of cathodic current correlates to the number of attached fastener, since potential difference between a fastener and the panel goes down if other fasteners are attached.

• Current of each fastener indicates that scribes are not just interacting with the closest fasteners, also interacting with distant ones. And current of fasteners decrease if scribes are far away from them.

• Mass loss results quantitatively prove coupling with SS 316 fasteners caused most severe corrosion attack and can be an accelerated corrosion method to rapidly evaluate coating systems.

• Corrosion attack areas are wider on topcoat than chromate primer, because topcoat blocks the release of soluble chromate from conversion coating.
Table 3.1. Anodic currents of the panel after exposure for different time.

<table>
<thead>
<tr>
<th>Time in B117</th>
<th>Anodic current of the panel at different fasteners attached / µA</th>
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<tbody>
<tr>
<td></td>
<td>$I_{p/2}$</td>
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<tr>
<td>30 min</td>
<td>61</td>
</tr>
<tr>
<td>2 days</td>
<td>92</td>
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<tr>
<td>5 days</td>
<td>94</td>
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<tr>
<td>7 days</td>
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<td>9 days</td>
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<td>11 days</td>
<td>80</td>
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<tr>
<td>13 days</td>
<td>82</td>
</tr>
</tbody>
</table>
Figure 3.1. Schematic illustrations of the test sample configurations. a: Standard test sample with four SS316 fasteners in AA 7075-T6 panel coated with chromate primer. Notation for fasteners and positions of scribes are shown. b: Schematic of sample configuration for ZRA test. Dotted lines beneath #2 and #4 fasteners represent scribes.
Figure 3.2. Anodic current of the panel after exposure in B117 environment for 30 min.
Figure 3.3. Galvanic current between the panel and each fastener during exposure in B117 for 4 hours.

\[ I_{p/1} = 16 \text{ nA}; I_{p/2} = 49 \text{ uA} \]
\[ I_{p/3} = 27 \text{ uA}; I_{p/4} = 61 \text{ uA}; \]
Figure 3.4. Anodic current of the panel after exposure in B117 environment for 2 days.
Figure 3.5. Galvanic current between the panel and each fastener during exposure in B117 for 2 days.

\[ I_{p/1} = 73 \text{ uA}; I_{p/2} = 97 \text{ uA}; I_{p/3} = 80 \text{ uA}; I_{p/1} = 91 \text{ uA}; \]
Figure 3.6. Cathodic current of #4 fastener when different fasteners attached after exposure in B117 for 7 days.
Figure 3.7. Anodic current of the panel after exposure in B117 environment for 9 days.
Figure 3.8. Cathodic current of each fastener at different connection situation after exposure in B117 for 9 days. a. #1 fastener; b. #2 fastener; c. #3 fastener and d. #4 fastener.
Figure 3.9. Cathodic current of each fastener at different connection situation after exposure in B117 for 13 days. a. #1 fastener; b. #2 fastener; c. #3 fastener and d. #4 fastener.
Figure 3.10. Anodic current change of the panel with function of exposure time at different fasteners attached in B117 environment.
Figure 3.11. Current $I_{p/1}$ and $I_{p/4}$ after exposure in B117 for different time, only #4 fastener is scribed. a. $I_{p/1}$; b. $I_{p/4}$. 
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Figure 3.13. Top morphology of the sample with only scribed #4 fastener after exposure in B117 for 4 days.
Figure 3.14. Cathodic current of each fastener when the panel attached with SS 316 or Ti-6Al-4V fasteners. a – d: chromate primer sample; e – h: chromate primer + top coat sample.
Figure 3.15. Anodic current of AA7075-T6 panel coupling with SS 316 and Ti-6Al-4V fasteners. a: chromate primer sample; b: chromate primer + top coat sample.
Figure 3.16. Morphology of scribes on chromate prime panel coupling with different fasteners after exposure to ASTM B117. a, b: SS 316 fasteners; c, d: Ti-6Al-4V fasteners; e, f: no fasteners.
Figure 3.17. Morphology of scribes on chromate prime + topcoat panel coupling with different fasteners after exposure to ASTM B117. a, b: SS 316 fasteners; c, d: Ti-6Al-4V fasteners; e, f: no fasteners.
Figure 3.18. Schematics of probable surface electrolyte layer on the top of sample. a. exposure for less 4 h; b. exposure for more than 2 days.
Figure 3.19. Mass loss of the panel measured by current and OP analysis after exposure to ASTM B117 for 3 weeks.
Figure 3.20. Corrosion depth profile of panels with different coatings and coupling with different fasteners. a, b: chromate primer panel coupling with Ti-6Al-4V fasteners; c, d: chromate primer + topcoat panel coupling with Ti-6Al-4V fasteners; e, f: chromate primer panel coupling with SS 316 fasteners; g, h: chromate primer + topcoat panel coupling with SS 316 fasteners.
3.6 References


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Chapter 4: Quantification of Accelerated Corrosion Testing of Coated AA7075-T6

4.1 Introduction

Aluminum alloy (AA) 7075-T6 (UNS A97075) is a high-strength aluminum alloy that is widely used in structural aircraft applications due to the combination of good mechanical properties and light weight \(^1\). However, AA7075-T6 is very susceptible to localized corrosion, including pitting, intergranular and crevice corrosion when exposed to an aggressive environment \(^2\)\(^-\)\(^5\). As a result, aluminum alloys for aircraft applications are usually protected from the corrosion attack using multi-layered coating systems \(^6\)\(^-\)\(^8\). Because of the generally good corrosion resistant properties by coating systems, a long period is required to observe their degradation or failure even when exposed to aggressive environments, which makes comparison of different coating systems difficult. Therefore, a new accelerated corrosion test sample was design to be efficient and rapid for assessing coatings \(^9\)\(^,\)\(^10\). It incorporates a painted Al alloy panel, uncoated through-hole noble fasteners, and scribes in the coating under the fasteners. The introduction of noble fasteners in such sample design activates galvanic corrosion and provides cathodic current to drive severe corrosion attack at scribes after only 567 h exposure to ASTM B117. Galvanic current, morphology and corroded volume data were provided \(^9\)\(^,\)\(^10\), but quantitative descriptions of the acceleration extent for galvanically-connected fasteners
were not discussed. A quantitative method for assessing degradation is critical to be able to use these new test specimens in research and development, materials specifications, and assessments for the life of coating systems.

Many conventional methods for assessing coatings have been studied in recent decades, including ASTM B117 exposure, field exposure, electrochemical impedance spectroscopy (EIS), and adhesion tests. The corrosion extent of samples exposed to ASTM B117 or to field environments is typically only qualitatively assessed, providing only a subjective evaluation of the coatings. EIS can be used to characterize the protective properties of coatings on aluminum alloys by evaluating the low frequency impedance magnitude (|Z|) representing coating resistance and by the coating capacitance, which dominates at higher frequency. Nevertheless, EIS data have not been well correlated to the field performance. Another very significant coating parameter in the performance of coated metals is the ability to maintain adhesion to a metal substrate in the presence of water or electrolyte, which can be determined by different adhesion measurements. Assessment of adhesion parameter should be a good approach to evaluate coatings, but most adhesion tests are qualitative, performed in dry conditions, non-reproducible, or overestimate adhesion strength as a result of secondary dissipation energies related to test geometry plastic deformation and other reasons. Therefore, more quantitative and reliable methods are needed for rapidly evaluating different coating systems.

In the present chapter, the galvanic charge and the volume loss of galvanic panels with different coating systems during 3 weeks exposure to ASTM B117 were determined.
An acceleration factor was introduced to describe quantitatively the extent of corrosion acceleration from galvanic coupling of the fasteners and substrate.

### 4.2 Experimental

AA7075-T6 panels with size of 150 x 75 x 6.5 mm were used as substrates for the galvanic panels. The arrangement of holes and fasteners was identical to the sample design described previously \(^9,^{10}\). Two rows of 5 mm diameter holes were created on each panel for attaching noble material fasteners. Two different coating systems were tested. One coating system was used previously \(^9,^{10}\) and included a chromate conversion coating (CCC) and a chromate epoxy primer (PPG CA7233, MIL-PRF-23377 Type I, Class C coating). The other coating system involved pretreatment with Prekote adhesion promoter and then a Pr-rich primer (Deft 084, MIL-PRF-23377J Type I, Class N coating). The same flat grey polyurethane topcoat (PPG CA9311/F36375, MIL-PRFL-85285D Type IV, Class H coating) was used to paint half of every panel. The samples were cut in half to assess the extent of corrosion attack on primer-only and topcoated panels without interactions between the two sections.

Two types of noble material fasteners and washers (SS316 and Ti-6Al-4V) were used for galvanic coupling with AA7075-T6 panels. The SS316 fasteners were passivated by immersion in 25-45 vol% nitric acid solution at 21 to 32 °C for 30 min, rinsing with cold and then hot water and then air drying. The Ti-6Al-4V fasteners were not pretreated before use, and had natural-formed oxide on the surface. To allow measurement of galvanic current between fasteners and the panel, the fasteners were electrically isolated by applying several layers of plastic tape between bolts, nuts, washers and the panel. A
numbering scheme was used to identify the four fasteners: #1 and #3 were inserted in the top unscribed holes and #2 and #4 were inserted in the bottom scribed holes, which is identical to the scheme used previously \(^9, ^{10}\). Fasteners #1 and #2 were Ti-6Al-4V fasteners; #3 and #4 were SS316 fasteners, as shown in Figure 4.1. Some experiments were performed on panels with only stainless steel fasteners.

“X” pattern scribes were manually created across the holes in the bottom row on the panel through to the Al alloy substrate using a carbide scribe and the fasteners were attached. The distance from the end of scribes to the edge of the washer under each fastener was about 10 mm. The width of the carbide scribe tip was about 400 μm. Copper wires were connected to the panel and each fastener for electrical connection. The panel was then embedded in epoxy resin to expose only the top surface to the environment. The sample was exposed in an ASTM B117 chamber with the wires connecting the various components reaching outside the chamber \(^{12}\).

Galvanic currents were measured between the AA7075-T6 panels and different fasteners using a zero resistance ammeter (ZRA) once a day during 3 weeks exposure to ASTM B117 and also during immersion in 5 wt% NaCl bulk solution at room temperature (RT). The solution was not changed constantly during the immersion test. A specific subscript notation was used to indicate the details of the galvanic coupling current. The current was measured between materials on the left and right of “/” with materials on the same side of “/” physically contacted to each other. For example, \(I_{p/2}\) represents the coupling current between the panel and #2 fastener. \(I_{p/24}\) is the coupling current between the panel and the combined #2 and #4 fasteners. In this case, the wires
from both the #2 and #4 fasteners were physically connected to one pole of the ZRA. $I_{p2/4}$ represents the galvanic current between #4 fastener and combined #2 fastener and panel. After the galvanic current measurements, the wires connected to the panel and all fasteners were shorted together so that the assembly components were electrically connected for most of the exposure time.

After the exposure tests, the samples were broken out of the epoxy mount and immersed in concentrated nitric acid to remove the coating and corrosion product. Weight change was monitored after repeated 10 min periods of immersion in nitric acid until the weight loss was less than 0.01 g between two consecutive weight measurements. The weight loss was not used to assess the extent of corrosion. Instead, topographic analysis of the scribed areas on the stripped panels was then performed using an optical profilometer (OP, Veeco Contour GT-K)\textsuperscript{9,10,22}. The topographic image generated by OP can be analyzed by a software package (Visio64TM v5.30 from Bruker) to determine the volume of a scribe below the level of the uncorroded areas. However, the scribe volume after exposure was not the corroded volume because the initial condition included a scribe that penetrated into the panel. The original volume scribe of the pair of scribed Xs was estimated to be about 1.5 mm\textsuperscript{3} from repeated analysis of 2 different control samples that were scribed but not exposed to corrosive conditions. Therefore, 1.5 mm\textsuperscript{3} was subtracted from each of the scribe volumes reported.

### 4.3 Results

Figure 4.2 shows anodic currents of the AA7075-T6 panel when coupled with two SS316 and two Ti alloy fasteners during 3 weeks exposure to ASTM B117 and 5 wt%...
NaCl bulk solution. The coating system on the panel was CCC/chromate primer with topcoat. Galvanic current $I_{p/2}$ between the panel and the #2 Ti alloy fastener at a scribe was monitored during the first 250 s of each measurement. Then the #1 Ti alloy fastener was connected to the #2 fastener, which increased the galvanic current ($I_{p/12}$) both in ASTM B117 and 5 wt% NaCl solution because of the increase in the cathode/anode area ratio. The galvanic current reached a maximum value when coupling the panel with all fasteners ($I_{p/1234}$), where the cathode/anode area ratio was largest. The current decreased after disconnecting the two Ti alloy fasteners, leaving the current between the panel and the two SS316 fasteners ($I_{p/34}$). Finally, the current of the panel when coupling with only the #4 SS316 fastener at a scribe was measured. The current trend in Figure 4.2 indicates that the anodic current of panel coupling with SS316 fasteners was higher than with Ti alloy fasteners in both environments, probably because SS316 fasteners provide more cathodic current than Ti alloy fasteners, which has been found previously $^9, ^{23}$.

Figure 4.2 also indicates that galvanic currents in ASTM B117 were larger than in 5 wt% NaCl bulk solution. ASTM B117 was performed at 35 °C whereas the bulk electrolyte immersion was at RT. The solubility of oxygen decreases with increasing temperature, but the diffusivity of oxygen increases. Furthermore, the thin electrolyte layer present on the surface in ASTM B117 results in a smaller diffusion layer thickness. The cumulative effect of these differences was that the cathodic currents of the fasteners in ASTM B117, and thus the measured galvanic current, were larger than for immersion in NaCl solution of the same nominal composition. It should be noted that, because the
bulk solution was not refreshed during the exposure, its aggressiveness could have
decreased owing to leaching of chromate from the coatings.

The galvanic currents between each individual fastener and the panel coupled to all
the other fasteners were monitored over time to determine the galvanic current from each
fastener, as shown in Figure 4.3. The currents from the SS316 fasteners, $I_{p124/3}$ and $I_{p123/4}$
(around 70 μA) were higher than those from Ti alloy fasteners, $I_{p234/1}$ and $I_{p134/2}$ (around
18 μA) in both environments. The cathodic currents of SS316 fasteners in B117 (around
70 μA) were much higher than those in 5 wt% NaCl solution (around 30 μA), whereas
the cathodic currents of Ti alloy fasteners were approximately the same in the two
environments. Moreover, the currents of fasteners at scribes ($I_{p134/2}$ and $I_{p123/4}$) were
usually a little higher than at holes without scribes ($I_{p234/1}$ and $I_{p124/3}$), due to the ohmic
drop between the fastener and the exposed Al alloy.

Figure 4.4 shows optical profilometry analysis of the corrosion attack caused by
SS316 and Ti alloy fasteners after 3 weeks exposure in ASTM B117. It is clear that the
SS316 fastener caused more corrosion than the Ti fastener for the two different coating
systems, which is consistent with the galvanic current results. Comparison of the two
coating systems indicates that the attack in the CCC/chromate primer/topcoat sample was
deeper, but it was much wider in the adhesion promoter/Pr primer/topcoat sample. This
difference could be caused by the different surface pretreatments of these two coating
systems: chromate conversion coating and adhesion promoter, respectively.

Because SS316 and other stainless steel fasteners and inserts provide more galvanic
acceleration and typically cause more corrosion damage on actual aircraft than titanium
alloy fasteners and inserts $^9$, $^{10}$, they create a more difficult challenge for protective coatings. Therefore, Al alloy panels with only SS316 fasteners were used in the following exposure tests. Figure 4.5 shows anodic currents of panels with two different coatings during 3 weeks of exposure in B117 and 5 wt% NaCl bulk solution. The error bars are from two or three individual experiments. There was very little difference between the primer-only (Figure 4.5a) and topcoated (Figure 4.5b) samples as the topcoat had essentially no effect on the galvanic interaction of the fasteners and Al alloy exposed at the through-scribe. The anodic currents of adhesion promoter/Pr primer samples were higher than those of CCC/chromate primer samples in both environments, indicating that CCC/chromate primer samples had better performance on coated Al alloy panels than adhesion promoter/Pr primer samples. As shown previously, anodic currents of panels in ASTM B117 were higher than that in 5 wt% bulk NaCl solution, which indicates that ASTM B117 exposure is a more accelerated method for rapid coating assessment than full immersion in NaCl solution. From Faraday’s law, the integral of anodic current over time can be used to determine an effective mass loss that reflects the extent of corrosion attack, which will be discussed in the following.

Cathodic currents flowing out of each SS316 fastener contributed to the anodic current flowing into the panel. To assess the contribution of each fastener, cathodic currents of fasteners were measured in ASTM B117 and 5 wt% NaCl bulk solution by using one fastener as the working electrode and other fasteners and the panel physically contacted to each other as the other electrode, as shown in Figure 4.6. Every fastener had the same current order: adhesion promoter/Pr primer sample in ASTM B117 >
CCC/chromate primer sample in ASTM B117 > adhesion promoter/Pr primer sample in bulk solution > CCC/chromate primer sample in bulk solution, which was the same order found for the anodic currents shown in Figure 4.5. The cathodic currents flowing from fasteners at scribed holes (I_{p134/2} and I_{p123/4}) in ASTM B117 were a little higher than those at unscribed holes due to the ohmic drop, which is consistent with the results in Figure 4.3 for the mixed fastener samples. The sum of the net cathodic currents of all fasteners should be equal to the net anodic current of the panel. Figure 4.7 shows that in fact the sum of cathodic currents from the fasteners was quite close to the anodic current to the panel for the two different coatings at every daily measurement during 3 weeks exposure in ASTM B117.

