Investigation of Chemically Vapor Deposited Aluminum as a Replacement Coating for Cadmium

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**SUPPLEMENTARY NOTES**
26th Replacement of Hard Chrome and Cadmium Plating Program Review Meeting, January 24-26, 2006, San Diego, CA. Sponsored by SERDP/ESTCP.
Problem Statement

• Cadmium provides unique combination of properties when used as a coating on weapon and support systems
  – Ease of application, not line-of-sight limited, good adhesion and corrosion resistance, lubricity, low electrical (contact) resistance

• However, cadmium is associated with environmental, health and safety issues
  – Listed as a hazardous chemical
  – Emission levels set by the EPA, OSHA, various state and local agencies, as well as by Executive Orders

• Suitable replacement needed for high-strength steels other than currently used Ion Vapor Deposited (IVD) or sputtered aluminum
  – Line of sight deposition techniques
  – Vacuum requirement limits throughput and results in high cost
  – Usually require post-treatments to be effective
While CVD processes are well established, APCVD is currently used only for small-scale applications in the electronics industry ….

Thus, objective is to develop a high throughput/low cost atmospheric pressure chemical vapor deposition (APCVD) process to produce aluminum coatings on high-strength steel parts and components that:

- Meet environmental/compliance, health and safety goals
- Provide conformal surface coverage to desired thickness
- Have desirable physical, chemical, and mechanical properties that meet specified performance requirements
- Can be used in military (and commercial) aircraft
- Reduce life cycle costs while meeting mission (and industry) requirements
Technical Background

• Replacement candidates under investigation include electroplated Al-Mn, Zn-Ni and Sn-Zn alloys, metal-filled polymer composites, novel stainless steel alloys, and electroplated Al
  – Problems associated with all of these processes
  – Many not suitable for high-strength steels

• Aluminum has advantages over cadmium
  – Not a hazardous material
  – Good corrosion resistance (galvanic protection)
  – Good chemical resistance to aircraft fluids/chemicals
  – Withstands higher operating temperatures
  – Higher vapor pressure (necessary for space applications)
  – Acceptable alternative under MIL-DTL-83488
Key Technical Issues Addressed by APCVD Process

• Processes involving a vacuum process not required
  – Less complicated equipment; high throughput possible
• Low processing temperatures for high-strength steels
  – Mechanical properties of substrate material retained
• Avoidance of hydrogen uptake during processing
  – No environmentally assisted cracking (e.g., H₂ embrittlement)
• Conformal coatings of desired thickness and microstructure, compatible with substrate material
  – Protects substrate from damage and extends useful life
• Adherent coatings with required chemical, physical and mechanical properties
  – Protects part/component from corrosive/erosive environments and allows required function(s) to be performed
APCVD Process & Schematic of APCVD Reactor

• APCVD process involves a gas that reacts chemically at low temperatures with the surface of a part placed in a reaction chamber to form an Al coating.

• Process needs to be optimized for high-strength steel parts.

• Microstructure and properties can be controlled by adjusting deposition parameters.

Horizontal Tube Reactor Basic Design
[Other configurations exist, including rotating barrels for small parts]
Experimental Procedures

• Coating Deposition:
  – **Deposition Temperatures:** 300°C, 325°C
  – **Operating Pressure:** 760 mm (atmospheric)
  – **Substrates:** AISI 4130 steel coupons and fasteners (unpolished, roughness ~160nm rms)
  – **Precursors:** tetra-ethyl aluminum (TEA), tri-isobutyl aluminum (TIBA)
  – **Carrier Gas:** nitrogen

• Coating Characterization:
  – **Appearance, Thickness, Roughness:** metallurgical mounting and sectioning, optical microscopy, scanning electron microscopy, atomic force microscopy
  – **Composition, Structure:** energy dispersive x-ray analysis, x-ray diffraction, AES, XPS, NRA
  – **Hardness, Young’s Modulus:** nano-indentation
  – **Adhesion:** pull test
Results - TIBA Precursor

Findings: steel bolts

- Consistent conformal Al surface coverage, even in defects
Results - TIBA Precursor

Findings: steel coupons

- **SEM** image showed dense coverage of Al coating on steel substrate
- **AFM** analysis on the grains showed *relatively* rough surface

Roughness (RMS) = 917 nm
Film thickness = 20 um
Findings: Steel bolts and coupons

- **XRD** patterns of Al coating is very similar to that of Al powder (FCC) showing polycrystalline structure with high degree of crystallinity
Results - TIBA Precursor

Findings: Steel bolts and coupons

- AES Analysis - coating composition: Al=92.6%, C=6.1%, O=1.3%
Results - TIBA Precursor

• **XPS Analysis** - APCVD Al coating close to pure Al in bulk
Results - TIBA Precursor

