# Sacrificial Anode Based Cathodic Prevention Using Mg, Al, and MgAl Metal Rich Primers Applied to AA 7075-T651:

An Assessment of Coating Performance and Substrate Protection

A Thesis

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#### **Thesis Abstract**

Age-hardenable aluminum alloys are vital to aerospace applications due to their high specific strength; as such, their corrosion resistance is critical to ensuring long-term sustainable use. To date, the aerospace industry has focused on legacy Al-Mg, Al-Cu-Mg, and Al-Zn-Mg-Cu alloys. These alloys are often prone to intergranular corrosion (IGC) as a result of their alloying composition, aging process, and environmental conditions. It is well established that individual microstructural features, such as constituent particles and precipitates, establish local anodes and cathodes that lead to micro-galvanic corrosion. Aerospace aluminum alloys are prone to exposure to coastal and marine environments increasing IG/IG-SCC susceptibility. The challenge is to mitigate this degradation process by imposing sacrificial cathode prevention (SCP). SCP is a strategy which involves creating a new galvanic couple below the electrode potential of the susceptible metallurgical phases.

Metal rich primers (MRP) are a class of active corrosion protection coatings containing sacrificial metallic pigments that are more electrochemically active than the underlying substrate. They inhibit the corrosion of the substrate by providing sacrificial anode based cathodic protection. Metal rich primers provide corrosion protection in three ways, galvanic protection, chemical inhibition, and barrier effect. Various accelerated laboratory tests and electrochemical methods have been employed to assess the corrosion performance of metal rich coatings, such as corrosion potential measurements, electrochemical impedance spectroscopy (EIS), galvanic corrosion, full immersion testing, hydrogen evolution testing, polarizability testing, ASTM B117 accelerated exposure testing, and high-fidelity testing in the form of scanning vibrating electrode technique (SVET) testing. Historically, the indoor laboratory accelerated cabinet style corrosion tests, in the form of ASTM B117, have been utilized to characterize the corrosion performance of age-hardenable Al alloys in various environments over a wide range of exposure times.

The objective of the proposed work is twofold. The mechanisms of substrate protection were elucidated and efforts were made to develop an assessment methodology for evaluating the corrosion protection performance and environmental cracking mitigation of MgRP, AlRP, and a composite MgAlRP applied to AA7075-T651. The degree of protection was quantified by interrogating corrosion potential suppression as well as reduced galvanically coupled potential afforded by the MRP relative to the electrode potential of susceptible grain boundary phases such

as MgZn<sub>2</sub>. Characterization of corrosion products formed during electrochemical testing and accelerated environmental testing was conducted with X-ray diffraction (XRD) and Raman spectroscopy in plan-view. In conjunction, backscatter electron imaging (BSI) and elemental distribution maps using energy dispersive spectroscopy (EDS) were used to visualize the progression of damage through the coating cross-section indicated by various markers such as oxidation in the coating and corrosion product penetration into the substrate. Suppression was directly assessed by comparing pigmented coatings to unprotected substrate. In addition, the evaluation of corrosion performance in MRP coatings was not confined to a single electrochemical test but rather a suite of electrochemical testing was needed to evaluate the intricate and elusive aspects pertaining to corrosion performance in MRP coatings. For instance, insight into the mechanisms of corrosion protection and coating performance was made possible with in situ pH measurements collected during galvanic couple testing and the use of chemical stability modeling. This showed that the multiple pigment chemistries available in the composite MgAlRP coating give rise pH changes during dissolution at the reacting electrode interface which shift the stability of species away from the formation of corrosion products and into a region of stable Mg<sup>2+</sup> and Al<sup>3+</sup> allowing for additional pathways for coating utilization via the activation of Al-5wt%Zn pigment resulting in enhanced corrosion performance. This performance was not noticed in the MgRP as the coating was comprised of a single pigment chemistry, pure Mg, which is susceptible to rapid dissolution limiting the duration of protection offered to the AA 7075-T651. The Al pigment in the MgAlRP was chemically identical to the Al pigment within the AIRP which was determined to be ineffective in providing sacrificial anode based cathodic protection and operated as a cathode opposite to the intended galvanic coupling with AA 7075-T651. This showed a significant departure from conventional testing which predominantly relies on accelerated environmental testing in the form of ASTM B117. This alone was not capable of discerning between the capacity of to which an MRP coating was able to operate as an effective form of sacrificial anode based cathodic protection or the mechanisms of protection.

The key scientific contributions produced in this thesis showed that the composite MgAlRP outperforms both the MgRP and AlRP in terms of sacrificial anode based cathodic protection and was able to polarize AA 7075-T651 below the corrosion potential of AA 7075-T651 and the pitting potential of MgZn<sub>2</sub>, maintained anodic potentials throughout galvanic

coupling, suppressed localized corrosion on bare AA 7075-T651, provided scribe protection, and output a greater amount of charge. All of the qualities observed in the composite MgAlRP were a result of the pigment additions of Mg + Al in a single coating, which represents a major technological achievement. This gives insight into future studies and coating design criteria which may consider the alloying of pigment, integration of multiple pigment chemistries (pure or alloyed) into a single coating, and effective electrochemical analysis techniques to evaluate performance.

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Figure 5-8. SVET derived surface plots showing the distribution of normal current density  $j_z$  emerging from an intact MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-9. SVET derived surface plots showing the distribution of normal current density j<sub>z</sub> emerging from an intact MgAlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-10. SVET derived surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half AlRP coated AA7075-T651sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-11. SVET derived surface plots showing the distribution of normal current density  $J_z$  emerging from a half bare AA7075-T651 half MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

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Figure 5-S1. Surface plots showing the distribution of normal current density  $j_z$  emerging from a bare AA7075-T651 alloy sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-S2. Surface plots showing the distribution of normal current density  $j_z$  emerging from an intact AIRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-S3. Surface plots showing the distribution of normal current density  $j_z$  emerging from an intact MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-S4. Surface plots showing the distribution of normal current density  $j_z$  emerging from an intact MgAlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-S5. Surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half AlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-S6. Surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-S7. Surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half MgAlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-S8. Digital optical imaging showing the visual appearance of post 48-h full immersion in 0.6 M NaCl shown for a) AlRP:7075, b) MgRP:7075, and c) MgAlRP:7075.

Figure 5-S9. Digital optical imaging showing the visual appearance of post 48-hour full immersion in 0.6 M NaCl shown for AIRP, MgRP, and MgAIRP. Optical imaging is taken over the intact MRP, CDI, and bare AA 7075-T651 regions.

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Figure 5-S11. Scanning electron BS imaging of post 48-hour full immersion in 0.6 M NaCl over the uncoated region at the CDI for **a**) AIRP, **c**) MgRP, and **e**) MgAIRP. EDS oxygen signal is shown next to each micrograph as a marker for oxidation for **b**) AIRP:7075, **d**) MgRP:7075, and **f**) MgAIRP:7075.

Figure 5-S12. Raman spectra collected for AlRP:AA7075 samples after 48-hour immersion in quiescent 0.6 M NaCl in the intact MRP, MRP:AA7075 interface, and within the bare AA7075 region.

Figure 5-S13. Raman spectra collected for MgRP:AA7075 samples after 48-hour immersion in quiescent 0.6 M NaCl in the intact MRP, MRP:AA7075 interface, and within the bare AA7075 region.

Figure 5-S14. Raman spectra collected for MgAlRP:AA7075 samples after 48-hour immersion in quiescent 0.6 M NaCl in the intact MRP, MRP:AA7075 interface, and within the bare AA7075 region.

Fig. A-1: Cross sectional EDS analysis of the three Al- / Mg-rich primers on 5456-H116, NAMLT 65 mg/cm<sup>2</sup>, illustrating the pigment type, size, and primer thickness for each.

Fig. A-2: Graphical representation of the cycle test, illustrating coupled potential results for each metal-rich primer, the potentiostatic hold steps at the 5456-H116 OCP of -0.85  $V_{SCE}$ , as well as the OCP in between potential holds. The detailed OCP and charge from each hold on each MRP are indicated in Figures 3, 4 and 5.

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Fig. A-4: The progression of cumulative anodic charge output per cycle (Cycles A – M/S) during the PS hold stages at -0.85 V<sub>SCE</sub> of the cycle test in 0.6 M NaCl for (a) MgRP (Epoxy,26%) and (b) AlRP (Epoxy,27%). The charge density output per cycle as well as the standard deviation for all of the candidate MRPs is summarized in (c).

Fig. A-5: Metal-rich primer activation times in 0.6 M NaCl, reflecting the influence of primer resin and pigment type / PWC on the initiation and magnitude galvanic protection offered by the MRP over 24 hours at natural coupled OCP with the 5456-H116, NAMLT 65 mg/cm<sup>2</sup> substrate.

Figure A-6. Long term open circuit potential is shown in **a**) for bare 5456 and each MRP. Galvanically coupled currents and potentials of each MRP – 5456-H116 are shown in **b**) and **c**) respectively with solid lines representing 1:1 area ratio and lines with square symbols representing 15:1 area ratio. The open circuit potential of the bare 5456 was -0.85 V<sub>SCE is</sub> represented by the green dashed line in c).

Figure A-7. Cumulative galvanic protection charge density supplied to remote bare 5456 for each MRP throughout the duration of the galvanic couple exposure of 5456 to either MRP (AlRP, MgRP, Al-MgRP). The galvanic charge was calculated from integration of the coupled current density with time.

Figure A-7. Cumulative galvanic protection charge density supplied to remote bare 5456 for each MRP throughout the duration of the galvanic couple exposure of 5456 to either MRP (AlRP, MgRP, Al-MgRP). The galvanic charge was calculated from integration of the coupled current density with time.

Figure A-8. Local pH modification monitored throughout the galvanic coupling of each MRP – 5456-H116 exposure tested in 0.6M NaCl shown in **a**) over the bare 5456 and **b**) over the MRP coating. The lines with square symbols denote the 15:1 (MRP: bare 5456) area ratio while the square symbols indicate 1:1 (MRP: bare 5456) area ratios.

Fig. A-9: EIS Bode Magnitude plots showing results for cycle testing on each MRP in 0.6 M NaCl, as well as for epoxy-coated, highly sensitized 5456-H116 as reference. Impedance modulus trends observed on uncoated AA5456-H116, NAMLT 65 mg/cm<sup>2</sup> may be found elsewhere [1]. With time of exposure at -0.85 V<sub>SCE</sub>, loss of impedance typically occurs during primer activation followed by increase in impedance by corrosion product formation.

Fig. A-10: Average impedance modulus at 0.01 Hz for each MRP throughout cycle testing in 0.6 M NaCl, with standard deviations for each to demonstrate variabilities in coating performance. The epoxy coated 5456 does not contain pigment.

Fig. A-11: Cycle test EIS phase angle plots in 0.6 M NaCl for cycles A-M/S for each MRP. Trends towards negative phase angles correlate to more capacitive coating behavior, whereas more positive phase angle trends relate to resistive behavior. Phase angle trends observed on uncoated AA5456-H116, NAMLT 65 mg/cm<sup>2</sup> may be found elsewhere [1].

Figure A-12. Electrochemical impedance spectroscopy of pre and post galvanic coupling of each MRP primer in 0.6M NaCl. The lines denote pre-galvanic coupling where the lines with square symbols indicate post exposure galvanic coupling.

Fig. A-13: Scanning electron microscopy micrographs demonstrating the pristine, untested Al-Zn / Mg-rich primer cross sections, in comparison to the cross sections of these MRPs following cycle testing where pigment oxidation / corrosion product precipitation may have occurred.

Fig. A-14: Scanning electron microscopy micrographs demonstrating the pristine, untested Al-Zn / Mg-rich primer surfaces in comparison to the surfaces following cycle testing where oxidation / corrosion product precipitation may have occurred.

Fig A-15: Energy dispersive spectroscopy analysis demonstrating the deep solution penetration achieved throughout the Al-MgRP (Epoxy,28/19%) during the cycle test in 0.6 M NaCl. In (**a**) the entire elemental spectrum is illustrated, while in (**b**) Mg is selected and in (**c**) only oxygen is shown, which highlights the oxidized Mg pigments and the filiform corrosion propagating towards the center of a Mg pigment.

Fig. A-16: A chemical stability diagram for the Al/Mg system, depicting the thermodynamic conditions for Mg dissolution at an initial pH of 5.7 and  $[Mg^{2+}]$  of  $1x10^{-10}$  M. The green and blue lines indicate equilibrium concentration-pH conditions for  $Mg^{2+}/Mg(II)$  or  $Al^{3+}/Al(III)$  products indicated. The black line indicates Mg2+ trajectory. These predictions demonstrate the ability of the Mg to active the Al in Al-MgRP (Epoxy,28/19%). Chloride complexation effects are unsubstantial for this system and are not incorporated here.

#### Forward

This work must be regarded within a greater context. This research is a continuation of the research first pioneered by Andrew King in the thesis " Corrosion Protection of 2024-T351 by a Mg-Rich Primer", carried on by Balaji Kannan in the thesis " Evaluation of the Performance of a Magnesium Rich, Non-Chromated Primer With/Without Topcoat on 2024-T351: The Role of Various Substrate Pretreatments", and subsequent research by Raymond Santucci in the thesis "Magnesium and Magnesium-Oxide Primer on 2024-T351: Assessment and Characterization of Mg-Based Protection Mechanisms". I am indebted to those before me who paved the way giving me the foundation upon which to build and expand. Their dedication and insight have provided invaluable guidance, shaping the trajectory of this study. This work strives not only to advance the field but also to honor the collective effort of researchers past and present. Through collaborative endeavors and a shared commitment to excellence, we propel the boundaries of understanding forward, inch by inch, towards a brighter and more informed future.

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## Chapter 1: Introduction

### **Thesis Organization**

This project is organized around four tasks. Task 1 aims to identify critical potentials of MgZn<sub>2</sub> phase, AA 7075-T651, and MRP coated AA7075-T651 through standard benchtop techniques. Task 1 also identifies a window of protection for AA 7075-T651, potential dependence of environmentally assisted cracking, and includes baseline MRP cross-sectional BSI and EDS characterization. Task 2 aims to evaluate the corrosion performance of an Al-5wt% MRP with a suite of electrochemical testing techniques and a variety of characterization techniques. Task 3 aims to evaluate the corrosion performance of a MgRP and MgAlRP with a suite of electrochemical testing techniques and a variety of characterization techniques. The mechanistic factors contribution to the corrosion performance of each MRP will be assessed via the electrochemical evaluation conducted in Task 2 and 3 with the aid of chemical stability modeling. The goal of task 4 is to assess the ability of each MRP to suppress localized corrosion to AA 7075-T651. The critical unresolved issues in our current understanding of AlRP, MgRP, and MgAlRP, will be addressed in each task. The methodology employed to address these unresolved issues is outlined for each pertinent task.

Task 1 – On the applied potential dependence of environment-assisted cracking behavior of AA 7075-T651 in marine environments: towards informing metal-rich primer-based mitigation strategies

- Identify the potential window of protection on AA 7075-T651 and hydrogen evolution rate as a function of applied potential.
- Determine the critical potentials of MgZn<sub>2</sub> phase, AA7075-T651, and MRP coated AA7075-T651 such that E<sub>ocp, MRP</sub> < E<sub>ocp, η</sub>, E<sub>ocp, MRP</sub> < E<sub>pit, η</sub> and dependency on solution chemistry.
- Inform MRP corrosion mitigation strategies in the ability to provide protection again environmentally assisted cracking of AA 7075-T651.

Task 2 – Electrochemical Evaluation of Al-5 wt% Zn Metal Rich Primer for Protection of Al-Zn-Mg-Cu Alloy in NaCl

- Evaluate MRP anode based cathodic protection and persistency using suite of diagnostic electrochemical testing methods.
- Explore the evolution of coating-substrate interface oxidation over intact and scribed panels for each MRP coating applied to AA7075-T651 with ASTM B117 testing compared to bare control panels.
- Compare lab high fidelity diagnostic tests to accelerated life testing to ascertain which high fidelity test in the available suite correlates best with B-117 results.

Task 3 – Electrochemical Evaluation of Mg and a Mg-Al 5%Zn Metal Rich Primers for Protection of Al-Zn-Mg-Cu Alloy in NaCl

- Explore the evolution of coating-substrate interface oxidation over intact and scribed panels for each MRP coating applied to AA7075-T651 with ASTM B117 testing compared to bare control panels.
- Determine the role of pH, [Cl<sup>-</sup>], [Mg<sup>2+</sup>] on the electrochemical kinetics of MgZn<sub>2</sub> and AA 7075-T651.
- Compare lab high fidelity diagnostic tests to accelerated life testing to ascertain which high fidelity test in the available suite correlates best with B-117 results.
- Investigate the galvanic corrosion behavior and pH modification of solution as a result of dissolution processes at each MRP electrode interface.

Task 4 – Spatially Resolved Assessment and Analysis of Al-Zn, Mg, and Mg/Al-Zn Metal Rich Primers applied to AA 7075-T651 in Full Immersion

- Assess the spatial potential and current distribution over uncoated AA 7075-T651.
- Determine the ability of each intact MRP coating to operate as a sacrificial anode based cathodic protection.

- Evaluate the reduction in peak anodic current density over a region of bare AA 7075-T651 that is partially protected by each MRP coating systems.
- Compare the electrochemical behavior and characterize the corrosion products formed within the defect region before and after full immersion exposure.

Appendix – Extra Dissertational Work

Mechanistic Insight into Al-Zn, Mg, and Al-Mg Rich Primer Design for Enhanced Cathodic Prevention on Sensitized Al-Mg Alloys

### Motivation

Aluminum alloy 7075-T651 (Table 1-1) is a peak-aged Al-Cu-Mg-Zn alloy which derives its metallurgical strength in part from precipitation hardening, due to intermetallic precipitates, which results in a high specific strength desirable for commercial and military aerospace applications <sup>1–</sup> <sup>3</sup>. The main alloying elements present in AA7075 are zinc (5.1-6.1wt%), magnesium (2.1-2.9wt%), and copper (1.2-2.0wt%). Zinc is commonly used in aluminum alloys for its heat treatability and provides the basis by which necessary strengthening phases form. Magnesium is present to provide solid-solution strengthening, work hardening and is necessary for the formation of strengthening phases <sup>4,5</sup>. The aluminum-magnesium phase diagram exhibits a positive sloping solvus necessary for precipitation strengthening systems <sup>6</sup>. The 7XXX-series aluminum alloys containing copper have the highest strength and increased resistance to stress corrosion cracking (SCC); however, these alloys display reduced resistance to general corrosion <sup>5,7</sup>. The presence of Cu in grain boundary precipitates (GBP), which is controlled through the aging process especially during overaging, correlates with a lower electrochemical activity, and lowers the hydrogen generation rate resulting in improved SCC resistance <sup>5,8,9</sup>. The formation of metastable and stable precipitate phases occurs through decomposition of the solid solution during aging <sup>4,5,8</sup>. The Gunier-Preston (GP) zones and meta-stable MgZn<sub>2</sub> ( $\eta'$ ) phases formed during aging are believed to be responsible for the peak hardening effect in Al-Zn-Mg-Cu alloys <sup>5,8</sup>. Copper enrichment within the  $\eta$  and  $\eta'$ phases present at peak aging (T6) shows that Cu stabilizes metastable phases in 7XXX-series

aluminum alloys <sup>8,10</sup>. Over-aging (T7) has been shown to increase resistance to environmentally assisted cracking (EAC) in 7XXX-series aluminum alloys with greater Cu content attributed to the coarsening and increased discontinuity of GBP's <sup>8</sup>. Increasing the extent of over-aging can provide some improvement to SCC in the T73 or to exfoliation corrosion in the T76 condition. A common method of reducing the level of internal residual stress is to provide stress relief by stretching as is the case in temper T651 with 1 to 3% stress relief by stretching <sup>11</sup>. The micro-structural differences among the T6, T73 and T76 tempers of these alloys are variations in size and type of precipitate, which changes from predominantly Guinier-Preston (GP) zones in T6 tempers to  $\eta'$ , the metastable transition form of  $\eta$  (MgZn<sub>2</sub>) in T73 and T76 tempers<sup>12,13</sup>. For 7xxx-T6 peak aged condition, the  $\eta'$  phase is the main precipitate and for the over-aged temper (T7x), the  $\eta$  phase is the main precipitate<sup>4,5,8,10</sup>.

The formation of the MgZn<sub>2</sub> ( $\eta$ ) precipitates in the matrix contributes to strengthening. The MgZn<sub>2</sub> also precipitates at the grain boundary (GB) causing precipitate free zones (PFZ) adjacent to the GB which do not contribute to the overall yield strength of the alloy<sup>14–18</sup>. These PFZs are deleterious towards mechanical and corrosion performance<sup>19</sup>. There are, in general, many phases present in AA 7075-T651 from constituent particles, dispersoids, and precipitates that are populated across various length scales. Constituent particles include the following chemistries: Al<sub>12</sub>(Fe,Mn)<sub>3</sub>Si, Al<sub>6</sub>(Fe,Mn), Mg<sub>2</sub>Si and Al<sub>7</sub>Cu<sub>2</sub>Fe. These particles are generally of the order 1 – 10  $\mu m$  and contribute toward improving the toughness and ductility of aluminum alloys<sup>5,20</sup>. Dispersoids, generally of the order 0.05-0.5  $\mu m$  such as Al<sub>12</sub>Mg<sub>2</sub>Crm, are present from the melt and contribute to microstructural control<sup>5,20</sup>.

The precipitates present in AA 7075, such as MgZn<sub>2</sub> and Al<sub>2</sub>CuMg, can be present in a range of sizes from *nm to*  $\mu$ *m* with the Al-Zn-Mg-Cu system, providing the basis for precipitation strengthening<sup>5,20</sup>. These precipitates can form during heat treatment occurring in the bulk via homogeneous nucleation, or can heterogeneously nucleate on grain boundaries. The precipitates contribute towards strengthening the alloy via precipitation hardening. Solution treatment and aging are used to modify the distribution and size of the intermetallic precipitates<sup>21</sup>. All precipitates and particles that have different chemistry, and electrochemical potential, then that of the surrounding Al matrix while sharing electrical continuity allows for the formation of a microgalvanic couple<sup>20,22</sup>. The potential difference between the intermetallic precipitates such as MgZn<sub>2</sub> and the surrounding Al matrix promote micro galvanic corrosion where phases which are considerably more active in the electromotive series than the Al-rich matrix corrode selectively  $^{10,23,24}$ . Intermetallic precipitates (IMP) of concern to corrosion performance include  $\eta$  phase, MgZn<sub>2</sub>, primarily those heterogeneously nucleated on GB. The selective dissolution of precipitates residing on GBs generates hydrogen which increases susceptibility to stress corrosion cracking (SCC) and intergranular stress corrosion cracking (IGC-SCC)  $^{25-29}$ .

The environmentally assisted cracking (EAC) of Al-Zn-Mg-Cu alloys in aqueous environments, including water vapor, has been heavily studied with many proposed models investigating the origins of the SCC mechanism <sup>9,30–34</sup>. Crack initiation or incubation is largely thought to be dominated by anodic dissolution of bare Al, which in turn forms critical defects such as pits <sup>32,35,36</sup>. In the presence of an electrolyte, the constituents, dispersoids, and precipitates mentioned all meet the prerequisite conditions necessary to form micro-galvanic couples with the surrounding aluminum matrix each of which has different composition and electrochemical potential. The corrosion potential of each phase depends upon the Nernst potential of each phase, composition of each phase (which can change during exposure), and electrolyte chemistry (pH and metal ion concentration).

The constituent particles are subdivided into two categories: 1) particles such as Al, Mg, and Zn, which are anodic with respect to the matrix; and 2) particles behaving as cathodic with respect to the matrix and that tend to promote corrosion or disintegration of the adjoining matrix, such as Fe, Cu and Mn <sup>5</sup>. The presence of these two distinctly categorized constituent particles tends to cause galvanic effects, resulting in the development of corrosion pits at these particle interfaces. Once corrosion pits are formed, they act as sites for stress concentration, leading to stress corrosion cracking failure <sup>37</sup>. The precipitate particles such as MgZn<sub>2</sub> act as anodes to the cathodic aluminum matrix<sup>20</sup>. This continuous precipitate at the grain boundaries act as anodic tunnels of intergranular corrosion and enhance the SCC rate of the alloy by accelerating the hydrogen transportation which further embrittles the grain boundaries <sup>4,27,28,30</sup>. In 7xxx Al series, the SCC mechanism involves repeated sequences of 1) generation of hydrogen at crack tips; 2) diffusion of hydrogen ahead of crack tips; 3) "brittle" fractures when a critical hydrogen concentration is reached over a critical distance<sup>29,37</sup>. The conditions of each micro-galvanic couple are a telling sign of how each intermetallic particle (IMP) interacts with the surrounding alloy. These micro-galvanic coupling

conditions may enhance localized anodic dissolution and increase surface defects present during initiation/incubation. This can be reduced by cathodically preventing localized anodic particles within AA7075 by suppressing the OCP below the  $E_{pit, particle}$  serving to minimizing the potential difference between the anodic particle and cathodic matrix.

The stage II crack propagation of Al-Zn-Mg-Cu alloys in aqueous environments is dominated by hydrogen environment assisted cracking (HEAC), in which the reaction of aluminum with water vapor produces a high fugacity hydrogen gas responsible for controlling EAC via hydrogen embrittlement (HE) <sup>9,28,30</sup>. Hydrogen generation may take the form of a two-electron step and form hydrogen gas directly or by single electron transfer to produce atomic hydrogen which may recombine to form hydrogen gas or be absorbed into the metal <sup>30</sup>. It is the production of atomic hydrogen by single electron transfer that makes water vapor an aggressive environment for Al-Zn-Mg-Cu alloys <sup>30</sup>. It has been reported that the presence of Mg along the grain boundaries has a larger electronegativity difference between Mg and H atoms than between Al and H atoms providing a larger affinity for hydrogen adsorption Mg bearing GBP. This leads to grain boundary embrittlement and accelerates the propagation of SCC<sup>28,30,32,38</sup>.

Aerospace aluminum alloys are in frequent exposure to marine environments containing chloride, a particularly aggressive ion known to induce and exacerbate pitting of micro-galvanic couples and oxide breakdown. These phases are connected by an electrolyte; thus, a galvanic cell will be formed between the intermetallic phase and the surrounding Al matrix. Anodic reactions (such as Mg/Zn dissolution) are enhanced on the more active phase ( $\eta$  in this example) and cathodic reactions (such as the Hydrogen Evolution Reaction, or HER) are enhanced on the more cathodic phase Al matrix but also occurs at anodes. The rapid dissolution and self-corrosion of Mg is a result of the high electrochemical activity of the MgZn<sub>2</sub> precipitate <sup>24,39,40</sup>. This corrosion damage (grain boundary attack, pitting, trenching, etc.) is detrimental to the aluminum alloy's structural integrity, as damaged regions can act as crack initiation sites which propagate to mechanical failure under cyclic loading<sup>41,42</sup>. This corrosion-induced damage can be prevented by a coating system which incorporate active corrosion protection to mitigate corrosion processes such as micro-galvanic couples or fissures for crack/pit formation. These coating systems serve to stop galvanic corrosion in the alloy by suppressing potential beneath critical breakdown potentials and release cations into solution that are available to hydrolyze and re-deposit onto an uncoated

surface to provide enhanced protection. This is a delicate balance, as overly cathodic polarization results in localized cathodic corrosion occurring on or around the surrounding constituent particles, and issues regarding hydrogen production may arise due to the activity of the pigment used.

Active corrosion protection in the form of coatings such as metal rich primers (MRP) are commonly employed, and work by disrupting electrolyte contact with the substrate through the presence of a coating layer. These coating systems are created to afford the underlying substrate protection in the form of galvanic protection, chemical inhibition, and secondary barrier properties. The performance of a coating is undermined by the presence of coating defects such as pores formed upon application and the development of scratches formed from abrasive impact, cracks formed under stress, or degradation under ultraviolet radiation exposure during service. Such coating defects decrease the barrier properties of the coating and lead to electrolyte ingress to the exposed substrate which initiates corrosion<sup>43,44</sup>. Active protection is required to protect the underlying substrate where barrier protection is insufficient, and at macro-defects such as within a scratch. Traditional methods of active protection of aerospace aluminum alloys have involved the use of chromium-based primer. These chromate conversion coatings (CCC) operate by releasing a corrosion inhibiting chromate ion which impedes cathodic/anodic reactions on the exposed substrate and its micro-galvanic couples and forms a chromate barrier film which prevents corrosion<sup>45-47</sup>.

However, hexavalent chromium is well-known for its toxicity and carcinogenicity. The use of hexavalent chromium-based technologies is mandated to be phased out of use in preference to safe and reliable alternative active corrosion protection methods<sup>48–51</sup>. Alternative pigments such as Mg and Al pigmented coatings have shown promise as reliable alternatives for the replacement of hexavalent Cr-based coatings<sup>52–54</sup>.

#### Background

Metal rich primer (MRP) coatings have been developed for the active protection of aerospace aluminum alloys <sup>14,55–63</sup>. Their cathodic protection scheme has proven to be an effective strategy for protection of structural engineering materials<sup>64–69</sup>. Mg has been chosen as a sacrificial anode whereby electrochemical dissolution of Mg within the coating suppresses the dissolution of

secondary phases present in the precipitation aged hardened alloy and is responsible for galvanically coupling below their corrosion potentials. This greatly reduces the oxidation of the substrate caused by the presence of micro-galvanic couples. The challenge in protecting Mg-Zn compounds is providing a sufficient cathodic shift in potential to suppress the active dissolution; in the case of MgZn<sub>2</sub>,this occurs at potentials more positive than  $E_{corr}$  (-1.1 V<sub>SCE</sub>)<sup>23</sup>.

There are many techniques that have proven effective in testing MRP electrochemical performance of MRP coatings. Electrochemical impedance spectroscopy allows for the determination of the state of barrier properties afforded to a given MRP coating in the form of insoluble precipitated corrosion products or multiple coating layers<sup>70–74</sup>.

The high electrochemical activity according to the electromotive series establishes an optimal relationship between the galvanic coupling of Mg-pigment with an aluminum substrate as the corrosion potential of Mg is well below the open circuit potential of AA7075 matrix and its strengthening GB precipitate. This develops a galvanic coupling relationship in which the coating is operating as a sacrificial anode permitting Mg oxidation to occur and maintaining a cathodic aluminum substrate. This is an effective strategy to suppress the dissolution of otherwise susceptible phases by maintaining a potential below critical threshold potentials required for localized corrosion damage to occur, such as  $E_{pit}$  and  $E_{IGC}$  (the threshold potentials for stable pitting and preferential attack of sensitized grain boundaries, respectively). In order for an MRP coating to operate as intended, it must be electrically and ionically connected to the AA7075-T651 substrate.

Companion work conducted on sensitized AA5456-H116 revealed that  $\beta$  phase, Al<sub>3</sub>Mg<sub>2</sub>, also renders the alloy susceptible to IGC-SCC attack at the GB's<sup>61</sup>. The mitigation of IG-SCC is hypothesized to be caused by the lowering of the crack tip potential below the critical pitting potentials to suppress the  $\beta$  phase as well as matrix breakdown which inhibits the development of an aggressive crack tip chemistry thus restricting the generation of hydrogen and subsequent embrittlement<sup>9,58,60,61</sup>. To this end, a zinc rich primer (ZnRP) was able to suppress IG-SCC of AA5456 in 0.6 M NaCl solution by providing suppression below  $E_{pit,\alpha}$  (-0.72 V<sub>SCE</sub>) and  $E_{pit,\beta}$  (-0.92 V<sub>SCE</sub>)<sup>59,61</sup>. The variation in the level of mitigation observed in various bulk environments was found to scale with the corresponding changes in critical breakdown potentials for the matrix and  $\beta$  phase in closely correlated environments<sup>58</sup>.

The susceptibility for IG-SCC is similar in AA7075-T651 with MgZn<sub>2</sub> as the detrimental phase; however, this poses greater issues as  $E_{OCP,\eta} = -1.1 V_{SCE}$ ,  $E_{OCP,7075} = -0.75 V_{SCE}$ , and  $E_{pit,\eta} = -0.85 V_{SCE}$ . There is a potential dependence on the cracking behavior identified for AA 7075; however, it does not show as potent of a reduction in cracking behavior as AA5456-H116 does <sup>31,75</sup>. This poses a greater challenge to protecting AA 7075 from the deleterious effects of IG-SCC.

An MRP system consists of an epoxy-based primer with embedded metallic pigment applied over bare AA7075-T651. The pigments considered are a spherical Al alloyed with 5wt% Zn (AlRP), a flaked Mg (MgRP), and a composite spherical Mg + spherical Al-5wt%Zn (MgAlRP). The primary purpose of assessing the corrosion performance of the MRPs is to better understand whether candidate coating systems are capable of providing IGC suppression to AA 7075-T651. In addition, a comparison of the electrochemical behavior between the MRP coatings and AA 7075-T651 substrate without the effects of pretreatments and topcoats can be made.

There have been studies conducted on fresh MRP coatings to assess the extent and longevity of galvanic coupling through a variety of standardized laboratory testing procedures and laboratory accelerated life testing (LALT) such as ASTM B117<sup>37,76</sup>. In order for a Mg<sup>2+</sup>-based protection mechanism to be effective, it must be viable both over the intact coating and also within a remote coating defect which exposes the AA7075-T651 substrate.

## **Knowledge Gap and Challenges**

- There are challenges of developing new testing methods that are aimed at assessing the efficacy of the newly proposed composite coating system.
- There has been little research addressing the application and performance of MRP coating systems on AA 7075-T651. The majority of research regarding MRP coatings have been conducted on AA 2024-T351 and AA 5456-H116.
- Do candidate MRP coatings provide adequate protection and IG-SCC suppression to AA 7075-T651 as they have been shown for 2xxx and 5xxx aluminum alloys.
- Do the candidate MRP coatings provide adequate protection under static corrosion condition to AA 7075-T651 as they have been shown for 2xxx and 5xxx aluminum alloys.
- The heterogeneous composition of AA 7075-T651 with many constituent phases and precipitates impacts the cathodic protection of the substrate and ability to suppress localized corrosion.
- The mechanistic factors contributing to the performance of composite coating systems which contain multiple pigment chemistries.

Legacy testing methods may not be sufficient to extrapolate the requisite knowledge required to determine if the advanced coating system are protective as detection of scribe protection does not inform us the mechanism responsible. While there have been studies performed on isolated pigment systems applied to 2xxx and 5xxx aluminum alloys [31,48-51,63-66,68], there are no studies conducted on AA 7075 nor do they explain the unique behavior observed for their composite coating system counterparts. It is necessary to determine how the Mg<sup>2+</sup> protection differs from MgRP to MgAIRP to better understand the influences on corrosion prevention and pigment choice. Improved understanding of pigment dissolution, active protection mechanisms, and solution chemistry dependence will inform the electrolytes used in testing to better replicate the actual service conditions observed in the field and their effects. A continuing challenge faced by corrosion engineers is the design of accelerated testing protocol which reliably mimics the results obtained from field testing in a fraction of the time.

A technological challenge of this work is to develop reliable alternatives to chromate conversion coatings for the protection of AA 7075-T651. While MgRP have been shown to be effective there are differences in performance of hybrid coating systems that contain multiple pigment chemistries including Mg pigment. There are challenges in developing assessment methods to evaluate the differences in protection afforded by single pigment and composite coating containing multiple pigment chemistries as well as metrics by which comparisons can be made. Once developed, these test methods can be used to screen both single pigment and composite coating systems for desirable sacrificial anode based cathodic protection attributes which enhance corrosion performance.

# **Overall Objective**

The aim of this investigation is to first assess the electrochemical behavior and susceptibilities of AA 7075-T651 and critical intermetallic phases present in varying solution chemistries that are present in field. This will shed light on the critical potential windows in which AA 7075-T651 will become susceptible to IGC/IG-SCC due to selective electrochemical dissolution of active phases. The primary objective of the proposed study is then to understand whether AlRP, MgRP, and MgAlRP are capable of providing cathodic protection or some other means of chemical protection such that susceptible phases are protected. The corrosion performance afforded to each primer will determine the galvanic protection, chemical inhibition, and barrier effects present. A suite of testing will be used in the assessment of corrosion performance as no single test will elucidate all requisite information. Standard benchtop testing in the form of OCP, potentiostatic polarization, and EIS is used to monitor the electrochemical behavior and barrier properties of each MRP coating. More advanced forms of electrochemical testing in the form of OCP/AC/DC cycle testing can be used to investigate an MRP's available charge capacity, barrier properties, and cathodic protection potential. The polarizability of each MRP coating is investigated using galvanostatic cycle testing to assess the ability of each MRP to provide IGC/IG-SCC mitigation under the demanding conditions of crack advance. ASTM B-1117 salt spray exposure testing is used to visualize the evolution of corrosion and the ability of each MRP to provide scribe and under-paint protection.

Comparisons between testing method will be made to contrast results obtained under freecorrosion conditions from imposed potential control. The assessment of the galvanic couple cathodic protection available to each fresh MRP as well as throughout laboratory accelerated life testing and primer depletion is necessary to understand how MRP corrosion prevention varies at long lifetimes. This body of work also aims to understand the effect of the composite primer system and the mechanisms available for protection. Results from the proposed study will further inform the advance and technological development of reliable coating for the protection of AA7075-T651. This research will have broader implications through an increase in the general understanding of the attributes of primers and how they could be tailored to a specific alloy.

# Hypothesis

The differences in electrochemical behavior of the composite MgAIRP have favorable performance as a protective coating for AA 7075-T651 compared to the MgRP and AIRP, it is hypothesized here that the composite coating contains additional utilization pathways due to the dual pigment nature of the composite MgAIRP that are not present in the case of MgRP or AIRP. Since the utilization of MgAIRP results in greater anodic charge output than the MgRP with comparable quantity of Mg pigment there must be additional mechanisms available to the MgAIRP not found in the MgRP. The dissolution of Mg to Mg<sup>2+</sup> and subsequent alkalization of solution activates the corrosion of AI-5wt%Zn pigment in the MgAIRP, not present in the MgRP, as AI is amphoteric and susceptible to corrosion opening an additional avenue for utilization in the MgAIRP. It is hypothesized that this basic shift in pH in the MgAIRP stabilizes both Mg<sup>2+</sup> and Al<sup>3+</sup> giving rise to enhanced performance. The combination of measurements during pH monitoring over the MRP interface throughout galvanic corrosion testing and predications from chemical stability diagram analysis will inform the relative stability of corrosion products and their respective cation species.

# Approach

Initially, global electrochemical measurement of AA 7075-T651, MgZn<sub>2</sub>, and commercially pure Al, Zn, and Mg will be made to assess critical electrochemical parameters such as the open circuit potential and pitting potential across a range of cation concentrations. This testing allows for the development of prevention criteria in which mitigation to IGC can be posited. Evaluation of the changes in the developed cathodic prevention criteria will be made by considering a range of electrolyte solutions from  $[10^{-3} - 10^{0}]$  molar concentration of  $[Mg^{2+}]$  and  $[Cl^{-}]$  with pH ranging from acidic (pH 3), near neutral (unadjusted, UA (pH 5.8)), to basic conditions (pH 9, 10, 11). The impact on the electrochemical kinetics will be observed by comparing the influence of each cation species to standard 0.6 M NaCl solution. Testing will include the assessment of electrochemical behavior of Al-5wt% Zn found within AlRP and MgAlRP. The electrochemical factor contributing to the applied potential dependence of environmentally assisted cracking AA 7075-T651 will be evaluated by various potentiostatic potential hold while capturing the evolved hydrogen gas produced. This analysis in combination with assessing varying electrochemical kinetics due to pH changes, which arise during hydrogen evolution, will inform mechanism responsible for susceptibility of AA 7075-T651 to stress corrosion cracking.

A series of diagnostic coating testing will be performed to evaluate the corrosion performance of each MRP. The approach will consist of a set of cyclic OCP/AC/DC laboratory testing and accelerated laboratory exposure testing in the form of ASTM B117. Cyclic OCP/AC/DC laboratory testing is used as a method by which each MRP coating is evaluated for its ability to discharge anodic current under an imposed potential which is deemed to be protective an minimize susceptibility to IGC, maintain coupled potential bellow the corrosion potential of AA 7075-T651, and monitor barrier properties. Accelerated environment exposure testing will compare the corrosion products formed over the intact and scribed region of each MRP coating through both plan-view and cross-sectional view to show the progression of corrosion. Comparisons are drawn from the observed oxidation through the cross-section view of each MRP for both methodologies of testing.

The galvanic corrosion behavior of a two electrode MRP coated AA 7075-T651 coupled to bare AA 7075-T651 array will be tested using a ZRA array outfitted with pH probes to quantify solution changes over each reacting electrode. The altered solution chemistry as a result of dissolution processes at the MRP coated AA 7075-T651 electrode will impact the electrochemical kinetics and stability of corrosion products formed. The MRP coated AA 7075-T651 corrosion products will be characterized with the use of XRD and Raman spectroscopy as well as SEM BSI cross-sections with EDS elemental maps.

In order to semi-quantitatively assess the spatial potential and current distribution, reduction in peak anodic current density over a region of bare AA 7075-T651 that is partially protected by three MRP coating systems (AIRP, MgRP, and MgAIRP), and the mechanisms of protection for each coating by utilizing SVET. The SVET will be used on the rectangular electrode with an intact coating and bare area to ascertain the ability of each MRP to provide cathodic protection. The freely corroding SVET samples will be characterized with Raman spectroscopy to analyze any corrosion products that may be formed on each half MRP coated electrode as well as SEM BSI plan-view and cross-sections with EDS elemental map profiles. The SVET testing should include monitoring both defect and intact MRP to observe the spatial distribution of current between MRP coated AA7075 and bare AA7075 as well as any localized corrosion events occurring on the electrode surface. The ability to suppress peak anodic current densities associated with localized corrosion in the form of pitting define a new conceptualization of providing sacrificial anode based cathodic protection to a substrate as opposed to the notion of throwing power where the entirety of the substrate is cathodically suppressed. This becomes increasingly unlikely as local compositional heterogeneity promotes localized dissolution due to the micro galvanic couples formed.

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# Tables, Chapter 1: Introduction

Table 1-1. AA 7075-T651 nominal	composition.
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AA7075-T651		
Element	Wt. %	
AI	Bal.	
Zn	5.1-6.1	
Cu	1.2-2.0	
Mg	2.1-2.9	
Fe	0.5	
Si	0.4	
Cr	0.18-0.28	
Ti	0.2	

Chapter 2 Task 1 – On the applied potential dependence of environment-assisted cracking behavior of AA 7075-T651 in marine environments: towards informing metal-rich primer-based mitigation strategies

Alen Korjenic, Zachary D. Harris, James T. Burns, John R. Scully

# Abstract

Metal-rich primers (MRPs) have been shown to effectively attenuate the environment-assisted cracking (EAC) susceptibility of 5xxx-series Al alloys exposed to marine environments, suggesting that such galvanic protection schemes may be suitable for use on 7xxx-series Al alloys. A detailed understanding of the relationship between EAC susceptibility and the applied electrochemical potential is needed to design effective MRPs, but such relationships are not wellunderstood in 7xxx-series Al alloys. Hydrogen evolution experiments were performed on AA7075-T651 in quiescent hydrogen charge 0.6 M NaCl solution at applied potentials -1.3 to -0.6 V vs Saturated Calomel Electrode (V<sub>SCE</sub>). These experiments quantified the amount of hydrogen evolved from the surface of AA7075-T651 throughout a six-hour duration at each potential hold. Corrosion morphology at each applied potential were characterized throughout cross-section characterization via back scatter imaging (BSI). Potentiodynamic polarization (PDP) and open circuit potential (OCP) monitoring of AA7075-T651 and MgZn<sub>2</sub> in quiescent 0.6 M NaCl at pH 3, unadjusted (UA, pH 5.8), 9, 10, 11 were conducted to evaluate corrosion characteristic in a range of conditions relevant to solution chemistries that occur at crack tips. Fracture mechanics experiments were performed on AA7075-T651 in 0.6 M NaCl at applied potentials ranging from -1.3 to -0.75 V<sub>SCE</sub> and fixed loading rates (dK/dt) ranging from 0 to 2.0 MPa√m/hr. A small potential window of reduced susceptibility is observed in AA7075-T651, but crack growth kinetics remain sufficiently severe such that MRPs are unlikely to prevent EAC.

### Introduction

Aluminum alloy (AA) 7075-T651 (**Table 1**) is a peak-aged Al-Cu-Mg-Zn alloy which derives its metallurgical strength in part from precipitation hardening which results in a high specific strength desirable for commercial and military aerospace applications<sup>1–3</sup>. These alloys derive their

high strength from the alloying elements and heat treatments conditions which result in the precipitation of intermetallic particles; however, this process is also responsible for the increased susceptibility to intergranular corrosion (IGC) and intergranular stress corrosion cracking (IG-SCC)<sup>4–7</sup>. The aging of 7xxx-series aluminum alloys results in the formation of the homogeneously nucleated MgZn<sub>2</sub>( $\eta$  phase) precipitates in the matrix contributes to strengthening. The MgZn<sub>2</sub> also precipitates heterogeneously during artificial or natural aging at the grain boundary (GB) causing precipitate free zones (PFZ) adjacent to the GB which do not contribute to the overall yield strength of the alloy <sup>3,8–10</sup>. These PFZs are deleterious towards mechanical and corrosion performance <sup>3</sup>. These alloys have experienced in-service stress corrosion cracking (SCC) and intergranular stress corrosion cracking (IG-SCC) due to the degradation of the heterogeneously nucleated precipitate phase  $\eta$  phase. The  $\eta$  phase dissolves preferentially to the matrix and rapidly corrodes in aggressive (e.g. aqueous chloride) environments, enabling severe IGC and intergranular stress corrosion cracking (IG-SCC) under sufficient applied load <sup>7,8,11</sup>. These aluminum alloys (AA) are in frequent exposure to marine environments in which chloride is abundant and serves to accelerate corrosion. The enhanced localized corrosion susceptibility of AA 7075-T651 is due to its heterogeneous microstructure and a wide range of constituent particles and precipitates introducing local chemical inhomogeneity and enhanced localized breakdown in the form of matrix-phase boundary attack <sup>11-</sup> <sup>14</sup>, selective dissolution  $^{17-21}$ , and pitting  $^{12,14,22-25}$ .

The main alloying elements present in AA 7075 are zinc (5.1-6.1 wt%), magnesium (2.1-2.9 wt%), and copper (1.2-2.0 wt%). Zinc is commonly used in aluminum alloys for its heat treatability and provides the basis by which necessary strengthening phases form <sup>3,26</sup>. Magnesium is present to provide solid-solution strengthening, work hardening and is necessary for the formation of strengthening phases <sup>3,26</sup>. The aluminum-magnesium phase diagram exhibits a positive sloping solvus necessary for precipitation strengthening systems <sup>3,27</sup>. The 7XXX-series aluminum alloys containing copper have the highest strength and increased resistance to stress corrosion cracking (SCC); however, these alloys display reduced resistance to general corrosion<sup>9,28</sup>. The presence of Cu in grain boundary precipitates (GBP), which is controlled through the aging process especially during over-aging (T7x), correlates with a lower electrochemical activity, and reduces the hydrogen generation rate resulting in improved SCC resistance<sup>7,9</sup>. The precipitates formed during the aging process is a function of the alloying constituents in 7xxx-series aluminum alloys. Increases in the alloying content of Cu promote the formation of CuAl<sub>2</sub> (θ phase). However, when

the Cu content is lower the phase composition is mainly affected by the Zn/Mg ratio<sup>7,29</sup>. In the case of near equal Zn/Mg ratio the phase present are composed of Al matrix ( $\alpha$  phase), Al<sub>2</sub>CuMg (S phase), and Al<sub>2</sub>Mg<sub>2</sub>Zn<sub>3</sub> (T phase). In the case of AA 7075 with an increased Zn/Mg ratio and the formation of  $\eta$  phase begins to appear and is present along with S phase and T phase.

There are many phases present in AA 7075-T651 from constituent particles, dispersoids, and precipitates that are populated across various length scales. Constituent particles include the following chemistries: Al<sub>12</sub>(Fe,Mn)<sub>3</sub>Si, Al<sub>6</sub>(Fe,Mn), Mg<sub>2</sub>Si and Al<sub>7</sub>Cu<sub>2</sub>Fe. These particles are generally of the order  $1 - 10 \,\mu m$  and contribute toward improving the toughness and ductility of aluminum alloys <sup>3,26</sup>. Dispersoids, generally of the order 0.05-0.5  $\mu m$  such as Al<sub>18</sub>Mg<sub>2</sub>Cr<sub>3</sub>, are present from the melt and contribute to microstructural control <sup>3,26</sup>. The constituent particles are subdivided into two categories: 1) particles such as Al, Mg, and Zn, which are anodic with respect to the matrix; and 2) particles behaving as cathodic with respect to the matrix and that tend to promote corrosion or disintegration of the adjoining matrix, such as Fe, Cu and Mn <sup>11,14,21,30</sup>. The  $\eta$  phase act as an anode to the surrounding cathodic aluminum matrix <sup>30</sup>.

The homogeneously precipitated phases present in AA 7075-T651, such as MgZn<sub>2</sub> and Al<sub>2</sub>CuMg, can be present in a range of sizes from *nm to*  $\mu$ *m* with the Al-Zn-Mg-Cu system, providing the basis for precipitation strengthening via precipitation hardening<sup>3</sup>. Solution treatment and aging are used to modify the distribution and size of the intermetallic precipitates<sup>3,26</sup>. All precipitates and particles that have different chemistry, and electrochemical potential, then that of the surrounding Al matrix forming many micro-galvanic couples <sup>21,30</sup>. The potential difference between the intermetallic precipitates such as MgZn<sub>2</sub> and the surrounding Al matrix promote micro galvanic corrosion where phases which are considerably more active in the electromotive series than the Al-rich matrix corrode selectively<sup>30</sup>. Intermetallic precipitates (IMP) of concern to corrosion performance include  $\eta$  phase, MgZn<sub>2</sub>, primarily those heterogeneously nucleated on GB. The selective dissolution of precipitates residing on GBs generates hydrogen which increases susceptibility to stress corrosion cracking (SCC) and intergranular stress corrosion cracking (IGC-SCC)<sup>31–38</sup>.

The precipitation sequence of forming  $\eta$  phase in 7xxx-series aluminum alloys follows three formation pathways from super saturated solution (SSS): 1) Guinier-Preston (GP) zones, 2) vacancy-related clusters (VRC), and 3) phase transformation from T phase. Pathways 1 and 2

result in the formation of metastable MgZn<sub>2</sub> ( $\eta'$  phase) and subsequent  $\eta$  phase. The 3<sup>rd</sup> pathway is influenced by the Zn/Mg ratio but in general all three pathways may occur simultaneously throughout the heat treatment and aging process. The formation of metastable and stable precipitate phases occurs through decomposition of the solid solution during the aging process <sup>7,39</sup>. The formation of  $\eta'$  phase from GP zones have been noticed to be coherent with the Al matrix while  $\eta$  phase is incoherent with the surrounding Al matrix <sup>7,39</sup>. The aging process results in the formation of Guinier-Preston (GP) zones and meta-stable MgZn<sub>2</sub> ( $\eta'$ ) phases and are responsible for the peak hardening effect in Al-Zn-Mg-Cu alloys<sup>7,39</sup>. However, the formation and coarsening of heterogeneously precipitated  $\eta$  phase is responsible for a decreasing in the yield strength of 7xxx-series aluminum alloys<sup>7,40,41</sup>. Copper enrichment occurring within both the  $\eta$  and  $\eta'$  phases present at peak aging (T6) shows that Cu stabilizes metastable phases in 7XXX-series aluminum alloys  $^{7,42,43}$ . In the T6 condition, the precipitated  $\eta$  phase at the grain boundaries act as anodic tunnels of intergranular corrosion and enhances the SCC rate of the alloy by accelerating the hydrogen generation and transportation which further embrittles the grain boundaries<sup>7</sup>. The corrosion of  $\eta$  phase at the GB develops a scenario which support a) the generation of both atomic hydrogen and hydrogen gas, b) trapping sites for atomic hydrogen, and c) diffusion pathways along GBs. The confluence of these factors facilitates hydrogen assisted IGSCC due to the presence of  $\eta$  phase at the GB. Over-aging (T7) in 7XXX-series aluminum alloys with greater Cu content has been shown to increase resistance to environmentally assisted cracking (EAC)<sup>7</sup>. This is attributed to the coarsening and increased discontinuity of grain boundary precipitates (GBPs)<sup>7,15,44</sup>.

The environmentally assisted cracking (EAC) of Al-Zn-Mg-Cu alloys in aqueous environments, including water vapor, has been heavily studied with many proposed models investigating the origins of the SCC mechanism<sup>35,45,46</sup>. Crack initiation or incubation is largely thought to be dominated by anodic dissolution of bare Al, which in turn forms critical defects such as pits<sup>7,47,48</sup>. In the presence of an electrolyte, the constituents, dispersoids, and precipitates mentioned all meet the prerequisite conditions necessary to form micro-galvanic couples with the surrounding aluminum matrix each of which has different composition and electrochemical potential. The corrosion potential of each phase depends upon the Nernst potential of each phase, composition of each phase (which can change during exposure), and electrolyte chemistry (pH and metal ion concentration). The conditions of each micro-galvanic couple are a telling sign of how each intermetallic particle (IMP) interacts with the surrounding alloy. These micro-galvanic

coupling conditions may enhance localized anodic dissolution and increase surface defects present during initiation/incubation. This can be reduced by cathodically preventing localized anodic particles within AA7075-T651 by suppressing the OCP below the  $E_{pit, \eta}$  serving to minimizing the potential difference between the anodic particle and cathodic matrix.

