CAMT

Center for Aerospace Manufacturing Technologies

Environmentally Friendly Coatings for Corrosion Protection of Aluminum Alloys

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Coatings Overview

- **Goal:** Investigate materials and processes for a non-chromate coating system for corrosion protection for high strength aluminum alloys
- **Focus areas:** Develop processes for deposition of cerium-based conversion coating (CeCC) for 2024-T3 and integrate with non-chromate primers
- **Cooperative Research with Boeing**
  - Testing of CeCCs with non-chromate primers
  - Deft and PRC DeSoto primers
  - Five separate spray series, over 500 panels
  - Neutral salt spray testing to ASTM B117
- **Outcomes:**
  - CeCC spray deposition process was developed
  - Corrosion performance was inferior to chromates
  - Corrosion in scribes

FIB Acquisition Overview

- **Goal:** Acquisition of a dual beam focused ion beam (FIB) scanning electron microscope system
- **Outcome:** A Helios Nanolab 600 from FEI was installed in B-18 McNutt and is available for use through the Materials Research Center

Coatings Outline

- **CeCC deposition processes**
  - **Spray deposition**
  - **Influence of organic additives and process parameters**
  - **Coating microstructure, properties, and performance**
- **Coating system evaluation**
  - **Non-chromate primers on CeCCs**
  - **Chromate control samples for comparison**
  - **Adhesion testing**
  - **Corrosion performance**

