

Year 2 Update: Investigation of Chemical Vapor Deposited Aluminum as a Replacement Coating for Cadmium

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- **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

Aluminum has advantages over cadmium

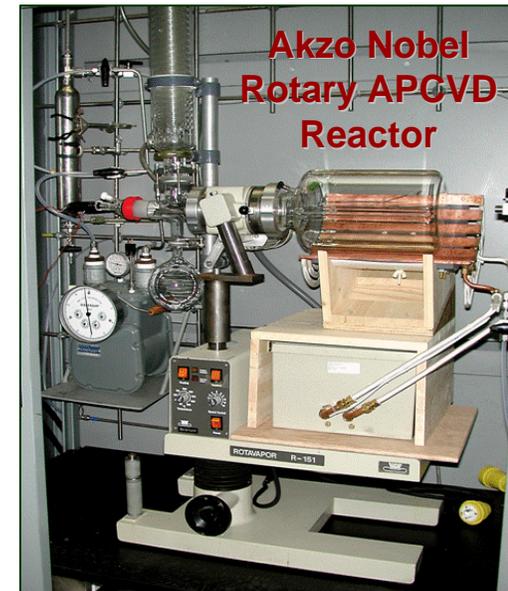
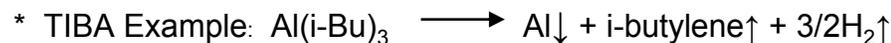
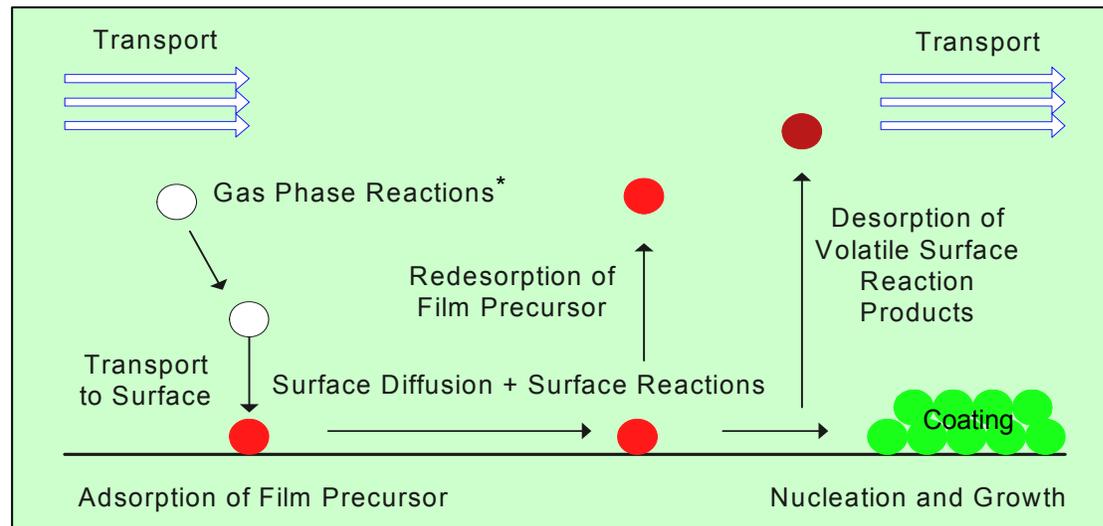
- Not a hazardous material
- Good corrosion resistance (galvanic protection)
- Good chemical resistance to aircraft fluids/chemicals
- Withstands higher operating temperatures
- Lower vapor pressure (necessary for space applications)
- Acceptable alternative under MIL-DTL-83488

Key Technical Issues to be Addressed by APCVD Process

- **Process not involving a vacuum process preferred**
 - Less complicated equipment; higher throughput possible
- **Low processing temperature for high-strength steels**
 - Mechanical properties of substrate material must be 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**
 - Protect substrate from damage and extends useful life
- **Adherent coatings with required chemical, physical and mechanical properties**
 - Protect part/component from corrosive/erosive environments and allow required function(s) to be performed

