CORROSION PROTECTION OF AL5086 AND SENSITIZED AL5086 USING A TITANATE BASED CONVERSION COATING

Andrew Murphy

University of Rhode Island, ajaymurphy@my.uri.edu

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CORROSION PROTECTION OF AL5086 AND SENSITIZED AL5086 USING A TITANATE BASED CONVERSION COATING

BY

ANDREW MURPHY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
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OF

ANDREW MURPHY

APPROVED:

Thesis Committee:

Major Professor Richard Brown

Michael Greenfield

Leon Thiem

Nasser H. Zawia

DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND

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ABSTRACT

Chromate conversion coatings have been widely used in the materials industry, particularly on aluminum, to provide corrosion protection. Due to their toxicity and harmful environmental effects, replacement coatings have been sought. An alternative process to chromate conversion coatings using the titanate ion was developed and tested on 5086-H32 aluminum alloy and sensitized 5086-H32 aluminum alloy.

Electrochemical impedance spectroscopy (EIS) was employed to quantify the performance of the coating, while scanning electron microscopy (SEM) along with energy X-ray dispersive spectroscopy (EDS) were used to examine the surface and surface composition of the samples. Auger electron spectroscopy (AES) was used to determine the coating composition as a function of depth.

The titanate conversion coating provided good corrosion protection on 5086-H32 samples, based on impedance data. SEM micrographs revealed light and dark areas on the surface on the coating, while AES determined that the light area was predominantly magnesium and the dark area mostly aluminum oxide.

For sensitized samples, the titanate coating provided increased corrosion protection on samples sensitized at or below 100°C for less than two weeks. Samples with a higher degree of sensitization exhibited a greater increase in pitting failure and did not exhibit adequate corrosion protection.
ACKNOWLEDGMENTS

I would like to thank Dr. Brown for all his guidance and support over the past two years. His expertise, dedication, and positive research outlook made this a rewarding and enjoyable experience. I’d also like to thank the Coast Guard for providing me the opportunity to pursue this degree. Several other people, including Amy Zeno, Andrew Walker, and Patrick McKiernan, provided invaluable assistance during my research. I’d also like to thank Mike Platek, who provided excellent guidance and expert knowledge using the scanning electron microscope and multi-surface technique analyzer. Finally, I’d like to thank all my fellow chemical engineering graduate students and the entire chemical engineering department. Everyone in Crawford Hall made this whole experience great.
PREFACE

The Manuscript Format is used to organize the contents of this Thesis. The first manuscript, titled “Development of Chromate Free Coating for Corrosion Protection of 5xxx Series Aluminum using the Titanate Ion,” deals with applying a previously developed titanate conversion coating to 5xxx series aluminum alloy. The goal of the first manuscript is to determine whether the coating reduces corrosion on the aluminum alloy. The second manuscript, titled “Titanate Based Conversion Coating for Corrosion Protection on Sensitized 5086-H32 Aluminum Alloy,” explains the results of corrosion testing and analysis on coated samples of sensitized 5086 aluminum alloy. In both manuscripts, the same analysis techniques were used to evaluate the quality of the coatings on the alloy.
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Chapter – 1

For publication in Corrosion

Development of Chromate Free Coating for Corrosion Protection of 5xxx Series Aluminum using the Titanate Ion

Andrew Murphy and Richard Brown

Department of Chemical Engineering, University of Rhode Island, Kingston, RI, USA

Corresponding Author: Richard Brown, Ph.D.

Department of Chemical Engineering
University of Rhode Island
110 Crawford Hall, 16 Greenhouse Rd.
Kingston, RI, 02881, USA
Phone: 1-401-874-2655
Email: rbrown@egr.uri.edu
CHAPTER 1

1.1 Abstract

An alternative process to chromate conversion coating using the titanate ion was developed and tested on 5086-H32 aluminum alloy. The coating was applied by an immersion batch process. Electrochemical impedance spectroscopy (EIS) was employed to quantify the performance of the coating, while scanning electron microscopy (SEM) along with energy x-ray dispersive spectroscopy (EDS) were used to examine the surface and surface composition of the samples. Auger electron spectroscopy (AES) was used to determine the coating composition as a function of depth. The coated samples exhibited strong corrosion resistance over a 1000 hour (42 day) test in 0.5N NaCl solution. SEM examination revealed a relatively uniform coating with minor defects. Auger electron spectroscopy indicated the surface composition contained aluminum oxide and magnesium oxide, with an underlying layer of titanium oxide.

1.2 Introduction

Aluminum, specifically 5xxx series aluminum, finds extensive use in the maritime and automotive industries due to its superior corrosion resistance. Aluminum naturally forms a protective oxide layer that is corrosion resistant.\(^\text{[1]}\) However, this natural layer provides poor long-term corrosion resistance and inhibits paint from properly adhering to the surface of the aluminum.\(^\text{[2]}\) As a result, coatings were developed to provide better long-term corrosion resistance and to provide a sufficient base layer for paint adhesion. This resulted in the development of chromate conversion coatings, based on the hexavalent chromium ion.
Chromate conversion coatings (CCC’s) are an electrochemically driven process, consisting of 3 steps starting with activation, then coating initiation, and finally growth of the coating. Generally, an activator, such as fluoride, is used to attack the natural aluminum oxide layer, releasing Al\(^{3+}\) ions.\(^{[2]}\) This allows the reduction of chromium, as well as aluminum, onto the surface of the aluminum to form a porous chromium oxide, aluminum oxide, and chromium hydroxide layer.\(^{[2]}\) The porosity allows the dissolution of aluminum and the reduction of chromium to continue and the coating to grow.\(^{[2]}\) CCC’s derive their good corrosion resistance from their ability to inhibit cathodic half-cell reactions, particularly the oxygen reduction reaction.\(^{[2]}\)

Several features of chromate conversion coatings make them very desirable. The application process is simple and inexpensive. The coatings can be applied through a batch immersion process and the solutions are re-usable and easily maintained. The porous structure of the coatings, a distinct feature, allows good paint adhesion for improved corrosion protection. In many cases, CCC’s are applied primarily for their strong adhesion to paint.\(^{[3]}\) Furthermore, the hexavalent chromium ion exhibits excellent corrosion resistance, while demonstrating the ability to self heal. When underlying metal is exposed due to a mechanical or chemical defect, migration of Cr \(6^+\) ions to the defect occur, where the ion reduces to a Cr \(3^+\) hydroxide to rebuild the protective coating \(^{[3]}\).

However, due to concerns over health effects and toxicity, some countries have recently enacted stringent regulations and laws governing the use of chromates.
Several studies have found that hexavalent chromium is carcinogenic.\[^4\] More specifically, the reduction of the hexavalent chromium to trivalent chromium leaves molecular debris that has been linked to DNA damage.\[^4\] This new insight has led to stricter handling requirements for chromates, as well as tighter environmental laws, driving up the process cost. Thus, there has been considerable interest in developing chromate free coatings.

