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

[SERDP Project Number PP-1405]

Major Timothy Allmann
Dr. Eric Brooman
Air Force Research Laboratory, WPAFB, OH
Prof. Roland Levy
New Jersey Institute of Technology, Newark, NJ

Presentation

Joint Cadmium Alternatives Team Meeting

San Diego, CA

29 January, 2006

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **29 JAN 2006**	2. REPORT TYPE	3. DATES COVERED **00-00-2006 to 00-00-2006**
4. TITLE AND SUBTITLE **Investigation of Chemically Vapor Deposited Aluminum as a Replacement Coating for Cadmium**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Air Force Research Laboratory,Wright Patterson AFB,OH,45433**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

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

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**24**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

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

Project Technical Objective

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

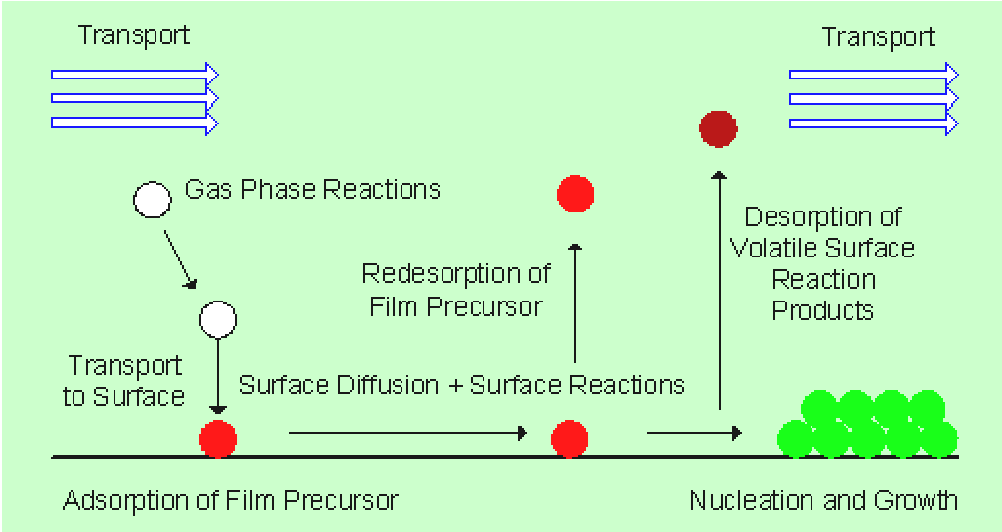
- **Aluminum has advantages over cadmium**
  - Not a hazardous material
  - Good corrosion resistance (galvanic protection)
  - Good chemical resistance to aircraft fluids/chemicals
  - Withstands higher operating temperatures
  - Higher vapor pressure (necessary for space applications)
  - Acceptable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

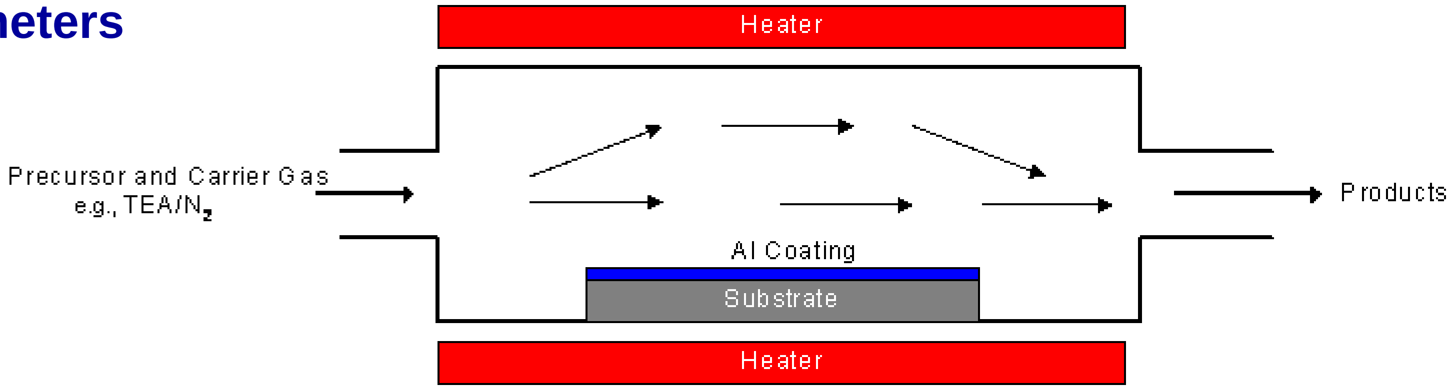
Key Technical Issues Addressed by APCVD Process