• Coating Deposition

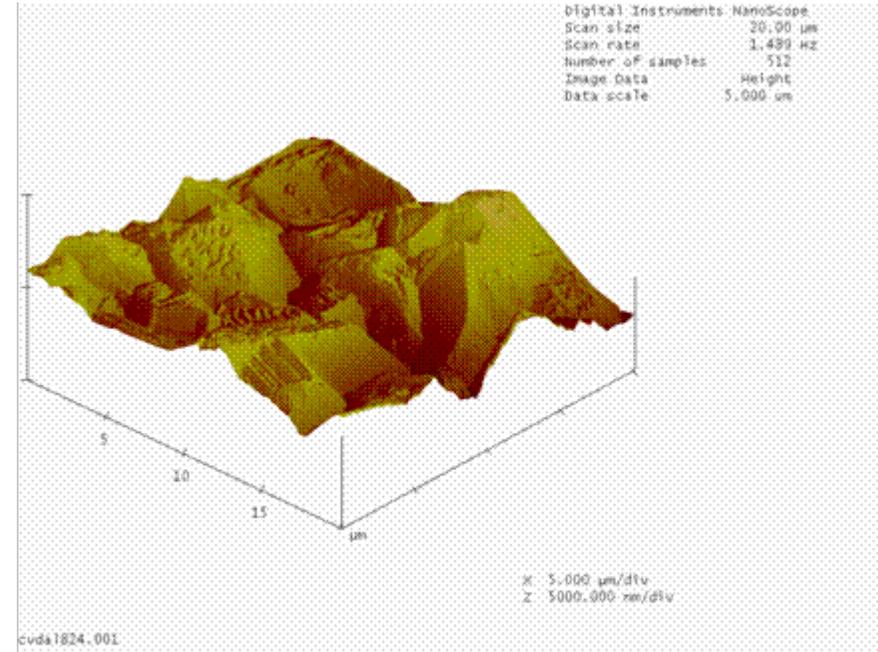
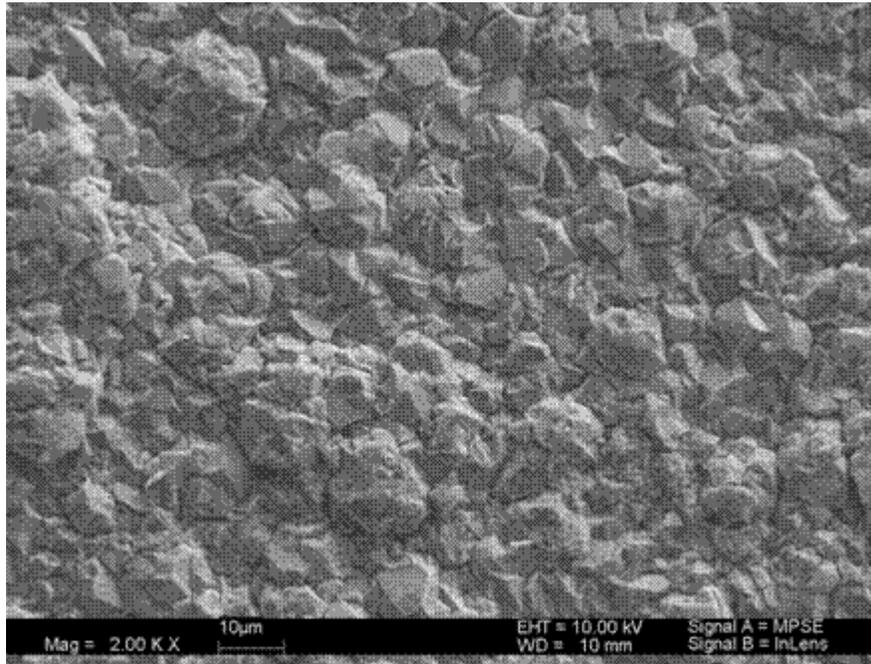
- **Precursors:** pure tri-isobutyl aluminum (TIBA); blended TIBA
- **Carrier Gas:** nitrogen
- **Deposition Temperatures:** 275°C, 300°C
- **Operating Pressure:** 760 mmHg (atmospheric)
- **Substrates:** AISI 4130 steel coupons, tubes, and fasteners



- **Year 2 Coating Characterization Testing**
 - **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 calculations
 - **Adhesion:** pull off test, tape adhesion, scribed panels
 - **Electrical resistivity:** four-point probe
 - **Step Coverage:** hollow rivet sleeve with inside step
 - **Throwing Power:** Al coating deposition on open and closed tubes with 0.1875" (3/16") and 0.3125" (5/16") OD, 2" length, and 0.0350" wall thickness

