Electrodeposition of Aluminum on a CRES A286 Substrate from Ionic Liquids

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Abstract

Galvanic corrosion is a serious issue that affects all aircraft platforms within the Naval Aviation Enterprise. Often deposition of a metal film as a sacrificial coating is utilized as a method of protection. One process is the deposition of aluminum onto high strength steel substrates via the ion vapor deposition (IVD) process. While this process is effective in mitigating corrosion, the facilities required to perform this task are highly specialized, and the deposition process is line-of-sight only. To address these shortfalls, we have developed a method allowing for the electrodeposition of aluminum onto stainless steel using ionic liquid chemistries utilizing a relatively simple deposition setup. This increases the ease with which the system could be installed on-site while increasing the rate at which components could be repaired. This chemistry, coupled with an optimized pulse plating process, has led to a system which can successfully deposit high quality pure aluminum onto A286 stainless steel, providing protection against galvanically-driven corrosion. Furthermore, when exposed to corrosive environments, an A286 threaded bolt conformally coated in the aluminum film was galvanically coupled via salt water immersion for 177 days without film failure.
Introduction

One of the largest degraders to aviation fleet readiness and cost is corrosion. In 2016 alone, the Department of the Navy spent $9.8 billion on corrosion mitigation, with $2.9 billion being devoted to aviation-based issues. [1] Secondly, the effect of corrosion on air vehicle availability is significant. In FY16, corrosion was identified as the root cause for 31.3% of all aircraft non-available days. [2] The same report also noted that corrosion associated with airframe structure or skin was the most commonly occurring corrosion-based reason for non-available aircraft.

Due to the nature of aircraft design, galvanic corrosion is a significant concern. Often ribs or struts made of aluminum alloys will be connected using steel fasteners, introducing the risk of a galvanic couple due to dissimilar metal contact. In order to prevent corrosion from occurring, multiple techniques may be employed, either as a stand-alone process or in conjunction with other protection schemes. These include passivation of the steel, painting, or the use of sealant to prevent water intrusion. [3] Certain designs however, do not accommodate most of these methods, either due to dimensional tolerances or other operational concerns. To address these instances, coating the steel fasteners with aluminum via the ion vapor deposition (IVD) process or plating with cadmium are effective means to reduce the risk of galvanic corrosion. [4] However, both processes face current limitations. Cadmium has been identified as a toxic metal and environmental regulations continue to restrict the application of this process. [5] Aluminum coatings by the IVD process requires a highly specialized setup with significant technical training for all operators. These factors result in long lead times for certain components and reduce the ability to quickly repair damaged coatings. In contrast, aluminum electrodeposition via an ionic liquid requires a simple inert atmosphere apparatus in combination with a one-step chemical synthesis. This reduction in complexity increases the number of locations that can facilitate repair, thereby reducing the amount of time to repair or replace damaged components. The research presented here will provide a proof-of-concept demonstration for the deposition of aluminum on a corrosion resistant steel (CRES) A286 threaded bolt using a chloroaluminate-based room temperature ionic liquid (RTIL), while also demonstrating the film’s ability to provide galvanic corrosion protection.

Ionic liquids are defined as a mixture of salts which exist as a liquid below 100 °C. [6] This loose definition is often augmented with other, more attractive properties including an expanded electrochemical window, relative ease of synthesis, low vapor pressure and the ability to fine tune chemical composition to match desired parameters. [7] Typically, the liquid
comprises two solid species that, when mixed, form a liquid. The liquid formation is due to weak coloumbic interactions between the molecules, preventing the formation of an ordered crystalline structure. [8] Early research had shown that bulky organic compounds \textit{(i.e.} imidazolium- or pyridinium-based compounds) in combination with haloaluminate compounds yielded mixtures capable of aluminum deposition on various metallic substrates. [9] Since then, other mixtures with more varied characteristics have been developed, but none of these deposit aluminum as efficiently as the first generation of ionic liquids. [7]

An ionic liquid consisting of aluminum chloride mixed with 1-ethyl-3-methyl imidazolium chloride (EMIC) has demonstrated the ability to electrochemically deposit aluminum on various metallic substrates [10, 11, 12]. This is critical because aluminum electrodeposition is not possible in traditional aqueous-based systems as the deposition potential for aluminum is more negative than the electrolysis potential of water. Use of the EMIC/AlCl$_3$ mixture, capitalizing on the expanded electrochemical window, is what allows for the aluminum electrodeposition process to occur. While this liquid has been well characterized, the application for aluminum deposition on CRES A286 has yet to be investigated.