- **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., H_2 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]

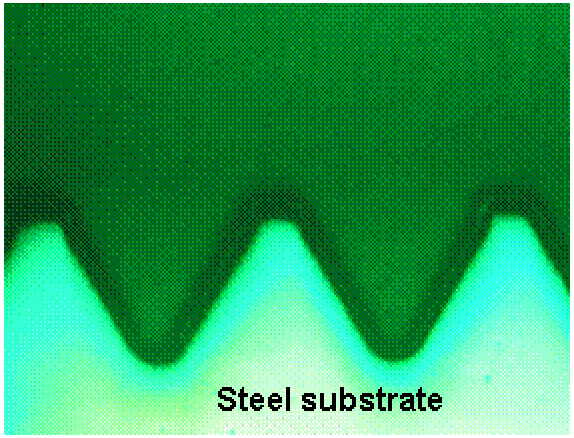
Experimental Procedures

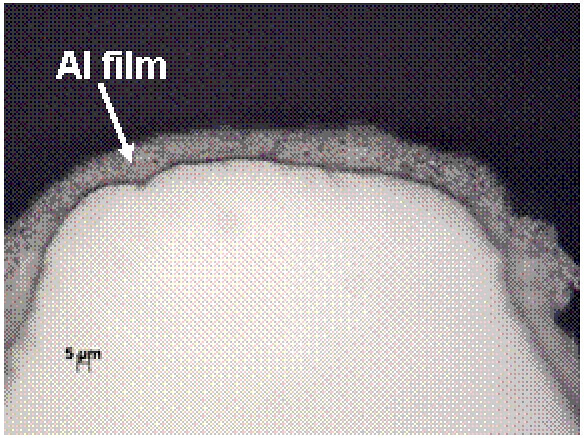
- **Coating Deposition:**
  - **Deposition Temperatures:** 300°C, 325°C
  - **Operating Pressure:** 760 mm (atmospheric)
  - **Substrates:** AISI 4130 steel coupons and fasteners (unpolished, roughness ~160nm rms)
  - **Precursors:** tetra-ethyl aluminum (TEA), tri-isobutyl aluminum (TIBA)
  - **Carrier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

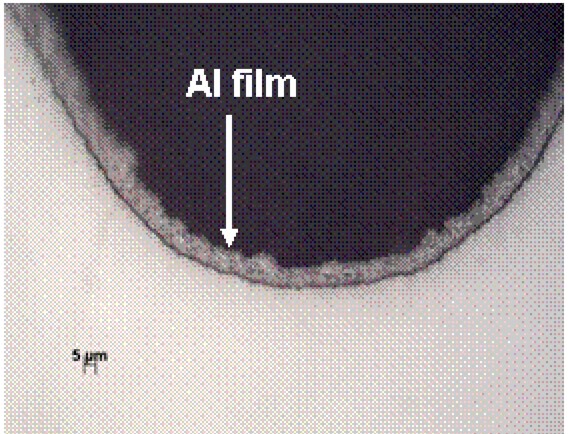
- **Coating Characterization:**
  - **Appearance, Thickness, Roughness:** metallurgical mounting and sectioning, optical microscopy, scanning electron microscopy, atomic force microscopy
  - **Composition, Structure**: energy dispersive x-ray analysis, x-ray diffraction, AES, XPS, NRA
  - **Hardness,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