Aluminum is a highly reactive metal that likes to react with oxygen, forming the protective oxide layer for which aluminum is known. Under most conditions, this oxide layer will provide adequate protection by resisting dissolution and preventing the cathodic reaction of water or oxygen at the aluminum matrix/oxide layer interface.\[^5\] However, in aggressive environments, such as seawater, halide ions can break down the thin (1 nm thick) oxide layer and corrosion can occur. Chlorides in salt water are the most common type of aggressive halide ion.\[^5\] This type of chloride attack most generally results in pitting corrosion, shown in Figure 1-1. Areas with high concentration of chlorides can create potential differences along the surface, facilitating breakdown of the oxide layer.\[^5\] This can also occur along a defect or scratch, where the oxide layer is not as thick. Once a pit forms, the pit breakdown of the aluminum inside the pit attracts chloride ions, increasing the acidity and preventing the formation of the protective oxide layer.\[^6\] The oxide layer forms in environments around neutral pH, as shown by the aluminum Pourbaix Diagram.

Intergranular corrosion, also called “sensitization,” is also of concern in aluminum alloys. Some alloying elements, particularly magnesium in concentrations greater than 3% in solution, have a different corrosion potential than the aluminum
matrix. In some cases of prolonged exposure to elevated temperatures, magnesium will diffuse to the grain boundaries, forming an area along the grain boundary that is now anodic to the depleted aluminum matrix.\[7, 8\] This area along the grain boundary then is susceptible to corrosion and can compromise the strength of the aluminum if the corrosion is severe enough. A few other forms of corrosion, such as crevice corrosion, biological corrosion, fretting corrosion, and stray current corrosion can impact aluminum alloys. However, they are mostly prevented through proper maintenance and engineering design and coatings are not as effective at preventing these types of corrosion.

Of particular concern in this study is 5xxx series aluminum, specifically 5086-H32 aluminum alloy. The 5xxx series aluminum are a wrought, non-heat treatable alloy that is generally considered the strongest of the non-heat treatable alloys with a high corrosion resistance.\[8, 9\] The primary alloying element is magnesium, which provides solid solution hardening. Additional strength is added to the alloy through cold-working.\[8\] For 5086-H32, the H designates strain hardened (cold worked), the 3 implies cold worked and stabilized as a secondary treatment, and the final number 2 indicates residual hardening of ¼ hard.\[9\]

An alternative to chromates using a titanate based coating process was developed by Guo and Brown and tested on Al2024-T3 aluminum alloy by Maddala with success.\[10, 11\] Further study through the same research group completed by Williams and Pierce occurred on 6061 and 7075 aluminum alloys using the same coating process with mixed results.\[12,13\] Additionally, Pierce added a post conversion coating step to repair defects and improve the coatings performance.\[13\]
The basis of this study is to determine the effectiveness of the titanate conversion coating process in reducing corrosion on 5xxx series aluminum, specifically 5086-H32 aluminum alloy. To date the titanate process has not been attempted on this alloy. The titanate ion has a significant advantage over the chromate ion in that it does not have any toxicity or negative health effects. Furthermore, titanium and chromium exhibit similar properties and are very close in potential. The titanate based conversion coating is applied through a batch immersion process very similar to chromates, and activators are also necessary for the conversion process to work.

1.3 Experimental Methods

The aluminum 5086-H32 alloy used in this study was procured from Alcoa Inc. and is composed of 4% magnesium, 0.43% manganese, 0.24% iron, 0.11% silicon, 0.08% chromium, 0.07% zinc, 0.06% copper, and 0.02% titanium. The alloy was cut into 1.25” by 1.25” samples using a press cutter to avoid heating the alloy.

To remove any dirt and oil, the samples were cleaned with acetone. Then samples were submerged in sodium hydroxide for chemical cleaning at 40°C and 12.75 pH for 10 minutes, then rinsed with de-ionized water. A 10-minute soak in a de-oxidizer called SMUTGO (room temperature, 1.5 pH) followed with a second thorough rinse with de-ionized water. The samples were then submerged in a titanate solution consisting of 6 g/L of potassium titanate and 4 g/L of sodium fluoride for 3 minutes. The titanate solution is maintained at 5.5 pH and 62°C. A third rinse with de-ionized water occurred after the conversion coating. Finally, the samples were submerged in a post treatment solution of 6 g/L potassium titanate to repair any
defects or impurities on the surface of the coating. The batch immersion process described above is shown in Figure 1-2.

After the conversion coating process, some samples were prepared for salt water exposure. The samples were mounted on an electrically insulating piece of polycarbonate and exposed to 0.5N sodium chloride solution. The sodium chloride was poured into a 1” spherical glass joint tube that was clamped to the exposed side of the aluminum sample. Between the joint and the aluminum sample, a gasket was placed with a small amount of vacuum grease to provide a watertight seal. The top of the joint tube was plugged with a rubber stopper.

Once the samples were mounted, they were tested using electrochemical impedance spectroscopy (EIS). A saturated calomel electrode acted as the reference electrode. A corner of the sample that had been polished to expose bare aluminum provided the working electrode connection. A third counter electrode was a piece of platinum foil placed in the electrolyte. The samples were tested at intervals of 1, 3, 5, 10, 20, 31, and 42 days as long as the coating remained intact. The 42 days is equivalent to 1000 hours. Regularly, the samples were also visually examined for signs of corrosion or crystal formation on the surface of the sample, which indicated that the coating had failed. An electrical circuit model was used to compare the coated sample data.

For imaging the surface of the coated samples, Scanning Electron Microscope (SEM) was used with the capability to conduct energy dispersive x-ray spectroscopy (EDS). Images of the coating surface were desired to observe the surface features of the coating and to identify defects and impurities that may be compromising the
performance of the coating. EDS provided analysis of the sample composition and any impurities on the surface.

Coating composition was analyzed using a Multi-technique Surface Analyzer with the capability to conduct either X-ray Photoelectron Spectroscopy (XPS) or Auger Electron Spectroscopy (AES). The AES capability was used for analysis due to its smaller spot size. Several samples had dark and light areas that were observed with the naked eye and then confirmed through the SEM that required separate analysis. XPS would not be able to focus the instrument on a small enough area to accurately read the composition of the desired area. Therefore, AES was chosen as the preferred technique for analysis.

