Testing Room-Temperature Ionic Liquid Solutions for Depot Repair of Aluminum Coatings

Elizabeth Berman, Ph.D., AFRL/RXSCP
Natasha Voevodin, Ph.D., AFRL/RXSCP/UDRI
Paul Brezovec, P.E., CEF, CTC
Michael Miller, CTC

E2S2 2011
Ernest N. Morial Convention Center
New Orleans, Louisiana
### Testing Room-Temperature Ionic Liquid Solutions for Depot Repair of Aluminum Coatings

Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 9-12 May 2011 in New Orleans, LA.

---

<table>
<thead>
<tr>
<th>1. REPORT DATE</th>
<th>2. REPORT TYPE</th>
<th>3. DATES COVERED</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAY 2011</td>
<td></td>
<td>00-00-2011 to 00-00-2011</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4. TITLE AND SUBTITLE</th>
<th>5a. CONTRACT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Testing Room-Temperature Ionic Liquid Solutions for Depot Repair of Aluminum Coatings</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6. AUTHOR(S)</th>
<th>5b. GRANT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Force Research Laboratory, AFRL/RXSCP, 2179 12th St, Ste 122, Wright Patterson AFB, OH, 45433-7718</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</th>
<th>5c. PROGRAM ELEMENT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Force Research Laboratory, AFRL/RXSCP, 2179 12th St, Ste 122, Wright Patterson AFB, OH, 45433-7718</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8. PERFORMING ORGANIZATION REPORT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</th>
<th>10. SPONSOR/MONITOR’S ACRONYM(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>11. SPONSOR/MONITOR’S REPORT NUMBER(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
</tbody>
</table>

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 9-12 May 2011 in New Orleans, LA.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

<table>
<thead>
<tr>
<th>a. REPORT</th>
<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>unclassified</td>
<td>unclassified</td>
<td>unclassified</td>
</tr>
</tbody>
</table>

17. LIMITATION OF ABSTRACT

Same as Report (SAR)

18. NUMBER OF PAGES

33

19a. NAME OF RESPONSIBLE PERSON

Standard Form 298 (Rev. 8-98)

Prescribed by ANSI Std Z39-18
Outline

A. Background of need
B. Incumbent coating process
C. Ionic liquids technology
D. Ionic liquids for aluminum deposition
E. Coating acceptance criteria
F. Technical challenges and process development
G. Summary
Background

An aluminum electrodeposited on a high-strength steel coupon. The deposit was produced using an ionic liquid electrolyte containing a dissolved aluminum salt.

- Aluminum (Al)
  a) Suitable replacement for cadmium
  b) Has a standard electrode potential of -- 1.676 volts versus the normal hydrogen electrode
  c) Requires specialized processing -- impossible to obtain the electrodeposition of aluminum from an aqueous solution (water hydrolyzes)
Drivers

• Need to repair Al coatings
  a) Pure (> 99%) Al coating electrodeposit
  b) Steel part surfaces
  c) Coating is not all within the line of sight

• Two major requirements:
  a) The repair process must comply with a facility’s environment, safety and occupational health (ESOH) requirements
  b) The coating must conform with MIL-DTL-83488, “Detail Specification Coating, Aluminum, High Purity”
Incumbent Aluminum Coating

- Original equipment manufacturers (OEMs) use incumbent Al coating on the part
  - Serves as a cadmium coating replacement
  - Al coating itself is considered to be safe
- Incumbent Al coating technology poses processing issues for a repair facility’s operation
  - Plating bath and its fumes ignite spontaneously in air
  - Stringent controls are required to eliminate moisture contact and mitigate the fire hazard in the facility
  - Currently only plated at coating vendor’s facilities
  - Weeks of delay in plating due to outsourcing
An “ionic liquid” (IL) is a salt in the liquid state

- Discussion will be limited to a “room-temperature IL” (RTIL), which has a melting point that is less than 100°C
- For example, “BMIM-PF₆” is an RTIL; table salt is not

Table Salt (NaCl) Crystal
Melting Point = 801°C

Ionic Liquid (BMIM-PF₆)
Melting Point = 11°C
RTIL Features

• High solvency (i.e., electrolyte for metal salt)
• Negligible vapor pressure (no VOC issues)
• Non-flammable
• Remain liquid within a wide temperature range
• Other properties may be tailored by the anion/cation selection
  o Physicochemical properties
  o Electrochemical properties
## Example RTIL Anions/Cations