- **Year 2 Coating Performance Testing**
 - **Corrosion Resistance:** ASTM B 117 Neutral Salt Fog Test; unscribed and scribed specimens, painted specimens
 - **Paint Adhesion:** ASTM D 3359 Method A
 - **Hydrogen Embrittlement:** ASTM F 519 incremental (rising) step load test
 - **Lubricity/Wear:** ASTM G 99 Coefficient of Friction, Pin-on-Disk abrasive wear
 - **Tensile Strength and Fatigue Resistance:** MIL-STD-1312

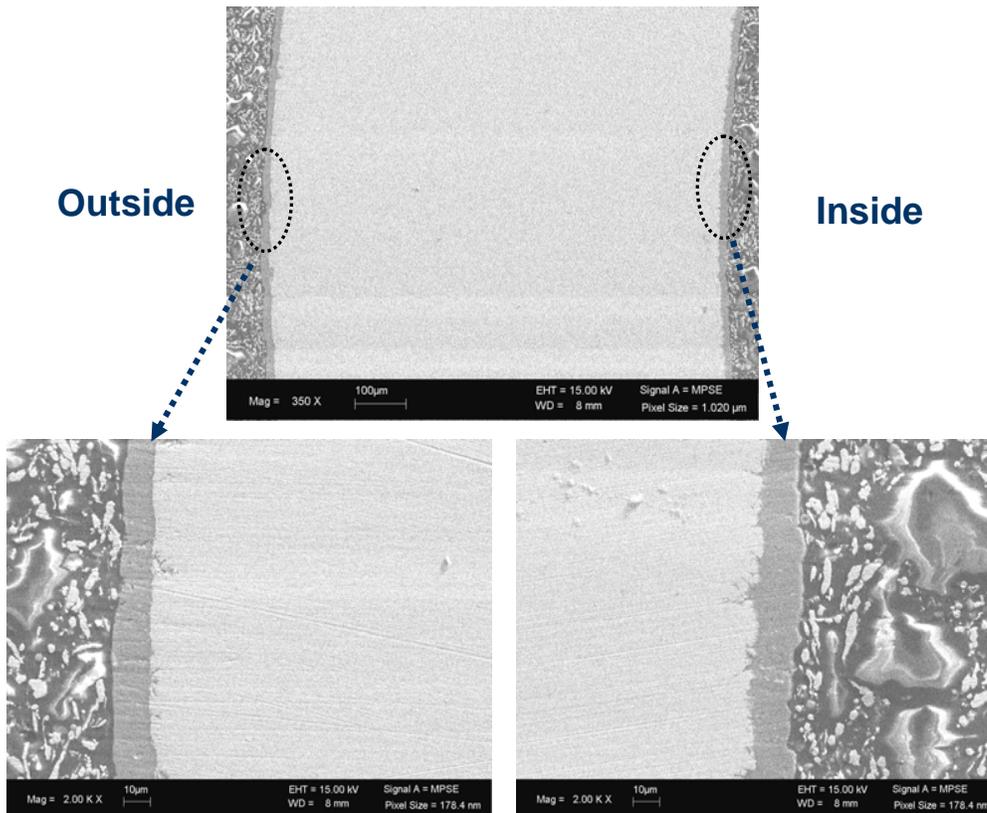
Findings: steel coupons, pure TIBA at 300°C



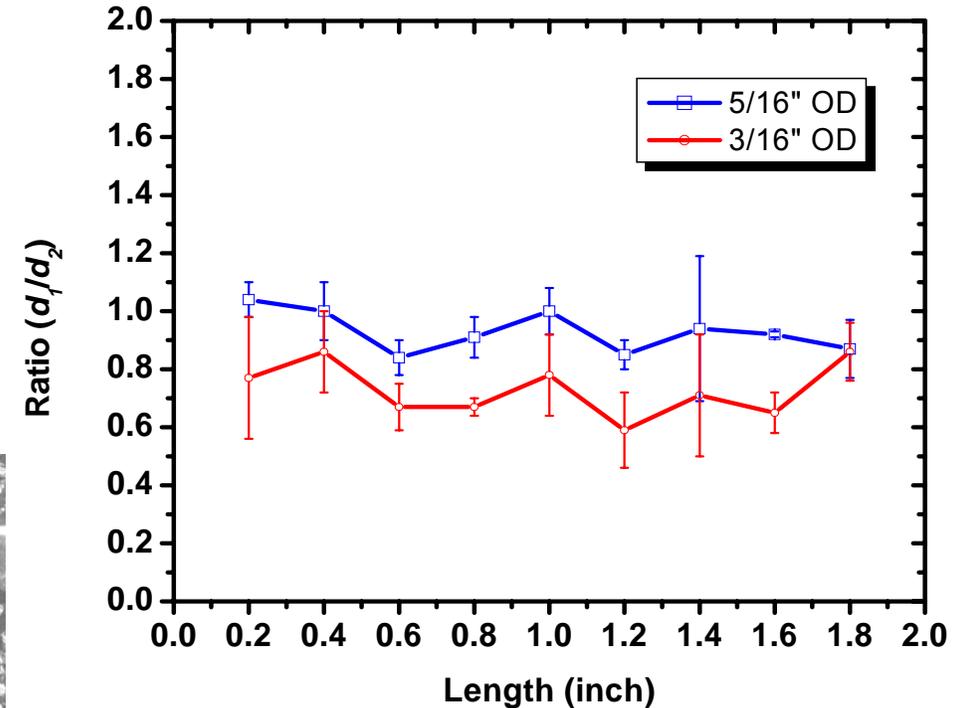
Roughness (RMS) = 917 nm
Film thickness = 20 µm