1.4 Results and Discussion

EIS data, specifically the impedance values at low frequency, provided a reasonable initial analysis of coating quality. Generally, the higher the impedance value at low frequency, the better the coating. Impedance data for uncoated samples is shown in Figure 1-3 and data for coated samples is shown in Figure 1-4. Uncoated samples performed extremely poorly compared to coated samples. The uncoated samples were not tested for the full 42 day (1000 hour) test period because visible corrosion formed on the surface of the samples. Impedance values for the uncoated samples were on average 15 times less at 0.01 Hz than for coated samples. This indicates that at first glance, the titanate coating provides a good improvement to corrosion resistance on the alloy.

For coated samples, two distinct behaviors were noted depending upon post conversion conditions. In the first condition, the majority of the samples were treated
with a post conversion treatment beyond 30 minutes and the impedance values generally trended upward over the 42 day test. The second condition included samples that were treated for less than 30 minutes and the data is not included because the samples showed premature failure well before the end of the 42 day test period. In Figure 1-4, sample E showed a unique drop after day 5, and then steadily climbed upward again. One explanation for the drop in impedance is that the electrolyte solution attempted to initiate a pit or other defect in the coating, causing the rapid drop in impedance. However, the titanate ions were able to repair the coating by depositing on the surface with oxygen to form a titanium oxide layer. No corrosion was visible on this sample after 42 days.

To determine a better measure of the quality of the coatings than just through basic analysis of impedance values, the EIS data was fit to an equivalent electrical circuit model. The electrical circuit model used is shown in Figure 1-5. The use of a circuit model for analysis of impedance data was first introduced by Kendig et al. and further modified by Zeller and Savinall. The model uses basic electric circuit elements such as resistors and capacitors, and equates them to physical electrochemistry of the coating system. If a sample had a perfect coating applied to the surface with no defects, the physical electrochemistry could be modeled using a basic circuit of just a resistor and capacitor in series. However, rarely are coatings perfect. Thus, a more complex model is used such as the one in Figure 1-5. \( R_s \) refers to the solution resistance of electrolyte solution, or the 0.5N salt-water solution. To model the quality of the coating, a resistance, \( R_c \), is added. The charge buildup from the coating in represented by a constant phase element, \( \text{CPA}_c \). \( R_p \) and \( \text{CPA}_{dl} \) represent
the polarization resistance and a double layer constant phase element, respectively. Polarization resistance accounts for the degree to which the electrode is forced away from its equilibrium potential value at open circuit or corrosion potential.[16] The double layer capacitance accounts for charges of ions that attach to the electrode surface.[16]

Results of the electrochemical models are shown in Figure 1-6. The data was more scattered than the raw EIS data from Figure 1-4, but this is most likely due to individual elements changing, while the raw data averages the changes of each circuit element. In several of the samples, there are drops from a peak, then recovery and stabilization. Several of the samples, including samples B and E, showed multiple drops. This may be a sign of continuous surface attack before the coating finally stabilized. All the samples displayed relatively high resistance values at day 42, indicating a good corrosion resistance provided by the coating.

Several samples were examined by SEM prior to exposure to 0.5N sodium chloride solution and are shown in Figures 1-7 through 1-10. Some common features were present on the surfaces for different post conversion treatments. These features included the presence of light and dark areas determined by backscatter electron imaging, large particles, and cracking amongst the coating in the darker areas.

A difference in composition was apparent due to the differing shades in the micrographs captured in backscatter mode (BEI) before EDS was even conducted. A backscatter detector works by collecting electrons from the electron beam that collide with atoms in the sample being viewed. The higher the atomic number of the atom, the larger the cross sectional area of the atom and more electron collisions will
occur.[17] This produces the different shades. From Figure 1-7, the EDS spectra for the two areas analyzed (B and C) show that the light area and dark area are composed of primarily aluminum and magnesium. This makes sense because the primary alloying element is magnesium. However, area C shows no trace of titanium, which is unexpected. There are two possibilities that explain the lack of titanium. The first possibility is that titanium is not depositing anywhere on the surface. This is highly unlikely due to the good EIS results for multiple coated samples. The second possibility is that a very thin but good layer of titanium is deposited on the surface, but the EDS is unable to detect it due to the limitations of the detector. A third possibility is that a thick aluminum oxide coating is formed under which lies the titanium, out of reach of the EDS detectors capabilities. For backscatter electrons, the specimen interaction volume is much larger than secondary or auger and generally the beam voltage is too high to accurately determine the immediate surface composition.[17] This third scenario is the most likely scenario that is occurring. In Figure 1-9, the EDS spectra for area B show similar results for the lighter phase region, with the presence of titanium.

Several impurities on the surface, such as large particles, were also noted in the SEM micrographs. In Figure 1-8 and 1-9, EDS spectra show the results for the particle analysis. The particle is primarily composed of iron with some manganese and silicon. The particles are most likely a result of the coating process, with the de-oxidation step producing the undesirable particles. During this step, a propriety de-oxidizer called SMUTGO is used that contains ferric sulphate. The current rinsing process is not adequate to remove all of these particles as they are found on almost
every micrograph. Furthermore, the particles cause depressions in the surface where they lie, further eroding the effectiveness of the coating. The iron may also cause an potential difference on the surface, leading to areas that are more anodic than the rest of the coating surface and causing corrosion or initiation of pit formation.

The final issue involves the cracking of the coating. In Figure 1-7 through 1-9, the dark areas of the coating all show significant cracking. All three figures show three separate samples that were immersed in post conversion solution for differing times. Each sample shows significant cracking in the darker phase areas. At this point, it is unknown if immersion time is a contributor to the degree of cracking as any type of quantitative stereology on the micrographs was not performed. However, it is believed that the cracking does not negatively affect the coating due to the good EIS and good visual results of several samples that have post conversion immersion times well beyond 1 hour.

More conclusive results were desired for the coating composition as a function of depth, which led to AES analysis of several samples. In order to better determine the composition of the light and dark phases, a scribe was used to mark a sample, as shown in Figure 1-10. The scribe provided orientation to direct the AES instrument to light and dark areas. Figure 1-11 shows the results of the AES analysis for a dark area. The sample was sputtered for 6s to clean off contamination, analyzed, and then sputtered for 5 minutes and analyzed again. In Figure 1-11A, the results of the 6s sputter are shown, with aluminum oxide, aluminum and titanium making up the majority of the composition. After the 5-minute sputter, shown in Figure 1-11B, the composition did indicate titanium was present. This implies that a thick layer (greater
than 120 nm) of aluminum and titanium oxide is deposited on the surface of the sample.

In Figure 1-12, the light phase was analyzed. The results after a 6 second sputter are shown in Figure 1-12A and after a 5-minute sputter in Figure 1-12B. The results are radically different from area 1, the dark phase. After the 6 second sputter, the entire composition of the coating is magnesium, with small traces of titanium. After the 5 minutes sputter, aluminum oxide and titanium are present with no magnesium. The presence of magnesium in such great quantity on the surface of the coating may cause differences in electrochemical potential and lead to anodic and cathodic sites. However, the fact that a layer of aluminum oxide and titanium rests under the magnesium, the coating should maintain good corrosion resistance, as demonstrated by EIS results.