CeCC Spray Process

Al Panels

Cleaning

Spray Process

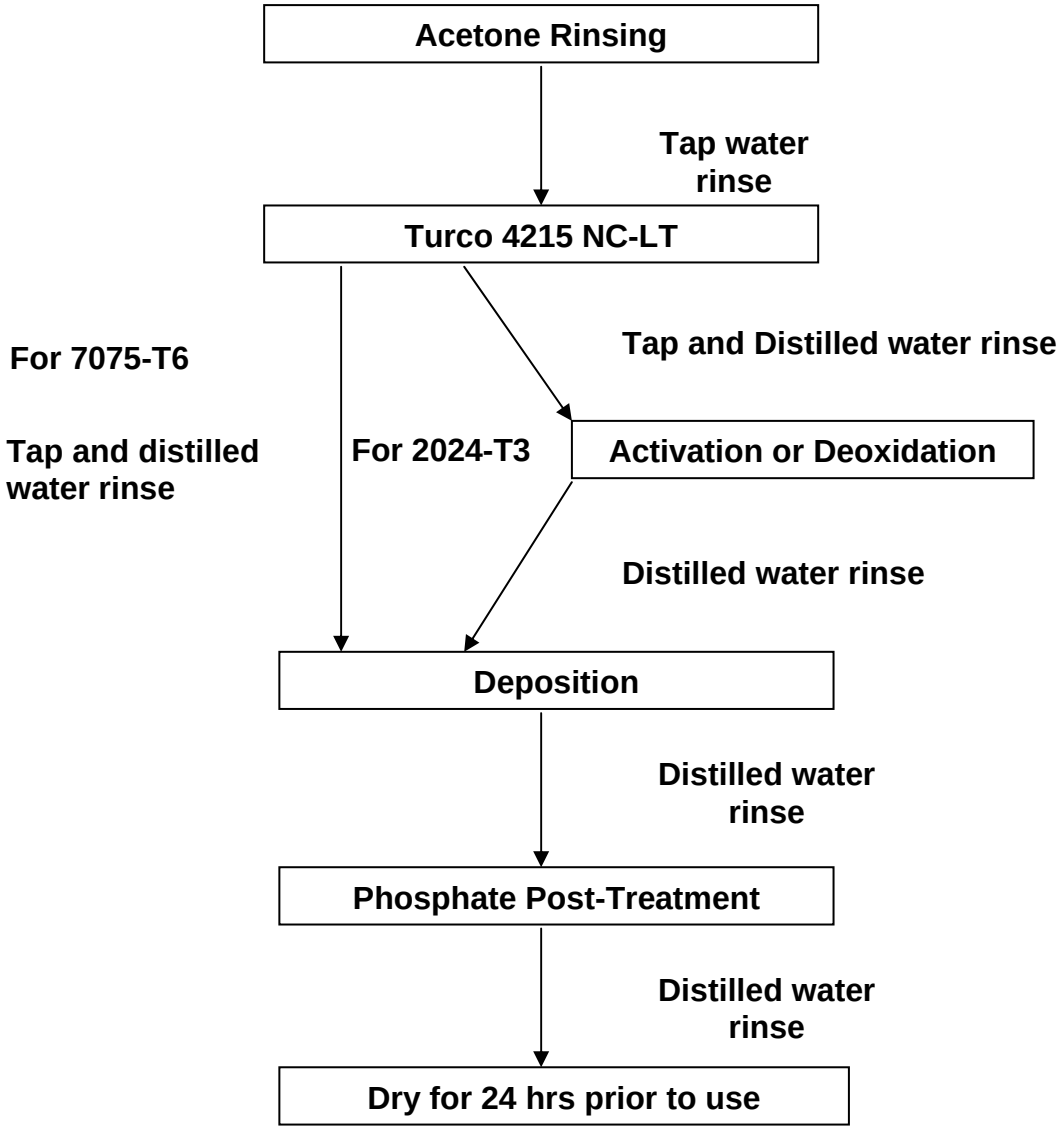
CeCC on 2024-T3 after salt spray

Water Rinsing

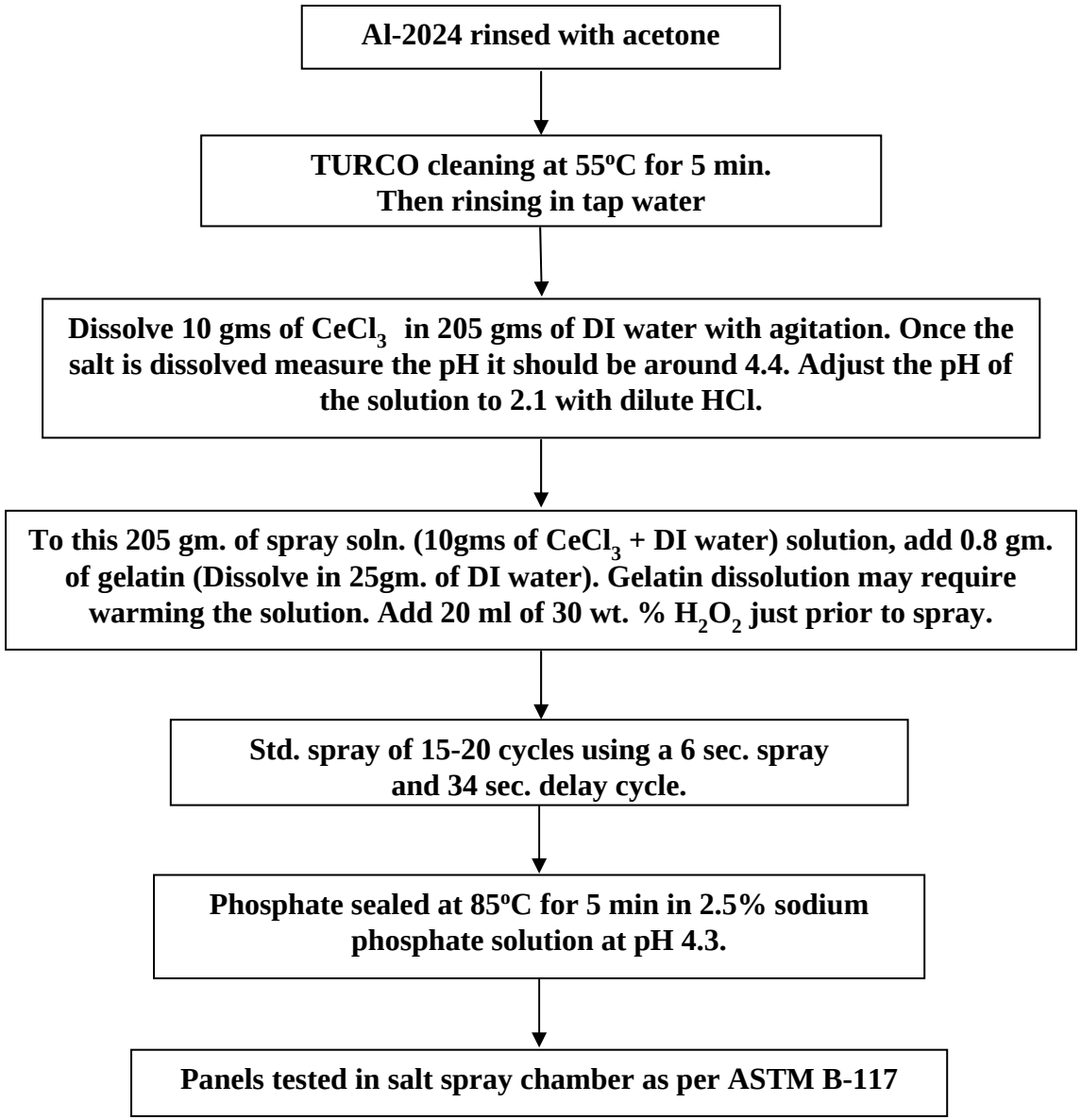
Post-Sealing

Coated Panel

Al Alloy Surface Preparation

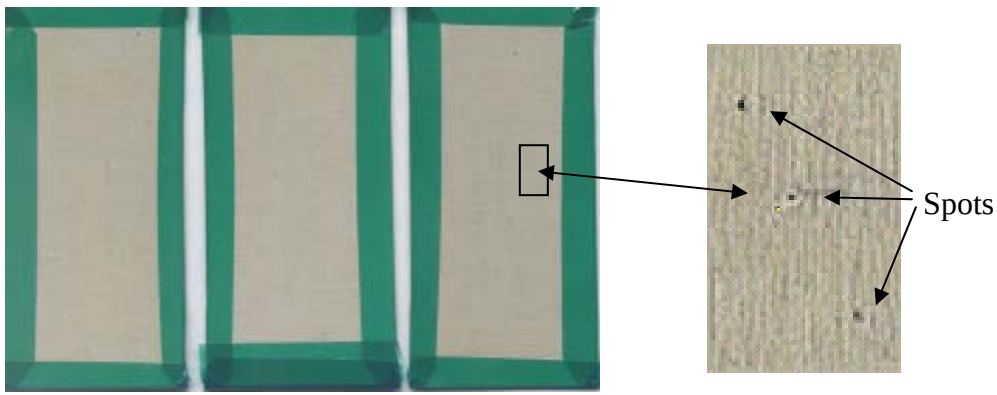


CeCC Deposition on Al 2024-T3



CeCC Deposition on 2024-T3