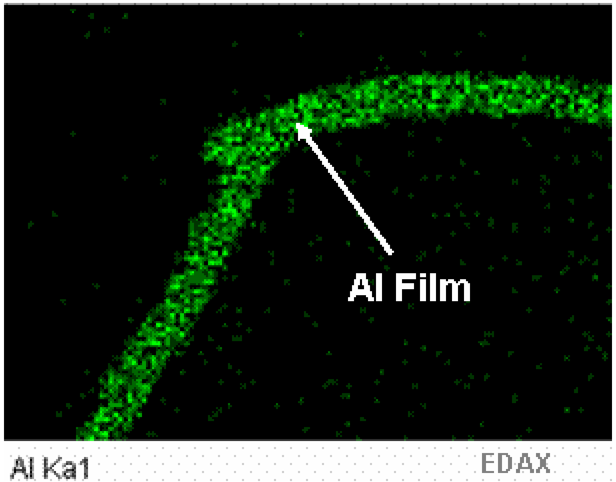
Results - TIBA Precursor

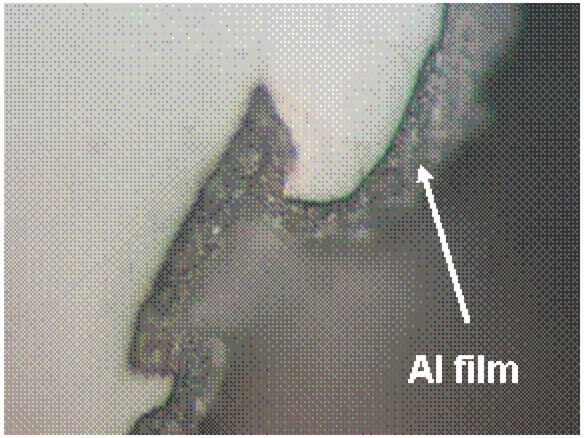
Findings: steel bolts







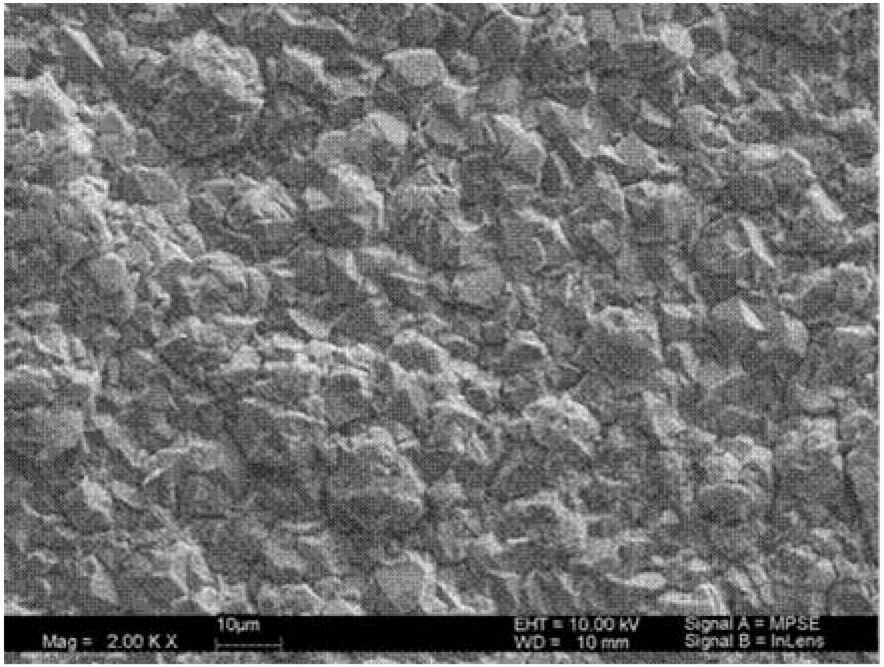


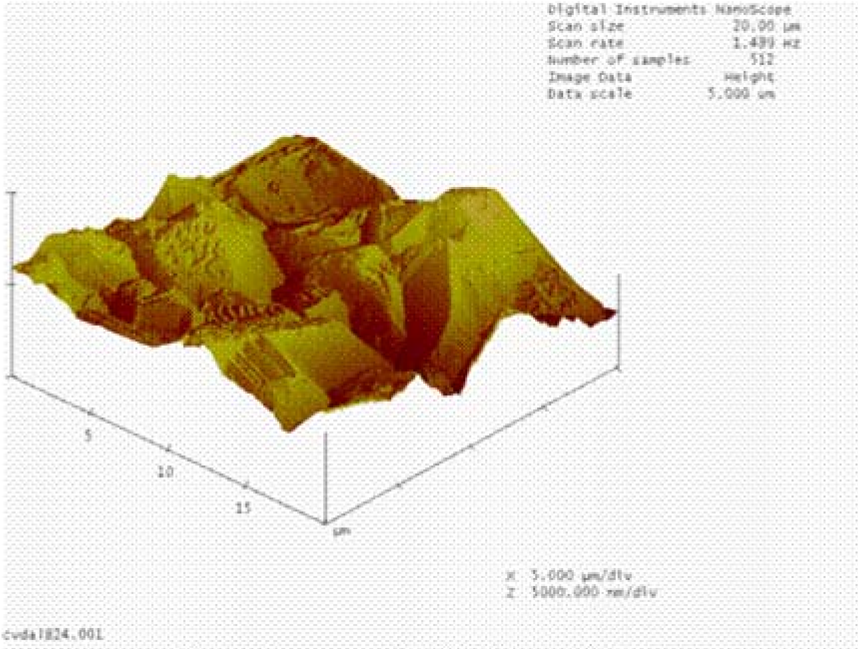


- Consistent conformal Al surface coverage, even in defects

Results - TIBA Precursor

Findings: steel coupons



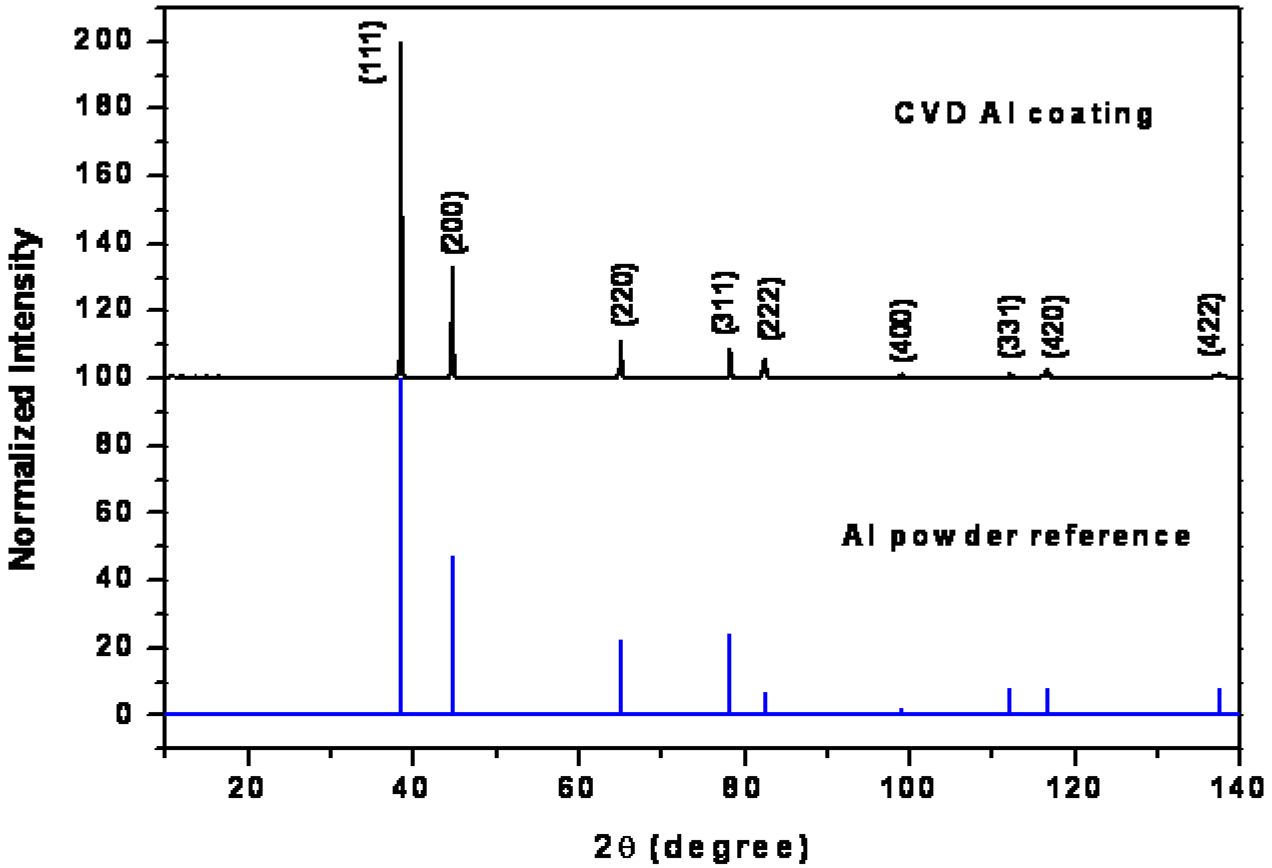


Roughness (RMS) = 917 nm