- **SEM** image showed dense coverage of Al coating on steel substrate
- **AFM** analysis of the surface showed a roughness on a nano-scale

Findings: Al on outside and inside of tubes; pure TIBA at 300°C



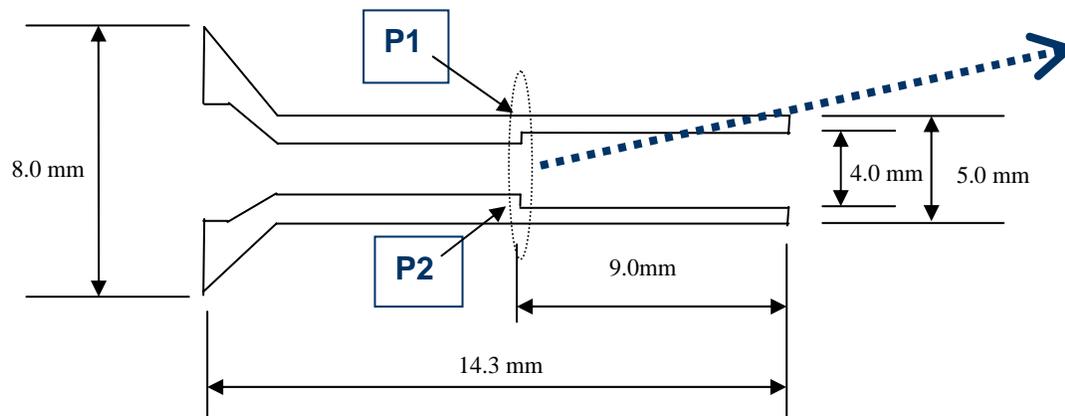
FE-SEM image showing cross section of Al coated tube (middle point)



d_1 = inside coating thickness
 d_2 = outside coating thickness

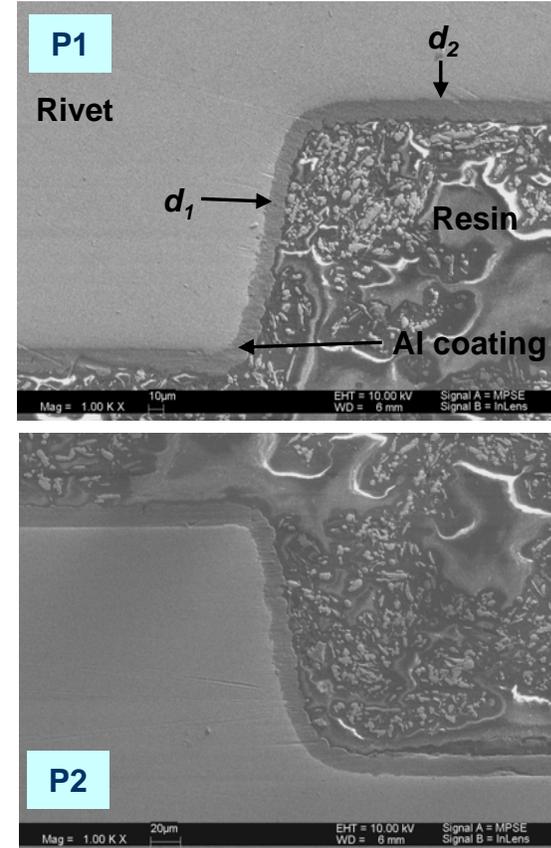
- **Al coatings exhibit excellent throwing power**