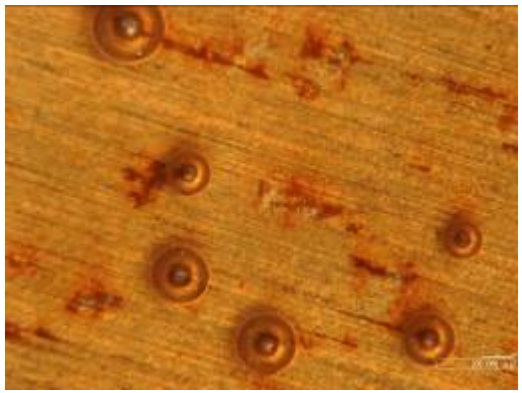
As deposited before salt spray



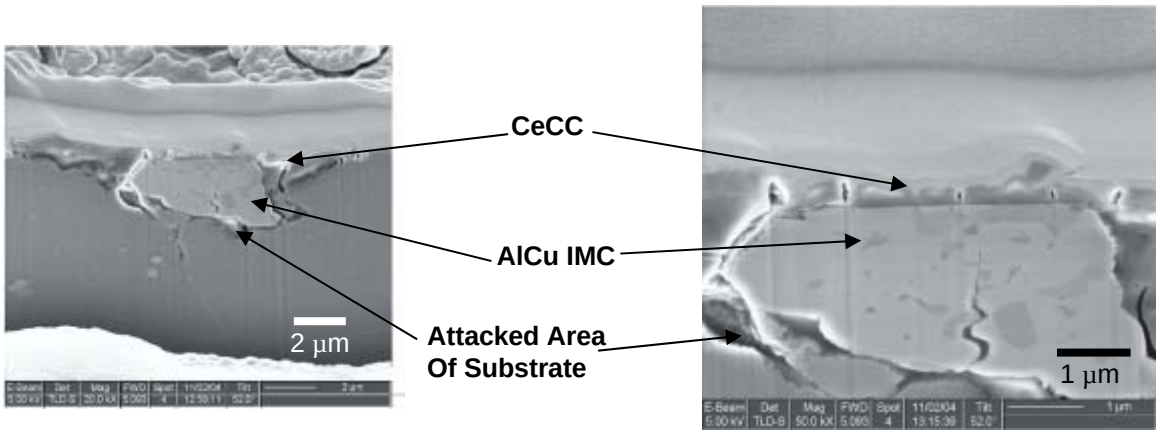
After 2 weeks salt spray

- Pits but no tails
- About 50% pass rate

CeCC Deposition Studies

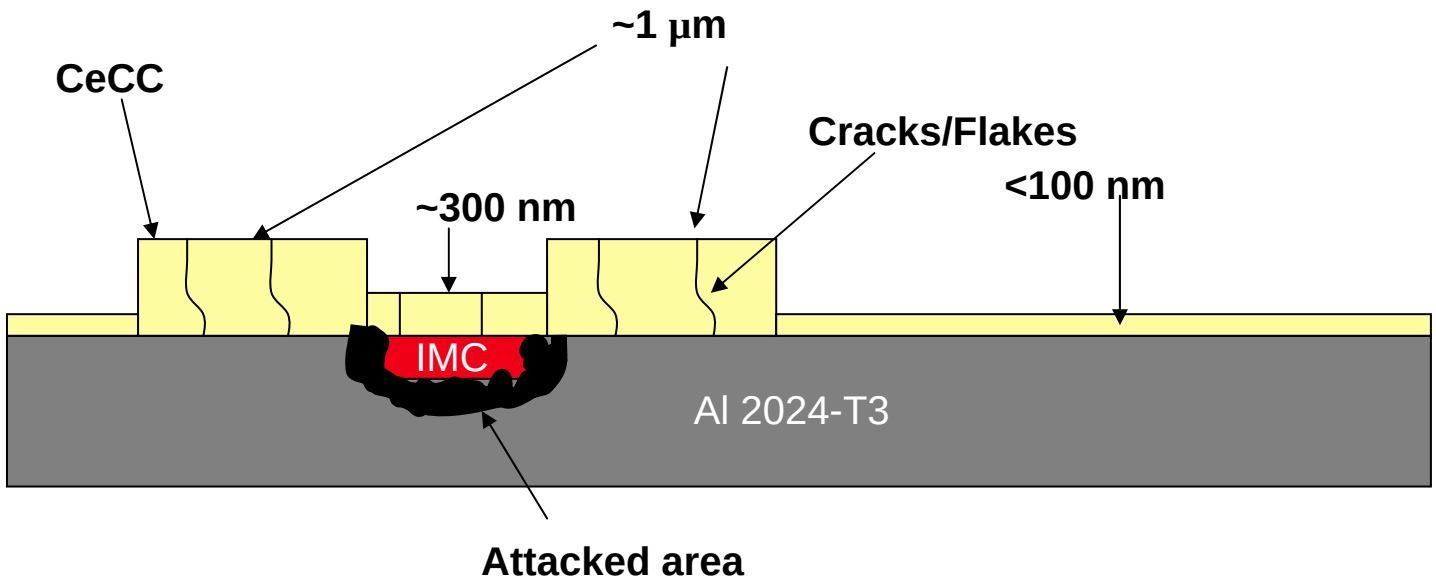


Gas bubbles form on surface at preferential deposition locations



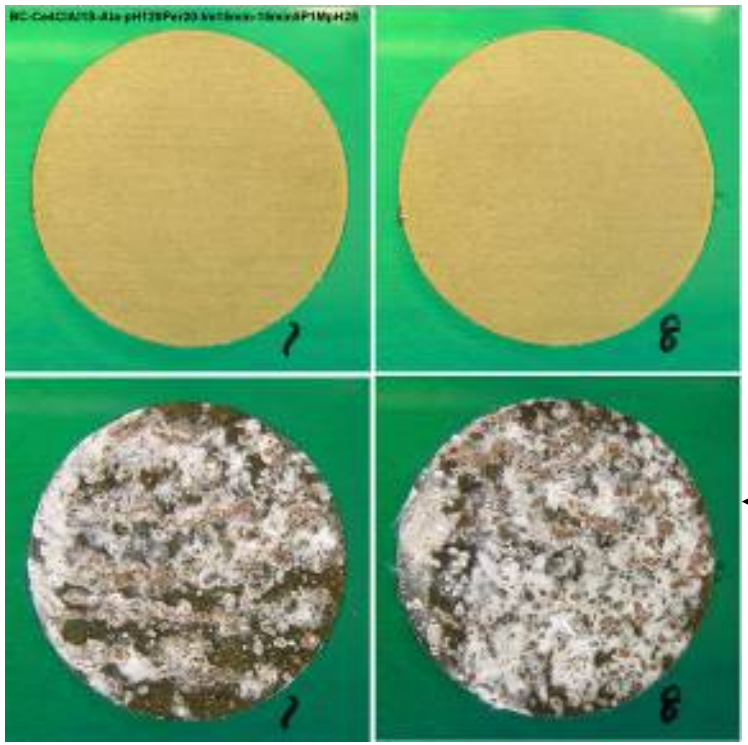