Figure 4.8 displays optical images and the surface morphology of scribes for CCC/chromate primer samples with or without topcoat after 3 weeks exposure in ASTM B117. At the top-left in Figure 4.8 is the image just after the sample was taken out from the salt fog chamber and the top-right image is after the coatings were removed using concentrated nitric acid. The bottom images in Figure 4.8 show the 2-D topographic maps of scribes in primed-only and topcoated samples. The adhesion promoter/Pr primer samples are shown in Figure 4.9. As shown above for samples containing a mixture of SS316 and Ti alloy fasteners, these two coating systems had very different corrosion responses after 3 weeks in ASTM B117. The CCC/chromate primer sample exhibited no obvious blisters on the samples and the Al alloy corrosion only occurred at the scribes but went into the substrate very deeply. The deepest attack was 380 - 400 μm, but the width of corroded areas was only 1 – 3 mm, as shown in Figure 4.10. The original width of
scribe was around 400 μm, which was the diameter of the scribe tool tip. The adhesion promoter/Pr primer sample exhibited many large blisters. Attack occurred not just at scribes, but also around unscribed fasteners and even on some spots far away from fasteners and scribes. The OP images indicate that corrosion spread out very widely from the scribes and unscribed holes along the coating/substrate interface but did not penetrate deeply into the substrate. It should be noticed that blisters around unscribed fasteners in Figure 4.9 only appeared on the primed-only sample, with no attack at unscribed fasteners on the topcoated sample. This was replicated in the repeat experiments.

4.4 Discussion

ASTM B117 and 5 wt% NaCl bulk solution are different environments even though they have the same NaCl concentration. Much corrosion and protection work of metals has been performed on samples immersed in bulk electrolyte because full immersion is a relatively stable condition and is easily controlled in the lab. However, the field environment for many metals, in particular high strength Al alloys, is atmospheric exposure in which the sample surface is covered with an adsorbed moisture layer in equilibrium with humid air, droplets of spray, condensation, or precipitation. Such atmospheric environments can influence the initiation and growth of various forms of corrosion by changing local aggressiveness and the solution resistance between active anodes and cathodes. The ASTM B117 salt fog chamber does not replicate most atmospheric corrosion environments. Nonetheless, the comparison of corrosion behavior in ASTM B117 with the behavior in bulk solution of the same composition is of interest because of the differences in the two conditions. The electrolyte layer in ASTM B117 is
very thin and not uniform or stable owing to droplet initiation, growth, agglomeration, sliding down, falling off, etc. which are phenomena that occur in real environments. In this chapter, the temperature in the ASTM B117 chamber was about 35 °C which was higher than the room temperature of the full immersion tests. The higher temperature and thinner electrolyte layer in ASTM B117 accelerated the cathodic reaction on fasteners causing more corrosion attack on Al alloy panel than in bulk solution. This explains why galvanic currents in ASTM B117 were higher than in bulk solution in Figure 4.2, Figure 4.3, Figure 4.5 and Figure 4.6. However, as mentioned above, the bulk solutions used in these experiments might have become less aggressive over time because of release of inhibitors from the coatings.

In the same environment, the cathodic current density associated with oxygen reduction in the mass transport controlled range should be the same on different electrode surfaces because the limiting current density theoretically only depends on the dissolved oxygen concentration, diffusivity, and oxygen diffusion layer thickness. However, this is only true for ideal electronic conductors. In the present work, Ti alloy and SS316 fasteners both have a layer of oxide film on the surface, TiO₂ and Cr₂O₃ respectively, which can be diffusion barriers for oxygen and interfere with electron charge transfer reactions. Differences in these oxides result in the SS316 fasteners providing more cathodic current than Ti alloy fasteners and therefore more corrosion attack on scribed areas as shown in Figure 4.4, even though the potential difference of SS316 and aluminum alloys is close to that of Ti-6Al-4V and aluminum alloys. Cathodic
polarization curves for samples immersed in 5 wt% NaCl bulk solution also showed that the current of a SS316 fastener was higher than a Ti-6Al-4V fastener.\(^9\) Coatings protect the underlying substrate because they prevent access of the electrolyte and oxygen to the surface and in some cases release chemical inhibitors to reduce corrosion attack. In an aggressive environment, a protective coating should minimize attack at any defect in the coating, such as the scribes intentionally added to the samples in this work, and adhere well to the edge of the defect to prevent the attack from propagating underneath, so-called scribe creep. A direct comparison of the two coating systems studied in this work is seen in Figure 4.10, which shows topographic maps and cross sections from optical profilometry after 3 weeks of ASTM B117 exposure. It shows the depth profiles at different distances from a fastener. The white areas below the zero line represent the corroded volume. For both coating systems the scribe attack extended horizontally and vertically. For the CCC/chromate primer system the attack broadened and deepened only at selective sites. It should be noted that optical profilometry is a top-down line-of-sight method. Therefore, any attack that might have propagated horizontally at a depth to result in undercutting would not be detected. This is a source of error, particularly for wrought Al alloy samples that might exhibit intergranular or selective grain attack along the working direction.\(^{25, 26}\) Nonetheless, the small amount of horizontal broadening of the attack indicates the good adhesion and protection provided by the coating system.

The wider corroded areas in the adhesion promoter/Pr primer sample indicate that the interface was not resistant to penetration by the electrolyte. A few sites in this sample
also exhibited deep attack, but it was not as deep as in the CCC/chromate primer sample and the average depth of penetration was much less. Even though the samples with these two coatings exhibited very different corrosion morphologies, the corroded volumes, which can be calculated by the integral across the sample of the area under the zero line, were similar in magnitude. Note that the holes in the panels were not considered in the data analysis. The adhesion promoter/Pr primer sample should have larger substrate corrosion volume than CCC/chromate primer sample, because larger anodic currents flowed into the promoter/Pr primer panel, as shown in Figure 4.5. Moreover, the local electrolyte at the substrate/coating interface probably had different compositions for these two coatings, even though they were exposed to the same environment, because soluble chromate or Pr ions can be released from the coatings, migrate to defects or corrosion sites and inhibit further damage 27-31. The chromate released from the CCC/chromate primer sample was one reason why corrosion attack did not propagate widely in CCC/chromate primer sample.

In the present work, current distribution on the fastener/panel structure involved cathodic currents that flowed from each fastener into the exposed substrate to create anodic current at the scribes. Therefore, the anodic current of the panel had to be balanced by the total cathodic current of the fasteners, as shown in Figure 4.7. However, the local anodic current density along the scribes and under the coating varied considerably, partly because the resistance between the cathodes (fasteners) and local anode sites increased with the distance between them. Sites more distant from fasteners should have less attack because of the higher resistance. There will be no effect of
galvanic corrosion if the distance between fastener and expose site is too far, which has been shown previously for fasteners far from the scribe. The corrosion profiles at lines 2 to 4 in Figure 4.10 show that corroded area and depth decreased with distance away from the fastener due to the increasing resistance between fastener and exposed sites. The corroded areas at line 1 were underneath a 10 mm diameter washer, where crevice corrosion occurred. The scribe regions below the fastener had more corrosion attack than the scribe region above the fasteners in Figure 4.8 and Figure 4.9, probably because of the effect of gravity on the concentrated solutions created by the corrosion reactions.

The goal of this chapter was to quantify the extent of accelerated corrosion testing of coated Al alloy panels. Two different approaches that were previously introduced to calculate the effective mass loss under the coatings, galvanic charge and OP analysis of the scribed area, were also used in the present work. In short, the volume loss determined from OP analysis and integration of the galvanic charge data can both be converted to an equivalent mass loss. Figure 4.11 shows the equivalent mass loss of panels with different coating systems after 3 weeks ASTM B117 exposure. The mass loss of adhesion promoter/Pr primer samples was larger than that of CCC/chromate primer, which is consistent with the current measurement in Figure 4.5 and morphology results in Figure 4.8 and Figure 4.9. Similarly, when comparing with effects of different type fasteners in chromate primer/CCC sample, it can be seen that coupling with SS316 fasteners caused more mass loss than with Ti alloy fasteners, which is also consistent with the results in Figure 4.2 - Figure 4.4.
The equivalent mass loss determined by each of the two methods might contain errors that would underestimate the extent of attack. The optical profilometry measurements might not sense attack that undercut the metal surface so the measured lost volume and mass might be less than the actual amounts. The sample with chromate primer and topcoat was sectioned through a spot of deep attack. An undercut region was observed, and it was estimated that the area not observable from above by the line-of-sight OP method was less than 12% of the total area at the plane of sectioning. Another section on the same sample indicated no undercut at all. The galvanic charge measurements might also underestimate the extent of attack because the actual anodic current from a scribe might be only partially consumed by cathodic reactions at distant fasteners. Local hydrogen evolution always accompanies pitting corrosion of Al, and the amount of local cathodic reaction has been estimated to be about 15% \(^{32}\). The equivalent mass loss for the two methods were quite similar for the samples with SS316 fasteners, which suggests that the errors in the two measurements were either both small or similar in magnitude. For the adhesion promoter/Pr primer samples, the values of equivalent mass determined from the galvanic charge were significantly less than those determined from optical profilometry. The attack along the coating/substrate interface in this case was likely accompanied by a larger extent of local cathodic reaction occurring under the coating rather than at the distant fasteners. This “self-corrosion” was not sensed by the galvanic current so that the equivalent mass determined from the galvanic charge was erroneously low.
Also shown in Figure 4.11 are values of equivalent mass loss determined by optical profilometry for scribed samples that had no fasteners in the holes. Galvanic charge measurements were of course not possible for these samples. However, the analysis of the last paragraph suggests that the mass loss determined by optical profilometry should be rather accurate, which allows comparison of values for samples with and without fasteners. The acceleration factor (AF) describing the effect of galvanic coupling on the rate of attack can be defined by:

\[ AF = \frac{m_g}{m_{ng}} \]  

where \( m_g \) and \( m_{ng} \) are the equivalent mass loss values for samples with coupling and with no coupling, respectively. The acceleration factors for SS316 fasteners were calculated to be 43 and 21 for adhesion promoter/Pr primer samples without and with topcoat, respectively, and 48 and 26 for CCC/chromate primer samples without and with topcoat, respectively. The mass loss values of non-galvanic chromate panels were very small, which creates a lot of error in the calculated AF values. For example, the volume change calculated for the non-galvanic chromate sample was \( 1.77 \pm 0.10 \, \text{mm}^3 \) where the standard deviation was determined by multiple analyses of the sample. The volume change for the scribed control sample was \( 1.52 \pm 0.19 \, \text{mm}^3 \). The difference in average values multiplied by 2.7 mg/mm\(^3\) resulted in the plotted mass change of 0.65 mg. The error in this number can be considered to be the sum of the standard deviations of the two measurements, or 0.78 mg, which is as large as the reported mass change value. Because the average mass change for the non-galvanic sample is the denominator in Eq. (1), the error in the reported AF is large. It should be noted that the volume changes for the
chromate sample with topcoat and for the adhesion promoter/Pr primer samples were relatively large so the errors are much less. Despite this error, it is quite interesting that the acceleration factors describing the effects of SS316 fasteners were similar for the two different coating systems that had very different attack morphology. This similarity is because the available cathodic current from these fasteners was the same, regardless of the coating system. The cumulative galvanic attack was clearly dependent on the available cathodic current. The adhesion promoter/Pr primer samples with topcoat and SS316 fasteners exhibited less attack than those without topcoat, whereas this effect of the topcoat was not observed for the CCC/chromate primer samples. As shown in Figure 4.9, blisters formed around the SS316 fasteners at unscribed holes for adhesion promoter/Pr primer samples without topcoat, but not at the same fasteners when the samples had a topcoat. The adhesion promoter did not passivate the Al alloy surface and galvanic coupling could occur through the primer without the topcoat in the absence of a scribe. In contrast, CCC passivated the Al alloy surface and provided protection even without a topcoat.

The analysis also shows that the acceleration factors for SS316 fasteners were higher than those for Ti alloy fasteners (A = 12 and 7 for without and with topcoat, respectively). As shown previously and above, SS316 fasteners provide higher cathodic current and accelerate more galvanic corrosion attack. The effect of Ti alloy fasteners was only determined for the CCC/chromate primer system as experiments with Ti alloy fasteners in the other coating system were not performed. The two methods for assessing
equivalent mass loss were also quite reproducible for the Ti alloy fasteners in the chromate coating system.

4.5 Conclusion

Effects of different type fasteners on accelerated corrosion test panels for coated Al alloy were compared. Galvanic corrosion in ASTM B117 and in 5 wt% NaCl bulk solution was also compared. Moreover, mass loss by charge and optical profilometry analysis was calculated to quantitatively to characterize the accelerated corrosion extent on two different coatings. Specific conclusions are as following:

- The galvanic current measured with SS316 fasteners was higher than with Ti fasteners because of differences in cathodic current each alloy provides.
- Galvanic current in ASTM B117 was larger than that in 5 wt% NaCl bulk solution, because of higher temperature, thinner electrolyte layer and greater availability of oxygen in ASTM B117.
- Corrosion degradation of two different coating systems was compared. CCC/Chromate primer panels exhibited deeper corrosion near scribes; while adhesion promoter/Pr primer samples showed relative wider corrosion. This difference was most likely from the different pretreatments due to their different ability to passivate the aluminum substrate.
- An approach was developed to determine acceleration factor that describes influence of galvanic coupling between fastener and substrate to accelerate coating degradation relative to situation with no galvanic coupling. The acceleration factors for SS316 fasteners were estimated to be 45 and 25 for coating systems without and with a
topcoat, respectively. The acceleration factors for Ti alloy fasteners were smaller, 12 and 7 for samples without and with a topcoat, respectively.
Figure 4.1. Schematic illustrations of the test sample configurations. Fasteners #1 and #2 are Ti-6Al-4V fasteners; #3 and #4 are SS316 fasteners; or all 4 fasteners are SS316. Note that primer-only and topcoated panels were always mounted together to ensure that the exposure conditions were identical. However, they were electrically isolated from each other.
Figure 4.2. Anodic currents of panels connected with different fasteners during 3 weeks exposure to (a) B117 and (c) 5 wt% NaCl solution. The multiple curves in (a) and (c) represent measurements made at different times from 0.25 to 21 days. Currents as function of time during exposure in (b) B117 and (d) 5 wt% NaCl solution. #1 and #2 are Ti-6Al-4V fasteners; #3 and #4 are SS316 fasteners.
Figure 4.3. Cathodic currents of each fastener during 3 weeks exposure to B117 (a) and 5 wt% NaCl solution (b). #1 and #2 are Ti-6Al-4V fasteners; #3 and #4 are SS316 fasteners.
Figure 4.4. Topographic maps and linescans of two different coating systems after 3 weeks exposure in ASTM B117. A Ti fastener was on the left and a SS316 fastener on the right. a: CCC/chromate primer with topcoat. b: Adhesion promoter/Pr primer with topcoat.
Figure 4.5. Anodic current of AA7075-T6 panel with different coating systems during three weeks exposure in two environments. Panels were coupling with only SS316 fasteners. Error bars are standard deviation from experiments that were repeated 2 or 3 times. a: Primer-only panels. b: Primer and topcoat panels.
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Figure 4.8. Surface morphology of CCC/chromate primer samples with or without topcoat after 3 weeks exposure in B117. Top-right is the image after removing coatings by nitric acid.
Figure 4.9. Surface morphology of adhesion promoter/Pr primer samples with or without topcoat after 3 weeks exposure in B117. Top-right is the image after removing coatings by nitric acid.
Figure 4.10. Topographic maps and depth cross sections at different distances from fastener. The circular dashed line represents the washer edge. a: CCC/chromate/with topcoat. b: adhesion promoter/Pr primer/with topcoat.
Figure 4.11. Equivalent mass loss of panels with different coating systems after 3 weeks B117 exposure measured by galvanic charge and OP analysis. “T” in the X axis labels means topcoat. The error bars are from two or three individual experiments.
4.6 References


Chapter 5: Effect of Surface Pretreatment on Galvanic Attack of Coated Al Alloy Panels

5.1 Introduction

Aluminum alloy (AA) 7075-T6 (UNS A97075) is widely used in structural aircraft applications because of its high strength to weight ratio. Unfortunately, the heterogeneous microstructure of AA7075-T6 (UNS A97075) makes it very susceptible to localized corrosion\(^1\)\(^-\)\(^7\). Therefore, multilayer protective coating systems are commonly applied on AA7075-T6. The first layer is usually a surface pretreatment coating, such as a conversion coating, which can provide some corrosion protection to the substrate, good adhesion to organic coatings applied on top, and active corrosion inhibition in some cases. Chromate conversion coating (CCC), a well-known coating formed by immersion in an acidic solution of chromate and fluoride salts, has been widely used for surface treatment of Al alloys and other metal alloys because of its excellent corrosion protection\(^8\)\(^-\)\(^13\). However, hexavalent chromium is toxic and carcinogenic, and non-hexavalent chromium based conversion coatings have been developed as an alternative to CCC\(^12\).

U.S. Naval Air Systems Command (Patuxent River, MD) has developed a Trivalent Chromium Pretreatment (TCP) coating, which has performed well as a replacement for CCC on Al alloys\(^14\)\(^-\)\(^18\). It is formed by immersion in a non-hexavalent chromium bath mainly containing potassium hexafluorozirconate (K\(_2\)ZrF\(_6\)) and basic chromium sulfate...
(Cr₄[SO₄]₅[OH]₂). The concentration can vary from 5 to 25% depending on the use. Even though the coating bath contains no Cr(VI) species, Li et al. found a transient formation of Cr(VI) oxide species in TCP coating by Raman Spectroscopy.

Chromium-free conversion coating baths (Non-Chromium Pretreatment, NCP) have also been formulated for treating non-ferrous alloys. The typical inorganic components in NCP are hydrofluotitanic acid (H₂TiF₆), zirconium hydroxide/carbonate (ZrO(OH)(CO₃)₀.₅), and silicon dioxide. It can be applied by immersion, spray, or wiping with a few minutes dwell time, similar to CCC pretreatment. Rincon Troconis et al. utilized the artificial blister test to compare the adhesion of an acetoacetate coating to AA2024-T3 panels with different surface pretreatments, including CCC, TCP, and NCP. The NCP treated sample exhibited better adhesion properties than the samples with TCP and CCC, regardless of whether the panel surfaces were first pretreated by cleaning and desmutting.

Adhesion promoters comprise another widely used non-chromium pretreatment. A typical contains less than 4% diethylene glycol monobutyl ether (DGBE), less than 4% N-Methyl-2-Pyrrolidone (NMP), and 80-95% water. The treatment forms a molecular layer on the metal surface, which bonds strongly to the organic primer. However, the adhesion promoter layer is not a conversion coating and does not passivate the surface of substrate. Such an adhesion layer was found previously not to perform as well as chromate conversion coatings.