EAC readily initiates and propagates when pre-cracked specimens are loaded to near the critical stress intensity ( $K_{1C}$ ) and are exposed to humid gases <sup>7,46,49</sup>. Stage II crack growth in Al-Zn-Mg alloys depend linearly on the water vapor pressure <sup>7,46,49</sup>. This linear dependence of crack growth rate on RH indicates that the crack tip is not filled with condensed water and therefore metal dissolution does not control crack growth. Under low RH conditions crack growth is observed where water condensation is unlikely to occur at crack tips. However, the oxidation of aluminum with concurrent water reduction produces high hydrogen fugacity which supports hydrogen embrittlement (HE) mechanisms driving EAC in 7xxx-series aluminum alloys.

The stage II crack propagation of Al-Zn-Mg-Cu alloys in aqueous environments is dominated by hydrogen environment assisted cracking (HEAC), in which the reaction of aluminum with water vapor produces a high fugacity hydrogen gas responsible for controlling EAC via hydrogen embrittlement (HE) <sup>35</sup>. Hydrogen generation may take the form of a two-electron step and form hydrogen gas directly or by single electron transfer to produce atomic hydrogen which may recombine to form hydrogen gas or be absorbed into the metal <sup>35</sup>. It is the production of atomic hydrogen by single electron transfer that makes water vapor an aggressive environment for Al-Zn-Mg-Cu alloys<sup>36,50,51</sup>. It has been reported that the presence of Mg along the grain boundaries has a larger electronegativity difference between Mg and H atoms than between Al and H atoms providing a larger affinity for hydrogen adsorption Mg bearing GBP. This leads to grain boundary embrittlement and accelerates the propagation of SCC.

There have been many mechanisms proposed to explain the governing SCC mechanisms in aluminum alloys <sup>7,31,52,53</sup>. The most contested theories being film induced cleavage, hydrogen embrittlement, and anodic dissolution. Of course, there can be many contributing factors that are present simultaneously and make determinations into a single mechanism difficult. The film-induced cleavage is predicated on local dealloying at the crack tip which results in the formation of a brittle film <sup>54,55</sup>. This brittle film is thought to be responsible for SCC as it is mechanically susceptible to rupture<sup>54</sup> and subsequently inducing cleavage. Generally, this mechanism is not

applicable to SCC in aluminum alloys where crack growth is predominantly intergranular <sup>7,52</sup>. The crack growth arrest marks observed ( $\mu$ ms) <sup>56</sup> and critical distances for cleavage fracture <sup>57</sup> are significantly greater than the thin (10s of nm) <sup>55,56,58</sup> nature of the hypothesized dealloyed brittle film<sup>54</sup>.

A variety of studies have interrogated the hydrogen-based mechanisms contributing to SCC in aluminum alloys<sup>43,59–64</sup>. Hydrogen embrittlement in aluminum alloys proceeds through the generation and uptake of atomic hydrogen at the crack tip followed by diffusion into the fracture zone and the deleterious interaction between hydrogen within the fracture zone accelerating plastic damage accumulation<sup>35,65,66</sup>. There are numerous viable local failure mechanisms that can be used to describe hydrogen within the fracture zone <sup>67,68</sup>. These include hydrogen modified in the mobility of dislocation <sup>67,68</sup> and the rate at which they organize <sup>69,70</sup>, hydrogen stabilization of strain-induced vacancies<sup>71,72</sup>, the formation of hydrides which embrittle the fracture zone <sup>73,74</sup>, adsorption-induced dislocation emission at the crack tip <sup>75</sup>, and reduction in the cohesive strength <sup>76</sup>. These mechanisms are widely debated with recent evidence suggesting that failure is driven by the combination of hydrogen induced modifications of grain boundaries resulting in a reduction of the cohesive strength<sup>71,77</sup>.

The IG-SCC behavior is hypothesized to be governed by a coupled anodic dissolution process (i.e. electro-dissolution of the grain boundary  $\eta$  phase and the surrounding matrix), which also catalyzes the formation of an aggressive acidified local crack tip chemistry that, in turn, facilitates the enhanced generation of crack tip hydrogen and uptake enabling embrittlement in the fracture process zone. The IG-SCC crack initiation tendencies and growth rate of AA 7075-T651 exhibit a great deal of potential dependence under potentiostatic conditions (PS) in 0.6 M NaCl. Therefore, the mitigation of both IGC and IG-SCC is possible through the establishment of potentials that are more negative than the pitting potential,  $E_{pit}$ , of the  $\eta$  phase,  $E_{pit}(\eta)$ . The potential dependence of environmentally induced fracture susceptibility of AA 7075-T651 has been investigated previously by Harris et al., who reported variation in the crack growth rate and threshold stress intensity (K<sub>TH</sub>) with applied potential. Stage II crack growth rate develops a minimum potential between -0.9 V<sub>SCE</sub> or above -1.0 V<sub>SCE</sub>. This range of minimum crack growth potentials is theorized to minimize  $\eta$  phase corrosion, hydrolysis, and acidification. The

environmental fracture susceptibility of numerous 7xxx series aluminum alloys such as AA 7050-T651 exhibits an identical potential window for crack growth suppression <sup>81</sup>. This illuminates a possible mitigation strategy for this class of alloys based on galvanic protection for use in marine service such that  $[da/dt]_{II}$  is minimized at the galvanic couple potential. This situation can be described by the term "sacrificial cathode prevention" where the goal is to polarize below selected critical potentials where susceptibility is indicated.

Aerospace aluminum alloys are in frequent exposure to marine environments containing chloride, a particularly aggressive ion known to induce and exacerbate pitting of micro-galvanic couples and oxide breakdown. These phases are connected by an electrolyte; thus, a galvanic cell will be formed between the intermetallic phase and the surrounding Al matrix. Anodic reactions (such as Mg/Zn dissolution) are enhanced on the more active phase ( $\eta$  in this example) and cathodic reactions such as the hydrogen evolution reaction (HER) are enhanced on the more cathodic phase Al matrix but also occurs at anodes. The rapid dissolution and self-corrosion of Mg is a result of the high electrochemical activity of the MgZn<sub>2</sub> precipitate facilitate an increased rate of hydrogen generation <sup>7</sup>. This corrosion damage (grain boundary attack, pitting, trenching, etc.) is detrimental to the aluminum alloy's structural integrity, as damaged regions can act as crack initiation sites which propagate to mechanical failure under cyclic loading <sup>7</sup> This corrosioninduced damage can be prevented by a coating system which incorporate active corrosion protection to mitigate corrosion processes such as micro-galvanic couples or fissures for crack/pit formation<sup>82</sup>. These coating systems serve to stop galvanic corrosion in the alloy by suppressing potential beneath critical breakdown potentials and release cations into solution that are available to hydrolyze and re-deposit onto an uncoated surface to provide enhanced protection. This is a delicate balance, as overly cathodic polarization results in localized cathodic corrosion occurring on or around the surrounding constituent particles, and issues regarding hydrogen production may arise due to the activity of the pigment used.

Active corrosion protection in the form of coatings such as metal rich primers (MRP) are commonly employed, and work by disrupting electrolyte contact with the substrate through the presence of a coating layer. These coating systems are created to afford the underlying substrate protection in the form of galvanic protection, chemical inhibition, and secondary barrier properties. The performance of a coating is undermined by the presence of coating defects such as pores formed upon application and the development of scratches formed from abrasive impact, cracks formed under stress, or degradation under ultraviolet radiation exposure during service. Such coating defects decrease the barrier properties of the coating and lead to electrolyte ingress to the exposed substrate which initiates corrosion <sup>83–86</sup>. Active protection is required to protect the underlying substrate where barrier protection is insufficient, and at macro-defects such as within a scratch.

The protection offered by MRPs is intricate and may include 1) sacrificial anode based cathodic protection, 2) chemical inhibition, and 3) secondary barrier protection. The performance of an MRP is tied to these forms of protection which in general vary based on a) metal/metal oxide pigment composition, b) physical coating characteristics such as PVC, and c) characteristics of the resin/binders used. There are a great deal of pigment chemistries and combinations to consider and depend on the substrate and service conditions. The use of Al, Mg, and Zn pigments have been used on aluminum alloys (2xxx, 5xxx, and 7xxx) indicating a capacity to provide active protection to the galvanic couples formed between precipitates and matrix of each alloy system <sup>80,84,87–91</sup>. However, mitigating EAC is an ongoing challenge which needs to be addressed. Previous work on Zn-based MRPs (ZnRPs) and cold mounted Zn anode achieved IGSCC mitigation when applied to AA 5456-H116 <sup>82</sup>. This mitigation was not observed when additional topcoats was applied to an inorganic ZnRP <sup>92</sup>. The chemical effects of Zn2+ was assessed separately with the use of ZnCl<sub>2</sub> salt instead of the use of a ZnRP and was shown to reduce the IGSCC growth rate by three orders of magnitude over a range of stress intensities in the presence of Zn<sup>2+</sup> ions <sup>93</sup>.

This study focuses on assessing the electrochemical factors contributing to EAC of AA 7075-T651 under applied potentials as well as the feasibility of mitigation strategies such as MRPs to provide protection against EAC. The electrochemical characteristics of AA 7075-T651 and MgZn<sub>2</sub> will be established in 0.6 M NaCl at varying pH conditions relevant to bulk electrolyte environments as well as conditions that may be present at the crack-tip. This includes assessing the potential dependence of hydrogen evolution on AA 7075-T651 in 0.6 M NaCl. The electrochemical factors contributing to EAC will be compared to fracture mechanics-based testing and fractography in 0.6 M NaCl. Insight is drawn from the potential dependence of K<sub>TH</sub> and stage II crack growth rate on AA 7075-T651.

### **Experimental**

#### Materials

Fracture mechanics testing samples were created starting from a single material heat of AA 7075-T651 (Alcoa, Pittsburgh, Pa, USA). Samples were machined from a 50.8 mm thick plate with the elemental composition reported in **Table 1**. The T651 heat treatment has been used previously to replicate the alloy composition of AA 7075 found in legacy aircraft structures [ref]. Present day compositions of AA 7075 have a lower concentration of Fe than the legacy aircraft structures [ref]. The rolling of aluminum plate deforms the grain structure into an elongated 'pancaked' grain structure with a more detailed microstructural analysis of this material shown elsewhere [ref]. The mechanical properties of the AA 7075-T651 specimen, shown in **Table 2**, is obtained from tensile testing oriented such that loading occurred parallel to the short transverse (S-T) orientation of the rolled plate.

# Fracture Mechanics-Based Testing

Fracture mechanics testing was performed on single edge notch tensile (SEN(T)) specimens of gauge dimensions  $6.60\pm0.52$  mm in thickness (B),  $17.25\pm0.055$  mm in width (W). The SEN(T) specimens were oriented to align the loading parallel to the S-T direction of the plate wherein Mode I crack propagation occurred parallel to the short-longitudinal orientation (S-L). A notch of 0.2 mm in height was positioned at the mid thickness (t/2) of the plate to a total depth of (a<sub>0</sub>) of  $1.90\pm0.05$ mm with the use of electrical discharge machining (EDM).Specimens were loaded using a pinned-ends configuration via a clevis-based load train. The threaded ends of the SEN(T) were screwed into tangs that were pin-fastened into clevises and connected to the mechanical load frame crosshead and actuator, respectively. The pins, clevises, and tangs were all machined from 17-4 precipitation hardened (PH) steel tempered to the H900 condition (ref]. After being placed in the mechanical load frame, specimens were aligned with the clevises to allow for free rotation, in compliance with the K solution boundary conditions for this geometry and fixture condition.

Open air fatigue pre-cracking was done prior to EAC testing using the following protocol: fixed  $K_{max} = 5 \text{ MPa}\sqrt{m}$  from the initial notch depth (1.9 mm) to a total notch depth plus crack length of X mm at a constant stress ratio (R) of 0.2 and a frequency of 5 Hz. This reduced precrack distance was utilized to minimize crack closure-induced shorting of the direct current potential difference (dcPD) system and was sufficient in length to ensure the crack-tip stress field was not influenced by the stress field associated with the notch. EAC testing was conducted under full immersion in 0.6 M NaCl (pH 5-6) in a 200-mL acrylic cell through which 0.25 L was circulated at a flow rate of 20 mL/min at ambient temperature. The SEN(T) specimens were grounded through the grips and electrochemical testing was conducted using a constant applied potential of -0.8 V<sub>SCE</sub>, -0.85 V<sub>SCE</sub>, -0.9 V<sub>SCE</sub>, -0.95 V<sub>SCE</sub>, -1.0 V<sub>SCE</sub>, or -1.1 V<sub>SCE</sub>, -1.2 V<sub>SCE</sub>, -1.3 V<sub>SCE</sub> via a Gamry 600 potentiostat at ambient temperature. In this electrochemical testing cell, the SEN(T) specimens served as the working electrode (WE) with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as reference. Slow rising displacement testing first consisted of a 5-h or 10-h hold under an applied force of 1 kN and at the polarization of interest. Following this initial hold, the specimen was loaded at an initial dK/ dt of 0.25 MPa $\sqrt{m}$ /hr, achieved under grip displacement-controlled rates of 0.0002 mm/min until final fracture.

The crack length was actively monitored to a resolution of 0.5- $\mu$ m throughout both the fatigue pre-crack and EAC segment of each experiment via the dcPD technique [ref] using a constant applied current of 6.000 ± 0.005 A. Voltage measurements were taken using 36-gage copper wires spot welded above and below the EDM notch at a distance of ~0.6–0.75 mm from the notch mid-plane, yielding a dcPD gage length of 1.2 to 1.5 mm. The conversion of dcPD-measured potentials to crack lengths are described in detail elsewhere [ref]. Each potential measurement was corrected for thermally induced voltages using current-polarity reversal and represented the average of at least 500 individual voltage readings. Crack growth rates (da/dt) were then calculated from the measured crack length data using the incremental (n = 3) polynomial method in ASTM E647-13 Appendix XI.

Two traditional fracture mechanics-based metrics of IG-SCC susceptibility will be reported:  $K_{TH}$  and Stage II crack growth rates (da/dtII). In the current work, two criteria are used to establish the  $K_{TH}$ : (1) the onset of Stage I crack growth which is typified by a significant increase in the slope of the da/dt versus KJ relationship, and (2) exceeding the resolution limit. Stage I crack growth is terminated by a (nearly) K-independent plateau; this plateau value is traditionally deemed the Stage II crack growth (da/dtII). Prior work established a function resolution limit (by testing in a dry nitrogen environment) largely associated with increases in crack tip plasticity that scales with K for the current slow rising displacement testing protocol <sup>81</sup>.

#### Electrochemistry Investigation on Bare Materials

Coupons of peak aged stress relieved AA7075 - T651 were machined to dimensions 1.5 mm thick, 20 mm long, and 30 mm wide cleaned of all grease from the surface via alcohol bath. All electrochemical testing techniques are carried out over a 0.785 cm<sup>2</sup> area (S-L orientation). Electrochemical testing in form of long-term OCP (24 hours) and potentiodynamic polarization (PDP) of the AA 7075-T651 and the MgZn<sub>2</sub> is carried out in quiescent 0.6 M NaCl across a range of pH conditions (pH 3, unadjusted (UA, pH 5.8), pH 9, pH 10, and pH 11). PDP is carried out at a scan rate of 1mV/s and limiting the cathodic sweep to 50 - 100 mV below OCP prior to scanning to more positive potentials. This set of testing is conducted to evaluate the potential corresponding to no net current flow as well as anodic electrochemical kinetics. The hydrogen evolution experiments of AA 7075-T651 (S-L orientation) was conducted in a vertical electrochemical cell modified with an inverted burette serving as a collection vessel to capture and measure the evolved hydrogen content. The application of multiple PS holds at varying potentials (-0.6 V<sub>SCE</sub>, -0.7 V<sub>SCE</sub>, -0.75 V<sub>SCE</sub>, -0.8 V<sub>SCE</sub>, -0.9 V<sub>SCE</sub>, -1.0 V<sub>SCE</sub>, -1.1 V<sub>SCE</sub>, -1.2 V<sub>SCE</sub>, -1.3 V<sub>SCE</sub>, -1.4 V<sub>SCE</sub>, -1.5 V<sub>SCE</sub>, -1.6 V<sub>SCE</sub>) allowed for the evaluation of current, and its polarity, while capturing evolved hydrogen gas (H<sub>2</sub>) that is formed at the electrode surface. The hydrogen evolution tests were conducted in H<sub>2</sub> saturated 0.6 M NaCl solution by the use of a polarizing a Pt/Pt cell at -1.6V<sub>SCE</sub> for 1.5 hours and transferring solution to the vertical hydrogen testing cell to avoid loss of evolved H<sub>2</sub> to solution solubility. The hydrogen evolution rates was conducted for a duration of six-hour and averaged over three experiments for each potential hold. Samples are cleaned in 70% nitric acid to rinse corrosion products and washed with deionized water prior to cross-sectioning. Cross-section sample preparation is carried out by machining with a Mager BR220 precision cut off saw, epoxy mounting, and wet-polishing to 1200 grit using SiC polishing pads. Characterization of posthydrogen evolution testing samples was performed by Hirox digital optical microscopy of polarized AA 7075-T651 cross-sections to view the evolution of damage profiles as a function of polarization. The MgZn<sub>2</sub> sample was procured through the Kurt J. Lesker company in 3-6-gram pellets. Typical synthesis procedures follow induction melting under slight vacuum in argon containing environment to reduce volatilization and oxidation.

#### Results

#### Fracture Mechanics Testing

There are a variety of sources that may lead to inaccurate crack growth measurements related to dcPD voltage increases which can obscure crack growth rates in both rising K and static K approaches. It is essential to improve the accuracy of crack extension measurements indicated through dcPD by correcting the static K-generated data in order report 'true' crack extension rates. The 'as measured' crack growth vs K is skewed from 'true' crack growth rates as it may include contributions corresponding to inaccurate crack growth extensions rates. A correction can be performed by subtracting the crack growth response in dry  $N_2$  from the asmeasured data thereby isolating 'true' crack growth extension. Testing in this inert environment represents the magnitude of inaccurate crack extension as a function of K given that these experiments were conducted at a fixed dK/dt. The crack growth rate data versus K with varying applied potential of AA 7075-T651 (S-L) are shown in **Figure 1** at a dK/dt of 0.5 MPa $\sqrt{m}$ /hr in 0.6 M NaCl under full immersion conditions with the 'as measured' data shown in **Figure 1a**. It is important to note, this subtraction-based corrections can be carried out using either the da/dt vs K or K vs crack length criterion. This study conducts the subtraction-based corrections is conducted using the K vs crack length criterion. There have been other methods proposed to accomplish the corrections to minimize inaccurate crack growth contributions arising from dcPD signals. However, these methods assume that the inaccuracies in crack growth contributions are insignificant upon the onset of real crack extension. These assumptions are not rigorous due to the potential for slow crack growth as will be shown for the current alloy under certain environmental conditions.

The crack growth data measured in dry N<sub>2</sub> (RH < 5%) environment (**Figure 1a**), which was then used to correct the applied potential data collected in 0.6 M NaCl full immersion condition. This correction to crack growth data as a function of K for a range of potentials is shown in **Figure 1b**. The crack growth rates  $(5 \times 10^{-6} \frac{\text{mm}}{\text{sec}})$  measured at a K = 19 MPa $\sqrt{\text{m}}$  in 0.6 M NaCl in the range of applied potentials between -0.8 V<sub>SCE</sub> to -0.85 V<sub>SCE</sub> (**Figure 1b**). There is a modest decrease (1/2 order of magnitude) of the crack growth rates  $(1.02 \times 10^{-6} \text{ m})$ 

 $10^{-6} \frac{\text{mm}}{\text{sec}}$ ) measured at a K = 19 MPa $\sqrt{\text{m}}$  in 0.6 M NaCl in the range of applied potentials between -0.9 V<sub>SCE</sub> to -1.0 V<sub>SCE</sub> and is referred to as a potential 'well' in the crack growth data (**Figure 1b**). This is followed by an increase in the crack growth rates  $\left(4.5 \times 10^{-6} \frac{\text{mm}}{\text{sec}}\right)$ measured at a K = 19 MPa $\sqrt{\text{m}}$  in 0.6 M NaCl in the range of applied potentials between -1.1 V<sub>SCE</sub> to -1.3 V<sub>SCE</sub> (**Figure 1b**).

The threshold stress intensity and stage II crack growth rates as a function of potential on AA 7075-T651 immersed in 0.6 M NaCl is shown in **Figure 2**. The effect of applied potential on the K<sub>TH</sub> of AA 7075-T651 (S-L) immersed in 0.6 M NaCl under full immersion conditions is shown in **Figure 2a**. The K<sub>TH</sub> exhibits a maximum of 9 MPa $\sqrt{m}$  at an applied potential of -0.9 V<sub>SCE</sub>. This potential is within the potential 'well' identified in **Figure 1b**. The effect of applied potential on the Stage II crack growth rate for AA 7075-T651 (S-L) immersed in 0.6 M NaCl under full immersion conditions is shown in Figure 2b. Elevated crack growth rates are observed at applied potentials near the OCP, followed by a decreased crack growth rate by a half-order of magnitude between the applied potentials of -0.9  $V_{SCE}$  to -1.0  $V_{SCE}$ , and then an increase in crack growth rates more negative than -1.0 V<sub>SCE</sub> (Figure 2b). The Stage II crack growth rates on either side of the potential 'well' are approximately equal showing the susceptibility of AA 7075-T651 in 0.6 M NaCl. Mechanical properties AA 7075-T651 summarized in Table 2. The results of the fracture mechanics testing are shown in the BSI micrographs provided in **Figure 3**. The fracture mechanics BSI micrographs at an applied potential of  $-0.8 V_{SCE}$  and  $-1.3 V_{SCE}$  is shown in **Figure 3a** and **3b**, respectively. The BSI micrographs generated at an applied potential of -0.8 V<sub>SCE</sub> show a continuous crack (Figure 3a) propagating throughout AA 7075-T651 whereas the BSI micrographs generated at an applied potential of-1.3 V<sub>SCE</sub> shows a discontinuous crack path (Figure 3b).

### Evaluation of the Potential Window for Reduced SCC Susceptibility via Potentiostatic Holds

The current densities and hydrogen generation rate resulting from the application of a range of PS hold can be seen in **Figure 4**. The current densities observed throughout the PS holds can be seen to increase with increasingly cathodic potentials. The application of -0.6  $V_{SCE}$  and -0.7  $V_{SCE}$  (anodic to AA7075-T651) can be seen to produce anodic current shown in **Figure 4a**. The PS holds between the range of potentials -0.75  $V_{SCE}$  to -1.1  $V_{SCE}$  resulted in no

meaningful increase in current density recorded (**Figure 4a**). The PS holds between the range of potentials -1.2 V<sub>SCE</sub> to -1.3 V<sub>SCE</sub> increase in current density recorded -0.8 mA/cm<sup>2</sup> by the end of six-hour PS hold (**Figure 4a**). The most substantial increase in the current density recorded was between -1.2 V<sub>SCE</sub> to -1.3 V<sub>SCE</sub> to -5.2 mA/cm<sup>2</sup> by the end of six-hour PS hold (**Figure 4a**). The greatest current density witnessed throughout testing was -8 mA/cm<sup>2</sup> at a potential hold of -1.6 V<sub>SCE</sub> by the end of the six-hour PS hold (**Figure 4a**). The potential window for reduced SCC susceptibility via PS holds, as determined from **Figure 4a**, is -0.75 V<sub>SCE</sub> to -1.1 V<sub>SCE</sub> as there does not appear to be a meaningful increase in current densities associated with these potentials.

The collection of evolved hydrogen from the surface of AA7075-T651 allowed for the quantification of hydrogen evolution rate over the six-hour PS hold collection time at each potential. The current density and average hydrogen evolution rate is shown in **Figure 4b**. It can be seen that the application of increasingly cathodic potentials results in an increase in the observed average hydrogen evolution rate. It can be seen that a minimum in the average hydrogen evolution rate develops in a potential range of -0.75 V<sub>SCE</sub> and -1.0 V<sub>SCE</sub>. The trends observed in both current density and average hydrogen generation rate are shown rescaled on a narrower linear axis for aid decerning each point within the potential window in **Figure 4c** and **4d**, respectively. It should be noted that the minimum hydrogen evolution occurred at OCP, -0.75 V<sub>SCE</sub>, as there is minimal driving force. The potential window for reduced SCC susceptibility via average hydrogen evolution rate, as determined from **Figure 4b**, is -0.75 V<sub>SCE</sub> to -1.1 V<sub>SCE</sub> matching the results gathered from PS holds and recorded current densities.

The cross-section depth profiles can be seen in **Figure 5** for each potential hold. The cross-section profiles clearly show anodic dissolution extending well into the depth of the AA 7075-T651 up to a maximum depth of 100  $\mu$ m after the six-hour PS hold at -0.7 V<sub>SCE</sub> (**Figure 5**). There does not appear to be corrosion into the depth as seen in cross-section view between -0.75 V<sub>SCE</sub> to -1.1 V<sub>SCE</sub> (**Figure 5**). There is a transition at -1.2 V<sub>SCE</sub> with the first signs of corrosion through the depth of the AA 7075-T651 cross-section; however, it does not appear to be significant (**Figure 5**). The PS hold at -1.3 V<sub>SCE</sub> experience a greater degree of corrosion through the depth of the cross-section (**Figure 5**). This cathodic corrosion is characteristic trenching and continues to increase in severity throughout the range of PS holds -1.3 V<sub>SCE</sub> to -1.6 V<sub>SCE</sub> (**Figure 5**). The potential window for reduced SCC susceptibility via cross-section depth profiles, as

determined from **Figure 5**, is -0.75 V<sub>SCE</sub> to -1.1 V<sub>SCE</sub> matching the results gathered from recorded current densities and average hydrogen evolutions rates throughout the range of PS holds measured. It is noted that while the applied potential of -1.2 V<sub>SCE</sub> does not experience significant corrosion through the depth that this is likely a result of the six-hour exposure time and not indicative of benign depth attach resulting from corrosion at longer time scales.

Long term OCP (24 hours) and PDP of AA 7075-T651 is shown in **Figure 6** tested in 0.6M NaCl under full immersion conditions across a range of pH conditions. All pH ranges excluding pH 11 experienced OCP of  $-0.8 V_{SCE} \pm 0.1 V_{SCE}$  across a 24-hour monitor under full immersion (**Figure 6a**). It can be seen that the OCP of AA 7075-T651 in the unadjusted 0.6 M NaCl solution is -0.74 V<sub>SCE</sub>. The OCP of AA 7075-T651 in pH 11 0.6 M NaCl solution is  $-1.2 V_{SCE}$  (**Figure 6a**). The PDP of AA 7075-T651 can be seen in **Figure 6b** for a variety of solution pH conditions. The PDP of AA 7075-T651 in acidic pH 3 0.6 M NaCl solution resulted in a corrosion potential of -0.765 V<sub>SCE</sub> with near identical anodic kinetics and a slight reduction in cathodic kinetics (**Figure 6b**). It can be seen that pH 9 and pH 10 solutions resulted in lowering the corrosion potential of AA 7075-T651 to -0.85 V<sub>SCE</sub> and -0.9 V<sub>SCE</sub> while a decrease in the current density is noticed, respectively. The corrosion potential observed in pH 11 solution is lowered substantially to -1.5 V<sub>SCE</sub> while the current density is increasing. The alkaline pH 9, pH 10, and pH 11 in 0.6 M NaCl solution experience a pitting potential of -0.7 V<sub>SCE</sub>.

Long term OCP (24 hours) and PDP of MgZn<sub>2</sub> is shown in **Figure 7** tested in 0.6 M NaCl under full immersion conditions across a range of pH conditions. The acidic pH 3, unadjusted, and pH 9 solution all resulted in an OCP of -0.95 V<sub>SCE</sub> (**Figure 7**). The pH 10 0.6 M NaCl solution initially started off as low as -1.1 V<sub>SCE</sub> eventually polarizing to -0.95 V<sub>SCE</sub> after six-hour (**Figure 7**). The pH 11 solution witnessed the most negative OCP of -1.3 V<sub>SCE</sub>. The PDP of MgZn<sub>2</sub> can be seen in **Figure 7b** for a variety of solution pH conditions. The PDP of MgZn<sub>2</sub> in acidic pH 3 0.6 M NaCl shows a corrosion potential of  $-1.04 V_{SCE}$ . It can be seen that the corrosion potential of MgZn<sub>2</sub> in the unadjusted 0.6 M NaCl solution is  $-1.13 V_{SCE}$ . The alkaline pH's of 9, 10, and 11 produce corrosion potentials of  $-1.06 V_{SCE}$ ,  $-1.13 V_{SCE}$ , and  $-1.58 V_{SCE}$ , respectively. All alkaline pH conditions as well as the unadjusted 0.6M NaCl solution experienced pitting at a pitting potential of  $E_{pit,MgZn_2} = -0.86 V_{SCE}$ . The only testing condition that did not experience MgZn<sub>2</sub> pitting was the acidic pH 3 solution.

The pitting potential and corrosion potential of both AA7075-T651 and MgZn<sub>2</sub> are shown in **Figure 8** across a range of pH conditions displayed with the reversible H<sub>2</sub> reduction line. It can be seen in **Figure 8a** that the pitting potential of MgZn<sub>2</sub> is very consistent and does not vary greatly over the range of pH values tested. Pitting was only observed in AA7075-T651 in alkaline conditions with pH 9, 10, and 11 (**Figure 8a**). The variation in corrosion potential for both AA7075-T651 and MgZn<sub>2</sub> across the range of pH solutions tested is shown in **Figure 8b**. It can be seen that under all circumstances the corrosion potential of AA7075-T651 remains above that of the MgZn<sub>2</sub>. The reversible hydrogen line is included to show the stability of hydrogen, below which gaseous hydrogen production is stable. Under alkaline conditions (pH 9, 10, 11) in 0.6 M NaCl AA 7075-T651 exists above the hydrogen evolution line and remains within the stable water region (**Figure 8a**). However, MgZn<sub>2</sub> remains below the reversible hydrogen promoting the stability of hydrogen gas (**Figure 8a**). There is a greater potential difference between the corrosion potential of MgZn<sub>2</sub> and the reversible hydrogen line than AA 7075-T651 under all pH ranges (**Figure 8b**).

#### Discussion

The hydrogen embrittlement process occurs during IGSCC through a series of steps wherein monatomic hydrogen must: 1) evolve and adsorb on the Al surface, 2) diffuse to the crack tip, and 3) interact deleteriously with the microstructure causing hydrogen embrittlement. The adsorption of hydrogen near to the crack tip is critical to its influence towards EAC. The results presented demonstrate that both cathodic and anodic polarization results in bulk hydrogen evolution rates that are similar in magnitude (**Figure 4b**). Fracture mechanics testing shows environmental cracking behavior that is equally susceptible near the open circuit potential of AA 7075-T651 as well as potentials  $\leq -1.1 \text{ V}_{\text{SCE}}$ . These findings warrant more detailed investigation as to the mechanism of IGSCC susceptibility of AA 7075-T651 under increasingly cathodic polarization. Specifically, the following questions are considered here and may require further elucidation in future work:

 What are the relevant hydrogen generation mechanisms that occur during both anodic and cathodic polarization of AA 7075-T651?

- 2) What influence does anodic and cathodic polarization of AA 7075-T651 have on the solution chemistry and in turn affect the susceptibility to EAC?
- 3) How do the results gathered herein inform mitigation strategies such as metal rich primers in the pursuit of reducing susceptibility to EAC on 7xxx-series aluminum alloys?
- 4) How do the results collected in this study compare to previous investigation in similar aluminum alloys?

#### Mechanisms of Hydrogen generation during Polarization

The evolution of corrosion during anodic or cathodic polarization of Al-Zn-Mg-Cu alloys varies due to differences in the localized surface chemistry as a result of the numerous intermetallic particles (IMCs) present <sup>30</sup>. In the regions adjacent to the grain boundaries which are solute depleted due to the precipitation aging of AA 7075-T651 comparisons can be drawn to commercially pure (CP) aluminum to assess the hydrogen evolution behavior in the region of the crack tip for simplicities sake <sup>65</sup>.

# Hydrogen Evolution during Anodic Polarization of Peak Aged AA 7075

The stability of an oxide layer is crucial when subjected to anodic polarization conditions, as this layer governs the rate of anodic and cathodic reactions occurring on the surface of aluminum  $^{94}$ . The stability of the oxide layer, Al<sub>2</sub>O<sub>3</sub>, decreases with increasingly anodic polarization (**Figure 9**) predominantly through pitting and the solution pH is acidified  $^{94-96}$ . In regions of high strain, such as crack tips, there are two phenomena that may occur under anodic polarization 1) strain-induced dislocation motion and 2) the dissolution of MgZn<sub>2</sub> and matrix phase. In the first scenario, bare aluminum is exposed due to dislocation motion may disrupt the oxide layer. In the second scenario, the dissolution of  $\eta$  phase and matrix phase releases Mg<sup>2+</sup>, Zn<sup>2+</sup>, and Al<sup>3+</sup> which can lead to ingress of Cl<sup>-</sup> assisting in charge balance <sup>97</sup>. This ingress of Cl<sup>-</sup> decreases the resistance of the Al<sub>2</sub>O<sub>3</sub> layer in turn increasing susceptibility to mechanical rupture caused by strain rates at the crack tip<sup>82.97,98</sup>. The stability of the Al<sub>2</sub>O<sub>3</sub> layer decreases with increasing Cl<sup>-</sup> concentration. The increase in exposed surface area of aluminum by either mechanical disruption or dissolution of

oxide layers at the crack tip results in an increase in the rate of the hydrogen evolution reaction (HER).

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \to \mathrm{H}_{2} \tag{1}$$

The HER reaction can involve an intermediate step involving the formation of atomic hydrogen  $^{94,99-101}$ , a crucial step in hydrogen embrittlement process. The transport of oxygen is tortuous at the crack tip leaving HER to be the dominant cathodic reaction. The dissolution of  $\eta$  phase and matrix phase and subsequent release of Mg<sup>2+</sup>, Zn<sup>2+</sup>, and Al<sup>3+</sup> allows for proton formation through the following hydrolysis reactions:

$$Al^{3+} + H_2 0 \rightarrow AlOH^{2+} + H^+$$
 (2)

$$Mg^{2+} + H_2O \rightarrow MgOH^+ + H^+$$
(3)

$$Zn^{2+} + H_2O \rightarrow ZnOH^+ + H^+$$
(4)

These hydrolysis reactions resulting in proton formation lead to an acidification of the aqueous environment during anodic polarization which is particularly detrimental when occurring at the crack tip. This acidification can become quite aggressive where previous studies have demonstrated the ability to attain negative pH values and high Cl<sup>-</sup> concentrations <sup>82,102</sup>. The high Cl<sup>-</sup> concentrations only further increase the activity of hydrogen causing exposed aluminum surfaces to experience an increased rate of HER. These contributing factors locally increase the overpotential for hydrogen evolution at the crack tip aiding in the adsorption and diffusion of hydrogen at the crack tip, all of which are necessary for hydrogen embrittlement mechanisms enhancing IGSCC<sup>82,98,103</sup>. The anodic polarization creates the conditions locally to acidify crack tip chemistries driving aggressive IGSCC<sup>82,98</sup>.

The dissolution of AA 7075-T651 and MgZn<sub>2</sub> under acidic conditions can be seen in **Figure 6b** and **7b**, respectively. The polarization behavior of AA 7075-T651 (**Figure 6b**) shows increased current densities driving further dissolution. According to **Figure 9**, acidification pushes the stability of  $Al_2O_3$  into a region where  $Al^{3+}$  is dominant. The polarization data of MgZn<sub>2</sub> under acidic conditions results in increased current density and absence of passivation (**Figure 7b**). In an acidified solution both Mg and Zn exist within a region of stable Mg<sup>2+</sup> and Zn<sup>2+ 104</sup>. This poses a particularly insidious reaction as continued dissolution, resulting in release of cations, enables

proton formation hydrolysis only to further stabilize the release of cations in solution. In the T6 condition a continuous precipitation of MgZn<sub>2</sub> occurs at the grain boundary aiding in supplying the local crack tip environment with active corrosion dissolution products exacerbating the conditions at the crack tip. The PS hold of AA 7075-T651 at -0.6  $V_{SCE}$  in **Figure 5** shows particularly aggressive dissolution in the cross-section view and substantial increase in hydrogen evolution rate (**Figure 4b**) associated with generation of both atomic hydrogen and molecular hydrogen from HER. The anodic reactions supported by the dissolution of Al, Mg, and Zn are shown below.

$$AI \to AI^{3+} + 3e^{-} \tag{5}$$

$$Mg \to Mg^{2+} + 2e^{-} \tag{6}$$

$$Zn \to Zn^{2+} + 2e^{-} \tag{7}$$

## Hydrogen Evolution and Alkaline Corrosion during Cathodic Polarization of Peak Aged AA 7075

Corrosion during cathodic polarization is possible due to the amphoteric nature of both aluminum and zinc <sup>104</sup>. This cathodic polarization drives the reduction of water which promotes the alkalinization of the aluminum surface including the crack wake environment <sup>104–106</sup>.

$$H_2 0 + e^- \rightarrow \frac{1}{2} H_2 + 0 H^-$$
 (8)

Under these conditions the oxide present at the crack tip may adsorb hydroxyl ions chemically dissolving the oxide layer <sup>104</sup> promoting a more negative aluminum surface potential increasing the driving force, overpotential, for HER <sup>106,107</sup>.

$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2O$$
 (9)

The region of stability of  $Al_2O_3$  is dependent on the concentration of  $Al^{3+}$ , initially the solution can be considered dilute (10<sup>-6</sup> M) and as dissolution continues the concentration of  $Al^{3+}$  in solution increases <sup>104</sup>. The initial conditions of corrosion present satisfy the criteria of being considered dilute and a pH above ~8.6 promotes chemical dissolution of the oxide layer (**Figure 9**) <sup>104</sup>. Whether the increase in exposure area of aluminum occurs via chemical dissolution processes or mechanical processes the result is an increased rate of HER due to exposure of an

increased surface area of aluminum. In the absence of the oxide layer the rate of aluminum corrosion is equal to the rate of electrochemical reaction <sup>107,108</sup>.

The formation of H<sub>2</sub> (Eqn. 8) at atomic hydrogen due to HER (Eqn. 1) occurs across the alloy surface under these alkaline conditions<sup>104</sup>. Cathodic polarization increases the rate at which cathodic corrosion occurs in the form of trenching <sup>94</sup>, which can be seen in the cross-section characterization in **Figure 5**. Under cathodic polarization the formation of hydrogen does not occur preferentially in the crack tip environment but rather across the bulk aluminum surface. The chemical inhomogeneity of AA 7075-T651 may disturb the electrochemical reactions occurring on the surface as IMCs may act as fast cathodic reaction sites <sup>30</sup>. Additional contributions from ohmic voltage drop effects will decrease the hydrogen overpotential at cathodically polarized crack tips.

In addition to the increased rate of HER as a result of exposed aluminum surfaces, the rate of HER may also be increased due to the dissolution of MgZn<sub>2</sub>. The Nernst potential Mg and Zn is far lower than that of Al and further accelerates the rate of HER as MgZn<sub>2</sub> corrosion occurs. This situation is made worse due to the nature of the MgZn<sub>2</sub> precipitate occurring along the grain boundary of AA 7075-T651 where the dissolution of MgZn<sub>2</sub> and production of hydrogen results in increased susceptibility of to EAC via hydrogen embrittlement. The change in solution chemistry at the crack tip is determined by the relative rates of reduction of water on  $Al_2O_3$  (Eqn. 8) and proton formation hydrolysis due to the release of Mg<sup>2+</sup>, Zn<sup>2+</sup>, and Al<sup>3+</sup> (Eqn. 2,3,4).

The alkalization of solution, over the bulk alloy and at the crack tip, influence the electrochemical kinetics of dissolution processes. This can be seen as a pH shift 11 results in a increase in the current densities on AA 7075-T651 (Figure 6b) and MgZn<sub>2</sub> (**Figure 7b**) as well as a decrease in the corrosion potential. The decrease in the open circuit potential as a function pH for AA 7075-T651 (**Figure 6a** and **6b**) and MgZn<sub>2</sub> (**Figure 7a** and **7b**) can be seen to be well within the region of stable H<sub>2</sub> evolution. The generation of both atomic and molecular hydrogen increases the susceptibility of AA 7075-T651 with increasingly cathodic potentials (**Figure 8**). The pitting potential of AA 7075-T651 and MgZn<sub>2</sub> appears to be independent of the pH as shown in **Figure 8a**. This shows that the breakdown of AA 7075-T651 and MgZn<sub>2</sub> remaining in a region of stable H<sub>2</sub> production below the HER equilibrium (**Figure 8a**). The potential

difference between the HER and the open circuit potential is a measure of the driving force for the evolution of H<sub>2</sub> (**Figure 8b**). The cathodic polarization shifts the solution pH to more alkaline values pushing the stability of Al<sub>2</sub>O<sub>3</sub> into a region in which  $AlO_2^-$  is stable (**Figure 9**). The cathodic corrosion of AA 7075-T651 does experience trenching can be observed at negative potentials (**Figure 5**), however, it is unable to sufficiently blunt crack tips and lower crack growth behavior (**Figure 2b**).

#### Hydrogen Production, Adsorption, Trapping/Uptake Behavior, and Role of Microstructure

The hydrogen production rates measured in this study are reflective of steady state bulk hydrogen evolution and not necessarily reflective of atomic hydrogen generation which is responsible for hydrogen assisted cracking behavior. The induced pH change as a result of polarization in either anodic or cathodic impacts the quantity of hydrogen present at the crack tip which is able to diffuse contributing to crack advance. The amount of hydrogen at the crack tip can be represented by equation 10 below.

$$C_{\rm H,crack\,tip} = C_{\rm H,Diff} \exp\left(\frac{\sigma_{\rm H} V_{\rm H}}{RT}\right)$$
 10

Where  $\sigma_H$  is the hydrostatic stress state present at the crack tip,  $V_H$  is the partial molar volume, and  $C_{H,Diff}$  the concentration of diffusible hydrogen. The production of hydrogen must be considered through the cathodic reaction rate ( $i_{ca}$ ) for the combined H<sup>+</sup> and H<sub>2</sub>O reduction is given below in equation 11.

$$i_{ca} = i_{o,H^+} 10^{\left(\frac{-\eta}{b_{c,H^+}}\right)}$$
 11

Where  $i_{o,H^+}$  is the exchange current density,  $\eta$  is the cathodic hydrogen overpotential and  $b_{c,H^+}$  is the Tafel slope ( $b_{c,H^+} < 0$ ). This expression can also be written for the reduction of water under charge transfer control given below in equation 12.

$$i_{H_2O} = i_{o,H_2O} 10^{\left(\frac{-E_{app}}{b_{c,H_2O}}\right)}$$
 12

66

Where  $i_{0,H_2O}$  is the exchange current density,  $E_{app}$  is the applied potential and  $b_{c,H_2O}$  is the Tafel slope ( $b_{c,H_2O} < 0$ ). The  $i_{0,H_2O}$  and  $b_{c,H_2O}$  maybe be influenced by the change in solution chemistry. Assessing the contributions from local and crack tip hydrogen production, cathodic polarization data can be used to gain a better understanding of the reaction mechanisms of H<sup>+</sup> and H<sub>2</sub>O reduction. This is crucial as the mechanism determines the relationship between hydrogen overpotential, cathodic current density, and hydrogen surface concentration. The measured hydrogen production which results from HER occurs by the coupled discharge and recombination mechanisms. The relationship between surface concentration of hydrogen is shown below in equation 13.

$$\frac{\theta_{ads}^{2}}{1-\theta_{ads}} = \frac{k_{1}}{k_{2}} C_{H} + \exp\left(\frac{-\alpha \eta F}{RT}\right)$$
 13

Where  $\theta_{ads}$  is the surface concentration of adsorbed hydrogen,  $k_1$  is the hydrogen discharge rate constant,  $k_2$  is the hydrogen recombination rate constant  $C_{H^+}$  is the hydrogen ion concentration,  $\alpha$  is the transfer coefficient (0.5), and  $\eta$  is the cathodic hydrogen overpotential. This expression can be rewritten in terms of the cathodic current density for  $\theta_{ads} \ll 1$ .

$$\theta_{ads} = \sqrt{\frac{k_1}{k_2} C_{H^+}} \exp\left(\frac{-\alpha \eta F}{2RT}\right)$$
 14

It should be noted that the role of grain boundary morphology plays a significant role in the production of hydrogen and which has been shown to impact the SCC susceptibility of 7xxx-series aluminum alloys. In the T6 condition the grain boundary is populated continuously with MgZn<sub>2</sub> whereas the T7 results in a discontinuous precipitation of MgZn<sub>2</sub> which is coarsened and enriched in Cu content to (Mg(Cu)Zn<sub>2</sub>)<sup>109,110</sup>. The T7 aging condition increases the resistance to SCC in part due to the higher OCP of Mg(Cu)Zn<sub>2</sub>, which lowers the potential difference, and therefore galvanic driving force, at the grain boundary in turn lowering the dissolution rate at the grain boundary <sup>109</sup>. The continuous precipitation of MgZn<sub>2</sub> along the grain boundary in the T6 condition results in a persistent saturation of atomic hydrogen resulting from HER whereas the coarsened Mg(Cu)Zn<sub>2</sub> precipitates allow for the desaturation of hydrogen present at the crack tip.

The hydrogen surface concentration may be trapped at atomic defects such as interstitial, octahedral, and tetrahedral sites in the aluminum matrix as well as vacancies, solute atoms, and dislocations. That being said, with respect to the surface concentration of trapped hydrogen at a

crack tip the dominant trapping sites will be the interstitial aluminum sites, vacancies, and dislocation present within the fracture process zone. The concentration of diffusible hydrogen can be given by the sum over the fractional coverage of a trap site and the number of a given trap given below.

$$C_{H,diff} = \theta_{interstitial} N_{interstitial} + \theta_{diss} N_{diss} + \theta_{vac} N_{vac}$$
 15

The effectiveness of a trap site to capture hydrogen at the surface is dependent on the binding energy of a particular defect. It should be noted that the solubility of hydrogen in aluminum is low which suggests that the majority of the surface concentration of hydrogen will be saturated at the crack tip rather than diffuse within the solute free zone adjacent to grain boundaries.

#### Influence of Material/Environment Susceptibility on Potential Dependence of EAC

The results presented above demonstrate that AA 7075-T651 exhibits a modest dependence on the potential dependence on EAC in 0.6 M NaCl under full immersion conditions at a dK/dt of 0.5 MPa $\sqrt{m/hr}$ . In this testing protocol a maximum K<sub>TH</sub> was observed within the potential range identified with reduced crack growth rates (Figure 1b), specifically at a potential of -0.9 V<sub>SCE</sub> (Figure 2a). There appears to be a potential 'well' in the stage II crack growth rate in the potential ranges between -0.9  $V_{SCE}$  to -1.0  $V_{SCE}$  in which a  $\frac{1}{2}$  order of magnitude decrease was observed (Figure 2b). These align with a minimum in the hydrogen evolution rates that can be seen in Figure 4c. At the applied potential of -0.9 V<sub>SCE</sub> pitting of MgZn<sub>2</sub> is suppressed in UA solution as well as in all alkaline solutions tested (Figure 8b). The application of potentials more negative than  $-1.1 V_{SCE}$  result in a decrease in the K<sub>TH</sub> (Figure 2a) and increase in stage II crack growth (Figure 2b) which can be attributed to an increase in the hydrogen evolution rate with increasingly negative potentials. This can be rationalized by the rise in hydrogen evolution rates (Figure 4b) which alter the solution chemistry at the crack tip and shift to alkaline values with increasingly cathodic polarization. The electrochemical behavior of both AA 7075-T651 and MgZn<sub>2</sub> testing in 0.6 M NaCl at pH 9, 10, and 11 show an OCP below the equilibrium HER line remaining in a region of stable  $H_2$  production (**Figure 6b** and **7b**). The potential difference between the OCP and equilibrium HER line represents the driving force for H<sub>2</sub> evolution which is greater for MgZn<sub>2</sub> than AA 7075-T651 (Figure 8b). This evidence show that even under cathodic polarization the production of hydrogen from MgZn<sub>2</sub> outpaces that of AA 7075-T651.

This maintains susceptibility as cathodic corrosion via trenching is unable to sufficiently blunt the crack tip, as is shown in the crack tip achieved under the application of  $-1.3 V_{SCE}$  in **Figure 3b**.

## **Comparison to Previous Studies**

The combination of fracture mechanics testing and electrochemical testing methods such as hydrogen evolution testing allow for the evaluation of potential ranges in which EAC susceptibility may be reduced. Fracture mechanics testing was able to identify a potential window in which there is a decrease in crack growth rates; however, the decrease does not signify a meaningful reduction in crack growth rates implying AA 7075-T651 is susceptibility to EAC is not reduced. Electrochemical testing in the form of assessing hydrogen evolution rates as a function of applied potential identified a potential well in which minimal evolved hydrogen is noticed. In combination with optical characterization of damage cross-sections shows a transition between different types of corrosion that are noticed. Previous work on AA 5456-H116, evaluated under similar conditions, resulted in comparable damage cross-sections via hydrogen evolution testing <sup>94</sup>. However, AA 5456-H116 was noticed to see an appreciable decrease in stage II crack growth rate effectively reducing the susceptibility of AA 5456-H116 under the application of cathodic potentials <sup>94</sup>. This was largely due to crack tip blunting under the application of cathodic potentials attributed to cathodic corrosion and alkalinization of the solution <sup>94</sup>. The trenching was able to blunt the crack tip, reducing the stress intensity, and therefore diminishing the rate of stage II crack growth <sup>94</sup>. These results were not observed in this study on AA 7075-T651 owing to the intrinsic susceptibility of the alloy in this heat posited to be a consequence of the precipitation of MgZn<sub>2</sub> at the grain boundary. This accelerates IGSCC through the combination of anodic dissolution of MgZn<sub>2</sub> at the grain boundary assisting hydrogen embrittlement. In the fracture micrographs polarized to -1.3 V<sub>SCE</sub> shown in Figure 3b that the crack tip which shows discontinuities in the crack path which can be explained by the 1) dissolution of MgZn<sub>2</sub>, 2) production of both monatomic and gaseous hydrogen, and 3) transport of hydrogen ahead of the crack tip causing embrittlement of AA 7075-T651. These discontinuities in the crack path can be attributed to the transport of hydrogen ahead of the crack tip (Figure 3b). In AA 5456-H116 the crack tip and wall experienced significant cathodic

corrosion in turn blunting the crack tip<sup>94</sup>, this was not observed in AA 7075-T651 showing a higher intrinsic susceptibility to EAC.

The influence of applied potential on the loading rate dependence to AA 7075-T651 in a previous publication showed a similarly modest reduction in crack growth rates <sup>81</sup>. This study showed evidence that EAC in AA 7075-T651 is likely mediated by a time-dependent process <sup>81</sup>. The data suggested that continued crack extension does not require an increased mechanical driving force implying that EAC in AA 7075-T651 is a stress-controlled fracture process <sup>81</sup>. As suggested in the present study and in a wider range of the literature, EAC in 7xxx-series aluminum alloys is driven by hydrogen embrittlement process that is assisted by the anodic dissolution of grain boundary precipitates and that the rate of crack propagation during EAC under stress-controlled conditions is related to hydrogen diffusion <sup>81</sup>. The hydrogen embrittlement process thereby reduces the intrinsic material resistance increasing susceptibility to EAC <sup>81</sup>. These contributions have also been observed in 5xxx-series aluminum alloys <sup>94</sup>. The hydrogen content <sup>94</sup>. The sluggish diffusion of hydrogen in aluminum alloys <sup>35,36</sup> suggests that diminished crack propagation rates would be anticipated, even when under stress-controlled fracture conditions.

Previous studies have investigated the influence of crack tip blunting on local crack tip stress field where finite element analysis (FEA) modeled the hydrostatic stress distribution in front of the crack/notch <sup>94</sup>. These calculations depended on the geometry (curvature of crack tip), the loading conditions (stress and stress intensity), and distance from the crack tip <sup>94</sup>. The reduction in hydrostatic stress at a blunt notch is attributed to a transition from plane strain to plane stress due to a traction free surface <sup>94</sup>. The hydrostatic stress distribution influences the local hydrogen concentration. This occurs due to an increase in the hydrostatic stress resulting in an increase in the lattice hydrogen solubility thereby increasing the hydrogen concentration at regions of high hydrostatic stresses such as crack tips <sup>94,97</sup>. This implies that a reduction in the hydrostatic stress would result in a decrease in both the stress intensity and the local hydrogen concentration.