AFRL FIB images of preferred deposition sites
– Cu intermetallic compounds (IMCs) found

CeCC Deposition Schematic



Non-uniform coating thickness due to presence of IMCs
- Variations can be minimized by proper surface preparation and deposition parameters

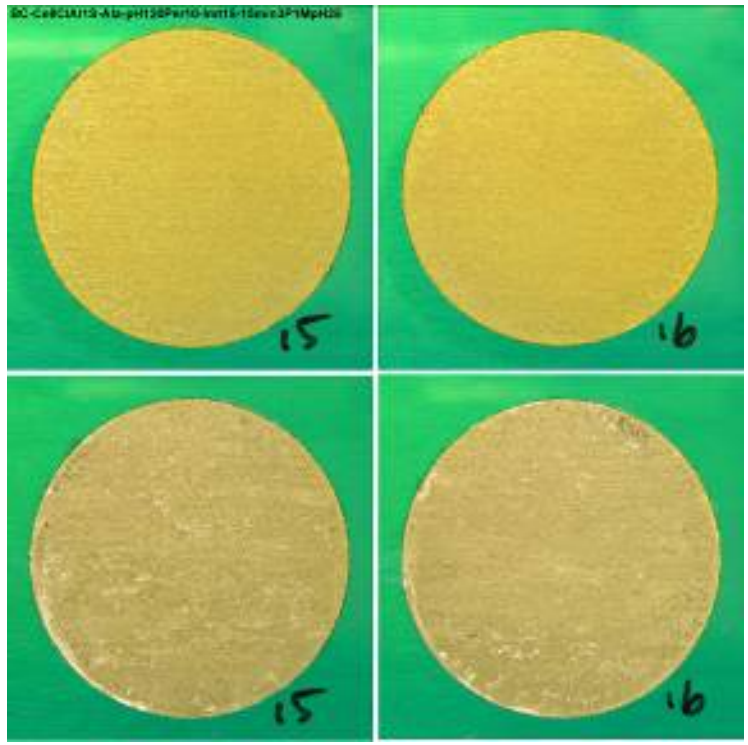
CeCC: Effects of [Ce] and [H_2O_2]