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylated imidazolium</td>
<td>Trifluoroacetate</td>
</tr>
<tr>
<td></td>
<td>Bromide (Br⁻)</td>
</tr>
<tr>
<td></td>
<td>Chloride (Cl⁻)</td>
</tr>
<tr>
<td>Alkylpyridinium</td>
<td>Hexafluorophosphate</td>
</tr>
<tr>
<td>Dialkylpyrrolidinium /</td>
<td>Tri-fluoromethane sulfonate</td>
</tr>
<tr>
<td>Dialkylpiperidinium</td>
<td></td>
</tr>
<tr>
<td>Tetraalkylammonium</td>
<td>Tricyanomethide</td>
</tr>
<tr>
<td>Tetraalkylphosphonium</td>
<td>Tetrafluoroborate</td>
</tr>
<tr>
<td>Trialkylsulfonium</td>
<td>Bis(trifluoromethyl sulfonyl)imide</td>
</tr>
</tbody>
</table>

- Listing is not comprehensive, particularly for anions
- Dissolving additives into the RTIL adjusts electrolyte properties further
**Claimed Plating Opportunities**

- **Opportunity of new plating alloys** (e.g., Nb)
- **Plating of active elements** (e.g., Mg, Mo, Ta, Ti)
- **Quality of plating** is not quantitatively reported

---

Select Al Electroplating in RTIL

- Based options on the research literature
  - Cation
    - Dialkyimidazolium
    - Tetraalkylammonium
    - Tetraalkylphosphonium
    - Dialkylpyrrolidinium
  - Anion
    - Chloride
    - Bis(trifluoromethylsulfonyl)imide (“TFSI”)
- Based selection on commercial availability
  - 1-ethyl,3-methylimidazolium chloride ([EMIM]Cl)
Electroplating Al in [EMIM]

- Aluminum chloride (AlCl$_3$) dissolves in [EMIM]Cl, forming [EMIM] chloroaluminates:
  
  \[
  \text{[EMIM]Cl} + \text{AlCl}_3 \rightarrow \text{[EMIM]AlCl}_4,
  \]
  
  \[
  \text{[EMIM]AlCl}_4 + \text{AlCl}_3 \rightarrow \text{[EMIM]Al}_2\text{Cl}_7
  \]

  - Electrolyte is supplied pre-mixed

- Al is plated (Al↓) when there are more dissolved Al atoms than EMIM molecules:
  
  \[
  4\text{[EMIM]Al}_2\text{Cl}_7 + 3e^- \rightarrow \text{Al↓} + 4\text{[EMIM]AlCl}_4 + 3\text{AlCl}_4^-
  \]

  - 100% plating efficiency at 4 amperes/decimeter$^2$ (A/dm$^2$) has been claimed
Overview:

1. Remove soils/corrosion products/plating from surfaces
2. Activate the substrate (standard method); dry
3. Electroplate Al onto the activated areas:
   - Pure Al anodes
   - Elevating electrolyte temperature above room temperature (~90°C) improves activity
   - Mechanical agitation
   - Current density of 4 A/dm² (example)
4. Rinse and dry plating; Inspect the plating quality
Plating Candidates