Modern multi-layered protective coating systems containing any of the above pretreatments generally provide good corrosion resistance properties to Al alloy.
substrate. As a result, a long time is required to observe their degradation or failure even during exposure to aggressive environments, making comparison of different coating systems costly and time consuming. Therefore, a galvanic sample design, which incorporates a painted and scribed Al alloy panel and uncoated through-hole noble fasteners, was developed as a new accelerated corrosion test sample to assess coatings efficiently and rapidly. Noble fasters in such a sample design activate galvanic corrosion by providing a large cathodic current, and they can cause severe attack at scribes after only 3 weeks exposure to a salt fog chamber. In this work, galvanic test structures were used to compare the influence of different surface pretreatments on the corrosion protection after exposure to ASTM B117. The surface pretreatments tested include TCP, CCC, NCP, adhesion promoter and no pretreatment as a control. The same primer and topcoat were applied to all panels after surface pretreatment. The corroded area, pit depth, mass loss, and corrosion rates were assessed for different times of exposure. The acceleration factors associated with the galvanic coupling of 316 stainless steel (SS316, UNS S31600) fasteners were also determined.

5.2 Experimental

The substrates for the galvanic samples were AA7075-T6 (UNS A97075) panels containing 4 through-holes as described previously. Five different surface pretreatments were applied on the panels for comparison, including TCP (SurTec 650 chromitAL, Surtec International), CCC (Alodine 1200S, Henkel Surface Technologies), NCP (Alodine 5700, Henkel Surface Technologies), adhesion promoter (PreKote, Pantheon Industries), and clean-only. The clean-only sample was treated by degreasing.
and desmutting to remove lubricants, salt, organic contaminants, and metallic oxide particles that might have been embedded during rolling or machining.

After pretreatment, all the pretreated panels were coated with the same chromate-containing epoxy primer (PPG CA7233, which is a MIL-PRF-23377 Type I, Class C2 coating\textsuperscript{31}) and flat gray polyurethane topcoat (PPG CA9311/F36375, which is a MIL-PRF-85285D Type IV, Class H coating\textsuperscript{32}). Two “X” pattern scribes through to the Al alloy substrate were manually created across the two holes in the bottom row on the panel by a carbide tip. Holes were generated before surface pretreatment and painting. Since surface pretreatments and coatings are applied by dip, brush, swap, or spray, internal surface of holes was also treated, even though they were not painted intentionally. Gray topcoat was observed inside the holes unevenly. Uncoated type 316 stainless steel (SS316, UNS S31600) fasteners with 6 mm inner and 11 mm outer diameter washers were then attached, making sure that they had good electrical contact to the panel. The scribes extended under the washer to the edge of the through-hole and outwards along the panel about 10 mm past the edge of the washer. The distance between two fasteners in a row was about 25 mm. As was reported previously, interaction between such closely located fasteners reduces the cathodic current that each provides below what they can provide individually\textsuperscript{30}. The back and edges of each galvanic panel were masked using combined layers of lacquer and epoxy, so only the top surface of the galvanic panel was exposed to the environment.

Galvanic panels with different surface pretreatments were exposed in an ASTM B117 standard Salt Fog Test chamber\textsuperscript{33} and then removed after 2, 7, 14, 21, 35, or 49 days
exposure. Different panels were used for each exposure period, and only one sample per coating and exposure time was analyzed. After exposure, the fasteners were detached and the panels were immersed in concentrated nitric acid (HNO₃) to remove the coating and corrosion product. The panel weight was monitored after repeated 10 min periods of immersion in nitric acid until the weight loss was less than 0.01 g between two successive weight measurements. Topographic analysis of the scribed areas on the stripped panels was then performed using an optical profilometer (OP) and the topographic image created by OP was analyzed by a software package to determine the corroded volume of a scribe below the level of the uncorroded areas. The initial volume of scribes (1.5 mm³) was subtracted from the final volume to get the corroded volume, as reported previously.

The preparation of galvanic panels for current measurement was slightly different than that for chamber exposure samples. The panel was isolated from each SS316 (UNS S31600) fastener using two layers of plastic tape (Scotch Tape, 3M). Insulated copper wires were connected to the panel and each fastener for electrical connection. Electrical isolation between the fasteners and panel, even for fasteners located at holes with scribes, was checked with a meter. The assembled sample was embedded in epoxy instead of masking the back and edges with lacquer. These epoxy-embedded assemblies were then exposed in an ASTM B117 chamber with the copper wires reaching outside the chamber. Galvanic currents were measured between the Al alloy panel and the four SS316 (UNS S31600) fasteners using a zero resistance ammeter (ZRA) each day during 21 days of exposure in the chamber. The 21-day monitoring period was selected to be consistent with previous work. Furthermore, the galvanic currents plateaued after 21 days. The
wires connected to the panel and all fasteners were shorted together after each galvanic current measurement so the assembly components were electrically connected for most of the exposure time. OP was also used for topographic analysis of the samples used for galvanic current measurements after the 21-day exposure.

Potentiodynamic experiments on bare AA7075-T6 (UNS A97075) were carried out at room temperature in aerated 3.5 wt% NaCl solution without and with $2.6 \times 10^{-3}$ M $K_2CrO_4$ addition. Pt mesh and a Saturated Calomel Electrode (SCE) were used as counter and reference electrodes, respectively. Cathodic and anodic polarization scans were performed separately starting from the open circuit potentials (OCPs) at a scan rate of 0.167 mV/s and ending at -1100 mV SCE and -600 mV SCE, respectively. Before that, AA 7075 samples were etched in 1.25 M NaOH at 60 °C for 1 min followed by immersion in 70% HNO$_3$ for 0.5 min to remove the altered surface layer. Cathodic polarization was performed on SS316 in 3.5 wt% NaCl solution.

5.3 Results

Figure 5.1 to Figure 5.5 show optical microscopy and topographic OP images of galvanic panels with TCP, CCC, NCP, adhesion promoter and clean-only pretreatments, respectively, after 2, 7, 14, 21, 35 and 49 days exposure to ASTM B117. Since the corrosion attack was focused primarily in and near the scribes around the bottom fasteners, only the bottom holes are shown in these figures. The coatings and corrosion products were removed using nitric acid before imaging to reveal the attack. The diameter of the holes was 5 mm, so the holes can be used as a scale for all the figures. The extent of corrosion attack of all the galvanic panels, including attack depth and
corroded area, became more severe with increasing exposure time. The worst attack was found in the regions of the scribes close to the edges of the SS316 washers, consistent with previous work. For the exposed scribe region, the ohmic potential drop was lowest near the washers, so the attack was greatest in this region. Interestingly, there was not much attack on the substrate under the washers. It is possible that the scribe through the coatings created a gap that was too large to generate substantial crevice corrosion. Also, not much corrosion attack was observed inside the holes or on the edges, probably because they were coated unintentionally, as mentioned in experimental section.

Comparing the corrosion attack of different surface pretreatments shown in Figure 5.1 to Figure 5.5, samples with TCP and CCC exhibited similar corrosion morphology, whereas samples with adhesion promoter pretreatment and clean-only were similar. Samples with NCP were in the middle between those two groups. The attack depth profile and delamination areas of different surface pretreatment panels are summarized in Figure 5.6, which shows the depth profiles of galvanic panels with different surface pretreatment as a function of exposure time. The profiles were taken along the black lines shown in Figure 5.1 to Figure 5.5, which were located close to the washer along a scribe on each sample. For samples with TCP and CCC pretreatment, the attack depth was very deep, reaching as much as 400 µm after 49 days. The attack width also increased with exposure time, changing from 0.5 mm to around 3 mm during the 49-day exposure. For comparison, the width and depth of the as-formed scribes were about 200 and 20 µm, respectively. Therefore, the scribe attack in TCP and CCC samples was deep but narrow. Cracks have been shown to initiate from pits in Al alloy samples that were previously
exposed to corrosive conditions. One concern is that the deep and relatively sharp attack exhibited by the CCC and TCP samples might act as a stress concentration site for initiation of SCC or fatigue cracking under an applied load.

The TCP and CCC samples showed no evidence of delamination under the coating that originally reached to the scribe edges. The very straight and vertical sides of the profiles are not representative of the expected morphology for localized corrosion in Al alloys. This is probably an artifact associated with the inability of OP to detect undercutting attack morphologies, which is discussed below.

In contrast, samples with NCP, clean-only and adhesion promoter pretreatments exhibited attack that was less deep but spread out across the sample surface beneath the coating. The maximum depth was less than 300 μm, but the deepest regions were only about 100 μm below the shoulders that developed in the profiles, so the likely stress concentration of such attack is much less than for the TCP and CCC samples. On the other hand, the corroded regions for samples with NCP, clean-only and adhesion promoter treatments were very wide, reaching as much as 10 mm. The propagation of attack shown in Figure 5.6 can be used to predict the time for pit penetration or full coating detachment, depending on the attack morphology, for a coated and scribed galvanic panel exposed in the ASTM B117 chamber.

The cathodic reactions on the uncoated SS316 fasteners provide the main driving force for anodic dissolution in these galvanic panels. To quantify the anodic dissolution, galvanic current was measured between all four fasteners and Al-alloy panels with different surface pretreatments during 21 days of exposure to ASTM B117, as shown in
The galvanic current results varied with the pretreatment even though the fasteners, the Al alloy substrates, and the organic coatings were identical. The integral of the galvanic current over exposure time can be quantitatively converted to an amount of panel dissolution based on Faraday’s law, as shown in Figure 5.7b. OP can also be utilized to quantify an effective mass loss from the volume of the corroded areas shown in Figure 5.1 to Figure 5.5. The equivalent mass loss values calculated by galvanic current and OP are also shown in Figure 5.7b. Mass loss results from charge follow a consistent trend with those from OP for different surface pretreatments. Furthermore, the results in Figure 5.7b indicate that the two measures of mass loss are very close for the samples with CCC and TCP, but that higher mass loss was found from the OP data than from charge for panels with NCP, clean-only and adhesion promoter pretreatments. The different behavior lines up with the forms of attack; the values from the two methods are close for the cases where the attack was narrow and deep, but different for the cases where the attack was shallow and wide.

All of the samples contained a chromated primer, so chromate ions released from the primer were likely available at all of the scribes. It should be noted that the samples also all contained a topcoat so any chromate released into the scribe from the primer would have come primarily from the thin edge of primer exposed at the scribe. The samples with CCC might have had more chromate available at the scribes, but the difference is not expected to be significant. The equivalent mass loss for the samples with CCC was lower than for the other samples, but was of similar magnitude. Chromate ions dissolved into solution are known to be an efficient cathodic inhibitor for high strength Al alloys.
For example, Na$_2$CrO$_4$ additions as small as $10^{-5}$ M to aerated 0.01 M NaCl solution were observed to significantly decrease the oxygen reduction reaction kinetics on AA7075-T651, resulting in decrease in corrosion current density of about 20x along with a decrease in corrosion potential $^{38}$. Figure 5.8 shows polarization curves of SS316 and bare AA7075-T6 in aerated 3.5 wt% NaCl solution without and with 2.6x$10^{-3}$ M K$_2$CrO$_4$ addition. CrO$_4^{2-}$ addition significantly decreased the cathodic reactions on AA7075-T6, resulting in the cathodic curve shifting to the left by one order of magnitude, which is consistent with previous reports $^{38}$. Anodic inhibition of chromate has been also reported $^{38, 39}$. However, in Figure 5.8, the pitting potentials and the anodic curves above the pitting potentials were essentially the same in both conditions, indicating that the CrO$_4^{2-}$ addition did not change the anodic kinetics. In the galvanic corrosion couple studied in this work, the aluminum alloy panel was the anode, and cathodic inhibition of the Al provided by chromate released from the CCC would not be expected to have a large effect on the extent of Al corrosion. Instead, the corrosion attack at the scribes in the coated AA7075-T6 panels was mainly driven by the cathodic reactions on the SS316 fasteners, which were distant from the released chromate and thus probably not exposed to the inhibitor. The intersection in Figure 5.8 shows the expected galvanic currents between SS316 and Al alloy would be the same in the solutions with and without CrO$_4^{2-}$ addition (assuming equal areas). Therefore, the high cathodic current provided by oxygen reduction on the SS316 fasteners still could cause a large amount of attack, even on Al alloy samples exposed to chromate from a CCC or a chromated primer, if the fasteners were not inhibited by the chromate. Even if chromate does cause anodic inhibition in
AA7075-T6 and increases the pitting potential, as has been observed previously\textsuperscript{38, 39}, the high cathodic current associated with transport limited oxygen reduction, will polarize the sample above the pitting potential. Bare stainless steel fasteners are used in real aircraft applications, thereby accelerating the corrosion attack on Al alloy. In order to reduce this galvanic attack, those bare fasteners should be coated to minimize the cathodic currents associated with them.

Because of the presence of chromated primer at the scribed edge of the coatings for all samples, released chromate ions were likely not the primary reason for the behavior of samples with CCC. Furthermore, samples with TCP behaved similarly. The results show that the main effect of the CCC and TCP was retention of the adhesion of the primer layer so that the attack could not spread outwards and was instead focused down into the scribe region.

The galvanic sample design used in this work has been shown to provide accelerated coating degradation response during atmospheric corrosion testing in the field and laboratory chambers\textsuperscript{26, 27, 30}. To assess the extent of acceleration of galvanic coupling, non-galvanic panels with the different surface pretreatments were exposed to ASTM B117 for 100 days. Figure 5.9 shows the non-galvanic panels after removal of the coating and corrosion product. The extent of corrosion for the TCP, CCC, NCP, and clean-only non-galvanic samples follows the same trend as for the galvanic samples: more attack for the NCP and clean only samples than for the TCP and CCC. It should be noted that the NCP looks worse than the clean-only sample in Figure 5.9, but the depth of attack was greater for the clean-only, particularly for the scribe on the left.
Interestingly, the adhesion promoter non-galvanic samples exhibited very little attack even after 100 days of ASTM B117 exposure, whereas the galvanic adhesion promoter samples exhibited wide regions of attack under the coatings. In general, the galvanic coupling caused more corrosion than on samples without galvanic coupling, and OP allows for a direct comparison and determination of acceleration factors associated with the galvanic coupling.

Table 5.1 shows the equivalent mass loss results of galvanic panels after 21 days exposure and non-galvanic panels after 100 days exposure in ASTM B117. These values were determined from the OP data. It also shows the acceleration factors (AF) of associated with the effect of galvanic coupling on the rate of attack, as defined by:

\[ AF = \frac{m_g/t_g}{m_{ng}/t_{ng}} \]  \hspace{1cm} (1)

where \( m_g \) and \( m_{ng} \) are the equivalent mass loss values for samples with galvanic coupling and with no galvanic coupling, respectively, and the \( t \) values are the respective exposure times. The acceleration factors vary with the surface pretreatments in the range of 100 – 600. The largest AF by far was for the adhesion promoter sample, which exhibited very little corrosion on the non-galvanic panel. The clean-only sample had a small value of AF because of the deep attack of left “X” pattern scribe on non-galvanic sample, as mentioned above.

5.4 Discussion

Many multilayer protective coating systems, such as chromate-containing systems, confer a high degree of corrosion resistance to the substrate.\(^8\sim10,40\) A very long period of
time is required to observe coating degradation or failure, even if they are exposed to rather aggressive environments like ASTM B117, wet/dry cyclic tests, or beach conditions. It is therefore quite time consuming to assess coating protectiveness and predict coating lifetime before failure. Bierwagen et al. \(^{28}\) used electrochemical impedance spectroscopy (EIS) to obtain the low frequency impedance of coatings as a function of exposure time and then extrapolate the lifetime of different coating systems. The low frequency impedance of the bare Al-alloy substrate was used as a critical condition for coating failure and coating lifetime was assessed by extrapolation of coated sample impedance to this value. Leidheiser et al. \(^{41, 42}\) proposed that a threshold impedance of \(10^7 \ \Omega \text{cm}^2\) should be used as a limit to indicate coating degradation. This threshold resistance is much higher than resistance of the bare Al-alloy substrate so the coating lifetime using bare metal resistance as a threshold would be much less conservative. Scully et al. \(^{40}\) developed a correlation of threshold impedance and the percentage of visual corroded area on epoxy polymide-coated steel and Araldite-coated Mg alloy. A visual corroded area of 3% (ASTM D 610 rating of 5) was defined arbitrarily as coating failure. The threshold low frequency impedance was about \(10^6\) to \(10^7 \ \Omega \text{cm}^2\) for coated steel and about \(4 \times 10^8 \ \Omega \text{cm}^2\) for coated Mg alloy. All of these studies were performed on full coatings without scribes, so the failure predictions were really for coating degradation.

This work is focused on corrosion attack at scribes for different coating systems under galvanic coupling stimulus. Attack at scribes on coated panel can propagate both along the surface and into the depth. Figure 5.6 shows that the dominant propagation
direction is correlated to surface pretreatment. Pit growth is a typical form of vertical propagation of artificial defects. Figure 5.10 shows the deepest pit depths in Figure 5.6 for galvanic panels with different surface pretreatments changes as a function of exposure time. The deepest pit on each sample was usually immediately adjacent to SS316 washers because that was the region of the lowest ohmic drop. The deepest pit depth increased with exposure time for all the surface pretreatments. Panels with TCP and CCC treatments have the highest slopes, indicating fastest pit growth. It is expected that such pits could eventually perforate the panel and cause it to fail. Another failure mode for coated galvanic panels is complete detachment of the coating from the Al alloy substrate, which can be assessed by the scribe propagation in the in-plane direction. Figure 5.11a displays the projected corroded area under delaminated coatings as a function of exposure time. Figure 5.11b gives an example of how the corroded area was determined, with the boundary between uncorroded and corroded areas marked by a red line. As was found for the deepest pit, the corroded area also increased with exposure time. However, in this case, the panels with TCP and CCC treatments had much smaller attack area rates of growth than the other pretreatments. With increasing exposure time, the whole coating would eventually delaminate from the Al-alloy substrate. From Figure 5.10 and Figure 5.11, the galvanic panels with TCP and CCC pretreatments may have a higher chance for failure by pit perforation and samples with NCP, clean only and adhesion promoter pretreatments may have a higher tendency for failure by full coating detachment. However, as mentioned, the sharp and deep pits in samples with TCP and CCC
pretreatments could provide a stress concentration to initiate SCC or fatigue cracking, which could accelerate the failure of coated Al alloy.