As part of the characterization, the chemical process facilitating the deposition of aluminum has been studied and described. [13] The initial reaction between the aluminum chloride and EMIC results in EMIC acting as a Lewis base, donating a chloride ion to aluminum chloride. (Eqn. 1.) If the molar ratio between aluminum chloride and EMIC is at least 1:1 then an aluminum chloride dimer can form. (Eqn. 2).

\[
\text{AlCl}_3 + \text{EMIC} \rightarrow \text{AlCl}_4^− + \text{EMIC}^+. \quad \text{(Eqn. 1)}
\]

\[
\text{AlCl}_4^− + \text{AlCl}_4^− \rightarrow \text{Al}_2\text{Cl}_7^− + 2\text{Cl}^− \quad \text{(Eqn. 2)}
\]

The formation of the dimer is critical to the deposition process, as it is the complex that facilitates aluminum deposition. (Eqn. 3)

\[
4\text{Al}_2\text{Cl}_7^− + 3e^- \rightarrow \text{Al}_3 + 7\text{AlCl}_4^− \quad \text{(Eqn. 3)}
\]

To aid in the deposition process, micromolar amounts of manganese chloride are added to the liquid. The addition of manganese aids in the deposition process by lowering the deposition potential, controlling both the crystallinity of the film. Grain size can also be controlled by the addition of manganese due to a reduction in the surface energy of each grain, enabling smaller grain formation. [14] Both of these factors are essential to the development of a thin, dense aluminum layer capable of providing corrosion protection.

As a deposition process, pulse plating provides the means to optimize film performance. [15] When a reductive current is applied, aluminum deposition occurs on the target substrate.
After a certain amount of time, the current is reversed to apply a weak oxidative current, allowing for the removal of high energy or poorly adhered aluminum from the film, reducing potential defects from the surface and increasing the uniformity of the film. The present study aims to demonstrate that utilization of the previously mentioned chemistry and pulsed electrochemical techniques have provided means of aluminum film deposition on A286 CRES threaded bolts. Furthermore, an evaluation of the film performance will demonstrate a proven ability to inhibit galvanic corrosion in both salt fog and immersive conditions.

**Experimental Section**

Aluminum chloride (99.99%), aluminum granules (99.7%, <1 mm), aluminum sheets (99.999%), manganese chloride (98%), and 1-ethyl-3-methyl imidazolium chloride (EMIC, >95%) were purchased from Sigma Aldrich. The aluminum, aluminum chloride, and manganese chloride were used without further purification, while the EMIC was dried to remove water, as described below. *Aluminum chloride reacts vigorously with water from the atmosphere to form HCl gas and must be handled carefully in a water-free atmosphere to avoid hazardous fumes.*

Acetone (ACS grade, >95%), ethanol (200 proof absolute), n-hexanes (ACS grade), diethyl ether (ACS grade), aluminum wire (99.999%), polyimide tape, Whatman ReZist PTFE syringe filters, and sodium chloride (USP crystalline, 99.0 %) were purchased from Fisher Scientific.

CRES A286 threaded bolts (1 inch long, 20 threads per inch) were purchased without any surface treatments from McMaster-Carr.

Before initiating the ionic liquid synthesis, the EMIC was dried in a vacuum oven at 110°C for 48 hours. Synthesis of the ionic liquid was done under a nitrogen environment to prevent water contamination in a glovebox made by Terra Universal. The aluminum chloride was combined with EMIC at a very slow rate, controlling the highly exothermic reaction, until \( \chi_{\text{AlCl}_3} = 0.66 \). After the correct amount of \( \text{AlCl}_3 \) had been added, aluminum granules, acting as scavengers for any hydrochloric acid byproduct, were added to the mixture and left to stir overnight. The liquid was then filtered successively through 5.0, 1.0 and 0.2 μm PTFE filters and doped with 5 mM of Mn\(^{2+}\) in the form of MnCl\(_2\). Unless otherwise noted, we refer to this solution as “ionic liquid” throughout the remainder of this work.