1. Ionic liquid #1, to be used at CTC in evaluating processing scale-up at a depot and also submitted for plating tests

2. Ionic liquid #2, plated by a vendor

3. Ionic liquid #3, plated by a vendor; aluminum-zirconium (Al-Zr) alloy

4. Incumbent Al coating, as a baseline

5. Ion Vapor Deposition (IVD) Al, another baseline
# Coating Screening Acceptance Criteria

<table>
<thead>
<tr>
<th>Quality (MIL-DTL-83488)</th>
<th>Coating must be smooth, fine grained, adherent, uniform in appearance, free from staining, pitting, and other defects; coating must show no excessively powdery or darkened areas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion (ASTM B117)</td>
<td>Specimens shall show no evidence of corrosion of the base metal for a minimum of 504 hours, as specified in Table 1 of MIL-DTL-83488 for Class 1, Type I coatings. Additionally, the appearance of white corrosion products on the Al coating during the test period shall not be cause for rejection.</td>
</tr>
<tr>
<td>Thickness (ASTM B499 &amp; ASTM B487)</td>
<td>Al coatings shall be applied to a minimum thickness of 0.0010 in (1 mil), but no greater than 0.0015 in (1.5 mil)</td>
</tr>
<tr>
<td>Adhesion (Bend) (ASTM B571)</td>
<td>No separation of the coating from basis metal at interface shall be evident when examined at a minimum of 4X magnification (as per Section 4.4.2.2 of MIL-DTL-83488)</td>
</tr>
<tr>
<td>Porosity</td>
<td>Fewer identified pores on average than the average number of pores in baseline panels</td>
</tr>
</tbody>
</table>
Coating Morphology (ASTM B-487)

Back-Scattered Electron

- Incumbent at 200X
  - (as-plated)
  - >99% Al

- IVD Al at 200X
  - (glass shot peened)
  - >99% Al

- Alternative IL#1 at 200X
  - (as-plated, preliminary)
  - >99% Al

- Alternative IL#2 at 200X
  - (scuffed, preliminary)
  - >99% Al

Secondary Emission

(not tested)
Cross-Sectional Analysis (ASTM B-487)

**Incumbent**
Coated Panel at 500X

- **Statistics (Mil)**
  - Minimum: 0.940
  - Maximum: 1.270
  - Mean: 1.110
  - Std Dev.: 0.133

**IVD Al**
Coated Panel at 500X

- **Statistics (Mil)**
  - Minimum: 1.110
  - Maximum: 1.630
  - Mean: 1.440
  - Std Dev.: 0.245

**Alternative IL #2**
Coated Panel at 500X

- **Statistics (Mil)**
  - Minimum: 0.570
  - Maximum: 1.070
  - Mean: 0.802
  - Std Dev.: 0.217
CTC is resolving issues with coating thickness and adhesion via in-house IL #1 plating
  - Adjusting agitation to improve coating thickness uniformity
  - Adjusting pretreatment if necessary to improve adhesion consistency
  - Adding filtration to control debris in the bath

Identifying electroplating equipment required to plate aluminum from RTIL
  - Investigating use of tank liners vs. Teflon® tanks
  - Evaluating inert gas blankets and liquid seals for environmental isolation
  - Examining importance of timing between processing steps
Adhesion (ASTM B-571 Modified)

Panel S-9 Panel S-10 Panel S-11

IVD Al Coating

3-Point Bend (PASS)

Panel S-9

Bend-to-Break (FAIL)

Panel S-10

Panel S-11
The Need for Particle Filtration

Particle redeposited into the coating

SEM MAG: 203 x  
HV: 20.0 kV  
DET: BSE  
500 um
Details of 1-Liter Test Cell Arrangement

**Electroplating Bath Lid Arrangement**

- Thermometer
- Purge gas vent
- Anode lead
- Cathode lead (Extractable from the lid)
- Purge feed gas

**Electroplating Ionic Liquid Bath Set-up**

- Purge gas feed
- Anode (pure Al)
- Cathode (steel)
- Mixing stir
- Hot plate
Tooling Views of Lid for 1-Liter Test Cell

Top View

Side View

Rotated View

Ionic liquid containing a dissolved aluminum salt
Electroplate Arrangement for 1-Liter Test Cell

- Resistance
- Heat variable transformer
- Power supply
- In-situ cyclic voltammetry
- 1-liter test cell (insulated)
Cyclic Voltammetry for RTIL Contamination

Electrodes (3) Arranged in Lid Insert

Electrodes (3) Arranged in Lid Insert in Plating Solution, Connected to Potentiostat Leads

Cyclic Voltammetry Measurement In-Situ for Al Plating Solution

- Room temperature
- No agitation
- 0.07 cm² Pt disk area
- 100 mV/s scan rate
• indication of water contamination is observed via shape changes to the voltammogram, particularly that of the shaded section versus the voltammogram of the fresh electrolyte
Scale-up to Rectangular Tank