Film thickness = 20 um

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

Results - TIBA Precursor

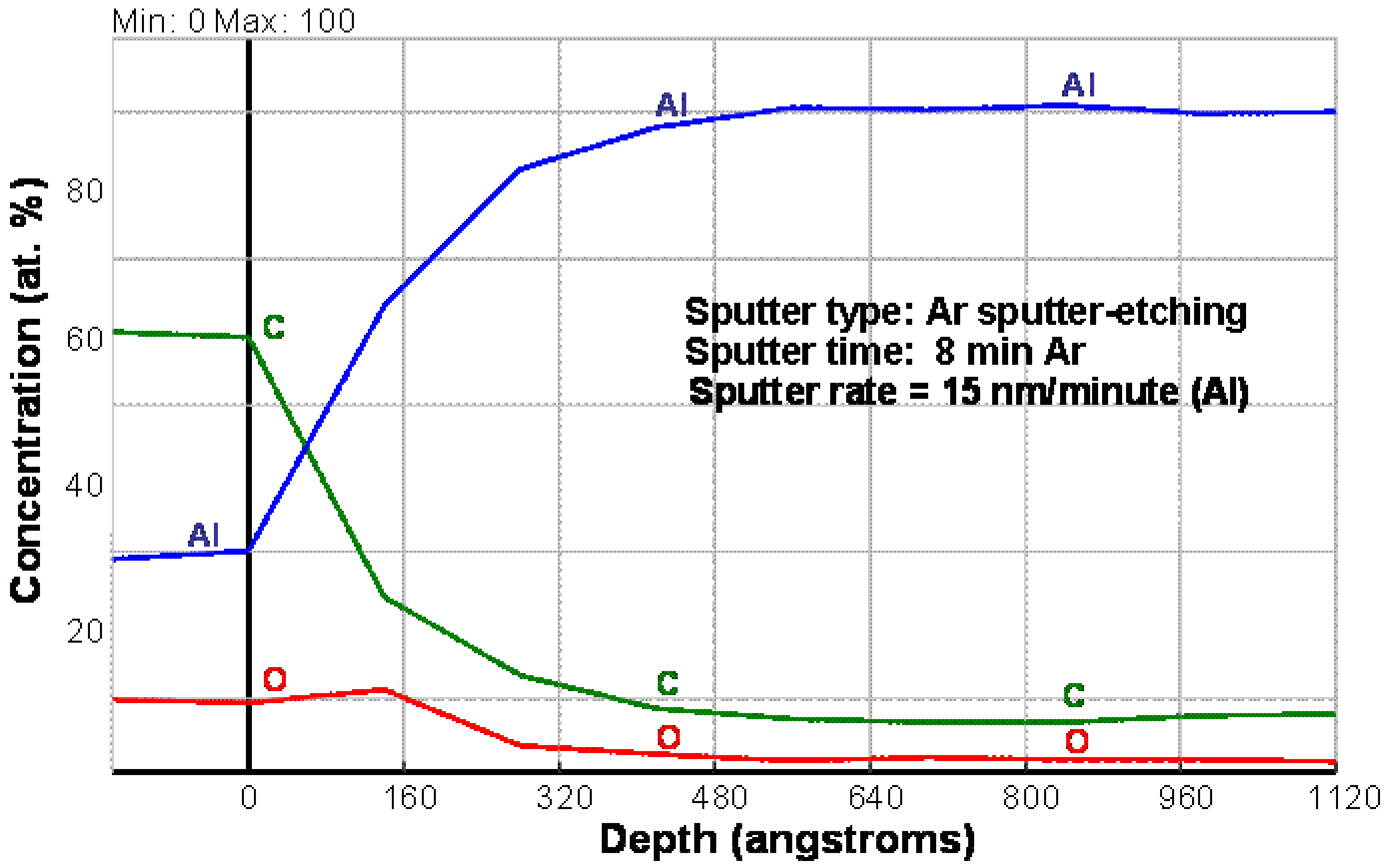
Findings: Steel bolts and coupons



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

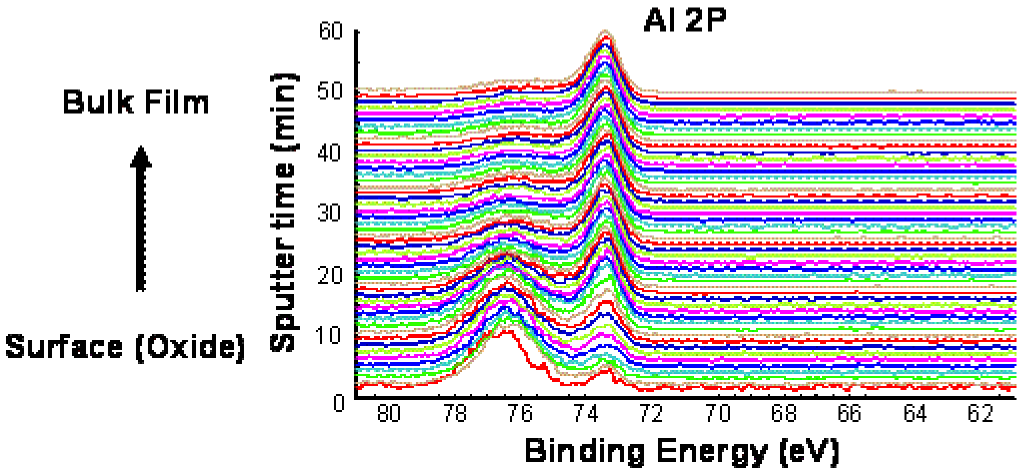
Results - TIBA Precursor

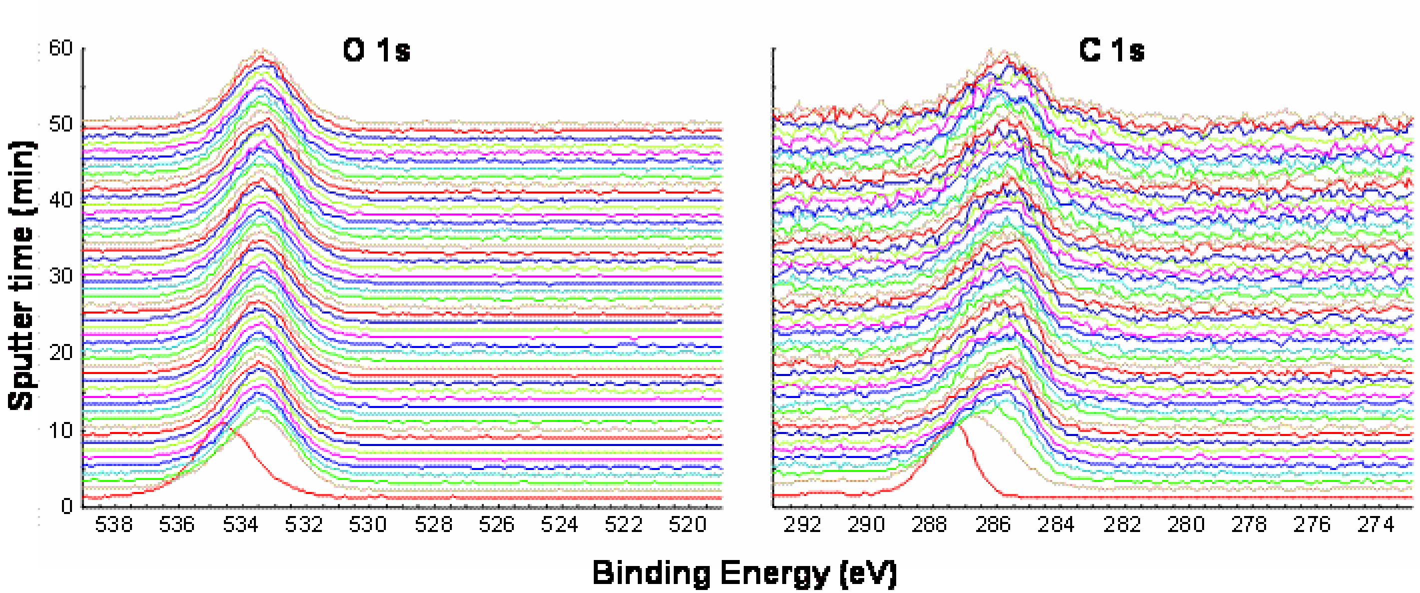
Findings: Steel bolts and coupons



- **AES Analysis** - coating composition: Al=92.6%, C=6.1%, O=1.3%