Low [Ce] and High [H_2O_2]

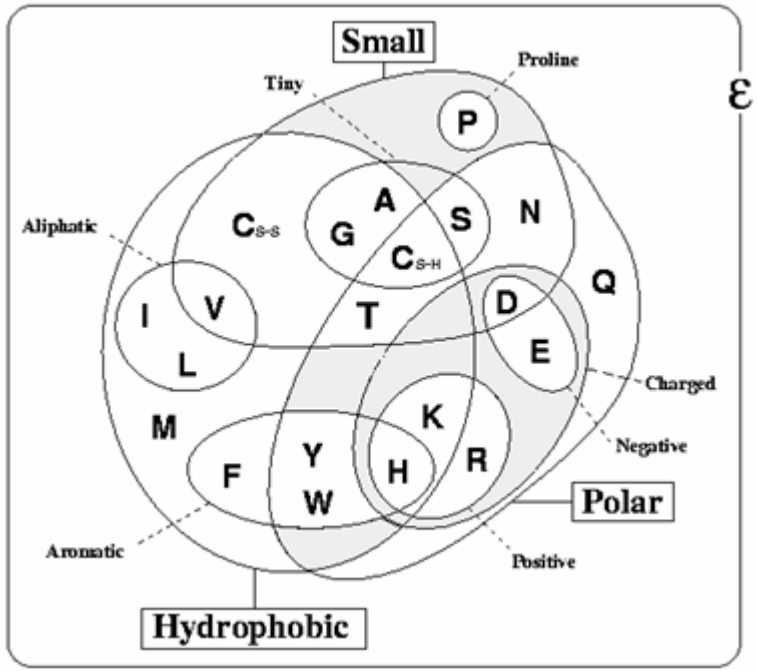
← As Deposited →

← After Salt Spray →

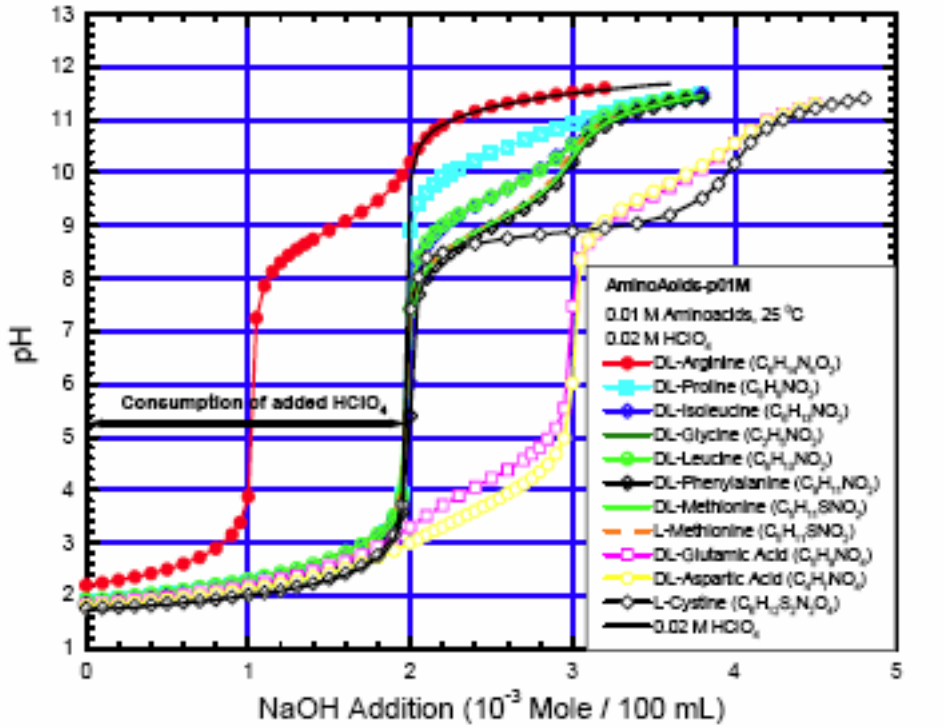


Standard [Ce] and Standard [H_2O_2]

Gelatin/Amino Acid Studies



Venn diagram of the amino acids found in gelatins.