To obtain more accurate corrosion rates for the samples with different surface pretreatment, the actual areas exposed to the environment should be determined, rather than the projected corroded areas shown in Figure 5.11. The actual exposed Al-alloy substrate surface area is 3 dimensional with surface roughness, internal areas of pits, and internal areas of the attack shoulder. The actual exposed area for each sample was determined by OP and a software package. Figure 5.12a shows the exposed surface area of samples with different surface pretreatments as a function of exposure time. The values are 2 to 3 times larger than the projected corroded areas for all the samples. Figure 5.12b shows equivalent mass loss of all the samples with exposure time, as calculated by OP. Based on mass loss, surface areas and exposure time, the corrosion rates of different pretreatment galvanic panels with artificial defects can be obtained by:

$$\text{Corrosion Rate} = \frac{\Delta m}{At} \quad (2)$$

where $\Delta m$ is the mass loss difference between before and after a certain period of time exposure. A and t are surface area and exposure time, respectively. Figure 5.12c shows the corrosion rates of each surface pretreatment galvanic panel changing with exposure time. These values are average corrosion rates over the whole metal area exposed to the environment, including scribe and delaminated areas. In contrast to the behavior of the deepest pits, which tended to exhibit a constant growth rate as shown in Figure 5.10, the average corrosion rates of all the galvanic panels decreased with exposure time. The corrosion rates were approximately equal to each other after 49 days exposure, and,
interestingly, were similar to the average corrosion rate of uncoated and uncoupled AA7075-T6 in ASTM B117, which is shown as a dashed line in Figure 5.12c. The AA7075-T6 corrosion rate was determined from a small piece of partially masked AA7075-T6 that was exposed in ASTM B117 for 21 days. The masked area acted as uncorroded reference for analysis by OP, which determined a corrosion rate of 0.116 ± 0.026 mg/cm$^2$ day (equal to 14 ± 3 μA/cm$^2$). The observation that the corrosion rates of the galvanic panels approached the rate of the uncoated and uncoupled alloy indicates that effects of galvanic coupling decreased with exposure time, probably as the result of increasing ohmic drop and that the effects of released chromate were small at this period of exposure. The increasing ohmic drop may be from the increasing distance between the fastener and the end of the delaminated zone as the delamination spread across the surface.

The SS316 fasteners provided a large cathodic current that accelerated the corrosion attack at the scribes, which were the anodes in the galvanic couple. Cathodic reactions on the anode are often ignored in galvanic corrosion assessments because they are assumed to be small. However, the local cathodic reaction is not negligible for the case of Al pitting and coating delamination. A fraction of the electrons generated by Al alloy corrosion are consumed by local hydrogen evolution and so would not be measured using the galvanic current technique. As a result, the mass loss values determined by the galvanic currents in Figure 5.7b are erroneously low.

To estimate the effects of local hydrogen evolution, volumetric measurement of hydrogen was carried out during immersion in 5 wt% NaCl solution for a galvanic panel
with adhesion promoter/chromate primer/topcoat, as shown in Figure 5.13a. The amount of H$_2$ collected each day during 21 days of exposure is shown in Figure 5.13b. The H$_2$ volume measured each day fluctuated, but the average was about 0.3 mL/day, which is equivalent to 2.6x10$^{-6}$ mol/cm$^2$day. The total amount of Al dissolution is therefore the equivalent mass determined by adding the mass associated with total amount of hydrogen collected to the charge calculated from the galvanic current, which was simultaneously measured. It should be noted that the collected hydrogen was all from the local cathodic reaction on Al. The dominant cathodic reaction on the SS 316 fasteners was likely the oxygen reduction reaction. Figure 5.13c displays the mass loss results of adhesion-promoter/chromate primer/topcoat samples after 21 days of immersion in 5 wt% NaCl solution calculated by charge both before and after modifying to account for the local hydrogen evolution. The local H$_2$ evolution was about 24% of the total, which is close to the 15% difference found during the growth of 2-D pits in thin film aluminum$^{43}$.

The value of mass loss determined by OP also contained some error. OP is a line-of-sight interferometric method in that it only senses the area with direct exposure to the instrument, which was positioned directly above the sample. Therefore, any undercutting of the surface would not be detected. To obtain the true extent of corrosion, undercutting must be accounted for. The effects of undercut were estimated by analyzing the cross section of samples exposed in ASTM B117 for 21 days, as shown in Figure 5.14. Two cross sections (lines 1 and 2) at the deepest corroded areas are presented. Obvious undercut attack can be seen shown in cross section “1”, whereas not much undercut is evident in cross section “2”. To estimate the effects of undercut, software (Image J) was
used to extract and analyze optical photos of cross sections, as shown in Figure 5.14. The area bounded by red lines presents the detectable area for OP, while the real area including undercut attack is indicated by black lines. The effect of undercut can be defined by:

\[ \text{undercut effect} = \frac{A(\text{real}) - A(\text{OP})}{A(\text{real})} \]  

where \( A(\text{real}) \) and \( A(\text{OP}) \) are the areas indicated by black and red lines, respectively. It turns out that the effect of undercut is about 11% for cross section “a” and less than 1% for cross section “b”. The mass loss determined by OP was therefore modified by adding an average of these values, or 6%. The two modified equivalent mass loss values for the immersed sample are shown in Figure 5.13c to be quite close.

Figure 5.15 shows equivalent mass loss results from ASTM B117 exposure by charge and OP after modification using the percentage differences determined by the hydrogen collection and undercut analyses. These data can be compared to those in Figure 5.7b, which were not modified to account for local hydrogen evolution and undercut. The differences in the values of equivalent mass loss determined by the galvanic charge and OP methods are much less after modification for these factors. The largest differences in the results from the two methods are for the clean-only and adhesion promoter samples.

5.5 Conclusions

The corrosion attack of coated galvanic panels with different surface pretreatments was compared after different periods of exposure to ASTM B117. The corroded areas, deepest pit depth, equivalent mass loss, and calculated corrosion rates were determined.
Also volumetric H$_2$ measurements and undercut attack were carried out to increase the accuracy of the measurements. Specific conclusions are as follows:

- Galvanic panels with TCP and CCC pretreatment exhibited narrow but deep corrosion attack, while samples with NCP, Clean only and adhesion promoter pretreatment had wide corrosion attack under the delaminated coating.

- Corroded area and largest pit depth increased with exposure time for all the surface pretreatment panels. Samples with TCP and CCC pretreatment have higher chance of pit perforation, whereas samples with NCP, clean-only and adhesion promoter pretreatment have higher chance of full coating detachment.

- The corrosion rates of galvanic panels decrease with exposure time for all the surface pretreatment samples, and eventually reached the rate of uncoated and uncoupled AA7075-T6.

- Mass loss results were modified to account for local H$_2$ evolution and undercut. The effects of local H$_2$ evolution and undercut were estimated to be 24% and 6%, respectively. That means that the galvanic current measurement underestimated mass loss by 24% and the OP method underestimated mass loss by 6%.

- Acceleration factors associated with the galvanic coupling in ASTM B117 are in the range of 100 to 600 for the different surface pretreatments even though the galvanic panels had the same substrate and fastener.
Table 5.1. Equivalent mass loss of galvanic and non-galvanic panels with different surface pretreatments. 21 and 100 days exposure in ASTM B117 are for galvanic and non-galvanic samples, respectively. Only one sample for each surface pretreatment was exposed. Five measurements were made on each sample to get average mass loss and standard deviation. AF is acceleration factor for the galvanic attack.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Non-galvanic (mg)</th>
<th>Galvanic (mg)</th>
<th>AF</th>
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<tbody>
<tr>
<td>TCP</td>
<td>1.65 ± 0.21</td>
<td>42.1 ± 2.1</td>
<td>123 ± 18</td>
</tr>
<tr>
<td>CCC</td>
<td>1.18 ± 0.25</td>
<td>46.3 ± 0.2</td>
<td>192 ± 32</td>
</tr>
<tr>
<td>NCP</td>
<td>3.12 ± 0.48</td>
<td>82.7 ± 2.7</td>
<td>130 ± 30</td>
</tr>
<tr>
<td>Clean only</td>
<td>4.02 ± 0.15</td>
<td>94.3 ± 0.5</td>
<td>112 ± 4</td>
</tr>
<tr>
<td>Adhesion promoter</td>
<td>0.90 ± 0.10</td>
<td>105 ± 0.9</td>
<td>559 ± 61</td>
</tr>
</tbody>
</table>
Figure 5.1. Optical images (left) and OP topography maps (right) showing the corrosion morphology of galvanic panels with TCP/chromate primer/topcoat after different exposure times in ASTM B117. The diameter of the hole is 5 mm.
Figure 5.2. Optical images (left) and OP topography maps (right) showing the corrosion morphology of galvanic panels with CCC/chromate primer/topcoat after different exposure times in ASTM B117. The diameter of the hole is 5 mm.
Figure 5.3. Optical images (left) and OP topography maps (right) showing the corrosion morphology of galvanic panels with NCP/chromate primer/topcoat after different exposure times in ASTM B117. The diameter of the hole is 5 mm.
Figure 5.4. Optical images (left) and OP topography maps (right) showing the corrosion morphology of galvanic panels with adhesion promoter/chromate primer/topcoat after different exposure times in ASTM B117. The diameter of the holes was 5 mm.
Figure 5.5. Optical images (left) and OP topography maps (right) showing the corrosion morphology of galvanic panels with clean-only/chromate primer/topcoat after different exposure times in ASTM B117. The diameter of the hole is 5 mm.
Figure 5.6. Depth profile of different surface pretreatment samples changes as a function of exposure time. Depth data is obtained from the lines shown in Figure 5.1 to Figure 5.5. TCP and CCC have deep but narrow damage, while NCP, clean-only, and adhesion promoter have shallow but wide corrosion attack.
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Figure 5.11. Projected corroded areas of different surface pretreatment samples change as a function of exposure time, indicating scribe propagation in the in-plane direction.
Figure 5.12. Surface area (a), mass loss (b), and corrosion rate (c) of different surface pretreatment samples changes as a function of exposure time. The dash line in (c) represents corrosion rate of bare AA7075-T6 in ASTM B117.
Figure 5.13. (a) A setup for H$_2$ collection during galvanic current measurement. (b) Amount of H$_2$ collected per day during 21 days current measurement in 5 wt% NaCl solution. (c) Mass loss data of adhesion promoter/chromate primer/topcoat sample calculated by charge and OP before and after modification.
Figure 5.14. Cross section of scribe (1) and (2). Area around by black curves is real attack. Area around by red lines is the attack measured by OP. The difference between these two areas is from undercut attack.
Figure 5.15. Equivalent mass loss of different surface pretreatment panels calculated by charge and OP data after modification. Galvanic panels with different pretreatments were exposed to ASTM B117 for 21 days.
5.6 References


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Chapter 6: Galvanic Attack of Coated Al Alloy Panels in Laboratory and Field Exposure

6.1 Introduction

Modern multi-layered protective coating systems on Al alloys have been widely studied in laboratory accelerated tests \(^1\text{-}^6\) including ASTM B117, a continuous 5 wt\% NaCl salt fog spray at 35 °C \(^7\), ASTM G85, a wet/dry cycle standard using 0.35 wt\% \((\text{NH}_4)_2\text{SO}_4\) and 0.05 wt\% NaCl electrolyte \(^8\), and ASTM 154, which uses ultraviolet (UV) light and humidity to create a wet/dry cycle that accelerates weathering effects \(^9\). However, the rank-order of coatings performance exposed in laboratory accelerated tests can be quite different from that achieved in field exposure, even if the critical environmental factors are included in the laboratory accelerated test \(^10\). Laboratory tests often use very high levels of these factors in an attempt to rapidly monitor the early stage of coating degradation, characterize corrosion propagation underneath the coating, and predict coating lifetime. For example, ASTM B117 contains an unrealistically high concentration of NaCl, constant high temperature and continuous, almost 100% relative humidity, which combines to create a condition that is much more severe than most field conditions. Continuous high concentration of salt fog provides aggressive species and the environment for the oxygen reduction reaction \(^6\), which can result in a different failure mechanism at the metal/coating interface from field exposure \(^10\text{-}^14\). Also, the elevated
temperature in accelerated test chambers influences the loss of plasticizer in a polymer coating, further causing unnatural coating degradation. To accurately mimic real field environments, realistic environmental factors have been considered in laboratory acceleration tests, such as wet/dry cycling, thermal cycling, UV, and ozone.

However, real environments are very complex and can vary enormously with time and location. Of importance are the deposition of aerosols and particulate, wet/dry cycling corresponding to water condensation at night or early morning and evaporation during the daytime, weather-driven relative humidity changes, and episodic precipitation. This time-varying field environment can even result in a discontinuous corrosion process on metal surface. During the initial stage of water condensation or water uptake by deposited salt, corrosion can initiate at local sites under saturated electrolyte droplets. Dissolved oxygen and chloride ion in the electrolyte droplets often cause severe localized corrosion attack. With water condensation or uptake increasing, electrolyte droplets become larger or merge with other droplets to form a thick electrolyte layer, diluting the salt concentration and increasing oxygen solubility and diffusion coefficient. Corrosion is active during this stage of large limiting rate of the oxygen reduction reaction. After the thickness reaches a certain value, electrolyte layers can be considered as a bulk solution, which could decrease the corrosion process due to the large diffusion distance of oxygen transporting to the metal surface. Frankel et al. used a Kelvin Probe Potentiostat to monitor the limiting cathodic current density for different thickness of 1M NaCl solution layer. The limiting cathodic current was almost constant after a thickness
of about 500 μm, indicating the solution layer with thickness greater than this could be considered as a bulk solution. The whole corrosion process is reversed during drying and there is no more corrosion occurring after the surface is completely dry until the next period of wetness. The corrosion process could be much more complicated and harder to reproduce if other natural environmental factors are taken into account, such as UV, ozone, thermal cycling, and local climate.

Lab accelerated testing is often utilized for lifetime assessment of coated metals, even though the tests are not in realistic environments. The correlation between lab and field exposure has been long studied from many perspectives. The corrosion attack on coated and scribed metals has been compared visually after lab and field exposure for establishing a correlation between them. Corrosion products of metals in the lab and field have also been analyzed by X-ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Raman spectroscopy, and X-ray Photon-electron Spectroscopy (XPS). Visualization and corrosion product analysis are comparisons that can generate support for mechanism speculation, but they do not provide sufficient information for accurate lifetime assessment. Other methods, such as Electrochemical Impedance Spectroscopy (EIS), mass loss, and Scanning Kelvin Probe (SKP) have also been utilized to quantify the correlation between lab and field exposure and might be useful for predicting field lifetime of metals or coatings from lab results. Bierwagen et al. used EIS to obtain the low frequency impedance of coatings as a function of exposure time, which was then extrapolated to estimate the lifetime of different coating systems. EIS is able to characterize the degradation of coated metals
before visual corrosion attack is evident by estimating water uptake and defect area\textsuperscript{31, 32}. SKP was used recently to study cathodic delamination kinetics on polymer-coated steel after field exposure\textsuperscript{13, 14}. The steel/coating interface stability assessed by SKP was considered to be a critical criterion to correlate field and lab environments. However, these are all post exposure techniques, not in-situ measurements during the field exposure. Additionally, these lab-based accelerated tests do not include any galvanic degradation of coated metals. In many applications of Al alloys, such as in aircraft, a major driving force for corrosion attack is the galvanic interaction of Al substrate and noble fasteners\textsuperscript{4, 5}.

In the present work, a galvanic test sample incorporating coplanar coated Al alloy with scribes and bare 316 stainless steel (SS316, UNS S31600) fasteners was used to continuously monitor the galvanic currents changing with electrolyte conditions in field. Acceleration factors were determined by comparing the currents provided by a bare 316 SS fastener in lab and field environment.

6.2 Experimental

AA2024-T3 panels of size 100 × 75 × 0.8 mm with 5 mm diameter through-holes were used as the substrates for the galvanic panels. Different coating systems were painted on the substrates to test their performances during laboratory and field exposure. One of the coating systems contained a chromate conversion coating (Alodine 1200S, Henkel) and a chromate primer (02Y040, Deft). The other is a non-chromate coating system including non-chrome deoxidizer pretreatment (RECC 1015, Deft) and epoxy primer (02GN093 (Y), Deft) primer. The active agent in both the pretreatment and primer
is yttrium. The same flat gray polyurethane topcoat (99GY001, Deft) was applied on all the samples on top of the primer.

A separate comparison was made using two other coating systems that were only exposed in the field. One set of these samples had a chromate conversion pretreatment (Turco Liquid Alumigold C, Henkel) with an Mg-rich primer (AE2100, AkzoNobel Aerospace Coatings) and polyurethane topcoat (99GY001, Deft). The other set had an adhesion promoter pretreatment (PreKote) with the same Mg-rich primer and polyurethane topcoat.

An “X” pattern was manually scribed across the four holes making certain to expose fresh Al metal to the environment. The width and depth and length of the as-formed scribes were about 250 μm, 20 μm and 60 cm, respectively. The four holes were distributed at symmetric positions corresponding to the center of the “X”, as shown in Figure 6.1. Uncoated hexagonal fasteners of type 316 SS and round washers with 11 mm outer diameter were attached to the panel at the through-holes for galvanic corrosion tests. The back and edges of each galvanic panel were covered by uninhibited green epoxy (3M Scotchkote Liquid Epoxy Coating), exposing only the top surface of the galvanic panel to the environment, as shown in Figure 6.2a and Figure 6.2b. All of the galvanic panels were positioned horizontally on the roof of a shack near Daytona Beach, as shown in Figure 6.2c. The samples were located about 125 m above the Mean High Tide Line and corrosion monitoring at this specific point showed it had an Environmental Severity Index (ESI) level at about the 95th percentile of the world, land-based severity distribution.
Samples were periodically removed for topographic analysis of the area surrounding each bolt using an Optical Profilometer (OP, Veeco Contour GT-K). Before the analysis, samples were immersed in concentrated nitric acid to remove the coating and corrosion product. Weight change was monitored after repeated immersion for 10 min periods in nitric acid until the weight loss was less than 0.01 g between two consecutive weight measurements. The topographic image created by OP was analyzed by a software package (Vision64TM v5.30 from Bruker) to determine the corroded volume of the scribe below the level of the uncorroded areas according to a procedure described previously. One panel of each coating system was cut in half and exposed in the field without galvanic coupling as a control sample, which was used to quantify the extent of acceleration of coating degradation from the galvanic interaction.