The dissolution of MgZn<sub>2</sub> is undoubtedly a significant contributor to the susceptibility of 7xxx-series and plays a crucial role in SCC. The anodic dissolution of MgZn<sub>2</sub> determines the

crack growth rate differ by ~3 orders of magnitude. Therefore, additional influences impacting the EAC susceptibility of 7xxx-series aluminum alloys must be present. There is compelling evidence in this study, as well as a number of other investigations, that anodic dissolution assisted hydrogen embrittlement is a major contributor to SCC in 7xxx-series aluminum alloys<sup>7</sup>. The modification of crack tip solution chemistry plays a crucial role in the electrochemical kinetics pertaining to dissolution processes and their impact on EAC susceptibility.

#### **Implications of Results on EAC Mitigation Strategies**

In aluminum alloys the mitigation of corrosion can be achieved through the application of MRPs used to provide sacrificial anode cathodic protection. There is a wide range of pigment chemistries and combinations that can be used to varying effectiveness. The service life of a particular MRP coating is dependent on a number of factors including physical attributes of the coating (pigment volume concentration (PVC), surface area of pigment, pigment compositions and combinations, resin/binder choice, etc.), environmental factors (solution composition, wet/dry cycling, UV exposure), and surface conditions of the substrate (polished, sandblasted, level of Cl<sup>-</sup> contamination). In addition to the attributes mentioned above, the level of protection desired must be considered as corrosion protection to SCC can provide more challenges than under static conditions. Previous studies on aluminum-rich primers (AlRP), magnesium-rich primers (MgRP), and a hybrid dual pigment magnesium-aluminum rich primer (MgAlRP) with a macro defect (scribe) were exposed to six weeks of B117 salt spray testing in 0.6 M NaCl <sup>90,91</sup>. In these studies, the AIRP was shown to be ineffective to providing both static corrosion protection and scribe protection against IGC 90,91, however both the MgRP and MgAlRP were shown to provide scribe protection against IGC throughout the duration of six-week exposure to 0.6 M NaCl salt spray testing <sup>91</sup>.

The dissolution of pigment within MRP coatings leads to the release of cations that can influence IGSCC crack growth rates. The composition and chemistry of pigments in a MRP coating dictates the type of cation released into solution where the corrosion rate determines the rate of cation release. The dissolved cations in solution can chemically inhibit corrosion processes on bare aluminum surfaces and have been shown for  $Cr^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$  on a 2xxx-, 5xxx-, and 7xxx-series aluminum alloys. It should be noted that not all dissolved cations inhibit

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corrosion to the same extent and some cations such as Al<sup>3+</sup> can accelerate corrosion <sup>37</sup>. In addition to chemical inhibition, the precipitation of corrosion resistant scales can form on bare aluminum surfaces once equilibria criteria are achieved and vary based on the chemistry of the precipitate <sup>91,111</sup>. Further studies investigating the SCC inhibition characteristics of MRP coated AA 7075-T651 in 0.6 M NaCl is warranted. These studies should include the influence of varying concentration of relevant cation concentrations.

### Conclusions

The effects of applied potential dependence on the EAC behavior of AA 7075-T651 immersed in 0.6 M NaCl solution was assessed using a fixed dK/dt methodologies in combination with various electrochemical techniques including hydrogen evolution experiments. Based on the results gathered in these experiments the following insights were obtained.

- 1. AA 7075-T651 immersed in 0.6 M NaCl exhibit a decrease in stage II crack growth rate by  $\frac{1}{2}$  order of magnitude under the applied potentials of -0.9 V<sub>SCE</sub> and -1.0 V<sub>SCE</sub>.
- 2. The potentials associated with minimal hydrogen evolution overlaps with the potential associated with reduced stage II crack growth rates. These potential ranges exhibit the least corrosion damage as viewed in optical cross-section characterization.
- 3. The crack growth rates are still sufficiently high, even within the potential 'well', and does not constitute a meaningful reduction in EAC.
- 4. The mechanism of SCC in 7xxx-series aluminum alloys involves anodic dissolution assisted hydrogen embrittlement.
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Tables, Chapter 2 – Task 1

**Table 1: Composition data** 

Al	Zn	Mg	Cu	Cr	Fe	Si	Mn	Ti
Bal	5.7	2.5	1.7	0.19	0.26	0.06	0.03	0.03

Table 2: Mechanical properties – we will likely provide just averages in the paper.

$\sigma_{YS}$ (MPa)	σ <sub>UTS</sub> (MPa)	E (GPa)	RA
470	561	72.1	0.086

## Figures, Chapter 2 – Task 1

## Figure 1



**Figure 1:** Measured stress intensity versus crack growth rate relationships for AA7075-T651 fully immersed in 0.6 M NaCl as a function of applied potential. The dashed black line in (a)

reflects the measured relationship in a dry  $N_2$  (RH < 5%) environment, which was then used to correct the applied potential data, shown in (b).





**Figure 2:** Effect of applied potential on the (a) threshold stress intensity and (b) Stage II crack growth rate for AA7075-T651 immersed in 0.6 M NaCl.



Figure 3. Scanning electron micrographs of the crack tip achieved during constant dK/dt = 0.5 MPa $\sqrt{m/hr}$  at a potential hold of a) -0.8VSCE and b) -1.3V<sub>SCE</sub> under full immersion in 0.6 M NaCl.





Figure 4: a) Monitored current density across a range of applied potentials for AA7075-T651 during 6-hour full immersion in 0.6M NaCl, b) the combined plot of applied potential vs current density (y-left) and average H<sub>2</sub> evolution rate (y-right), c) a narrowed potential window [-1100 to -750 mV<sub>SCE</sub>] shown for each current density, and d) and average evolution rate. These data consider the entire 0.785 cm<sup>2</sup> exposed area to contribute to hydrogen formation.

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Figure 5
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Figure 5: Optical microscopy with cross-sectional analysis on AA7075-T651 after exposure to six-hour full immersion hydrogen evolution experiment in  $H_2$  saturated 0.6 M NaCl showing the transition in corrosion morphology in the applied potential range of -0.6 V<sub>SCE</sub> to -1.6 V<sub>SCE</sub>.





Figure 6: Long term OCP (**a**) with polarization curves for AA 7075 – T651 shown in **a**) and **b**) in 0.6M NaCl at pH 3, unadjusted (6), 9, 10, and 11.





Figure 7: Long term OCP (**a**) with polarization curves for MgZn<sub>2</sub> shown in **a**) and **b**) in 0.6M NaCl at pH 3, unadjusted (6), 9, 10, and 11.

Figure 8



Figure 8: The pitting potential and corrosion potential shown respectively in **a**) and **b**) obtained from the polarization curves of AA7075-T651 and MgZn<sub>2</sub>.





Figure 9. Aluminum E-pH diagram showing the effects of both cathodic (red) and anodic (black) polarization from bulk electrolyte conditions (blue) and the effects on the potential/pH of the electrochemical system which is demonstrated schematically. The specific crack tip potential/pH values are not experimentally verified in this study. The concentration of Al<sup>3+</sup> is taken to be 10<sup>-6</sup> M.

# Chapter 3 Task 2 – Electrochemical Evaluation of Al-5 wt% Zn Metal Rich Primer for Protection of Al-Zn-Mg-Cu Alloy in NaCl

A. Korjenic, L. Blohm, A. Druschitz, J.R. Scully

#### **Abstract**

An intact and X-scribed Al-5wt%Zn rich primer (AlRP) without pretreatment or topcoat was evaluated for its ability to suppress potential dependent intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGC-SCC) of peak aged AA7075A-T651 in NaCl salt fog and full immersion. The ability of the primer to provide sacrificial anode-based cathodic prevention of peak aged AA7075-T651 substrate was evaluated both under the primer coating and at scratches. The AIRP evaluated consisted of an epoxy-based resin embedded with spherical Al-5wt%Zn pigment particles. Performance was evaluated under full immersion in 0.6 M NaCl solution and compared to ASTM B117 salt spray exposure using two approaches. These consisted of the University of Virginia (UVA) cycle test on intact coatings and the full immersion galvanic couple testing on simulated scratched panels created when intact coatings form bimetal couples with bare AA7075-T651. Focus was placed on the ability of the AlRP to achieve a targeted intermediate galvanic couple potential near a "prevention" potential which suppresses stress corrosion crack growth, intermetallic particle corrosion as well as intergranular corrosion. The long term (24-hour) open circuit potential (OCP) of AIRP coated AA7075-T651 in 0.6 M NaCl indicated that the AIRP provided less than 100mV of cathodic potential shift of the intact coating from its OCP in 0.6 M NaCl. Electrochemical cycle testing conducted at a potentiostatic hold of -0.95 V<sub>SCE</sub> demonstrates that the AIRP did not enable sacrificial anode-based cathodic protection as the coupled potential remained at the corrosion potential of bare AA7075-T651. Furthermore, the current observed throughout galvanic corrosion experiments coupling of AIRP to AA7075-T651 indicated the AIRP coating was a cathode in the bimetal galvanic couple. ASTM B117 salt spray exposure of the AIRP revealed oxidation of the AA 7075-T651 substrate below the primer detected as a continually growing oxygen signal at the primer-substrate interface that did not arrest corrosion over the exposure period.

## **Introduction**

AA7xxx-series alloys are often used in aerospace industry due to their high strength-toweight ratio and general corrosion resistance<sup>1,2</sup>. These aerospace aluminum allovs (AA) are in frequent exposure to marine environments in which chloride is abundant and serves to accelerate corrosion <sup>1–4</sup>. These alloys have experienced in-service intergranular corrosion (IGC) and stress corrosion cracking (SCC) due to the corrosion of the strengthening precipitate phase  $MgZn_2$ <sup>5,6</sup>. The  $\eta$  phase, MgZn<sub>2</sub>, is highly anodic to the matrix and rapidly dissolves in aggressive (e.g. aqueous chloride) environments, enabling severe IGC and intergranular stress corrosion cracking (IG-SCC) under sufficient applied load<sup>7-12</sup>. The  $\eta$  phase can be heterogeneously precipitated on grain boundaries during heat treatment as well as by natural aging. The IG-SCC behavior is hypothesized to be governed by a coupled anodic dissolution process (i.e. electro-dissolution of the grain boundary  $\eta$  phase and the surrounding matrix), which also catalyzes the formation of an aggressive acidified local crack tip chemistry that facilitates the enhanced generation of crack tip hydrogen and uptake which then enables embrittlement in the fracture process zone<sup>7,13,14</sup>. The IG-SCC crack growth rate exhibits a great deal of potential dependence under potentiostatic conditions (PS) in 0.6 M NaCl<sup>15</sup>. Therefore, the mitigation of both IGC and IG-SCC is possible through the establishment of more negative potentials than the pitting potential of the  $\eta$  phase,  $E_{pit(\eta)}$ . This furnishes a possible mitigation strategy based on electrochemical galvanic protection for use in marine service. This situation can be described by the term "sacrificial cathodic prevention" where the goal is to polarize below selected critical potentials that are associated with local corrosion 3,16,17

In marine environments the susceptibility for environmentally assisted cracking (EAC) and stress corrosion cracking (SCC) is high. The environmentally assisted cracking (EAC) of Al-Zn-Mg-Cu alloys in aqueous environments, including water vapor, has been heavily studied with many proposed models investigating the origins of the SCC mechanism <sup>7,13,18</sup>. Crack initiation or incubation is largely thought to dominated by anodic dissolution of bare Al which in turn forms critical defects such as pits <sup>6,15</sup>. The suppression of environmental fracture presents a more demanding objective than does the typical static protection of an underlying substrate against uniform corrosion.

Metal rich primers (MRP) are a promising corrosion prevention technique as they exhibit active corrosion control by incorporating metallic pigments which are selected to be electrochemically more active than the substrate and/or its detrimental phases<sup>19–21</sup>. There are a variety of pigment options that function as an active anode such as Al, Al-Co-Ce<sup>22-24</sup>, Zn<sup>25-32</sup>, Mg <sup>19,20,33-43</sup> as well as composite coating systems combining multiple pigment types into the same coating <sup>44–46</sup>. These active anode pigments are tasked with providing corrosion protection; however, each pigment system offers varying types of protection such as operating a sacrificial anode when galvanically coupled to the aluminum substrate, active inhibitor release in the form of dissolved cations in solution which protect bare scratches, and barrier properties that may develop as the corrosion products form on the surface of the coating. Moreover, there are a range of passivated metal-oxide pigments such as MgO, which is novel in its own regard as a Mg-based coating. MgO primers showed evidence of prolonged chemical dissolution of pigments that resulted in Mg(II) compound formation at scratches, chemistry change to suppress local corrosion and reductions of corrosion in field exposure samples at Kennedy Space Center (KSC) <sup>39,47,48</sup>. The oxidized MgO pigment did not provide sacrificial anode-based protection by electrochemical processes.

In order for an MRP to provide cathodic protection by electrochemical processes, a given MRP must maintain electrical and ionic connection to the AA7075-T651 substrate establishing a mixed potential based galvanic couple where the AA7075-T651 is cathodically polarized below the corrosion potential of AA7075-T651 ( $E_{corr, 7075}$ ) and  $E_{pit(\eta)}$  by the MRP which improves corrosion resistance <sup>36,39,47-49</sup>. Sacrificial anode-based cathodic protection is an active protection mechanism as the cathodic polarization of the substrate can extend from the intact coatings into coating defects of various dimensions (e.g. pores, scratches, pinholes). Pigmented primers for the sacrificial anode based cathodic protection have been found to depend on the pigment volume concentration (PVC), shape, and distribution of pigment on the properties <sup>39,47,50–53</sup>. The distance over which the protection is available in the defect is termed the throwing power of the coating <sup>33,48,54</sup>. A range of MRP with varying pigment chemistries (Al, Mg, Zn) have been tested on 2XXX and 5XXX-series aluminum alloys indicating an ability to provide active protection <sup>7,48,55–61</sup>. However, little work has been conducted on assessing the corrosion behavior and performance of these MRP applied to 7XXX-series aluminum alloys.

Each pigment systems offer these modes of protection, however, to varying effectiveness. In the Al-Co-Ce system, for example, release rates of Co- and Ce-based inhibitors depend on pH and  $[Cl-]^{62}$ . Sacrificial aluminum anodes for the protection of aerospace aluminum alloys range from the use of Al-Zn-In <sup>63,64</sup> and Al-Zn-Mg <sup>65</sup>. Moreover, the addition of Sn has been observed to have a positive influence on the corrosion properties and increase the resistance to IGC of a Al-Zn-Mg alloy with alloying additions of < 1wt% <sup>65</sup>The addition of Si to Al-Zn-In pigment tends to increase the degree of uniform corrosion due to the formation of refined, reduced grain size, smaller spacing between dendritic arms, and formation of equiaxial disk-shaped precipitate structure <sup>64</sup>. The use of Li carbonate as a corrosion inhibitive pigment has also been shown to be an effective chemical inhibitor increasing defect protection via leachable lithium salt which forms lithium carbonates and oxalates in scratches <sup>66,67</sup>.

Rare earth metal salt (REMS) containing corrosion resistant polymer coatings have been investigated using a range of rare earth metals such as Ce<sup>68–73</sup>, lanthanum<sup>74–76</sup>, and praseodymium<sup>77</sup> where inhibition effects were observed on AA2024. The work of Warner et al showed that the molybdate ions were proven to be an effective inhibitor to environmentally assisted fatigue crack growth propagation in AA7075-T651 during full immersion in chloride containing solution<sup>78</sup>. Previous investigations showed that an increase in the local pH due to cathodic corrosion at the interface of AA2024 leads to the formation of cerium hydroxy-complexes when the Ce is present as inhibitor in the form of Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O <sup>79</sup>. Interest has been increasing in the properties of layered double hydroxides (LDH) as functional materials for corrosion protection in the form of inhibitors, pigments, and pretreatment layers <sup>80</sup>. These LDH have been observed to increase corrosion resistance to filiform corrosion on AA2024 <sup>80</sup>.

Hence, numerous Al-based primers have been considered to achieve long-term cathodic protection on Al alloy substrates, however little published work exists pertaining to their overall performance in aggressive saline environments with limited literature in this area on AA7075-T651<sup>36,38,39,48</sup>. Aluminum pigments such as Al/Al<sub>2</sub>O<sub>3</sub> flaked pigments embedded within polypyrrole have been observed to not show evidence of electrochemical interaction with the AA2024-T3 substrate via scanning vibrating electrode technique (SVET) which is distinctly different from sacrificial Mg pigments <sup>81</sup>. This aluminum flake was shown to activate gradually as the passive Al<sub>2</sub>O<sub>3</sub> outer layer dissolves or as electrolyte saturation of the binder film under de-

aerated conditions in Dilute Harrison's Solution (DHS) occurs. However, it is observed to have little ability to suppress the potential below the OCP of the AA2024-T3 substrate <sup>81</sup>. The close proximity of the OCP of these coatings to that of Al substrates (low  $\triangle OCP$ ) makes this technology a promising candidate for long-term cathodic protection without the danger of over-protection and cathodic corrosion, as long as the pure Al or alloyed pigments can activate and then remain active (anodic) relative to the substrate. The use of an Al-based rich primer is challenged by the requirement to balance effective cathodic prevention while avoiding cathodic corrosion <sup>82–86</sup>. This means that the OCP of the AIRP must be tuned to protection, on one hand, and not overprotection. In the case of AA 5456 the range of protective potentials extends from -0.85 V<sub>SCE</sub> to -1.0 V<sub>SCE</sub> whereas AA7075-T651 ranges from -0.75 V<sub>SCE</sub> to -1.0 V<sub>SCE</sub> <sup>87–89</sup>. The observation of corrosion suppression is the first step – in separate testing it has been established that the protection potentials suppressed IGC. Namely, when the potential established is in a certain range below E<sub>pit,matrix</sub> and near E<sub>pit,n</sub> intergranular corrosion is suppressed.

Traditional legacy systems have used chromate-based coatings which function based on the release of chromate ions to chemically inhibit corrosion on aluminum alloys <sup>84,90–92</sup>. Although chromate-based coatings are very effective, there are concerns over toxicity of hexavalent chromium as well as growing requirements in Department of Defense (DoD) and aerospace industry that motivate the quest for alternative coating solution <sup>93–96</sup>. This study focuses on a prospective alternative to chromate-based coating systems by investigating an AlRP applied to AA7075-T651 free of inhibitors, pretreatment, and top coatings. This may not be reflective of realistic field implementation of a multilayered coating systems; however, this allows for the determination of the effectiveness of a specific primer system free of the influences of multilayered coating systems.

Related investigations evaluated organic and inorganic Zn-rich primers on highly sensitized AA5456-H116, demonstrating a robust ability in this primer technology to achieve intermediate cathodic potentials in 0.6 M NaCl<sup>97</sup>. This study focuses on assessing the capacity of an AIRP that is alloyed with 5 wt% Zn to provide sacrificial anode based cathodic protection to an AA7075-T651 substrate. The alloying of Al pigment with Zn is intended to lower the electrochemical potential promoting the MRP to serve as an anode with respect to AA7075-T651 in accordance with the galvanic series in seawater <sup>98,99</sup>. Electrochemical comparisons between Al-

5wt%Zn pigment and its bulk alloy were made to elucidate the differences in the pigment chemistry without the influences of the epoxy coating. The present work will utilize a previously developed combination of test methods targeted to evaluate the AIRP sacrificial anode based cathodic prevention without cathodic corrosion <sup>38-40,51,59,100</sup>. This was achieved by galvanic corrosion testing with the use of a zero-resistance ammeter (ZRA) <sup>49,87,101–103</sup>, the anodic charge capacity of the pigment via the UVA cycle test <sup>32,39,51,57,104</sup>, and accelerated environmental exposure in the form of ASTM B117 with post-mortem analysis <sup>33,35,48,92,105,106</sup>. The UVA cycle test method is a type of diagnostic DC/AC/OCP cycle testing and is a well-proven evaluation of the ability of a candidate coating ability to provide sacrificial cathodic protection in the presence of a remote cathode such as exposed AA7075-T651 substrate at the site of a macro-defect <sup>48</sup>. Greater mechanistic information is gathered than provided in the case of ASTM B117 salt spray alone and field exposure followed by postmortem characterizations. However, there is no correlation between life in service and life in the field nor a universal relationship between the number of cycles in a test and the coating lifetime in the field. The UVA cycle tests herein consist of a repetition of OCP, potentiostatic electrochemical impedance spectroscopy (EIS) (at OCP), and a potentiostatic holds (at -0.95V vs SCE) to assess the coating charge capacity, galvanic couple, and primer barrier properties after various amounts of charge utilization (i.e., discharge). A comparison of the benefits and pitfalls of testing using the aforementioned electrochemical testing methods is provided. The application of an MRP coating under service conditions is often accompanied by a pretreatment layer and finished with a topcoat to improve barrier protection. In this study, MRP on bare AA 7075-T651 was tested for simplicity.

### **Experimental Procedure**

## Materials: AA7075-T651, Al-5wt% Zn, and Al-Rich Primer

Rectangular plates of peak aged and stress relieved AA7075-T651, with composition shown in **Table 3-1**, were machined to dimensions 1.5 mm thick, 200 mm long, and 76 mm wide via Mager<sup>TM</sup> high speed cut off saw. Coupons of AA7075-T651 were cleaned of all grease from the surface via alcohol bath and air dry prior to spray coating application. Luna Innovations, Inc. and DEVCOM Army Research Lab performed the cold spray-coating process of the AlRP using thoroughly mixed formulations as shown in **Table 3-2** to Milspec. As shown in **Table 3-2**, the

resin/pigment combination of the AIRP as produced by Randolph Coatings (Chicopee, Massachusetts) and designation is: epoxy resin, 27 pigment volume percent (PVC) Al-5wt% Zn pigment. These pigments embedded in the AIRP are approximately spherical. No pretreatments or topcoats were considered and all coatings were tested in both as-received intact condition as well as in the presence of a conventional X-scribe defect of 250 – 300 µm exposing the underlying substrate AA7075-T651 in accordance with ASTM D1654 using a tungsten carbide scribing tool <sup>72,73</sup>. A bulk Al-5wt%Zn cylinder was synthesized at Virginia Tech via melting in a Thermo Scientific box resistance furnace with molybdenum disilicide elements melting 5 times to increase homogeneity. Melting and casting was conducted in a graphite crucible. The MgZn<sub>2</sub> sample was procured through the Kurt J. Lesker company in 3-6-gram pellets. Typical synthesis procedures follow induction melting under slight vacuum in argon containing environment to reduce volatilization and oxidation.

## **Coating Characterization**

The candidate coating cross-sections were characterized through scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) on a Quanta 650 system for imaging and elemental analysis under magnification of 500x, spot size of 5 nm, and accelerating voltages of 10 kV at 10<sup>-8</sup> torr to mitigate charging. All samples were embedded in epoxy and sputter coated using a Cressington-108 Au-Pd sputter coater at 30mA for 40 seconds at a standoff distance of 5 cm to aid in micrograph acquisition with Au and Pd eliminated from EDS elemental analysis. The average pigment size and primer thickness values are reported in **Table 3-2**. The average pigment size and coating thickness were confirmed through the consideration of 10 vertical thickness measurements on 3 pristine AlRP cross-sectional areas under SEM. Cross-section polishing was carried out by wet polishing in water to 1200 grit using an abrasive silicon carbide pad.

Metal rich primer crystalline composition and corrosion product identity were analyzed using X-ray diffraction (XRD), which measured the intensity of the pigment content before and after cyclic testing. A Cu-Ka source (1.54nm) was used on an Empyrean diffractometer with a 40-mA beam accelerated at 45 kV to perform continuous scans from  $20 - 120^{\circ}$  at a step size of 0.02. Previous analyses on similar thickness Zn-rich primers demonstrated the continual presence of a major Al peak at approximately 44.5°, which proved that the entirety of the AlRP was being

sampled <sup>50</sup>. Al-5wt.% Zn pigment peaks were not differentiable from the 7075-T651 substrate, and thus Al-rich pigment depletion was not evaluated. Raman spectroscopy was utilized for crystalline as well as amorphous corrosion product identification. Raman measurements were conducted using a 200 mW, 514 nm laser at 50% power under a 50x objective lens through an 1800 1/mm visible grating. Scans were accumulated 5 times at 15 second acquisition duration through a range of 200-1300 cm<sup>-1</sup>, the Raman shift peaks were characterized based on the RUFF database. This relatively surface sensitive Raman spectroscopic analysis complemented the XRD findings in the identification of corrosion product formation.

## **Initial Corrosion Electrochemistry Investigation**

Potentiodynamic polarization scans were conducted on AA7075-T651 (ST rolling orientation), MgZn<sub>2</sub>, AlRP coated AA7075-T651, as well as 99.99% pure Al, Zn, Cu, and Mg, and a synthesized a bulk Al-5wt%Zn alloy. Potentiodynamic scan started at 50mV below the open circuit potential and scanned upward at a rate of 1mV/s with an exposed area of 0.785 cm<sup>2</sup>. Long term open circuit potential monitoring was carried out for both AA7075-T651 and AIRP coated AA7075-T651. All samples aside from AIRP coated AA7075-T651 are polished to 1200 grit SiC paper until a mirror finish was obtained. Electrochemical tests were conducted with a standard three electrode cell with sample as the working electrode (WE), saturated calomel reference electrode (SCE), and a Pt counter electrode (CE) using a Gamry 600 potentiostat. Electrochemical testing is conducted in non-aerated quiescent 0.6 M (3.5wt%) NaCl solution under full immersion. According to mixed potential theory, the quantity of exposed sacrificial particles connected to the substrate will affect the coupled potential and the overall corrosion rate in the substrate. The galvanic couple is mediated by the electron transfer kinetics of the anodic pigment, the cathodic substrate, and the electrical and ionic resistances between the two. Fine tuning the galvanic couple potential of an MRP coating with its substrate may be achieved by purposeful alloying of the pigments used within the coating reaching a balance between fast sacrificial anode kinetics, maintaining a galvanically coupled potential below that of the substrate, and activity of the pigment to resist passivation and deactivation. The variation in electrochemical behavior of AA 7075-T651, AIRP coated AA 7075-T651, and bulk Al-5wt%Zn as a function of chloride concentration ([Cl<sup>-</sup>]) is conducted by varying NaCl concentration under non-aerated quiescent full immersion conditions. All electrochemical testing was triplicated for consistency.

## The UVa DC/AC/OCP Cycle Test: Charge Output and Barrier Assessment of Al-Rich Primer

The AIRP coating system was evaluated under full immersion conditions in a controlled laboratory environment to assess electrochemical characteristics and performance as a sacrificial anode during cathodic prevention owing to the galvanic couple between the AIRP and the AA7075-T651. The UVa DC/AC/OCP test has been used extensively and is of great merit for a variety of primers because the DC hold potential can be tuned to match the galvanic couple potential sought or that prevails for a given alloy and pigment. Similar MRP systems have been tested using a variety of realistic exposure conditions on AA2xxx-, 5xxx, and AA7xxx-series alloys, though limited analyses has been reported to understand the behavior of a MRP on AA-7xxx with or without topcoat <sup>42,107–109</sup>. The anode charge capacity, residual coating barrier characteristics, and galvanic couple potential of the primer-substrate system after various states of discharge were recorded throughout DC/AC/ OCP testing. The cycle testing follows a 14 OCP/EIS/PS hold procedure summing up to a 100 hours of polarization time as shown in **Table** 3-4. Herein the selected galvanic couple potential for AA7075-T651 was selected to be -0.95  $V_{SCE}$ and cumulative 15 hours OCP collection time, and 100 net hours of DC polarization time. The basis for -0.95 V<sub>SCE</sub> galvanic couple potential is to polarize below critical potentials that are posited to provide protection such as the pitting potential of MgZn<sub>2</sub>. Cycle testing was performed in triplicate to confirm reproducibility.

The OCP stage of cycle testing demonstrated the level of continuity of galvanic coupling between the AIRP and the peak aged stress relieved AA7075-T651 relative to the primer pigment. Metal rich primers are considered activated at the point of the most negative established OCP during cycle testing. Mixed potential theory dictates that the magnitude of the galvanic couple potential is affected by the surface area of the metal pigments, their polarization characteristics (i.e., electrochemical reactivity) as well as the exposed surface area ratio between the bare AA7075-T651 and AIRP coated AA7075-T651<sup>32,54,56</sup>. The subsequent EIS stage then assesses the barrier properties of the intact primer with a frequency between 10<sup>5</sup> and 10<sup>-2</sup> Hz, 10 points per decade, and an AC amplitude of 65mV rms. Equivalent circuit fitting of the EIS results in terms of a resistive-capacitive (RC) circuit then enabled the quantification of the pore, coating, and solution resistances as well as coating and double layer capacitance <sup>38,39,42,51,59,108,110–113</sup>.

## Galvanic Corrosion Analysis using Mixed Potential Theory, DC Corrosion Electrochemistry, and Zero-Resistance Ammetry

The galvanic corrosion between the AA7075-T651 substrate simulating a bare scratch and the AIRP was assessed through the use of a zero-resistance ammeter (ZRA). During the test, a previously unexposed (hereafter referred to as a pristine and intact) AA7075-T651 and AIRP coated AA7075-T651 was coupled with bare alloy simulating a scratch as a bimetal couple in a galvanic corrosion cell. The galvanically coupled currents and galvanically coupled potential associated with the dissimilar electrodes were monitored throughout a 24-hour exposure period in 0.6 M NaCl using natural aeration. The bare 7075-T651 substrate operates as the WE where the AIRP coated alloy was connected as the CE and a SCE as reference. Thus, a negative or cathodic current on the bare 7075 indicates electron flow entering the cathode. The distance between WE and CE was > 4 cm limiting chemical, but not electrochemical, interactions. Galvanic couple testing was conducted in a 1:1 (AIRP: bare 7075) area ratios to assess the effect of a drop covering a scratch with a small adjacent area covered with coating referred to as 1:1 area ratio. This may be similar to discrete electrolyte drops near a scribe as in atmospheric corrosion. Galvanic corrosion testing was conducted with an exposure area of 0.785 cm<sup>2</sup>. In order to further understand the influence of pigment chemistry of the Al-5wt%Zn on the electrochemical properties of the AlRP coating the monitoring of galvanic corrosion between bulk synthesized Al-5wt% Zn alloy (WE) and AA 7075-T651 (CE) was conducted. A positive anodic current between the galvanic corrosion of Al-5wt% Zn alloy (WE) and AA 7075-T651 (CE) indicates the Al-5wt% Zn alloy as an anode. The tests conducted were triplicate to ensure the trends shown are characteristic.

## **ASTM B117 Q-Fog Salt Spray Testing**

Accelerated life testing (ALT) of AlRP was performed on intact as well as scribed AlRP panels in accordance with ASTM B117 at DEVCOM ARL using an Auto Technology salt fog chamber <sup>65,77</sup>. During ALT, both intact and scribed panels were exposed for a six -week window with samples being removed from the testing chamber every two weeks for characterization. Each two -week sampling of salt spray exposure testing consisted of 3 intact and 3 scribed panels. Unexposed intact and scribed samples were maintained to provide a baseline characterization profile as a control to determine the extent of damage accumulation. All samples were rinsed with deionized water prior to handling and storage for subsequent characterization. Electrochemical

testing in the form of OCP monitoring, potentiodynamic polarization, and EIS testing was conducted following each 0, 2, 4, 6-week ASTM B117 salt spray testing panel for intact AIRP coatings. Damage profile characterization across the six -week exposure window was documented with SEM back-scatter imaging (BSI) microscopy conducted with a Phenom SEM and EDS elemental mapping to the same specification as the parameters described above. The oxygen signal from elemental map is shown as a marker for the observed oxidation in both cross-section map scan and plane view with line scan profiles across the scribed region. Scribe corrosion and protection against IGC was assessed by washing unexposed and uncoated AA7075-T651, post six -week bare AA7075-T651, and AIRP coated AA7075-T651 ASTM B117 samples in 70% nitric solution for 5 minutes with gentle pipetting to remove accumulated corrosion products from the surface of the MRP and interior of the scribe. Once exposed to 70% nitric solution, the AIRP coating was dissolved within 2-3 minutes, therefore micrographs do not show the presence of the AIRP at the scribed regions due to dissolution of the coating. Comparison are drawn from a scribed bare AA 7075-T651 post six -week ASTM B117 panels.

### **Results**

## Characterization of As-Received AA7075-T651/Al-Rich Primer

Baseline assessment utilized BS-SEM imaging with EDS elemental mapping on AlRP-7075 cross-sections to assess primer thickness and particle size at 500x magnification. These characteristics are seen in **Table 3-2** and **Figure 3-1** for Al-5wt% Zn. The AlRP contains spherical pigment with average diameter of 10.3  $\mu$ m. The micrographs in **Figure 3-1** shows that the pigments are close packed enough to provide some electrical contact throughout the thickness of the epoxy-based coating applied to a AA7075-T651 substrate via the individual primer particles but not every particle is connected to one another. The AlRP was not mechanically tested in the present study to differentiate adhesion/elasticity properties, through no deficiencies in primer adhesion to the 7075-T651 substrate were observed in the samples before or after cycle testing utilizing the -0.95V<sub>SCE</sub> DC hold.

## **Initial Corrosion Electrochemistry Investigation**

Investigation in the polarization behavior of AA7075-T651, pure elements, and detrimental MgZn<sub>2</sub> phase are shown in **Figure 3-2**. Recall the strengthening phase in 7xxx alloy is eta phase, MgZn<sub>2</sub>, which forms heterogeneously formed on the grain boundary. The potentiodynamic polarization provides the basis for assessing potential ranges in which IGC may be the predominant mechanism of SCC according to an anodic dissolution mechanism based on differences in critical potentials. The AA7075-T651 shows a corrosion potential of -0.75 V<sub>SCE</sub>. The MgZn<sub>2</sub> phase is seen to have a corrosion potential of -1.1 V<sub>SCE</sub> with pitting potential at -0.85 V<sub>SCE</sub>. The electrochemical theory of Galvele posits that IGC occurs when the applied potential or E<sub>app</sub> is such that E<sub>pit,MgZn<sub>2</sub></sub>  $< E_{app} < E_{pit}$  or  $E_{repass,7075}$  <sup>82,83</sup>. One concept for cathodic prevention posits that protection is achieved when the eta, MgZn<sub>2</sub>, is cathodically protected below  $E_{pit,MgZn_2}$ <sup>82,83</sup>. The electrochemical behavior of MgZn<sub>2</sub> is in good agreement with the findings of Birbilis et al<sup>88</sup>. The polarization behavior of AIRP coated AA7075-T651 is shown in Figure 3-3 compared with the bare AA7075-T651. The AIRP coated AA7075-T651 is shown to have a reduction in the current density by as much as three orders of magnitude compared to bare AA7075-T651 (Figure 3-3). A long term, 24-hour, OCP monitoring shown in Figure 3-4 for both bare and AIRP coated AA7075-T651 shows the AIRP remains at or below the OCP of AA7075-T651 by up to 80mV. (Figure 3-4). The AIRP is witnessed to activate periodically throughout the 24-hour scan dropping in OCP 80mV or less ultimately which could polarize to the OCP of the AA7075-T651 substrate. This potential shift is insufficient to provide protection against IGC and IG-SCC as the potential is not depressed below E<sub>pit,MgZn<sub>2</sub></sub>by the Al-5wt% Zn pigment in the AlRP.

Understanding the effect of chloride concentration, [Cl<sup>-</sup>], on the electrochemical properties of bulk Al-5wt%Zn alloy is shown in **Figure 3-5**. Recall Al-5wt%Zn is the same composition of aluminum pigment within AlRP MRP coating system. Electrochemical testing in the form of 24hr OCP, PDP, and EIS is conducted by varying the concentration of NaCl between 1mM, 10mM, 100mM, and 1000 mM (1M) on uncoated Al-5wt% Zn ingot. **Figure 3-5a** shows the 24-hour OCP of Al-5wt%Zn alloy across a range of [Cl<sup>-</sup>] which indicates a decrease in the OCP with increasing [Cl<sup>-</sup>]. The 24-hour terminal OCP of bulk Al-5wt%Zn at 1 M NaCl rests at -0.99 V<sub>SCE</sub> which is 40 mV below the  $E_{pit(\eta)}$ . The variation in polarization behavior and electrochemical impedance spectra are shown in **Figure 3-5b** and **3-5c** respectively. The corrosion potential and pitting potential of Al-5wt%Zn alloy are shown to vary as a function of [Cl<sup>-</sup>]. The corrosion potential of Al-5wt%Zn alloy at 1 M NaCl, approximately equal to lab made seawater ranging from 0.6 M NaCl, is -0.95 V<sub>SCE</sub> very near to the pitting potential. The pitting potential become more negative with increasing [Cl<sup>-</sup>] as seen in **Figure 3-5b**). The Bode magnitude impedance spectrum shown in **Figure 3-5c** with phase angle progression shown in **Figure 3-5d**. The barrier properties of the passivated Al-5wt%Zn electrode can be seen to vary as a function of [Cl<sup>-</sup>] with an apparent decrease in low frequency modulus behavior ( $Z_{mod}^{0.01 Hz}$ ) at a concentration of 1 M NaCl ostensibly due to dissolution behavior by the pitting of Al-5wt%Zn at high [Cl<sup>-</sup>] or more global depassivation. The variation in 24-hour terminal OCP for AA 7075-T651, MgZn<sub>2</sub>, AlRP coated AA 7075-T651, and bare bulk Al-5wt%Zn alloy is compared in **Figure 3-5e** across [Cl<sup>-</sup>] ranging from 10<sup>-2</sup> M to 2M NaCl concentrations. In summary, it is seen that bare Al-5wt% Zn can offer galvanic protection when depassivated or pitted at high Cl<sup>-</sup>. This is not consistent with the AlRP coating presumably due to low Cl<sup>-</sup> at the interface as well as the additional resistances present in the coating compared to a bulk alloy at the same composition of pigment.

## The UVa DC/AC/OCP Cycle Test: Charge Output and Barrier Assessment of Al-Rich Primer

The magnitude of the established OCP throughout DC/AC/OCP cycle testing is shown compared with the 7075-T651 OCP (-0.75 V<sub>SCE</sub>, black dashed line) in **Figure 3-6a**. The AIRP attained an OCP of -0.73 V<sub>SCE</sub> on the first cycle (10 minutes of polarization). The Al-5wt% Zn became activated to the fullest extent possible at a potential of -0.83 V<sub>SCE</sub> by cycle six (490 minutes). The AIRP sustains an E<sub>OCP</sub> between -0.8 to -0.83 V<sub>SCE</sub> for the remainder of the DC/AC/OCP cycle testing aside from cycle 12 which rose to an OCP of -0.77 V<sub>SCE</sub> (**Figure 3-6a**). The AIRP at cycle 1 polarized to -0.95 V<sub>SCE</sub> or E<sub>app</sub> < E<sub>pit,MgZn<sub>2</sub></sub> initially produced a current density of  $-0.87 \,\mu A/cm^2$  averaged over the total area of 0.785 cm<sup>2</sup> that decayed to and remained at  $-0.25 \,\mu A/cm^2$  after 1000 seconds (**Figure 3-6b**). The peak current produced occurred in cycle 13 at  $-1.62 \,\mu A/cm^2$  that decayed and remained at  $-0.3 \,\mu A/cm^2$  after 1000 seconds. These are cathodic current densities that do not contribute to protection of AA 7075 as the AIRP is not the anode. **Figure 3-6c** demonstrates the cumulative charge output associated with Al-5wt% Zn pigment oxidation for AIRP throughout DC/AC/OCP cycle testing. The electrochemical characteristics and performance of AIRP throughout the DC/AC/OCP are shown in **Table 3-3**. The

resulting charge accumulation is negative (-) indicating cathodic current density not contributing to the intended sacrificial anode-based cathodic prevention.

AIRP barrier properties were assessed via potentiostatic EIS (at the primer OCP) intermittently throughout PS cycle testing to monitor impedance and coating defect area progression with increasing exposure time <sup>98</sup>. Figure 3-6d and 3-6e show the Bode magnitude impedance spectrum as well as the phase angle progression throughout DC/AC/OCP testing sequence. The AIRP had low frequency impedance (Z\_{mod}^{0.01\,Hz})~response of 8.9  $\times~10^{5}ohm\cdot cm^{2}$ that decayed to 8  $\times$  10<sup>3</sup> ohm  $\cdot$  cm<sup>2</sup> after 100 hours of PS hold at -0.95 V<sub>SCE</sub>. Figure 3-6d reports the Bode phase angle progression throughout the cycle testing exposure in 0.6 M NaCl. This data is useful for the determination of defect area through use of methods such as the breakpoint frequency or saddle point frequency <sup>25,31,42,43,53</sup>. However, Al pigment was not consumed to the point where this was a factor. The variation in low frequency modulus of impedance can seen for each cycle in **Figure 3-7a** with very little degradation in barrier properties. The variation in OCP established at the end of each OCP cycle within DC/AC/OCP cycle testing can be seen in Figure 3-7b. The AIRP coating is considered activated at its lowest potential. The lowest potential observed throughout DC/AC/OCP cycle testing was in cycle 13 with a potential of -0.83  $V_{SCE}$ (Figure 3-7b). SEM BSI and EDS cross section characterization is shown in Figure 3-8 to assess the oxidation through the AIRP. The oxidation observed in the intact AIRP coating appears to occur throughout the interior pigment of the AIRP coating after 100 hours of imposed potential control at -0.95 V<sub>SCE</sub>. Evaluation of primer galvanic couple kinetic behavior may provide further evidence towards understanding these differences in MRP performance.

## Substrate – Primer Coupled Potential and Current Densities

Galvanic couples were investigated with a bimetal couple consisting of intact coating electrically connected to bare AA7075-T651. The AlRP does not suppress the open circuit potential of the substrate as seen in **Figure 3-9a**. The unadjusted pH of quiescent 0.6 M NaCl is measured experimentally at pH 5.5-6.0 and remains the same throughout the duration of the galvanic coupling of AlRP coated AA7075-T651 to bare AA7075-T651. The galvanic couple potential never drops below -0.75 V<sub>SCE</sub> and the galvanic current is positive with respect to the bare AA7075-T651 which is the WE. This indicates that the AlRP is the cathode, and the bare scratch is the anode. The AlRP:7075 galvanic couple results in  $0.5 \mu A/cm^2$  of anodic current

(Figure 3-9b). This galvanic relationship will not protect the bare AA7075-T651 in the mixed potential framework developed here as discussed below. This is further reinforced by the integration of the current density vs time revealing a positive charge on the bare AA7075-T651. The charge supplied by the AIRP indicates cathodic current (-) suggesting the AIRP does not protect. The AIRP does not function as a sacrificial anode when applied to AA7075-T651. A bimetal galvanic couple between bare AI-5wt% Zn alloy (WE) to a bare AA 7075 (CE) was also investigated as shown in Figure 3-10. The galvanically coupled potential between the AI-5wt% Zn alloy to a bare AA 7075 is stable at -0.96 V<sub>SCE</sub> with a galvanically coupled current of +14  $\mu$ A/cm<sup>2</sup> (Figure 3-10). The galvanically coupled potential as well as the anodically coupled current between the AI-5wt% Zn alloy and the bare AA 7075 indicates an ability of the bulk AI-5wt% Zn alloy to provide sacrificial anode based cathodic protection to AA 7075-T651 (Figure 3-10). This illustrates one of the challenges in pigment and coating design as the galvanic coupling of bare bulk samples does not entirely reflect the coating corrosion performance of MRP coated systems. This may be due to factors such as the added resistances of individual pigment-epoxy junctions, the number of isolated pigment particles, and low PVC of the AIRP.

## Lab Accelerated Testing – ASTM B117 Salt Spray

Intact and X-scribed AIRP was tested in humid marine environments carried out with ASTM B117 salt spray cabinet to assess the corrosion progression with increasing exposure time and scratch protection. Open circuit potential monitoring of the AIRP through the progression of ASTM B117 salt spray testing is shown in **Figure 3-11a**. A decrease to -0.95 V<sub>SCE</sub> occurs after six weeks of accelerated exposure testing in 0.6 M NaCl. **Figures 3-11b** and 3-11c show the Bode magnitude impedance spectrum and progress of phase angle intermediately collected throughout ASTM B117 salt spray testing. The AIRP had low frequency impedance of 2.26 × 10<sup>6</sup> ohm ·  $cm^2$  that decreased to 1.28 × 10<sup>3</sup> ohm ·  $cm^2$  after six weeks of accelerated exposure testing (**Figure 3-11b**).

Under paint and scratch corrosion evolution throughout ASTM B117 exposure is reported in **Figure 3-12** and **Figure 3-13** using BSI and the oxygen signal from EDS. The oxygen signal is used to track corrosion damage. The intact AIRP coated AA7075-T651 with no exposure is seen in **Figure 3-12a**) and **3-12b**). They provide a basis for comparison to conditions after exposure to ASTM B117 salt fog. The BSI micrograph shows the cross-sectional view of the AIRP coated AA7075-T651 with no apparent oxidation present from oxygen EDS signal in zero-week or untested condition (**Figure 3-12a**). The two-week ASTM B117 exposure is seen to indicate oxidation present at the coating-electrolyte interface, coating-substrate interface, within the scribed region, and on the interior of the coating (**Figure 3-12b**). The increasing exposure time is seen to increase the intensity of oxygen signal present in the EDS map indicating increased severity of oxidation (**Figure 3-12**). The evolution of oxidation over the scribed AIRP seen in **Figure 3-13** follows similar trends. The control is free of any observed oxidation in the zero-week condition (**Figure 3-13a**). The scribed AIRP proceeds to accumulate oxygen signal at the coating-electrolyte interface, coating-substrate interface, within the scribed region, and on the interior of the coating with increasing exposure time (**Figure 3-13**). The oxygen signal intensity increases at these critical locations with increasing exposure time. The oxygen signal present at the scribe develops with the greatest intensity of all oxidized regions suggesting that AIRP does not protect the scratch. Breakdown of the coating barrier in marine or coastal environments is largely due to the presence of Cl<sup>-114,115</sup>.

## **Coating Deterioration and Corrosion Product Identification**

Subjecting the AIRP to 14 PS hold stages at -0.95V<sub>SCE</sub> for a total of 100 hours resulted in anodic pigment oxidation (**Figure 3-6**). The post-DC/AC/OCP cycle testing of AIRP shows evidence of coating breakdown in the form of increased porosity as well as the presence of increased oxygen signal associated with the pigment as measured via EDS throughout the thickness of the coating (**Figure 3-8**). The increase in apparent porosity in the post DC/AC/OCP cycle testing is seen consistently throughout testing. The observed cathodic current throughout DC/AC/OCP cycle testing during the application of -0.95 V<sub>SCE</sub> indicates that the AIRP coating is not functioning as a sacrificial anode in the galvanic couple but instead as a cathode. AIRP was further examined via XRD analysis to identify the composition and relative intensity of the crystalline components in each sample throughout ASTM B117 testing. No corrosion products were detected for lab diagnostic testing in the XRD spectra, suggesting that any such products were either amorphous or occurred at volume percentages lower than 3-5%.

However, corrosion products were detected and identified for lab ASTM B117 accelerated salt spray testing shown in **Figure 3-14** and **Figure 3-15**. The BSI micrographs are shown for pristine 0-week exposure in **Figure 3-14a**) and six-week ASTM B117 salt spray exposure in

**Figure 3-14b**) with the EDS line scans shown in **Figure 3-14c**) and **Figure 3-14d**). The EDS line scans show a maximum Al intensity in the intact coating equal in the scribed region; however, with greater irregularity due to the nature of the buried pigments within the epoxy-based MRP coating in **Figure 3-14c**). After six weeks of ASTM B117 salt spray testing the signal intensity of Al within the intact region of the coating decreases 84% while unexposed buried pigments are seen to reduce in Al intensity by 14% compared to the pristine intact coating. The six-week ASTM B117 sample is seen to reduce Al intensity within the scribe by 84% with an overlap of Al signal and O signal implying the oxidation of Al throughout the intact and scribed region. The six-week ASTM B117 sample is also observed to show an overlap between the Zn and Cl signal over the intact coating that is consistent with location of the light region in the BSI micrograph shown in **Figure 3-13b**.

X-ray diffraction was conducted through the intact coating as well as a narrow 3mm x 5mm rectangular window over the scribed area shown in **Figure 3-15 a**) and **3-**15b). The corrosion products identified were predominately  $Al_2O_3$  and  $Al(OH)_3$  with less intense peaks aligning with the formation of  $AlO \cdot OH$  and  $AlCl_3 \cdot 6H_2O$ . The products are identified in the intact scenario as the signal to noise ratio was greater than the scribed substrate. The peak corresponding to  $AlCl_3 \cdot 6H_2O$  at 42° was observed to have the greatest intensity increase throughout the exposure testing. The corrosion products ranked in terms of XRD intensity to determine relative abundance are  $AlCl_3 \cdot 6H_2O$ ,  $Al(OH)_3$ ,  $Al_2O_3$ , and  $AlO \cdot OH$ . The depletion of the buried Al-5wt.% Zn pigments could not be detected given the Al substrate. Raman spectroscopy was performed to further confirm corrosion product identification revealing the formation of  $Al_2O_3$ ,  $Al(OH)_3$ ,  $AlO \cdot OH$  and  $AlCl_3 \cdot 6H_2O$  under the intact coating in **Figure 3-15c** and in the scribe in **Figure 3-15d**. The  $Al_2O_3$  is present in the unexposed scenario and does not diminish throughout the salt spray exposure testing. The formation of  $Al(OH)_3$ ,  $AlO \cdot OH$  and  $AlCl_3 \cdot 6H_2O$  all occur at lower intensity than  $Al_2O_3$  but increase with increasing exposure time (**Figure 3-15**).

The ability to provide protection against scribe corrosion can be seen in cross-section BSI profiles in **Figure 3-16** showing a comparison between the bare unexposed AA 7075 in the intact (**Figure 3-16a**) and scribed (**Figure 3-16b**) condition to the post six-week ASTM B117 salt spray exposure over both intact (**Figure 3-16c**) and scribed (**Figure 3-16d**) regions of bare AA 7075-T651 and AlRP coated AA 7075-T651 (**Figure 3-16e**). **Figure 3-16a** shows the control BSI over

an unexposed intact (as-ground) bare region of AA 7075-T651 with the scribed region shown in **Figure 3-16b**. The post six-week ASTM B117 exposure of uncoated bare AA 7075-T651 shown in the intact and scribed regions in **Figure 3-16c** and **Figure 3-16d**. The intact bare AA 7075-T651 shows pit formation (**Figure 3-16c**) and a widening of the scribe area indicating increased dissolution (**Figure 3-16d**). The cross-section BSI of AIRP coated AA 7075-T651 within the scribed region is shown in **Figure 3-16e** with a large pit formed with extensive depth beyond the scribe indentation of 115  $\mu$ m. There appears to be a portion of the corroded scribe side wall that has dissolved in **Figure 3-16e**. The corrosion exposure damage experienced within the scribed area of AIRP coated AA 7075 is more severe than that of the intact uncoated AA 7075 exposed under the same conditions consistent with an unfavorable galvanic couple between the AA7075-T651 substrate and Al-5wt%Zn pigment.

## **Discussion**

The use of Al/Zn-based pigments for cathodic protection purposes is not a new concept. Al/Zn composite coating systems have been sought out for the protection of carbon steel substrates for decades due to two main complementary attributes: the galvanic couple potential is a beneficial balance between the OCP vales of Zn and Al, and the Zn content selectively dissolves to form corrosion product that will slow down the Al oxidation <sup>117,118</sup>. Both Al and Zn are amphoteric anodes, but the Zn is often observed to selectively dissolve at more acidic pH values up to pH 8 while the Al is stable up at pH 5, in fact Al<sub>2</sub>O<sub>3</sub>. has maximum insolubility at pH 5.9 and dissolves more rapidly at more alkaline pH values as the protective oxide becomes unstable. The performance of a metal rich primer coating is based on three basic mechanisms: 1) galvanic protection, 2) chemical inhibition, and 3) secondary barrier formation <sup>38,39,41,50,52,53</sup>. It was posited herein that the former could be achieved by reaching a galvanic couple potential below  $E_{pit(\eta)}$ . In many ways the protection of AA7075-T651 is more difficult than 2XXX or 5XXX aluminum alloys due to the greater cathodic polarization (**Figure 3-2**) required to suppress pitting of MgZn<sub>2</sub>, the detrimental phase responsible for IGC and IGSCC, placing a higher demand on given coating.

The AIRP has been seen in the present work exposed to NaCl under full immersion and B117 salt fog is shown to have limited galvanic protection as the primer is not capable of
cathodically polarizing the AA7075-T651 substrate to the potential  $E_{pit (\eta)}$  in near neutral NaCl. Passivation of Al inhibits galvanic protection as passivation of Al pigment renders it polarizable and the primer coating is polarized to the corrosion potential of the substrate (**Figure 3-4** and **Figure 3-6b**). The passive barrier formed does not allow protection by serving as an anode in a chloride containing solution which is abundant in marine atmospheres <sup>2</sup>. It is interesting to note that attributes of bulk Al-5wt%Zn might be expected to function as a sacrificial anode especially at high Cl<sup>-</sup> (**Figure 3-5e**). However, this is not the case for the AlRP, presumably because of low depassivating Cl<sup>-</sup> concentration at the coating metal interface which is not severe enough to pit or otherwise activate Al-5wt%Zn (**Figure 3-5b**). This is particularly the case at short exposure times.