• Hydrogen in Al coating
  – $^1\text{H}^{\text{15N}, \alpha\gamma}^{12}\text{C}$ NRA method
    • Ion beam energies of 7, 7.2, and 7.4 MeV were used to probe hydrogen concentration at different depths
    • Average concentration at these energies was found to be close to 1% (at.) indicating negligible hydrogen incorporation in the Al coatings during deposition

• Mechanical Properties of Al coating
  – Nanoindentation Test (diamond tip)
    • Hardness is ~550 MPa (not a critical performance parameter)
    • Young’s Modulus is ~36 GPa (some ductility; compare with bulk Al ≈70 GPa)
Results - TIBA Precursor

- Mechanical Properties of Al coating (cont’d.)
  - Adhesion (Pull) Test
    - Maximum load = 1,755 kg/cm²; accuracy within 1% at 20 ± 4 °C
    - Aluminum coating sample shows good adhesion (698 kg/cm²)

- Electrical Properties of Al coating
  - Electrical Resistivity
    - Resistivity = 11.9 μohm.cm (for an ~80 μm coating on Si₃N₄-coated steel sample)
    - Value higher than bulk Al (2.7 μohm.cm) probably because of lower purity and some porosity in this thick coating
Summary of Results

- Cross sectional analysis showed good conformal coating with uniform coating thickness
- Morphological analysis by SEM and AFM revealed that APCVD Al coating is dense and exhibits a rough surface
- XRD analysis revealed that the APCVD Al coating exhibits a pattern that is identical to that of the Al powder reference (FCC polycrystalline structure)
- Compositional depth profile by AES and XPS showed that APCVD Al coatings are oxidized on the surface but pure within the bulk
- NRA analysis reveals negligible hydrogen incorporation in the Al coatings
- APCVD Al coatings exhibit desirable adhesion
Transition Plan

• **Current Project will demonstrate viability of technology**
  – Process optimized for coating high-strength steel components
  – All performance requirements for coating high-strength steel components met
  – Technical and cost data made available to assess risk of technology implementation

• **Follow On Work will involve the following activities**
  – Optimizing coatings (e.g., lowering deposition temperature to ~200 °C
  – Designing, constructing and demonstrating a prototype production scale APCVD reactor
  – Conducting field trials on weapon system and other components
  – Demonstrating suitability of using an APCVD process in a depot working environment
  – Working with the Air Force, Army and Navy to transition to their applications for MRO operations
  – Working with industrial partner(s) to use technology on OEM parts
Key Team Members

• **Air Force Research Laboratory (WPAFB, OH)**
  *DoD requirements, program management, technical support*
  – Major Timothy P. Allmann
  – Dr. Eric W. Brooman

• **Army Research Laboratory (Aberdeen Proving Ground, MD)**
  *DoD requirements, testing of coatings*
  – Dr. John H. Beatty
  – Mr. Brian E. Placzankis

• **Naval Air Systems Command (Patuxent River, MD)**
  *DoD requirements, testing of coatings*
  – Mr. William Nickerson

• **New Jersey Institute of Technology (Newark, NJ)**
  *Process, coating and equipment development*
  – Prof. Roland A. Levy

• **The Boeing Company (St. Louis, MO)**
  *Industry liaison and technology insertion assistance*
  – Mr. Steven P. Gaydos
Acknowledgments

• NJIT (Coating Characterizations)
  – Yong Seok Suh
  – Sungmin Maeng
  – Sipeng Gu

• Acton Materials, Inc. (TEA-based Depositions)
  – Mr. John Kane

• Akzo Nobel Chemicals (TIBA-based Depositions)
  – Mr. Dennis Davenport
Back Up Exhibits
Joint Test Protocols

- JG-PP BD-P-1-1 (1999): “Validation of Alternatives to Electro-deposited Cadmium for Corrosion Protection and Threaded Part Lubricity Applications” (general surfaces and threaded parts)

- JG-PP J-00-MF-024B-P1 (2000): “Validation of Alternatives to Electrodeposited Cadmium for Electrical Connector Applications”

- USAF JTP (2003): “Validation of Alternatives to Low Embbrittlement Cadmium for High-Strength Steel Landing Gear and Component Applications”
## Adhesion Screening Test Methods for APCVD Al

<table>
<thead>
<tr>
<th>Engineering Requirement</th>
<th>Test</th>
<th>Acceptance Criteria/Measurements</th>
<th>Reference</th>
<th>Facility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion</td>
<td>Water Boil</td>
<td>No separation (flaking, peeling, or blistering) from the basis metal or from any under plating at the edge</td>
<td>ASTM B 571-91</td>
<td>NAVAIR</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Conical Mandrel Bend</td>
<td>Coatings visually examined for cracking: crack length is measured and using the length of the crack versus the mandrel diameter, the total elongation of the coating can be calculated.</td>
<td>ASTM D 522</td>
<td>ARL</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Pull-off Adhesion</td>
<td>Adhesion values &gt; 3,500 psi * Panels &gt; 1/8&quot; for steel must be used</td>
<td>ASTM D 4541</td>
<td>ARL</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Tape Adhesion</td>
<td>Ratings of 4 or 5 (X-Cut and Cross-cut methods)</td>
<td>ASTM D 3359</td>
<td>NAVAIR</td>
</tr>
</tbody>
</table>
# Test Methods/Assignments