One galvanic panel of each coating system was utilized to continuously monitor the coupling current during a 9 month field exposure. For those samples, each SS316 fastener was insulated from the substrate by a plastic O-ring and concentric cylinder. Electrical isolation between the fasteners and panel was checked with a meter and was determined to be greater than $10^7 \, \Omega$. Each fastener was electrically connected to the counter and reference electrode clips in a potentiostat (Intertech Systems PGS-151) by four insulated copper wires. One fastener remained shorted to the panel and was connected to the working electrode lead of the potentiostat. This fastener was top-coated and was only for electrical connection between the substrate and the copper wire, not for providing galvanic interaction. The applied potential was set to zero, which enabled the potentiostat to act as a zero-resistance ammeter. Anodic current flowing into the panel was balanced.
by the cathodic currents flowing out of the fasteners. They both represent the value of galvanic current between the panel and fasteners, measured by the potentiostat. A data logger (Veriteq) was plugged into the back of the potentiostat for recording and collecting galvanic current data every two minutes during approximately 280 days of field exposure. These currents were extracted from the data logger and plotted afterwards. The fasteners and the substrate were shorted together by the potentiostat throughout the testing, which is the same connection situation as for fasteners physically contacting the panel. OP was also used for topographic analysis of the galvanic panels used for current measurements.

The samples exposed to ASTM B117 were also cut in half. One half was attached with two uncoated SS316 fasteners for galvanic corrosion measurement and one fastener used for electrical connection painted by red Microstop lacquer (Tolber), as shown in Figure 6.2d. The two uncoated fasteners were insulated from the panel by two layers of plastic tape (Scotch Tape, 3M). The other halves were exposed without attached fasteners as control samples. The backs and edges of both half samples were painted by lacquer. Three long copper wires connected to each fastener reached out of the chamber. The galvanic current between the two uncoated fasteners and the panel was monitored once each day for 5 months. The wires connected to the panel and all fasteners were shorted together after each galvanic current measurement. Similar measurements in the ASTM B117 chamber were made previously. However, the substrate alloy, orientation of fasteners, and scribe length were different in this work, and the same as for the field exposed samples.
6.3 Results

Figure 6.3a-Figure 6.3d show the surface morphology of galvanic panels with chromate coating systems after 2, 5, 7, and 9 months exposure, respectively, at Daytona Beach. Corrosion attack was only observed near the fastener hole and scribes due to the galvanic interaction of the fasteners and scribed substrate. Not much corrosion was observed at the end of scribes because of the large ohmic potential drop and possibly inhibition effects of chromate released from the primer. The corrosion attack under the coatings surrounding fasteners became more severe with exposure time, indicating that corrosion initiated at scribed areas and then spread along the substrate/coating interface. The corrosion attack under the coating was not evenly distributed on the two sides of the scribes as shown in Figure 6.3d, possibly because corrosion will spread along preferential paths, such as weak adhesion spots, defects, and pores of the coatings. Figure 6.3e-Figure 6.3h show the surface morphology of galvanic samples with the non-chromate coating system after 2, 5, 7, and 9 months exposure at Daytona Beach, respectively. The corrosion attack also tended to occur near fasteners and scribes and become more severe with exposure time. Samples with the non-chromate coating system have much wider corrosion that is spread farther out along the metal/coating interface at each exposure period of time. This is consistent with a previous study on exposure in ASTM B117 \(^{34}\) and might indicate that the non-chromate coating has worse adhesion than the chromate coating. It should be noted that the behavior of other non-chromate coating systems could be different than the specific deoxidizer pretreatment (RECC 1015, Deft) and epoxy primer (02GN093 (Y), Deft) used here.
Figure 6.4 shows the surface morphology after removal of the coatings for non-galvanic samples with chromate or non-chromate coating systems after 204 or 460 days exposure in the field. The two non-galvanic samples have much less corrosion attack than the galvanic samples, as was shown in Figure 6.3. Accelerated corrosion attack as the result of galvanic interactions between fasteners and a coated panel has also been discussed previously $^5,6$. Corrosion attack on the samples with non-chromate coating became more severe with exposure time and both halves were worse than the samples with chromate coating. It is very difficult to see corrosion attack on samples with chromate coating, indicating better corrosion resistance than the non-chromate coating. To determine the extent of acceleration of the corrosion by galvanic coupling, the corrosion attack on non-galvanic samples has to be quantified and compared to a galvanic sample of the same type $^5,6$. However, there was little corrosion on chromate samples and much attack on the non-chromate sample after 460 days field exposure. The very small and large amounts of corrosion attack on these samples makes accurate quantification difficult due to the sensitivity range of the OP. Therefore, the non-galvanic sample with the non-chromate coating after 204 days exposure was used for determining acceleration factors, as described in the discussion section.

Figure 6.5 shows the surface morphology, topographic map, and depth profile of galvanic and non-galvanic samples after 5 months exposure in ASTM B117. Figure 6.5a and Figure 6.5b show the samples with chromate and non-chromate coating systems, respectively. The galvanic samples (top images) have obviously worse corrosion attack near the fastener holes and scribes than the non-galvanic samples (bottom images) for
both the chromate and non-chromate samples. This accelerated corrosion by galvanic interaction during laboratory exposure is consistent with that shown above for samples exposed in the field. The depth profiles of the galvanic samples (lines 1 and 3) indicate that the attack in galvanic samples can penetrate about 800 μm. Galvanic samples with chromate and non-chromate coating systems have very similar extents of corrosion attack, which is not consistent with the results during field exposure as shown in Figure 6.3. The ASTM B117 environment is so aggressive with galvanic coupling that both the chromate and non-chromate systems exhibited severe attack. Neither coating system could protect the Al alloy panel. The non-galvanic chromated sample exhibited no obvious corrosion attack after 5 months of ASTM B117 exposure, as shown in the bottom half of the panel in Figure 6.5a. The depth of the scribe was about 25 μm after exposure (line 2 in Figure 6.5a), which increased only slightly, by around 5 μm, from the depth of original scribe. The chromated coating could provide considerable corrosion protection to the Al alloy in the absence of galvanic coupling. On the other hand, the non-galvanic sample with the non-chromate coating exhibited two obvious corrosion spots. One was near the hole and scribe and the other was at the end of the scribe, as shown in the bottom half of the panel in Figure 6.5b. The depths of both corrosion spots were deeper than 100 μm (line 4 in Figure 6.5b), indicating worse corrosion protection of the non-chromate system. This is consistent with the results of galvanic and non-galvanic samples during field exposure in Figure 6.3 and Figure 6.4.

The galvanic currents between the uncoated fasteners and coated Al alloy panels were continuously monitored during the field and lab exposures. Figure 6.6a shows the
galvanic currents during the first 24 hours in the field exposure. For galvanic corrosion in the field, the controlling factor is the electrolyte on the surface, which strongly depends on the local weather, even for samples that were very close to the sea. The corrosion will be different for a thick layer of electrolyte and good ionic connection between fasteners and scribes than for a thin layer of electrolyte and poor ionic connection. Heavy dew, rain, aerosol deposition, and evaporation will all affect the condition of the surface electrolyte. At the start of the exposure, bottled water and sea water were splashed on the surface of two individual samples to assess the response and set the current range. The galvanic currents promptly responded to the electrolytes on the two samples, as shown in Figure 6.6a. The galvanic currents resulting from the sea water were much higher than from the bottled water as expected. The currents decayed rapidly after the bottled water splash because evaporation left a clean surface between the fasteners and scribes. The current after the seawater splash stayed high for many minutes. Another current spike was observed when rain started after the sea water splash. This rain shower also flushed away the ionic species from the sea water on the sample surface, leading to a lower current and then a lower peak when the second rain shower started. Galvanic currents above zero lasted around 20 hours in the first 24 hours of exposure. The diurnal formation of dew at night and evaporation during the day resulted in repeated fluctuations in current, Figure 6.6b. The current associated with each fastener was less than 5 μA. Chromate and non-chromate samples were connected to individual potentiostats for simultaneous current measurements. The current transients were similar for the two samples, as shown in Figure 6.6. The galvanic currents were continuously measured for about 280 days, as
shown in Figure 6.6b. This sample design essentially behaved as a sensor for the local weather. The galvanic current values were larger than zero 85% of the time, indicating that the Daytona Beach weather supported galvanic interaction between the fasteners and panel almost constantly during the 280 days exposure. The accuracy of the galvanic interaction time is limited by the frequency of measurement, 2 min. The current of the non-chromate sample was mostly similar to the chromate sample although it was a little higher during the first 150 days and lower after that. However, even though the magnitudes of the current for the two coating systems was similar, the extent of corrosion could be different. The corrosion attack in this type of sample is balanced by the sum of the cathodic galvanic current flowing from the fasteners and the local cathodic current on the Al alloy panel. Figure 6.3 shows that the extent of attack in the field for non-chromate coating system was much worse than that of the chromated systems for galvanic samples even though the galvanic current was similar. This indicates that the corrosion of the non-chromated sample involved more local cathodic current than the chromated sample during the field exposure. The attack was spread across the surface underneath the coating of the non-chromate sample, possibly because of poor adhesion. This physical separation of the local anodes from the cathodic fasteners resulted in a large ohmic potential drop under the coating, and promoted the activation of local cathodes. The attack on the non-galvanic, non-chromate sample shown in Figure 6.4 also indicated poor adhesion of this coating system.

Figure 6.7 shows the galvanic currents between fasteners and Al alloy panel during ASTM B117 exposure. The current per bolt was about 50 μA in ASTM B117, much
larger than that in the field exposure. Furthermore, unlike the field exposure, no current transients were observed, indicating that a stable layer of electrolyte existed on the surface of galvanic panel in the salt spray chamber. The chromate and non-chromate samples exhibited similar currents during the first 100 days. However, the current for the non-chromate sample continued to increase after that time while the chromated sample exhibited a significant decrease in current and became lower than that of the non-chromate sample.

6.4 Discussion

Atmospheric field exposure is usually less aggressive than laboratory exposure, including chambers and immersion, even if the NaCl concentration in seawater is used for the laboratory tests, because the surface concentration is variable, and ionic connection between anode and cathode is uncertain in atmospheric field exposure. The changes in local aggressiveness and potential drop influence the initiation and growth of various forms of corrosion. The electrolyte on the sample surface is covered with an adsorbed moisture layer in equilibrium with humid air, water droplets, precipitation, condensation, or rain. A very long time is required for the corrosion on scratched galvanic panels with chromated coatings during exposure in the field to reach the stage where it is visibly noticeable. Additionally, multi-layered coatings on the top surface can make it hard to observe the corrosion attack underneath using bare eyes. OP was used to characterize the small amount of localized corrosion in previous work due to its high sensitivity and resolution. To guarantee accurate corrosion quantification, in particular for the first sample removed from the environment, the corrosion attack has to be greater
than the detection sensitivity threshold of the optical profilometer. Galvanic currents were continuously monitored during field exposure, simultaneously giving the corrosion extent of samples by charge and an indication of the appropriate period of time to remove the first samples.

Due to the curvature of the thin plate samples, small areas had to be analyzed individually and then summed to quantify the corrosion attack on the whole sample. For example, Figure 6.8a shows the topographic map of the top left hole of the first sample with chromate coating removed from the field, which was after 2 months of exposure (Figure 6.3a). The optical profilometer is a much more sensitive technique than bare eye observation and it provides a depth profile of the whole scanned surface area. However, curvature of the sample is evident. Figure 6.8b is the zoomed-in area of the yellow rectangle in Figure 6.8a and Figure 6.8c is the depth profile along the yellow line in Figure 6.8b. Figure 6.8b and Figure 6.8c show no curvature and provide a clear boundary between the corroded and uncorroded areas, allowing for an accurate analysis of the corroded volume and area, which are shown in Figure 6.9a and Figure 6.9b. Corroded area and volume increased with exposure time for the samples with both coatings systems. The corroded areas and volumes are larger for the non-chromate samples, which is consistent with the morphology results in Figure 6.3. Based on the corroded volume, corroded area, and exposure time, the corrosion rate of galvanic panels with different coatings can be determined \(^{34}\). Figure 6.9c shows that the area-normalized corrosion rates decreased during the exposure time. The decreasing corrosion rate might be caused by corrosion product blocking the surface or by increasing ohmic potential drop between the
fasteners and the end of the attack under the coating with exposure time. The chromate and non-chromate samples have very similar corrosion rates at 5, 7 and 9 month of field exposure, even though the corrosion morphologies are very different. This apparent contradiction is the result of the difference in corroded area. Even though the corroded volume was much greater for the non-chromate system, the corroded area was also much greater.

The galvanic current can also be utilized to quantify the corrosion attack through Faraday’s law \(^5, 6\). The volume loss of galvanic panels in field and during ASTM B117 exposure was determined by OP and charge, as shown in Figure 6.10. OP and charge both have limitations for quantifying corrosion, such as undercut attack and local cathodic reaction, respectively, as discussed in Chapter 4. There are also other possible factors that might affect the volume loss results. A small amount of corrosion attack on the back side of samples might have occurred, even though the back side was painted as shown in Figure 6.2b. This small amount corrosion might consume a part of cathodic current from the fasteners. It is possible (though probably unlikely) that physical removal of the Al alloy substrate could be caused by wind or sand erosion, which might be sensed by the OP but not by the galvanic current measurement. Corrosion quantification by OP performed by summing the volume loss of many small areas on a curved sample surface might result in some errors due to overlap of the areas. Furthermore, the current measurement has errors associated with out of range currents, low frequency monitoring, and drift of the multiplier factor between the potentiostat and data logger. The results shown on the potentiostat front panel and those collected by data logger were offset by a
multiplier factor of 20 that was used to account for this offset. However, this multiplier changed for unknown reasons during the field exposure within the range of 14 to 34. An average multiplier was used to generate the galvanic currents shown in Figure 6.6, which caused error in the analysis.

Despite these possible errors, the current measurements and optical profilomotery data both provide means for quantification of the corrosion in galvanic and non-galvanic samples 5, 6, which allows for the determination of acceleration factors (AF) associated with the effect of galvanic coupling on the rate of attack, as defined by:

\[ AF_{galv-nongalv} = \frac{m_g / t_g}{m_{ng} / t_{ng}} \]  

(1)

where \( m_g \) and \( m_{ng} \) are the equivalent mass loss values for samples with and without coupling, respectively, and the \( t \) values are the respective exposure times 34. Table 6.1 shows the values of \( AF_{galv-nongalv} \) in field exposure and in ASTM B117. Some of the corroded volume values were normalized by multiplying by 2, because only one half of the panels was exposed in those conditions. It should be noted that the non-chromate coating system after 204 days exposure was used to determine the acceleration factor because no corrosion attack was observed on non-galvanic samples with chromate coatings, as shown in Figure 6.4 and Figure 6.5a. This mass loss of galvanic samples at different exposure times allowed determination of the acceleration factor for galvanic corrosion as a function of time, even though only the non-galvanic sample after 204 days exposure was used in the comparison shown in Eq. (1). Table 6.1 indicates that the \( AF_{galv-nongalv} \) during the field exposure increased with time, apparently reaching a plateau
value around 8. Only one $AF_{\text{galv-nongalv}}$ was determined for ASTM B117 because of limited samples, and it was found to be about 60, or 10x larger for the same time period in the field. SS316 fasteners provide much more cathodic current in ASTM B117, causing larger $AF_{\text{galv-nongalv}}$ than in the field exposure, even though the sample configurations were identical: the same type of fasteners, Al alloy panel, and coating system.

It is also interesting to compare the corrosion of samples exposed in the field and ASTM B117 for either galvanic or non-galvanic panels after 5 months exposure to determine the acceleration factors of ASTM B117 versus the field, $AF_{\text{B117-field}}$. The $AF_{\text{B117-field}}$ values are 3.8 and 38 for non-galvanic and galvanic panels, respectively, indicating that ASTM B117 is much more aggressive for the galvanic panels because of the ionic pathway to the SS316 fasteners, which results in a continuous cathodic current.

The different extents of galvanic attack of chromate samples between ASTM B117 and field exposure are the result of a different amount of cathodic current provided by the fasteners in the two environments. The cathodic current from fasteners highly depends on oxygen solubility, diffusion distance, and ohmic potential drop between scribed area and fastener, which are all relevant to the electrolyte situation on the sample surface. In the ASTM B117 environment, the electrolyte layer is not very uniform due to droplet initiation, growth, agglomeration, sliding down, falling off, etc., which are phenomena that also occur in real environments. However, unlike in field, the electrolyte never evaporates in ASTM B117 because the chamber maintains almost 100% relative humidity and 35 °C. The combination of temperature and continuous exposure to a thin
electrolyte layer results in a large and continuous oxygen reduction reaction on fasteners in ASTM B117. The electrolyte in the field exposure is more complicated than that in ASTM B117 chamber, owing to the changing temperature and RH from day to night, water droplet evaporation and condensation, precipitation, and wind. Evaporation of water droplets in the field increases the ohmic potential drop and might even break the ionic path between scribed substrate and fasteners. As a result, the SS316 fasteners cannot provide the same extent of cathodic current as in the ASTM B117 chamber. Bulk salt solutions are commonly used for corrosion studies in the lab because full immersion is a stable condition and is easily controlled. However, the diffusion layer thickness is much larger than that in ASTM B117 chamber or in the field, which decreases the cathodic limiting current on the SS316 fastener.

The cathodic current per SS316 fastener when coupled with coated panels is shown in Figure 6.7 for ASTM B117, in Figure 6.6 for the field, and was shown previously for bulk 5 wt% NaCl solution. Comparison of the average current values, which are given in Table 6.2, provides another means to quantify the acceleration factor of one environment to the other. The ratio of currents is essentially an acceleration factor for the oxygen reduction reaction on a SS316 fastener in the different environments. The oxygen reduction AF values listed in Table 6.3 are very similar for the chromate and non-chromate coatings, with AF_{B117-field} being the largest and AF_{B117-solution} being the smallest. The AF_{B117-field} for corrosion attack is smaller than for cathodic current because the corrosion attack in field was not driven only by the cathodic reaction occurring on the fasteners. Local cathodic reactions (oxygen reduction and hydrogen evolution) on the
non-galvanic non-chromate samples caused a large extent of corrosion attack on the panel, as shown in Figure 6.4. The oxygen reduction AFs should be useful for lifetime prediction of materials and coatings in the field using lab results.