Findings: Al coating deposited on hollow rivet sleeve



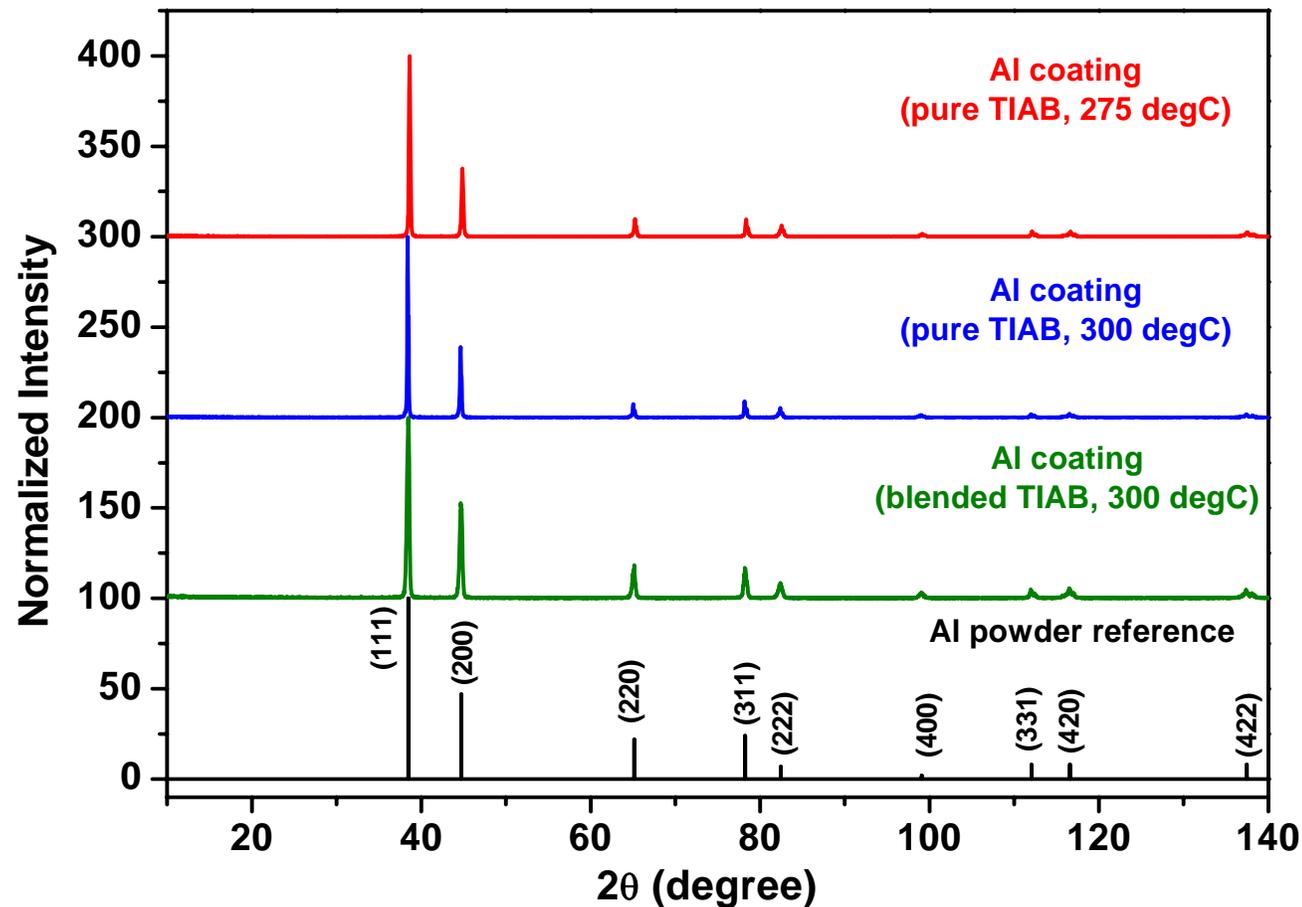
$$r = \frac{d_1}{d_2} = \frac{13.56 \mu\text{m}}{14.12 \mu\text{m}} = 0.96$$

[where d_1 and d_2 are average coating thickness]