To remedy this situation, suggestions include Al alloys with more negative potentials, nonpolarizable Al pigments, and inhibitor containing Al pigment. In general, these conditions can be met by using a pigment from an electrochemically active alloy. These active non-passivating conditions in Al alloys can be achieved with the alloying of Mg, Zn, Li, In, Ga, Hg, and Sn. These are commonly used elements in aluminum anode design with OCP ranging from -0.95 V<sub>SCE</sub> to - $1.23 V_{SCE}$  in artificial seawater <sup>66,70,118,119</sup>. This is well below the OCP of bare AA 7075-T651 and satisfies the criteria discussed above. There has been some limited testing of aluminum anode materials for the protection of aluminum alloys. Moreover, an Al-Zn-In pigment has shown ability to cathodically protect AA 2024-T3 in 0.1 M NaCl <sup>120</sup>. The Al-Zn-In pigments used were passivated using TCP pretreatment so the electrochemical properties reported are not representative of a non-passivated anode grade Al-Zn-In MRP free of pretreatment.

The use of Li as a passivator for organic coatings where Li-containing salts in the form of  $Li_2CO_3$  have been shown to form a polycrystalline layer on pure aluminum, AA 1100, AA 2024, AA 6061, and AA 7075 <sup>66,67,121–123</sup>. This layer is thought to originate from the dissolution of  $Li_2CO_3$  and release of Li<sup>+</sup> resulting in the formation of a hydrated lithium-aluminum-hydroxide-carbonate layer ( $Li_2[Al_2(OH)_6]_2 \cdot CO_3 \cdot nH_2O$ ) that can be categorized as a layered double hydroxide. Li-containing salts have been shown promise as leachable corrosion inhibitor in model organic coatings for the protection of AA 2024-T3 where protective Al/Li layered double hydroxides were detected in the scribe under neutral salt spray conditions <sup>121</sup>.

#### Electrochemical and Chemical behavior of AIRP – 7075 T651 galvanic coupling

The galvanic coupled potential between the AIRP coated AA 7075-T651 and bare AA 7075-T651 rests near the open circuit potential of AA 7075-T651. The buried AIRP is not capable of quickly de-passivating. Once Al pigment is passivated it becomes highly polarizable and ineffective in providing the galvanic protection ability. The Al-5wt% bulk alloy showed more electrochemically active potentials than was observed in the AIRP coating. A contributing factor to the difference in properties is the additional resistance in the form of corrosion products, oxides layers, pores, and the epoxy-based coated.

The oxide/corrosion product barrier formed and tracked throughout ASTM B117 does not appear to offer a high impedance barrier ( $10^3$  ohm · cm<sup>2</sup>) after the six-weeks of accelerated environmental exposure testing in NaCl. This suggests but does not prove that pigment is removed or resin degraded but that pores are not blocked by corrosion products. **Figure 3-13h**) detected the presence of overlapping Zn-Cl signals over an apparent precipitate formed on the intact AlRP region seen in **Figure 3-13d**) that was not detected with Raman spectroscopy of XRD analysis. These may be hydrated or de-hydrated ZnCl<sub>2</sub> salt precipitates formed through the dissolution of Zn originates from within the Al-5wt%Zn pigment. These are non-protective precipitates and include Cl<sup>-</sup> which may serve to trap Cl<sup>-</sup> on the surface leading to sustained persistent contamination. These Zn-Cl products are not detected within the scribed region (**Figure 3-14d**). However, does contain Al<sub>2</sub>O<sub>3</sub> which is non-protective in chloride containing solutions <sup>124</sup>.

### **Diagnostic Testing vs Lab Accelerated Testing**

Initial investigation into the electrochemical behavior of AA7075-T651, pure elements, critical intermetallic compound, and AIRP coated AA7075-T651 by laboratory diagnostic testing identified critical threshold potentials for local corrosion in NaCl solutions. It is likely that the environmental conditions and chemistry alters the functionality of the Al-rich primer system towards AA7075-T651 protection. The polarization behavior of MgZn<sub>2</sub> is critical as the pitting potential of this intermetallic compound defines the boundary in which IGC and IGSCC behavior is anticipated <sup>89,125–129</sup>. The dissolution of intergranular phases is responsible for increased susceptibility to IGSCC <sup>7,15,99,125-129</sup>. Any accelerated tests should not alter the electrochemistry and chemistry that defines the electrochemical framework established herein. Cathodic protection is viable assuming the specific criteria defined are achieved. For instance, the acidified salt fog test might be appropriate technologically in acid rain but too aggressive to mimic the passive and active

corrosion electrochemistry of 7XXX series aluminum alloys that governs IGC such as  $E_{pit, \eta} < E_{GB} < E_{pit, 7075}$ . If this relationship was changed then the circumstances that dominate marine exposure with salt deposition may not apply.

The AIRP was not capable of preventing scribe corrosion within the interior of the scribed region as shown in **Figure 3-16d** and **Figure 3-16e** showing the large accumulation of pit and precipitate damage compared to the unexposed control samples shown in **Figure 3-16a** and **Figure 3-16b**. The purpose of bare AA 7075-T651 exposed to ASTM B117 salt spray testing is to show the results of unmitigated corrosion accumulation around the scribe-defect region that exposes bare metal. The intention of active corrosion protection by an MRP coating systems in the absence of cathodic protection occurs, ideally, through the selective dissolution of pigment within the coating. Such dissolution releases metal ions into solution which may form protective insoluble compounds that have corrosion inhibition properties. The results gathered confirm a lack of protection AIRP offers to defect regions which expose unprotected substrate under the conditions tested herein. The observation of corrosion suppression is the first step – in separate testing it was established that the protection potentials suppressed IGC and IGSCC tests. These studies are ongoing. Future work could investigate the influence of PVC on sacrificial anode based cathodic protection of AIRP in marine environments, expand testing in solutions containing buffers and complexing agents, as well as explore a greater extent of alloying or a range of alloying elements.

#### Conclusions

Metal-rich primer-based cathodic protection was investigated to understand its viability to protect AA7075-T651 by achieving intermediate cathodic potentials which mitigate IGC and IGSCC. In order to mitigate IGSCC, the MRP must achieve an intermediate cathodic potential as well as low polarizability in order to maintain  $E_{couple} < E_{pit,MgZn_2}$  in neutral quiescent NaCl. The present work utilized a newly developed combination of experimental methods to evaluate these performance attributes in Al-based primers, which established the following conclusions.

- An electrochemical corrosion framework was established to define the conditions for successful protection of AA7075-T651 over the time frame of Cl<sup>-</sup> exposure. It is suggested

that maintaining  $E_{couple} < E_{pit, MgZn_2}$ . This is a necessary but alone not sufficient methodology.

- The use of Al-5wt%Zn pigment in an epoxy-based MRP is not capable of providing cathodic protection to AA7075-T651 in quiescent 0.6 M NaCl solution or salt fog as the difference in open circuit potential of AlRP coated AA7075-T651 and bare AA 7075-T651 over the time frame of the tests is minimal. The 5wt% Zn alloying within the Al pigment is apparently not sufficient to depassivate the AlRP.
- AlRP cannot achieve a target galvanic couple potential of -0.95  $V_{SCE}$  in 0.6 M NaCl deemed necessary to protect AA 7075-T651 ultimately polarizing to the corrosion potential of AA7075-T651.
- The galvanic coupled current of AlRP coated AA7075-T651 and bare AA7075-T651 exhibits positive coupled polarity indicating the AlRP is the cathode and the bare substrate is the anode. Suggestions are made to improve the AlRP concept.

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# Tables, Chapter 3 – Task 2

AA7075-T651			
Element	Wt. %		
Al	Bal.		
Zn	5.1-6.1		
Cu	1.2-2.0		
Mg	2.1-2.9		
Fe	0.5		
Si	0.4		
Cr	0.18-0.28		
Ti	0.2		

Table 3-1. Nominal Composition of AA7075

Table 3-2. Metal Rich primer systems included in this study

Code	Primer	Resin	PVC	Thickness	Pigment	Pigment
	Commercial		(%)	(µm)	Diameter/	Morphology
	Name				Dimensions	
					(µm)	
AlRP	LN4841	Epoxy	27	$47.2\pm4.2$	$10.3 \pm 5.4$	spheroid
(Epoxy,27%)						

Coating manufactured by Randolph Coatings, PVC = pigment volume concentration.

Table 3-3. Metal-Rich Primer Charge Capacities and Cathodic Protection Performance

Metal-Rich	Theoretical	Maximum	Anodic	Initial	OCP Upon
Primer	Anodic Q	Experimental	Q Usage	Activated	Completion
	from MRP	Q Output	by End	ОСР	of the
	(C/cm <sup>2</sup> )*	(C/cm <sup>2</sup> ) by End	of Cycle		Cycle Test
		of Cycle Test	Test**		
AlRP	32.2	0.025	N/A	-0.83 ±	$\textbf{-0.8} \pm 0.03$
(Epoxy,27%)				0.01 V <sub>SCE</sub>	V <sub>SCE</sub>

Q = charge, C = Coulombs, XRD = X-Ray Diffraction, OCP = open circuit potential, Activated OCP = stabilized OCP following immersion and sufficient coating wetting, MRP = metal-rich primer

Cycle	Test	Duration (min)
0	ОСР	60
1	EIS	30
	PS Hold	10
	ОСР	60
2	EIS	30
	PS Hold	20
	ОСР	60
3	EIS	30
	PS Hold	40
	ОСР	60
4	EIS	30
	PS Hold	60
	ОСР	60
5	EIS	30
	PS Hold	120
	ОСР	60
6	EIS	30
	PS Hold	240
	ОСР	60
7	EIS	30
	PS Hold	480
	ОСР	60
8	EIS	30
	PS Hold	600
	ОСР	60
9	EIS	30
	PS Hold	600
	ОСР	60

Table 3-4. Potentiostatic cycle testing sequence for each MRP at a potential of  $-0.95V_{SCE}$ 

10	EIS	30
	PS Hold	600
	ОСР	60
11	EIS	30
	PS Hold	600
	ОСР	60
12	EIS	30
	PS Hold	600
	ОСР	60
13	EIS	30
	PS Hold	600
	ОСР	60
14	EIS	30
	PS Hold	1500
	ОСР	60

# Figures, Chapter 3 – Task 2





Figure 3-1. (a) Cross sectional BSI electron micrographs, (b) EDS elemental maps of pristine unexposed AlRP applied on AA7075 – T651.



# Figure 3-2

Figure 3-2. Initial electrochemical evaluation of the AA 7075-T651, pure elements, and detrimental phases related to IGC included in the potentiodynamic polarization diagram tested in full immersion 0.6 M NaCl.

Figure 3-3



Figure 3-3. Potentiodynamic polarization scan of bare AA7075-T651 and AlRP coated alloy in full immersion quiescent 0.6 M NaCl.





Figure 3-4. Long term open circuit potential of AlRP and AA 7075-T651 in full immersion 0.6 M NaCl.











Figure 3-5. The experimental determination of effect of Cl<sup>-</sup> concentration on bulk Al-5wt%Zn alloy tested via (a) long term (24-hour) OCP, (b) potentiodynamic polarization, **c**) electrochemical impedance spectrum, (d) phase angle progression, and (e) the variation in post 24-hour OCP vs chloride concentration for bare AA 7075-T651, AlRP coated AA 7075-T651, bare MgZn<sub>2</sub>, and bare bulk Al-5wt%Zn alloy. Electrochemical testing is conducted in varying chloride concentration with NaCl without pH adjustments under quiescent full immersion conditions.





Figure 3-6. Potentiostatic cycle testing of AlRP applied on AA7075 T651 with potential hold at -0.95  $V_{SCE}$  and the legend denoting the cycle indicated in Table 4. (a) OCP shown with a black dashed line at the OCP of AA7075-T651 (-0.75 $V_{SCE}$ ), (b) The current density output shown with a red dashed line through zero, (c)The accumulated charge density as calculated from the current density, (d) The residual barrier properties are determined by the Bode impedance response, and (e) phase angle progression. Testing is conducted in non-aerated 0.6 M NaCl under full immersion.

Figure 3-7



Figure 3-7. (a) Variation of low frequency limit (0.01Hz) of  $Z_{mod}$  against each potentiostatic cycle, and (b) the OCP step shown against each potentiostatic cycle.

Figure 3-8



Figure 3-8. Post-Potentiostatic polarization testing cross-sections of AlRP coated AA7075-T651 after 100 hours of polarization at  $-0.95V_{SCE}$  under full immersion in 0.6 M NaCl. (a) BSI SEM micrographs, (b) layered EDS map, and (c) oxygen signal from EDS shown individually.

# Figure 3-9



Figure 3-9. Galvanic corrosion of the coupled bare AA7075-T651 to AlRP coated AA7075-T651 tested in quiescent 0.6 M NaCl for a 1:1 area ratio. (a) The galvanically coupled potentials, and

(g) galvanically coupled current densities. The dashed line represents the OCP of bare AA7075-T651 (- $0.75V_{SCE}$ ) in quiescent 0.6 M NaCl.



## Figure 3-10

Figure 3-10. Galvanic corrosion of the coupled Al-wt% Zn alloy (WE) to bare AA7075-T651 (CE) tested in quiescent 0.6 M NaCl for a 1:1 area ratio with the coupled potentials and current densities.

Figure 3-11



Figure 3-11. (a) Evolution of open circuit potential, (b) electrochemical impedance spectrum Bode plot, and (c) phase angle progression across 0, 2, 4, and 6 weeks of accelerated environmental exposure via ASTM B117 conducted in 0.6 M NaCl.





Figure 3-12. (a), (b), (c), and (d) BSI SEM micrographs of ASTM B117 salt spray testing on coated and intact AIRP applied on AA7075-T651 across a 0, 2, 4, 6-week accelerated

environmental exposure in 0.6 M NaCl. (e), (f), (g), and (h) EDS elemental mapping showing individual oxygen signal shown to the right of the respective BSI micrographs.





Figure 3-13. (a), (b), (c), and (d) BSI SEM micrographs of ASTM B117 salt spray testing on coated and scribed AIRP applied on AA7075-T651 across a 0, 2, 4, 6-week accelerated

environmental exposure in 0.6 M NaCl. (e), (f), (g), and (h) EDS elemental mapping showing individual oxygen signal shown to the right of the respective BSI micrographs.



Figure 3-14

Figure 3-14. (a) Planar view BSI SEM micrograph of 0-week (pristine) AIRP coated AA 7075-T651 across the scribed region, (b) Planar view BSI SEM micrograph of 6-week accelerated environmental exposure testing via ASTM B117 in 0.6 M NaCl, (c) EDS line profile across the pristine scribed region, and (d) EDS line profile across the 6-week accelerated environmental exposure in the scribed region. The EDS line scan profile is shown in each BSI SEM micrograph.

# Figure 3-15



Figure 3-15. (a) X-ray diffraction analysis on intact and (b) scribed AlRP condition following ASTM B117 exposure in 0.6M NaCl. (c) Raman spectroscopy performed on intact and (d) scribed AlRP coated AA7075-T651 also following exposure for the times indicated in ASTM B117 testing. Purple stars indicating FCC aluminum, blue circles indicate Al(OH)<sub>3</sub>, orange upward triangles indicate Al<sub>2</sub>O<sub>3</sub>, green stars for AlO · OH, and yellow downward triangle for AlCl<sub>3</sub> ·  $6H_2O$ .

Figure 3-16

mode A+B+C



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Figure 3-16. (a) Nitric washed unexposed bare AA 7075-T651 control BSI with no protection scheme shown over the uncoated intact region, (b) over the uncoated scribe. (c) Nitric washed post 6-week bare AA 7075-T651 ASTM B117 BSI with no protection scheme shown over the intact region, and (d) scribed region. (e) The post 6-week AIRP coated AA7075-T651 ASTM B117 salt spray testing over the scribed region.

# Chapter 4 Task 3- Electrochemical Evaluation of Mg and a Mg-Al 5%Zn Metal Rich Primers for Protection of Al-Zn-Mg-Cu Alloy in NaCl

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#### **Abstract**

High purity magnesium and a Mg-Al 5wt% Zn metal rich primer (MRP) were compared for their ability to suppress intergranular corrosion (IGC) and intergranular stress corrosion cracking (IG-SCC) in peak aged AA 7075-T651 by sacrificial anode-based cathodic prevention. Tests were conducted in 0.6 M NaCl solution under full immersion. These evaluations considered the ability of the primer to attain an intermediate negative open circuit potential (OCP) such that the galvanic couple potential with bare aluminum alloy (AA) 7075-T651 resided below a range of potentials where IGC is prevalent. The ability of the primer to achieve an OCP negative enough that the AA 7075-T651 could be protected by sacrificial anode-based cathodic prevention and the ability to sustain this function over time were evaluated as a first step by utilizing a NaCl solution. The primers consisted of epoxy resins embedded with either (1) Mg flake pigments (MgRP) or (2) Mg flake pigments and spherical Al-5 wt.% Zn together as a composite (MgAlRP). A variety of electrochemical techniques were used to evaluate the performance including OCP monitoring, electrochemical impedance spectroscopy (EIS), diagnostic DC/AC/OCP cycle testing, and zero resistance ammeter tests with simultaneous pH measurements. Electrochemical DC/AC/OCP cycle testing in 0.6 M NaCl demonstrated that MgRP reached a suitable OCP for cathodic protection of AA 7075-T651. MgRP was an effective coating for cathodic protection but dispensed less anodic charge than the composite MgAlRP. Cross-sectional analysis demonstrated that some Mg flakes dissolved while uniform surface oxidation occurred on the remaining Mg flakes which led to impaired activation. The composite MgAIRP maintained a suitably negative OCP over time, remained activated, dispensed high anodic charge, and remained an anode in zero resistance ammeter testing. Chemical stability modeling and zero resistance ammeter testing suggest that Mg corrosion elevates the pH which dissolved aluminum oxides and hydroxide thereby activates the Al-5wt.% Zn pigments, thereby providing a primary (i.e. Mg corrosion) and secondary process to enable superior (activation of Al-5wt%Zn) sacrificial anode-based cathodic protection.

#### **Introduction**

Aircraft aluminum alloys range widely in composition due to a large range in the demand for optimal material properties and performance. The wing-spar of commercial aircraft structures is largely comprised of 7XXX-series aluminum alloys<sup>1–3</sup>. Aluminum alloy (AA) 7075 is a naturally aged precipitation hardened Al-Zn-Mg-Cu alloy that owes its IGC susceptibility to its grain boundary phase MgZn<sub>2</sub>, known as  $\eta$  phase. The 7XXX-series aluminum alloy AA 7075-T651 is commonly used commercial aircraft. This alloy is hardened through peak-aging and stress relieved by stretching (3%). Peak age (T6x) hardening of AA 7075-T651 results in a maximum yield strength (0.2% offset) of 455 MPa<sup>2,4,5</sup>; however, this process is also responsible for the increased susceptibility to intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC)<sup>4,6-10</sup>. The enhanced localized corrosion susceptibility of AA 7075-T651 is due to its heterogeneous microstructure and a wide range of constituent particles and precipitates introducing local chemical inhomogeneity and enhanced localized breakdown in the form of matrix-phase boundary attack<sup>11–16</sup>, selective dissolution<sup>17–22</sup>, and pitting<sup>11,13,23–26</sup>. The peak aging of AA 7075 results in a greater phase fraction of intragranular precipitates and grain boundary ( $\eta$  phase) precipitates as well as solute-depleted zones<sup>4,12,27</sup>. Intragranular coherent precipitates increase the yield strength of AA 7075-T651, but the peak aging treatment also forms heterogeneously nucleated  $\eta$  phase increasing IGC/IGSCC susceptibility <sup>1,2,4,5,7,28–31</sup>.

Marine environments, which are abundant in Cl<sup>-</sup> and subject to wet-dry cycles, are particularly aggressive increasing the susceptibility for environmentally assisted cracking (EAC) and stress corrosion cracking (SCC) <sup>2,32–36</sup>. EAC of 7xxx-series aluminum alloys in both aqueous environments and water vapor have been studied extensively with numerous proposed models aimed at understanding SCC mechanisms <sup>2,6,8,31,37–41</sup>. Localized breakdown contributes to EAC as environmental exposure facilitates the breakdown and evolution of pits on the surface acting as stress concentrators ultimately lowering the SCC resistance<sup>7,31,42,43</sup>. The IG-SCC behavior is hypothesized to be governed by a coupled anodic dissolution process (i.e. electro-dissolution of the grain boundary  $\eta$  phase and the surrounding matrix), which also catalyzes the formation of an aggressive acidified local crack tip chemistry that, in turn, facilitates the enhanced generation of crack tip hydrogen and uptake enabling embrittlement in the fracture process zone<sup>10,36,44–52</sup>. The IG-SCC crack initiation tendencies and growth rate of AA 7075-T651 exhibit a great deal of potential dependence under potentiostatic conditions (PS) in 0.6 M NaCl<sup>28,49</sup>. Therefore, the
mitigation of both IGC and IG-SCC is possible through the establishment of potentials that are more negative than the pitting potential,  $E_{pit}$ , of the  $\eta$  phase,  $E_{pit(\eta)}^{39,53,54}$ . The potential dependence of environmentally induced fracture susceptibility of AA 7075-T651 has been investigated previously by Harris et al., who reported variation in the crack growth rate and threshold stress intensity with applied potential<sup>28</sup>. Stage II crack growth rate develops a minimum potential between -0.9 V<sub>SCE</sub> and -1.0 V<sub>SCE</sub>. This range of minimum crack growth potentials is theorized to minimize  $\eta$  phase corrosion, hydrolysis, and acidification. The environmental fracture susceptibility of numerous 7xxx series aluminum alloys such as AA 7050-T651 exhibits an identical potential window for crack growth suppression<sup>55</sup>. This illuminates a possible mitigation strategy for this class of alloys for use in marine service such that stage II crack growth is minimized based on the establishment of potentials more negative than the pitting potential of the  $\eta$  phase,  $E_{pit(\eta)}$ . This situation can be described by the term "sacrificial cathodic prevention" where the goal is to polarize below selected critical potentials where susceptibility is indicated<sup>225,56,57</sup>.

Protecting against environmental fracture whether it be SCC or IGSCC is a larger challenge than providing static protection against localized or uniform corrosion. The challenge is to develop a substrate protection system that can suppress environmental fracture. Traditional legacy systems have used chromate-based coatings, which function based on the release of chromate ions, to chemically inhibit corrosion on aluminum alloys<sup>17,58–65</sup>. Although chromate-based coatings are very effective, there are concerns over the toxicity of hexavalent chromium as well as growing requirements in the aerospace industry that motivate the quest for alternative coating systems<sup>66–71</sup>. Metal rich primers are often accompanied by anodizing treatments to the substrate, conversion coatings, and the application of a topcoat layer<sup>58,60,72,73</sup>. Conversion coatings vary in composition from Cr <sup>59,60,64,74–76</sup>, Zr<sup>77–79</sup>, Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub><sup>80–83</sup>, or Ce<sup>.84–86</sup>. They generally serve the purpose of providing corrosion inhibition through the dissolution of cation species. The MRP layer is found between the anodizing layer and the top-coat layer; this arrangement functions as an active coating system that has multiple modes of protection. In general, an MRP coating system is comprised of a metallic pigment embedded within an epoxy-based resin.

MRP protection of an aluminum alloy substrate is multifaceted and may include 1) sacrificial anode based cathodic protection of the substrate, particularly through intermetallic

compounds (IMC) which normally induce micro-galvanic attack with the FCC matrix phase, 2) chemical inhibition of oxygen reduction reaction (ORR) at some IMC, and 3) a secondary barrier effect. The corrosion performance of an MRP is intimately tied to these three possible forms of protection, which vary based on the physical coating attributes such as pigment volume concentration (PVC) and type of pigment used. A range of MRP with varying pigment chemistries (Al, Mg, Zn) has been tested on 2XXX and 5XXX-series aluminum alloys, indicating a capacity to provide active protection of the micro-galvanic couple between the IMC and matrix<sup>54,58,60,72,74,87–102</sup>. However, mitigating environmental fracture remains an unmet challenge. Previous work on zinc-rich primers applied to AA 5456-H116 indicated that IG-SCC mitigation was achieved when using either cold mounted Zn anode or a Zn-based metal rich primer (ZnRP) coating<sup>99,103</sup>. Mitigation was not observed when a topcoat was applied to an inorganic ZnRP<sup>99</sup>. The chemical effects afforded by the primer and the addition of ZnCl<sub>2</sub> salt. In this case, the observed IG-SCC growth rate was reduced by as much as three orders of magnitude over a range of stress intensity in the presence of just Zn<sup>2+</sup> ions<sup>104</sup>.

A few criteria must be satisfied for a given MRP to provide sacrificial anode based cathodic protection to an underlying substrate which include 1) an electrical connection between the AA 7075-T651 substrate and electrolyte, 2) an ionic connection between the AA 7075-T651 substrate and electrolyte, and 3) contain pigment which maintains the ability to support an anodic reaction leaving the substrate to support the cathodic reaction. In this situation a mixed potential based galvanic couple is formed between the pigment within the coating and the AA 7075-T651 substrate and is polarized below the corrosion potential,  $E_{corr}$ , of the AA 7075-T651 ( $E_{Corr, 7075}$ ) <sup>98,99</sup>. Ideally the mixed potential is also capable of suppressing below critical threshold potential such as  $E_{pit(\eta)}$  <sup>39,89</sup>. There is a lack of prior studies assessing the corrosion characteristics and coating performance of these MRPs applied to 7xxx- series aluminum alloys susceptible to EAC with these target goals in mind. An effective MRP might also provide chemical inhibition via pigment dissolution and redeposition of beneficial species within macro-defects such as scribes/scratches as well as preventing blistering and under-paint corrosion<sup>72,98,105</sup>.

In a complementary study, preliminary experiments were conducted assessing the electrochemical behavior of an AIRP applied to AA 7075-T651 consisting of Al-5wt%Zn

pigment<sup>89</sup>. This AIRP was not shown to provide potential suppression below the  $E_{pit(\eta)}$  when tested in 0.6 M NaCl<sup>89</sup>. The electrochemical investigation measured a cathodic current density over the AIRP-coated AA 7075-T651 sample during galvanic coupling with bare AA 7075-T651 which indicated the AIRP coating is operating as a cathode instead of an anode to the AA 7075-T651<sup>89</sup>. Additional electrochemical diagnostic testing assessing the ability of the AIRP coating to discharge anodic current at a potential deemed protective, below the  $E_{pit(\eta)}$  (-0.85 V<sub>SCE</sub>), concluded that the coating discharges cathodic current opposite to the intended sacrificial anode capability<sup>89</sup>. Examination of the oxidation behavior of the intact buried AIRP during ASTM B117 salt spray exposure indicated no oxidation of the coating-electrolyte interface and the interior of the coating<sup>89</sup>. The combination of measured electrochemical behavior and the negligible oxidation observed suggested the AIRP was inadequate to protect AA 707-T651<sup>89</sup>. It was noted that the alloying of 5wt%Zn in the Al pigment is likely insufficient to provide adequate sacrificial anode-based cathodic protection to AA 7075-T651<sup>89</sup>.

MgRPs are known to be effective at providing sacrificial anode-based cathodic prevention, scribe defect protection, and possess high impedance secondary barrier effects on aluminum alloys<sup>90,96,98,106,107</sup>. The use of MgRP's, first developed by Bierwagen et al., was introduced for the protection of aluminum alloys<sup>90,108–111</sup>. The galvanic effects of a MgRP applied to AA 2024-T3 provide sacrificial anode based cathodic protection via cathodic polarization of the substrate and have been shown to provide protection to a defect region sufficient to suppress pitting<sup>72,74,98,105,112</sup>. The more challenging verification of  $\eta$  phase protection was not attempted. Polarization of AA 7075-T651 below  $E_{pit}(\eta)$  might be better achieved with Mg and MgO rich primer due to its low electrode potential<sup>72,87,98</sup>. However, the criterion for protection proposed herein was not attempted elsewhere in the literature. The use of high purity Mg pigment in MgRP is limited by its high self-corrosion rate<sup>58,60,98,102</sup>. The dissolution of Mg pigment to Mg<sup>2+</sup> within MgRP was shown to precipitate corrosion products within the scribed region, providing a surface modified layer to the otherwise bare defect<sup>60,72,73,87,102,113</sup>.

Studies on the influence of MgO or derivative compounds on aluminum alloys have shown similar corrosion performance, as seen with zinc-rich primers for the galvanic protection of steel and their fasteners<sup>72,87,114–119</sup>. These MgO pigments may dissolve and precipitate at the substrate and modify the Al surface by filling pores within the Mg oxide layer, increasing the stability of the layer to Cl<sup>-72,87</sup>. Studies performed on AA 2024-T3 in chloride-containing environments

showed that the introduction of Mg<sup>2+</sup> ions leads to a pH rise and a negative shift in the E<sub>corr</sub> common to aluminum alloys exposed to alkaline environments given its amphoteric nature. The dissolution of Mg from either the coating or the dissolution of Mg-based corrosion products such as  $Mg(OH)_2$  enables the supply of a reservoir of  $Mg^{2+}$  similar to a coating that dispenses a possible chemical inhibitor. Here, Mg<sup>2+</sup> products precipitate chemically in a scratch at high pH sites, such as IMCs, where the pH becomes quite alkaline<sup>72,87</sup>. Such repartitioning of Mg<sup>2+</sup> was observed in the case of MgRP and MgORP on AA 2024-T3<sup>60,72,87,102,112</sup>. These repartitioning effects occur due to chemical dissolution of the passivated MgO pigment (MgORP). A greater amount of Mg<sup>2+</sup> repartitioned for MgRP than MgORP. However, both were observed to exhibit similar amounts of reduced corrosion damage within the scribe after 2.5 years of field exposure at Kennedy Space Center (KSC)<sup>72,87,98,100</sup>. The work of Mokaddem et al. shows the variation in the dissolution rate of Mg, Al, and 2024 (Al-Cu-Mg) using atomic emission spectroscopy, indicating that when Mg is present in the solid solution of 2024, the co-dissolution of Mg and Al occurs together until the pH increases, allowing the Mg to form Mg(OH)<sub>2</sub> and thereby reducing the dissolution of Mg and increasing that of Al<sup>120</sup>. In Mg and MgO pigments, the MgO species was soluble at the initial neutral pH solutions containing Cl<sup>-100,102</sup>. It was shown that Mg(OH)<sub>2</sub> was deposited at alkaline sites in the cathodically protected scratch<sup>60,102</sup>.

Zn-based RP has also been used extensively on mild<sup>116,117,121,122</sup>, carbon<sup>77,123–126</sup>, and stainless steels <sup>82,127–129</sup> for galvanic protection in aqueous and marine atmospheric environments. ZnRP used on steels has shown the ability to perform as an effective sacrificial anode-based form of cathodic protection in marine environments<sup>118,119,130–133</sup>. Composite ZnRP pigment coating systems have been used before for the protection of carbon steel in marine environments<sup>134–137</sup>. These ZnRP have been shown to be an effective system for providing sacrificial anode-based cathodic protection to aircraft aluminum such as 2XXX and 5XXX-series aluminum alloys in marine environments<sup>99,133,138,139</sup>. The utilization of ZnRP on either steel or aluminum substrates results in the conversion of Zn to ZnO pigment via oxidation<sup>58,133,140</sup>, which is considered "depleted" yet continues to provide barrier protection<sup>126,134,141</sup>. Zn is viewed as a "p-metal" and thought to have the character of a p-type semiconductor, whereas ZnO is a n-type semiconductor<sup>142,143</sup>. Thus, the combination of Zn–ZnO may form a p–n junction, which permits the flow of electrons and can control the electrochemical reaction of corrosion<sup>143</sup>.

Another possible candidate for the replacement of chromated conversion coating is the use of aluminum-lithium passivation processes, including immersion in alkaline lithium salt solutions which has proven effective for aluminum and aluminum alloys<sup>144</sup>. Previous work has shown the formation of a stable corrosion-resistant film within a scribe defect that has stoichiometry of  $Li_2[Al_2(OH)_5]_2 \cdot CO_3 \cdot nH_2O$  <sup>145–147</sup>. Lithium salts have been proposed as potential replacements for chromate-containing pigments in organic MRP coating systems<sup>144</sup>. Testing on AA 2024-T3 showed that the leaching lithium carbonates and lithium oxalates from an organic coating formed a protective layer in an artificial defect <sup>145</sup>. The effective corrosion protective properties of these layers were demonstrated by Visser et al. in a study based on electrochemical techniques<sup>145–148</sup>. However, none of this work has elucidated whether this substrate protection strategy can suppress IGC/IGSCC.

There has been limited research conducted on composite primers with multiple dissimilar pigments combined into a single coating. This shows another design parameter by which a coating can be tuned for the protection of the underlying substrate and suppression of IGC. The addition of multiple pigment chemistries within the same coating allows for a more robust protection scheme as the utilization (conversion of pigment), galvanic protection, and secondary barrier properties are a function of the pigment within the primer. The current literature on composite coatings is primarily focused on the combination of Mg, Zn, and their oxides mixed in various proportions to create composite primers <sup>138,149</sup>. The work of Shen et al. indicated enhanced sacrificial anode-based cathodic protection of a composite Mg + ZnO primer compared to MgRP analyzed on AZ91D magnesium alloy<sup>150</sup>. The secondary barrier properties of the composite Mg + ZnO primer were shown to form a robust passive layer with greater stability compared to MgRP<sup>150</sup>. Another study by Fayomi et al. investigated a Zn + MgO composite primer and found that the addition of MgO enhanced the corrosion performance of the coatings applied to mild steel<sup>151,152</sup>. There have also been efforts to understand the influence of additions of graphene and carbon nanotubes on both single pigment and composite coatings<sup>132–135</sup>. However, none of this work has elucidated whether this substrate protection strategy can suppress IGC/IGSCC. The limited work available in literature indicates a gap in the knowledge that merits further investigation into the electrochemical behavior of composite coatings compared to their single pigment primer counterparts.

This study focuses on a prospective alternative to chromate-based coating systems and single pigment primers by investigating a composite MgAlRP applied to a challenging substrate susceptible to IGC such as AA 7075-T651 free of any other inhibitors, pretreatment, and top coatings. The objective is to determine the relative performance of each system as a sacrificial anode, protection of the substrate, and examine the governing mechanisms. The performance of MgRP is used as a control in order to make an accurate determination as to the efficacy of the composite MgAlRP in providing sacrificial anode based cathodic protection to AA 7075-T651. The electrochemical behavior and coating performance of an Al-based MRP (AlRP) applied to AA 7075-T651 were reported in a previous publication<sup>89</sup>. Each MRP is evaluated using multiple electrochemical diagnostic techniques and characterization methods to identify performance and corrosion products formed.  $E_{pit (\eta)}$  is used as a critical potential to determine susceptibility to EAC and IG-SCC. Moreover, these studies were combined with ASTM B117 exposure testing under salt fog. This initial work was conducted in NaCl but diagnostic experiments included variations in both Cl<sup>-</sup> concentrations and pH. Future work should consider wet/dry cyclic exposures, variation in pigment chemistry, and other relevant coating properties such as PVC.

## **Experimental**

## Materials: AA 7075-T651, MgRP, and MgAlRP

Peak aged and stress relieved AA 7075-T651 rectangular plates were machined to dimensions 1.5 mm thick, 200 mm long, and 76 mm wide via Mager<sup>TM</sup> high speed cut off saw. Samples were de-greased via alcohol bath and dried in lab air before the spray coating application. The composition of AA 7075-T651 is shown in **Table 4-1**. All bare uncoated samples were wetpolished to 1200 grit SiC paper until a mirror finish was obtained. The DEVCOM Army Research Lab (ARL) conducted spray-coating of the MgRP and composite MgAlRP according to the formulations shown in **Table 4-2** and applied to Milspec. The resin/pigment combination of the MgRP as produced by AkzoNobel (AN) Coatings (Amsterdam, Netherlands) and designation consists of epoxy resin and non-passivated 99.9% pure Mg pigment with flaked morphology at 26% PVC. The resin/pigment combination of the MgRP and an Aluminum Rich Primer (AlRP) produced by Randolph Coatings (RC, Chicopee, Massachusetts US). The RC AlRP coating contains a spherical aluminum

pigment alloyed with 5wt% Zn with spherical morphology. The combination of the AN MgRP with RC AlRP is possible due to the use of similar organic resin-hardener combinations with specifications listed in **Table 4-2**. The AA 7075-T651 panels area free of pretreatment. The MRP coated AA 7075-T651 samples do not include passivated pigments and do not include topcoats of any variety. Both intact and X-scribed defect MRP coated samples are tested. The MRP coated samples with X-scribed defect are made with the use of a tungsten carbide tip exposing the underlying substrate AA 7075-T651 in accordance with ASTM D1654<sup>73,74</sup>. A bulk Al-5wt%Zn cylinder was produced, in effort to represent the Al-5wt%Zn pigment within the MgAlRP, via melting in a National Element electric resistance furnace conducted in ambient conditions. A graphite crucible was utilized, subject to 5 repeated melting cycles to achieve increased homogeneity. The MgZn<sub>2</sub> specimen was synthesized by the Kurt Lesker Company weighing between 3 to 6 grams. Conventional synthesis methods involve induction melting under vacuum with an argon-enrich atmosphere to mitigate volatilization and oxidation effects.

## **Coating Characterization: Metal Pigment**

Characterization of as-received, electrochemically tested, and accelerated environmental testing of MRP coating cross-sections were conducted with the use of scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) on a Quanta 650 system for imaging and elemental analysis. The SEM cross-sections are gathered under back scatter imaging (BSI) at a magnification of 500x, spot size of 5 nm, and an accelerating voltage of 10 kV at 10<sup>-8</sup> torr to mitigate charging. Cross-sectioned MRP coating were mounted in epoxy and wet polishing in water to 1200 grit using an abrasive silicon carbide pad. The polished epoxy mounted MRP cross-sections were sputter coated with a conductive Au-Pd layer using a Cressington-108 at 30mA for 40 seconds with a standoff distance of 5 cm. The Au and Pd signal was excluded from EDS elemental analysis. The SEM BSI of each MRP cross-section was used to determine physical attributes (**Table 4-2**) such as average pigment size and coating thickness using 10 vertical thickness measurements on 3 pristine MgRP and MgAIRP cross-sections.

Metal rich primer crystalline composition and corrosion product identity were analyzed using X-ray diffraction (XRD). The Empyrean diffractometer XRD source used was a Cu-Ka source (1.54nm) with a 40-mA beam accelerated at 45 kV to perform continuous scans from 20–120° at a step size of 0.02. Previous work on Zn-rich primers with similar thickness demonstrated

the presence of major Al peak at approximately 44.5°, which showed that the entirety of the MRP was being sampled <sup>33</sup>. Due to the pigment choice in the MgAlRP and the composition of AA 7075-T651 the Al-5wt.% Zn pigment peaks could not be differentiated from the substrate making the depletion of Al-rich pigment unattainable by XRD methods.

## **Corrosion Electrochemistry Investigation on Bare Materials**

The initial potentiodynamic polarization (PDP) scans of AA 7075-T651 (S-T rolling orientation), MgZn<sub>2</sub>, MgRP coated AA 7075-T651, MgAlRP coated AA 7075-T651, 99.9% pure Mg, and an Al-5wt%Zn alloy were conducted in quiescent 0.6 M NaCl solution under full immersion conditions. The PDP provides the basis for assessing potential ranges in which IGC may be the predominant mechanism of SCC according to an anodic dissolution mechanism based on differences in critical potentials. The E<sub>corr</sub> evaluated by PDP and E<sub>OCP</sub> evaluated via OCP monitoring were recorded to examine galvanic relationships and potential relative to critical potentials. The anodic portion of the potentiodynamic scan started at 50mV below the OCP and scanned upward at a rate of 1mV/s. The cathodic leg of the potentiodynamic polarization scan started at 50 mV above the OCP and scanned downwards at a rate of 1mV/s. All electrochemical testing was conducted over a 0.785 cm<sup>2</sup> surface area.

The influence of  $[Mg^{2+}]$  concentration in the presence of Cl<sup>-</sup> on the electrochemical properties of AA 7075-T651 as well as Al-5wt%Zn was assessed by conducting PDP scans as well as 24-hour OCP monitors across a range of pH conditions from pH 3, unadjusted (UA, pH 5.8), pH 9, pH 10, and pH 11. The  $[Mg^{2+}]$  concentration was adjusted with the addition of MgCl<sub>2</sub> and titrated to the appropriate pH using stock solutions of 1 M HCl and 1 M NaOH. The influence of Cl<sup>-</sup> on the PDP behavior and 24-hour OCP at near neutral conditions was conducted separately using NaCl to avoid convoluting the influence of Cl<sup>-</sup> with the presence of Mg<sup>2+</sup> for bare AA 7075-T651, Al-5wt%Zn, MgZn<sub>2</sub>, MgRP coated AA 7075-T651, and MgAlRP coated AA 7075-T651. The NaCl concentration is varied between 1, 10, 100, and 1000 mM at near neutral unadjusted pH conditions.

Additionally, PDP testing was conducted on AA 7075-T651, MgZn<sub>2</sub>, Mg (99.9% pure), and Al-5wt%Zn in 0.6 M NaCl under quiescent full immersion conditions in unadjusted pH (5-5.5) as well as pH 11 to aid in understanding the galvanic coupling conditions of the intact and scribed coating scenarios in accordance with mixed potential theory. Galvanic couples of all types

are mediated by the electron transfer kinetics between the anode, cathode, and the electrical and ionic resistances between the two. The pigments within MRP coating systems can be alloyed to achieve a certain charge capacity and balance between rapid sacrificial anode kinetics and maintain galvanically coupled potential ( $E_{GC}$ ) below that of the substrate. The quantity of exposed sacrificial particles electrically connected to the substrate affects the coupled potential and the overall corrosion rate in the substrate. All electrochemical tests were conducted using a Gamry 600 potentiostat and a standard three-electrode cell containing a saturated calomel reference electrode (SCE) and a Pt counter electrode (CE); each specimen was used as the working electrode (WE).

## The UVA DC/AC/OCP Cycle Test: Charge Output and Barrier Assessment of Mg/MgAl-Rich Primers

The MgRP and MgAlRP coating systems' performance as a sacrificial anode during cathodic prevention and electrochemical characteristics was evaluated under full immersion conditions in quiescent 0.6 M NaCl. The UVa DC/AC/OCP laboratory accelerated cycle test has been widely employed and holds significant value across various primer applications. This is due to its capability to adjust the PS hold potential to align with the desired galvanic couple potential and can be tailored to any specific alloy compositions and MRP choice <sup>54,87,89,100</sup>. The charge capacity of the primer can be assessed by integrating the current density vs time measured during the PS hold potential is an indication of the sacrificial anode cathodic protection a given MRP is able to offer. Extensive studies have been conducted on analogous MRP systems across a range of realistic exposure scenarios, encompassing 2xxx and 5xxx series aluminum alloys.

The laboratory accelerated cycle testing method stands as a reliable means to assess a candidate coating's capacity for sacrificial cathodic protection, particularly in the presence of a macro-defect (scribe) exposing the underlying substrate <sup>54,87,89,98,100,102</sup>. This testing method is advantageous to alternative forms of exposure testing and yields greater mechanistic information that can be obtained instead of relying on pos-mortem characterization from accelerated environmental testing solely. The electrochemical characteristics pertaining to MRP coating performance in the form of charge capacity (and polarity), residual barrier impedance, and

progression of the primer-substrate galvanic couple potential system after various states of discharge were recorded throughout DC/AC/OCP testing. The laboratory accelerated cycle testing involves a 14-cycle series of repeated OCP/EIS/PS hold procedure summing up to 100 hours of polarization time. The PS hold stage which imposes a galvanic couple potential for the MRP-substrate system was selected to be -0.95 V<sub>SCE</sub>. This testing procedure includes a cumulative 15 hours of OCP collection time and 100 hours of PS polarization time. A detailed description of the test scheme and associated times is shown elsewhere<sup>89</sup>. Establishing a PS hold at -0.95 V<sub>SCE</sub> aims to evaluate each MRP's capability to discharge anodic current under conditions designed to guard against IGC (i.e.  $E_{PS hold} < E_{pit (\eta)}$ ). All laboratory accelerated cycle testing was performed in triplicate to confirm reproducibility and ensure the trends shown are characteristic.

The extent of galvanic coupling between the MRP and AA 7074-T651 substrate was observed via the OCP stage of cycle testing as a greater pool of connected active MRP pigment is capable of suppressing coupled potential below the corrosion potential of AA 7075-T651. The OCP of the primer also gives a qualitative indication of the remaining pigment. The activation of metal rich primers occur at the most negative established OCP during cycle testing. According to mixed potential theory, the galvanic couple potential is influenced by the surface area of pigments, their polarization characteristics, and the exposed surface area between the bare AA 7075-T651 and the MRP coated AA 7075-T651<sup>54,89,98,100</sup>. In the following EIS stage of laboratory accelerated cycle testing the barrier properties of the intact primer and the remaining primer after discharge were examined. EIS testing is evaluated between 10<sup>5</sup> and 10<sup>-2</sup> Hz, 10 points per decade, and an AC amplitude of 65mV rms.

## Galvanic Corrosion Analysis using Mixed Potential Theory, PS Corrosion Electrochemistry, and Zero-Resistance Ammetry

The evaluation of galvanic corrosion between the AA 7075-T651 substrate, mimicking a bare scratch, and the Mg/MgAlRP was performed using a zero-resistance ammeter (ZRA) test. Throughout the galvanic corrosion testing, an unexposed MgRP/MgAlRP coated AA 7075-T651 was galvanically coupled to a pristine bare AA 7075-T651 electrode. This galvanic coupling scenario simulates a scratch and forms a bimetal galvanic couple between the MRP coated AA 7075-T651 and the bare AA 7075-T651. This is advantageous as the galvanic coupled potential

and galvanically coupled current density are formed naturally and not imposed or forced by a potentiostat. The galvanic couple potential is permitted to vary freely between the OCP of the primer and the exposed bare metal surface. The galvanic corrosion was monitoring over a 24-hour period of the dissimilar electrodes in quiescent 0.6 M NaCl. The bare 7075-T651 substrate with an exposure area of 0.785 cm<sup>2</sup> is connected as the WE, the MRP coated 7075-T651 operating as the CE, and an SCE is used as the reference electrode. In this setup, if a negative current on the bare 7075-T651 WE is measured this indicates electron flow entering the cathode. The indication that the MRP (CE) is acting as an anode is represented by a negative current measured over the WE. The distance between WE and CE was greater than 4 cm in the galvanic corrosion test which limits corrosion product transfer but does not limit electrochemical interactions. The galvanic coupling of the MRP coated AA 7075-T651 to bare AA 7075-T651 and ensuing electrochemical reactions may induce local pH change due to the dissolution of active pigment within the MRP coating. The local pH fluctuations were monitored with the use of a Mettler Toledo dual ISM pH microprobe positioned at a standoff distance of 5mm from each electrode surface. Galvanic couple testing was conducted in a 1:1 (MRP: bare 7075-T651) area ratio to assess the effect of a drop covering a scratch. Galvanic couple testing was also conducted in a 15:1 (MRP: bare 7075-T651) area ratio to simulate the conditions present near a scribe where a greater area of MRP is present than bare 7075-T651 substrate. All galvanic corrosion monitoring experiments were conducted in triplicate to ensure the trends shown are characteristic.

## **ASTM B117 Q-Fog Salt Spray Testing**

DEVCOM ARL conducted accelerated life testing (ALT) on both intact and scribed MgRP and MgAlRP coated AA 7075-T651 panels, following ASTM B117 standards, using an Auto Technology salt fog chamber<sup>157</sup>. Testing occurred for a total duration of six weeks with three intact and three scribed MRP coated AA 7075-T651 panels removed from the camber at two-week intervals for characterization purposes. In order for comparisons to be drawn unexposed intact and scribed samples were set aside, as controls, to provide a baseline characterization profile. Once specimens were removed from the chamber at each two-week sampling period, they were promptly rinsed with deionized water and dried prior to handling and storage for characterization. Electrochemical testing that tracked the progression of OCP and EIS impedance behavior throughout the six-week exposure period to B117 ALT was conducted on intact MgRP and MgAIRP coated AA 7075-T651. Characterization was conducted in the form of SEM BSI crosssections with EDS elemental mapping throughout the six-week exposure window taken to document the progression of damage profiles. The oxygen signal detected through EDS elemental mapping was used as a marker for the oxidation of pigment and substrate in both cross-section map scan and plan view with line scan profiles across the scribed region. The evaluation of scribe corrosion and protection against IGC involved washing ASTM B117 samples post six-week exposure in 50% nitric solution for two-three minutes. This was done to remove accumulated corrosion products from both the surface of the MRP and the interior of the scribe. Comparisons are drawn from control samples that were unexposed as well as six-week exposed panels without protection scheme to determine whether or not the candidate MRP coating were capable of preventing entirely or reducing both scribe corrosion and protecting against IGC.

#### **Results**

## Characterization of As-Received Mg/MgAIRP coated AA 7075-T651

Characterization of as received MRP-AA7075-T651 cross-sections are conducted using BSI with EDS elemental mapping to assess primer thickness and particle size at 500x magnification. These physical characteristics of each coating can be shown in **Table 4-2** with cross-section micrographs shown in **Figure 4-1** for MgRP coated AA 7075-T651, and **Figure 4-2** for MgAlRP coated AA 7075. The MgRP coating contains flaked pigment of 26.5  $\mu m$  major axis and 12.2  $\mu m$  minor axis. The MgAlRP composite primer contains flaked Mg pigment of 18.2  $\mu m$  major axis and 6.6  $\mu m$  minor axis and spherical Al-5wt%Zn pigment with an average diameter of 9.8  $\mu m$ . It should be noted that the MgRP and MgAlRP both contain the same AN MgRP pigment and resin combination and the difference physical dimensions of Mg pigment may be a result of sampling during characterization.

The micrographs in **Figure 4-1** and **Figure 4-2** show a well-connected MRP coating layer that is capable of providing electrical connection throughout the thickness of the coating that is provided by the individual primer particles. However, not every particle is connected to the surrounding particles. The pigment volume concentration (PVC) has been studied elsewhere and is not the focus of this paper<sup>92,116,158</sup>. The total PVC of Mg pigment within the MgRP was 26% compared to the PVC of Mg pigment within the MgAlRP of 19%. This indicates a lower PVC for the Mg pigment in the composite MgAlRP than in the MgRP. However, if Al is activated, the

MgAlRP has a greater combined PVC including Mg pigment (19%) and Al pigment (28%) with a gross Mg + Al pigment surface area of 14.5 cm<sup>2</sup> of the combined Mg and Al pigment per cm<sup>2</sup> of MgAlRP. This is contrasted with the gross surface area of 4.81 cm<sup>2</sup> for the Mg pigment per cm<sup>2</sup> of MgRP.

## **Corrosion Electrochemistry Investigation**

Investigation of the polarization behaviors of bare AA 7075-T651, Al-5wt%Zn alloy,  $\eta$  phase , MgRP coated AA 7075-T651, and MgAlRP coated AA 7075-T651 is shown in **Figure 4-3**. Recall the strengthening phase in 7xxx alloy is the  $\eta$  phase which forms homogeneously in grain interiors and heterogeneously on the grain boundary. The PDP provides the basis for assessing potential ranges in which IGC occurs by dissolution of a boundary phase or zone. This is achieved by comparing critical potentials (E<sub>corr</sub>, E<sub>OCP</sub>, E<sub>pit</sub>) to ascertain potential ranges for IGC as discussed above. Such potential-dependent dissolution contrast may provide the predominant framework for IGC and IGSCC according to an anodic dissolution mechanism based on differences in critical potentials<sup>39,53,54,89</sup>. The AA 7075-T651 exhibits an E<sub>corr</sub> of -0.75 V<sub>SCE</sub> which appears to be very near its E<sub>pit</sub> (**Figure 4-3**).

The  $\eta$  phase is seen to have an Ecorr of -1.0 V<sub>SCE</sub> with E<sub>pit</sub> at -0.86 V<sub>SCE</sub> (**Figure 4-3**). The Al-5wt% Zn indicates an E<sub>corr</sub> of -0.94 V<sub>SCE</sub> which appears to be very near to its E<sub>pit</sub> (**Figure 4-3**). The electrochemical theory of Galvele posits that IGC occurs when the applied potential, E<sub>app</sub>, is such that E<sub>pit ( $\eta$ )</sub> < E<sub>app</sub> < E<sub>pit, 7075</sub> or E<sub>OCP, 7075</sub> <sup>39,53</sup>. One concept for cathodic prevention posits that protection is achieved when the grain boundary precipitate,  $\eta$  phase, is cathodically protected below E<sub>pit ( $\eta$ )</sub> <sup>39,53</sup>. Therefore, the potential range to expect IGC to occur is between -0.86 V<sub>SCE</sub> < E<sub>app</sub> < -0.75 V<sub>SCE</sub>.