However, the acceleration factor of lab versus field is just a comparison of the corrosion extent in two environments. Care should be taken when using these factors to predict lifetimes in the field from lab tests when they have different corrosion or failure mechanisms. An accelerated test should determine the susceptibility of a component to degradation or failure in a shorter period of time than that required in field exposures without changing the failure mechanism. A review of an accelerated lab test method for atmospheric corrosion presented the following disagreements between lab and field exposure: (a) lab exposure simulating industrial sites caused heavy rusting and rust staining on the cut edges, which was not observed during natural exposure at an industrial site. (b) Edge blistering was followed by edge flaking in the field exposure, which was not found in accelerated testing. Similar differences were also shown in the present work. Large delaminated areas were observed on non-chromate coated panels in field exposure shown in Figure 6.3e to Figure 6.3h, which were not seen in the ASTM B117 exposure shown in Figure 6.5b. (c) The rank-order of the accelerated tests is not always the same compared with exposure results and (d) Accelerated tests may cause rapid reduction in gloss paint, providing a disproportionate rate of acceleration. The different performance of materials between ASTM B117 and field exposure indicates the limitation of using ASTM B117 as an accelerated corrosion test. The results in ASTM B117 are of questionable relevance in practice for some systems. Therefore, extreme care
must be taken when utilizing the results in ASTM B117 and other acceleration factors to predict field performance or lifetime of materials.

Non-galvanic chromate samples did not exhibit any corrosion attack after 460 days of field exposure, as shown in Figure 6.4, and after 150 days of ASTM B117 exposure, as shown in Figure 6.5a, indicating strong inhibition by chromate. However, galvanic panels with chromate coatings have obvious corrosion in even short periods of field exposure, as shown in Figure 6.3a-Figure 6.3d, and severe corrosion attack in ASTM B117, as shown in Figure 6.5a. The large extent of corrosion at scribed areas in galvanic panels does not imply a bad performance of the chromate coating system because such corrosion attack was mainly driven by the cathodic currents provided by the bare SS316 fasteners. The fasteners were distant from the released chromate and thus probably not exposed to the inhibitor 34. A difference in inhibiting power can still be observed between chromate and non-chromate coatings by comparing the corrosion attack in the field-exposed galvanic panels in Figure 6.3, because the chromate can inhibit the local cathodic reactions on the Al alloy substrate. The small amount of cathodic current of fasteners in the field exposure indicates that the cathodic reaction on bare fasteners might not be the dominant driving force in the corrosion attack. However, the fasteners dominate in the ASTM B117 chamber because of the excess electrolyte, which is why the corrosion attack is similar for chromate and non-chromate coated galvanic panels. Therefore, galvanic acceleration of corrosion is more appropriate for field exposure than in the aggressive ASTM B117 chamber to quantitatively evaluate protection of different coating systems.
This experimental approach was also used to assess different surface treatments (chromate conversion coating or adhesion promoter) with an Mg-rich primer, as described in the experimental section. The galvanic panels with the two pretreatments had similar corrosion attack near fasteners and scribes after 135 days field exposure as shown in Figure 6.11. Both had more corrosion than the sample with the chromate coating system in Figure 6.3b, but less attack than the sample with the non-chromate coating system in Figure 6.3f, even though they all had the same topcoat. It is not a surprise that the sample with chromate conversion coating and chromate primer exhibited better performance than the sample with other coatings, including non-chromate system and chromate pretreatment with Mg-rich primer. The galvanic currents of these two panels were also monitored in the field as shown in Figure 6.12. The current transients are similar to the results shown in Figure 6.6. However, a galvanic current between the fasteners and scribes was measured only in 65% of the exposure time, less than the 85% in Figure 6.6b, indicating the difficulty of reproducibility of field exposure. The exposure of the second set took place during a different period of time, subsequent to the first exposure. To obtain accurate reproducibility in field, the same samples have to be exposed in the same location for the same period of time, such as the two simultaneous galvanic current tests in Figure 6.6, which presented the same current response to the environment.

6.5 Conclusions

AA2024-T3 panels with different scribed coatings and with or without galvanic connections to 304 stainless steel fasteners were exposed in ASTM B117 and the field
near an ocean beach. Galvanic currents and corrosion attack were quantified in both environments. Specific conclusions are as follows:

- Galvanic current measurements were performed during field exposure. Current transients depended strongly on the electrolyte on the sample surface, corresponding to changes in relative humidity, water drop evaporation, condensation, and precipitation. Galvanic currents are much lower in the field near an ocean beach than in the ASTM B117 chamber.

- Corrosion attack under the coatings was quantified for both field and lab exposure by optical profilometry and galvanic charge.

- Volume loss, corroded areas and corrosion rates as a function of exposure time were determined after field exposure. Volume loss and corroded areas increased, but corrosion rates decreased with exposure time.

- Acceleration factors for galvanic coupling in the field and lab exposure were determined and compared. Acceleration factors associated with cathodic current from a SS316 fastener were also determined. These acceleration factors could be used as a correlation factor between field and lab exposure.

- Care must be taken when utilizing ASTM B117 as an accelerated test because it may change the corrosion mechanism. The acceleration factors of lab versus field are just a comparison of the corrosion extent in two environments.

- Obvious corrosion attack was observed on chromate coated galvanic panels in both field and ASTM B117 exposure, because chromate is not able to inhibit the oxygen reduction reaction on distant bare fasteners, which drives galvanic attack.
This is not indicative of poor performance of chromate coating systems. Chromate coatings did perform well in the field and in the ASTM B117 chamber on non-galvanic panels.
Table 6.1. Acceleration factors (AF) of galvanic interaction between field exposure and ASTM B117. Samples in ASTM B117 and non-galvanic sample in field exposure were cut in the half. Their volume was normalized by multiplying by 2. Only the non-chromate coating system was used to determine $\text{AF}_{\text{galv-nongalv}}$.

<table>
<thead>
<tr>
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<th>2 month</th>
<th>5 month</th>
<th>7 month</th>
<th>9 month</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{galv}} / \text{mm}^3$</td>
<td>0.33</td>
<td>2.99</td>
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<td>7.12</td>
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<td>$2 \times V_{\text{nongalv}} / \text{mm}^3$</td>
<td>-----</td>
<td>-----</td>
<td>0.67</td>
<td>-----</td>
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<tr>
<td>$\text{AF}_{\text{galv-nongalv}}$</td>
<td>1.7</td>
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<td>8.2</td>
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<table>
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<th>5 month</th>
<th>7 month</th>
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<tr>
<td>$2 \times V_{\text{galv}} / \text{mm}^3$</td>
<td>-----</td>
<td>114</td>
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<tr>
<td>$2 \times V_{\text{nongalv}} / \text{mm}^3$</td>
<td>-----</td>
<td>1.86</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>$\text{AF}_{\text{galv-nongalv}}$</td>
<td>-----</td>
<td>61</td>
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Table 6.2. Cathodic currents per fastener coupling with chromate and non-chromate coated Al alloy panels in ASTM B117 chamber, 5 wt% NaCl solution, and field exposure.

<table>
<thead>
<tr>
<th></th>
<th>Coupling with chromate coated panel</th>
<th>Coupling with non-chromate coated panel</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ASTM B117</strong></td>
<td>69 ± 18 μA</td>
<td>84 ± 15 μA</td>
</tr>
<tr>
<td><strong>5 wt% NaCl solution</strong></td>
<td>18 ± 3.2 μA (^6)</td>
<td>27 ± 3.0 μA (^6)</td>
</tr>
<tr>
<td><strong>Field (Daytona Beach)</strong></td>
<td>0.69 ± 0.68 μA</td>
<td>0.95 ± 0.92 μA</td>
</tr>
</tbody>
</table>
Table 6.3. Acceleration factors of an environment relative to the other determined by corrosion attack and cathodic current of one fastener, respectively.

<table>
<thead>
<tr>
<th>Corrosion attack (non-galvanic panel with non-chromate coating)</th>
<th>Corrosion attack (galvanic panel with non-chromate coating)</th>
<th>Oxygen reduction reaction (galvanic panel with non-chromate coating)</th>
<th>Oxygen reduction reaction (galvanic panel with chromate coating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF_{solution-field}</td>
<td>-----</td>
<td>-----</td>
<td>29</td>
</tr>
<tr>
<td>( \text{AF}_{B117-field} )</td>
<td>3.8</td>
<td>38</td>
<td>88</td>
</tr>
<tr>
<td>AF_{solution}</td>
<td>-----</td>
<td>-----</td>
<td>3</td>
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</tbody>
</table>
Figure 6.1. Schematics of test sample configurations. (a) Coated AA2024-T3 panel coupling with four uncoated SS316 fasteners. Sample dimension, scribe length, and fastener position are shown. (b) Schematic of ZRA test in field exposure. Data logger was connected to the potentiostat to record and collect data.
Figure 6.2. Images of galvanic test sample preparation. (a) Top of sample showing scribes and fasteners. (b) Bottom of sample showing connections to fasteners and panel. (c) Location of galvanic samples on the roof of shack near the beach. (d) Galvanic test sample exposed in B117. Top half of the panel was coupling with two uncoated SS316 fasteners. Bottom half of the panel was a non-galvanic control.
Figure 6.3. Surface morphology of stripped galvanic samples after different periods of exposure in the field. (a - d) Samples with chromate coating systems after 2, 5, 7, and 9 months exposure. (e - f) Samples with non-chromate coating system after 2, 5, 7, and 9 months exposure.
Figure 6.4. Surface morphology of non-galvanic samples with chromate (a) and non-chromate (b) coating systems after field exposure. (c) Topographic image of non-chromate sample after 204 days field exposure. It is used for determining acceleration factors.
Figure 6.5. Surface morphology, topographic maps, and depth profile of galvanic (top of a and b) and non-galvanic (bottom of a and b) samples after 5 months exposure in ASTM B117. (a) Samples with chromate coating system. (b) Samples with non-chromate coating system.
Figure 6.6. Galvanic currents between fasteners and scribed coated Al alloy panel during field exposure. (a) Currents correspond to surface electrolyte situation at the first 24 h. (b) Current profile of the whole field exposure. 85% of currents are larger than 0.
Figure 6.7. Galvanic currents between fasteners and scribed coated Al alloy panel during ASTM B117 exposure.
Figure 6.8. (a) Topographic map of the top left hole of chromate coated sample after 2 months field exposure. (b) Zoomed in area of the yellow rectangle in (a). (c) Depth profile of the line in (b).
Figure 6.9. Volume loss, corrosion area, and corrosion rate of galvanic chromate and non-chromate samples in the field for different exposure times.
Figure 6.10. Volume loss of galvanic samples between field (DAB or Daytona Beach) and ASTM B117 exposure for non-chromate (NC) and chromate (C) samples determined by OP and charge.
Figure 6.11. Surface morphology and topographic maps of AA 2024-T3 coated with Alumigold/Mg-rich primer/topcoat (top) and PreKote/ Mg-rich primer / topcoat (bottom) after 135 days field exposure.
Figure 6.12. Galvanic currents between fasteners and Al alloy panel with two different non-chromate coating systems in field exposure. 65% of currents are larger than 0.
6.6 References


34. Z. Feng, J. Boerstler, G. S. Frankel, and C. A. Matzdorf, *Corrosion*, 2015, **71**(6), 771-783.

Chapter 7: Coating Evaluation of Al Alloy Using Breakpoint

Frequency Method

7.1 Introduction

High strength aluminum alloys are widely used in structural aircraft applications because of the combination of good mechanical properties and light weight. However, during the exposure to corrosive environments, Al alloys are prone to localized corrosion such as pitting, intergranular and crevice corrosion \(^1\)\(^-\)\(^4\). Therefore, Al alloys for aircraft applications are usually protected from the corrosion attack using multi-layered organic coating systems \(^5\),\(^6\). Most applications of organic coatings are either immersed in water or exposed to wet conditions such as humid air, droplets of spray, and condensation. Unfortunately, no organic coatings can behave as a perfect barrier to completely block water transport through them, due to their free volume and defects offering possible paths for water penetration where corrosion attack occurs \(^7\),\(^8\). So, the active area percentage of coatings can be used to indicate the coating quality.

A good coating providing a large ohmic potential drop makes the metal substrate unpolarizable, so that DC electrochemical methods like linear polarization are unable to evaluate the corrosion rate of coated metals \(^9\). Electrochemical impedance spectroscopy (EIS) is a technique capable of characterizing the electrochemical interface of coated metals and assessing corrosion resistant properties of coatings \(^10\)-\(^13\). The equivalent circuit
shown in Figure 7.1 has been widely used to analyze impedance spectra for coated metals, quantitatively providing important parameters such as coating capacitance, pore resistance in the coating, and metal/interface capacitance and resistance \(^{14-20}\). The metal/electrolyte interfacial capacitance measurement is one possible method to quantify the electrochemically active area in the coating. This assumes the specific capacitance (capacitance per unit area) of the metal/electrolyte interface is a constant. In typical aqueous environments, metal/electrolyte interfacial specific capacitance is usually about 15 to 30 \(\mu F/cm^2\) \(^{21,22}\). The electrochemically active area is equal to the measured metal/electrolyte interfacial capacitance divided by the specific capacitance \(^{12}\).

Additionally, the change of pore resistance in the coating has been used by Haruyama et al. \(^{23}\) to determine the electrochemically active area via the following expression:

\[
R_{po} = \rho d / A_d
\]  

where \(R_{po}\) is the pore resistance in the coating, \(A_d\) is the electrochemically active area. \(\rho\) and \(d\) are the specific bulk resistivity and coating thickness, respectively. The above approaches require computer modeling of the measured EIS spectra. Haruyama et al. proposed another method, the breakpoint frequency method, to determine electrochemically active area of the coating without modeling \(^{23}\). Based on that, Scully et al. proposed the low breakpoint frequency theory, which allows determination of the electrochemically active area ratio as small as 0.01% \(^{11,12}\). More detail information about breakpoint frequency is provided in the following.

The purpose of this work was to use the low and high breakpoint frequency methods to monitor the coating defect area with time on different coating systems. The appearance
of a high breakpoint frequency was proposed as the time when the visually localized corrosion occurred. The defect areas estimated by the breakpoint frequency method were compared with that measured by optical profilometry after a long-term EIS test. The breakpoint frequency and low frequency resistance $Z_{0.01Hz}$ values were also used to rank the performance of chromate primer on different surface pretreatments.

### 7.2 The Breakpoint Frequency Method

A nested simplified Randles circuit is used to model coated metal with defects, as shown in Figure 7.1. Scully $^{11, 12}$ utilized it to figure out the correlation between the defect area ratio change and the breakpoint frequency shift, based on the theory of Haruyama et al. $^{23}$. A layer of intact coating covering most a metal provides very high resistance such that it can be considered as a pure capacitor of value $C_c$. Small defects, usually pores, existing through coating thickness create an ionic path from the substrate to the bulk solution, which is modeled by a resistor $R_{po}$. Faradaic processes occur on the electrolyte/metal interface at the end of the pores, including the capacitance associated with the double layer, dissolution, or/and diffusion. This is modeled using a capacitance $C_d$ in parallel with a resistor $R_d$ representing the defect capacitance and resistance, respectively. Many papers refer to the double layer capacitance and the charge transfer resistance instead $^{10-13}$. The values of $R_{po}$, $R_d$ and $C_d$ change as a function of defect area, offering a possible method to evaluate defect area variation with exposure time.

A family of synthetic Bode magnitude and phase plots shown in Figure 7.2 was obtained using the nested simplified Randles circuit by varying the defect area percentage. These curves were reproduced based on Scully’s work $^{10, 12}$. Table 7.1 shows
the defect area ratios and the corresponding values of each component assumed for the curves in Figure 7.2. The overlapped Bode magnitude curves in the high frequency range for all the defect area ratios reflect the constant values of $R_s$ and $C_c$. The two resistance plateaus and the capacitive region in between shift downward with increasing defect area ratio, which lowers $R_{po}$ and $R_d$ and increases $C_d$. Figure 7.2 also show ASTM visual ratings for these same defect areas $^{10,12}$.

Breakpoint frequencies in the Bode magnitude plot are defined as a boundary where a capacitive region with slope equal to -1 transitions to a resistive region with a horizontal plateau when the frequency shifts from high to low values. At the transition, the impedance of the capacitance is equal to the plateau resistance and the phase angle is about $45^\circ$ $^{11,12}$. So the breakpoint frequency can also be determined in the Bode phase plot where, following the curve from higher to lower frequency, the phase angle first shifts down below $45^\circ$ $^{11,12}$. For coatings with relatively large defect areas, the frequency where the coating impedance ($1/\omega C_c$) equals the summation of pore resistance $R_{po}$ and solution resistance $R_s$ is named the higher breakpoint frequency $f_h$ $^{12}$. It is directly correlated to the defect area ratio, as follows:

$$R_s + R_{po} = \frac{1}{2\pi f_h C_c} \quad (2)$$

$$R_{po} = \rho d / A_d \quad (3)$$

$$C_c = \varepsilon \varepsilon_0 (A - A_d) / d \quad (4)$$

where $A$ and $A_d$ are the total exposed coating area and defect area, respectively, $\rho$ and $d$ are the resistivity in pores and coating thickness, respectively, and $\varepsilon$ and $\varepsilon_0$ are dielectric
constants for the coating saturated with water and permittivity of free space, respectively. Rs is usually negligible compared to R_po. For the defect area A_d less than 1% of the total coating area, A − A_d is approximated to A. Thus:

\[ f_h = \frac{1}{2\pi \varepsilon \varepsilon_0 \rho} \frac{A_d}{A} \]  

(5)

The relationship between f_h and the defect area ratio is independent of the substrate.