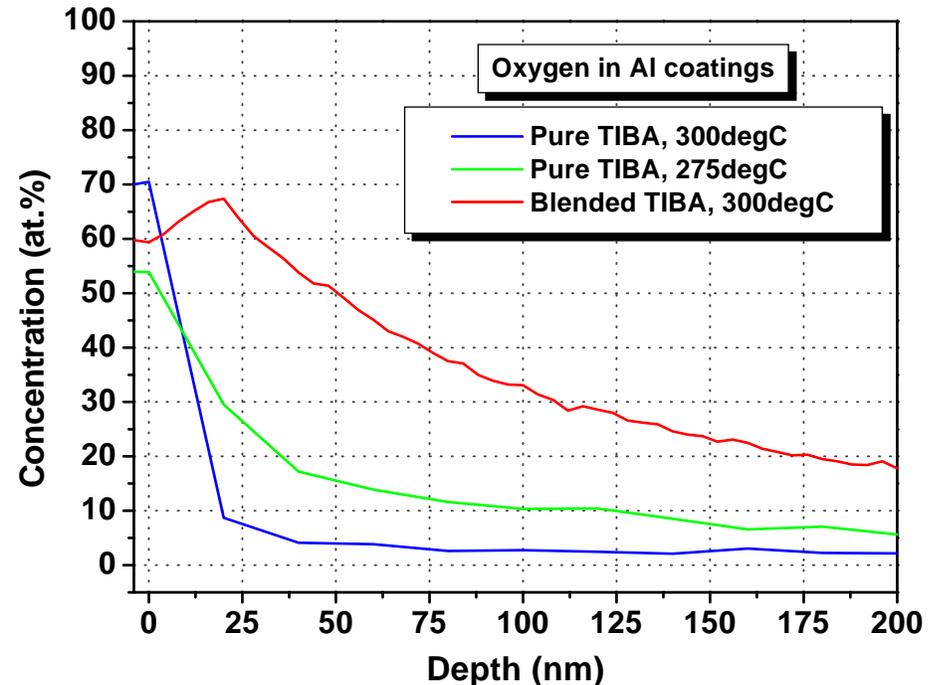
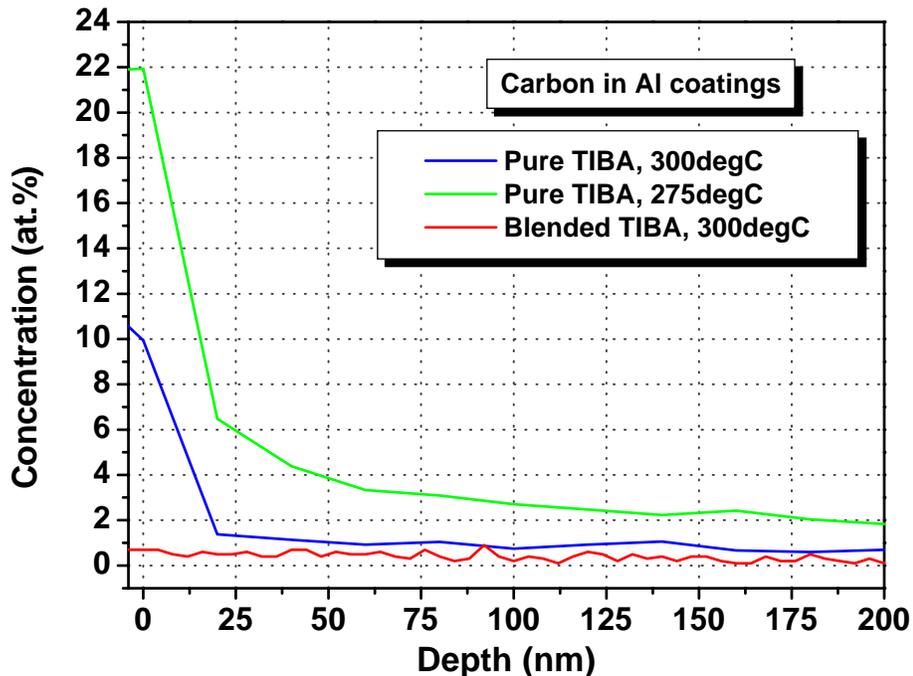
- **Al coatings exhibit excellent conformal coverage ($r = 0.96$)**