Plot of pH vs amount of NaOH base addition for various amino acids

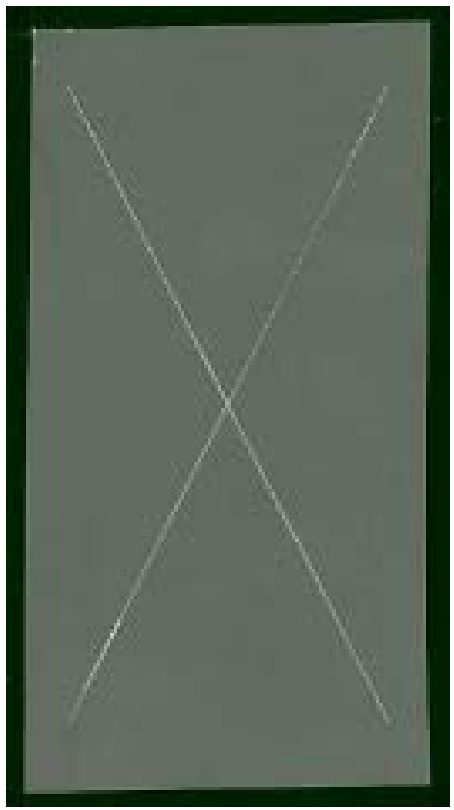
Gelatins/amino acids buffer local pH and influence the coating process

Evaluation of Coating System

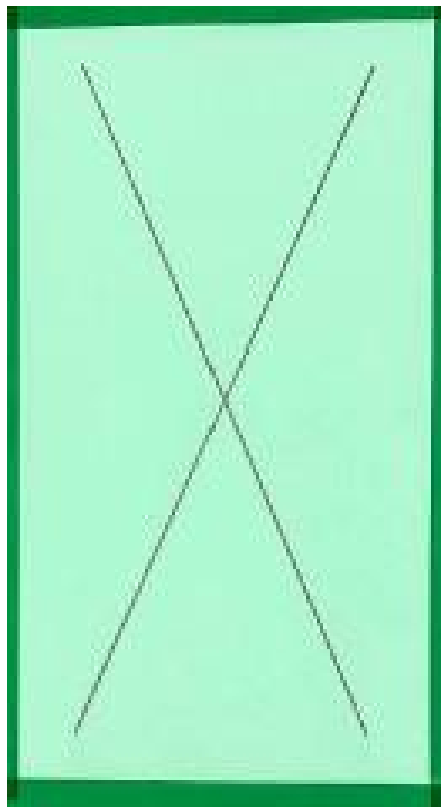
- **Commercial Deft non-chromate primer on CeCC panels**
  - **Wet and dry tape adhesion studies**
  - **All panels pass tests**

Evaluation of Coating Systems

- **Reference standards after 3000 hours of salt spray testing**
  CrCC with chromate primer: shiny scribe
  CrCC with non-chromate primer: dark scribe, no salting