Based on the EDS spectra and the results of the AES analysis, a suggested coating was created to provide a visual representation of the coating composition, shown in Figure 1-13. The presence of the light phase, which is predominantly magnesium, and the dark phase, which is predominantly aluminum oxide, with some titanium, conclude that the surface of the coating is interspersed with islands of magnesium overlaying a thick layer of aluminum oxide. Directly below the aluminum oxide is a layer of titanium oxide.

1.5 Conclusions

The coating has proven that it is capable of providing good corrosion resistance on Al5086-H32 aluminum alloy when exposed to a simulated salt water environment. EIS data shows that at low frequency, the impedance of the coatings in
at least 7 samples is very high, indicating a good uniform coating deposition on the surface of the aluminum. SEM micrographs reveal minor defects, such as iron particles, surface cracking, and light and dark phases. Despite the defects, the majority of the samples performed well during the 42 day 0.5N NaCl exposure test. However, it is still unknown how much of a role the defects play in the performance of the coating.
Figure 1-1: Mechanism of pit formation.
Figure 1-2: A sample of 5086-H32 during (A) chemical cleaning, (B) de-oxidation, (C) conversion coating, and (D) post conversion treatment.
**Figure 1-3:** EIS data for uncoated samples A and B.
Figure 1-4: Impedance data for several samples over 1000 hours (42 days). (A) PC 30 minutes, (B) PC 1 hour, (C) PC 45 minutes, (D) PC 4 hours, (E) PC 45 minutes, (F) PC 45 minutes.
Figure 1-5: Electrical circuit used to model coating resistance, where: Rs = solution resistance, Rc = coating resistance, Rp = polarization resistance, CPAc = a constant phase element for the coating, CPAdl = a constant phase element for the double layer.
Figure 1-6: Results of Rc Modeling. (A) PC 30 minutes, (B) PC 1 hour, (C) PC 45 minutes, (D) PC 4 hours, (E) PC 45 minutes, (F) PC 45 minutes.
Figure 1-7: A sample conversion coated for 3 minutes, then followed by a 4 hour PC treatment with (A) SEM micrograph, (B) EDS spectra from the dark area, (C) EDS spectra from the light area.
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Figure 1-13: Theoretical layers of coating.
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Titanate Based Conversion Coating for Corrosion Protection on Sensitized 5086-H32 Aluminum Alloy

Andrew Murphy and Richard Brown

Department of Chemical Engineering, University of Rhode Island, Kingston, RI, USA

Corresponding Author: Richard Brown, Ph.D.
Department of Chemical Engineering
University of Rhode Island
110 Crawford Hall, 16 Greenhouse Rd.
Kingston, RI, 02881, USA
Phone: 1-401-874-2655
Email: rbrown@egr.uri.edu
CHAPTER 2

2.1 Abstract

An alternative process to chromate conversion coatings using the titanate ion was developed and tested on sensitized 5086-H32 aluminum alloy. Samples were sensitized for one or two weeks at 75°C, 100°C or 125°C in a standard lab oven. The samples were then coated using a previously developed batch immersion process. ASTM G67 Nitric Acid Mass Loss Test (NAMLT) was used to determine the susceptibility of the samples to intergranular corrosion (IGC). Electrochemical impedance spectroscopy (EIS) was employed to quantify the performance of the coating, while scanning electron microscopy (SEM) along with energy x-ray dispersive spectroscopy (EDS) were used to examine the surface and surface composition of the samples. Auger electron spectroscopy (AES) was used to determine the coating composition as a function of depth. Samples sensitized at 100°C or less exhibited good corrosion resistance over a 1000 hour (42 day) test in 0.5N NaCl solution. Auger electron spectroscopy indicated the surface composition contained predominantly magnesium oxide with some aluminum oxide and small amounts of titanium oxide.

2.2 Introduction

Aluminum, more notably, 5xxx series aluminum, continues to find significant use in the maritime and automotive industries. The main alloying element in 5xxx series aluminum alloy is magnesium, which provides increased corrosion resistance, but also subjects the alloy to a form of attack called intergranular corrosion.\textsuperscript{[1, 2]} This
form of corrosion only exists under certain conditions, but if it is not recognized or dealt with, serious degradation can occur to the alloy.

The mechanics of intergranular corrosion (IGC) are not well agreed upon. In a general sense, IGC occurs when the areas adjacent to grain boundaries in the alloy become anodic to the bulk matrix and corrosion occurs.\textsuperscript{[2, 3]} This mechanism is shown in Figure 2-1. For 5xxx series aluminum alloy, exposure to elevated temperatures will cause the magnesium to diffuse to the grain boundaries, resulting in “sensitization” of the material. At this point, the magnesium is anodic to the depleted aluminum matrix, and corrosion will occur, removing the magnesium. There are generally two preventative methods that have been employed to inhibit IGC. The first involves deliberate heat treatments during manufacturing for alloy with magnesium content above 3% wt.\textsuperscript{[3]} The second method for IGC prevention limits the amount of magnesium in the alloy below 3% wt when possible to reduce the likelihood of IGC.\textsuperscript{[3]}

However, these methods do not completely eliminate the threat of IGC, especially for alloys with magnesium greater than 3% wt. IGC is most prevalent after a period of years in service, when the material is continuously subjected to elevated temperatures, resulting in slow but steady movement of magnesium to the grain boundaries.

IGC has seen significant research and study, but most of the research has dealt with the mechanics and behavior of the Mg\textsubscript{2}Al\textsubscript{3} phase and what happens to fatigue and stress corrosion cracking as a result. Few studies have looked at prevention of IGC through a coating process. Holtz et al. analyzed fatigue crack growth on 5083-H131 aluminum alloy at 175°C, and concluded that full continuous grain boundary coverage of the beta phase, Mg\textsubscript{2}Al\textsubscript{3} occurred around 200 hours.\textsuperscript{[4]} Furthermore, Holtz et al.
utilized the NAMLT test and found that below 30 mg/cm$^2$ mass loss has no effect on the corrosion fatigue threshold.$[4]$ Oguocha et al. studied the effects of sensitization of 5083 aluminum alloy by looking for decreases in the chemical and mechanical properties of the alloy with respect to time and sensitization.$[5]$ They found that samples sensitized for up to 80°C and 672 hours are resistant to intergranular corrosion while also concluding that the most susceptible IGC temperature lies between 150 and 200°C.$[5]$ Further studies by Lyndon et al. found that dissolution rates for the beta phase to the grain boundaries, Mg$_2$Al$_3$, was pH dependent, with acidic pH having greater dissolution rates.$[6]$ Several other studies looked at the behavior of the precipitates under differing conditions and all concluded definitively that IGC occurred when samples were sensitized, usually between 50 and 150°C over the course of several hundreds of hours.$[7-10]$ 