Results - TIBA Precursor



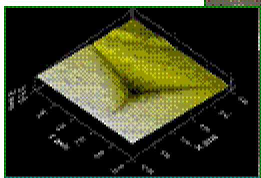


- **XPS Analysis** - APCVD Al coating close to pure Al in bulk

Results - TIBA Precursor

- **Hydrogen in Al coating**
  - **$^{1}H(^{15}N, \alpha\gamma)^{12}C$ 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)

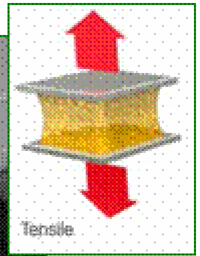


Typical Indentation

Nano-indenter Equipment

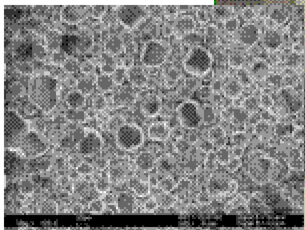
Results - TIBA Precursor

- **Mechanical Properties of Al coating (cont'd.)**
  - **Adhesion (Pull) Test**
    - Maximum load = 1,755 kg/cm^2; accuracy within 1% at 20 $\pm$ 4 °C
    - Aluminum coating sample shows good adhesion (698 kg/cm^2)

Pull Off Test Fixture

- **Electrical Properties of Al coating**
  - **Electrical Resistivity**
    - Resistivity = 11.9 μohm.cm (for an ~80 μm coating on Si_3N_4-coated steel sample)
    - Value higher than bulk Al (2.7 μohm.cm) probably because of lower purity and some porosity in this thick coating




Resistivity Test Equipment

Results - TIBA Precursor

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 ^{o}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 Embrittlement Cadmium for High-Strength Steel Landing Gear and Component Applications"**