The PDP of MgRP and MgAlRP coated AA 7075-T651 shifts the  $E_{corr}$  to -1.14 V<sub>SCE</sub> and -1.06 V<sub>SCE</sub> respectively as shown in **Figure 4-3**. A 24-hour exposure at OCP is shown in **Figure 4-4** for bare AA 7075-T6511, MgZn<sub>2</sub>, Al-5wt% Zn, and MgRP/MgAlRP coated AA 7075-T651. This shows the MgRP activates to a potential of -1.15 V<sub>SCE</sub> and maintains a potential of -1.07 V<sub>SCE</sub> up to the end of the 24-hour period (**Figure 4-4**). This potential shift may be sufficient to provide protection against IGC and IG-SCC as the potential is depressed below  $E_{pit(\eta)}$  by the MgRP. This will depend on the galvanic couple potential attained. The MgAlRP is observed to attain a potential of -1.25 V<sub>SCE</sub> and remains below the OCP of bare AA 7075-T651 by the end of the 24-hour OCP monitor at -1.08 V<sub>SCE</sub>. This potential shift is sufficient to provide protection against IGC and IG-SCC as the potential is depressed below  $E_{pit(\eta)}$  by the composite Mg-Al-5wt% Zn pigment in the MgAlRP provided the galvanic couple potential remains near the OCP.

The effects of magnesium concentration,  $[Mg^{2+}]$ , and pH on the electrochemical properties of AA 7075-T651 are shown in **Figure 4-5**. The variation in the OCP of AA 7075-T651 is influenced by the  $[Mg^{2+}]$ , which decreases the E<sub>OCP</sub>. However, there was a greater dependency noticed across varying pH (**Figure 4-5a**). Similarities are noticed with the E<sub>corr</sub> of AA 7075-T651 and can be seen to decrease to -1.3 V<sub>SCE</sub> in a basic pH 11 solution (**Figure 4-5b**). There is small variation (85mV) in the E<sub>pit</sub> of AA 7075-T651 as a function of pH (**Figure 4-5c**). However, all alkaline solutions are observed to have similar decreasing trend in E<sub>pit</sub> as a function of  $[Mg^{2+}]$ (**Figure 4-5c**). The effect of magnesium concentration,  $[Mg^{2+}]$ , and pH on the electrochemical behavior of Al-5wt% Zn is shown in **Figure 4-6**. Both the variation in E<sub>OCP</sub> and E<sub>corr</sub> of Al-5wt% Zn can be seen to decrease as the solution becomes more alkaline (**Figure 4-6a and 4-6b**). The variation in E<sub>pit</sub> of Al-5wt% Zn decreases as  $[Mg^{2+}]$  and pH increase (**Figure 4-6c**). The variation of the E<sub>OCP</sub> with [Cl<sup>-</sup>] independent from of the effects of  $[Mg^{2+}]$  in near neutral solution can be seen for pristine bare AA 7075-T651, Al-5wt%Zn, MgZn<sub>2</sub>, MgRP, and MgAlRP in **Figure 4-7**. This data implies that the relationship between key potentials suggested to be pertinent to IGC remain roughly similar across all  $[Mg^{2+}]$  and pH levels tested.

The influence of [Cl<sup>-</sup>] on the electrochemical behavior of AA 7075-T651, Al-5wt%Zn, and MgZn<sub>2</sub> is shown in **Figure 4-8** at near neutral unadjusted pH conditions. The PDP of AA 7075-T651 in **Figure 4-8a** shows a decrease in the  $E_{corr}$ , and  $E_{pit}$  with increasing [Cl<sup>-</sup>]. The  $E_{corr}$  can be seen to decrease approximately 300 mV<sub>SCE</sub> from a NaCl solution concentration of 1 mM to 1 M (in **Figure 4-8a**). The Al-5wt%Zn shows similar trends to AA 7075-T651; however, with increasing [Cl<sup>-</sup>] the passive window vanishes and  $E_{corr}$  decreases by 200 mV<sub>SCE</sub> between 1 mM and 1 M NaCl as seen in **Figure 4-8b**. The MgZn<sub>2</sub> possesses the lowest  $E_{corr}$  at 1 M NaCl at -1.05 V<sub>SCE</sub> and decreases by 300 mV<sub>SCE</sub> from a NaCl solution concentration of 1 mM to 1 M NaCl as shown in **Figure 4-8c**. These results suggest that MgRP and MgAlRP have an OCP favorable towards sacrificial protection. Even at different Cl<sup>-</sup> concentrations, the relationships are preserved such that EOCP, MRP <  $E_{OCP,(n)}$  <  $E_{pit(n)}$  <  $E_{OCP, 7075$ .

The PDP behavior of AA 7075-T651 shows a to decrease in  $E_{corr}$  from -0.76 V<sub>SCE</sub> at near neutral conditions (**Figure 4-9a**) to -1.3 V<sub>SCE</sub> under pH 11 conditions (**Figure 4-9b**) with the

development of a passive region until E<sub>pit</sub> at -0.74 V<sub>SCE</sub> (Figure 4-9b). The bare Al-5wt%Zn alloy shows similar trends, with E<sub>corr</sub> decreasing from -0.97 V<sub>SCE</sub> at near neutral conditions (Figure 4-9a) to -1.28 V<sub>SCE</sub> with the development of a passive region under pH 11 conditions until pitting at -0.9 V<sub>SCE</sub> (Figure 4-9b). The MgZn<sub>2</sub> shows a decrease in E<sub>corr</sub> from -1.13 V<sub>SCE</sub> at near neutral conditions (Figure 4-9a) to -1.33 V<sub>SCE</sub> under pH 11 conditions until pitting at -0.85 V<sub>SCE</sub> (Figure **4-9b**). The Mg displays a decrease in E<sub>corr</sub> from -1.55 at near neutral conditions (Figure 4-9a) to -1.65 under pH 11 conditions (Figure 4-9b). Furthermore, the mixed potentials describing the galvanic coupling of bare AA 7075-T651, Al-5wt%Zn alloy, MgZn<sub>2</sub>, and pure Mg can be seen by the junctions formed in the PDP shown in Figure 4-9. The galvanic couple potentials of Mg and MgRP coupled to bare AA 7075-T651 were -1.47 V<sub>SCE</sub> and -0.8 V<sub>SCE</sub>, respectively. The MgAlRP galvanic coupled potential was -0.75 V<sub>SCE</sub>. The galvanically coupled potentials of MgRP and MgAlRP identified by PDP are static and do not represent how the galvanically coupled potential evolves over time. Judging from the E - log i data, polarization below  $E_{pit(\eta)}$  requires a potential below -0.85 V<sub>SCE</sub> on AA 7075-T651 so that embedded MgZn<sub>2</sub> is polarized below E<sub>pit (n)</sub>. Therefore, a long-term potential hold was conducted on bare AA 7075-T651 at potentials to assess the current density that must be supplied from the MRP to the AA 7075-T651 to attain a coupled potential sufficient to protect  $E_{pit(\eta)}$ .

The effect of 24-hour PS polarization in quiescent 0.6 M NaCl on the protection of AA 7075-T651 can be seen in **Figure 4-10a** for PS holds at of -0.95 V<sub>SCE</sub>, -1.1 V<sub>SCE</sub>, and -1.4 V<sub>SCE</sub>. It is clear that the optimal potential is -0.95 V<sub>SCE</sub>. This is done to determine whether the galvanic couples formed by each MRP:AA 7075-T651 galvanic couple is sufficient to provide protection to AA 7075-T651. It can be seen from **Figure 4-10a** that a PS hold of -0.95 V<sub>SCE</sub> and -1.1 V<sub>SCE</sub> requires 6  $\mu$ A/cm<sup>2</sup> and 10  $\mu$ A/cm<sup>2</sup> after 24 hours, respectively. The PS hold of -1.4 V<sub>SCE</sub> results in 2.6 mA/cm<sup>2</sup> after 24 hours, as seen in **Figure 4-10a**. Plan view optical characterization (**Figure 4-10b**) indicates negligible surface degradation is noticed for the -0.95 V<sub>SCE</sub> potential hold. The -1.1 V<sub>SCE</sub> potential hold results in minor surface degradation in the form of enhanced dissolution near stinger precipitates as seen in the plan view optical characterization shown in **Figure 4-10b**. The -1.4 V<sub>SCE</sub> potential hold resulted in major surface degradation in the form of gross-scale cathodic corrosion as seen in the plan view optical characterization shown in **Figure 4-10b**. These differences are best observed in the SEM BSI cross-section micrographs shown in **Figure 4-10c** where the cathodic corrosion progresses through the depth of the AA 7075-T651 sample at -1.4

V<sub>SCE</sub>. It can be seen from **Figure 4-10a** that polarization to -0.95 V<sub>SCE</sub> and -1.1 V<sub>SCE</sub> requires a supply of 6  $\mu$ A/cm<sup>2</sup> and 10  $\mu$ A/cm<sup>2</sup> after 24 hours, respectively. The PS hold of -1.4 V<sub>SCE</sub> results in 2.6 mA/cm<sup>2</sup> after 24 hours. However, this latter potential is too severe and leads to high rates of H<sub>2</sub> evolution. The long-term anodic current density which must be supplied from the MRP to the AA 7075-T651 to attain a coupled potential of -0.95 V<sub>SCE</sub> is 6  $\mu$ A/cm<sup>2</sup> (**Figure 4-10a**).

## The UVa DC/AC/OCP Cycle Test: Charge Output and Barrier Assessment of Mg/MgAl-Rich Primers

The cycle test was performed on intact pigmented coatings. The magnitude of the established OCP of intact MgRP throughout DC/AC/OCP cycle testing is shown compared to the 7075-T651 OCP (-0.75 V<sub>SCE</sub>, dotted red line) in **Figure 4-11a**. The MgRP applied to AA 7075-T651 activated to an OCP of -1.53 V<sub>SCE</sub> on the first cycle (10 minutes of polarization). The MgRP activated to its most negative potential on cycle 1 and sustained an E<sub>OCP</sub> between E<sub>app</sub> until cycle 13 (75 hours) of the DC/AC/OCP cycle testing (Figure 4-11a). The MgRP at cycle 1 polarized to -0.95 V<sub>SCE</sub> or  $E_{app} < E_{pit(\eta)}$  initially produced a net anodic current density of +0.5  $\mu A/cm^2$ averaged over the total area of 0.785 cm<sup>2</sup> (Figure 4-11b). The peak current produced occurred in cycle 4 at + 34  $\mu A/cm^2$  that decreased and remained at +2  $\mu A/cm^2$  after 1000 seconds (Figure 4-11b). These are anodic current densities that contribute to protection of the AA 7075-T651, as the MgRP is the anode and the AA 7075-T651 substrate sits below its OCP. Figure 4-11c shows the Bode magnitude electrochemical impedance spectra collected throughout the DC/AC/OCP cycle testing. A cross-sectional EDS oxygen map can be seen in Figure 4-11d showing the oxidation profile of the post-DC/AC/OCP cycle testing MgRP sample. The oxygen EDS map shows the oxidation of the Mg pigment perimeter as well as the MgRP- AA 7075-T651 interface (Figure 4-11d).

The MgAlRP activated to an OCP of -1.15 V<sub>SCE</sub> on the first cycle (10 minutes of polarization) (**Figure 4-12a**). The MgAlRP activated to its most negative potential on cycle 4 and sustained an E<sub>OCP</sub> lower than -0.95 V<sub>SCE</sub> until cycle 11 (56 hours) of the DC/AC/OCP cycle testing (**Figure 4-12a**). The MgAlRP at cycle 1 polarized to -0.95 V<sub>SCE</sub> or E<sub>app</sub> < E<sub>pit ( $\eta$ )</sub> initially produced a current density of +7.5  $\mu$ A/cm<sup>2</sup> averaged over the total area of 0.785 cm<sup>2</sup> (**Figure 4-12b**). The peak current produced occurred in cycle 2 at + 10.6  $\mu$ A/cm<sup>2</sup> that decreased and remained at +2  $\mu$ A/cm<sup>2</sup> after 1000 seconds (**Figure 4-12b**). These are anodic current densities that do

contribute to the protection of AA 7075-T651, as the MgAlRP is the anode. **Figure 4-12c** shows the Bode magnitude electrochemical impedance spectra collected throughout the DC/AC/OCP cycle testing. A cross-sectional EDS oxygen map can be seen in **Figure 4-12d** showing the oxidation profile of the post-DC/AC/OCP cycle testing MgAlRP sample. The oxygen EDS map shows the oxidation of both the Mg and Al-5wt% Zn pigment extending beyond the perimeter of the pigment with more uniform oxidation throughout the exposed pigment surface (**Figure 4-12d**). The electrochemical characteristics and performance of MgRP and MgAlRP throughout DC/AC/OCP cycle testing are shown in **Table 4-3**.

The remaining anodic charge capacity in these MRPs is not necessarily assessed because pigment particles may be electrically isolated by loss of particles in close proximity and passivation by oxide of hydroxide formation. It is suggested that OCP increase during cycle testing (**Figure 4-11** and **4-12a**) occurs mostly due to passivation and electrically isolated pigment rather than substantial pigment loss, which is supported by the Backscatter Electron (BSE) micrographs taken on post-cycle testing MRP specimens (**Figure 4-11d, Figure 4-12d**). The MgRP shows partial Mg pigment oxidation because the interior of the Mg pigment is relatively unperturbed. Moreover, there is a layer of oxidation at the MRP-substrate interface (**Figure 4-11d**). In the MgAIRP, complete oxidation is apparent in Mg pigments as indicated by oxygen EDS signal through the entire thickness of the primer following the cycle test (**Figure 4-12d**).

The MgRP and MgAlRP barrier properties were assessed via PS EIS (at the primer OCP) intermittently throughout PS cycle testing to monitor impedance and coating defect area progression with increasing exposure time. The variation in low frequency (0.01 Hz) modulus of impedance can be seen for each cycle in **Figure 4-13a** with very little degradation in barrier properties limited to variation of 1 order or magnitude for MgRP over 100 hours of polarization at -0.95 V<sub>SCE</sub>. The MgRP had  $Z_{mod}^{0.01 \text{ Hz}}$  response of  $1.9 \times 10^5$  ohm  $\cdot$  cm<sup>2</sup> that decayed to  $2.1 \times 10^4$  ohm  $\cdot$  cm<sup>2</sup> after 100 hours of PS hold at -0.95 V<sub>SCE</sub>. The MgAlRP is observed to have a higher  $Z_{mod}^{0.01 \text{ Hz}}$  over 100 hours of polarization at -0.95 V<sub>SCE</sub> varying from  $4 \times 10^6$  ohm  $\cdot$  cm<sup>2</sup> to  $1.3 \times 10^6$  ohm  $\cdot$  cm<sup>2</sup> (**Figure 4-13a**).

The variation in OCP established at the end of each OCP cycle within DC/AC/OCP cycle testing can be seen in **Figure 4-13b**. The lowest potential obtained for MgRP throughout DC/AC/OCP cycle testing after cycle 3 was -1.25 V<sub>SCE</sub>. The lowest potential obtained for MgAlRP throughout DC/AC/OCP cycle testing was in cycle 2 with a potential of -1.16 V<sub>SCE</sub> (**Figure 4-**

**13b**). The MgRP produced the least charge as indicated in **Figure 4-13c** showing the charge accumulated throughout DC/AC/OCP for each cycle. A decrease in the charge density was observed after cycle 9 proceeding to a rise again after cycle 12 (**Figure 4-13c**). The MgAlRP produced the greatest charge density observed and unlike the MgRP, continued to increase in utilization over time (**Figure 4-13c**). Evaluation of primer galvanic couple kinetic behavior may provide further evidence towards understanding these differences in MRP performance.

The theoretical anodic charge capacity of each MRP, reported in **Table 4-3**, was assessed based on average primer thickness and volume per cm<sup>2</sup> (**Table 4-2**), the density of Mg / Al-5wt.%Zn, the molar volume, the exchange of two electrons necessary for Zn or Mg oxidation (Zn<sup>2+</sup> / Mg<sup>2+</sup>) and/or the exchange of three electrons necessary for Al oxidation (Al<sup>3+</sup>). For comparison, the maximum total anodic current output exhibited by each MRP during cycle testing was computed by integrating the anodic current output from each stage of PS potential hold at -0.95 V<sub>SCE</sub> (**Table 4-3**). The theoretical anodic charge (Q) output analysis demonstrated that MgRP has the lowest theoretical anodic Q capacity at 16.7 C/cm<sup>2</sup>, while MgAIRP has a higher capacity at 27.2 C/cm<sup>2</sup> (**Table 4-3**). The maximum experimental anodic Q output for each specimen based on three series of cycle testing demonstrated that the MgAIRP has a maximum output of 0.5 C/cm<sup>2</sup> followed by the MgRP with 0.1 C/cm<sup>2</sup>.

The fraction of experimental to theoretical anodic charge output demonstrated anodic charge usage (ACU) of 1.8% for MgAlRP, and 0.6% for MgRP, as shown in **Table 4-3**. Therefore, these primers have considerable protective capacity remaining following the cycle test, indicating that a considerable reservoir of Al-Zn and Mg remains available for local galvanic protection should a defect develop proximate to buried pigment. However, it should be mentioned that there is self-corrosion of MgRP and galvanic corrosion of MgAlRP consumes an unknown amount of charge rendering it unavailable. In summary, MgAlRP performs better than MgRP according to a number of metrics when polarized to -0.95 V<sub>SCE</sub> to mimic a galvanic couple with bare AA 7075-T651.

## Substrate – Primer Galvanically Coupled Potential and Current Densities

Galvanic couples investigated consisted of intact MRP coating electrically connected to bare AA 7075-T651. The galvanic couple test is an excellent complement to the cycle test, as the galvanic potential spontaneously forms, is not static, and is not assigned. The coupled galvanic potential of MgRP and MgAIRP coupled to bare AA 7075-T651 in a 1:1 area ratio is shown in **Figure 4-14a** with the green dotted line denoting the OCP of AA 7075-T651 (-0.75 V<sub>SCE</sub>). The coupled potential of MgRP and MgAIRP to AA 7075-T651 is -0.9 V<sub>SCE</sub>; however, the MgAIRP is more stable and subject to fewer changes in the coupled potential as seen in **Figure 4-14a**. The galvanically coupled potentials shown in **Figure 4-14a** are free to evolve with time. The galvanically coupled current densities are shown in **Figure 4-14b** for MgRP and MgAIRP coupled to AA 7075-T651 in a 1:1 area ratio. The galvanic coupled current density of MgRP produces current spikes up to  $+7.5\mu A/cm^2$  and decreases to below  $1\mu A/cm^2$  by the end of the 24-hour bimetal galvanic couple. The MgAIRP produces current spikes up to  $+7.5\mu A/cm^2$  and decreases to  $+1.7\mu A/cm^2$  by the end of the 24-hour bimetal galvanic couple. This is consistent with the current density of 6  $\mu A/cm^2$  required to polarize bare AA 7075-T651 to -0.95 V<sub>SCE</sub>.

The coupled galvanic potential of MgRP and MgAIRP to bare AA 7075-T651 in a 15:1 area ratio is shown in **Figure 4-15a** with the green dotted line denoting the OCP of AA 7075-T651 (-0.75 V<sub>SCE</sub>). The coupled potential of MgRP and MgAIRP to AA 7075-T651 is -1.0 V<sub>SCE</sub>; however, the MgAIRP is more stable and subject to fewer changes in the coupled potential, as seen in **Figure 4-15a**. Again, there are differences in the galvanically coupled potentials identified through PDP in **Figure 4-9a** as they are static points while the galvanic coupled potentials of **Figure 4-15a** are allowed to evolve over time. Comparing the galvanic coupled potentials of **Figure 4-14a** and **4-15a** there is a lower galvanic couple potential by 100 mV given larger MRP:substrate area ratios. The galvanically coupled current densities are shown in **Figure 4-15b** for MgRP and MgAIRP coupled to AA 7075-T651 in a 15:1 area ratio. The galvanic coupled current density of MgRP produces current spikes up to  $+10\mu A/cm^2$  and decreases to  $2.5 \mu A/cm^2$  by the end of the 24-hour bi-metal galvanic couple. The MgAIRP produces current spikes up to  $+7.5\mu A/cm^2$  and decreases to  $+5\mu A/cm^2$  by the end of the 24-hourbi-metal galvanic couple A-15b. This is consistent with the current density of 6  $\mu A/cm^2$  required to polarize bare AA 7075-T651 to -0.95 V<sub>SCE</sub>.

The MRP CE alters the solution chemistry near the reacting electrode interfaces causing changes in the solution pH throughout the galvanic coupling experiments in both 1:1 and 15:1 area ratios as shown in **Figure 4-16**. The change in pH in front of the bare AA 7075-T651 WE can be seen in **Figure 4-16a**. Changes in pH were only observed when the area ratio 15:1 was over the WE. The MgRP exhibits an increase in the local pH near the bare AA 7075-T651 WE from an

initial pH of 6 to 8.5-9.1 (**Figure 4-16a**). The local pH near the bare AA 7075-T651 WE changed from 6 to 8.0-8.5 in the case of MgAlRP. The MgRP CE in the 15:1 area ratio exhibits a slightly greater pH increase to a peak of 10.3 decreasing as low as 8.4 by the end of the 24-hour monitoring period (**Figure 4-16b**). In summary, it is seen that the pH shifts toward 10 at the bare AA 7075-T651 surface couple to MRP. This will affect activation and deactivation of Al-5wt%Zn, as changes in pH may correspond to regions in which dissolution of Al is favorable over solid oxide or hydroxide formation<sup>159</sup>.

## Lab Accelerated Testing – ASTM B117 Salt Spray

Intact and X-scribed MgRP and MgAlRP were tested in 0.6 M NaCl with a Q-Fog salt spray cabinet to assess scratch protection ability and performance of each MRP as a function of exposure time. Periodic OCP and EIS monitoring of the MRP coated AA 7075-T651 panels was conducted in 0.6 M NaCl tracking the progression of coating deterioration throughout B117 testing (Figure 4-17). The MgRP is shown to maintain protection potential at -1.1 V<sub>SCE</sub> over the course of six weeks of ALT (Figure 4-17a). The composite MgAlRP was capable of maintaining an EOCP of -1.3 V<sub>SCE</sub> after six weeks of ASTM B117 salt spray testing in 0.6 M NaCl as seen in Figure 4-**17b.** It is also useful to compare the impedance behavior. The Bode magnitude electrochemical impedance spectra progression throughout the six weeks of accelerated laboratory testing can be seen for both MgRP and MgAIRP taken after 1-hour OCP monitoring in Figure 4-17c and Figure 4-17d, respectively. The MgRP at zero weeks in the as-received condition shows a  $Z_{mod}^{0.01 \text{ Hz}}$  of 5.9  $\cdot$  10<sup>5</sup>  $\Omega \cdot$  cm<sup>2</sup> as seen in **Figure 4-17c**. The MgAlRP initially recorded a  $Z_{mod}^{0.01 \text{ Hz}}$  of 2.8  $\cdot$  10<sup>7</sup>  $\Omega \cdot$  cm<sup>2</sup> as seen in **Figure 4-17d**. The MgAlRP sustains an order of magnitude greater  $Z_{mod}^{0.01 \text{ Hz}}$  (1.2 · 10<sup>6</sup>  $\Omega$  · cm<sup>2</sup>) compared to the MgRP with a  $Z_{mod}^{0.01 \text{ Hz}}$  of 1 · 10<sup>5</sup>  $\Omega$  · cm<sup>2</sup> after six weeks of ASTM B117 testing. The phase angle progression can be seen for MgRP in Figure 4-17e and MgAlRP in Figure 4-17f.

Under paint and scratch corrosion behavior of the MgRP throughout ASTM B117 exposure are reported in **Figures 4-18** and 4-**19** with BSI showed in conjunction with magnesium and oxygen signal from EDS. The oxygen signal is used to track corrosion damage herein. The intact MgRP is shown in **Figure 4-18** and can be observed to oxidize at the coating-electrolyte interface and at Mg pigment particles throughout the thickness of the intact MgRP coatings. The oxidation predominantly occurs on the pigments throughout the MgRP coating and not at the MRP-substrate interface (**Figure 4-18**). The scribed MgRP cross-section is shown in **Figure 4-19** and is seen to oxidize throughout the coating thickness as well as at the scribe wall (defect region). The scribed MgRP experiences an increase in magnesium and oxygen signal within the scribed region seen in **Figure 4-19** without MRP-substrate oxidation. The oxidized Mg pigments can be seen to reduce the Mg signal intensity (**Figure 4-19**).

Concerning mass transfer of pigment to the scratch, **Figure 4-20** shows BSI imaging and EDS line scans of oxygen and Mg for MgRP in both the 0-week as-received condition as well as after 6-weeks of ASTM B117 salt spray exposure testing. The as-received 0-week MgRP shows a high magnesium signal intensity within the intact region of the coating, with the alloying elements of AA 7075-T651 shown with increasing signal intensity within the scribed (uncoated) region (**Figure 4-20**). The post 6-week ASTM B117 condition reveals a reduction in the magnesium signal intensity within the intact region of the coating with an increase in the magnesium signal intensity within the scribed region by 3.5x. The magnesium signal intensity overlaps with the oxygen signal intensity implying the oxidation of magnesium within the MgRP. The EDS line scan is only capable of detecting AA 7075-T651 substrate within the scribed region to background levels (< 200 counts) suggesting the presence of magnesium and oxygen corrosion products. The 6-week ASTM B117 BSI micrographs shown in **Figure 4-20** show a significant coverage of magnesium and oxygen-rich corrosion products identified via EDS line scan throughout the scribed region, showing the ability to heal defected regions.

Under paint and scratch corrosion evolution of the MgAlRP throughout ASTM B117 exposure is reported in **Figures 4-21** and 4-22, showed in conjunction with magnesium and oxygen signal from EDS. The oxygen signal is used to track corrosion damage herein. The intact MgAlRP is shown in **Figure 4-21** and can be observed to oxidize at the coating-electrolyte interface as well as throughout the thickness of the MgAlRP coating. However, the extent of oxidation in the MgAlRP is lower than that in the MgRP (**Figure 4-18**). The oxidation is restricted to the Mg pigments throughout the MgAlRP coating, and does not appear in the Al-5wt%Zn pigments (**Figure 4-21**). There does not appear to be any MRP-substrate interface oxidation (**Figure 4-21**). The scribed MgAlRP is shown in **Figure 4-22** and is seen to oxidize throughout the coating thickness as well as at the scribe wall (defect region). The scribed MgAlRP has an increase magnesium and oxygen signal within the scribed region, as seen in **Figure 4-22**, without MRP-substrate oxidation. The increased Mg concentration is an indicator of transfer and redeposition of

dissolved Mg released from the MgAlRP coating and transferred to the scribe. This indicates some ability of the MgAlRP to precipitate corrosion products on defected regions of the coating (scribe).

**Figure 4-23** shows BSI imaging and EDS line scans of MgAIRP in the 0-week as-received condition to serve as control when comparing oxidation effects to 6-week ASTM B117 salt spray exposure testing . The post 6-week ASTM B117 condition reveals a reduction in the magnesium signal intensity within the intact region and an increase in the magnesium signal intensity within the scribed region. The post 6-week ASTM B117 condition reveals a reduction in the aluminum signal intensity within the intact region and a decrease in the aluminum signal intensity within the intact region and a decrease in the aluminum signal intensity within the scribed region. The overlapping magnesium and oxygen EDS signal shown in **Figure 4-23** are present throughout the intact coating as well as the scribed region. The 6-week ASTM B117 BSI micrographs shown in **Figure 4-23** exhibit good coverage of the corrosion products produced throughout the scribed region.

Corrosion products were tracked throughout ASTM B117 cycle testing on each MRP XRD analysis identified the composition and relative intensity of the crystalline phase seen in each primer (**Figure 4-24**). The MgRP can be seen to produce crystalline Mg(OH)<sub>2</sub> corrosion products as identified in **Figure 4-24a**, present in the 2- and 4- week MgRP samples with the 6-week Mg(OH)<sub>2</sub> peaks broadening into a weaker signal-to-noise ratio XRD spectra. The MgAlRP can be seen to produce crystalline Al(OH)<sub>3</sub>, present in the initial condition, as well as a weak peak at 58° sharing position with the previously identified Mg(OH)<sub>2</sub>. However, the peak at 52° fades into the background with continued ASTM B117 salt spray exposure (**Figure 4-24b**). It is worth noting that there may be additional corrosion products that are not detected within the diffraction spectrum either due to lack of crystallinity or due to sampling and detection limitations.

It is necessary to evaluate the ability of each primer to provide protection against scribe corrosion and IGC of the substrate which can be made by considering the cross-section BSI micrographs in **Figure 4-25**. In order to determine whether each coating can protect against scribe corrosion a control needs to be considered by which comparisons can be made. The pristine uncoated AA 7075-T651 in both bare and scribed conditions serve as a control and can be seen in **Figure 4-25a** and 4-25b, respectively. The six-week B117 exposure of AA 7075-T651 in the bare (**Figure 4-25c**) and scribed (**Figure 4-25d**) conditions without MRP protection scheme serve as a means of comparing the amount of degradation that occurs under equivalent conditions and exposure time. These two controls provide a means of comparing each MRP coating to a baseline

as opposed to making qualitative judgements compared to one another. Comparing the pristine bare AA 7075-T651 (Figure 4-25a) to the six-week exposure of unprotected bare AA 7075-T651 to B117 salt spray testing (Figure 4-25c) shows dissolution of AA 7075-T651 up to a depth of 20 µm as well as what looks to be dissolution of IMC and fine hair-like cracks left behind characteristic of IGC. Comparing the pristine scribed AA 7075-T651 (Figure 4-25b) to six-week exposure of unprotected scribed AA 7075-T651 (Figure 4-25d) shows an increase in the scribe dimensions along the depth of the scribe by 10 µm and width of the scribe by 80 µm after six weeks of B117 testing. The cross-section BSI of MgRP coated AA 7075-T651 within the scribed region is shown in Figure 4-25e with no apparent dissolution through the thickness of the crosssection after six weeks of B117 testing. The cross-section BSI of MgAlRP coated AA 7075-T651 within the scribed region in **Figure 4-25f** does not show any signs of scribe deterioration. The deterioration of the bare AA 7075-T651 surface, widening of the scribe wall, and increase in the scribe depth can be attributed to increased dissolution due to the lack of MRP protection scheme. The indentation shown within the scribed region of the MgAIRP in Figure 4-25f originates from the scribe tool as the tip hardness is substantially greater than the aluminum substrate. These results may not fully represent the severity of corrosion as the field of view does not encompass a large portion of the sample in comparison to the area exposed and may be a conservative representation.

## **Discussion**

The present study indicates that the MgAlRP system is superior to the MgRP system. This is supported by suitably negative and stable OCP over time, dispenses high anodic charge, remains an anode in zero resistance ammeter testing, and possesses superior barrier properties measured via EIS. It is noted that pigment physical attributes are not equal as far as pigment volume concentration and surface area. The total PVC of Mg pigment within the MgRP was 26% compared to the PVC of Mg pigment within the MgAlRP of 19%. This indicates a lower PVC for the Mg pigment in the composite MgAlRP than in the MgRP. However, if the Al is activated, the MgAlRP has a greater combined PVC including Mg pigment (19%) and Al pigment (28%) with a gross Mg + Al pigment in MgAlRP possess different pigment dimensions (**Table 4-2**) with a surface area of 6.58 cm<sup>2</sup> of Mg pigment per cm<sup>2</sup> of MgAlRP. This is contrasted with the gross surface area of 4.81 cm<sup>2</sup> for the Mg pigment per cm<sup>2</sup> of MgRP. The combined Mg + Al pigment surface area of

the MgAIRP is greater than the Mg pigment surface area in the MgRP by a factor of 3. The differences in physical attributes of the primer reflect a greater Mg surface area in the MgAIRP than in the MgRP by a factor of 1.37. This does not reflect considerations of electrically disconnected pigments or pigment fallout and assumes 100% utilization of pigment in each coating. As mentioned previously, the MgAIRP is a mixture of the AN MgRP and an AIRP produced by RC, therefore, the differences in Mg pigment dimensions may be a result of different sampling areas during scanning electron microscopy and not entirely reflective of the MgAIRP tested.

## Oxidation of Mg and Al in Hybrid MgAl-Rich Primer Systems

The oxidation observed in the intact MgRP during cycle testing (**Figure 4-11d**) and ASTM B117 accelerated environmental testing (**Figure 4-18**) show similarities in the presence of partial oxidation of Mg pigment. This is apparent as the perimeter of flaked Mg pigment appears oxidized with an unoxidized interior. The oxidation of Mg pigment and formation of corrosion products can be considered to occur spontaneously in aqueous environments through the following electrochemical half-cell and overall reactions described in Equations 1-3 or 4:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \text{ (overall)}$$

$$Mg+2H_2O = MgO + H_2$$

4

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$$
 5

The chemical equilibrium between the  $Mg^{2+}$  hydroxide and  $Mg^{2+}$  and  $OH^-$  in solution is described by Equation 5. The corrosion products identified in **Figure 4-24** are described by the above reactions and can be plotted to produce equilibria lines for the formation of stable Mg-based corrosion products in aqueous solution dependent on the initial amount of species present and the pH, as seen in **Figure 4-26**. This is described elsewhere<sup>159</sup>. The formation of solid Mg(OH)<sub>2</sub> requires a higher concentration of available Mg<sup>2+</sup> for the equilibrium formation of a stable corrosion product compared to the stability of solid MgO, as seen in **Figure 4-26**. The precipitated corrosion products present after ASTM B117 are an indication of utilization of the pigment and of the alkaline conditions developed throughout the duration of testing.

The oxidation behaviors observed in the intact MgAlRP during cycle testing (**Figure 4-12d**) and ASTM B117 accelerated environmental testing (**Figure 4-21**) show similarities in the presence of complete oxidation of Mg pigment. The observed oxidation cross-section profiles are distinctly different than those observed in the MgRP coating (**Figure 4-11d** and **4-18**). It is a given that Al-Mg interaction may form a local galvanic cell between pigments as well as the substrate. Moreover, the dissolution of Mg within the composite MgAlRP coating changes the local pH under equilibrium conditions governed by reaction 5. The equilibrium pH describing the stability between Mg<sup>2+</sup> and Mg(OH)<sub>2</sub> for a [Mg<sup>2+</sup>] of 10<sup>-6</sup> M is 11.3. This in turn impacts the relative corrosion product stability of AlO<sub>2</sub><sup>-</sup>, stabilizing AlO<sub>2</sub><sup>-</sup> at pH 11-12<sup>160</sup>. Therefore, this could be a pathway for AlRP pigment activation unique to the MgAlRP system. It can be seen that at pH 11-12 that AlO<sub>2</sub><sup>-</sup> is more stable than either Al(OH)<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> (**Figure 4-26**). This can be shown below.

Now, let us consider the oxidation and dissolution of Al described by the relevant electrochemical reactions for the formation of the corrosion products shown below by Equations 6-10. Starting with a neutral pH, Al is spontaneously oxidized in water to form Al(OH)<sub>3</sub> or  $Al_2O_3 \cdot nH_2O$ .

$$3H_{2}O + 3e^{-} \rightarrow 3H_{ads} + 3OH^{-} \qquad 6$$

$$Al + 3H_{2}O \rightarrow Al(OH)_{3} + 3e^{-} + 3H^{+}$$

$$7$$

$$2Al + 6H_{2}O \rightarrow 2Al(OH)_{3} + 3H_{2} \text{ (overall)} \qquad 8$$

$$Al^{3+} + 2H_{2}O \leftrightarrow AlO_{2}^{-} + 4H^{+} \qquad 9$$

$$2Al + 3H_{2}O = Al_{2}O_{3} + 3H_{2} \qquad 10$$

The  $Al^{3+}$  corrosion products identified in the above reactions can be plotted to produce equilibria lines for the formation of stable Al-based corrosion products in aqueous solution dependent on the initial amount of  $Al^{3+}$  and  $Mg^{2+}$  species present and the pH, as seen in **Figure 4-26** for Al<sub>2</sub>O<sub>3</sub> and Al(OH)<sub>3</sub>. The formation of Al(OH)<sub>3</sub> requires a lower concentration of available  $Al^{3+}$  for the formation of a stable corrosion product than  $Al_2O_3$ , as seen in **Figure 4-26**. A mixed Al-Mg product has not been identified.

This process explains the origins of the cooperative or synergistic effect between the performance of Mg and Al. The local pH brought about by Mg oxidation in an Al/Zn/Mg system is speculated to affect the dissolution of Al. This is understood through the use of a chemical stability diagram for Al/Mg described by Santucci et al.<sup>159</sup>. Defects such as scribes may expose additional aluminum from the substrate where corrosion products are allowed to dissolve and form corrosion products as found in line EDS profiles showing an increase in the Mg signal within the scribed region in both scribed MgRP (Figure 4-20) and scribed MgAlRP (Figure 4-23). The corrosion product formation is hypothesized to play an important role in the protection of the AA 7075-T651 substrate during exposure to marine conditions; therefore, the conditions of stable product formation and dissolution trajectories will determine the corrosion product protection capacity of a particular MRP. To address this issue requires discussion of the effects of the pH on corrosion electrochemistry. The dissolution trajectory, or dissolution pathway toward equilibrium, of the composite primer is then altered by the participation of both pigments in the oxidation and corrosion process of MgAlRP, as shown in Figure 4-26. The dissolution trajectory of the Mg-Al can be seen in Figure 4-26 and is shown to activate the Al as the dissolution of Mg increases the basicity of solution pulling the dissolution trajectory into a region of Al activity or stable Al<sup>3+</sup>. The dissolution trajectory of Mg-Al crosses the equilibria line of Al(OH)<sub>3</sub>/Al<sup>3+</sup> at a pH of 8.8 as opposed to the Mg dissolution trajectory remaining within the stable Al(OH)3 region. This is the premise of enhanced electrochemical performance of the composite primer showing increased utilization of depassivated Al pigment.

# Electrochemical behavior of MRP – 7075-T651 galvanic coupling explaining the Mg-Al synergy

Two findings must be discussed: (a) the increased utilization of the composite MgAlRP, and (b) the electrochemical differences of Al-5wt% Zn pigment within MgAlRP and bulk Al-5wt% Zn alloy. These can be explained with mixed potential theory and the corrosion thermodynamics of the governing electrochemical and chemical reactions written above. This analysis requires that pH be taken into consideration. Consider the dissolution of Mg within the MgRP below pH 11 for which reactions 1-5 are operative. Mg is unstable in water and

spontaneously corrodes with water reduction resulting in  $H_2$  evolution (reactions 1-2) and overall reaction 3. The pH rises due to the production of hydroxyl ions seen in reaction 1 which raises the local pH to an equilibrium pH of 10.4 established by the equilibrium pH of reaction 3.

The chemical effects of  $[Mg^{2+}]$ ,  $[Cl^{-}]$ , and pH on the dissolution behavior of AA 7075-T651 and an Al-5wt% Zn alloy are shown in **Figure 4-5** through **Figure 4-8**. The Al-5wt% Zn alloy appears to show similar trends as AA 7075-T651 under the same pH range and  $[Mg^{2+}]$ conditions; however, the Al-5wt%Zn alloy activates more readily at pH 10 than AA 7075-T651 (**Figure 4-6**). The AA 7075-T651 shows greater dependence of E<sub>OCP</sub> on pH for all  $[Mg^{2+}]$  with activation seen at pH 11 shown in **Figure 4-5**. The polarization behavior of AA 7075-T651, Al-5wt% Zn, and MgZn<sub>2</sub> (**Figure 4-8**) shows strong effects on lowering the E<sub>corr</sub> as a function of  $[Cl^{-}]$ independent of  $[Mg^{2+}]$  at near neutral conditions. It is important to examine whether AlRP can function as a sacrificial anode under these changes in pH,  $[Mg^{2+}]$ , and  $[Cl^{-}]$ .

The MgRP in the 1:1 area ratio initially responds by supplying a strong anodic current from the oxidation reaction of  $Mg^0$  to  $Mg^{2+}$  (reaction 2). The reaction is non-polarizable, remaining close to the Nernst potential associated with reaction 2. The cessation of dissolution activity decreases limiting the utilization of all Mg pigment within the MgRP (**Figure 4-14b**). The region separating the chemical reaction between  $Mg^{2+}$  and  $Mg(OH)_2$  is defined by the equilibrium of reaction 4. For an  $Mg^{2+}$  concentration of  $10^0 - 10^{-6}$  M the equilibrium pH for reaction 4 will vary between 8.4 and  $11.6^{-161}$ . This allows for the assessment of ion concentration within the aqueous electrolyte by measuring the pH near the reacting electrode surface.

An assessment of the dissolution of Mg via pH monitoring is shown in **Figure 4-16** for a galvanic coupling of the bare AA 7075-T651 and MgRP coated AA 7075-T651. The 1:1 and 15:1 area ratio reached a peak pH of 9.8 and 10.3 for the MgRP electrode interface corresponding to a  $Mg^{2+}$  concentration in the electrolyte of  $10^{-3}$  and  $10^{-4}$  M, respectively as determined from the chemical stability modeling proposed by Santucci et al.<sup>159</sup> and shown in **Figure 4-26**. The 1:1 and 15:1 area ratio attained a pH of approximately 8.6 over the coating after 24-hour galvanic coupling to bare AA 7075-T651, substrate indicating an  $Mg^{2+}$  concentration of  $10^{-1}$  M at equilibrium with  $Mg(OH)_2$ . The sequence of reactions 1-5 describes spontaneous corrosion of the Mg pigment yielding aggressive self-corrosion of magnesium systems in the presence of water and NaCl.

Similar results were reported by McMahon et al in the determination of Mg-Al synergy between the same MgRP and a MgAlRP<sup>54</sup>.

Consideration should be made as to the fate of Al within the MgAIRP. Pure Al starting at pH 6 in NaCl solution is passive at  $10^{-6}$  M Al<sup>3+</sup> with a minimum equilibrium solubility at pH 4.7, as shown by Santucci et al.<sup>159</sup>. The Al spontaneously passivates by half-cell reactions 1 and 2 to form Al(OH)<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> and becomes polarizable. This can be seen in the work of McMahon et al., in which the E<sub>GC</sub> of an AIRP (Al-5wt%Zn pigment) polarizes the potential of a 5456 substrate (-0.8 V<sub>SCE</sub>)<sup>54</sup>. The equilibrium chemical stability of AlO<sub>2</sub><sup>-</sup> with Al(OH)<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> is governed by Equation 9. For a concentration of  $10^{-6}$  M, AlO<sub>2</sub><sup>-</sup> is stable at pH 8 and above. McMahon et al. measured pH over an AIRP throughout the duration of a galvanic corrosion experiment in which an AIRP coated 5456 coupled to bare AA 5456 remained at a pH of 6.0-6.5, which is well within the thermodynamic stability region of Al(OH)<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub>. It should be noted that Al<sup>3+</sup> cation buildup in solution has been noted to accelerate HER on Al alloys<sup>162</sup>, which accelerates self-corrosion. The alloying of 5wt% Zn in the aluminum pigments cannot be ignored, as the stability of Zn(OH)<sub>2</sub> at pH 6 is also pertinent to the enhanced activity of MgAIRP. The formation of Zn(OH)<sub>2</sub> is thermodynamically stable at a 1 M Zn<sup>2+</sup> with a minimum solubility at pH 5.6<sup>163</sup>.

Al is activated by the high pH, as suggested by the chemical stability modeling in **Figure 4-26**. The chemical stability modeling implies that Mg oxidation and the resulting pH rise to 8.6 thermodynamically activates the Al-5wt% Zn pigments (**Figure 26**). The production of hydroxyl ions as reaction by-products of Mg oxidation changes the electrolyte to pH 8.6 during the galvanic couple. The Mg-Al pigment oxidation was observed to shift the pH to 9 over the MRP in the 15:1 area ratio and 8.2 pH for the 1:1 area ratio which requires a very high concentration of  $10^{-3}$  M for  $Al^{3+}$  and  $10^{-2}$  for Mg<sup>2+</sup> for Al(OH)<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and Mg(OH)<sub>2</sub> to remain the stable species, respectively. This could explain how the Al-5%Zn pigment is activated to oxidize to  $AlO_2^-$ . This pH change renders the Al-Zn pigment susceptible to active dissolution as the dissolution trajectory is forced outside of the passive Al(OH)<sub>3</sub> stability region. Once this pH is achieved, Al is expected to oxidize to  $AlO_2^-$  according to reaction 4, providing a second pathway to support the long-lasting cathodic protection achieved by the Al-5wt% Zn / Mg composite primer. These findings should be explored in a variety of other relevant environments and during wetting and drying typical of field exposures.

A simplified treatment of the galvanic coupling of MgRP and MgAlRP with AA 7075-T651 is illustrated in **Figure 4-27**. This treatment is not representative of all of the complexities within MRPs; however, serves the role of illustrating the influences of multiple pigments, resistive nature of the polymer matrix ( $R_{polymer}$ ), and resistance at the surface of the MRP ( $R_{surface}$ ). This treatment incorporates real polarization data collected in **Figure 4-9a** tested in unadjusted 0.6 M NaCl under quiescent condition. The limiting current density of AA 7075-T651 in 0.6 M NaCl under quiescent conditions is taken to be 1.2 x 10<sup>-5</sup> A/cm<sup>2</sup> which was evaluated via finite element modeling (FEM) and experimental methods <sup>164,165</sup>. The bi-metal galvanic couple formed between the Mg pigment in MgRP and the AA 7075-T651 is shown without resistance by the junction of the cathodic AA 7075-T651 in black and the Mg oxidation line in green (**Figure 4-27**).

The bi-metal galvanic couple formed between the Mg pigment in the MgAlRP and the AA 7075-T651 is shown by the junction of the cathodic AA 7075-T651 in black and the Mg oxidation line in blue (Figure 4-27). The Mg oxidation lines cross the cathodic AA 7075-T651 curve within the region dominated by the hydrogen evolution reaction (HER). The Mg oxidation line representing the bi-metal galvanic couple formed between MgAIRP and AA 7075-T651 experiences a larger quantity of current (charge) output due to the differences in Mg surface area between the Mg within MgRP (4.81 cm<sup>2</sup>) and the Mg within MgAlRP (6.58 cm<sup>2</sup>) which differs by a factor of 1.37. This illustrates that the increase in surface area of the Mg pigment does not have a significant impact on the galvanic couple formed between the Mg pigment in each coating and the AA 705-T651 substrate. The bi-metal galvanic couple formed between the Al-5wt%Zn pigment in the MgAIRP and the AA 7075-T651 is described by the junction of the cathodic AA 7075-T651 in black and the Al-5wt%Zn oxidation line in red (Figure 4-27). The oxidation of Al-5w%Zn crosses the cathodic portion of AA 7075-T651 within the current limiting oxygen reduction reaction (ORR) region. The galvanic couple formed between the Al-5wt%Zn and AA 7075-T651 does not have a great influence on the amount of charge supplied to the AA 7075-T651 substrate as the galvanic couple is limited by low mass transport-controlled ORR kinetics.

The net galvanic couple formed between the MgAlRP and AA 7075-T651 is shown in the dotted blue line as the sum of oxidation reactions occurring on both Mg pigment and Al-5wt%Zn pigment within the MgAlRP coating (**Figure 4-27**). This net galvanic couple for MgRP with AA

7075-T651 is represented by the yellow circle and similarly for MgAIRP with AA 7075-T651 by the pink circle, is relevant when there is no polymer present and ohmic contributions are negligible. As ohmic contributions become more relevant through the solution, polymer, and surface resistance this modifies the galvanic coupling formed at the interface between the AA 7075-T651 and the Mg pigment. The amount of resistance that is experienced between a given pigment within the MgRP or MgAIRP is dependent on the PVC and whether the pigment can be considered to be exposed to electrolyte or buried within the coating.

## **Conclusion**

Metal-rich primer-based cathodic protection was investigated to understand its viability in protecting AA 7075-T651 by achieving intermediate cathodic potentials to mitigate IGC and IG-SCC. The guiding attribute considered to mitigate IG-SCC, MRP was  $E_{couple} < E_{pit,MgZn_2}$  in neutral quiescent NaCl. The MgRP was capable of maintaining cathodic polarization of 100-150 mV below the OCP of AA 7075-T651 throughout galvanic coupling in 0.6 M NaCl. This potential meets the criteria of sacrificial cathodic prevention of 7075-T651 by maintaining potentials below  $E_{OCP,7075} = -0.75 V_{SCE}$  and  $E_{pit,\eta} = -0.85 V_{SCE}$ .

- Mg flake pigment in epoxy-based MRP rapidly activated and performed as a sacrificial anode. Mg piment was only partially expended as evident from scanning electron cross-sections. The cathodic protection criteria were met with the MgRP and achieved an activated potential of -1.5 V<sub>SCE</sub> on AA 7075-T651.
- The combination of Al-5wt% Zn pigment and Mg pigment in an epoxy-based MRP achieves intermediate cathodic potentials of approximately -1.1 V<sub>SCE</sub> on AA 7075-T651.
- The composite MgAlRP primer has shown enhanced galvanic protection, increased anodic charge output, and stable coupled potentials below the OCP of AA 7075-T651 suggesting that these MRPs may be utilized in static galvanic coupling condition on AA 7075-T651.
- The dissolution trajectory of the Mg-Al system is shown to have delayed activation of the Al as the dissolution of Mg increases the basicity of the solution, pulling the dissolution trajectory into a region of Al activity or stable Al<sup>3+</sup>. This is the premise of enhanced electrochemical performance of the composite MgAlRP system showing increased utilization.

- Composite MgAlRP systems are capable of (1) maintaining cathodic polarization of 200-250 mV below the OCP of AA 7075-T651 throughout galvanic coupling in 0.6 M NaCl, and (2) supplying positive current indicating the MRP is operating as intended with coating acting as anode.
- MRP utilization produces a pH increase associated with Mg oxidation that shifts the thermodynamic stability of Al<sup>3+</sup> to AlO<sub>2</sub><sup>-</sup>. In this way, Al corrosion occurs spontaneously in NaCl solution.

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### Tables, Chapter 4 – Task 3

AA7075-T651					
Element	Wt. %				
AI	Bal.				
Zn	5.1-6.1				
Cu	1.2-2.0				
Mg	2.1-2.9				
Fe	0.5				
Si	0.4				
Cr	0.18-0.28				
Ti	0.2				

Table 4-1. Nominal composition of AA 7075-T651 and Al-5wt%Zn.

Al-5wt%Zn				
Elements	Wt. %			
AI	Bal.			
Zn	5			

Table 4-2. Metal Rich primer systems included in this study.

Code	Primer	Provider	Resin	PVC	Thickness	<b>Pigment Diameter/</b>
	Commercial			(%)	(µm)	Dimensions (µm)
	Name					
MgAlRP	N/A	UVa-ARL	Epoxy	28 (Al-	$46.2 \pm 6.1$	$9.8 \pm 4.8$ (Al-Zn)
(Epoxy,19/28%)				Zn)		Length: $18.2 \pm 6.2$
						(Mg)
				19 (Mg)		Width: 6.6 (Mg)
MgRP	Aerodur 2100	AN	Epoxy	26	$44.5 \pm 6.4$	Length: $26.3 \pm 8.4$
(Epoxy,26%)						
						Width: $12.2 \pm 4.4$

AN = AkzoNobel, PVC = pigment volume concentration.

Metal-Rich Primer	Theoretical Anodic Q from MRP (C/cm <sup>2</sup> )	Maximum Experimental Anodic Q Output (C/cm <sup>2</sup> ) by End of Cycle Test	Anodic Q Usage by End of Cycle Test	Initial Activated OCP	OCP Upon Completion of the Cycle Test	Average Scribe Width (µm)
MgAlRP	27.2	0.5	1.8%	-1.15 ±	$-0.9\pm0.02$	171 <u>+</u> 15
(Epoxy,				0.06 V <sub>SCE</sub>	V <sub>SCE</sub>	
19/28%)						
MgRP	16.7	0.1	0.6%	-1.5 ±	$-0.95\pm0.03$	$225 \pm 20$
(Epoxy,26%)				0.04 V <sub>SCE</sub>	V <sub>SCE</sub>	

Table 4-3. Metal rich primer charge capacities and cathodic protection performance

Q = charge, C = Coulombs, XRD = X-Ray Diffraction, OCP = open circuit potential, Activated OCP = stabilized OCP following immersion and sufficient coating wetting, MRP = metal-rich primer

# Figures, Chapter 4 – Task 3

### Figure 4-1



Figure 4-1. **a**) Cross sectional BSI electron micrographs and **b**) EDS map scan of pristine unexposed MgRP applied on AA7075-T651.





Figure 4-2. **a**) Cross sectional BSI electron micrographs and **b**) EDS map scan of pristine unexposed MgAlRP applied on AA7075-T651.

Figure 4-3



Figure 4-3. Potentiodynamic polarization scan of bare AA7075-T651, MgZn<sub>2</sub>, Al-5wt%Zn, MgRP, and MgAlRP coated AA 7075-T651 under full immersion conditions in quiescent 0.6 M NaCl.





Figure 4-4. Long term open circuit potential of bare AA 7075-T651, Al-5wt% Zn, MgRP, and MgAlRP coated AA7075-T651 under full immersion conditions in quiescent 0.6 M NaCl.





Figure 4-5. Effect of  $[Mg^{2+}]$  in the presence of Cl<sup>-</sup> and influence of pH on the electrochemical behavior of AA 7075-T651 with **a**) the post 24-hour open circuit potential, **b**)the corrosion potential obtained through potentiodynamic polarization, and **c**) the pitting potential obtained through potentiodynamic polarization. Electrochemical testing was conducted under quiescent full immersion conditions. Variation in  $[Mg^{2+}]$  is achieved with MgCl<sub>2</sub> and pH is adjusted via titrations of NaOH and HCl for either basic or acidic conditions.