The fact that sensitization can occur at temperatures as low as 50°C and up to 200°C can cause significant problems, even in standard atmospheric conditions. The lower end of this temperature range is the most dangerous, since many of these temperatures are regularly encountered in warm weather climates. However, even long-term exposure to temperatures below 50°C over many years will result in some magnesium precipitation to the grain boundaries, resulting in sensitization.$[10]$ 

Aluminum hulled ships can be susceptible to IGC especially around cooling water discharges, where cooling water that absorbs heat from an engine is discharged out a through hull fitting below the waterline. This area will see prolonged exposure to elevated temperatures compared to the rest of the hull. This is just one of many examples where IGC attack can occur.
Previous work by the author dealt with a titanate based conversion coating and its effectiveness at preventing corrosion on 5xxx series alloy, specifically 5086-H32 alloy, with good results.\textsuperscript{[11]} This study will determine the effectiveness of the same titanate coating process in preventing intergranular corrosion on sensitized samples of aluminum 5086-H32 alloy.

2.3 Experimental Methods

The 5086-H32 aluminum alloy for use in this study was procured from Alcoa Inc. and is composed of 4% magnesium, 0.43% manganese, 0.24% iron, 0.11% silicon, 0.08% chromium, 0.07% zinc, 0.06% copper, and 0.02% titanium. A large sheet of 5/16-inch thick alloy was cut into 1.25” by 1.25” samples using a press cutter to avoid heating the alloy. These samples were then sensitized at 75, 100, and 125°C in a standard lab oven for 1 week and 2 week periods. The sensitized samples were then coated with a titanate conversion coating. Several samples were also coated first, then sensitized for 1 or 2 week periods at 75, 100, and 125°C.

To determine the degree of sensitization, the NAMLT as described in ASTM standard G 67 was employed.\textsuperscript{[12]} This test subjected the sensitized samples to Nitric Acid for 24 hours, which dissolved away the precipitated phase at the grain boundaries. To start the test, sensitized samples were cleaned with acetone and measured using a micrometer for length, width and height dimensions. To clean, the samples were submerged in a 5% weight NaOH solution for 1 minute, rinsed with deionized water, and then submerged in HNO₃ for 30 seconds. The samples were then weighed to thousandths of a gram. Once weighed, the samples were placed in HNO₃ for 24 hours. The setup is shown in Figure 2-2. After the samples were removed, they
were rinsed, allowed to air dry, and then weighed again using the same lab scale. At this point, the mass loss, in mg/cm$^2$, was determined. Samples used for the NAMLT test were not coated due to the significant change to the microstructure.

The coating process started with acetone cleaning and roughening with 600 grit silicone carbide paper. The samples were then submerged in sodium hydroxide solution at 40$^\circ$C and 12.75 pH for 10 minutes. This provides a chemical cleaning to remove any impurities. Next, a thorough rinsing with de-ionized water occurred to remove the sodium hydroxide. A 10-minute soak in a de-oxidizer called SMUTGO (room temperature, 1.5 pH) followed with a second thorough rinse with de-ionized water. The samples were then submerged in a titanate solution consisting of 6 g/L of potassium titanate and 4 g/L of sodium fluoride for 3 minutes. The titanate solution is maintained at 5.5 pH and 62$^\circ$C. A third rinse with de-ionized water occurred after the conversion coating. Finally, the samples were submerged in a post treatment solution of 6 g/L potassium titanate. The pH was held at 11.5 and the temperature was held at 62$^\circ$C.

The samples were then mounted on an electrically insulating piece of polycarbonate and exposed to 0.5N sodium chloride solution. The 0.5N solution was poured into a 1” spherical glass joint tube that was clamped to the exposed side of the aluminum sample. A watertight seal was achieved by using a rubber gasket with vacuum grease between the joint and the aluminum sample. The top of the joint tube was plugged with a rubber stopper.

Once the samples were mounted, they were tested using electrochemical impedance spectroscopy (EIS). A saturated calomel electrode acted as the reference
electrode. A corner of the sample that was polished to expose bare aluminum provided the working electrode connection. A third counter electrode, a piece of platinum foil, was placed in the electrolyte. The samples were tested at intervals of 1, 3, 5, 10, 20, 31, and 42 days as long as the coating remained intact. The 42 days is equivalent to 1000 hours. Regularly, the samples were also visually examined for signs of corrosion or crystal formation on the surface of the sample, which would indicate that the coating failed. An electrical circuit model was used to compare the coated sample data.

For imaging the surface of the coated samples, a scanning electron microscope was used with the capability to conduct EDS. Images of the coating surface were desired to observe the surface features of the coating and to identify defects and impurities that may be compromising the performance of the coating. EDS provided analysis of the sample composition and any impurities on the surface.

Coating composition was analyzed using a Multi-technique Surface Analyzer with the capability to conduct either X-ray Photoelectron Spectroscopy (XPS) or AES. The AES capability was used for analysis due to its smaller spot size. Several sample areas were selected to analyze the coating composition with respect to depth.

2.4 Results and Discussion

The first concern was employing a reliable method to verify sensitization and susceptibility to intergranular attack of the aluminum alloy samples. The ASTM G 67 standard is regularly used in industry and is the only standard for determining the degree of sensitization on 5xxx series alloys. Generally, a sample that has lost more than 30 mg/cm² is considered sensitized. The results of the NAMLT test are
shown in Table 2-1. Clearly, the data shows that the samples are sensitized, especially the samples that were heated for 2 weeks at 100°C and 125°C. Three as received samples were also tested and showed 15-23 mg/cm² mass loss. The mass loss of the sample sensitized for 1 week at 75°C was in the same range, indicating no sensitization. Thus, any sample heated for only 1 week at or below 75°C was not considered sensitized. All other samples had mass loss above 30 mg/cm² and were considered sensitized.

EIS data provided visible trends for the sensitized samples. Raw data for impedance at low frequency is provided in Figure 2-3. The plot indicates that as the degree of sensitization increased, the coating performance suffered. Sample E and F, both sensitized for 2 weeks, fared poorly. The coating did not prevent corrosion for the 42-day period. After about 31 days, small pits were visible on the surface of the coating. Unlike samples A-F, sample G was coated first and then sensitized and also performed poorly. It displayed visible coating failure due to pitting after 20 days. Sample A-D, all sensitized for 1 week and then coated, performed well over the 42 day period with no visible corrosion. The good impedance data indicates a strong coating. For samples E-F, the longer sensitization times had a significant impact on the performance. For sample G, the sensitization that occurred after the coating caused failure. It is believed that greater amounts of magnesium diffuse through the titanium layer to the surface during heating disturbing the titanium based layer to then form areas of magnesium oxide. If enough titanium diffuses, tunnels of magnesium oxide form through the coating, creating islands of titanium oxide instead of the desired uniform distribution. The magnesium oxide, which has a greater electrochemical
potential than the aluminum or titanium, then becomes anodic to the matrix and corrosion forms.