- TEFLON LID ASSEMBLY
- LINED STAINLESS STEEL INNER TANK
- STAINLESS STEEL OUTER TANK
Initial Cost-Benefit Analysis

- ALC plating Al remains financially favored after the 4th year, even with modified or new plating system installation ($1 million capital cost estimated)
- Cumulative present value savings = $5 million during 12 years operation

Note: Continuing search for “more defendable” cost data, which can be rapidly plugged into spreadsheet for updated CBA
Safety Considerations: Primarily Water

1. Water (H₂O) contamination
   - Reacts with chloroaluminate (AlCl₄⁻) anions:
     \[
     \text{AlCl}_4^- + \text{H}_2\text{O} \rightarrow \text{AlOCl}_2^- + 2\text{HCl} \uparrow
     \]
   - Liberates hydrogen chloride (HCl) gas
   - Forms oxychloroaluminate (AlOCl₂⁻)
     - Slows plating rate; requires AlCl₃ additions
     - Build-up of AlOCl₂⁻ requires recycling
   - Design limits H₂O contamination
     - Process allows for < 0.1 % H₂O by weight
Safety Considerations (continued)

2. Voltage excursion above ~2.7 volts
   • Chloride anion oxidizes to chlorine at anode:
     \[4\text{AlCl}_4^- \rightarrow 2\text{Al}_2\text{Cl}_7^- + \text{Cl}_2 + 2e^-\].

3. Candidate RTIL electrolyte handling
   • Electrolyte is a superacid
   • Plating bath operates at ~90 C
   • Personal protective equipment is required
     o Face shield, goggles
     o Nitrile gloves with elbow extension
   • Hands-on experience indicates hazards are manageable
1. AFRL/RXSCP and CTC are investigating a method for a depot to repair electroplated aluminum, using a near-commercial RTIL electrolyte, [EMIM]Cl-AlCl₃.

2. Al coatings are suitable cadmium replacements and lack watch-list chemicals like nickel.

3. RTILs offer the potential of a non-line-of-sight operation that is superior to spray coatings such as IVD Al plating.

4. The current test criteria for coatings produced from RTIL electrolyte are in conformance with the specification for pure aluminum deposits, MIL-DTL-83488.
5. Competitive plating rates have been achieved.

6. Adoption of this RTIL process at an ALC avoids outsourcing delays.

7. Preliminary CBA shows cost savings over alternatives.

8. As part of the processing activity, compliance with ESOH requirements are under preliminary review, including designs for container covers.

9. Process development is an ongoing effort; this is not currently an off-the-shelf technology for depot repair.

10. Testing of other ionic liquid technologies is pending.
Future Work

• Completing coating tests to confirm viability
• Examining more complicated geometries that are representative of aircraft
  o Hollow tubes with blind ends
  o Pins for hydrogen embrittlement testing
• Examining alloys based on aircraft applications
  o Fe-Co-Ni alloy, UNS K92580
  o Aluminum-bronze alloy, UNS C63000
  o Alloy Steel, UNS G41400
• Focusing tests on field-oriented needs, for example, strip-and-repair for a depot
Contacts

Elizabeth S. Berman, Ph.D.
USAF AFMC AFRL/RXSCP
Pollution Prevention Group
Materials & Manufacturing Directorate
Air Force Research Laboratory
2179 12th St, Ste 122
WPAFB, OH 45433-7718
Phone: (937) 656-5700
Elizabeth.Berman@wpafb.af.mil

Paul Brezovec, P.E., CEF
Concurrent Technologies Corporation
100 CTC Drive
Johnstown, PA 15904
Phone: (814) 269-2844
E-mail: brezovec@ctc.com

Natasha Voevodin, Ph.D.
USAF AFRL/RXSCP (UDRI)
Pollution Prevention Group
Materials & Manufacturing Directorate
Air Force Research Laboratory
2179 12th St, Ste 122
WPAFB, OH 45433-7718
Phone: (937) 656-5699
E-mail: natasha.voevodin@wpafb.af.mil

Michael Miller
Concurrent Technologies Corporation
7995 114th Avenue
Largo, FL 33773-5026
Phone: (727) 549-7285
Email: millermi@ctc.com
Putting ideas into action.™

1-800-CTC-4392
www.ctc.com