CrCC + Chromate
Deft Primer

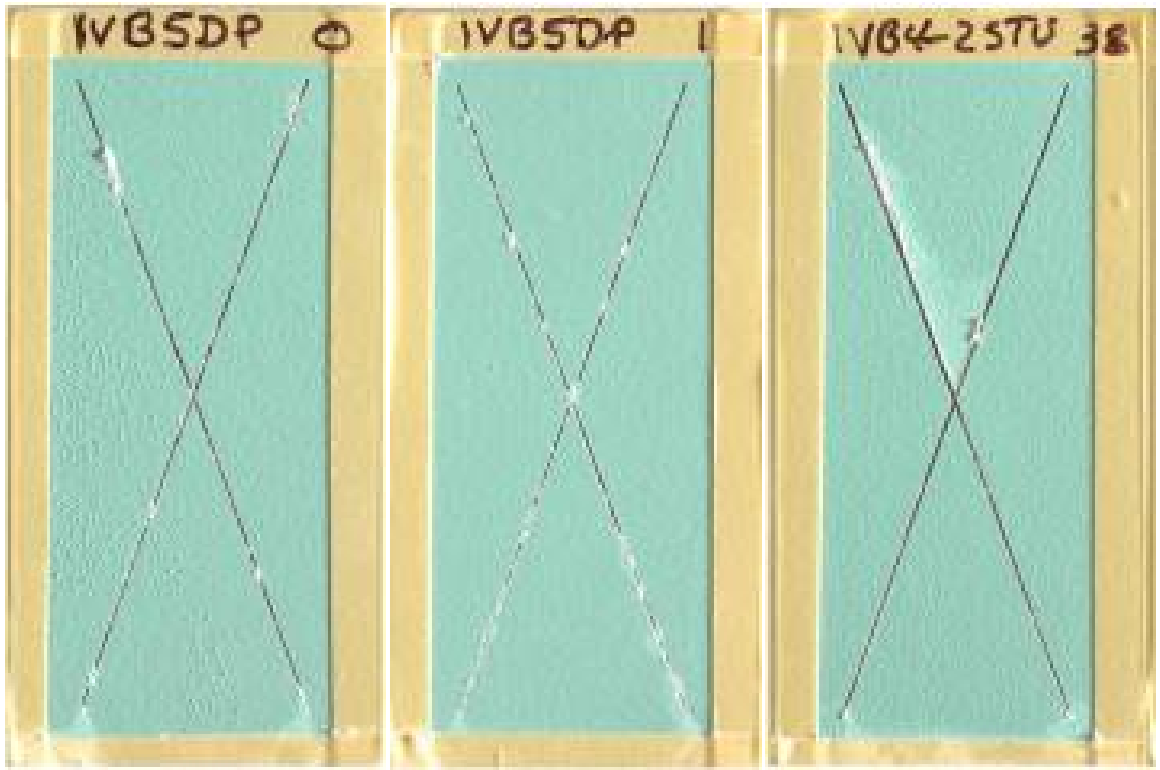


CrCC + Non-Chromate
Solvent Borne Deft Primer

Evaluation of Coating Systems

Round 2 Panels After 1500 Hours Salt Spray

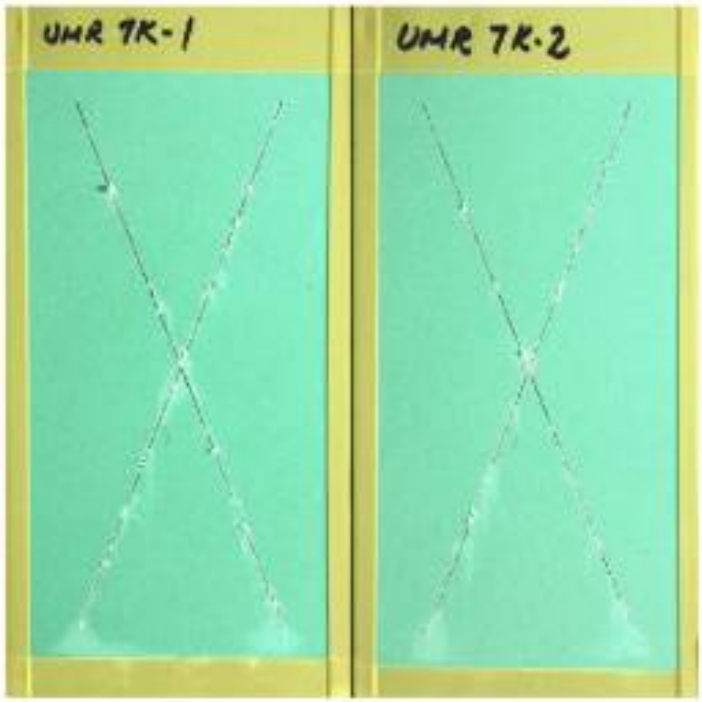
CrCC + Non-Chromate,
Solvent Borne Deft Primer



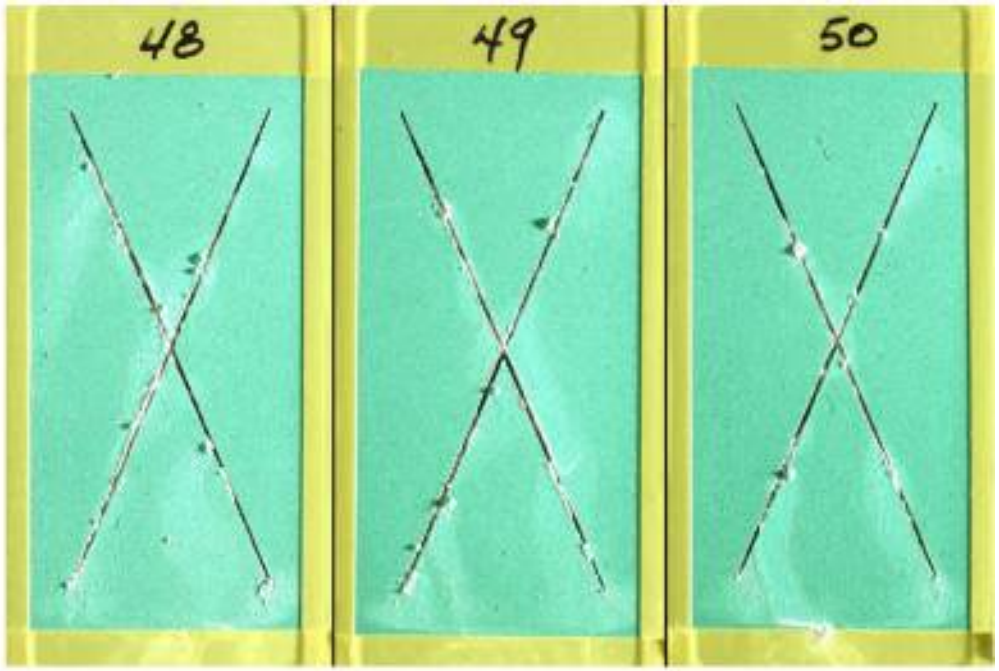
CeCC + Non-Chromate,
Solvent Borne Deft Primer