Findings: Al coatings on steel coupons



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

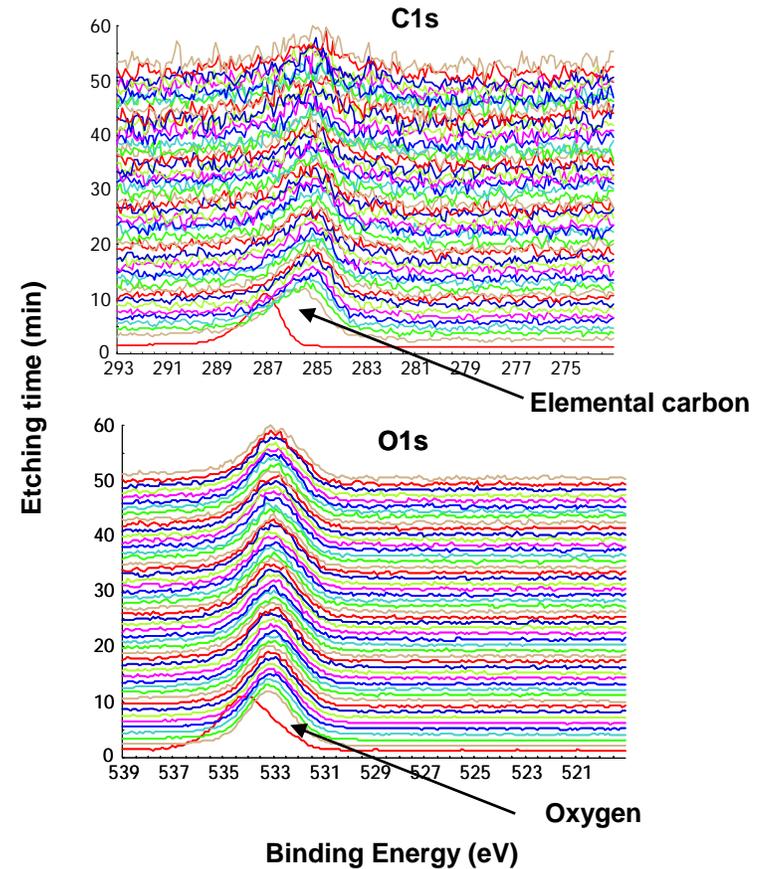
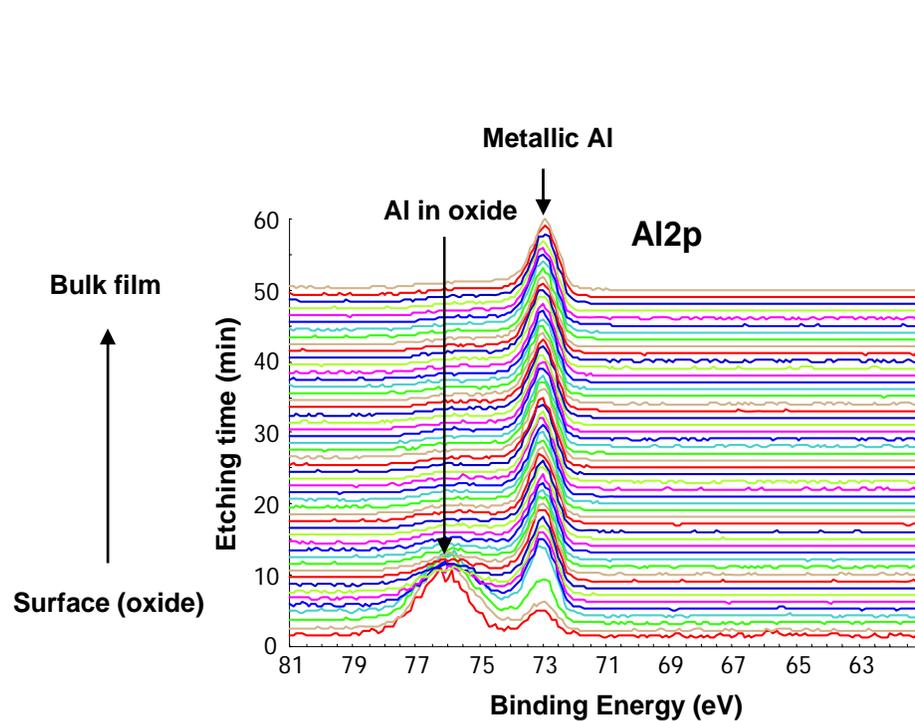
Findings: Steel coupons and fasteners; pure and blended TIBA



■ AES Analysis Summary:

- C contamination in Al coatings affected by process temperature
- Low C contamination observed in Al coatings using blended TIBA
- Low O₂ content observed in Al coatings using pure TIBA