In preparation for aluminum deposition, the bolts were ultrasonically cleaned successively in n-hexanes, diethyl ether, acetone and ethanol for 10 minutes each to remove any residual contamination from the bolt fabrication process. After the bolt had air-dried, it was immersed in a 50% hydrochloric acid solution for 10 minutes, then rinsed twice with water and once with ethanol to ensure a spot free surface. Immediately after this, the bolt was set

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2. Thermo Fisher Scientific, 4500 Turnberry Dr., Hanover Park, IL 60133
3. McMaster-Carr, 600 County Line Rd., Elmhurst, IL 60126
4. Terra Universal Inc., 800 S Raymond Ave., Fullerton, CA 92831

**⁺ Trade Name**

inside of the plating cell. As seen in Figure 1, the cell consisted of high-purity aluminum counter electrodes creating a cage around the A286 bolt. All of the electrodes were held in place by a polylactic acid-based 3D printed cap, maintaining electrode orientation and distances. The bolt and the counter electrodes were connected to the Gamry Ref 600+ potentiostat\(^5\) cables by short pieces of 0.5 mm aluminum wire and the reference electrode was placed outside of the counter electrode cage. The reference electrode placement was chosen so that there would be no interference of the electric field lines facilitating deposition. The reference electrode, designed specifically for this process, consisted of a reference electrode glass body and Teflon heat shrink tubing from Princeton Applied Research\(^6\) and a borosilicate glass frit (4 – 8 μm pore size; Ace Glass\(^7\)). A 0.5 mm diameter aluminum wire (99.999% purity) was inserted through a rubber cap into the glass body which contained ionic liquid. In order to preserve stability of the reference electrode measurements, the liquid was saturated with aluminum chloride and contained no manganese chloride. After each experiment, the aluminum wire was removed and abraded to remove any impurities from the wire.

Figure 1
A schematic depicting the orientation of electrodes for the aluminum electrodeposition process.

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5. Gamry Inc., 734 Louis Dr., Warminster, PA 18974
7. Ace Glass Inc., 1430 NW Blvd., Vineland, NJ 08360

\(^*\) Trade Name
Before plating was initiated, the bolt was electrochemically activated in a bath of ionic liquid by applying a potential of +2.9 V vs a saturated aluminum electrode (SAE) [16] for 20 minutes to remove any remaining contamination on the surface. At the end of this process, all aluminum counter electrodes were replaced with clean aluminum electrodes and the cell was immersed in a second bath of ionic liquid for aluminum deposition. The galvanically driven pulse plating process was executed by applying a -8.6 mA/cm² reductive current for two seconds followed by a 125 μA/cm² oxidative current for 5 seconds. This cycle was repeated 9,257 times for a total deposition time of 18 hours, yielding an aluminum-coated bolt. Immediately after the deposition was completed, the bolt was removed from the bath and immersed in ethanol until gas evolution on the bolt surface had stopped. Neutralizing the residual ionic liquid was the cause of the gas formation and the neutralization must be done immediately to eliminate damage from the ionic liquid, which is highly corrosive.

After the deposition process was completed, verification of film deposition was confirmed using a Keyence VK-250 confocal laser profilometer [8]. To evaluate the improvement in corrosion resistance, two different methods were used. Evaluation of the film’s resistance to breakdown under immersive conditions were done by using a zero resistance ammeter technique with an aluminum-coated bolt as the working electrode, a polished A286 coupon as the counter electrode, and a saturated calomel reference electrode (SCE). The electrolyte was 3.5% (w/w) sodium chloride in ultrapure (18 MΩ·cm) water and the electrochemical testing was completed on a BioLogic VMP-300 [9]. For salt fog testing, three untreated A286 bolts and three aluminum-coated bolts were threaded through aluminum 7075-T6 alloys and secured with nylon washers. The bolts were tested according to GMW 14872 [17] for seven days and then removed. After disassembly and washing with ultrapure water, the side of the 7075-T6 coupon in contact with the underside of the bolt head was measured by laser profilometry and the total volume of material loss was determined. Film adhesion was evaluated using ASTM method D3359-17 and testing was done on the top face of the bolt hex head. [18]

**Results and Discussion**

The underlying methodology of the aluminum deposition process was developed on flat A286 coupons. [16] The process consists of four steps: 1) surface grinding and acetone/ethanol cleaning; 2) chemical activation in 50% (v/v) HCl; 3) masking followed by electrochemical activation at 2.9V vs. SAE in an ionic liquid bath; and finally, 4) electrodeposition from another ionic liquid bath. On these flat coupons, crystalline aluminum films with thicknesses between 45-60 μm, were deposited uniformly over the 1.7 cm² A286 substrates. Deposition of the film used a current-based pulsed plating scheme, focusing on the

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8. Keyence Corporation of America, 500 Park Boulevard, Itasca, IL 60143
9. BioLogic USA, LLC, 9050 Executive Park, Knoxville TN 37923

† Trade Name

use of both reductive and oxidative currents pulsed for fixed amounts of time to develop a high-quality film. The plating cycle for the flat A286 coupons comprised a \(-15 \text{ mA/cm}^2\) pulse, held for two seconds followed by a \(+60 \mu\text{A/cm}^2\) pulse held for 5 seconds. These pulses were repeated 9,258 times for a total of 18 hours of electrodeposition.