Figure 4-6



Figure 4-6. Effect of  $[Mg^{2+}]$  and influence of pH on the electrochemical behavior of **a**) Al-5wt%Zn bulk alloy with the post 24-hour open circuit potential, **b**) the corrosion potential obtained through potentiodynamic polarization, and **c**) the pitting potential obtained through potentiodynamic polarization. Electrochemical testing was conducted under quiescent full immersion conditions. Variation in  $[Mg^{2+}]$  is achieved with MgCl<sub>2</sub> and pH adjusted via titrations of NaOH and HCl for either basic or acidic conditions.

Figure 4-7



Figure 4-7. Effect of [Cl<sup>-</sup>] on the post 24-hour open circuit potential of bare AA 7075-T651, MgZn<sub>2</sub>, Al-5wt%Zn alloy, MgRP, and MgAlRP. Electrochemical testing is conducted under quiescent full immersion conditions. Variation in [Cl<sup>-</sup>] is achieved with NaCl at near neutral conditions.



Figure 4-8. Influence of  $[Cl^-]$  on the electrochemical behavior of **a**) AA 7075-T651, **b**) Al-5wt% Zn alloy, and **c**) MgZn<sub>2</sub>. Electrochemical testing is conducted under quiescent full immersion conditions. Variation in  $[Cl^-]$  is achieved with NaCl at near neutral conditions.

a)





Figure 4-9. Potentiodynamic polarization diagram for AA 7075-T651, MgZn<sub>2</sub>, Al-5wt%Zn alloy, and Mg (99.9%) in quiescent 0.6 M NaCl under full immersion in **a**) unadjusted pH (5-5.5), and **b**) pH 11. Solution pH adjustments are conducted with NaOH.

## Figure 4-10

a)



b) c) -0.95 V<sub>SCE</sub> -1.1 V<sub>sc</sub> -1.4 V<sub>SCE</sub>

Figure 4-10. a) Potentiostatic hold on pristine bare AA7075-T651 at DC potential holds of -0.95V<sub>SCE</sub>, -1.1 V<sub>SCE</sub>, and -1.4 V<sub>SCE</sub> for 24-hours. Testing is conducted under full immersion conditions in quiescent 0.6 M NaCl. b) Plan view optical microscopy for each DC potential hold. c) SEM BSI cross-sections showing penetration through the depth of the sample as a function of DC polarization.





Figure 4-11. OCP/AC/DC cycle testing of MgRP applied to AA7075-T651 with DC potential hold at -0.95  $V_{SCE}$  and the legend denoting the cycle indicated in Table 3. **a**) Open circuit potential is shown with a red dotted line denoting the OCP of AA7075-T651, **b**) the current

density output, **c**) with residual barrier properties shown in the Bode impedance response, and **d**) the oxygen EDS cross-section of MgRP after 100 net hours of DC potential hold at -0.95V<sub>SCE</sub>. Testing is conducted under full immersion conditions in quiescent 0.6 M NaCl.





Figure 4-12. OCP/AC/DC cycle testing of MgAlRP applied to AA7075-T651 with DC potential hold at -0.95  $V_{SCE}$  and the legend denoting the cycle indicated in Table 3. **a**) Open circuit potential is shown with a red dotted line denoting the OCP of AA7075-T651, **b**) the current

density output, **c**) residual barrier properties shown in the Bode impedance response, and **d**) the oxygen EDS cross-section of MgRP after 100 net hours of DC potential hold at  $-0.95V_{SCE}$ . Testing is conducted under full immersion conditions in quiescent 0.6 M NaCl.



Figure 4-13. **a**) Variation of low frequency limit (0.01Hz) of  $Z_{mod}$  against each potentiostatic cycle, **b**) the end of each OCP step shown against each cycle, and **c**) the charge density, as calculated from the current density, given for each DC/AC/OCP cycle.





Figure 4-14. Galvanic corrosion of the coupled MgRP and MgAlRP coated AA7075-T651 to bare AA7075-T651 tested in quiescent 0.6 M NaCl for a 1:1 area ratio with the **a**) coupled

potentials and **b**) coupled current densities. The green dashed line represents the OCP of bare AA7075-T651 (-0.75 $V_{SCE}$ ) in quiescent 0.6 M NaCl.



Figure 4-15

Figure 4-15. The galvanic corrosion testing of the coupled MgRP and MgAlRP coated AA7075-T651 to bare AA7075-T651 tested in quiescent 0.6 M NaCl for a 15:1 area ratio with the **a**) coupled potentials and **b**) coupled current densities. The green dashed line represents the OCP of bare AA7075-T651 (-0.75V<sub>SCE</sub>) in quiescent 0.6 M NaCl.

Figure 4-16



**Figure 4-16.** Local pH modification monitored throughout the galvanic coupling of each MRP – 7075-T651 exposure tested in 0.6M NaCl shown in **a**) over the bare AA7075-T651 WE and **b**)

over the MRP coating CE. The lines with square symbols denote the 15:1 (MRP:bare 7075) area ratio while the lines without symbols denote the 1:1 (MRP:bare 7075) area ratio.

Figure 4-17



Figure 4-17. The open circuit potential and electrochemical impedance spectroscopy shown for both intact MgRP and MgAlRP coated AA7075-T651 throughout the six-week ASTM B117 accelerated environmental exposure testing in 0.6 M NaCl. Long term open circuit potential

shown for **a**) MgRP, and **b**) MgAlRP; the Bode magnitude is plotted for **c**) for MgRP, and **d**) MgAlRP. The phase angle progression is illustrated for **e**) MgRP, and **f**) MgAlRP.



Figure 4-18

Figure 4-18. ASTM B117 salt spray testing on intact MgRP applied to AA7075-T651 across 0, 2, 4, and 6 weeks of accelerated environmental exposure in 0.6M NaCl as shown in BSI SEM micrographs with individual magnesium and oxygen signals from EDS elemental mapping.



Figure 4-19. ASTM B117 salt spray testing on scribed MgRP applied to AA7075-T651 across 0, 2, 4, and 6 weeks of accelerated environmental exposure in 0.6M NaCl as shown in BSI SEM micrographs with individual magnesium and oxygen signals from EDS elemental mapping.

Figure 4-20



Figure 4-20. ASTM B117 salt spray testing of MgRP shown in plan-view BSI SEM micrographs for zero and six-week in **a**) and **c**) with EDS line scans shown in **b**) and **d**).

Figure 4-21



Figure 4-21. ASTM B117 salt spray testing on intact MgAlRP applied to AA7075-T651 across 0, 2, 4, and 6 weeks of accelerated environmental exposure in 0.6M NaCl as shown in BSI SEM micrographs with individual magnesium and oxygen signals from EDS elemental mapping.

Figure 4-22



Figure 4-22. ASTM B117 salt spray testing on scribed MgAlRP applied to AA7075-T651 across 0, 2, 4, and 6 weeks of accelerated environmental exposure in 0.6M NaCl as shown in BSI SEM micrographs with individual magnesium and oxygen signals from EDS elemental mapping.



Figure 4-23. ASTM B117 salt spray testing of MgAlRP shown in plan-view BSI SEM micrographs are shown for zero and six-week in **a**) and **c**) with EDS line scans shown in **b**) and **d**).



Figure 4-24. X-ray diffraction analysis on **a**) intact MgRP and **b**) intact MgAlRP condition following ASTM B117 exposure in 0.6M NaCl. In the XRD spectra purple stars denotes FCC Al peaks, blue triangles denote Mg peaks, red triangles denote Mg(OH)<sub>2</sub>, and green circles denote Al(OH)<sub>3</sub>.

#### Figure 4-25



Figure 4-25. Nitric-washed pristine bare AA 7075-T651 control BSI with no protection scheme shown over the uncoated bare region in **a**) and over the scribe shown in **b**). Nitric washed post six-week bare AA 7075-T651 ASTM B117 BSI with no protection scheme is shown over the bare region in **c**) and scribed region **d**). The post six-week MgRP coated AA7075-T651 ASTM
B117 salt spray testing over the scribed region is shown in **e**). The post six-week MgAlRP coated AA7075-T651 ASTM B117 salt spray testing over the scribed region is shown in **f**).



### Figure 4-26

Figure 4-26. Chemical stability diagram depicting the chemical equilibria lines of  $Al^{3+}/Al_2O_3$ ,  $Al^{3+}/Al(OH)_3$ ,  $Mg^{2+}/MgO$ ,  $Mg^{2+}/Mg(OH)_2$  using solid lines. The dissolution trajectory of the corroding Mg (dashed black line) and MgAlRP (dashed blue line) systems is dependent on the initial solution chemistry.





Figure 4-27. Schematic representation of the galvanic couple between formed in both MgRP and MgAlRP coated AA 7075-T651 substrate exposed to unadjusted quiescent 0.6 M NaCl.

# Chapter 5 Task 4– Spatially Resolved Assessment and Analysis of Al-Zn, Mg, and Mg/Al-Zn Metal Rich Primers applied to AA 7075-T651 in Full Immersion

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#### **Abstract**

The scanning vibrating electrode technique (SVET) was utilized to provide a localized assessment of substrate protection of three metal rich primers (MRP). The ability to suppress localized corrosion (i.e. pitting and macro-galvanic coupling) and provide widespread cathodic polarization to enable sacrificial anode-based cathodic protection to AA 70705-T651 substrate were investigated. The coatings investigate in this study were an aluminum rich primer (AIRP), magnesium rich primer (MgRP), and a composite magnesium + aluminum rich primer (MgAlRP) in a polyamide-based epoxy primer. The substrate was AA 7075-T651. SVET testing was conducted under full immersion in 0.001 M (1 mM) NaCl. The efficacy of these metal rich primers to provide sacrificial anode-based cathodic prevention was evaluated considering both intact coatings as well as for a 1:1 coating/defect area ratio with a macro defect consisting of an unpainted region exposing the substrate. Pigments do not activate uniformly. Another finding is that local corrosion is suppressed on heterogeneous alloys and widespread cathodic polarization is absent. The notion of throwing power polarizing the bare substrate and finite element analysis of scratch sites do not capture the transient behavior. The MgRP and MgAlRP was shown to provide superior local corrosion suppression compared to the AIRP. The MgAIRP was determined to be the most effective coating for maintaining the ability to suppress local peak anodic current associated with pitting on AA 7075-T651.

#### **Introduction**

Aircraft aluminum alloys range widely in composition based on intended application <sup>1,2</sup>. The wing-spar of commercial aircraft structures is largely comprised of 7XXX-series aluminum alloys <sup>1,3,4</sup>. A common 7XXX-series aluminum alloy for this use is AA 7075-T651, a peak-age (PA) hardened stress relieved by stretching (3%). Aluminum alloy (AA) 7075 is an aged precipitation hardened Al-Zn-Mg-Cu alloy which are highly susceptible to localized corrosion due

to their heterogeneous microstructure and owes its intergranular corrosion (IGC) susceptible to its grain boundary phase MgZn<sub>2</sub>  $^{5-10}$ . It is common in commercial applications to use an over-aged tempers (T7x) which increases resistance to SCC and decreases crack growth rates  $^{11-13}$ . For the purposes of this study AA 7075-T651 was examined to determine if a metal rich primer is capable of providing protection to the most susceptible aging treatment of AA 7075.

The localized corrosion of AA 7075-T651 is due to its heterogeneous microstructure containing a wide range of precipitates and possible grain boundary solute depletion introducing local chemical inhomogeneity and enhanced localized breakdown that is determined by the chemical composition, heat treatment, and resulting microstructure <sup>9,14–16</sup>. Intragranular coherent precipitates increases the yield strength of AA 7075 but PA may also form heterogeneously nucleated MgZn<sub>2</sub>, η phase, on grain boundaries increasing IGC/IG-SCC susceptibility <sup>4,17–20</sup>. The grain boundary precipitate,  $\eta$  phase, is more electrochemically active than the surrounding matrix and rapidly dissolves in aggressive aqueous environments <sup>1,9,16</sup>. In order to suppress IGC it is necessary to minimize the dissolution of  $\eta$  phase at grain boundaries. Previous work has identified potential ranges that are suitable for the suppression of  $\eta$  phase dissolution by polarizing below the pitting potential ( $E_{pit}$ ) of  $\eta$  phase, ( $E_{pit,\eta}$ )<sup>21,22</sup>. The potential range in which IGC is minimized by polarizing below -0.85 V<sub>SCE</sub> to -1.1 V<sub>SCE</sub> in 0.6 M NaCl<sup>21,22</sup>. It should be noted that excessive cathodic polarization can lead to cathodic corrosion and should be avoided <sup>23</sup>. In addition to the suppression of IGC, it is desirable to suppress pitting and macro galvanic coupling on AA 7075-T651 which is made challenging due to the wide variety of constituent particles with varying electrochemical characteristics present in this alloy to ensure adequate performance throughout the duration of structural aircraft components<sup>24</sup>.

The protection of aluminum alloys for aerospace application is traditionally afforded by multilayered coatings to provide barrier protection and active corrosion protection to the underlying substrate <sup>25–31</sup>. These multilayered coating systems typically consist of a pretreatment layer (anodization, tri-valent chromium pretreatment (TCP), etc.) <sup>32–35</sup> applied to the substrate with active corrosion coatings protection (MRP, embedded inhibitors, etc.) <sup>36–39</sup> and topcoat (polyurethane, polyamide, etc.) <sup>27,31,40–42</sup>. A commercial organic coating system containing Mg-rich primer (MgRP) has been developed for the active corrosion protection of aerospace aluminum

alloys <sup>31,41,43–49</sup>. These MgRP coating systems contain metallic Mg-pigment embedded in an epoxy resin.

The active corrosion protection of any aluminum alloy is provided by the galvanic coupling of more active Mg pigment in the primer relative to the more noble AA 7075-T651 substrate. This general approach has been well established and widely reported in the design of zinc-rich primers (ZnRP) used for a variety of steels <sup>50–58</sup>. This same concept can be applied to a wider variety of scenarios such as AI-Zn cladding on carbon/mild steel <sup>51,59,60</sup>, the protection of marine vessels <sup>49,61–63</sup>, as well as the use of dissimilar pigments in MRP's <sup>64–67</sup>. The use of ZnRP on steel systems are typically contain pigment volume concentrations (PVC) as high as 60-90% <sup>68,69</sup> whereas the PVC of MgRP coating systems on aluminum alloys range between 30-50% <sup>41</sup>. Sacrificial protection of a substrate in this case can be modified by changing the dissolution behavior of the anode. The tuning of properties by either marine anodes or MRP pigment are achieved by alloying of other electrochemically active elements <sup>64,70–73</sup>, rare-earth <sup>74–76</sup>, and earth-alkali elements <sup>36,38,39</sup> to modify the behavior of active pigments. The properties of MRP pigment can be further tuned by the morphology of the pigment <sup>64,66,67,77</sup> as well as the use of composite MRP coatings which contain multiple pigment chemistries <sup>60,64,66,67</sup>.

The conditions describing conventional galvanic coupling of a MRP pigment to the substrate have historically been described by mixed potential theory <sup>35,44,46,49,78,79</sup>. The galvanic protection potential is derived from mixed potential theory and mediated by both the electrical and ionic resistances between the anode and cathode such as polymer barrier properties of the MRP, pretreatment resistances, electrolyte chemistry, electrolyte thickness and geometry, and anode/cathode area ratio <sup>64,80–82</sup>. Barrier protection is afforded to the substrate, the pretreatment layer, and the MRP itself <sup>30,44,46,83–88</sup>. Furthermore, chemical inhibition in the form of the release of dissolved cation species may arise from the pretreatment layer and are transported to the scratch or defect exposing bare Al. Moreover, pigments within the MRP may provide additional corrosion protection by precipitating corrosion products on constituent particles and inhibiting the anodic and cathodic kinetics of AA 7075-T651 <sup>46,49,78,89,90</sup>.

Previous studies on the sacrificial anode based cathodic protection of the same AIRP, MgRP, and MgAIRP applied to AA 7075-T651 evaluated in this study were tested using various electrochemical techniques and ASTM B117 accelerated exposure testing conducted in 0.6 M

NaCl<sup>21,22</sup>. The initial electrochemical framework sought out to determine potential ranges for protection based on the polarization behavior of the bare AA 7075-T651 alloy and the susceptible  $\eta$  phase. The potential range in which IGC was minimized is between -0.84 V<sub>SCE</sub> to -1.1 V<sub>SCE</sub> in 0.6 M NaCl<sup>21,22</sup>. The MRP's were studied by electrochemical testing involving long term (24-hr) OCP monitoring which showed that the MgRP activated to a potential of -1.5 V<sub>SCE</sub> and polarized to the potential of -1.1  $V_{SCE}$  by the end of the 24-hr monitoring period <sup>22</sup>. Advanced electrochemical testing was conducted in the form of AC/DC/OCP laboratory cycle testing (more details on laboratory cycle testing are described elsewhere)<sup>21,22</sup> and showed that the MgRP and MgAlRP are capable of discharging anodic current operating as sacrificial anode where the AlRP discharged cathodic current operating not as intended <sup>21,22</sup>. However, pigments were not fully utilized to reach the theoretical charge capacity owing to the low PVC. Galvanic corrosion testing coupling with pH monitoring showed a modification of the electrolyte chemistry at the MRP interface associated with dissolution processes in the MgRP and MgAlRP where the AlRP remained at near neutral conditions <sup>21,22</sup>. These pH shifts give insight into the mechanistic difference associated with the enhanced performance of MgAlRP in which the dissolution of Mg causes a shift to alkaline pH values that activates the Al-5wt%Zn pigment allowing for a secondary pathway of sacrificial anode based cathodic protection <sup>22</sup>.

In conventional thinking, the distance over which an active corrosion protection system can protect a scratch or a defect exposing a bare metal surface is termed 'throwing power' <sup>35,46,80,82,91</sup>. The assumption is that anodes and cathodes are constant with time and possess reaction rates that are fixed for both anode and cathode, which when considered result in static current and potential distributions in the primary and secondary current distributions across both anode and cathode electrodes. No local heterogeneity with different reaction rates at different locations is typically incorporated as spatial dependent boundary conditions even though actual precipitation age hardened AA alloys have many micro galvanic couples. This type of conceptualization assumes fixed anode and cathodes that do not change with time.

SVET has proven useful in the quantification of potential and current spatial distribution on pure elements, alloys, and protection schemes <sup>80,92–94</sup>. SVET provides the opportunity to map local current above the bare as well as coated metal planes (z-direction) to access the local heterogeneous behavior of local corrosion cells operating which is closer to the real time operando

behavior. SVET has been used previously to study the throwing power of MgRP's applied to AA 2024-T351 wherein various pretreatments (chromated, non-chromated, anodized) have been shown to modify the galvanic coupling between the MRP and the bare substrate under full immersion conditions in 2 M NaCl solution <sup>95</sup>. The pretreatments investigated showed galvanic coupling between MgRP and 2024-T3 for chromated and non-chromated pretreatments showing moderate galvanic coupling, and no galvanic coupling for anodized systems <sup>95</sup>. The anodized systems lack galvanic coupling is likely due to its large electrical resistance imparted by the anodized layer between metal and primer. This limited the primer's galvanic interaction between the Mg pigment and the AA2024-T351 surface <sup>95</sup>. The throwing power was observed on the bare substrate via SVET-derived current density profiles <sup>46,80,82,91</sup>. The suppression of localized corrosion in the form of pitting may be suppressed. However, alternative criteria may be sought after for more susceptible alloys with a greater tendency to breakdown locally via micro-galvanic couples that arising from chemical heterogeneity and pitting such as suppressing peak anodic pitting current densities. This is a measure of reducing the rate of dissolution via pitting that occurs on the surface of a bare electrode adjacent to a coating compared to the peak anodic current density associated with pitting on a bare uncoated alloy. One distinct limitation of SVET is that the x-y raster time of SVET is not instantaneous.

SVET has been extended to monitoring the progression of galvanic corrosion between dissimilar metals/alloys which have engineering relevant applications [<sup>80,96–98</sup>]. For instance, the galvanic coupling of stainless steel (SS) and aluminum alloys used in aerospace applications in the form of rivets which can be found on the fuselage, wings, tail, and nose of commercial aircraft <sup>99,100</sup>. There are a multitude of previous studies utilizing the SVET to investigate the corrosion of bare metals and their alloys <sup>92,93,97,101,102</sup>, the study of galvanic activity <sup>45,80,82,96,97,103</sup>, influence of surface treatment/modification on the corrosion properties of bare metals <sup>88,104–106</sup>, the influence of inhibitor species <sup>92,107–109</sup>, pitting corrosion <sup>101,110–113</sup>, scribed coatings <sup>35,41,80,91,107,114–117</sup>, the study of metal rich primers (MRPs) <sup>31,35,123,41,52,80,118–122</sup>, and the dissolution behavior of corrosion conversion coatings <sup>88,105,110,124</sup>. The spatial distribution of potential and current are useful in determining localized corrosion of both uncoated surfaces, activation and repassivation phenomena, the progression of galvanic corrosion, and the influence of added chemical species either in the form of dissolved species from an electrochemically active MRP or released inhibitors

on the electrochemical dissolution behavior <sup>80,97,107,117,124</sup>. Of course, the latter must be augmented with chemical and/or pH measurements.

The corrosion of galvanic systems has been studied previously using a variety of electrochemical techniques such as multi-electrode array (MEA) [<sup>80,100,125–127</sup>], finite element analysis (FEA) <sup>100,128</sup>, zero-resistance ammetry (ZRA) <sup>21,22,64,129–132</sup>, and scanning vibrating electrode technique (SVET) <sup>18,29,125, 39,41,43,45,63,73,115,124,126</sup>. These techniques aid in quantifying post-exposure volume loss, coupled current density, galvanically coupled potential, and defect protection. Each electrochemical technique has their advantages and disadvantages; for instance, MEA's make use of wires of systems of interest are often flush mounted in epoxy and the galvanically coupled current and potential distribution between the wires are studied using a separately addressable ZRA to assess the galvanic interactions across the array. However, limitations include the inability to study localized corrosion and its spread such as pitting in a continuous bare substrate as a flush mounted array of electrodes made from wires is limited by the dimensions of the wire <sup>125–127</sup>. One of the surprising things uncovered with the MEA is the unexpected switch of anodes and cathodes as well as partial activation/deactivation <sup>82,125,127</sup>.

The aim of this current study is to semi-quantitatively assess the spatial potential and current distribution, reduction in peak anodic current density over a region of bare AA 7075-T651 that is partially protected by three MRP coating systems (AIRP, MgRP, and MgAIRP), and the mechanisms of protection for each coating by utilizing SVET. This revisits our previous work using DC/AC/OCP cycle testing and other global analysis methods such as bi-electrode galvanic couples <sup>21,22</sup>. These coating systems are applied to bare non-pretreated, non-passivated AA 7075-T651 without inhibitors when fully immersed in NaCl solution. In this work the location and intensity of current density (j) distribution of bare AA 7075-T651, an intact MRP coated AA 7075-T651, as well as an MRP with an artificial defect was detected and mapped. The local anodic maxima (inferring the location and intensity of pits), the local current density profile at the coating defect interface (CDI) region and the total integrated anodic and cathodic current density values of defined areas in the defect regions are all relevant parameters to determine the efficacy of a given MRP coating system. This may not be reflective of realistic field implementation of a multilayered coating systems; however, this allows for the determination of the effectiveness of a specific primer system free of the influences of multilayered coating systems.

#### **Experimental**

AA 7075-T651 samples, with composition shown in **Table 5-1**, were cut to dimensions 1.5 mm thick, 200 mm long, and 76 mm wide via Mager<sup>TM</sup> high speed cut off saw. All samples were cleaned of grease from the surface via alcohol bath and air dried prior to spray coating application. All bare uncoated samples were polished to 1200 grit using SiC pad until a mirror finish was obtained. A cold spray coating process was performed by DEVCOM Army Research Labs (ARL) to apply AIRP, MgRP, and MgAIRP coating systems using thoroughly mixed formulations shown in Table 5-1 to Milspec. The AIRP formulation is sourced from Randolph Coatings (RC, Chicopee, Massachusetts US) and contains spherical aluminum pigments alloyed with 5wt% Zn. The MgRP formulation is sourced from AkzoNobel (AN) Coatings (Amsterdam, Netherlands) and contains non-passivated 99.9% pure Mg pigment with a flaked pigment morphology. The MgAlRP composite coating is a combination of the AN MgRP and the RC AlRP and is possible due to the use of similar organic resin-hardener combinations. The composite MgAlRP contains both flaked Mg pigment and spherical Al 5wt% Zn pigment. Characterization of these coatings has been shown in previous studies <sup>21,22</sup>. Specification for all physical attributes of each coating can be found in Table 5-1. Experiments were compared to an uncoated otherwise bared AA 7075-T651 sample used to define the peak current density values associated with anodic dissolution of the substrate as a basis to judge the ability to suppress pitting of each MRP coating. No pretreatments, passivated pigments, or topcoats were considered and all coatings were tested in both as-received intact condition (i.e. no intentional defects) (Figure 5-1a). Samples with macro-defects were considered in order to assess the ability to suppress pitting. These macro-defects were in the form of half MRP coated and half bare AA 7075-T651 samples (Figure 5-1b). The bare portion of these samples were hand polished to 1200 grit using SiC polishing pad to reveal the bare AA 7075-T651 substrate.

It should be noted that there are differences in the physical attributes of each coating as PVC and surface area vary. The total PVC of Mg pigment within the MgRP was 26% compared to the composite MgAlRP coating which contains a Mg PVC of 19%. The PVC of Al pigment in the AlRP is 27% while the composite MgAlRP coating contains an Al PVC of 28%. This results in a surface area of Mg pigment of 4.81 cm<sup>2</sup> per cm<sup>2</sup> of MgRP and 6.58 cm<sup>2</sup> per cm<sup>2</sup> of MgAlRP.

The surface area of Al pigment is 7.58 cm<sup>2</sup> per cm<sup>2</sup> of AlRP and 7.92 cm<sup>2</sup> per cm<sup>2</sup> of Al within the MgAlRP coating. If the MgAlRP is fully activated the net surface area of Mg + Al pigment present is 14.5 cm<sup>2</sup> per cm<sup>2</sup> of MgAlRP. The MgAlRP has a greater surface area of Mg pigment than the MgRP by a factor of 1.37 and a greater Al surface area than the AlRP by a factor of 1.04. This does not reflect considerations of electrically disconnected pigments of pigment fallout and assumes 100% utilization. As mentioned previously, the MgAlRP coating is a combination of the AN MgRP and the RC AlRP, therefore, the differences in pigment geometry may be a result of different sampling areas during scanning electron microscopy.

#### Laboratory Full Immersion Electrochemical Testing

The global galvanic protection potential of intact coating systems, bare substrate and the barrier properties of intact coating systems were examined non-destructively using open circuit potential (OCP), potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS). Long-term OCP is monitored over a 24-hour (hr) period. A 10-minute OCP is monitored prior to conducting PDP scans which started at 50 mV below the OCP and scanned upward at a rate of 1 mV/s. The PDP scans in the cathodic leg of the curve started 50 mV above the OCP and scanned downward at a rate of 1 mV/s. The EIS scan were acquired from 100 kHz to 0.01 Hz with 10 points per decade after a 1-hr OCP monitor intact coating samples and 10-minute OCP monitor for all bare AA 7075-T651 samples. Coated Panels with intact coatings exhibiting high impedance and were scanned with an alternating current (AC) amplitude of 65 mV to reduce noise. The bare uncoated AA 7075-T651 EIS scan was conducted with an AC amplitude of 10 mV. All electrochemical testing was conducted with a Gamry 620 potentiostat using a standard 3-electrode cell with a saturated calomel electrode (SCE) as reference and Pt mesh as a counter electrode (CE). Full immersion electrochemical testing was conducted in quiescent 0.6 M NaCl open to laboratory air over a 0.785 cm<sup>2</sup> surface area. All laboratory full immersion testing has been triplicated for consistency and reproducibility.

#### Scanning Vibrating Electrode Technique (SVET)

A Biologic M470 instrument was used for all SVET experiments. Experiments were conducted in freely corroding open circuit conditions and were performed on an exposed area of 1 cm<sup>2</sup> in each case masked with insulating tape to avoid edge effects. SVET testing is conducted under full immersion in 1 mM NaCl as signal-to-noise ratio decreases with increasing the solution concentration <sup>136</sup>. The SVET probe consisted of a platinum probe with a diameter specified by the manufacturer as between 5 µm and 50 µm. A complete description of the design and calibration of procedure for the SVET instrument is available in previous publications <sup>137</sup>. The SVET probe was positioned vertically and scanned at a constant height of 50 µm or 100 µm above the experimental area with an amplitude of 30 µm and frequency of 80 Hz. Scanning commenced immediately following specimen immersion with a scan time of approximately 18 minutes. Sampling of SVET scans is taken within the first hour of immersion to establish a baseline for evaluating the progression of localized corrosion followed by sampling every 12-hr for a net duration of 48-hr. SVET monitoring is conducted over bare unprotected AA 7075-T651, intact MRP coated AA 7075-T651 (Figure 5-1a), and 1:1 area MRP:AA 7075-T651 defect ratio (half coated half uncoated) which a representative schematic can be seen in Figure 5-1b. A schematic diagram of the half MRP coated and half bare AA 7075-T651 samples are shown in Figure 5-2. This schematic diagram is used to depict the full immersion SVET testing used to monitor the suppression in localized corrosion over the bare region of the half MRP coated samples (Figure 5-2). Characterization methods are shown over both intact regions and the coating defect interface (CDI) (Figure 5-2).

Al point current source was used to calibrate the obtained SVET-derived current densities according to the z-distance of the SVET probe above the sample surface. Al wire with a diameter of 250  $\mu$ m and purity of 99.5% (Goodfellow Cambridge Limited, England) was mounted into the epoxy in order to obtain an appropriate size for the SVET cell, then was gradually polished with SiC paper up to 1200 grit. The schematic of the Al point current source is presented in **Figure 5-3a**. The SVET probe was set up above the Al source at a distance of 50  $\mu$ m and the number of applied current densities (cathodic and anodic) from 2.4 A/m<sup>2</sup> to 480 A/m<sup>2</sup> was applied (see the applied current densities in **Figure 5-3c**). Then the z-distance between the probe and the Al current source was increased by 50  $\mu$ m to reach 100  $\mu$ m distance above the Al source and to determine how the SVET response changes for all applied current densities. This experiment was repeated several times, the z-distance was gradually increased with a step of 50  $\mu$ m until it reached 500  $\mu$ m

above the source surface. An example of the distribution of the SVET-derived (measured) current density above the surface of the Al point current source at 120 A/m<sup>2</sup> is presented in **Figure 5-3b**. The final distance-calibration results are presented in **Figure 5-3c** where each symbol is the SVET-derived peak current density at the certain applied current density and a certain distance above the source. The solid lines in **Figure 5-3c** are fitting lines according to the exponential law with the obtained equations presented. Considering the data obtained in **Figure 5-3c** for 0  $\mu$ m distance above the Al point current source surface and the distance of the probe in the SVET experiment above the sample surface 50  $\mu$ m for bare AA7075, coated samples, and half-coated samples for the coated part and 100  $\mu$ m for half-coated samples over the bare region, calibration lines were plotted in **Figure 5-3d** where x-axis shows a measured (SVET-derived) current density with different applied current densities, and y-axis shows the calibrated current density at the distance 0  $\mu$ m above the sample surface. Note that **Figure 5-3** presents only anodic current densities. Cathodic current densities were obtained and analyzed using the same procedure and the calibration curves obtained were symmetrical (y-axis) to anodic ones.

#### **Characterization**

Optical characterization of the post SVET exposure in the plane view were conducted with a Hirox digital optical microscope to track the change in visual appearance. Scanning electron microscopy (SEM) of the as-received MRP coated AA 7075-T651 cross-sections were paired with energy dispersive X-ray spectroscopy (EDS) on a Quanta 650 system for imaging and elemental analysis under magnification of 500x, spot size of 5 nm, and an accelerating voltage of 10 kV at 10<sup>-8</sup> torr mitigate charging. Imaging was conducted using a concentric-ring backscatter (CBS) detector. All samples were embedded in epoxy and sputter coated with a conductive layer using a Cressington-108 Au-Pd sputter coater at 30 mA for 40 seconds at a standoff distance of 5 cm to aid in micrograph acquisition with Au and Pd eliminated from EDS elemental analysis. The average pigment size, and primer thickness values are reported in **Table 5-1**. The average pigment size and coating thickness were confirmed through the consideration of 10 vertical thickness measurements on 3 pristine AlRP, MgRP, and MgAlRP cross-sectional areas under SEM. Cross-section polishing was carried out by wet polishing in water to 1200 grit using an abrasive silicon carbide pad.

#### **Results**

#### Laboratory Full Immersion Electrochemical Testing

The results for OCP and EIS Bode-magnitude scan conducted in 0.6 M NaCl under full immersion conditions are summarized in Figure 5-4a and 5-4b, respectively, for bare AA 7075-T651 and MRP coated AA 7075-T651. The bare AA 7075-T651 shows an OCP of -0.75 V<sub>SCE</sub> and periodic potential fluctuations between  $-0.72 V_{SCE}$  and  $-0.77 V_{SCE}$  characteristic metastable pitting throughout the 24-hr monitor (Figure 5-4a). The intact AIRP coated AA 7075-T651 is shown to have a stable potential throughout the 24-hr exposure period at -0.7 V<sub>SCE</sub> (Figure 5-4a). The intact MgRP coated AA 7075-T651 activates with an electrode potential decrease to -1.2 V<sub>SCE</sub> prior to rising to the potential of the substrate (-0.75  $V_{SCE}$ ) (Figure 5-4a). The MgAlRP activates to -1.25 V<sub>SCE</sub> similarly to the MgRP; however, maintains a potential of -1.1 V<sub>SCE</sub> after 24-hr monitoring period. The electrochemical impedance spectroscopy of bare AA 7075-T651 and intact AlRP/MgRP/MgAlRP-coated AA 7075-T651 can be seen in Figure 5-4b. The low frequency modulus impedance,  $Z_{0.01 \text{ Hz}}$  (ohm  $\cdot$  cm<sup>2</sup>), of bare AA 7075-T651 is  $6 \cdot 10^3$  ohm  $\cdot$  cm<sup>2</sup>. The MRP coatings are ranked according to largest low frequency modulus impedance with AlRP > MgAlRP > MgRP and  $2.3 \cdot 10^6$  ohm·cm<sup>2</sup> >  $2.4 \cdot 10^6$  ohm·cm<sup>2</sup> >  $2.8 \cdot 10^6$  ohm·cm<sup>2</sup>, respectively (Figure 5-4b). The phase angle progression for each intact MRP sample and bare AA 7075-T651 is shown in Figure 5-4c throughout the EIS scan. Investigation in the polarization behavior of AA 7075-T651, pure elements, and detrimental MgZn<sub>2</sub> phase are shown in Figure 5-5. The potentiodynamic polarization provides the basis for assessing potential ranges in which IGC may occur according to an anodic dissolution mechanism based on differences in critical potentials such as the pitting potential of MgZn<sub>2</sub>. The AA 7075-T651 shows a corrosion potential of -0.75 V<sub>SCE</sub> (Figure 5-5). The MgZn<sub>2</sub> phase is seen to have a corrosion potential of -1.15 V<sub>SCE</sub> with pitting potential at -0.85V<sub>SCE</sub> (Figure 5-5). Potentials above the pitting potential of MgZn<sub>2</sub> are said to define definite IGC  $(E > E_{pit})$ , potentials between the corrosion potential of MgZn<sub>2</sub> and its pitting potential (net anodic to MgZn<sub>2</sub>) define possible IGC ( $E_{pit} > E > E_{corr}$ ), and potentials below the corrosion potential of MgZn<sub>2</sub> are defined to be protective ( $E < E_{corr}$ ).

#### Localized corrosion of Bare AA 7075-T651

The localized corrosion of bare AA 7075-T651 and half MRP coated AA 7075-T651 half bare AA 7075-T651 is monitored via SVET over a 48-hr period under full immersion conditions in 1 mM NaCl. The SVET surface plots seen in **Figure 5-6** shows the distribution of normal current density ( $j_z$ ) emerging from the bare AA 7075-T651 sample under freely corroding conditions. The SVET raster time was 18 minutes per scan. The SVET-derived peak  $j_z$  of the anodic regions describes the peak anodic normal current density,  $j_z^a$ , which can be used as a marker for future evaluations. The current densities were not corrected for z-distance. The highest anodic value for the freely corroding AA 7075-T651 is 0.1 A/m<sup>2</sup>. The exposure of bare AA 7075-T651 starts off with numerous sites for anodic dissolution via pitting and progresses toward a smaller spatial distribution of active pits and pits of lower intensity (**Figure 5-6**). The lower spatial distribution of pits can be witnessed by the reduction in the number of sites of local anodic dissolution seen in **Figure 5-6**. The pits diminish in intensity as  $j_z$  decreases with increasing exposure time (**Figure 5-6**). The number of pits that were initiated within the detection limit of the SVET on the bare uncoated AA 7075-T651 sample after 48-hr immersion in 1 mM NaCl was 40 pits/cm<sup>2</sup>. The 3-D current distribution for the bare AA 7075-T651 sample can be found in **Figure 5-S1**.

#### Galvanic coupling of intact AIRP / MgRP / MgAIRP coated AA 7075-T651 monitored by SVET

Intact coated samples without artificial defects described in **Figure 5-1a**, were chosen to study the change in surface distribution of normal current density with increasing exposure time indicative of primer activation or self-corrosion when not connected to a bare area. This is done to evaluate how well each primer can operate as a sacrificial anode, in the intact condition, applied to AA 7075-T651. The evolution of normal current density across the surface of an intact AIRP can be seen in **Figure 5-7** and can be seen to begin net anodic  $(0.1 \text{ A/m}^2)$  and decreases throughout the exposure period  $(0.02 \text{ A/m}^2)$ . This suggests that with increasing time the AIRP coating in the intact condition has a reduced ability to maintain net anodic current densities and increases in cathodic contributions. The normal current density distribution across the surface of the intact MgRP showed an initial mix of net anodic and net cathodic sites and progressed to predominantly net anodic current density with increasing time (**Figure 5-8**). The initial net cathodic current density can be attributed to the hydrogen produced as a result of the cathodic reaction (H<sub>2</sub>O

reduction) balancing the rapid anodic dissolution of Mg pigment particles. The intact MgAlRP showed a mixed spatial distribution of net cathodic and net anodic current density that shows a decrease in the cathodic current density and maintains anodic current densities (**Figure 5-9**). The 3-D current distribution for the intact AlRP, MgRP, and MgAlRP coated AA 7075-T651 sample can be found in **Figure 5-S2**, **5-S3**, and **5-S4**, respectively.

# Galvanic coupling of half Bare AA 7075-T651 and half AlRP / MgRP / MgAlRP coated AA 7075-T651

Samples with artificial defects described in Figure 5-1b, were chosen to study the distance range of galvanic protection offered by various MRP-based coating systems and the ability to suppress pitting on the bare but connected AA 7075-T651. The evolution of normal current density across an AIRP : AA 7075-T651 (AIRP coated : bare AA 7075-T651) sample with defect area ration of 1:1 is shown in Figure 5-10. The SVET derived current density distribution of AlRP : AA 7075-T651 sample can be seen to experience local anode dissolution within the bare AA 7075-T651 as well as polarize a region of the AIRP coating showing both net anodic and net cathodic behavior (Figure 5-10). The AIRP : AA 7075-T651 sample experiences persistent pitting on the bare AA 7075-T651 throughout the duration of exposure as the AIRP coating becomes more cathodic (Figure 5-10). The AIRP does not show a great ability to suppress pitting at the CDI as the AA 7075-T651 substrate is the dominant anode and the AIRP coating shows more cathodic current densities than the substrate (Figure 5-10). The surface plots for the AIRP : AA 7075-T651 sample shown in Figure 5-10 shows no anodic activity over the AIRP coating with local cathodes and anodes (pits) such as seen over the bare AA 7075-T651 substrate. The maxima of  $j_z^a$  over the bare region of the AlRP : AA 7075-T651 sample is 0.1 A/m<sup>2</sup> and does not diminish over the 48hr exposure period. For these reasons, the AIRP can be said to not provide any ability to suppress pitting. The number of pits that were initiated within the detection limit of the SVET on the bare region of the half AIRP coated sample after 48-hr immersion in 1 mM NaCl was 34 pits/cm<sup>2</sup>. The 3-D current distribution for the half AIRP coated and half bare AA 7075-T651 sample can be found in Figure 5-S5.

The distribution of current density across the MgRP : AA 7075-T651 sample with a defect area ratio to coating ratio of 1:1 (**Figure 5-11**). The SVET-derived net current density distribution

of MgRP : AA 7075-T651 sample can be seen in **Figure 5-11**. Pits are developed over the bare AA 7075-T651 with the MgRP experiencing the same mixed anode/cathode behavior within the first hour that was observed in the intact condition. The MgRP : AA 7075-T651 sample progresses such that there is a decrease in the total number of pits over the bare AA 7075-T651 with increasing exposure time (**Figure 5-11**). The maxima of  $j_z^a$  over the bare region of the MgRP : AA 7075-T651 sample show the level of cathodic current density over the MgRP coating increasing with increasing exposure time (**Figure 5-11**). The surface plots of the MgRP : AA 7075-T651 sample show the level of cathodic current density over the MgRP coating increasing with increasing exposure time (**Figure 5-11**). The bare region of the uncoated bare AA 7075-T651 has fewer pits and shows a reduction in the maxima of  $j_z^a$  over the bare region with increasing exposure time (**Figure 5-11**). The bare region of the MgRP : AA 7075-T651 has fewer pits and shows a reduction in the maxima of  $j_z^a$  over the bare region with increasing exposure time (**Figure 5-11**). The maximum of  $j_z^a$  over the bare region of the MgRP : AA 7075-T651 has fewer pits and shows to 0.03 A/m<sup>2</sup> over 48-hr exposure (**Figure 5-11**). This shows that the MgRP is capable of suppressing pitting on the bare AA 7075-T651. The number of pits that were initiated within the detection limit of the SVET on the bare region of the half MgRP coated sample after 48-hr immersion in 1 mM NaCl was 14 pits/cm<sup>2</sup>. The 3-D normal current distribution for the half MgRP coated and half bare AA 7075-T651 sample can be found in **Figure 5-S6**.

The distribution of current density across the MgAlRP : AA 7075-T651 sample with a defect area ratio of 1:1 (**Figure 5-12**). The SVET derived current density distribution of MgAlRP : AA 7075-T651 sample can be seen in **Figure 5-12** to develop a well-defined separation between the anodic MgAlRP region towards a surface with local cathodes and anodes over the bare AA 7075-T651 (**Figure 5-12**). The number of pits formed in the first hour over the bare region of the MgAlRP : AA 7075-T651 sample are less than that observed AlRP or MgRP samples (**Figure 5-12**). The maxima of  $j_z^a$  over the bare region of the MgAlRP : AA 7075-T651 sample are less than that observed AlRP or MgRP samples (**Figure 5-12**). The maxima of  $j_z^a$  over the bare region of the MgAlRP : AA 7075-T651 sample and decreases to 0.01 A/m<sup>2</sup> over 48-hr exposure (**Figure 5-12**). The MgAlRP maintains anodic behavior throughout the exposure period (i.e. no polarity reversal) and decreases in magnitude with increasing exposure time (**Figure 5-12**). The bare region of the MgAlRP : AA 7075-T651 sample showed suppressed pitting near the CDI and further away in the bare region of AA 7075-T651. The number of pits that were initiated within the detection limit of the SVET on the bare region of the half MgAlRP coated sample after 48-hr immersion in 1 mM NaCl was only 7 pits/cm<sup>2</sup>. The 3-D current distribution for the half MgAlRP coated and half bare AA 7075-T651 sample can be found in **Figure 5-S7**.

The results obtained from the above SVET monitoring of 1:1 defect area ratios can be analyzed further by evaluating the net anodic and net cathodic current over the intact region of each sample with increasing exposure time (**Figure 5-13a** and **5-13b**). The bare AA 7075-T651 decreases from 8 A/m<sup>2</sup> to 3 A/m<sup>2</sup> in net anodic current density (**Figure 5-13a**) while the net cathodic current density increases from 1.5 to 2 A/m<sup>2</sup> (**Figure 5-13b**). The net anodic current density for the half AIRP coated AA 7075-T651 in **Figure 5-13a** starts and end around 3 A/m<sup>2</sup>. The net cathodic current density of the half AIRP coated AA 7075-T651 sample decreases from 5.3 A/m<sup>2</sup> to 3 A/m<sup>2</sup> (**Figure 5-13b**). The half MgRP coated sample decreases in net anodic current density from 4.3 A/m<sup>2</sup> to 1.1 A/m<sup>2</sup> (**Figure 5-13a**) and increases in net cathodic current density from 1.5 A/m<sup>2</sup> to 10 A/m<sup>2</sup> throughout the 48-hr monitoring (**Figure 5-13b**). The MgAIRP decreases in net anodic current density from 3.4 A/m<sup>2</sup> to 3 A/m<sup>2</sup> (**Figure 5-13a**) while the net cathodic current density from 3.4 A/m<sup>2</sup> to 3 A/m<sup>2</sup> to 3.1 A/m<sup>2</sup> by the end of the monitoring period (**Figure 5-13b**).

The SVET derived current density line profiles for bare AA 7075-T651 and each half bare AA 7075-T651 half MRP coated AA 7075-T651 sample are shown in **Figure 5-14**. The bare AA 7075-T651 which is used as a control is shown to produce a peak anodic current density associated with pitting of 0.026 A/m<sup>2</sup> after 1-hr (**Figure 5-14a**) and 0.046 A/m<sup>2</sup> by the end of the 48-hr exposure (**Figure 5-14b**). In the bare AA 7075-T651 region, the maximum anodic current densities of the half AIRP, half MgRP, and half MgAIRP coated samples after 1-hr were 0.028 A/m<sup>2</sup>, 0.03 A/m<sup>2</sup>, and 0.013 A/m<sup>2</sup>, respectively (**Figure 5-14a**). The half-coated region after 1-hr exposure resulted in a maximum anodic current density of 0.008 A/m<sup>2</sup> for the MgRP, 0.004 A/m<sup>2</sup> for the MgAIRP, and the AIRP providing a maximum cathodic current density of 0.007 A/m<sup>2</sup> (**Figure 5-14a**). The half MgAIRP-coated region after 48-hr of exposure fluctuates with maximum current density over the half-coated region after 48-hr of 0.008 A/m<sup>2</sup> and 0.006 A/m<sup>2</sup>, respectively (**Figure 5-14b**). The MgRP and AIRP show a maximum cathodic current density over the half-coated region after 48-hr of 0.008 A/m<sup>2</sup> and 0.006 A/m<sup>2</sup>, respectively (**Figure 5-14b**). The MgRP and AIRP show a maximum cathodic current density over the half-coated region after 48-hr of 0.008 A/m<sup>2</sup> and 0.006 A/m<sup>2</sup>, respectively (**Figure 5-14b**). The MgRP and AIRP show a maximum cathodic current density over the half-coated region after 48-hr of 0.008 A/m<sup>2</sup> and 0.006 A/m<sup>2</sup>, respectively (**Figure 5-14b**). The MgAIRP provides the greatest suppression of peak anodic current density followed by MgRP where the least protection is offered by the AIRP.

A more detailed view of the suppression of localized corrosion can be seen in **Figure 5**-**15**. The cumulative density function (CDF) showing the peak pit current density over the bare AA 7075-T651 region of each half MRP coated sample and the uncoated AA 7075-T651 sample used

as a control (Figure 5-15a). At 100% the CDF represents the maximum peak pit current density over the bare region of each half MRP coated sample which can be compared to the uncoated AA 7075-T651 control (Figure 5-15a). The control and half MgRP coated sample show the highest peak pit current density of  $3.5 \cdot 10^{-2}$  A/m<sup>2</sup> while the AlRP shows a maximum peak pit current density of  $2 \cdot 10^{-2}$  A/m<sup>2</sup> and the MgAlRP shows the lowest maximum of peak pit current density of  $1 \cdot 10^{-2}$  A/m<sup>2</sup> (Figure 5-15a). The number of pits and peak pit current density distribution is shown in Figure 5-15b. The number of pits and peak pit current density is greatest for the uncoated AA 7075-T651 control, as expected. The half AIRP coated sample does not show the ability to suppress localized corrosion as the number of pits and peak pit current density is very similar to the uncoated control sample (Figure 5-15b). The half MgRP coated sample shows a significant reduction in the number of pits and peak pit current density compared to the AlRP (Figure 5-15b). The MgAlRP shows the greatest reduction in the number of pits and peak pit current density (Figure 5-15b). Extending this approach to analyzing the anode and cathode area percentages over the bare region of each half MRP coated sample can be seen in Figure 5-16. This shows the anode and cathode area percentages during SVET testing within the first hour and after 48-hrs of exposure in 1 mM NaCl. The half AlRP coated sample shows no ability to suppress the anode area over the bare region where the MgRP and MgAlRP both show a significant reduction in the anode area percentage after 48-hr exposure (Figure 5-16). This detailed analysis definitively shows the superior ability of MgAlRP to provide suppression of localized corrosion to AA 705-T651 compared to the AlRP and MgRP (Figure 5-15 and 5-16).

#### Characterization after Full Immersion Testing in 1 mM NaCl

Optical characterization and the SEM BSI cross-section micrographs of bare AA 7075-T651 and half MRP (MgRP, AlRP, and MgAlRP) coated and half bare AA 7075-T651 after the SVET 48-hr immersion in 1 mM NaCl are presented in **Figures 5-17** through **5-19**. The localized corrosion on the surface of bare AA 7075-T651 can be seen in **Figure 5-17a** as well as in the SEM-BSI cross-section (**Figure 5-18a**) where the pits can be observed. These finding were also in correlation with the SVET recorded net current density distribution (**Figure 5-6 and S1**) showing the multiple net anodic currents maxima corresponded to pits. The bare AA 7075-T651 portion of the half AlRP coated sample showed a surface containing many pits are presented in

Figure 5-17b, which was also seen in SVET recorded data (Figure 5-10 and 5-S5). The CDI interface for the AIRP did not show evidence of deposit formation as it is shown in Figures 5-18b, 5-19a. The bare AA 7075-T651 portion of the half MgRP coated sample (Figure 5-17c) showed a surface with fewer pits than were present both in the uncoated condition (Figure 5-17a) and over the bare AA 7075-T651 portion of the half coated AlRP sample (Figure 5-17b). This was also confirmed in the SVET net current density distribution (Figure 5-11 and 5-S6). The subtle deterioration of the bare substrate with some deposit formation can be seen in the case of MgRP in Figures 5-18c, 5-19b. The bare AA 7075-T651 portion of the half MgAIRP coated (Figure 5-**17d**) sample showed a surface containing fewer pits than were present in the uncoated condition and over the bare AA 7075-T651 portion of both the half MgRP (Figure 5-17c) and the half AlRP (Figure 5-17b) coated samples. This reduced anodic current density and deceased number of active pits in the bare region of half MgAlRP coated sample is a defining feature indicating that the MgAIRP is capable of providing suppression against pitting (Figure 5-12 and 5-S7). The bare substrate adjacent to the CDI for MgAIRP did not show the presence of deposit formation Figures 5-18d, 5-19c. The general observation for AIRP (Figure 5-18b), MgRP (Figure 5-18c), and MgAlRP (Figure 5-18d) is the CDI interface found showed little deterioration over the bare AA 7075-T651 substrate. This necessitated further analysis in the form of full immersion testing over the same exposure period (48-hrs) in a solution of higher concentration (0.6 M NaCl) of each half MRP coated sample which can be found in the supplemental section.

#### **Discussion**

#### Conventional behavior expected for sacrificial anode based cathodic protection

The spatial current distributions, reduction in peak anodic current density over a bare region of AA 7075-T651 that is partially protected by AlRP, MgRP, and MgAlRP have been assessed. At open circuit potential the intact coatings should display anode and cathode sites unless there is a virtually no anode-cathode separation in which case a white-grey background would appear homogeneously across the MRP electrode. Upon galvanic coupling to an anode, nonlocal corrosion might shift monotonically to more bare cathodic area depicted in blue indicating net cathodic currents spread across the bare area (**Figure 5-11** and **5-12**). In contrast, the anodic MRP would increase in current density (charge output) indicating activation of the pigment providing

electrons for protection to the bare AA 7075-T651 which operates as the cathode resulting in the consumption of electrons (**Figure 5-12**). In equation form the corrosion process involves no charge accumulation and the charge neutrality requirement also means instantaneous anode and cathode currents at any one instance to satisfy the following equilibria.

$$\sum i_a A_a = \sum i_c A_c$$

The ideal situation is expected if  $E_{corr}^{MRP} \ll E_{corr}^{7075}$  even the situation where  $E_{corr}^{\eta} > E_{corr}^{MRP}$ . Instead, cathodic sites prevail on the sacrificial anode sites. There ideally would then be complete anode and cathode separation. This is not the case on AA 7075-T651 as there are many constituent particles (**Figure 5-6**). The suppression of local intense anodes is observed rather than a smooth secondary current distribution of current and potential where the anode MRP is 100% anode and the bare AA 7075-T651 is 100% cathode (**Figure 5-10** through **5-12**). This would be the situation given (a) constituent particles are local anode with  $E_{corr} \ll E_{corr}^{matrix}$  and (b) for unknown reasons why the MRP does not activate consistently or that activation of each pigment particle occurs.