Good coatings with very small defect area ratio may result in pore resistance R_po and defect capacitance C_d that are not visible in the Bode magnitude plot because of the poor separation of the two time constants \(^{12}\), as shown in Figure 7.2. In this case, the higher breakpoint frequency is not measurable, and the lower breakpoint frequency can be determined as the point where the coating impedance \(1/\omega C_c\), is equal to the pore resistance R_po and the defect resistance R_d (Rs is negligible) \(^{12}\). This frequency is directly correlated with the defect area ratio

\[ R_{po} + R_{d} = \frac{1}{2\pi f_l C_c} \]  

(6)

\[ R_{d} = \frac{r_d}{A_d} \]  

(7)

\[ f_l = \frac{\frac{d}{2\pi \varepsilon \varepsilon_0 (\rho d + r_d)}}{A} \frac{A_d}{A} \]  

(8)

where \(r_d\) and \(c_d\) are unit area resistance and area specified capacitance at the metal/electrolyte interface, respectively. The resistivity in a pore \(\rho\) and coating thickness \(d\) are on the order of 1 – 10 \(\Omega\)cm and \(10^{-2}\) cm, respectively, making the product of \(\rho \times d\) much lower than \(r_d\), which is on the order of \(10^3\) \(\Omega\)cm\(^2\) \(^{12}\). So the lower breakpoint frequency in Eq. (8) can be reduced to:
This lower breakpoint frequency is dependent on unit area resistance at the metal/electrolyte interface, which may correlate with the charge transfer resistance of the substrate. This indicates that the relationship between $f_l$ and the defect area ratio depends on the material. In this work, the substrate is always AA 7075-T6, and $f_l$ can still be used to evaluate coatings qualitatively. This area dependence of $f_l$ can only be observed for good coatings with a very small defect area.

The benefit of the breakpoint frequency method is its ability to monitor the defect area as a function of time only using the high frequency range of Bode magnitude plots, with no need for analyzing the complicated behavior in the low frequency range. Moreover, the double layer capacitance and charge transfer resistance of a specific bare metal are not needed when using the high breakpoint frequency method. A shortcoming of this method is that a relatively long exposure time is needed to clearly observe the appearance of $f_h$. Scully $^{12}$ stated that the measurable minimum and maximum values for $f_h$ and $f_l$ are 100 and 10 Hz, respectively. Therefore, it is easy to know which breakpoint frequency is measured based on its value.

**7.3 Experimental**

The substrates of coated samples were AA7075-T6 (UNS A97075) panels. The surfaces of the panels were treated five different ways: chromate conversion coating (CCC, Alodine 1200S, Henkel Surface Technologies), Trivalent chromium pretreatment (TCP, SurTec 650 chromitAL, Surtec International), non-chromate pretreatment (NCP,
Alodine 5700, Henkel Surface Technologies), adhesion promoter (PreKote, Pantheon Industries), and clean only. The clean-only sample was treated by degreasing and desmutting to remove organic contaminants, salt, lubricants, and metallic oxide particles that might have been embedded during rolling or machining. Two different primer coatings were painted on the pretreated panels: a chromate epoxy primer (PPG CA7233, MIL-PRF-23377 Type I, Class C2 coating) and a Pr-rich primer (Deft 084, MIL-PRF-23377J Type I, Class N coating). No topcoat was applied on top of the primer in this work. Two batches of coating systems were measured. The first batch of coated Al alloys contained chromate conversion coating (CCC) with chromate primer and adhesion promoter pretreatment with Pr-rich primer. The second batch of samples has the same chromate primer, but different surface pretreatments, including TCP, NCP, adhesion promoter, and clean only.

A cylindrical PTFE cell with an inner surface area of 5.50 cm² was positioned on the coated panel using silicone glue, which was allowed to dry for 24 h. The cell was filled with naturally-aerated 5 wt% NaCl solution. A graphite rod was used as the counter electrode and a Saturated Calomel Electrode (SCE) was the reference electrode. EIS were carried out using a Gamry Instruments Reference 600 potentiostat. The impedance was collected in the frequency range from $10^5$ to $10^{-2}$ Hz with a 10 mV voltage amplitude around the open circuit potential (OCP). 7 data points were collected per decade. EIS measurements were taken on the each coated Al alloy periodically (usually every day) for exposures of >100 days. The OCP was monitored for 15 min before each EIS measurement.
After the long-term EIS measurement, the coatings were stripped by immersing the samples into concentrated nitric acid (HNO₃) for 20 min. This also removes corrosion products forming under the coating. Topographic analysis of the stripped panel was then conducted using optical profilometry (OP, Veeco Contour GT-K). The topographic images produced by OP were analyzed using a software package (Vision64TM v5.30 from Bruker) to quantify the corroded area under coatings.

7.4 Results

Figure 7.3 shows Bode magnitude and phase angle plots for Al alloy coated with CCC pretreatment and chromate primer. The impedance data were collected periodically during 187 days exposure to 5 wt% NaCl solution. The low frequency resistance was higher than 10⁹ Ω and the magnitude plot was a straight line for the first 8 days, indicating that the coating blocked the electrode completely, separating the metal substrate and electrolyte. After 21 days exposure, the electrolyte penetrated the coating through pores and reached the substrate, activating the resistances in the pores and at the metal/electrolyte interface. This caused the magnitude plot to bend a little in the low frequency range, exhibiting a lower breakpoint frequency \( f_l \). With increasing time, the exposed metal area was enlarged due to corrosion and coating degradation, causing the low frequency resistance to decrease and the breakpoint frequency to shift to higher values. After a certain exposure time, 125 days exposure in this case, the electrochemically active area of the coating achieved a threshold value when an impedance plateau appeared associated with pore resistance in the middle frequency range. At this point, the high breakpoint frequency \( f_h \) appeared. Meanwhile, two separated
time constants in the Bode phase plot became obvious, as shown in Figure 7.3b. Poor separation of time constants before 125 days prevented their identification. The similarities of the Bode plots in Figure 7.3 and Figure 7.2 verified the use of the breakpoint frequency method for evaluating the active areas of these samples.

Figure 7.4a shows the change of $f_i$ and $f_h$ with exposure time for Al alloy coated with CCC and chromate primer. They were extracted from each Bode phase plot. $f_i$ could not be measured before 21 days, because the coating blocked the sample. After 21 days, $f_i$ was measured and slightly increased with exposure time from 0.1 to 2 Hz until 119 days. The appearance of $f_h$ occurred at 121 days, corresponding a sharp drop of OCP and the low frequency impedance, $Z_{0.01Hz}$, values as shown in Figure 7.4b. This may indicate that a significant defect initiated under the coating. With increasing time, the $f_h$ values elevated and approached the largest value, about $10^5$ Hz, indicating propagation of the attack. Before the appearance of $f_h$, the OCP values were stabilized at about -300 mV SCE because the CCC pretreatment passivated the substrate. After the initiation of attack on the substrate, the OCP values decreased to about -800 mV SCE, which is close to the OCP of bare AA 7075-T6 in this solution.

Based on the correlation between the breakpoint frequency and the active area ratio in Figure 7.2, the largest breakpoint frequency reaching to $10^5$ Hz in Figure 7.4a corresponds to the active area ratio in the range of 0.01% to 0.1%. Only one visual corrosion site was observed on the sample after 182 days exposure to 5 wt% NaCl solution as shown in Figure 7.5a and Figure 7.5b. Optical profilometry was utilized to obtain a topographical map of this site, as shown in Figure 7.5c. The depth and area of
the pit were about -120 μm and 0.67 cm², respectively. Because the total exposed area was 5.5 cm², the visual defect area ratio was around 0.12% after 182 days EIS measurements, which is slightly higher than the ratio range estimated from the breakpoint frequency method. The period of time before the appearance of \( f_h \) can also be considered as a criterion to evaluate the susceptibility to coating degradation.

For comparison, EIS measurements were conducted on the coating system consisting of adhesion promoter pretreatment and Pr-rich primer. Figure 7.6 shows the Bode magnitude and phase plots of this coating during 121 days exposure to 5 wt% NaCl solution. The breakpoint frequency was also observed to shift to higher values with increasing exposure time. A high breakpoint frequency occurred after only 12 hours exposure, much quicker than for the CCC pretreatment and chromate primer system, which was about 125 days. This indicates that attack initiated faster under the Pr-rich primer than the chromate primer or that the Pr-rich primer had more intrinsic defects than the chromate primer. The breakpoint frequency reached to the highest setting frequency \( 10^5 \) Hz after 70 days exposure, indicating the defect area ratio was at least higher than 0.1% after the propagation. The attack under the chromate primer was still in the incubation stage at this time. Figure 7.7 shows the effect of exposure time on the breakpoint frequency, OCP, and \( Z_{0.01Hz} \). The breakpoint frequency quickly shifted to high values and reached a plateau close to the maximum frequency \( 10^5 \) Hz. This corresponded to the sharp drop of \( Z_{0.01Hz} \) values at the early stage, ending up to about \( 10^5 \) ohms. OCP values increased from -900 to -650 mV SCE, and then dropped and stabilized around -800 mV SCE. The adhesion promoter pretreatment did not strongly passivate the substrate,
causing the OCP values reach to -800 mV (OCP of bare Al alloys) after only a short exposure. Although the breakpoint frequency was over $10^5$ Hz after 70 days corresponding to over 0.1% defect area ratio, it is still interesting to characterize and quantify the corroded area of the coatings after exposure. Figure 7.8 displays the corrosion morphology and the topographic image after 121 days of exposure. The corroded area and area ratio are 14.77 cm$^2$ and 2.7%, respectively. This ratio is one order of magnitude higher than that determined using $10^5$ Hz as a breakpoint frequency. An assumption for the breakpoint frequency method is the defect area ratio is less than 1%, allowing the derivation of Eq. (5). Therefore, for small cell area (5.5 cm$^2$ in this work), the breakpoint frequency method may be only valid for the determination of defect area ratio during the initiation of attack but not for the propagation to large regions of attack.

Because the breakpoint frequency method was successful for comparison of the two coating systems described above, it was also utilized to evaluate the second batch of coated samples with different surface pretreatments including TCP, NCP, adhesion promoter pretreatment, and clean only. All of the samples had the same chromate primer after the surface pretreatment. Figure 7.9 shows Bode magnitude plots of samples with each pretreatment exposed to 5 wt% NaCl solution for over 300 days. The low frequency resistance $Z_{0.01Hz}$ of all the samples decreased with exposure time due to water uptake and coating degradation. The resistance plateau at the medium frequency range was only observed on the sample with NCP pretreatment, indicating the high breakpoint frequency was measured and possibly visual attack initiated on the sample. The samples with other pretreatments exhibited only the low breakpoint frequency. Figure 7.10 shows Bode
phase plots of chromate primer coated Al alloys with each surface pretreatment. Similarly, the breakpoint frequency shifted to higher frequencies for all the samples with exposure time. $Z_{0.01Hz}$ and the breakpoint frequency values were extracted from the Bode magnitude and phase angle plots, respectively, and are shown in Figure 7.11. The higher values of breakpoint frequency correspond to the lower values of $Z_{0.01Hz}$, due to the larger defect area ratio of the coating. This indicates the performance rank of the chromate primer on the surface pretreatments is adhesion promoter > clean only ≈ TCP > NCP.

Figure 7.12 shows the surface morphology of samples with different surface pretreatment after over 300 days of exposure. The left and right side of each part are before and after the coating was stripped, respectively. Visual blisters were only exhibited on the coated sample with NCP pretreatment, as shown in the yellow rectangles in Figure 7.12b. Slight corrosion stains were observed after removing the coating. OP was not able to distinguish the two corrosion sites from the surrounding uncorroded areas, due to the very strong roughness of the substrate. Image J, a photo analysis software, was used to quantify the corroded area from the optical images. The area was about $2.3 \text{ mm}^2$ corresponding to a defect area ratio of about 0.4%, which is two orders of magnitude higher than the expected area ratio estimated from the highest breakpoint frequency, about 5000 Hz in Figure 7.11b. The chromate primer coated samples with TCP, clean only, and adhesion promoter pretreatment exhibited no obvious corrosion attack. From visual comparison, the performance rank-order of the surface pretreatments is adhesion promoter ≈ clean only ≈ TCP > NCP. It is almost consistent with the order ranked from
the breakpoint frequency and $Z_{0.01\text{Hz}}$ values, except the visual comparison is not able to distinguish the performance of adhesion promoter, clean only, and TCP.

TCP also passivated the substrate like CCC, causing the higher OCP values than other non-passivated pretreatments including NCP, clean only and adhesion promoter, as shown in Figure 7.13. The OCP values of non-passivating pretreatments were between -750 mV and -900 mV SCE, close to the value of the bare Al alloy. The TCP treatment increased OCP to around -500 mV SCE, which is lower than the value measured for the CCC pretreatment before significant corrosion occurred, about -300 mV SCE, as seen in Figure 7.4b.

7.5 Discussion

To understand how the pore resistance, metal/electrolyte resistance and capacitance change with expanding defect area, the observed spectra for samples with CCC pretreatment and chromate primer were fitted using the nested simplified Randles circuit, as shown in Figure 7.14. The corresponding fit values of each component are presented in Table 7.2. Since $R_s$ is independent of the defect area, it was fixed at 1 $\Omega$ during the computer fitting. One of the assumptions for the breakpoint frequency method is that the defect area is less than 1% of total cell area, making $A - A_d$ approximated to $A$ in Eq. (4). As a result, the coating capacitance is also independent of the defect area and does not change with exposure time, as shown in Table 7.2. It should be noted that the coating capacitance in this case is the value after the water uptake that occurred quickly, usually in the first 24 hours. The visual defect area ratio of the chromate coating system was around 0.12% (less than 1%) after 182 days EIS measurements, as shown in Figure 7.5.
which is in good agreement with the defect area ratio evaluated by the breakpoint frequency. For the Pr coating system as shown in Figure 7.8, however, the attack area ratio after 121 days EIS measurements was 2.7%. This is greater than the limit for the application of the breakpoint frequency method, which is 1% of total cell area. The attack area ratio is almost two order magnitudes higher than that estimated by the breakpoint frequency. This supports the notion that the breakpoint frequency is only valid for very small defect areas or for the initial stage of coating degradation, and not for the defect propagation to a large scale. The other assumption for the breakpoint frequency method is the constant unit area resistance and capacitance in defects, allowing the determination of defect area by measuring resistance and capacitance. Based on that, the measured resistance including $R_{po}$ and $R_d$ should decrease with expanding defect area. However, the measured defect capacitance $C_d$ should increase with expanding defect area. Such a trend is seen in Table 7.2. In addition, the resistance and capacitance should change by one order of magnitude when the breakpoint frequency or the defect area increases by one order of magnitude. However, the data in Table 7.2 do not show this relationship. This might be caused by the complexity of the metal/electrolyte interface, which is not modeled well by a pure capacitor parallel with a resistor. Instead of a pure capacitor, a constant phase element was usually utilized to model the capacitive behavior of coatings 26, 27.

Organic coatings protect the metal substrate in different ways. The primary mechanism is to act as a physical barrier separating metal and corrosive electrolyte. This barrier provides a large ohmic potential drop making metal substrate hard to be polarized.
For instance, multi-layered coatings on Al alloy panels can protect them from anodic polarization by adjacent noble material fasteners for a certain time \(^5,6\). However, water uptake occurs quickly, causing the ohmic potential drop to decrease due to the relatively low resistance of the solution in the pores of coatings. After water approaches the metal substrate, corrosion attack can happen at anodic and cathodic sites. The coating can still protect the metal substrate after water uptake by preventing formation of a bulk electrolyte at the coating/substrate interface and thus limiting the interaction between anodic and cathodic sites. The charge transfer reaction occurs easier on both cathodic and anodic sites in the presence of a bulk electrolyte. Even when a bulk electrolyte phase exists at the metal/coating interface, inhibitors such as soluble chromate and Pr ions can be released from the coatings, migrate to the corrosion sites and prevent further attack \(^28-30\).

The coating protectiveness mentioned above can be estimated by the important electrical parameters, including the low frequency resistance \(Z_{0.01Hz}\) and the breakpoint frequency. \(Z_{0.01Hz}\) and the breakpoint frequency in Figure 7.11 indicate the coating protectiveness rank on the surface pretreatments is adhesion promoter > clean only \(\approx\) TCP > NCP. The same chromate primer coated Al alloys with the same surface pretreatments, but with artificial scribes, were exposed to ASTM B117 for 100 days in previous work \(^24\). The corrosion attack of the sample with NCP pretreatment was worse than the samples with other pretreatments. The panel with adhesion promoter pretreatment exhibited no obvious corrosion attack on both “X” scribes. The corrosion extent of samples with TCP and clean only pretreatment was between NCP and adhesion...
pretreatment. These observations are consistent with the trends of low frequency resistance $Z_{0.01\text{Hz}}$ and breakpoint frequency in Figure 7.11. It is also interesting that the breakpoint frequency of TCP, clean only, and adhesion promoter remained at low values less than 10 Hz for over 300 days in NaCl solution. Also they maintained high $Z_{0.01\text{Hz}}$ values of more than $10^7 \, \Omega \text{cm}^2$ and exhibited no visual corrosion attack for over 300 days exposure. It should be noted that ASTM B117 is an extremely aggressive environment compared to a full immersion test. The good performance of samples with scribes in ASTM B117 and during immersion in chloride solution is strong evidence of the good performance of chromate primer combined with the adhesion promoter pretreatment.

The excellent performance of coatings makes it difficult to compare them or predict their lifetime in a short period of time. Bierwagen et al. plotted the low frequency resistance of different coatings as a function of time and extrapolated their lifetime using the impedance of bare metal as a failure criterion. It was assumed that $\log(Z_{0.01\text{Hz}})$ was a linear relationship with exposure time until coating failure. This assumption overlooked at least two very important realities. Firstly, $\log(Z_{0.01\text{Hz}})$ values exhibited a sharp drop at the very early stage involving water uptake and another drop when significant corrosion initiated, as shown in Figure 7.4b. Between those two times, $\log(Z_{0.01\text{Hz}})$ was almost a constant at around 7 to 8, probably because the coating limited the formation of bulk electrolyte phase at the metal/coating interface. So, it may be inappropriate to model the change of $\log(Z_{0.01\text{Hz}})$ vs. time using a linear relationship. Figure 7.11a also shows a non-linear relationship between $\log(Z_{0.01\text{Hz}})$ and exposure time, although the second resistance drop did not occur. Additionally, it might be not critical to consider the impedance of
bare metal as the coating failure criterion. A 3% visual corroded area (ASTM D 610 rating of 5) was defined arbitrarily as coating failure. A correlation of threshold impedance and visual corroded area percentage has been developed on epoxy polymide-coated steel and Araldite-coated Mg alloy. The threshold low frequency impedance was about $10^6$ to $10^7 \ \Omega \text{cm}^2$ for coated steel and about $4 \times 10^8 \ \Omega \text{cm}^2$ for coated Mg alloy, which are much higher than the impedance of bare metal. Therefore, a linear extrapolation of low frequency resistance to the bare metal impedance would be much less conservative to predict coating lifetime. EIS actually is a more useful technique to characterize coated metals before visual attack, such as water uptake and water saturation, small defect area estimation, and bulk electrolyte formation at the metal/coating interface.