EIS data was fit to an equivalent electrical circuit model. This analysis was useful because it provided a specific value for the resistance of the coating, rather than the entire system, which includes the resistance of the coating and several other elements together. The electrical circuit model used is shown in Figure 2-4. This circuit model for analysis of impedance data was first introduced by Kendig et al and further modified by Zeller and Savinall.[15, 16] The model equates basic electric circuit elements, such as resistors and capacitors, to the physical electrochemistry of the coating system.[17] The physical electrochemistry of a perfect coating with no defects could be modeled using a simple resistor and capacitor in series. However, coatings are not perfect and a more complex model is used such as the one in Figure 2-4. $R_s$ refers to the solution resistance of electrolyte solution, or the 0.5N salt-water solution. To model the quality of the coating, a resistance, $R_c$, is added. The charge buildup from the coating is represented by a constant phase element, CPA$_c$. $R_p$ and CPA$_{dl}$ represent the polarization resistance and a double layer constant phase element, respectively. Polarization resistance accounts for the degree to which the electrode is forced away from its equilibrium potential value at open circuit or corrosion potential.[17] The double layer capacitance accounts for charges of ions that attach to the electrode surface.[17]

The raw data from the EIS results was the input data for the modeling analysis. The modeling analysis for coating resistance, $R_c$, is shown in Figure 2-5. The model had a good fit on most of the sample data, as indicated by goodness of fit results. The
goodness of fit result, calculated through a non-linear least squares method and averaged over all the data points, was 5x10^{-3}. However, there is significantly more scatter associated with this data as compared to the impedance data from Figure 2-3. Most likely, the model is more sensitive to changing coating conditions, such as surface attack from the electrolyte solution. Samples A-C still showed strong resistance values toward the end of the 42-day test period, despite a drop off from their peak values. However, both sample A and C showed drops from a peak, indicating electrolyte attack, then recovery and stabilization. The behavior of sample D showed that the polarization resistance was on the order of 1.9 million ohms and the coating resistance was negligible. But, after 42 days, the coating on sample D was still intact and no corrosion product was visible on the surface. Either the electrochemistry of the sample changed significantly and was not visible, or the model was not an ideal fit for this sample. Samples E-G showed poor coating resistance values, in line with the poor impedance values from Figure 2-3.

The SEM micrographs in Figures 2-6 and 2-7 enabled the examination of the coating surface to determine the quality of the coating. Previous work by the authors determined that the light and dark phase on un-sensitized 5086-H32 aluminum alloy samples were magnesium oxide and aluminum oxide respectively. Similar results were expected for sensitized samples. Both micrographs in Figure 2-6 and 2-7 are taken in backscatter mode, and an apparent difference in composition is obvious on the surface in the form of light and dark areas. A backscatter detector works by collecting electrons from the electron beam that collide with atoms in the sample being viewed. The higher the atomic number of the atom, the larger the cross sectional area
of the atom and more electron collisions will occur.\cite{18} In Figure 2-6, the amounts of magnesium and titanium detected for area B and C are about the same. The best explanation for this is that the beam voltage is too high, and the specimen interaction volume too far below the surface to accurately determine the immediate surface composition.\cite{18} Furthermore, the greatest difference between B and C in Figure 2-6 is the large peak of chlorine and silicon. The presence of these elements was added either during sensitization in the oven, during the coating process, or during testing in the SEM. Figure 2-7 shows very similar results to the data in Figure 2-6.

AES analysis was employed to provide a more accurate depiction of the surface composition of the coating. Two random areas were sampled on the surface, with the blue line indicating area 1 and the red line indicating area 2. In Figure 2-8, plot 2-8A displays the surface composition after a 6 second sputter. Figure 2-8B shows the sample composition after a 5-minute sputter. After 6 seconds, titanium and aluminum are present, but magnesium is not detected. After 5 minutes, titanium is not detected and only aluminum and aluminum oxide are present. The lack of magnesium can be attributed to the sensitization of the sample, causing the magnesium to diffuse to the surface in clusters, or tunnels. Furthermore, the lack of titanium after a 5-minute sputter indicates the titanium coating is very thin. After 5 minutes, the sputter gun has removed approximately 1300 angstroms of material, with the titanium coating being less thick.

A second sample was tested and the results are shown in Figure 2-9. The results of the 6 second sputter are shown in Figure 2-9A. For both area 1 (blue line) and area 2 (red line), the composition is almost identical. However, after a 5-minute
sputter shown in Figure 2-9B, area one contains a large amount of magnesium and no aluminum. Area two is the complete opposite, having no magnesium and almost all aluminum and aluminum oxide. Again, titanium was not detected after the 5-minute sputter, indicating a very thin titanium layer (less than 120 nm). The drastic change in the two areas from Figure 2-9A to Figure 2-9B further reinforces the theory that the magnesium is diffusing and clustering, or forming tunnels at or near the surface of the coating. This is leading to a difference in electrochemical potential on the surface, causing corrosion, and helping to initiate pits that have been prevalent on the sensitized samples.

Based on the results from the EDS spectra and AES analysis, a suggested coating structure was created to provide a visual representation of the coating composition, shown in Figure 2-10A and 2-10B. It is believed that the sensitization of the aluminum alloy causes magnesium to diffuse through the titanium layer and cluster on the surface of the sample. For Figure 2-10A, the suggested coating composition is shown for samples sensitized at or below 100°C for less than two weeks. The magnesium diffuses to the surface but does not disrupt the titanium oxide layer. Figure 2-10B represents the suggested coating composition for samples sensitized beyond two weeks at a temperature greater than 100°C and also for samples coated and then sensitized. The magnesium diffuses to the surface and disrupts the titanium oxide layer, leading to islands of titanium oxide. It is believed that the rate of magnesium diffusion to the surface closely follows the degree of sensitization. As the degree of sensitization increases, the magnesium clusters grow and have a “tunneling effect” on the coating, where the magnesium provides an initiation point for pitting.
due to the difference in electrochemical potential with the rest of the alloy. This leads to the increased failure of the sensitized coatings.