The presence of many electrochemically active constituent particles within AA 7075-T651 provides a challenging situation to provide corrosion protection. While pitting was not prevented in its entirety the reduction in peak anodic current density and number of local sites is used as a metric to assess the ability of each primer to suppress pitting as compared to uncoated bare AA 7075-T651 (**Figure 5-10** through **5-12**). The MRPs ranked from most effective to least effective in reducing peak anodic current density of AA 7075-T651 are MgAIRP>MgRP>AIRP. The full immersion testing and subsequent electrochemical testing showed the precipitation of corrosion products in half MgRP coated and half MgAIRP coated samples that was not observed in the half AIRP coated sample and bare AA 7075-T651. The combination of both SVET testing (**Figure 5-10** through **5-12**) and full immersion testing allows for the confirmation of protection from current density mapping as well as post exposure microscopy (**Figure 5-17** through **5-19** and **5-S8-5** through **S11**) and corrosion product identification (**Figure 5-S12** through **5-S14**).

#### Sacrificial protection and the role of pigments

The premise of galvanic protection in MRP coating systems is predicated on reducing the corrosion of the substrate by allowing for the favorable dissolution of more reactive species, as is the case with galvanic couple between Mg and Al. The necessary conditions of galvanic corrosion being described by the junction of two dissimilar metals in electrical and ionic contact with one another through a conductive electrolyte. The difference in properties and performance observed, for instance, in the MgAlRP compared to the MgRP are a result of the benefits of composite coatings. The pigment within the MgAlRP coating are chemically indistinguishable from the pigment in the individual AlRP and MgRP coatings yet the MgAlRP outperforms both during the SVET testing. This can also be seen in the polarization of MgRP to the potential of the AA 7075-T651 substrate where the MgAlRP is capable of sustaining potentials 300 mV<sub>SCE</sub> lower than the OCP of AA 7075-T651 seen in **Figure 5-4a**. This is well within the region with is considered to be protective as the OCP of the MgAlRP intact coating is below the pitting potential of MgZn<sub>2</sub>.

The ability to sustain sacrificial protection, once a suitable galvanic couple is formed, is largely dependent on the dissolution behavior of the anode. The oxidation processes taking place on the anode and the chemical composition of the solution are of critical importance. The EDS oxygen profiles of MgRP applied to AA 7075-T651 seen in the appendix (Figure 5-S10) shows the oxidation around the perimeter of each Mg pigment. This oxidation behavior results in the formation of a partial barrier, thereby increasing the resistance of the pigment. This can be seen in the appendix clearly in the cross-sectional microscopy and oxygen EDS map as the CDI of the half MgRP coated sample contains the thickest oxygen rich layer on the bare AA 7075-T651 surface resulting in increased barrier resistance (Figure 5-S11). The MgRP is not without its issues, the high activity of Mg pigment resulting in rapid dissolution may lead to a scenario in which the Mg pigment is depleted. This shows how the trade-offs between dissolution of pigment (sacrificial protection) and the formation of corrosion products (secondary barrier properties) as well as the impact on the galvanic couple mediating the corrosion. Similar results were observed for the application of composite MgAlRP applied to AA 5456-H116 in 0.6 M NaCl<sup>64</sup> wherein the addition of Mg to an Al-Zn system showed two additional benefits: (1) the dissolution of Mg stabilizes insoluble Zn corrosion products, and (2) the increase in oxidation of Al reduces the corrosion rate of Mg<sup>64</sup>.

The galvanic couple formed between the intact MgRP and the AA 7075-T651 requires the electrical connection from the electrolyte through Mg pigment in the MRP to the AA 7075-T651 substrate. In this condition, the sacrificial capacity of an intact MRP with only one pigment chemistry is tied to the resistance through the thickness of the MRP. The oxidation and subsequent dissolution of Mg pigment can disconnect Mg pigment from participating in the sacrificial anode capacity of the MgRP coating thereby diminishing the current contributed. In the defect condition which reveals the underlying substrate a dissolving MgRP is dominated by the ohmic resistance of the solution. The greater the ohmic resistance, IR drop, of solution limits the galvanic couple of the pigment within the MRP. This is described by the schematic Evans diagram provided in previous publication <sup>19</sup>.

The MgRP, AlRP, and MgAlRP galvanically coupled to AA 7075-T651 were investigated in a previous study to evaluate the galvanically coupled potential and galvanically coupled current densities in both 1:1 and 15:1 MRP:bare AA 7075-T651 area ratios while monitoring the change in pH at each electrode over 24-hr period in 0.6 M NaCl<sup>21,22</sup>. This study was able to determine that the AIRP galvanically coupled to AA 7075-T651 and produced cathodic current densities suggesting the galvanic couple was not behaving as a sacrificial anode <sup>21</sup>. The MgRP and MgAlRP were both capable of producing anodic current densities and provided a galvanically coupled potential below the OCP of AA 7075-T651<sup>22</sup>. This shows that both the MgRP and MgAlRP are capable of providing sacrificial anode based cathodic protection <sup>22</sup>. A greater anodic coupled current density was witnessed in the MgAIRP leading to increased utilization requiring further analysis and mechanistic description. The MgRP was capable of shifting the solution pH to 10.3 near the reacting MRP electrode interface while the MgAlRP shifted the solution pH to 9.1<sup>22</sup>. The enhanced performance of the MgAlRP is attributed to the shift in pH activating the Al 5wt%Zn pigment pushing the chemical stability outside of the passive Al(OH)<sub>3</sub> region and into a region of stable Al<sup>3+ 22</sup>. This shift in pH could explain how the Al-5wt%Zn pigment is activated to oxidize to AlO<sub>2</sub><sup>-</sup> as aluminum is amphoteric and susceptible to corrosion in alkaline conditions <sup>22</sup>. The lack of corrosion products detected in the half MgAlRP sample may be a result of the pH shift into a region of stable  $Mg^{2+}$  and  $Al^{3+}$ , which is shown by chemical stability modeling in previous publication for the MgAlRP system<sup>19</sup>. This provides a secondary pathway for coating utilization supporting long lasting cathodic protection <sup>22</sup>. These secondary pathways are unique to the composite MgAIRP due to the different pigment chemistries available in the coating.

These studies were extended to evaluate the progression of corrosion damage over a sixweek exposure to 0.6 M NaCl with the use of accelerated exposure testing in B117 salt spray chamber on AlRP, MgRP, and MgAlRP coatings in the intact and scribed condition <sup>21,22</sup>. Postmortem analysis in the form of SEM and EDS map/line scans were collected throughout the cross-section view and plan view with oxygen signal being used as a marker to track the progression of corrosion <sup>21,22</sup>. This testing revealed that in the intact condition both the MgRP and MgAlRP are capable of suppressing substrate oxidation at the coating substrate interface while there is an increasing oxygen signal at the coating electrolyte interface for the intact AlRP which can be considered under-paint corrosion<sup>21,22</sup>. In the scribed condition there is an increasing oxidation of pigment at the scribe wall for the MgRP and MgAlRP suggesting enhanced protection in the defect region <sup>22</sup>. The AIRP showed increasing oxygen signal within the scribe throughout the duration of exposure testing <sup>21</sup>. The scribed MgRP and MgAlRP showed an increase in the magnesium and oxygen signal throughout the scribe with a decrease in the aluminum signal implying the precipitation of corrosion products <sup>22</sup>. The AlRP showed an aluminum and oxygen rich signal within the scribe while also detecting the presence of overlapping zinc and chloride signal at the scribe wall <sup>21</sup>. This suggests that the AIRP does not provide protection allowing the scribe to corrode, the zinc and chloride signal can be attributed to the dissolution of zinc from the Al-5wt%Zn pigment in the AlRP and precipitation of ZnCl<sub>2</sub> on the surface which is not protective and may lead to persistent contamination of the MRP surface <sup>21</sup>. The scribed samples after sixweek accelerated exposure testing were cleaned with nitric acid and compared to uncoated AA 7075-T651 exposed under the same conditions as MRP coated samples and pristine unexposed AA 7075-T651 as control. This showed that the scribe section of the AIRP coated sample increased in depth and width suggesting that the corrosion products formed were insufficient to protect the bare AA 7075-T651<sup>21</sup>. The MgRP and the MgAlRP both revealed no deterioration of the substrate within the scribe after six-week accelerated exposure testing <sup>22</sup>.

A further study to assess the long-term (>48-hr) immersion, cyclic wetting and drying, and field testing would enable a greater understanding of the evolution of the galvanic coupling condition that may reveal meaningful differences in the nature of the corrosion product layer observed. This would also aid discerning the effects of composite MRP on the dissolution and precipitation of corrosion products and the trade-offs between cathodic protection, chemical inhibition, and secondary barrier properties. Greater efforts should be made to consider the

alloying of Al pigments with greater than 5-wt%Zn or additional electrochemically active elements such as Mg and Li to provide sacrificial anode based cathodic protection to AA 7075-T651.

#### **Conclusion**

The ability of AIRP, MgRP, and MgAIRP coating systems to provide sacrificial anodebased cathodic protection as well as suppression of pitting on AA 7075-T651 was studied utilizing the SVET in conjunction with standard electrochemical tests. SVET revealed that the corrosion of uncoated otherwise bare AA 7075-T651 is characterized by the onset of local anodic current density maxima indicating dissolution via pitting where peak values of 0.1 A/m<sup>2</sup> and 40 pits/cm<sup>2</sup> were initiated during the 48-hr exposure period in 1 mM NaCl. Full immersion testing in 0.6 M NaCl showed the precipitation of corrosion product from MgRP and MgAIRP that increase the barrier resistance of AA 7075-T651 at the CDI compared to bare AA 7075-T651 taken as a baseline.

- Coating systems of three different pigment types (AlRP, MgRP, MgAlRP) were tested via EIS measurements ranked according to their barrier resistance of in the absence of a topcoat: AlRP > MgAlRP> MgRP.
- The OCP monitoring of each as-received MRP coating in the intact condition revealed the activation of Mg pigment within both MgRP and MgAlRP; however, the MgAlRP was the only MRP to maintain potentials lower than the AA 7075-T651 substrate and critical potentials for suppression of IGC such as the pitting potential of MgZn<sub>2</sub>.
- The SVET monitoring of MRP coating in the intact condition determined that MgRP and MgAlRP coatings have capacity to act as a sacrificial anode applied to AA 7075-T651 in the intact condition. The AlRP coating in the intact condition started out as an anode yet reduced in intensity with continued exposure implying eventual loss of sacrificial protection.
- The SVET monitoring of half bare AA 7075-T651 half MRP coated AA 7075-T651 with a defect area ratio of 1:1 showed the AIRP polarizing to become a cathode to an anodic AA 7075-T651 substrate (opposite to the expected sacrificial anode based cathodic protection).
  MgRP was capable of operating as a sacrificial anode and suppressed pitting of the bare

AA 7075-T651 substrate. The MgAlRP was capable of maintaining anodic activity over the MRP throughout the entire 48-hr exposure period and possessed the greatest suppression of pitting over the bare AA 7075-T651.

- The corrosion products identified are a result of the precipitation of soluble cation species associated with the dissolution of sacrificial pigment within the MRPs. The precipitated corrosion products detected for the MgRP and MgAlRP increased the barrier resistance of the AA 7075-T651 at the CDI. The AlRP sample did not witness any precipitated corrosion products and had the least ability to protect a defect exposing bare AA 7075-T651.
- The ability to suppress pitting within the defect region exposing bare AA 7075-T651 for each MRP is ranked from highest to lowest MgAlRP > MgRP > AlRP as characterized by the number of pits observed and suppressing the maxima of normal current density below values observed in uncoated bare circumstances monitored via SVET and confirmed with optical characterization.
- The number of pits that were initiated within the detection limit of the SVET in the defect region for AlRP, MgRP, and MgAlRP coated AA 7075-T651 samples after 48-hr immersion in 1 mM NaCl was 34 pits/cm<sup>2</sup>, 14 pits/cm<sup>2</sup>, and 7 pits/cm<sup>2</sup>, respectively. The number of pits that were initiated within the detection limit of the SVET for bare uncoated AA 7075-T651 is 40 pits/cm<sup>2</sup>.

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# Tables, Chapter 5 – Task 4

# Tables

Table 5-1. Metal Rich primer systems included in this study.

Code	Primer Commercial Name	Provider	Resin	PVC (%)	Thickness (µm)	Pigment Diameter/ Dimensions (μm)
AlRP (Epoxy,27%)	LN4841	RC	Epoxy	27	48.23 ± 4.2	$10.3 \pm 5.4$
Al-MgRP (Epoxy,28/19%)	LN4847	UVa-ARL	Ероху	28 (Al-Zn) 19 (Mg)	46.23 ± 6.12	9.8 ± 4.8 (Al-Zn) Length: 18.2 ± 6.2 (Mg) Width: 6.6 ± 2.1 (Mg)
MgRP (Epoxy,26%)	Aerodur 2100	AN	Ероху	26	$44.52 \pm 6.42$	Length: $26.3 \pm 8.4$ Width: $12.2 \pm 4.4$

# Figures, Chapter 5 – Task 4

## Figure 5-1



Figure 5-1. Representation of the intact coating shown in **a**) and coating/defect configuration shown in **b**) for a 1:1 exposed area ratio between the coating and bare AA7075-T651. All SVET full immersion testing is conducted in 1 mM NaCl solution.

### Figure 5-2



Figure 5-2. Schematic representation of a half MRP coated half bare AA 7075-T651 sample which experiences localized corrosion on the bare AA 7075-T651 region, corrosion product accumulation at the coating defect interface (CDI), characterization within the intact and defect regions of the coating, net current flux density along the z-direction, and electrochemical methodology across the sample

Figure 5-3



Figure 5-3. Calibration of the SVET data by the distance of the probe above the sample using Al point current source: **a**) schematic of the Al point current source and SVET probe position; **b**) the distribution of the SVET-derived current density depending on the z-distance of the probe above the Al point current source surface at applied current density of  $120 \text{ A/m}^2$ ; **c**) the distribution of the SVET-derived peak current densities depending on the z-distance of the probe above the Al point current applied current densities for the SVET-derived current densities.

Figure 5-4



Figure 5-4. **a)** The 24-h open circuit potential monitoring of AlRP, MgRP, MgAlRP coated AA 7075-T651 as well as bare AA 7075-T651 in the as received condition. **b)** The electrochemical impedance spectra of the bare AA 7075-T651 substrate and each MRP coating applied to AA 7075-T651 in the as received condition. **c)** The phase angle progression. Electrochemical testing is conducted in 0.6 M NaCl under full immersion conditions.
Figure 5-5



Figure 5-5. Initial electrochemical evaluation of the AA 7075-T651, pure elements, and detrimental phases related to IGC included in the potentiodynamic polarization diagram tested in full immersion 0.6 M NaCl.





Figure 5-6. SVET derived surface plots showing the distribution of normal current density  $j_z$  emerging from a bare AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.



Figure 5-7. SVET derived surface plots showing the distribution of normal current density  $j_z$  emerging from an intact AlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.





Figure 5-8. SVET derived surface plots showing the distribution of normal current density  $j_z$  emerging from an intact MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

10-

9-

8-

7-

6-

5-

4-

3-

2

1

0<mark>∔</mark>0 0

10

9-

8-

7-

6-

ż ż

1

Distance / mm





Figure 5-9. SVET derived surface plots showing the distribution of normal current density  $j_{\tau}$ emerging from an intact MgAlRP coated AA7075-T651 sample freely corroding in nonaerated 1mM NaCl solution.

10





Figure 5-10. SVET derived surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half AlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.



Figure 5-11. SVET derived surface plots showing the distribution of normal current density J<sub>z</sub> emerging from a half bare AA7075-T651 half MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.



Figure 5-12. Surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half MgAlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.

Figure 5-13



Figure 5-13. Total net z-corrected SVET derived (a) net anodic and (b) net cathodic current density as a function of exposure time for each half MRP coated AA7075-T651 half bare AA7075-T651 sample immersed in 1mM NaCl solution. The net anodic and net cathodic current densities are shown over the bare region of AA 7075-T651.



Figure 5-14. SVET derived current density line profiles for bare AA 7075-T651 and for each half bare AA 7075-T651 (0-5 mm) half MRP coated (5-10 mm) sample in a) 1-hr and b) 48-hr of immersion time in 1mM NaCl. The dashed black line is drawn through 0 to identify anode vs. cathode.



Figure 5-15. a) Cumulative distribution function and b) pit distribution vs peak pit current density over uncoated AA 7075-T651 and each half MRP coated AA 7075-T651 sample throughout SVET testing in 1mM NaCl after 48-hr exposure.

Figure 5-16







Figure 5-17. Digital optical imaging showing the visual appearance of post 48-hour SVET immersion in 1mM NaCl shown in **a**) bare AA7075, **b**) 7075: AlRP, **c**) 7075: MgRP, and **d**) 7075: MgAlRP.





Figure 5-18. Scanning electron BS imaging of post 48-hour SVET full immersion in 1mM NaCl for **a**) bare AA7075, **b**) AlRP:7075, **c**) MgRP:7075, and **d**) MgAlRP:7075.





Figure 5-19. Scanning electron BS imaging of post 48-hour SVET full immersion in 1mM NaCl over the uncoated region immediately adjacent to the coating defect interface for **a**) AlRP, **b**) MgRP, and **c**) MgAlRP.

### Figures, Chapter 5 – Task 4 – Supplemental





Figure 5-S1. Surface plots showing the distribution of normal current density  $j_z$  emerging from a bare AA7075-T651 alloy sample freely corroding in non-aerated 1mM NaCl solution.



Figure 5-S2. Surface plots showing the distribution of normal current density  $j_z$  emerging from an intact AIRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.





Figure 5-S3. Surface plots showing the distribution of normal current density  $j_z$  emerging from an intact MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.



Figure 5-S4. Surface plots showing the distribution of normal current density  $j_z$  emerging from an intact MgAlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM <sup>271</sup> NaCl solution.





Figure 5-S5. Surface plots showing the distribution of normal current density j<sub>z</sub> emerging from a half bare AA7075-T651 half AIRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution. 272



Figure 5-S6. Surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half MgRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.



Figure 5-S7. Surface plots showing the distribution of normal current density  $j_z$  emerging from a half bare AA7075-T651 half MgAlRP coated AA7075-T651 sample freely corroding in non-aerated 1mM NaCl solution.



Figure 5-S8. Digital optical imaging showing the visual appearance of post 48-h full immersion in 0.6 M NaCl shown for a) AlRP:7075, b) MgRP:7075, and c) MgAlRP:7075.

Figure 5-S9

MRP

CDI

AA 7075-T651



Figure 5-S9. Digital optical imaging showing the visual appearance of post 48-hour full immersion in 0.6 M NaCl shown for AlRP, MgRP, and MgAlRP. Optical imaging is taken over the intact MRP, CDI, and bare AA 7075-T651 regions.



Figure 5-S10. Scanning electron BS imaging of post 48-hour full immersion in 0.6 M NaCl over the intact coating for **a**) AlRP, **c**) MgRP, and **e**) MgAlRP. EDS oxygen signal is shown next to each micrograph as a marker for oxidation for **b**) AlRP, **d**) MgRP, and **f**) MgAlRP.

MgRP

AIRP

MgAIRP



Figure 5-S11. Scanning electron BS imaging of post 48-hour full immersion in 0.6 M NaCl over the uncoated region at the CDI for **a**) AlRP, **c**) MgRP, and **e**) MgAlRP. EDS oxygen signal is shown next to each micrograph as a marker for oxidation for **b**) AlRP:7075, **d**) MgRP:7075, and **f**) MgAlRP:7075.



Figure 5-S12. Raman spectra collected for AlRP:AA7075 samples after 48-hour immersion in quiescent 0.6 M NaCl in the intact MRP, MRP:AA7075 interface, and within the bare AA7075 region.



Figure 5-S13. Raman spectra collected for MgRP:AA7075 samples after 48-hour immersion in quiescent 0.6 M NaCl in the intact MRP, MRP:AA7075 interface, and within the bare AA7075 region.



Figure 5-S14. Raman spectra collected for MgAlRP:AA7075 samples after 48-hour immersion in quiescent 0.6 M NaCl in the intact MRP, MRP:AA7075 interface, and within the bare AA7075 region.

#### Chapter 6 – Thesis Summary, Conclusions, and Suggested Future Work

#### Summary

Three metal rich primers (MRP) (AlRP, MgRP, and MgAlRP) were analyzed in a variety of electrochemical analysis techniques as well as ASTM B117 accelerated environmental exposure testing to evaluate their ability to provide sacrificial anode based cathodic protection when applied to AA 7075-T651. Initially, standard electrochemical testing in the form of open circuit potential monitoring and electrochemical kinetics of AA 7075-T651, susceptible grain boundary phase MgZn<sub>2</sub>, and commercially pure elements Zn, Mg, and Al. This developed a method by which determining potential regions of IGC susceptibility could be determined. These potential regions were confirmed with potentiostatic holds through a range of applied potentials from the anodic and cathodic regions of -0.6, -0.7  $V_{SCE}$ , -0.75  $V_{SCE}$ , -0.8  $V_{SCE}$ , -0.9  $V_{SCE}$ , -1.0 V<sub>SCE</sub>, -1.1 V<sub>SCE</sub>, -1.2 V<sub>SCE</sub>, -1.3 V<sub>SCE</sub>, -1.4 V<sub>SCE</sub>, -1.5 V<sub>SCE</sub>, and -1.6 V<sub>SCE</sub>. At each of these potentials the hydrogen evolution rate was determined with the use an inverted burette to capture the evolved hydrogen gas and cross-sectional optical characterization was conducted to show the progression of corrosion through the depth of AA 7075-T651 as a function of applied potentials. This testing revealed a potential window in which current density and hydrogen evolution were minimized and associated with minimal crack growth rates. The minimum crack growth rates that were noticed within this potential window of reduced IGC susceptibility where, unfortunately, still considerably fast. This speaks to the nature of how susceptible and prone to SCC/IGSCC AA 7075-T651. This leaves little room for mitigation strategies such as MRPs to arrest crack growth as the reduction in crack growth rates, while present, are insignificant.

Further analysis in the form of laboratory diagnostic cycle testing and accelerated environmental exposure testing was conducted to evaluate corrosion performance metrics of each MRP. Cycle testing revealed that the AIRP was not able to suppress the potential below the corrosion potential of AA 7075-T651 or the pitting potential of MgZn<sub>2</sub>, produced cathodic current density under the application of -0.95 V<sub>SCE</sub> opposite of the intended galvanic coupling conditions. The MgRP was observed to suppress the potential below the corrosion potential of AA 7075-T651 or the pitting potential of MgZn<sub>2</sub>, produced anodic current density under the application of -0.95 V<sub>SCE</sub>. The current output of the MgRP was short-lived as the rapid oxidation of MgRP resulted in quick depletion as well as oxidation of the pigment perimeter leading to a reduction in the corrosion rate. The MgAlRP was observed to suppress the potential below the corrosion potential of AA 7075-T651 or the pitting potential of MgZn<sub>2</sub>, and produced a greater anodic current density under the application of -0.95 V<sub>SCE</sub> than the MgRP. This was an interesting discovery as the Mg pigment within the MgAlRP was identical to the MgRP and the Al pigment was identical to the AIRP which was determined to be ineffective. This enhanced performance of the MgAlRP requires additional utilization pathways not available to the MgRP motivating further analysis. Accelerated environmental testing in the form of ASTM B117 salt spray was conducted in order to determine the ability of each coating to protect defects within coating systems such as scribed which reveal the underlying substrate. This testing revealed that the AIRP was not able to protect against oxidation of the scribe and was shown to increase the scribe width and depth over the duration of exposure. These results directly show the lack of protection offered by the AIRP and the corrosion products that were detected where determined to be unprotective. The MgRP and MgAlRP both successfully protected against scribe corrosion into the depth and revealed that oxidation of pigment at the scribe wall was present which allows for enhanced protection of the scribe as corrosion products are redeposited within the scribe and form corrosion protective films to form. These laboratory diagnostic cycle testing and accelerated environmental exposure testing results showed a capacity for protection which can be offered to AA 7075-T651 by the MgRP and MgAlRP while the AlRP is ineffective. This testing also revealed that the MgAIRP outperforms the MgRP and results in a greater charge output under conditions deemed to be protective. The enhanced performance requires further analysis to determine the mechanisms responsible for the increased charge output of the composite MgAlRP coating.

Investigations in the form of galvanic couple testing between each MRP and the bare AA 7075-T651 substrate where conducted to evaluate the naturally occurring coupled potential and coupled current density. This situation is preferable as the galvanic couple formed is allowed to form naturally and spontaneously from the galvanic couple between each MRP and the substrate. This testing was conducted in a galvanic corrosion cell outfitted with port-holes that allow for the pH monitoring at each electrode interface throughout the duration of galvanic corrosion testing. The galvanic couple formed between AlRP and AA 7075-T651 resulted in a galvanic couple potential at the corrosion potential of AA 7075-T651 showing no ability to provide potential suppression and a galvanically coupled current density that showed the AlRP responds

with cathodic current density and no pH changes at the AlRP. These results confirmed that the AIRP is not an effective form of sacrificial anode based cathodic protection when applied to AA 7075-T651. The MgRP galvanically coupled to bare AA 7075-T651 produced a coupled potential bellow the corrosion potential of AA 7075-T651 showing an ability to provide potential suppression and produced an anodic galvanically coupled current density. The pH change in the at the MgRP was observed and shifted the pH of solution to 9.5 after 24-hr of galvanic coupling The MgAIRP galvanically coupled to bare AA 7075-T651 produced a coupled potential bellow the corrosion potential of AA 7075-T651 showing an ability to provide potential suppression and produced an anodic galvanically coupled current density. The MgAlRP was able to provide greater potential suppression and responded with a greater anodic current density than the MgRP, once again showing enhanced protection when compared to MgRP. The pH change in the at the MgAlRP was observed and shifted the pH of solution to 9.0 after 24-hr of galvanic coupling. With the aid of chemical stability diagram analysis, we can see the dependence of metal ion concentrations and pH on the relative stability of chemical species. The dissolution trajectory of MgRP, following equilibrium dissolution, starting at a solution pH of 7 resides within a region which contains stable Al(OH)<sub>3</sub>. While the measured pH exceeds the pH values indicated by equilibrium dissolution, implying non-equilibrium dissolution occurs, results in corrosion of the aluminum substrate (unwanted) due to the amphoteric nature of aluminum.

In the case of MgAlRP, much like the case of MgRP, results in a shift in the solution chemistry as pH shifts to more alkaline values. This shifts the dissolution trajectory away from stable Al(OH)<sub>3</sub> into a region of stable Al<sup>3+</sup> which gives rise to additional utilization pathways as the aluminum pigment within the MgAlRP is allowed to contribute to the sacrificial anode based cathodic protection of AA 7075-T651 by releasing AlO<sub>2</sub><sup>-</sup> into solution. Even in the case of non-equilibrium dissolution trajectory in which pH values may exceed that of predicted equilibrium dissolution trajectories the corrosion of aluminum may occur on the Al pigment and not the substrate as in the intact condition there Al pigment is more proximal to the reacting electrode interface and experiences less resistance than the substrate buried beneath the coating.

Further high-fidelity analysis was conducted in the form of SVET testing to quantify the ability of each MRP to suppress localized corrosion over the bare AA 7075-T651. It was shown that, when compared to uncoated AA 7075-T651 as control, the AlRP resulted no meaningful

decrease in the number of pits present, the anode area percentage over the bare AA 7075-T651, and the greatest peak pit current density of the three MRPs tested. The MgRP resulted in a reduction in the number of pits, the anode area percentage over the bare AA 7075-T651, and a lower peak pit current density over the bare AA 7075-T651 compared to the AIRP. The MgAIRP resulted in the greatest reduction in the number of pits, the anode area percentage over the bare AA 7075-T651, and the lowest peak pit current density over the bare AA 7075-T651 compared to the AIRP. The MgAIRP resulted in the greatest reduction in the number of pits, the anode area percentage over the bare AA 7075-T651, and the lowest peak pit current density over the bare AA 7075-T651 compared to the uncoated AA 7075-T651, AIRP, or MgRP. The numerous electrochemical techniques and exposure testing methods used have shown that there are consistent and measurable differences in the enhanced corrosion performance of MgAIRP which can be attributed to the multiple pigment chemistries available within the coating giving rise to additional utilization pathways that are unavailable in the MgRP and AIRP coatings.

#### Conclusion

- Initial electrochemical investigation into the corrosion protection properties of AA 7075-T651, MgZn<sub>2</sub> revealed potential windows of IGC susceptibility due to the dissolution of MgZn<sub>2</sub> present at the grain boundary in AA 7075-T651. The application of various potentiostatic holds was used as a means of comparing the current output, hydrogen evolution, and the corrosion extending into the depth of the sample through crosssectional characterization. This revealed that the overlap between minimized current output, hydrogen evolution, and corrosion damage characterization revealed a potential window in which corrosion can be mitigated. In the context of SCC susceptibility, this potential window was seen to overlap with minimums in the potential window of reduced SCC crack growth rate and gave insights toward informing mitigation strategies to EAC. The difference in anodic dissolution rate vs crack growth rate implying additional mechanisms of degradation are required to explain the crack growth rate such as hydrogen embrittlement and electrochemical processes relevant to crack tip environments.
- Initial electrochemical investigation into the corrosion protection properties of each MRP in 0.6 M NaCl revealed that the AlRP was not capable of providing potential suppression below the corrosion potential of AA 7075-T651 where MgRP and MgAlRP were both

able to provide potential suppression below the corrosion potential of AA 7075-T651 and the pitting potential of MgZn<sub>2</sub>. Global electrochemical properties of MgRP and MgAlRP show capacity to suppress below critical potentials revenant to AA 7075-T651.

- The laboratory cycle testing procedure in 0.6 M NaCl revealed that the AlRP was not able to suppress the potential below the corrosion potential of AA 7075-T651, responded with cathodic current density under applied potentials which are deemed to be protective from the initial electrochemical investigation conducted. In contrast, both the MgRP and MgAlRP were shown to suppress the potential below the corrosion potential of AA 7075-T651 and the pitting potential of MgZn<sub>2</sub> while producing anodic current density. The MgAlRP produced a greater amount of anodic charge output compared to the MgRP as well as a difference pigment oxidation morphology after 100 hours of polarization.
- Accelerated environmental salt spray testing in 0.6 M NaCl showed that the AlRP was
  not able to provide scribe protection over a 6-week exposure period. The MgRP and
  MgAlRP showed protection to the underlying substrate in the intact condition and scribe
  protection over the 6-week exposure period. The Mg pigment oxidation at the scribe wall
  was seen in the MgRP and MgAlRP showing an enhanced protection in the region of a
  defect which was confirmed throughout EDS line profiles in the plan-view as Mg signal
  increased in the scribe showing an ability to redeposit corrosion products in the scribed
  region.
- The ability of each MRP to protect the underlying AA 7075-T651 substrate was evaluated under conditions in which the natural galvanic couple between the MRP and A 7075 formed spontaneously. In similar fashion to the results gathered above the AIRP was not able to produce galvanically coupled potentials below the corrosion potential of AA 7075-T651 and produced cathodic coupled current density, opposed to the intended galvanic couple. The MgRP and MgAIRP both showed an ability to maintain a coupled potential below the corrosion potential of AA 7075-T651 and produces anodic coupled current density. The MgAIRP, once again, outperformed the MgRP under natural galvanic coupling conditions. The confirmation of enhanced performance across many electrochemical techniques requires a greater level of explanation into the mechanism which are present in the MgAIRP and not in the MgRP. This investigation into the mechanisms responsible for enhanced performance were made possible with the

combined use of pH monitoring throughout galvanic corrosion testing and chemical stability diagram analysis. The dissolution of Mg shifts the solution chemistry to more alkaline pH, which was measured. This shift in pH was noticed for both MgRP and MgAlRP. However, in due to the dual pigment nature of MgAlRP this pH shift resulted in the activation of Al pigment as Al is amphoteric and susceptible to corrosion in both acidic and basic conditions. The current output of the MgAlRP was then determined to be a result of the coordinated of both Mg and Al pigment giving rise to a greater utilization of the composite coating than the MgRP.

The ability to suppress localized corrosion in the form of pitting on the bare AA 7075-T651 was tested for each MRP and compared to uncoated AA 7075-T651 as a control. The AlRP was not capable of reducing the peak pit current density, number of pits, or the anode area percent over the bare region of AA 7075-T651. The MgRP and MgAlRP were capable of reducing the peak pit current density, number of pits, or the anode area percent over the bare region of AA 7075-T651. The MgRP and earea percent over the bare region of AA 7075-T651. The MgRP and MgAlRP were capable of reducing the peak pit current density, number of pits, or the anode area percent over the bare region of AA 7075-T651. The MgAlRP outperformed the MgRP in the ability to suppress localized corrosion, once again showing enhanced performance due to the additional utilization pathways available to the MgAlRP via the pH activation mechanisms of composite coatings.

#### Suggested Future Work

# Suggested future work to assess the impact of multiple pigment chemistries, alloyed pigments, and intermetallic pigments

This study has revealed that composite coatings show great promise in their ability to provide enhanced corrosion protection compared to single pigment coating systems. This opens a new avenue for the optimization of corrosion protection properties. The alloying of pigments optimizes electrochemically active pigments such as Al-Mg, Al-Li, Mg-Zn, Zn-Li as well as their three element alloy systems. The alloying of pigments to achieve optimal electrochemical properties for sacrificial anode cathodic protection allows for ease of manufacturing followed by atomization or ball milling to achieve suitable pigment sizes and morphologies. Multiple alloyed pigments can be used in the same composite coating or a variety of commercially pure elements

to tune the electrochemical properties of coatings. The advancement of intermetallic have been shown to create bulk (1 kg) rods of both Al<sub>2</sub>Mg<sub>3</sub> and MgZn<sub>2</sub>, both of which have the capacity to serve as a sacrificial pigment which may offer additional beneficial corrosion properties within coatings. The results gathered herein motivate future investigations in the possible of composite coatings and the tuning of electrochemical properties of coatings.

Suggested future work to assess the relevant chemical protection mechanisms in the presence of multiple inhibiting species

Previous studies have shown the beneficial effects of many cation species such as  $Zn^{2+}$ and  $Mg^{2+}$  while  $Al^{3+}$ has been shown to have antagonistic effects on the electrochemical behavior of aluminum alloys. These chemical effects, when studied in isolation, are only relevant to single pigment coating systems. However, in the presence of multiple pigment coating systems the cooxidation of electrochemically active pigment results in the release of multiple cations simultaneously. Chemical inhibition in the face of multiple inhibiting species are required to fully understand the protection capacity of hybrid composite coatings. In addition, the chemical dissolution and thermodynamic stability of species results from the balance between pH and metal ion concentration. Ambiguity arises when calculating cation concentrations from a current density and subsequent charge as corrosion rates and cation valency varies. The impact on chemical stability and the ability of common corrosion products to effectively buffer solution and resist acidification and alkalinization motivates further research efforts.
Appendix – Extra Dissertational Work

# Mechanistic Insight into Al-Zn, Mg, and Al-Mg Rich Primer Design for Enhanced Cathodic Prevention on Sensitized Al-Mg Alloys

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<u>Keywords</u>: aluminum alloy, sacrificial protection, cathodic prevention, aluminum primer, hybrid Al-Mg primer, magnesium primer, x-ray diffraction, electrochemical impedance spectroscopy

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#### <u>Abstract</u>

Three Al-Zn, Mg, and Mg-Al rich primers (RP) were evaluated for their ability to suppress intergranular corrosion (IGC) and intergranular stress corrosion cracking (IG-SCC) on highly sensitized aluminum alloy 5456-H116 by sacrificial anode based cathodic prevention and chemical deposition effects. Tests were conducted in 0.6 M NaCl solution under full immersion. These evaluations considered the ability of the primer to attain an intermediate open circuit potential such that the galvanic couple potential with bare 5456 resided outside a range of potentials where IGC prevention is observed. The ability of the primer to achieve open circuit potential's negative enough so that the 5456-H116 could be protected by sacrificial anode based cathodic prevention and the ability to sustain this function over time were evaluated. The primers consisted of epoxy resins embedded with either (1) spherical Al-5 wt.% Zn, (2) spherical Al-5 wt.% Zn and spherical Mg, or (3) Mg flake pigments. A variety of electrochemical techniques evaluated the performance specified including open circuit potential, electrochemical impedance spectroscopy, diagnostic cycle testing, as well as zero resistance ammeter tests with simultaneous pH measurement. Electrochemical cycle testing demonstrated that Al-5%Zn did not activate or provide cathodic prevention. MgRP had a suitable open circuit potential for cathodic protection of 5456 but the time to primer activation as well as the activated potential both decreased upon utilization of Mg flake content in the primer. The pure Mg-rich primer activated quickly but ceased to achieve protective

potentials after 1-11 cycles of DC/AC/OCP cycle testing. Cross sectional analysis demonstrated that some flakes dissolved while uniform surface oxidation occurred on the remaining Mg flakes. which in combination led to impaired activation. The composite Mg plus Al-Zn rich primer mixed primer maintained a suitably negative open circuit potential over time, remained activated, dispensed high anodic charge, and remained an anode in zero resistance ammeter testing. Chemical stability modeling and zero resistance ammeter testing suggests that Mg corrosion elevates the pH which activates the Al-5wt.% Zn pigments, thereby providing a secondary pathway for sacrificial anode based cathodic protection which supports the long-lasting cathodic protection achieved by the Al-5 wt.% Zn/Mg primer. These analyses set a baseline for the consideration of Al-Zn/Mg-based coatings to establish effective cathodic protection on highly sensitized 5456-H116 in aggressive alternate immersion environment and illustrate the merit of using Al-MgRP.

#### **Introduction**

AA5xxx-series alloys are often used in marine structures due to their high strength-toweight ratio and general corrosion resistance <sup>1,2</sup>, and serve as an alternative to heavier steel components. However, these alloys have experienced in-service intergranular corrosion and stress corrosion cracking degradation due to their solid solution strengthening by a supersaturation of the Al- ( $\alpha$ ) matrix with 5 wt. % Mg. Following prolonged exposure to in-service temperatures as low as 40°C (313 K), the diffusion of this Mg content can lead to precipitation of the  $\beta$  phase (Al<sub>3</sub>Mg<sub>2</sub>) on the grain boundaries in a process termed sensitization <sup>3</sup>. The  $\beta$  phase is highly anodic to the matrix and may rapidly dissolve in aggressive (e.g. aqueous chloride) environments, enabling severe intergranular corrosion (IGC) <sup>4</sup> and intergranular stress corrosion cracking (IG-SCC) under sufficient applied load <sup>5,6</sup>. The extent of sensitization, or the intergranular  $\beta$  phase density, is typically quantified by the ASTM G-67 Nitric Acid Mass Loss Test (NAMLT) <sup>7</sup>. The NAMLT value is often considered as a rough proxy for IG-SCC susceptibility; specifically, materials are rated as resistant at NAMLT < 15 mg/cm<sup>2</sup>, intermediate at 15 – 25 mg/cm<sup>2</sup>, and susceptible at > 25 mg/cm<sup>2 4,7–9</sup>. Long-term, low temperature sensitization may achieve NAMLT values as high as 65-70 mg/cm<sup>2</sup>, which is considered here as highly sensitized material <sup>10,11</sup>.

Al-Mg alloys experience high susceptibility to IGC and IG-SCC at electrochemical potentials more positive than the  $\beta$  phase pitting potential (-0.95 volts versus saturated calomel

electrode ( $V_{SCE}$ ),  $E_{pit, \beta}$ ), with these corrosion mechanisms increasing in severity with proximity to the  $\alpha$  matrix pitting potential (-0.7 V<sub>SCE</sub>, E<sub>pit,  $\alpha$ </sub>) (and IG-SCC continues to increase in severity past  $E_{pit, \alpha}$ ) as measured in 0.6 M NaCl<sup>12-14</sup>. The IG-SCC behavior is hypothesized to be governed by a coupled anodic dissolution process (of the  $\beta$  phase and the  $\alpha$  matrix), which also catalyzes the formation of an aggressive acidified local crack tip chemistry that facilitates the enhanced generation of crack tip H and enables embrittlement in the fracture process zone <sup>12,15–19</sup>. Passivation of the  $\beta$  phase and the  $\alpha$  matrix suppresses the formation of this aggressive H-generating chemistry; this phenomenon explains the observed three orders of magnitude reduction in IG-SCC crack growth rate for fracture testing under cathodic polarization <sup>13,20</sup>. Therefore, the mitigation of both IGC and IG-SCC is possible through the establishment of potentials more negative than  $E_{pit, \beta}$ , which inspires mitigation strategies based on galvanic protection, such as through metal-rich primers, for use in marine service. This does not come without limitations as potentials more negative than -1.3 V<sub>SCE</sub> have been noticed to induce cathodic corrosion in Al-Mg alloys and increase hydrogen generation <sup>21</sup>. It has been shown in previous work that AA 5456-H116, tested in 0.6 M NaCl, experiences crack tip blunting and non-localized H-generation under these cathodic conditions reducing IG-SCC susceptibility <sup>22</sup>. In general, this is not desirable as susceptibility may be induced with fatigue loading <sup>21</sup>.

Specifically-designed metal-rich primers may achieve cathodic potentials in the low to intermediate susceptibility IGC/IG-SCC zones on 5xxx-series alloy surfaces <sup>13,14,20</sup>. Therefore, these coatings could provide an economic means of establishing effective long-term cathodic prevention in modern naval vehicles provided that protection can be sustained over long times. The establishment of such protection would reduce maintenance and improve service life by mitigating IGC and IG-SCC. However, there are key differences in cathodic protection performance when utilizing a metal rich primer (MRP) instead of a potentiostat (which is untenable on the scale of a naval vessel). An MRP must maintain galvanic coupling between exposed anodic pigment and the underlying substrate, while also achieving sufficient response to dynamic galvanic coupling conditions, such as the rapid increase in 5456 surface area during IGC/IG-SCC advance (unlike a potentiostat, the MRP is a finite sacrificial anode). A companion study evaluated organic and inorganic Zn-rich primers on highly sensitized 5456-H116 demonstrating a robust ability in this primer technology to achieve intermediate cathodic potentials despite the application of high

magnitude anodic current in 0.6 M NaCl<sup>14</sup>. A variety of other metal-rich primers have also been formulated for Al alloy protection however, such as Al- and Mg-based primers, and hybrid alloy pigment systems (such as Al-Zn-In and Zn-Mg)<sup>23–31</sup>. Magnesium rich primer has been reported that it can exceed the neutral salt spray and filiform resistance of chromate-based primers that depend on leachability of the chromate-based inhibitor, when all of the primers are top coated <sup>32</sup>.

Numerous Al-based primers are under development to achieve long-term cathodic protection on Al alloy substrates, but little published work exists pertaining to their overall performance in aggressive saline environments (and no literature exists in this area for 5456-H116) <sup>23,28,33</sup>. The close proximity of the open circuit potential (OCP) of these coatings to that of Al substrates (low  $\triangle OCP$ ) makes this technology a promising candidate for long-term cathodic protection, as long as the pure Al or alloyed pigments remain active (anodic) relative to the substrate. On the other end of the cathodic protection spectrum lie the Mg-based primers, which have been thoroughly researched and developed to offer cathodic protection on AA2xxx- and AA7xxx-series alloys  $^{25-27,31,34-38}$ . These coatings have a high  $\triangle OCP$  and offer a high level of cathodic protection, though due to this fact they are also susceptible to fast depletion (loss of Mg pigment through oxidation to the extent of cathodic (-) current output predominance from the coating) or pigment passivation <sup>25,31</sup>. To combat these depletion and passivation concerns, hybrid Mg-based coatings have been developed to modify the coating oxidation rate and further the useful service life of the coating <sup>24</sup>. However, neither pure Mg-rich primers, Al-rich primers, nor hybrid Al-Mg based primers have been evaluated in the literature for the cathodic protection of IGC on highly sensitized 5456-H116 in simulated marine service conditions.

The suppression of intergranular cracking and environmental fracture presents a more demanding objective than does the typical static protection of an underlying substrate surface against uniform corrosion. Thus, the objective of the present work will be to utilize a suite of test methods to evaluate primer OCP, activation and sacrificial anode based cathodic protection, as well as the longevity of galvanic current output and charge capacity. Sacrificial cathodic prevention is of interest where attaining the potential of the  $\beta$  phase is targeted as a strategy to suppress IGC and IGSCC. Moreover, consideration of secondary barrier effects and pH driven activation and chemical deposition processes are considered. Systematic evaluation of galvanic and secondary chemical substrate protection strategies afforded by three commercial Al/Mg-rich

primers on highly sensitized (NAMLT 65 mg/cm<sup>2</sup>) AA5456-H116 was performed in 0.6 M NaCl immersion. In addition, the process by which an Al-MgRP composite primer maintains superior performance via early Mg activation and delayed Al activation triggered by high pH in neutral NaCl. This sequence of events is proposed as a strategy for a long-lasting high capacity means of attaining cathodic prevention. These analyses will establish the strategies and methodologies for determining key coating qualities of Al / Mg – based primers to achieve effective, long-lasting cathodic protection for IGC / IG-SCC mitigation on Al-Mg naval alloys in aggressive marine service environments.

#### **Experimental Procedures**

#### Materials: 5456-H116 and Al/Mg-Rich Primers

A non-recrystallized 5456-H116 (UNS A95456) plate of 57 mm thickness was exposed in the susceptible S-T orientation; the microstructural character and composition are reported elsewhere <sup>17</sup>. Rectangular plates were excised, sensitized, cleaned, and dried following the specifications and procedure reported elsewhere <sup>14</sup>. As shown in **Table A-1**, two of these coatings are products of Randolph Coatings (Chicopee, Massachusetts), where the resin/pigment combination and designation for identifying each coating is: epoxy resin, 27 pigment volume percent (PVC) Al-5wt.% Zn pigment (AlRP (Epoxy,27%)), and epoxy resin, 28 PVC Al-5wt.% Zn pigment + 19 PVC Mg pigment (Al-MgRP (Epoxy,28%/19%). (**Table A-1**). These pigments embedded in the primers produced by Randolph Coatings are all roughly spherical. The third epoxy coating is a product of AkzoNobel (Waukegan, Illinois), and the resin/pigment (MgRP (Epoxy,26%)) (**Table A-1**). No pretreatments or organic topcoats were considered, and all coatings were tested as-received, with no added defects (such as scribes) to expose the underlying 5456-H116.

#### **Coating Characterization: Metal Pigment Capacity**

The candidate coatings were characterized through scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to assess the average pigment diameter (or width/length for flakes) and average primer thickness following the specifications outlined in companion work <sup>14</sup>. Mg-containing primer crystalline composition, pigment depletion, and corrosion product formation were analyzed using X-Ray Diffraction (XRD), which measured the intensity of Mg crystalline content before and after cycle testing <sup>14</sup>. X-Ray diffraction characterizes crystalline content to a resolution limit of 3-5% volume fraction, with a typical penetration depth of up to 150  $\mu$ m on Al, depending on 2 $\Theta$ <sup>39,40</sup>. A Cu-K $\alpha$  source (1.54 nm) was used on a PANalytical X'pert powder XRD with a 40-mA beam accelerated at 45 kV to perform continuous scans from 20° to 120° at a step size of 0.05°. Previous analyses on similar thickness Zn-rich primers demonstrated the continual presence of a major Al peak at approximately 44.5°, which proved that the entirety of each MRP was being sampled <sup>14</sup>. This finding applies here to the MgRP (Epoxy, 26%), and is loosely applied to the Al-MgRP (Epoxy, 28/19%) due to the potential interference by Al-5wt.% Zn pigment, which enabled normalization of Mg peak intensity to account for primer thickness effects. Al-5wt.% Zn pigment peaks could not be differentiated from the 5456-H116 substrate, and thus Al-rich pigment depletion was not evaluated.

## The DC/AC/OCP Accelerated Cycle Test: Depletion Life and Barrier Assessment of Al/Mg-Rich Primers

The candidate coating systems were evaluated under full immersion conditions in a controlled laboratory environment to assess electrochemical characteristics and performance as a sacrificial anode during cathodic prevention owing to the galvanic couple of the MRP to the 5456. Similar MRP systems have been tested using a variety of realistic exposure conditions on AA2xxx- and AA7xxx-series alloys, though no analyses have yet considered Al/Mg-based primers on AA5xxx-series substrates <sup>25,35,36,41</sup>. Therefore, these accelerated tests offer an experimental baseline. Electrochemical tests were conducted with a working electrode, saturated calomel reference electrode fitted with a luggin capillary, and a Pt counter electrode, all immersed in 0.6 M NaCl electrolyte in quiescent, ambiently aerated conditions. Electroce potential and current were controlled and monitored with an electrochemical impedance spectroscopy (EIS)-capable

potentiostat connected to a three-electrode electrochemical flat cell, as described in detail elsewhere <sup>25,41</sup>.

The accelerated DC/AC/OCP <sup>1</sup>cycle test method is a well-proven evaluation of the ability of a primer to provide sacrificial cathodic protection in the presence of a remote cathode (such as exposed 5456-H116 area at the site of a coating macrodefect <sup>25,31,42</sup>. However, no universal relationship has been established between the number of cycles in a DC/AC/OCP test and coating lifetime in the field. The cycle test consists of a cyclic repetition of OCP, Potentiostatic (PS, DC), and EIS (AC) (at OCP) in stages for various times to assess the sacrificial anode attributes of the coating (OCP) throughout the full immersion exposure after periods of primer oxidation (DC) (with the timing of each stage detailed in companion work <sup>14</sup>). Anode charge capacity as well as anode potential at various states of discharge were recorded throughout testing, as well as associated residual coating barrier characteristics. In the case of the MgRP (Epoxy, 26%), the cycle test consisted of 13 OCP/EIS(AC)/PS(DC) Hold cycles (Cycle A through Cycle M) on an intact, macro-defect free, primer-coated specimen, which together summed to 76 hours of exposure at -0.85 V<sub>SCE</sub>, and 20 hours at the primer OCP (the same procedure applied to Zn-rich primers in companion work <sup>14</sup>). Due to their variable activation time, similarly intact, macro-defect free, primer-coated AIRP (Epoxy, 27%) and AI-MgRP (Epoxy, 28/19%) specimens underwent extended cycle testing to evaluate performance more thoroughly. This extended testing procedure consisted of 19 OCP/EIS/PS Hold cycles (Cycle A through Cycle S), summing to 136 hours at -0.85 V<sub>SCE</sub> and 28 hours at the MRP OCP. DC/AC/OCP cycle testing was performed three times for each MRP for statistical analysis.

The OCP stages of cycle testing demonstrate the driving force for galvanic coupling between the MRP and the sensitized 5456-H116 relative to the pure anodic pigment OCP by measuring the potential of the MRP-coated 5456-H116 as the working electrode. Mixed potential theory dictates that the magnitude of the galvanic couple potential is affected by the capacity of

<sup>&</sup>lt;sup>1</sup> The accelerated DC/AC/OCP cycle testing carried out is different than the AC/DC/AC testing found in the literature conducted at North Dakota State University in which the cathodic DC step is held for a period of time and a relaxation step where the coating is allowed back to a stable open-circuit potential ( $E_{OC}$ ) [22]. This relaxation time is used as a metric to quantify transport of ions through a coating, dielectric relaxation of the coating, and charge transfer at the metal/coating interface. The DC hold in the DC/AC/OCP testing conducting in this study maintains a potential hold at the potential of the substrate and quantifies the current and charge a given coating can supply to the substrate.

the metal pigments as well as the exposed surface area ratio between the 5456-H116 and Al-5wt.%Zn / Mg  $^{43,44}$ . The subsequent EIS stage then assesses the barrier properties of the intact primer, which utilizes frequencies between 10<sup>5</sup> and 10<sup>-2</sup> Hz at 10 points per decade and an AC amplitude ranging from 60 to 100 mV. In the DC potentiostatic hold stage, a worst-case galvanic coupling scenario is simulated between the MRP and a large 5456-H116 area by applying -0.85 V<sub>SCE</sub>, which is the OCP of NAMLT 65 mg/cm<sup>2</sup> 5456-H116 in 0.6 M NaCl immersion.

#### **Galvanic Corrosion Testing**

The galvanic corrosion between the 5456-H116 substrate and the designated MRP was assessed through the use of a zero-resistance ammeter test (ZRA). During the test, a previously unexposed, hereafter referred to as a pristine, 5456 and MRP coated 5456 were coupled in a galvanic corrosion cell. The coupled currents and galvanic potential associated with the dissimilar electrodes were monitored by a Gamry 600 throughout a 24-hour exposure period in 0.6 M NaCl using natural aeration. The bare 5456 – H116 substrate simulating a scratch operated as the working electrode (WE) where the MRP coated alloy was connected as the counter electrode (CE). A saturated calomel electrode (SCE) was used as the reference electrode. Thus, a negative or cathodic current on the bare 5456 indicates electron flow entering the cathode in the galvanic couple. The distance between WE and CE was > 4 cm limiting chemical interactions in 0.6 M NaCl. The subsequent cathodic reaction on bare 5456 may induce a local pH change due to the electrochemical reactions accelerated or suppressed by galvanic coupling.