In the present work, the appearance of $f_h$ (over $10^2$ Hz) corresponds to visual corrosion initiation. After that, the attack propagated causing the breakpoint frequency shift to even higher values. The critical $f_h$ of $10^2$ Hz could be considered as a criterion to assess the incubation time before visually localized corrosion under coatings to rank different coating systems. This method avoids fitting and analyzing complex impedance at very low frequency. However, excellent coating systems postpone the appearance of the high breakpoint frequency and enlarge the incubation time to over 300 days. This was the case for chromate primer coating on TCP, clean only, and adhesion promoter pretreatments, as shown in Figure 7.11b. Therefore, to compare different coating systems, it may be necessary to shorten the period before the appearance of the high breakpoint frequency in an appropriate way. Pre-polarizing coated metal can accelerate coating
degradation by speeding up either metal dissolution or cathodic reactions, because corrosion products, hydroxyl ion, and hydrogen are able to induce coating disbondment. A test cycle involving a sequence of OCP, EIS, and potentiostatic hold has been used to monitor the significant decrease of low frequency impedance of coatings in a few cycles. The same test protocol can also be used to observe the breakpoint frequency shift and then to characterize expansion of defect areas with the test cycle number. The other way to accelerate coating degradation may be galvanic coupling with a noble metal, which provides large cathodic current driving the metal dissolution, similar to anodic pre-polarization. The combined panel and fastener sample is also similar to structures used in real applications. A coated Al alloy panel coupling with bare stainless steel 316 fasteners has been recently been studied to provide an accelerated response to lab and field environments. A serial EIS measurement can be conducted on the coated area near the fasteners after pre-exposure. The fasteners may accelerate the coating degradation during pre-exposure and then EIS could be utilized to quantify the degraded area by monitoring the breakpoint frequency shift. More interestingly, the incubation time before reaching the critical breakpoint frequency ($10^2$ Hz) can be compared for the cases with and without galvanic acceleration. This comparison could also be considered as an acceleration factor.

7.6 Conclusions

Long-term EIS measurements were taken on chromate primer coated Al alloy panels with different surface pretreatments including CCC, TCP, NCP, clean only and adhesion
promoter pretreatment. The breakpoint frequency method was used to monitor the defect area expanding under different coating systems. The specific conclusions are as follows:

- A correlation was obtained between the high breakpoint frequency and the electrochemically active area on coated Al alloys. OP was used to quantify the active areas after long-term EIS measurements, which were one or two orders of magnitude larger than the area estimated by the breakpoint frequency. This is evidence of the limitation of the breakpoint frequency method; it may be only valid for very small defect area of the coating or for the initial stage of coating degradation, but not to assess defect propagation to a large scale.

- The breakpoint frequency shifted to larger values with coating deterioration. Visual corrosion attack occurred when the breakpoint frequency reached values higher than $10^2$ Hz.

- $Z_{0.01\text{Hz}}$ was also used to evaluate coatings, and it decreased with coating degradation. It has the opposite response to the breakpoint frequency. The higher breakpoint frequency means larger electrochemically active area, corresponding to lower $Z_{0.01\text{Hz}}$ values.

- The performance rank-order of chromate primer on the surface pretreatments is adhesion promoter > Clean only ≈ TCP > NCP, which is consistent with the rank-order of scribed samples during self corrosion exposure to ASTM B117.

- TCP and CCC pretreatment passivated the substrate and increased the OCP values to -500 mV and -300 mV SCE, respectively.
Table 7.1. Defect area ratio and values of each component assumed for curves in Figure 7.2.

<table>
<thead>
<tr>
<th>Assumed values</th>
<th>Defect area ratio, $A_{\text{total}} = 10 \text{ cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1%</td>
</tr>
<tr>
<td>$R_s = 1 \Omega$</td>
<td>1 $\Omega$</td>
</tr>
<tr>
<td>$C_c = 10^{-9} \text{ F/cm}^2$</td>
<td>$10^8$</td>
</tr>
<tr>
<td>$R_{po} = 1 \Omega \text{ cm}^2/A_d$</td>
<td>$10^1$</td>
</tr>
<tr>
<td>$R_d = 10^2 \Omega$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>$C_d = 10^{-3} \text{ F/cm}^2$</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

Rounded values.
Table 7.2. Fit values of each component in the equivalent circuit for modeling the spectra in Figure 7.14. Total cell area is 5.5 cm²

<table>
<thead>
<tr>
<th>Component</th>
<th>$f_1 = 10^{-1}$ Hz</th>
<th>$f_1 = 10^0$ Hz</th>
<th>$f_h = 10^2$ Hz</th>
<th>$f_h = 10^3$ Hz</th>
<th>$f_h = 10^4$ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s/\Omega$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$C_c/F$</td>
<td>$1.4 \times 10^{-9}$</td>
<td>$1.5 \times 10^{-9}$</td>
<td>$1.5 \times 10^{-9}$</td>
<td>$1.6 \times 10^{-9}$</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>$R_{po}/\Omega$</td>
<td>$1.3 \times 10^7$</td>
<td>$3.3 \times 10^6$</td>
<td>$7.2 \times 10^5$</td>
<td>$8.4 \times 10^4$</td>
<td>$1.2 \times 10^4$</td>
</tr>
<tr>
<td>$C_d/F$</td>
<td>$3.3 \times 10^{-9}$</td>
<td>$4.6 \times 10^{-9}$</td>
<td>$5.2 \times 10^{-8}$</td>
<td>$9.3 \times 10^{-8}$</td>
<td>$1.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>$R_d/\Omega$</td>
<td>$2.4 \times 10^8$</td>
<td>$4.0 \times 10^7$</td>
<td>$5.8 \times 10^6$</td>
<td>$2.9 \times 10^6$</td>
<td>$4.4 \times 10^4$</td>
</tr>
</tbody>
</table>
Figure 7.1. Nested simplified Randles circuit of a coated Al alloy with a defect.
Figure 7.2. Effect of defect area percentage on impedance magnitude and phase angle behavior of a coated steel equivalent circuit. Total cell area assumed is 10 cm$^2$.

Reproduced data $^{10, 12}$. 

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Figure 7.3. Bode plots of Al alloy coated with CCC pretreatment and chromate primer. EIS measurements were performed periodically during 162 days exposure to 5 wt% NaCl solution. Cell area is 5.5 cm$^2$. 
Figure 7.4. Effect of exposure time on (a) the breakpoint frequency $f_i$ or $f_h$ and (b) OCP and $Z_{0.01\text{Hz}}$ values.
Figure 7.5. Pitting corrosion morphology on Al alloy coated with CCC and chromate primer after 162 days EIS measurements. a. Before coating removed. b. After coating removed. c. Topography image by optical profilometry.
Figure 7.6. Bode plots of Al alloy coated with adhesion promoter pretreatment and Pr-rich primer. EIS measurements were performed periodically during 121 days exposure to 5 wt% NaCl solution. Cell area is 5.5 cm².
Figure 7.7. Effect of exposure time on (a) breakpoint frequency $f_1$ or $f_h$ and (b) OCP and $Z_{0.01Hz}$ values. The breakpoint frequency is higher than the measured frequency after 70 days.
Figure 7.8. Corrosion morphology on Al alloy coated with adhesion promoter pretreatment and Pr-rich primer after 121 days EIS measurements. a. Before coating removed. b. After coating removed. c. Topography image by optical profilometry.
Figure 7.9. Bode magnitude plots of Al alloy with (a) TCP pretreatment, (b) NCP pretreatment, (c) clean only, and (d) adhesion promoter pretreatment. They all have the same chromate primer after pretreatment. EIS measurements were performed periodically in 5 wt% NaCl solution. Cell area is 5.5 cm$^2$. 
Figure 7.10. Bode phase plots of Al alloy with (a) TCP pretreatment, (b) NCP pretreatment, (c) clean only, and (d) adhesion promoter pretreatment. They all have the same chromate primer after pretreatment. EIS measurements were performed periodically in 5 wt% NaCl solution. Cell area is 5.5 cm$^2$. 
Figure 7.11. Effect of exposure time on (a) $Z_{0.01\text{Hz}}$ and (b) breakpoint frequency $f_i$ and $f_h$ of different surface pretreatment samples. All the samples have the same chromate primer after pretreatment. Cell area is 5.5 cm$^2$. 
Figure 7.12. Morphology after over 300 days exposure to 5 wt% NaCl solution. (a) TCP, (b) NCP, (c) Clean only, (d) Adhesion promoter pretreatment. All the samples have the same chromate primer on the surface pretreatment.
Figure 7.13. OCP of different surface pretreatment samples changes as function of exposure time. All the samples have the same chromate primer after pretreatment.
Figure 7.14. The observed and fit Bode plots of Al alloy coated with CCC pretreatment and chromate primer. The solid lines are fit based on the equivalent circuit in Figure 7.1. Total cell area is 5.5 cm$^2$. 
7.7 References


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Chapter 8: Conclusions and Future Work

8.1 Conclusions

In this work, zero resistance ammeter and optical profilometery were utilized to measure the galvanic current between coated Al alloy panel and noble fasteners and quantify the galvanic corrosion attack. It has been compared with the corrosion attack of the panel without attaching fasteners to determine the acceleration factor for the galvanic corrosion. Additionally, the galvanic sample design was used to evaluate different coating systems in a short period of time exposure to ASTM B117. Furthermore, the galvanic attack was compared between lab and field exposure, providing an acceleration factor for lab environment to field environment. Finally, the breakpoint frequency method was used to evaluate the defect expanding of different coating systems. The specific conclusions are as follows:

- Galvanic interaction of fasteners with an AA7075-T6 panel indicates that anodic current of the panel increases with the addition of attached fasteners and decreases when fasteners are disconnected because of the cathode/anode area ratio.
- Interaction of fasteners with each other shows that cathodic current of each fastener decreases when other fasteners are attached to the panel and the decrease of cathodic current correlates to the number of attached fasteners, since potential
difference between a fastener and the panel goes down if other fasteners are attached.

- The current of each fastener indicates that scribes are not just interacting with the closest fasteners, also interacting with distant ones. And current of fasteners decrease if scribes are far away from them.

- The galvanic current measured with SS316 fasteners was higher than with Ti fasteners because of differences in cathodic current each alloy provides. Galvanic current and mass loss results quantitatively prove coupling with SS 316 fasteners caused most severe corrosion attack and can be an accelerated corrosion method to rapidly evaluate coating systems.

- Corrosion attack areas are wider for the samples with a topcoat than for those with only a chromate primer, because topcoat blocks the release of soluble chromate from conversion coating.

- Galvanic current in ASTM B117 was larger than that in 5 wt% NaCl bulk solution, because of higher temperature, thinner electrolyte layer and greater availability of oxygen in B117.

- Corrosion degradation of two different coating systems was compared. CCC/chromate primer panels exhibited deeper corrosion near scribes; while adhesion promoter/Pr primer samples showed relative wider corrosion. This difference was most likely from the different pretreatments due to their different ability to passivate the aluminum substrate.
An approach was developed to determine acceleration factor that describes influence of galvanic coupling between the fasteners and substrate to accelerate coating degradation relative to the situation with no galvanic coupling. The acceleration factors for SS316 fasteners were estimated to be 45 and 25 for coating systems without and with a topcoat, respectively. The acceleration factors for Ti alloy fasteners were smaller, 12 and 7 for samples without and with a topcoat, respectively.

Galvanic panels with TCP and CCC pretreatment exhibited narrow but deep corrosion attack, while samples with NCP, Clean only and adhesion promoter pretreatment had wide corrosion attack under the delaminated coating.

Corroded area and largest pit depth increased with exposure time for all the surface pretreatment panels. Samples with TCP and CCC pretreatment have a higher chance of pit perforation, whereas samples with NCP, clean-only and adhesion promoter pretreatment have higher chance of full coating detachment.

The corrosion rates of galvanic panels decrease with exposure time for all the surface pretreatment samples, and eventually reach the rate of uncoated and uncoupled AA7075-T6.

Mass loss results were modified to account for local H$_2$ evolution and undercut attack. The effects of local H$_2$ evolution and undercut attack were estimated to be 24% and 6%, respectively. That means that the galvanic current measurement underestimated mass loss by 24% and the OP method underestimated mass loss by 6%.
• Acceleration factors associated with the galvanic coupling in ASTM B117 are in the range of 100 to 500 for the different surface pretreatments even though the galvanic panels had the same substrate and fastener.

• Galvanic current measurements were performed during field exposure near an ocean beach. Current transients are related to the electrolyte situation on the sample surface, corresponding to changes in relative humidity, water drop evaporation, condensation, and precipitation. Galvanic currents are much lower in the field than in the ASTM B117 chamber.

• Corrosion attack under the coatings was quantified in field and lab exposure by optical profilometry and galvanic charge. In-situ quantification of corrosion by charge gave an indication as to when samples were removed from the field.

• Volume loss, corroded areas and corrosion rates changing with exposure time were determined after field exposure. Volume loss and corroded areas increased, but corrosion rates decreased with exposure time.

• Acceleration factors of galvanic coupling in field and lab exposure were determined and compared. More importantly, acceleration factors associated with different aggressive environment were addressed by corrosion attack and cathodic currents of a SS316 fastener, respectively, which can be used as a correlation factor between field and lab exposure.

• Care must be taken when utilizing ASTM B117 as an accelerated test because it may change the corrosion mechanism. The acceleration factors of lab versus field are just a comparison of the corrosion extent in two environments.
• Obvious corrosion attack was observed on chromate coated galvanic panels in both field and ASTM B117 exposure, because chromate is not able to inhibit the oxygen reduction reaction on distant bare fasteners, which drives galvanic attack. This is not indicative of poor performance of chromate coating systems. Chromate coatings did perform well in the field and in the ASTM B117 chamber on non-galvanic panels.

• A correlation was obtained between the high breakpoint frequency and the electrochemically active area on coated Al alloys. OP was used to quantify the active areas after long-term EIS measurements, which were one or two orders of magnitude larger than the area estimated by the breakpoint frequency. This is evidence of the limitation of the breakpoint frequency method, which is that it is only valid for very small defect areas of the coating or for the initial stage of coating degradation, but not to assess defect propagation to a large scale.

• The breakpoint frequency shifted to larger values with coating deterioration. Visual corrosion attack occurred when the breakpoint frequency reached values higher than $10^2$ Hz.

• $Z_{0.01Hz}$ was also used to evaluate coatings, and it decreased with coating degradation. It has the opposite response to the breakpoint frequency. The higher breakpoint frequency means larger electrochemically active area, corresponding to lower $Z_{0.01Hz}$ values.
• The performance rank-order of chromate primer on the surface pretreatments is adhesion promoter > Clean only ≈ TCP > NCP, which is consistent with the rank-order of scribed samples during self corrosion exposure to ASTM B117.

• TCP and CCC pretreatment passivated the substrate and increased the OCP values to -500 mV and -300 mV SCE, respectively.

8.2 Future Work

This work has provided understanding of the corrosion mechanism of the galvanic panel and presented how to use this sample design to evaluate coating systems. However, there are still some remaining questions need to be studied in the future:

• Noble fasteners cause the worst corrosion attack at the adjacent scribed area, but less corrosion at the scribed area far from the fasteners due to the ohmic potential drop. However, this dissertation does not quantify the ohmic potential drop changing as a function of distance away from the fastener. Scanning Kelvin Probe, as a powerful technique, can be utilized to monitor the potential in very localized areas, providing a potential mapping around the fastener. The potential mapping might indicate the higher local potential at the fastener adjacent scribe areas than the distant areas, which explains the ohmic potential drop increases with distance away from the fastener. It might also give the largest radius area of galvanic interaction from a fastener. Additionally, it is interesting to figure out how the potential mapping changes with time or with the different material type of fasteners.
• Surface pretreatments are able to improve the adhesion between the primer coating and the metal substrate. Different corrosion morphologies were observed on each individual surface pretreatment. However, this work does not provide details about how the coating adhesion affects the galvanic attack morphology at the scribed areas. Wet adhesion tests can be done on the coated galvanic panels after different exposure time. In this case, artificial defects might be not necessary.

• Electrolyte is always playing a significant role in corrosion attack. The electrolyte phase is very complex at the metal/coating surface. It penetrates to the metal substrate through the defects of coatings and accumulates at some specific sites such as pores of coatings, contamination at the metal/coating interface, or/and weak bonding areas. Additionally, it is unknown if the electrolyte moves in some preferential directions at the metal/coating interface. Corrosion attack would happen if the moving electrolyte connects the anodic sites and cathodic sites. It may be very challenging to characterize the electrolyte motion at the metal/electrolyte interface, because the high sensitive probe technique is required for such measurement.

• Artificial defects in coatings shorten the evaluation time. However, it is not the real situation of applied coating system at the early stage of service. It is more realistic to study the galvanically coated samples without any artificial defects, even though it may take very long time to detect the coating degradation. A serial EIS measurement can be conducted on such galvanically coated panels to monitor the breakpoint frequency shift. More interestingly, the incubation time before
reaching to the critical breakpoint frequency \( (10^2 \text{ Hz}) \) can be compared for the cases with and without galvanic acceleration. This comparison could also be considered as an acceleration factor.

- It is also very interesting to establish a model based on the galvanic panel design. The polarization curves of the fastener and Al panel can be considered as input data for the model to solve Laplace’s equation and then obtain the potential and current distribution on the surface of galvanic panels. The advantage of modelling is to predict the lifetime of a material or coating without preceding long time experiments.
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