Findings: Steel coupons and fasteners; pure TIBA at 300°C



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

- **Mechanical Properties:** TIBA at 300°C

- Adhesion (Pull) Test on AISI 4130

- 703±85 kg/cm² (pure TIBA)
 - 684±30 kg/cm² (blended TIBA)

- Nanoindentation Test

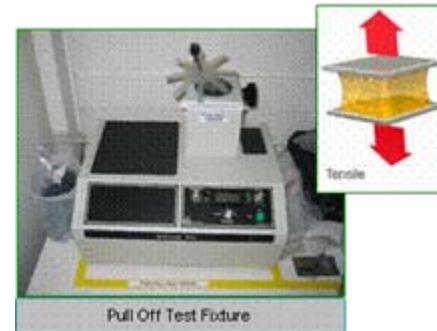
- Hardness is ~551 MPa
 - Young's Modulus is ~36 GPa

- Coefficient of Friction

- Greater for APCVD Al coatings than Cd coatings (as expected)

- **Electrical Resistivity:** TIBA at 300°C

- Resistivity = 3.5 ±0.1 μohm·cm (~14.7 μm coating on Si₃N₄-coated steel sample)
 - Value close to bulk Al (2.7 μohm·cm) indicating purity of Al coating



Preliminary Salt Fog Exposure: pure TIBA at 300°C

- 1"X 2" AISI 4130 steel coupon substrate
- ASTM B 117 salt fog testing

17 days in B117 salt fog



As deposited



Scribed as deposited



With TCP



Scribed with TCP

- Red rust began to form at 27 days - test discontinued
- Post treatment with TCP did not improve corrosion resistance
- TCP needs to be optimized for this coating

APCVD Al meets Type I, Class 1 Cd Coating Requirement

Preliminary Painted Corrosion Test: pure TIBA at 300°C

- 1" X 2" AISI 4130 steel coupons
- MIL-PRF-23377C primer and MIL-PRF-85285 topcoat
- ASTM B 117 salt fog testing

After 17 days in B117 Salt Fog



Unscribed



Scribed

- **All painted coatings exhibit good corrosion resistance - no blistering or red rust up to 27 days - test discontinued**

- Preliminary tensile strength measurements
 - Al coatings deposited on notched round bars (Control - AISI 4340 bar (ultimate tensile \approx 400 ksi))
 - *Notch tensile strength not in acceptable range*
 - H₂ relief bake after Al coating deposition
 - *Notch tensile strength in acceptable range*
- ASTM 519 rising step load method
 - Al coatings deposited on notched round bars (Control - AISI 4340 bar (ultimate tensile \approx 400 ksi))
 - *Failed HE rising step load test*
 - H₂ relief bake after Al coating deposition
 - *Passed HE rising step load test*

Round bar



Round bar test in progress

- Morphological analysis by SEM and AFM revealed that the APCVD Al coatings are dense and rough, but on a nano-scale
 - APCVD Al coatings exhibit excellent conformal coverage with uniform coating thickness
 - APCVD Al coatings exhibit excellent / good:
 - throwing power
 - step coverage
 - adhesion
 - hardness
 - Coefficient of friction of APCVD Al higher than for Cd, but still acceptable
-
- APCVD Al coatings exhibit face-centered cubic pattern that is identical to that of the Al powder reference (XRD)
 - Compositional depth profile shows that APCVD Al coatings are oxidized on the surface but relatively pure within the bulk (AES / XPS / NRA)
 - C, H₂ and O₂ impurity concentrations depend on deposition temperature and type of precursor used

Conclusions (cont.)

- Preliminary corrosion test (salt fog): APCVD Al (bare) met requirement for a Type I, Class 1 Cd coating
- Preliminary painted corrosion test (salt fog): No loss of adhesion for the exposure time used
- Tensile strength and hydrogen embrittlement tests: preliminary data promising when APCVD Al coatings receive the conventional hydrogen relief bake post treatment used for Cd

- **Further In-depth Physical Property Testing (i.e.adhesion, compatibility w/ substrate)**
- **Fluid / Cleaning Chemical Corrosion Resistance**
- **Optimization of Deposition / Processing Temperature**
- **Develop Plan to Scale Up APCVD AI Process**

- **NJIT (Coating Characterizations)**
 - Dr. Sung Min Maeng
 - Dr. Yong Seok Suh
 - Mr. Sipeng Gu