A few changes were necessary in order to modify the methodology developed on flat coupons for use on an A286 bolt. The surface of the bolt was not ground to improve adhesion; the surface finish was as-received. Given that the bolt was sourced commercially, a more rigorous solvent cleaning was employed wherein a polarity series of solvents (n-hexanes, diethyl ether, acetone and ethanol) was utilized to remove any contaminants from manufacture or packaging. A specialized counter electrode design (as depicted schematically in Figure 1) was developed to ensure appropriate current distributions and conformal coverage of the bolt, avoiding electrodeposition issues associated with geometry.

In addition to the necessary changes to the process steps, modifications were necessary for the electrochemical method as well. While optimizing the deposition methodology for the 1.7 cm² flat surface, the reductive current density was \(-14.7 \text{ mA/cm}^2\). However, scaling this current to match the surface area of the bolt (11.6 cm²) would require a total reductive current of approximately \(-175 \text{ mA per pulse}\). Based on preliminary experimentation not presented here, it was expected that the ionic liquid would be depleted of aluminum prior to the completion of the 18 hour (9,257 pulse cycles) deposition. To compensate for this depletion, two lower deposition currents were examined, \(-6.45 \text{ mA/cm}^2\), and \(-8.6 \text{ mA/cm}^2\).

It was anticipated that the lower deposition currents may result in incomplete coverage/gaps in the film, porosity, and/or reduced film thicknesses. For aluminum coatings deposited at \(-6.45 \text{ mA/cm}^2\), evidence of poor coverage was provided when examined microscopically (Figure 2) by the presence of striations related to the machining of the bolt. As discussed below, the corrosion properties of coatings deposited at \(-6.45 \text{ mA/cm}^2\) were also degraded. The aluminum coatings deposited at \(-8.6 \text{ mA/cm}^2\) displayed full coverage over the entire surface as can be noted in Figure 3. Further characterization by confocal profilometry of films deposited with the \(-8.6 \text{ mA/cm}^2\) current showed a surface roughness (Ra) of 4.47 μm (± 1.99 μm) and the average film thickness, as determined by cutting a groove in the aluminum film to the substrate with a razor, to be between 25 and 35 microns.

The successful deposition of a coating at the \(-8.6 \text{ mA/cm}^2\) current density also allows for an assessment of the effects of the omission of surface grinding, the change to the cleaning procedure, and the inclusion of a modified counter electrode as mentioned above. It would be expected that a surface that is highly oxidized or not sufficiently clean would result in poor film coverage or adhesion. The modified procedure appears to be adequate in this regard given the observed coverage and the fact that film adhesion was unaffected, with excellent adhesion and no loss of film when evaluated according to ASTM D3359-17. [18] This may indicate that the
critical step in preparing the surface for electrodeposition is the 2.9 V vs. SAE electrochemical activation, though more study is necessary to confirm this hypothesis. The conformal nature of the film would seem to indicate that the counter electrode acted as intended, allowing for equivalent current density and ion transport around the varied geometry of the bolt and resulting in a uniformly thick film.

![Figure 2](image)

**Figure 2**

Laser confocal profilometry images demonstrating the relationship between deposition current and surface coverage between two threads of an A286 bolt for films deposited with a reductive current of A) -6.45 mA/cm$^2$, and B) -8.6 mA/cm$^2$. The areas shaded red are the top of each thread, while the areas shaded blue are the valleys in between threads. Use of the -6.45 mA/cm$^2$ current resulted in inconsistent film deposition, identified by the presence of visible machine striations from the substrate as indicated by the red arrows. Increasing the deposition current to -8.6 mA/cm$^2$ removed these gaps in coverage and provided a continuous aluminum film over the entire surface.
A) A photomicrograph illustrating complete coverage of an aluminum coating on an A286 bolt electrodeposited with a pulse sequence utilizing a reductive current of -8.6 mA/cm² for 18 hours of deposition time. The dark section at the bottom of the threading is where the electrical connection was made with the potentiostat; and, B) a laser confocal microscopy image of the surface of the electrodeposited aluminum coating taken at 20x magnification.