Test Methods/Assignments

Adhesion Screening Test Methods for APCVD Al

Engineering Requirement	Test	Acceptance Criteria/Measurements	Reference	Facility
Adhesion	Water Boil	No separation (flaking, peeling, or blistering) from the basis metal or from any under plating at the edge	ASTM B 571-91	NAVAIR
Adhesion	Conical Mandrel Bend	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.	ASTM D 522 MIL-DTL-83488	ARL
Adhesion	Pull-off Adhesion	Adhesion values > 3,500 psi * Panels > 1/8" for steel must be used	ASTM D 4541	ARL
Adhesion	Tape Adhesion	Ratings of 4 or 5 (X-Cut and Cross-cut methods)	ASTM D 3359	NAVAIR

Test Methods/Assignments

Compatibility, General Properties, Lubricity Test Methods for APCVD Al

Engineering Requirement	Test	Acceptance Criteria/Measurements	References	Facility
Compatibility with Substrate	Metallographic Examination	No degradation of substrate properties introduced as a result of deposition	Microscopy X-ray	ARL/NAVAIR NJIT
Electrical Conductivity	Contact Resistance	ECR < 5,000 micro-ohms as coated ECR < 10,000 micro-ohms after B117	MIL-DTL-81706	NAVAIR
General Properties	Bent Cathode Thickness Uniformity	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	Fed-Std-QQ-P-416F	NAVAIR
General Properties	XRF Alloy Composition Uniformity	Composition stays within the process specification requirements	ASTM B 568-91 ASTM E 1621	NAVAIR
Lubricity	Pin on Disk Coefficient of Friction	Coefficient of friction (COF) measured and compared with cadmium plated controls	ASTM G 99	ARL
Lubricity w/Corrosion	Pin on Disk Coefficient of Friction	COF measured and compared with Cd-plated controls after several successive specimen exposures (accelerated corrosion methods)	ASTM G 99 ASTM B 117 GM 9540P	ARL
Throwing Power	Coating Uniformity on Inner Diameter of Cylinder	Coating thickness remains within specification requirements along entire length of interior cylinder	NAVAIR and AF requirement	NAVAIR

Test Methods/Assignments

Corrosion Screening Test Methods for APCVD Al

Engineering Requirement	Test	Acceptance Criteria/Measurements	References	Facility
Sacrificial Coating Protection	Unscribed salt fog exposure	3,000 hours minimum with no red rust	ASTM B 117 MIL-DTL-83488	ARL/NAVAIR
Sacrificial Coating Protection	Scribed salt fog exposure	1,000 hours minimum with no red rust	ASTM B 117 MIL-DTL-83488	ARL/NAVAIR
Sacrificial Coating Protection	Unscribed cyclic exposure	80 cycles with no red rust.	GM 9540P	ARL
Sacrificial Coating Protection	Scribed cyclic exposure	40 cycles with no red rust	GM 9540P	ARL
Sacrificial Coating Protection	E_{corr} vs. time (immersion)	Coating degradation greater than or equal to that of cadmium plated control specimens	ARL TR	ARL
Corrosion Resistance (fluid)	Fluid Corrosion Resistance	No coating degradation greater than that of cadmium plated control specimens	MIL-PRF-5624 MIL-H-6083 MIL-H-53282	NAVAIR

Test Methods/Assignments

Hydrogen Embrittlement & Fatigue Screening Test Methods for APCVD Al

Engineering Requirement	Test	Acceptance Criteria/Measurements	References	Facility
Susceptibility to Hydrogen Embrittlement	Rising Step Load	No degradation vs. Cd-plated controls on precracked CV2 (Charpy) specimens ESR4340, Aermet 100, 300M – at RC52	Incremental Step Loading per ASTM F1624 (Rising Step Load)	ARL
Fatigue Resistance	High Cycle Fatigue	No degradation vs. Cd-plated controls for fastener specimens ESR4340, Aermet 100, 300M – at RC52	MIL-STD-1312	NAVAIR