2.5 Conclusions

EIS and data modeling proved that the titanate based conversion coating is capable of preventing intergranular attack at low degrees of sensitization, at or below 100 degrees Celsius for times less than 2 weeks. Above these temperatures, the coating does a poor job of protecting the samples from corrosion. Furthermore, samples that are coated and then sensitized did not perform well. The poor performance of highly sensitized samples, as well as EDS and AES data showing surface composition with high levels of magnesium, indicate that the titanium coating does not provide a diffusion barrier to magnesium.
Figure 2-1: Mechanism of intergranular corrosion.
**Figure 2-2:** Nitric Acid Mass Loss Test (NAMLT), (A) when samples are first immersed, (B) after the samples have been submerged for 24 hours.
| Sensitization Time (Days) | Temperature (°C) | Mass Loss (mg/cm²) |
|---------------------------|------------------|--------------------|
| As Received               | None             | 20.67              |
| As Received               | None             | 23.19              |
| As Received               | None             | 15.01              |
| 14                        | 125              | 55.05              |
| 14                        | 125              | 50.00              |
| 14                        | 100              | 40.72              |
| 14                        | 100              | 42.11              |
| 14                        | 75               | 33.84              |
| 14                        | 75               | 30.15              |
| 7                         | 125              | 33.51              |
| 7                         | 100              | 32.79              |
| 7                         | 75               | 18.14              |

**Table 2-1:** Tabulated results of NAMLT test.
Figure 2-3: Impedance results for low frequency (0.01 Hz). A) PC 45 min, sens 1 week at 100°C B) PC 1 hour, sens 1 week 100°C C) PC 45 min, sensitized 1 week 75°C D) PC 45 min, sens 1 week 125°C E) PC 1 hour, sens 2 weeks 125°C F) PC 1 hour, sens 2 weeks 125°C G) coated first w/ PC 1 hour, then sensitized 2 weeks 100°C.
Figure 2-4: Electrical circuit used to model coating resistance, where: Rs = solution resistance, Rc = coating resistance, Rp = polarization resistance, CPAc = a constant phase element for the coating, CPAdl = a constant phase element for the double layer.
Figure 2-5: Results of modeling for the resistance of the coating, $R_c$, A) PC 45 min, sens 1 week at 100°C B) PC 1 hour, sens 1 week 100°C C) PC 45 min, sensitized 1 week 75°C D) PC 45 min, sens 1 week 125°C E) PC 1 hour, sens 2 weeks 125°C F) PC 1 hour, sens 2 weeks 125°C G) coated first w/ PC 1 hour, then sensitized 2 weeks 100°C.
Figure 2-6: A sample that was coated with PC of 1 hour then sensitized for 1 week at 125°C, A) Micrograph of sample in backscatter mode, B) EDS spectra of dark area shown on the micrograph, C) EDS spectra of the lighter area shown on the micrograph.
Figure 2-7: A sample that was coated with a PC of 1 hour, then sensitized for 2 weeks at 125°C. A) Micrograph of sample in backscatter mode, B) EDS spectra of dark area shown on the micrograph C) EDS spectra of the lighter area shown on the micrograph.
Figure 2-8: AES results for sample that was coated for 1 hour PC, then sensitized for 14 days at 100°C. The blue line designates the first area analyzed, and the red line the second area analyzed. A) Results for 6 second sputter, B) results for 5 minutes sputter.
Figure 2-9 AES results for sample that was coated for 1 hour PC, then sensitized for 14 days at 100°C. The blue line designates the first area analyzed, and the red line the second area analyzed. A) Results for 6 second sputter, B) Results for 5 minutes sputter.
Figure 2-10: Theory on sensitized sample coating composition; A) For samples sensitized at or below 100°C for less than two weeks; B) Samples sensitized at temperatures above 100°C for greater than two weeks.
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A.1 Significance of Study

Aluminum is a vital material used in almost every industry. It ranks only behind iron and steel in production of metals and its demand continues to grow rapidly.\[1\] As companies and governments seek to reduce energy usage, especially in the transportation sector, aluminum is finding more and more use because it is lighter than steel while still providing significant strength. Aluminum also is used extensively in the marine and aviation industries because of the superior corrosion resistant properties.\[1\] Corrosion of aluminum costs governments and companies millions of dollars a year in maintenance and replacement costs. For the maritime industry, corrosion is the most significant problem from both an economic and maintenance standpoint. According to a study conducting by NACE International on behalf of the US DOT, corrosion costs the USA $276 billion a year, with $2.7 billion of that cost associated with just the marine transportation sector.\[2\]

Aluminum naturally forms a protective oxide layer that is corrosion resistant.\[3\] However, this natural layer provides poor long-term corrosion resistance and inhibits paint from properly adhering to the surface of the aluminum.\[4\] Thus, coatings were developed to provide aluminum with better long-term corrosion resistance.

Historically, the most common coating for aluminum was the chromate based conversion coating. However, due to the toxicity of the chromates, governments have enacted legislation limiting the use of chromates.\[5\] There continues to be significant pressure on the coatings industry to develop adequate coatings that are less toxic and
hazardous to the environment. Thus the need to find better replacements for chromate coatings is evident. This study has proposed the use of the titanate ion to replace the chromate ion in a conversion coating.

**A.2 Overview of Aluminum Alloys**

Aluminum alloys are generally divided into two major categories, wrought alloys and cast alloys. For most marine applications, wrought alloys are used and a four-digit system is used to identify the alloying components, such as 2xxx series aluminum alloy, which has copper as its principle-alloying element.[6] Cast alloys use a 3-digit system followed by a decimal system describing the casting alloy limit.[7] Other wrought alloys include 3xxx, 4xxx, 5xxx, 6xxx, and 7xxx series aluminum alloys, in which manganese, silicon, magnesium, magnesium and silicon, and zinc are the primary allowing elements, respectively.[6] The wrought aluminum alloys are further divided into two groups of heat treatable and non-heat treatable alloys. Heat treatable alloys, such as the 2xxx series and 6xxx series, are strengthened through heating and cooling of the material.[7] Non-heat treatable alloys, such as the 3xxx, 4xxx, and 5xxx series, derive their strength from the hardening provided by the principal-alloying element. Further strengthening is then provided through cold working, such as rolling.[7]

For this study, a 5086-H32 series aluminum, consisting of magnesium as the primary alloying element, was used. The H32 designation describes the strengthening process through which the aluminum was subjected. For 5xxx series, only non-heat treatable methods of strengthening are used, mostly cold rolling.[7] The H designates strain hardened through cold working. The 3 designates that the aluminum was
A low temp thermal treatment, which results in improved ductility. The two indicates the degree of strain hardening on a scale from 1 through 9.