Analysis of electrochemical polarization data for the flat A286 coupons in 3.5% (w/w) aqueous NaCl solution revealed that $i_{corr}=1.98\times10^{-3}$ A/cm² and $E_{corr} = -948$ mV vs. SCE for the electrodeposited films. Zero resistance ammeter (ZRA) testing was performed on the Al-coated A286 bolts. The ZRA testing was designed to simulate a galvanic couple between the bolt and uncoated A286 while immersed in a 3.5% (w/w) aqueous NaCl solution. The galvanic current and potential for the bolts plated with aluminum at -6.45 mA/cm² and -8.6 mA/cm² deposition currents are presented in Figure 4. It is of note that the initial galvanic potential of the bolt plated at lower current is near -760 mV, while the bolt plated at a higher current has an initial galvanic potential near -880 mV, much closer to the $E_{corr}$ of the flat films. The bolt plated at lower current failed after 72 days in galvanic testing, while the bolt at higher current did not fail after 177 days of testing. These data are in line with the qualities of the films observed via optical microscopy. It stands to reason that if the bolt plated at lower current does not have full coverage, the potential of this electrode would be mixed with the A286 substrate and start at a lower galvanic potential. Additionally, a thinner or less complete film will not offer equivalent protection, as evidenced by the premature failure of this coating.
Figure 4

Zero resistance ammeter monitoring of the galvanic corrosion current (top) and potential (bottom) between electrodeposited aluminum coatings on A286 bolts and bare A286 in 3.5% (w/w) NaCl aqueous solutions. Coating life is assessed by monitoring potential and current with respect to time, with failure defined as a sudden increase in potential and decrease in current. These features are seen in the -6.5 mA/cm² plot, occurring at the 72-day mark. Plots are identified by the reductive current density used to deposit aluminum on the surface. All other parameters were held constant during the deposition events.

Lastly, cyclic salt fog testing according to GMW 14872 [17] was conducted on mock components as a means of comparison to evaluate if the aluminum films provided noticeable protection against galvanic corrosion between the coated bolts and aircraft-grade (Al 7075-T6) aluminum substrates. Three aluminum-coated and three untreated A286 bolts were fastened through Al 7075-T6 coupons and subjected to seven cycles, corresponding to seven days. This length of exposure was expected induce noticeable corrosion-based damage to the Al 7075-T6 coupons as a result of the galvanic couple to A286. After removing all the bolts, washing each coupon with 18.1 MΩ·cm water, and immersing in 50% HCl to remove any remaining corrosion product, confocal profilometry analysis was used to measure the volume of material lost from the Al 7075-T6 alloy and then calculate the total mass lost from the coupon. No means of
mechanical cleaning (brushing, sonication) were used in order to preserve the surface for profilometry measurements. Not only did the profilometry images (Figure 5) show more severe physical damage for the control coupons, it was also determined that, on average, for the aluminum coated bolts, the 7075-T6 coupons lost 0.11 mg (± 0.03 mg) of material while the control samples lost an average of 0.84 mg (±0.34 mg). The optical images coupled with the material loss data confirms that the aluminum coated bolts successfully decreased the galvanic corrosion pathway, reducing the effects of corrosion on the aluminum alloy. It is also worth noting that $E_{corr}$ for films deposited on flat coupons were determined to be -948 mV, while most aluminum alloys have an $E_{corr}$ between -700 mV and -775 mV. This means that if the two materials are galvanically coupled then the coating will behave as the anode in a galvanic cell, protecting the more noble aluminum alloy from corrosion.

![Figure 5](image)

**Figure 5**
Laser confocal profilometry images demonstrating the effect of seven cycles of GMW 14872 cyclic salt fog testing on aluminum 7075 coupled to A) uncoated, and B) aluminum-coated A286 bolts. The green and blue coloration noted in A corresponds to pits found on the surface of the coupon, while the dark red corresponds to corrosion product.
Conclusion

Use of the EMIC/AlCl3 ionic liquid chemistry in combination with a chronoamperometric pulse plating process resulted in the deposition of aluminum films over the entire surface of CRES A286 bolts. The design of the counter electrodes, coupled with the application of an electrochemical activation process, provided films that had complete, conformal coverage and excellent adhesion to the substrate. In addition to the physical characteristics, electrochemically, the films exhibit a potential which is more negative than most common alloys. This is an essential feature of a sacrificial coating as it means that the coating should always act as the anode, preserving the substrate materials. In addition, the films also exhibit the ability to resist galvanic corrosion in multiple environments including salt fog and immersion conditions. This successful proof-of-concept demonstrated the potential for the application of ionic liquids as a media for aluminum deposition on aviation-relevant materials. To continue improving the process, future studies may include the development of new, less hazardous ionic liquids capable of the same process while also exploring the application of aluminum deposition on other alloys.

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References