Two varying area ratios of bare 5456 to coated 5456 were used to simulate the effects of a drop of solution covering a scratch with a small adjacent area covered with coating and a mechanical defect (scribe) with large coated MRP and a small scribe area referred to as 1:1 or 15:1 (MRP: bare 5456 area ratio). The former represents an electrolyte drop near a mechanical defect site (scribe) as in atmospheric corrosion while the latter simulates a small scribe connected to a large surface area of MRP in full immersion. Simultaneous potential and current monitoring were combined with dual ISM micro-pH electrodes to monitor local solution pH fluctuations. The sensing probe was placed 5 mm from each reacting interface throughout the duration of the exposure. The tests conducted were triplicate to ensure the trends shown are characteristic. An electrochemical impedance spectrum was collected on the coated 5456 anode from 0.01 Hz to 100

kHz at 10 points per decade using an AC amplitude of 65 mV immediately before and after the end of galvanic exposure to assess the changes in barrier properties.

#### Characterization

The MRP-coated 5456-H116 cross-sections were characterized utilizing a Quanta 650 scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and PANalytical X'pert X-ray diffractometer for imaging, elemental analysis, and corrosion product identification under the specifications stated in companion work <sup>14</sup>.

#### **Results**

#### **Characterization of Coatings: Average Metal Pigment Size and Primer Thickness**

Baseline assessment utilizing EDS elemental mapping on MRP cross sections was performed to differentiate primer thickness and particle size at 1000x magnification. These are shown in **Table A-1** and **Figure A-1** for each MRP. The Al-Zn and Al-Zn/Mg-based primers contained spherical pigments, while the pure Mg-rich primer contained ellipsoidal flake pigments. The thickest primer was the Al-MgRP (Epoxy,28/19%) at  $51.16 \pm 8.74 \mu m$ , followed by MgRP (Epoxy,26%) ( $46.52 \pm 7.97 \mu m$ ), and finally AlRP (Epoxy,27%) ( $41.71 \pm 3.95 \mu m$ ) (**Table A-1**). The pigment size was largest in the MgRP (Epoxy,26%) (ellipse of length 24.46 ± 11.94 µm, width  $13.29 \pm 5.67 \mu m$ ), followed by AlRP (Epoxy,27%) (diameter of  $9.19 \pm 4.01 \mu m$ ), and lastly Al-MgRP (Epoxy,28/19%) (Al-5wt.% Zn of diameter  $8.64 \pm 3.78 \mu m$ , Mg of diameter  $8.16 \pm 3.70 \mu m$ ) (**Table A-1**). No deficiencies in primer adhesion to the 5456-H116 substrate were observed in these samples before or after cycle testing utilizing the -0.85 V<sub>SCE</sub> PS hold.

All Mg-based crystalline components within the primers were investigated through XRD analysis on the pristine and post-exposure primer samples. These analyses confirmed the presence of elemental Mg in the crystalline state in Al-MgRP (Epoxy,28/19%) and MgRP (Epoxy,26%). Despite the Al pigment being alloyed with 5 wt.% Zn, these pigment peaks overlapped with those of the 5456-H116 substrate so that the Al-rich pigment content could not be assessed. No oxidized

corrosion products were identified by XRD on these MRPs either before or after cycle testing through XRD.

## Global Galvanic Protection Potential, Charge and Residual Barrier Properties Afforded by MRP Throughout DC/AC/OCP Cycle Testing

The DC/AC/OCP cycle test interrogates the ability to supply anodic current at a fixed potential deemed desirable by mixed potential theory analysis to mimic a galvanic couple potential-enabled sacrificial-based anode cathodic protection. Subjecting the MRPs to 13/19 DC/AC/OCP hold stages at -0.85 V<sub>SCE</sub> for a total of 76 / 136 hours resulted in anodic pigment oxidation, the magnitude of which varied between primers. This potential simulates galvanic coupling between primer in intact coating and bare AA5456 at a scratch. The first step is to verify that the OCP of pigmented intact primer on 5456 is more negative than the bare 5456. Figure A-2 reports the potential of the intact MgRP (Epoxy, 26%), indicating the MRP-coated 5456-H116 global galvanic protection potential (OCP)<sup>2</sup>. Each MRP is considered activated at the point of the most negative established OCP during cycle testing. The primers are considered activated and indicated by a potential drop and then become more positive with respect to time and testing during the OCP stage of each cycle (cycles shown on bottom, A-M) as pigment is depleted by anodic dissolution or oxidized and partially depleted. The magnitude of the established global galvanic protection potentials (indicated as primer OCP in the Figure A-2 is shown comparatively with the pure Mg OCP in 0.6 M NaCl (-1.65 V<sub>SCE</sub>, dashed blue line) and with the bare 5456-H116 OCP (-0.85 V<sub>SCE</sub>, dotted red line). The magnitude and variance of established potentials as well as the MRP activation period are demonstrated in **Figure A-3** for each cycle. After each cycle of anodic polarization, the OCP assesses the ability of the remaining primer to serve as a sacrificial anode. This is indicated by an OCP more negative than bare 5456. Figure A-3 demonstrates that the MgRP (Epoxy, 26%) activates quickly by Cycle B (100 minutes of immersion in 0.6 M NaCl),

 $<sup>^2</sup>$  The open circuit potential corresponds to the point of equal anodic and cathodic reaction rates such that the total net current is zero. Thus, in a generalized case the OCP refers to a potential, in which the anodic and cathodic reactions occur on the same working electrode. However, the intact coating represents the galvanic coupling of anodic pigment and the buried 5456 substrate. The zero current condition is satisfied by anodic reactions on the sacrificial anode and cathodic reactions on the 5456, which also corresponds to an OCP value for the system; where necessary for this analysis, this OCP is technically a global galvanic protection potential. This is the most negative protection potential that could be achieved by the MRP when coupled to bare 5456.

however the achieved OCP quickly rises above the 5456-H116 OCP by the time Cycle H is reached such that cathodic protection is no longer provided and able to function as a sacrificial anode for protection of the 5456-H116 substrate. The AlRP (Epoxy,27%) reached an average stabilized OCP of -0.95 V<sub>SCE</sub> by Cycle K (3070 minutes of immersion in 0.6 M NaCl), and the Al-MgRP (Epoxy,28/19%) activated by Cycle H (1690 minutes of immersion in 0.6 M NaCl) to achieve an average stabilized OCP of -1.15 V<sub>SCE</sub> with high standard deviation only prior to becoming activated (**Figure A-3**).

**Figure A-4** demonstrates the cumulative charge output associated with Al-Zn / Mg oxidation for MgRP (Epoxy, 26%) (4a) and AlRP (Epoxy, 27%) (4b). These trends indicate the significant differences in the performance achieved by these primers. **Figure A-4c** summarizes the cumulative anodic charge output per cycle for each MRP, which indicates the "effective" anodic charge capacity provided by each MRP used to protect the 5456-H116 substrate during the cycle test. These data demonstrated that the MgRP (Epoxy, 26%) outputs the least anodic current overall, and this current output switched to cathodic current following Cycle I in the cycle test (**Figure A-4a**). The AlRP (Epoxy, 27%) provides the most anodic current on average following Cycle C (**Figure A-4b**, **A-74c**), and the Al-MgRP (Epoxy, 28/19%) achieved intermediate anodic current output following primer activation in Cycle H (**Figure A-4c**). The theoretical anodic charge capacity is defined as the quantity of charge an anodic pigment is capable of releasing. Note that this not only depends on the composition of the primer but the average primer thickness, the density of pigment, the primer particle pigment volume concentration, and the number of electrons transferred for each pigment type.

While the results in Figure 4 suggest that the AIRP may provide the greatest potential barrier properties for protection further tests are necessary to better elucidate the field performance of these primers. These significant differences in performance warrant further evaluation of the activation and passivation behavior of these MRPs. Assessment of the MRP OCP during cycle testing provides one metric of primer activation time and pigment depletion/passivation rate. However, these activation times are likely affected by the aggressive PS hold stages at -0.85  $V_{SCE}$  simulating coupling of the primer to bare AA 5456 and forcing anodic polarization.

#### Exposure of Primer at OCP and Forecasted Galvanic Couple Relationship with AA 5456

Considering the galvanic series in seawater, galvanic couple relationships can be predicted when the OCP of the intact primer (anode) is below the OCP or bare 5656 (cathode). **Figure A-5** illustrates the progression of the global galvanic protection potential (OCP) of intact primer when each is subjected to 24 hours' full immersion in 0.6 M NaCl, unperturbed with no cycle test. Similar to the cycle testing results (**Figure A-2, A-3**), the MgRP (Epoxy,40%) activates and achieves a potential of -1.6 V<sub>SCE</sub> and is repeatedly activated indicated by potential drops followed by potential increases. The overall potential gradually rises over time presumably as electrically connected pigment is used up (**Figure A-3**). These results also show that the MgRP (Epoxy,40%) global galvanic protection potential becomes more positive than the 5456-H116 OCP after 15 hours' immersion in 0.6 M NaCl. In contrast, the activation time and potential of Al-MgRP (Epoxy, 28/19%) as measured during both cycle test as well as long term OCP monitor are suitably negative after cycle G (**Figure A-3**) and this is underscored by the behavior during 16 hours at OCP (**Figure A-5**). The potential remains steady at about -1.15 V for the remainder of the exposure period. This potential meets the criteria of sacrificial cathodic prevention of 5456 maintaining potentials below  $E_{pit, \alpha} = -0.72 V_{SCE}$  and  $E_{pit, \beta} = -0.92 V_{SCE}$ .

Notably, the AlRP (Epoxy,27%) never reached potentials below the 5456-H116 OCP during the 24-hour OCP test. The forecasted inability of AlRP to provide potential suppression to the 5456-H116 after 24 hours suggests that a longer activation time may be necessary for AlRP (Epoxy,27%) otherwise it would be an ineffective primer for this alloy (**Figure A-5**). Evaluation of primer galvanic couple kinetic behavior may provide further evidence towards understanding these differences in MRP performance.

#### Substrate - Primer Galvanic Coupled Potential and Current Densities

The galvanic couple behavior of an intact coating and bare 5456 was revisited with a ZRA test. The long-term OCP of the MgRP reaches the lowest potential in the MRPs tested of -1.6 V<sub>SCE</sub>. It then rises approaching  $E_{OCP}^{5456}$ , -0.85 V<sub>SCE</sub> shown in **Figure A-6a**. The MgRP - 5456 galvanically coupled potential,  $E_{gal}^{MgRP-5456}$ , achieves more negative potentials than  $E_{OCP}^{5456}$  throughout the duration of the galvanic coupling. Both 1:1 and 15:1 ratios were tested, shown in **Figure A-6c**. The MgRP shows a steep activation period during which the Mg pigment rapidly reacts, leading

to a spontaneous increase in galvanic current (**Figure A-6b**). The large spikes of anodic current density subside and quickly decay with the maximum cathodic galvanic current of -1.5  $\mu$ A/cm<sup>2</sup> that slowly decreases to <-500 nA/cm<sup>2</sup> throughout the duration of the exposure. The MgRP at 15:1 area ratio does show a slight increased cathodic current output. However, the galvanic couple decays to <500 nA/cm<sup>2</sup> current similarly to the 1:1 couple. A comparison between each MRP charge output throughout galvanic coupling can be seen in **Figure A-7** with AlRP producing an ever-increasing cathodic charge, MgRP providing some cumulative anodic charge output, and the Al-MgRP producing an ever-increasing anodic charge output. The MgRP exhibits local pH change to 8.5 and 9.5 locally over the CE (MRP) in the 1:1 and 15:1 area ratio, respectively, shown in **Figure A-8**. The dominant cathodic reactions increase alkalinity over AA 5456-H116 in the 15:1 simulated scribe due to the consumption of protons and hydroxyl production. The MgRP does not show any discernible pH modification relative to the bare 5456 WE during the 1:1 coupling. The maximum pH obtained over the 5456 WE are 9.1 in the case of the 15:1 area ratio. The MgRP coating provides anodic charge densities of  $0.01^{\text{C}}/_{\text{cm}^2}$  (**Figure A-7**).

The Al-5wt% Zn does not suppress galvanically coupled potential below the open circuit potential of the 5456 substrate as seen in **Figure A-6a**. Therefore, the AIRP does not function as a sacrificial anode during full immersion in 0.6 M NaCl at natural aeration conditions which was also indicated above (**Figure A-5**). The galvanic couple potential is not more negative than -0.85  $V_{SCE}$  and the galvanic current is positive indicating that the MRP is the cathode, and the bare 5456 alloy is the anode or the substrate is protecting the Al pigment. The AIRP – 5456 1:1 galvanic couple results in +1  $\mu$ A/cm<sup>2</sup> that decays to <500 nA/cm<sup>2</sup> while the 15:1 shows a continual increase in coupled current near +1.2  $\mu$ A/cm<sup>2</sup>. This galvanic relationship is not favorable for the protection of bare 5456. This is further reinforced by **Figure A-7** which reports accumulated cathodic charge of 0.07  $C/_{cm^2}$ . Moreover, since the AIRP does not function as a sacrificial anode, it stands to reason that there is no pH change at either CE:WE ratio shown in **Figure A-8**.

The Al-MgRP sustains the lowest long-term open circuit potential at -1.1 V<sub>SCE</sub> well below the  $E_{OCP}^{5456}$  (**Figure A-6a**) and for extended time. The composite Al-MgRP coating in both 1:1 and 15:1 area ratio exhibits trends that are different from the observed trends of either of the individual material systems. The Al-MgRP - 5456 coupled potential achieved values of -1.0 V<sub>SCE</sub> and -1.05 V<sub>SCE</sub> for both 1:1 and 15:1 area ratio, respectively, show in **Figure A-6c**. This potential meets the criteria of sacrificial cathodic prevention of 5456 below  $E_{pit, \alpha} = -0.72 V_{SCE}$  and  $E_{pit, \beta} = -0.92 V_{SCE}$ .

The Al-MgRP in the 1:1 scenario achieves a maximum cathodic current output of  $-1.6 \,\mu\text{A/cm}^2$  that was sustained throughout the remainder of the galvanic couple. The 15:1 exposure shows a gradually increasing cathodic current throughout the entirety of the galvanic coupling, seen in **Figure A-6b**, ultimately reaching values of  $-4.5 \,\mu\text{A/cm}^2$ . The Al-MgRP exhibits similar behavior to the MgRP in that over the MRP in both 1:1 and 15:1 area ratio the Al-MgRP becomes increasingly alkaline and shows similar trends in the 15:1 area ratio. The Al-MgRP does not show any discernible pH modification over the 5456 WE in the 1:1 area ratio scenario. The maximum pH obtained throughout the 15:1 exposure is approximately 8.5 over both the MRP and bare 5456 alloy in **Figure A-8**. The composite Al-MgRP is the only primer that shows a continuous increase in the cathodic current throughout the duration of the ZRA experiment reaching a value of  $-4.5 \,\mu\text{A/cm}^2$  (**Figure A-6b**). The increased coupled current output of Al-MgRP results in the greatest cumulative charge density, as seen in **Figure A-2**, of 0.15  $\text{C/}_{cm^2}$  and therefore the greatest utilization of pigment for any MRP tested herein.

#### **Remaining Coating Barrier Properties Throughout the Electrochemical Cycle Testing**

Al/Mg-rich primer barrier properties were assessed via PS EIS (at the primer OCP) intermittently throughout cycle testing to monitor impedance and coating defect area progression with increasing exposure time. The cycle test as well as long term OCP exposure can provide opportunities to use EIS to examine residual primer barrier properties after some pigment depletion. **Figure A-9** shows the Bode Magnitude impedance response for each intact MRP as well as for epoxy-coated 5456-H116 (Cycles A-M or A-S). Directional trends in MRP impedance are illustrated on these plots by arrows correlated to the most relevant testing cycles (A-M or A-S). Previous EIS analyses on metal-rich coatings have concluded that assessment of coating impedance at the lowest measured frequency (0.01 Hz here) accurately represents overall conductive/resistive properties of the coating with time of exposure  $^{25,31,37,38,41,45}$ . These trends are illustrated in terms of the average low frequency impedance modulus (Z<sub>0.01 Hz</sub>) and standard deviation in **Figure A-10**. This analysis demonstrates the average primary (upon initial exposure)

and secondary (upon recovery following activation) primer impedance/barrier properties as well as performance variations during cycle testing. Specifically, the primary AIRP (Epoxy, 27%) impedance was the lowest of these MRPs, and  $Z_{0.01 \text{ Hz}}$  decreased half an order of magnitude from Cycle A  $(2x10^5 \ \Omega \cdot cm^2)$  to Cycle S  $(7x10^4 \ \Omega \cdot cm^2)$  which is the lowest impedance secondary barrier (Figure A-10). The Al-MgRP (Epoxy, 28/19%) achieved the highest primary impedance in Cycle A  $(2x10^6 \,\Omega \cdot cm^2)$ , which decreased nearly two orders of magnitude by Cycle K  $(6x10^4 \,\Omega \cdot$ cm<sup>2</sup>) before recovering half an order of magnitude by Cycle S ( $1x10^5 \Omega \cdot cm^2$ ) (Figure A-10). The MgRP (Epoxy, 26%) achieved the second highest primary impedance in Cycle A ( $2x10^6 \Omega$  · cm<sup>2</sup>) before decreasing an order of magnitude in impedance by Cycle D ( $3x10^5 \Omega \cdot cm^2$ ) during activation. Following this period, the MgRP (Epoxy, 26%) Z<sub>0.01 Hz</sub> recovered by half an order of magnitude by Cycle M ( $1 \times 10^6 \ \Omega \cdot cm^2$ ) to achieve the highest impedance secondary barrier (Figure A-10). Figure A-11 illustrates the Bode Phase Angle progression for each cycle throughout the cycle testing exposure in 0.6 M NaCl. These data are useful for the determination of defect area through use of methods such as the breakpoint frequency or saddle point frequency <sup>31,46–50</sup>. However, the lack of consistent presence of these points in the present dataset challenged the use of these data for porosity evaluation purposes.<sup>3</sup>

#### **Barrier Properties During Galvanic Coupling**

The electrochemical impedance, as shown in **Figure A-12**, evaluated the residual barrier properties of the intact primer for each coating system both before and after the galvanic couple exposure. The impedance modulus at  $Z_{0.01 \text{ Hz}}$  (**Figure A-12**) for MgRP, Al-MgRP, and AlRP was  $2.5 \times 10^6$ ,  $1 \times 10^6$ , and  $4.3 \times 10^4 \Omega \cdot \text{cm}^2$ , respectively, before exposure. The impedance modulus  $Z_{0.01 \text{ Hz}}$  after the exposure for MgRP, Al-MgRP, and AlRP dropped to  $3.3 \times 10^4$ ,  $7.27 \times 10^3$ , and  $6.18 \times 10^5 \Omega \cdot \text{cm}^2$ , respectively. Hence, there is considerable decrease in impedance in the case of MgRP and Al-MgRP. The Al 5wt% Zn primer passivates consistent with the  $Z_{0.01 \text{ Hz}}$  rise to  $6.18 \times 10^5 \Omega \cdot \text{cm}^2$ . This supports the notion that the AlRP pigment passivated

<sup>&</sup>lt;sup>3</sup> In cycle testing primer depletion by oxidation may leave behind porosity in the epoxy resin in the form of cavities where pigment once resided as well as produce other defects from corrosion product wedging and gas evolution.

and does not corrode away and hence does not increase coating porosity reflected by low impedance. The MgRP and Al-MgRP after galvanic coupling both contain a saddle point between 1 - 10 Hz suggestive of defect formation and growth bringing about the greatest decrease in low frequency modulus behavior (**Figure A-12**)<sup>46</sup>.

#### **Coating Depletion and Corrosion Product Identification**

Prior to and after cycle testing was completed on each MRP, XRD analysis identified the composition and relative intensity of the crystalline phase seen in each primer. No crystalline corrosion products containing  $OH^-$ ,  $O^{2-}$  or  $CO_3^{2-}$  were detected in the XRD spectra, suggesting that any such products were either amorphous or occurred at volume percentages lower than 3-5%. The depletion of Mg pigment was assessed through comparison of XRD Mg peak intensities following normalization to the highest Al peak at approximately 44.5°, which originates from the 5456-H116 substrate and therefore should not be affected by Mg pigment depletion. In the Al-MgRP (Epoxy, 28/19%), the overlap of the 5456-H116 and Al-5wt.% Zn peaks led to uncertainly in the 44.5° peak; however, the lack of significant variance in these peak intensities in pre- and postcycle testing analysis suggested that either (1) negligible Al-5wt.% Zn depletion occurred or (2) the 5456-H116 contributed more strongly to the peak intensity at 44.5°. This consistency validated the use of this normalization method on the Al-MgRP (Epoxy, 28/19%) to evaluate oxidation in the spherical Mg pigment. However, depletion of the Al-5wt.% Zn pigments was not detected. Depletion analysis considered the cycle test in which the maximum experimental anodic charge output was achieved for each MRP (Table A-2). Specifically, the Al-MgRP (Epoxy, 28/19%) experienced the greatest Mg depletion at 52%, followed by the MgRP (Epoxy, 26%) at 10% Mg depletion. To more effectively evaluate the depletion life of each primer, anodic charge capacity must also be assessed.

The theoretical anodic charge capacity of each MRP, reported in **Table A-2**, was assessed based on average primer thickness (**Table A-1**), the density of Mg / Al-5wt.%Zn (**Table A-3**), the primer pigment volume concentration (PVC, **Table A-1**), the exchange of two electrons necessary for Zn or Mg oxidation ( $Zn^{2+}$  / Mg<sup>2+</sup>) and/or the exchange of three electrons necessary for Al oxidation (Al<sup>3+</sup>). For comparison, the maximum total anodic current output exhibited by each MRP during cycle testing was computed by summing the anodic current output from each stage of PS

hold at -0.85 V<sub>SCE</sub> (**Table A-2**). The theoretical anodic charge (Q) output analysis demonstrated that AIRP (Epoxy,27%) has the highest theoretical anodic Q capacity at 32.2 C/cm<sup>2</sup>, followed by Al-MgRP (Epoxy,28/19%) at 27.2 C/cm<sup>2</sup> and MgRP (Epoxy,26%) at 16.7 C/cm<sup>2</sup> (**Table A-2**). The maximum experimental anodic Q output for each based on three series of cycle testing demonstrated that the AIRP (Epoxy,27%) achieved the highest anodic Q output (0.7 C/cm<sup>2</sup>), followed by Al-MgRP (Epoxy,28/19%) (0.2 C/cm<sup>2</sup>) and MgRP (Epoxy,26%) (0.1 C/cm<sup>2</sup>). The fraction of experimental to theoretical anodic charge output demonstrated anodic charge usage (ACU) of 2.1% for AIRP (Epoxy,27%), 1.6% for Al-MgRP (Epoxy,28/19%), and 0.2% for MgRP (Epoxy,26%), as shown in **Table A-2**. Therefore, these primers have considerable protective capacity remaining following the cycle test, indicating that a considerable reservoir of Al-Zn / Mg remains available for local galvanic protection should a defect develop proximate to buried pigment.

The remaining anodic charge capacity in these MRPs suggests that OCP increase during cycle testing (**Figure A-5**) is occurring mostly due to passivation rather than substantial pigment loss, which is supported by the Backscatter Electron (BSE) micrographs taken on post-cycle testing MRP specimens shown in **Figure A-13**. As shown in **Figure A-14**, surface imaging of each primer before and after cycle testing illustrates little corrosion product formation, with only local events being noticeable on Mg pigments but no product visible on Al-5wt.% Zn pigments. In the case of the AlRP (Epoxy,27%), there is no noticeable difference between the Al-5wt.% Zn pigments in the pristine and post-cycle testing cross sections. In the Al-MgRP (Epoxy,28/19%), oxidation is apparent in Mg pigments as indicated by O EDS signal through the entire thickness of the primer following the cycle test (**Figure A-15**). The MgRP (Epoxy,26%) shows Mg pigment oxidation on the very surface of the primer, which is visible as a transition in pigment brightness with proximity to the topmost primer surface, but the embedded Mg pigments in the epoxy resin are relatively unperturbed.

#### **Discussion**

The characterization of the cathodic protection performance of these three candidate MRPs through laboratory accelerated cycle testing and natural exposure demonstrated the different anodic pigment behaviors quantified electrochemically with greater fidelity than field or lab cabinet exposure allow. However, the environment and cyclic nature of the environment may differ between lab and field. Despite this forensic analysis yielded similar results in lab and field testing in previous studies on MgRP<sup>31</sup>. In other words, discrepancies were not observed which may be utilized to inform future coating design. These results must be evaluated in more detail including field testing in order to understand MRP design parameters necessary for optimized cathodic protection on Al-Mg alloys. In this study, parameters such as theoretical coating anodic charge capacity and ACU, anodic pigment corrosion mechanism, as well as secondary barrier formation were systematically assessed. It is worth noting that no single test provides all the information needed to evaluate each primer. Further discussion is warranted.

# Anodic Charge Usage and Relative Porosity/Secondary Barrier Formation Effects with Time of Exposure

Due to the differences in pigment choice and activation time, the theoretical anodic Q capacity of each MRP (**Table A-1**) correlates with the ACU (**Table A-3**), but these metrics do not translate to the sacrificial cathodic protection of each MRP in terms of an achieved primer OCP below that of 5456. For example, the AlRP (Epoxy,27%) has the highest theoretical anodic Q capacity at 32.22 C/cm<sup>2</sup> (**Table A-2**) and the highest achieved ACU at 2.06% (**Table A-3**). However, the most negative OCP achieved by the AlRP (Epoxy,27%) in Cycle S was -0.99 V<sub>SCE</sub> compared to -0.85 V<sub>SCE</sub> throughout the long term OCP exposure which is not sufficient to protect 5456. The Al-MgRP (Epoxy,28/19%) achieved 2/3 the ACU compared to AlRP yet maintained an OCP as negative as -1.17 V<sub>SCE</sub> in Cycle S (**Table A-2**). The low anodic Q requirement for the establishment of negative cathodic protection potential via Mg oxidation is encouraging, though passivation and porosity are factors that must be evaluated further.

The AIRP, unlike either MgRP or Al-MgRP, was not capable of performing as a sacrificial anode as the OCP (**Figure A-6a**) and galvanically coupled potential (**Figure A-6b**) both rest at the corrosion potential of AA5456. The AIRP is not capable of providing a cathodic shift in potential in either galvanic coupling scenario. The AIRP was the only MRP to perform as a cathode throughout galvanic coupling monitored by ZRA (**Figure A-6b**). This can also be seen in **Figure A-7** as the cumulative charge density is increasingly cathodic. The oxidation of AIRP after cycle testing is shown in **Figure A-13** reveals an un-perturbed coating cross-section which does not

appear to experience significant oxidation like the Al-MgRP. There is no beneficial galvanic coupling of AlRP to AA5456.

The significant differences in the cathodic protection performance of these MRPs may be further understood by considering the influence of corrosion product formation. In the case of the MgRP (Epoxy, 26%), the stark difference between the theoretical anodic Q capacity (16.7 C/cm<sup>2</sup>) and the maximum ACU (0.1 C/cm<sup>2</sup>) suggests that the Mg flake pigments may be kinetically hindered when buried in coating by corrosion product formation or sufficiently oxidized such that buried Mg pigment is not exposed in 0.6 M NaCl. In the post cycle testing MgRP (Epoxy, 26%), there is little evidence of Mg pigment dissolution below the uppermost MRP surface, where dense corrosion product is present (Figure A-13). This cross section demonstrates relatively uniform Mg surface corrosion, which may be slowed as the densification of corrosion product strengthens the secondary barrier properties of MgRP (Epoxy, 26%) (Figure A-13). This may also explain the intense early galvanically coupled current density that proceeds to diminish to <500 nA/cm<sup>2</sup> after 6 hours in both 1:1 and 15:1 scenarios (Figure A-6b). This is also witnessed in the low cumulative charge transfer of MgRP throughout galvanic coupling shown in **Figure A-7**. The decay of current witnessed throughout galvanic coupling may be a result of (1) the partial oxidation of Mg pigment and (2) formation of corrosion product that may hinder the utilization of the MgRP. This conclusion would be in agreement with prior findings concerning corrosion product densification in Zn-Mg coatings on steel <sup>51</sup>, and would explain the rapid reduction in the galvanic protection achieved by the MgRP (Epoxy, 26%) when the majority of the Mg pigment remains non-oxidized (Table A-2).

In contrast, the Mg pigments were partially or fully oxidized through the entire thickness of the Al-MgRP (Epoxy,28/19%) by the end of cycle testing (**Figure A-13**). This oxidation was evaluated through EDS, as shown in **Figure A-15**. When examining the oxygen signal (**Figure A-15c**) and the Mg signal (**Figure A-15b**), the considerable oxidation of the Mg pigment is evident through the primer thickness. The partially oxidized, roughly spherical Mg pigments within the composite Al-MgRP (Epoxy,28/19%) are far removed from the uppermost surface of the primer as well (while all of the corrosion product on MgRP(Epoxy,26%) had precipitated on the uppermost surface). This enhanced oxidation of Al-MgRP may explain the increase in coating utilization throughout galvanic couple testing shown in **Figure A-6b**. The Al-MgRP witnesses an

ever-increasing cathodic current while providing the most negative and stable galvanically coupled potential. This is also witnessed in the cumulative charge density shown in **Figure A-7** as Al-MgRP shows the greatest utilization of each MRP. The differences in pigment oxidation as a result of primer composition warrant a further investigation into expanding electrochemical testing and characterization of MRPs and their performance.

#### Complementary Mg and Al Oxidation in Hybrid Al/Mg-Rich Primer Systems

The corrosion products formed in an Al/Zn/Mg system have complex relationships that are not entirely understood, however there is good agreement that a dominance of Mg corrosion product may form a dense layer that promotes passivity of the sacrificial zinc (in agreement with the cycle testing results observed here for MgRP (Epoxy, 26%) <sup>52,53</sup>. Al/Zn hybrid coatings have been utilized on carbon steel substrates for decades due to two main complementary attributes: the galvanic couple potential is a beneficial balance between the OCP values of Zn and Al, and the Zn content selectively dissolves to form corrosion products argued to slow Al oxidation <sup>54–56</sup>. When Mg is added to an Al-Zn system, experimental results have demonstrated two additional benefits: (1) the Mg dissolution stabilizes insoluble Zn corrosion products, and (2) the increased oxidation of Al reduces the corrosion rate of the Mg <sup>53,57</sup>. A spherical pigment geometry may also serve to increase coating porosity and water permittivity in comparison to the dense packing and blocking effect caused by the flake morphology, as has been experimentally observed in Zn-rich primers <sup>58</sup>. This blocking effect was observed in the post cycle testing MgRP (flaked Mg) coating wherein the buried pigment below the uppermost surface is unreacted ultimately hindering the utilization of the coating system (Figure A-13). One other effect that may be significant for the Al-MgRP (Epoxy, 28/19%) performance is the local pH brought about by Mg oxidation in an Al/Zn/Mg system that may then affect Al dissolution, as understood through the use of a chemical stability diagram for Al/Mg in Figure A-16. The literature suggests that a chemical mechanism may also support the effective performance of the Al-MgRP (Epoxy, 28/19%), which may be evaluated via chemical stability modeling <sup>59</sup>. This thermodynamic analysis, which is based on solubility predictions will be used herein to help explain the beneficial combination of Al and Mg <sup>59,60</sup>.

# Electrochemical behavior of MRP – 5456-H116 galvanic coupling explaining the Mg-Al synergy

The galvanic coupled potential of the MRP (MgRP, AlRP, or Mg-AlRP) coated AA 5456-H116 to bare 5456 substrate reveals how much shift in galvanic couple potential from the OCP of the bare 5456 a given MRP is capable of providing (**Figure A-6b**). The MgRP and Al-MgRP are the only primers in this study to both maintain a coupled potential below the global OCP of the underlying 5456 substrates and supply electrons to protect bare 5456 (**Figure A-6b**). In contrast, the AlRP coupled potential ultimately increases to the potential of the substrate (**Figure A-6c**).

Three findings must be explained. They are (a) passivation of AIRP yet (b) activation of Al in Al-MgRP instead of passivation and (c) hydroxide formation on the surface of the remaining Mg pigment retained in the unconsumed pigment. These can all be explained with mixed potential theory and the corrosion thermodynamics of the governing electrochemical and chemical reactions. This analysis requires that pH be taken into consideration. Consider the MgRP during corrosion of Mg below pH 11 for which reactions 1 - 4 are operative. Mg is unstable in water and spontaneously corrodes with water reduction resulting in H<sub>2</sub> evolution (reactions 1-2) and overall reaction 3. The pH rises due to the production of hydroxyl ions seen in reaction 1 which raises the local pH to an equilibrium pH 10.4 established by the equilibrium pH of reaction 4.

$$2H_20 + 2e^- \rightarrow H_2 + 20H^-$$
 1

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \text{ (overall)}$$
3

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2OH^-$$
 4

The MgRP in the 1:1 area ratio initially responds by supplying a strong anodic current from the oxidation reaction of  $Mg^0$  to  $Mg^{2+}$  (reaction 2). The reaction is non-polarizable, so the potential is very negative and close to the Nernst potential associated with reaction 2. The current quickly decays limiting the utilization of all Mg pigment (**Figure A-6b**). The region separating the chemical reaction between  $Mg^{2+}$  and  $Mg(OH)_2$  is defined by the equilibrium of reaction 4. For an  $Mg^{2+}$  concentration of  $10^0 - 10^{-6}$  M the equilibrium pH for reaction 4 will vary between 8.4 and  $11.6^{-58}$ . This allows for the assessment of ion concentration within the aqueous electrolyte by

measuring the pH near the reacting electrode surface. The 1:1 and 15:1 area ratio reached a peak pH of 9.9 and 11.4 corresponding to a  $Mg^{2+}$  concentration in the electrolyte of  $10^{-3}$  and  $10^{-5}$  M, respectively (**Figure A-8**). The 1:1 area ratio attained a pH of 9 over the coating after 24-hour galvanic coupling to bare 5456 substrate indicating an  $Mg^{2+}$  concentration of  $10^{-1}$  M at equilibrium with  $Mg(OH)_2$ . The 15:1 area ratio reached a pH of 9.5 over the coating after 24-hour galvanic couple on the bare 5456 substrates indicating a required  $Mg^{2+}$  concentration of  $10^{-2}$  M to support the formation of partially protective  $Mg(OH)_2$ . This supports the observations that once the pigment starts corroding the  $Mg(OH)_2$  forms on the pigment particles and the reaction slows although easily disrupted by Cl<sup>- 57</sup>. However, the sequence of reactions 1-4 describes spontaneous corrosion of the Mg pigment yielding aggressive self-corrosion of magnesium systems in the presence of water and NaCl<sup>51</sup>.

There was no pH change seen at the bare 5456 during the galvanic coupling with MgRP coated 5456 ZRA experiment for the 1:1 area ratio. The 15:1 area ratio is seen to increase to a pH of 9 near the bare 5456 after 15-hour galvanic couple in full immersion 0.6 M NaCl (**Figure A-8**). The large 15:1 area ratio witnesses more severe activation as the increased surface area exposes a greater quantity of Mg pigment to electrolyte. The increased dissolution of Mg to Mg<sup>2+</sup> in the 15:1 area ratio may be responsible for the chemical protection effect over the bare 5456 WE where Mg(OH)<sub>2</sub> formation is possible (**Figure A-16**). Using the current throughout the galvanic couple, the concentration of Mg<sup>2+</sup> is estimated to be  $4.4 \times 10^{-8}$  M according to the chemical stability diagram in **Figure A-16**.

Here it is constructive to consider the AlRP. Pure Al starting at pH 6 in NaCl solution is passive at  $10^{-6}$  M Al<sup>3+</sup> with a minimum equilibrium solubility at pH 4.7, as shown in **Figure A-16**. The Al spontaneously passivates by  $\frac{1}{2}$  cell reactions 5 and 6 to form Al(OH)<sub>3</sub> / Al<sub>2</sub>O<sub>3</sub> and becomes fairly polarizable. This is seen in the galvanically coupled potential as the AlRP\_polarizes to the potential of the 5456 substrate.

$$3H_2O + 2e^- \rightarrow 3H_{ads} + 3OH^-$$

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3e^- + 3H^+$$

$$6$$

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \text{ (overall 5 and 6)}$$

$$7$$

310

$$Al^{3+} + 2H_20 \leftrightarrow AlO_2^- + 4H^+$$

$$Al(OH)_3 \leftrightarrow AlO_2^- + H^+ + H_20$$
9

The equilibrium chemical stability of  $AlO_2^-$  with  $Al(OH)_3 / Al_2O_3$  is governed by equation 9. For a concentration of  $10^{-6}$  M,  $AlO_2^-$  is stable at pH 8 and above. The measured pH over the AlRP throughout the duration of the galvanic couple remains at 6.0 - 6.5, well within the thermodynamic stability region of  $Al(OH)_3 / Al_2O_3$ . The 15:1 area ratio maintaining increased levels of cathodic coupled current density indicates the Al based MRP is not operating as a sacrificial anode. It should be noted that  $Al^{3+}$  cation buildup in solution has been noted to accelerate HER on Al alloys [24] which accelerates self-corrosion. This is another disadvantage of an Al primer.

The stability of  $Zn(OH)_2$  at pH 6 is also pertinent given the Al pigment composition. It is passive at a 1 M  $Zn^{2+}$  with a minimum solubility at pH 5.6 <sup>58</sup>. Thus, Zn may spontaneously passivate to  $Zn(OH)_2$  and become polarizable. The polarizability of the passivated Al-5wt% Zn pigment translates into an OCP above the formation potential of Al and Zn hydroxides and below the reversible water reaction (**Figure A-6c**). The Al-Zn pigment will be passive at the pH indicated in ZRA experiments. This disables the ability of the Al-Zn pigment to support cathodic protection by shifting the coupled potential to somewhere in between the OCP of the 5456 substrate and the more positive Al-Zn OCP in full immersion 0.6 M NaCl.

The Al-MgRP exhibits optimal behavior responding with an anodic coupled current density and a suitable galvanic couple potential to protect 5456 providing greater utilization (**Figure A-6b**). The Al-MgRP responds with the largest coupled anodic current density in the 1:1 scenario and persists throughout the galvanic coupling exposure (**Figure A-6c**). In this case, 5456-H116 is protected. The 15:1 scenario exhibits an increasing anodic current throughout the entirety of the galvanic coupling to the bare AA 5456-H116 substrate. The Al-MgRP is distinct in that both the galvanic couple potential is maintained below the global OCP of the 5456 and the galvanic coupled current of Al-MgRP coated AA 5456-H116 with bare AA 5456-H116 exhibits persistent anodic current densities. The Al-MgRP does not polarize to the corrosion potential of the 5456-substrate, maintaining 150 mV of suppression of the 5456  $E_{ocp}$  throughout the galvanic coupling (**Figure A-6c**).

Thus, Mg may form Mg(OH)<sub>2</sub> while Al is activated by the high pH (**Figure A-16**). This could explain how Al is activated to oxidize to  $AlO_2^{-}$  Chemical stability modeling suggests that Mg oxidation and resulting pH rise to 8.5 thermodynamically activates the Al-5wt% Zn pigments (**Figure A-16**). The production of hydroxyl ion as reaction by-products of Mg oxidation changes the electrolyte to pH 8.5 during the galvanic couple. The Mg-Al pigment oxidation was observed to shift the pH to 8.5 over the MRP for both area ratios which requires a very high concentration of  $10^{-3}$  M for Al<sup>3+</sup> and  $10^{-2}$  for Mg<sup>2+</sup> for Al(OH)<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and Mg(OH)<sub>2</sub> to remain stable respectively. This pH change renders the Al-Zn pigment susceptible to active dissolution as the dissolution trajectory is forced outside of passive Al(OH)<sub>3</sub> stability region. Once this pH is achieved, Al is expected to oxidize to AlO<sub>2</sub><sup>-</sup> according to reaction 8 providing a second pathway to support the long-lasting cathodic protection achieved by the Al-5wt% Zn / Mg composite primer.

The corrosion of Mg pigment in the presence of Al-Zn pigment shows 1) increased anodic current output 2) stable coupled potential during the galvanic coupling experiment and 3) stable pH change over the coated area. Quiescent 0.6 M NaCl is seen to have a pH of 5.5-6 during the start of galvanic coupling supporting the formation of  $Al(OH)_3$  or  $Al_2O_3$  which is stable with low concentration. However, Mg corrodes spontaneously as shown by reaction 2. Then the rise in pH is observed in **Figure A-8** by the corrosion of Mg to form Mg(OH)<sub>2</sub> which occurs shortly after the galvanic couple begins and reaches a stable intermediate pH of 8.5. The pH increase over the Al-MgRP shows how the presence of Al-Zn pigment serves as an MRP that can turn on after the corrosion of Mg pigment raises the pH. This pH rise shifts the oxidation predominance to Al and Zn pigment as the formation of Mg(OH)<sub>2</sub> slows Mg<sup>2+</sup> release as the pH increases to an equilibrium point. Near pH 6 the favored product remains  $Al(OH)_3/Al_2O_3$  which polarizes the MRP to the potential of the 5456 substrate. The pH rises due to the activation of Mg pigment. This shows the interplay between metal composite coating systems and the observations provide evidence to the secondary mechanism available to metal composite coating systems.

#### **Conclusions**

Metal-rich primer-based cathodic protection may increase Al-Mg service life in marine conditions by achieving intermediate cathodic potentials to mitigate IGC and IG-SCC. In order to mitigate IG-SCC the MRP must achieve an intermediate cathodic potential. The present work

utilized a newly developed combination of experimental methods to evaluate these performance attributes in three Al/Mg-based primers, which established the following conclusions. There is limited viable use of Al-5wt% Zn for the cathodic protection of AA 5456-H116 as **1**) the AlRP does not suppress galvanically coupled potential below the open circuit potential of AA 5456, and **2**) the positive galvanically coupled current density indicates the AA 5456 is acting as an anode and the AlRP is cathode at least in NaCl solution. The use of Mg flake pigment in epoxy-based MRP causes susceptibility to rapid activation and oxidation of pigment followed by cessation of cathodic protection and inhibition of MRP utilization on AA 5456 in 0.6 M NaCl due to the formation of corrosion products on Mg particles. The MgRP was capable of maintaining cathodic polarization of 100mV below the open circuit potential of AA 5456 throughout galvanic coupling in 0.6 M NaCl. This potential meets the criteria of sacrificial cathodic prevention of 5456 by maintaining potentials below  $E_{pit, \alpha} = -0.72 V_{SCE}$  and  $E_{pit, \beta} = -0.92 V_{SCE}$  but benefits are quite time limited.

- The combination of spherical Al-5wt.% Zn and spherical Mg pigment in an epoxy-based MRP achieves stable intermediate cathodic potentials of approximately -1.17 V<sub>SCE</sub> on 5456-H116 in 0.6 M NaCl, likely due to a combination of chemical and porosity effects.
- Al/Mg-based primers have low anodic charge output and enhanced galvanic protection suggesting that these MRPs be utilized in static galvanic coupling conditions on 5456-H116.
- Hybrid Al/Mg composite pigment systems are capable of **1**) maintaining cathodic polarization of 150mV below the open circuit potential of AA 5456 throughout galvanic coupling in 0.6 M NaCl, **2**) supplying negative current indicating the MRP is operating as intended with coating acting as anode and **3**) superior MRP utilization as the pH increase associated with Mg oxidation forces the Al/Mg product stability into a thermodynamically active region. This potential meets the criteria of sacrificial cathodic prevention of 5456 by maintaining potentials below  $E_{pit, \alpha} = -0.72 V_{SCE}$  and  $E_{pit, \beta} = -0.92 V_{SCE}$ .

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# Tables - Appendix - Extra Dissertational Work

### **Tables**

Table A-1: Metal-Rich primer characteristics studied in this system

Code	Primer	Provider	Resin	PWC	PVC	Thickness	Pigment
	Commercial			(%)	(%)	(µm)	Diameter/
	Name						Dimensions
							(μm)
AlRP	LN4841	RC	Epoxy	44	27	41.71 ±	$9.19 \pm 4.01$
(Epoxy,27%)						3.95	
Al-MgRP	LN4847	RC	Epoxy	33 (Al-	28 (Al-	51.16 ±	8.64 ± 3.78 (Al-
(Epoxy,28/19%)				Zn)	Zn)	8.74	Zn) $8.16 \pm 3.70$
							(Mg)
				14 (Mg)	19 (Mg)		
MgRP	Aerodur 2100	AN	Epoxy	40	26	46.52 ±	Length: 24.46 ±
(Epoxy,26%)						7.97	11.94
							Width: 13.29 $\pm$
							5.67

RC = Randolph Coatings, AN = AkzoNobel, PWC = pigment weight concentration (in the dry film), PVC = pigment volume concentration (in the wet mix)

Table A-2: Metal-Rich Primer Charge Capacities and Cathodic Protection Performance

Metal-Rich	Theoretical	Maximum	Anodic	Max.	Initial	OCP Upon
Primer	Anodic Q	Experimental	Q Usage	XRD	Activated	Completion
	from MRP	Anodic Q	by End	Depletion	ОСР	of the
	(C/cm <sup>2</sup> )*	Output (C/cm <sup>2</sup> )	of Cycle	at End of		Cycle Test
		by End of	Test**	Cycle		
		Cycle Test		Test		
AlRP	32.2	0.7	2.1%		-0.96 ±	$-0.96\pm0.03$
(Epoxy,27%)					0.01 V <sub>SCE</sub>	V <sub>SCE</sub>
Al-MgRP	27.2	0.2	1.6%	52%	-1.21 ±	$-1.14 \pm 0.03$
(Epoxy,				(Mg)	0.08 V <sub>SCE</sub>	V <sub>SCE</sub>
28/19%)				(Al)		
MgRP	16.7	0.1	0.2%	10%	-1.47 ±	$-0.74 \pm 0.07$
(Epoxy,26%)					0.09	V <sub>SCE</sub>
					V <sub>SCE</sub>	

Q = charge, C = Coulombs, XRD = X-Ray Diffraction, OCP = open circuit potential, Activated OCP = stabilized OCP following immersion and sufficient coating wetting, MRP = metal-rich primer

\*Based on Zn pigment volume concentration and coating thickness

\*\* Not designed for universal usage, is a test-and time of exposure-dependent value

**Table A-3:** Elemental Molar and Corrosion Product Volumes Potentially Produced per Mole of

 Cations

Pigment/Compound	Specific Density*	Volume Produced/mole		
		cations		
Al-5wt.% Zn	$2.79 \text{ g/cm}^3$	$09.94 \text{ cm}^3$		
Al(OH) <sub>3</sub> (Gibbsite)	$2.53 \text{ g/cm}^3$	$30.83 \text{ cm}^3$		
Al <sub>2</sub> O <sub>3</sub> (Corundum)	$4.05 \text{ g/cm}^3$	$12.59 \text{ cm}^3$		
Mg	$1.74 \text{ g/cm}^3$	$13.96 \text{ cm}^3$		
Mg(OH) <sub>2</sub> (Brucite)	$2.39 \text{ g/cm}^3$	$24.40 \text{ cm}^3$		
Mg(CO) <sub>3</sub> (Magnesite)	$3.00 \text{ g/cm}^3$	$28.10 \text{ cm}^3$		

\*Densities obtained / calculated from the WebMineral Database

## Figures - Appendix – Extra Dissertational Work

## Figure A-1



Al-MgRP (Epoxy,28/19%)



MgRP (Epoxy,26%)



Fig. A-1: Cross sectional EDS analysis of the three Al- / Mg-rich primers on 5456-H116, NAMLT 65 mg/cm<sup>2</sup>, illustrating the pigment type, size, and primer thickness for each.

#### Figure A-2



Fig. A-2: Graphical representation of the cycle test, illustrating coupled potential results for each metal-rich primer, the potentiostatic hold steps at the 5456-H116 OCP of -0.85  $V_{SCE}$ , as well as the OCP in between potential holds. The detailed OCP and charge from each hold on each MRP are indicated in Figures 3, 4 and 5.

Figure A-3



Fig. A-3: The OCP established by each MRP per cycle (Cycles A - M) during the OCP stages in 0.6 M NaCl full immersion.

### Figure A-4

a)






Fig. A-4: The progression of cumulative anodic charge output per cycle (Cycles A – M/S) during the PS hold stages at -0.85 V<sub>SCE</sub> of the cycle test in 0.6 M NaCl for (**a**) MgRP (Epoxy,26%) and (**b**) AlRP (Epoxy,27%). The charge density output per cycle as well as the standard deviation for all of the candidate MRPs is summarized in (**c**).

Figure A-5



Fig. A-5: Metal-rich primer activation times in 0.6 M NaCl, reflecting the influence of primer resin and pigment type / PWC on the initiation and magnitude galvanic protection offered by the MRP over 24 hours at natural coupled OCP with the 5456-H116, NAMLT 65 mg/cm<sup>2</sup> substrate.

Figure A-6









Figure A-6. Long term open circuit potential is shown in **a**) for bare 5456 and each MRP. Galvanically coupled currents and potentials of each MRP – 5456-H116 are shown in **b**) and **c**) respectively with solid lines representing 1:1 area ratio and lines with square symbols representing 15:1 area ratio. The open circuit potential of the bare 5456 was -0.85 V<sub>SCE is</sub> represented by the green dashed line in **c**).

Figure A-7



Figure A-7. Cumulative galvanic protection charge density supplied to remote bare 5456 for each MRP throughout the duration of the galvanic couple exposure of 5456 to either MRP (AlRP, MgRP, Al-MgRP). The galvanic charge was calculated from integration of the coupled current density with time.



Figure A-8. Local pH modification monitored throughout the galvanic coupling of each MRP – 5456-H116 exposure tested in 0.6M NaCl shown in **a**) over the bare 5456 and **b**) over the MRP

coating. The lines with square symbols denote the 15:1 (MRP: bare 5456) area ratio while the square symbols indicate 1:1 (MRP: bare 5456) area ratios.





Fig. A-9: EIS Bode Magnitude plots showing results for cycle testing on each MRP in 0.6 M NaCl, as well as for epoxy-coated, highly sensitized 5456-H116 as reference. Impedance modulus trends observed on uncoated AA5456-H116, NAMLT 65 mg/cm<sup>2</sup> may be found elsewhere [1]. With time of exposure at -0.85  $V_{SCE}$ , loss of impedance typically occurs during primer activation followed by increase in impedance by corrosion product formation.

Figure A-10



Fig. A-10: Average impedance modulus at 0.01 Hz for each MRP throughout cycle testing in 0.6 M NaCl, with standard deviations for each to demonstrate variabilities in coating performance. The epoxy coated 5456 does not contain pigment.





Fig. A-11: Cycle test EIS phase angle plots in 0.6 M NaCl for cycles A-M/S for each MRP. Trends towards negative phase angles correlate to more capacitive coating behavior, whereas more positive phase angle trends relate to resistive behavior. Phase angle trends observed on uncoated AA5456-H116, NAMLT 65 mg/cm<sup>2</sup> may be found elsewhere [1].

## Figure A-12



Figure A-12. Electrochemical impedance spectroscopy of pre and post galvanic coupling of each MRP primer in 0.6M NaCl. The lines denote pre-galvanic coupling where the lines with square symbols indicate post exposure galvanic coupling.



AIRP (Epoxy,27%)

Al-MgRP (Epoxy,28/19%)

MgRP (Epoxy,26%)

Fig. A-13: Scanning electron microscopy micrographs demonstrating the pristine, untested Al-Zn / Mg-rich primer cross sections, in comparison to the cross sections of these MRPs following cycle testing where pigment oxidation / corrosion product precipitation may have occurred.



Fig. A-14: Scanning electron microscopy micrographs demonstrating the pristine, untested Al-Zn / Mg-rich primer surfaces in comparison to the surfaces following cycle testing where oxidation / corrosion product precipitation may have occurred.

## Figure A-15



c)



50µm

Fig A-15: Energy dispersive spectroscopy analysis demonstrating the deep solution penetration achieved throughout the Al-MgRP (Epoxy,28/19%) during the cycle test in 0.6 M NaCl. In (**a**) the entire elemental spectrum is illustrated, while in (**b**) Mg is selected and in (**c**) only oxygen is shown, which highlights the oxidized Mg pigments and the filiform corrosion propagating towards the center of a Mg pigment.

Figure A-16



Fig. A-16: A chemical stability diagram for the Al/Mg system, depicting the thermodynamic conditions for Mg dissolution at an initial pH of 5.7 and  $[Mg^{2+}]$  of  $1x10^{-10}$  M. The green and blue lines indicate equilibrium concentration-pH conditions for  $Mg^{2+}/Mg(II)$  or  $Al^{3+}/Al(III)$  products indicated. The black line indicates Mg2+ trajectory. These predictions demonstrate the ability of the Mg to active the Al in Al-MgRP (Epoxy,28/19%). Chloride complexation effects are unsubstantial for this system and are not incorporated here.