## Compatibility, General Properties, Lubricity Test Methods for APCVD Al

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<tbody>
<tr>
<td>Compatibility with Substrate</td>
<td>Metallographic Examination</td>
<td>No degradation of substrate properties introduced as a result of deposition</td>
<td>Microscopy X-ray</td>
<td>ARL/NAVAIR NJIT</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>Contact Resistance</td>
<td>ECR &lt; 5,000 micro-ohms as coated</td>
<td>MIL-DTL-81706</td>
<td>NAVAIR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ECR &lt; 10,000 micro-ohms after B117</td>
<td></td>
<td></td>
</tr>
<tr>
<td>General Properties</td>
<td>Bent Cathode Thickness Uniformity</td>
<td>Plating thickness remains within class when measured after plating: composition of the coating must stay within the process range when measured using the X-ray Fluorescence (XRF) Alloy Composition Uniformity Test</td>
<td>Fed-Std-QQ-P-416F</td>
<td>NAVAIR</td>
</tr>
<tr>
<td>General Properties</td>
<td>XRF Alloy Composition Uniformity</td>
<td>Composition stays within the process specification requirements</td>
<td>ASTM B 568-91, ASTM E 1621</td>
<td>NAVAIR</td>
</tr>
<tr>
<td>Lubricity</td>
<td>Pin on Disk Coefficient of Friction</td>
<td>Coefficient of friction (COF) measured and compared with cadmium plated controls</td>
<td>ASTM G 99</td>
<td>ARL</td>
</tr>
<tr>
<td>Lubricity w/Corrosion</td>
<td>Pin on Disk Coefficient of Friction</td>
<td>COF measured and compared with Cd-plated controls after several successive specimen exposures (accelerated corrosion methods)</td>
<td>ASTM G 99, ASTM B 117, GM 9540P</td>
<td>ARL</td>
</tr>
<tr>
<td>Throwing Power</td>
<td>Coating Uniformity on Inner Diameter of Cylinder</td>
<td>Coating thickness remains within specification requirements along entire length of interior cylinder</td>
<td>NAVAIR and AF requirement</td>
<td>NAVAIR</td>
</tr>
</tbody>
</table>
## Test Methods/Assignments

### Corrosion Screening Test Methods for APCVD Al

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</thead>
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<tr>
<td>Sacrificial Coating Protection</td>
<td>Unscribed salt fog exposure</td>
<td>3,000 hours minimum with no red rust</td>
<td>ASTM B 117 MIL-DTL-83488</td>
<td>ARL/NAVAIR</td>
</tr>
<tr>
<td>Sacrificial Coating Protection</td>
<td>Scribed salt fog exposure</td>
<td>1,000 hours minimum with no red rust</td>
<td>ASTM B 117 MIL-DTL-83488</td>
<td>ARL/NAVAIR</td>
</tr>
<tr>
<td>Sacrificial Coating Protection</td>
<td>Unscribed cyclic exposure</td>
<td>80 cycles with no red rust.</td>
<td>GM 9540P</td>
<td>ARL</td>
</tr>
<tr>
<td>Sacrificial Coating Protection</td>
<td>Scribed cyclic exposure</td>
<td>40 cycles with no red rust</td>
<td>GM 9540P</td>
<td>ARL</td>
</tr>
<tr>
<td>Sacrificial Coating Protection</td>
<td>$E_{\text{corr}}$ vs. time (immersion)</td>
<td>Coating degradation greater than or equal to that of cadmium plated control specimens</td>
<td>ARL TR</td>
<td>ARL</td>
</tr>
<tr>
<td>Corrosion Resistance (fluid)</td>
<td>Fluid Corrosion Resistance</td>
<td>No coating degradation greater than that of cadmium plated control specimens</td>
<td>MIL-PRF-5624 MIL-H-6083 MIL-H-53282</td>
<td>NAVAIR</td>
</tr>
</tbody>
</table>
# Hydrogen Embrittlement & Fatigue Screening Test Methods for APCVD Al

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Susceptibility to Hydrogen Embrittlement</td>
<td>Rising Step Load</td>
<td>No degradation vs. Cd-plated controls on precracked CV2 (Charpy) specimens ESR4340, Aermet 100, 300M – at RC52</td>
<td>Incremental Step Loading per ASTM F1624 (Rising Step Load)</td>
<td>ARL</td>
</tr>
<tr>
<td>Fatigue Resistance</td>
<td>High Cycle Fatigue</td>
<td>No degradation vs. Cd-plated controls for fastener specimens ESR4340, Aermet 100, 300M – at RC52</td>
<td>MIL-STD-1312</td>
<td>NAVAIR</td>
</tr>
</tbody>
</table>