A.3 Corrosion of Aluminum

Basic corrosion relies on 4 processes in order to occur. These include an anodic half-cell reaction, a cathodic half-cell reaction, ion transport and electron transport. If one of these processes does not occur, then corrosion will not occur. For aluminum, the anodic and cathodic reactions that take place are:

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad \text{(anodic half cell reaction)}
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4(\text{OH}^-) \quad \text{(cathodic half cell reaction in basic solutions)}
\]

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad \text{(cathodic half cell reaction in acidic solutions)}
\]

However, these above reactions will not occur under certain conditions. These conditions, based on the thermodynamic stability of aluminum in certain pH environments, are shown in Figure A-1. The Pourbaix diagram in Figure A-1 relates pH to potential. Aluminum forms its protective oxide layer in the passive region between pH 4 and 9. No corrosion will occur in this region because the Al\text{3+} ions that oxidize react with oxygen to form an aluminum oxide film at the same rate. However, if aluminum is exposed to an acidic environment with a pH less than 4, corrosion will occur following the cathodic half cell reaction for acidic solutions. An electrolyte such as salt water provides the necessary electrical contact for ion and electron transport to occur. All forms of corrosion that are prevalent with aluminum follow this basic electrochemical behavior, including pitting, crevice and intergranular corrosion.
A.4 Feasibility of Titanate as a Chromate Replacement

Titanate possesses very similar properties to chromium, especially from an electrochemical standpoint. The success of chromates in preventing corrosion is well documented. The Pourbaix diagrams for both elements show similar regions of passivity, indicating that both elements form stable oxides under similar conditions to prevent corrosion. The Pourbaix diagrams for both elements are shown in Figure A-2 and Figure A-3.

The titanate ion acts as a corrosion inhibitor, even when not applied as a conversion coating to the surface of a metal. A basic test was conducted using as received aluminum samples. Five sensitized samples (100°C for two weeks) were immersed in 0.5N NaCl solution, with rubber bands placed around the center of the sample, as shown in Figure A-4. Two samples were placed in a beaker with just tap water. The other 3 samples were placed in beakers with solution and 1 gram/Liter, 3 g/L, and 5 g/L potassium titanate, respectively. Figure A-4A shows a sample with no potassium titanate and Figure A-4B shows a sample with 5 g/L of potassium titanate. The results of the test, which spanned over 6 months, are shown in Figure A-5A and B. Figure A-5A contained no potassium titanate and is severely degraded. The sample with the potassium titanate, shown in Figure A-5B, is mostly intact and exhibited very little corrosion over the 6 month period. The results show the viability of titanate in providing protection against corrosion.

A.5 Electrochemical Impedance Spectroscopy (EIS)

EIS is heavily used by industry and researchers to investigate the quality of coatings on materials. The analysis is a non-destructive test method that permits the
time-dependent behavior to be measured. Impedance testing is conducted using a Gamry Framework Software Program that controls a Gamry PC4 potentiostat. The potentiostat is connected to a saturated calomel electrode that acts as the reference electrode. The working electrode is connected to a corner of the sample that has been polished to expose bare aluminum. A third counter electrode is a piece of platinum foil placed in the electrolyte. The setup for the system is shown in Figure A-6. The Gamry EIS system investigates the quality of the coating by inducing a small voltage over a wide frequency range, and measuring the resulting current, which can be used to quantify the impedance of the system and eventually its ability to resist corrosion. The higher the impedance value measured at low frequency, the better the corrosion resistance. The samples were tested at intervals of 1, 3, 5, 10, 20, 31, and 42 days as long as the coating remains intact. The 42 days is equivalent to 1000 hours. Regularly, the samples were also visually examined for signs of corrosion or crystal formation on the surface of the sample, which indicated that the coating may have failed. In almost all samples, a strong correlation existed between a visual failure of the coating, and drop in impedance values.

**A.6 Comparison of Samples**

A total of 5 different sample variations were used and tested throughout the study. These variations included the following:

1) Uncoated as received aluminum with no sensitization.
2) Uncoated as received aluminum that was sensitized.
3) Titanate coated aluminum with no sensitization.
4) Sensitized aluminum samples that were then coated with titanate.
5) Titanate coated aluminum samples that were then sensitized.

The first manuscript dealt with variations 1) and 3). Manuscript 2 dealt with variations 2), 4), and 5). Very little data were presented on variations 1) and 2) because both variations displayed visible corrosion a few days after exposure to the 0.5N NaCl solution. Amongst the remaining variations, there was significant difference in coating performance. For variation 3), the titanate coating process significantly improved the corrosion resistance of the aluminum over the 42 day test period, when compared to uncoated as received samples. The sensitized samples in variation 4) fared slightly worse. Samples that were sensitized for less than 2 weeks at 100°C generally exhibited good corrosion resistance over the 42 day test period. Any sample with a higher degree of sensitization did not fare well. All samples in variation 5) performed poorly, with most samples exhibiting visual coating failure after 20-30 days.

A.7 Equivalent Circuit Modeling

An equivalent circuit model was used to take experimental (raw) EIS data and determine more useful forms, such as coating resistance. The experimental impedance data was collected over a range of frequencies and plotted as ZCurve, shown in Figure A-7. The data was then modeled using the equivalent circuit model and the resulting fit is shown in Figure A-7 as Fit 1. For each fit, 5 values were extracted. Those values correspond to $R_s$ (solution resistance), $R_c$ (coating resistance), $R_p$ (polarization resistance), $CPA_c$ (constant phase element for the coating), and $CPA_{dl}$ (constant phase element for the double layer). A goodness of fit value was provided for each fit that was calculated by a non-linear least
squares method. Constant phase elements were used instead of capacitors because the system was not ideal.

**A.8 Future Work**

Since the coating showed promise on small samples of 5086-H32 alloy, the next step would be to scale up to larger aluminum alloy panels. The larger panels, most likely 10" by 3", would then be tested in a salt spray machine. Further investigation should be conducted on titanate to determine whether or not it exhibits the same self-healing properties as chromates. Also, since chromates are applied in many cases as a base layer before painting, the titante coating should be tested with a paint system to see if similar corrosion resistance is achieved.
Figure A-1: Aluminum Pourbaix Diagram\textsuperscript{[10]}
Figure A-2: Titanium Pourbaix Diagram\textsuperscript{[11]}
Figure A-3: Chromium Pourbaix Diagram\textsuperscript{[12]}
Figure A-4: (A) A sensitized sample in 0.5 NaCl solution. (B) A sample immersed under the same conditions with the addition of potassium titanate, visible in the bottom of the beaker.
Figure A-5: Results of the long term exposure test. (A) A sensitized sample was immersed in 0.5NaCl solution, (B) a sensitized sample was immersed in 0.5NaCl solution with potassium titanate.
Figure A-6: The setup for electrochemical impedance spectroscopy is shown with the (A) working electrode, (B) reference electrode, (C) and counter electrode.
Figure A-7: A Bode plot is shown with the experimental (raw) EIS data, shown as ZCurve, plotted with the model results, shown as Fit 1.
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