Evaluation of Coating Systems

Round 3 Panels After 1000 Hours Salt Spray



CrCC + Non-Chromate
Water Borne Deft Primer

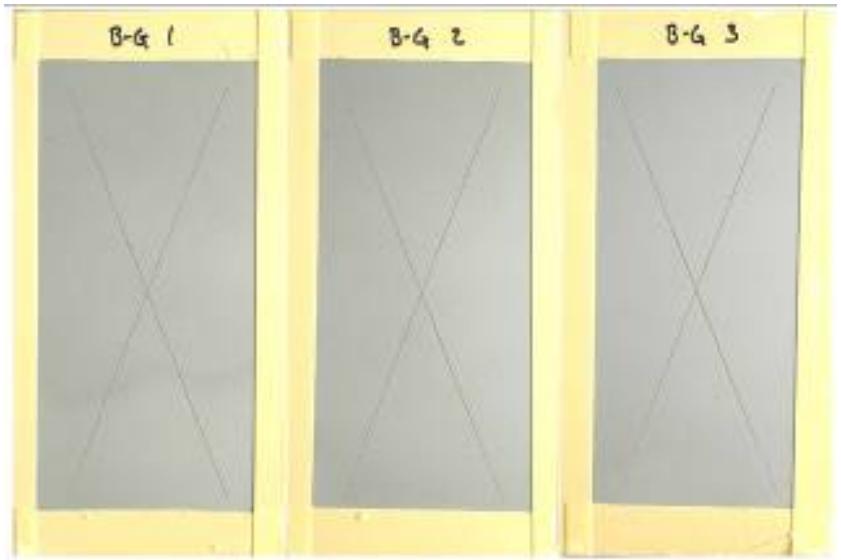


CeCC + Non-Chromate
Water Borne Deft Primer

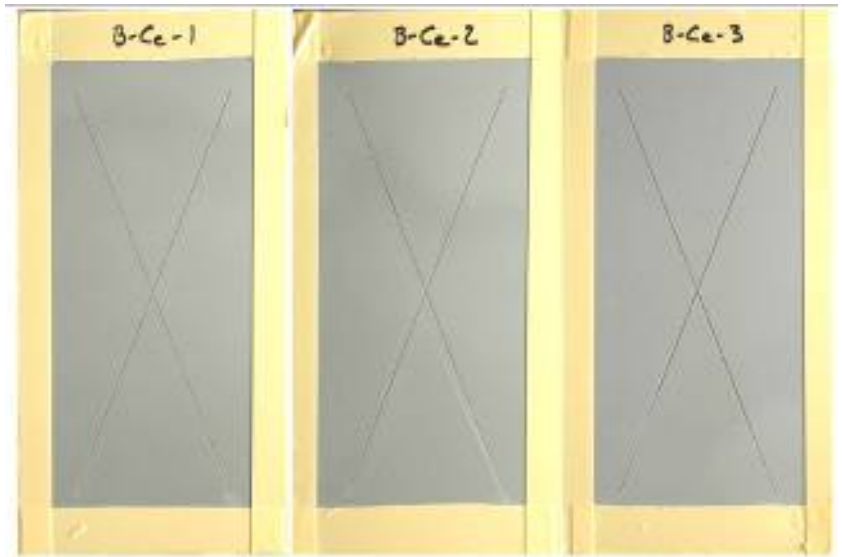
Round 3 water borne primer not commercial product at time of testing

Evaluation of Coating Systems

Round 5 Panels After 2000 Hours Salt Spray



CrCC + Chromate
Deft Primer

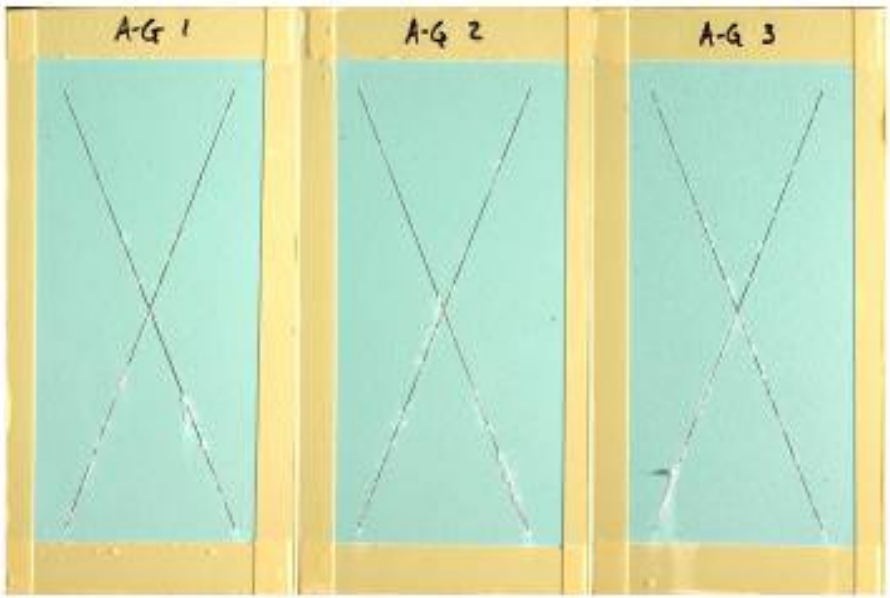


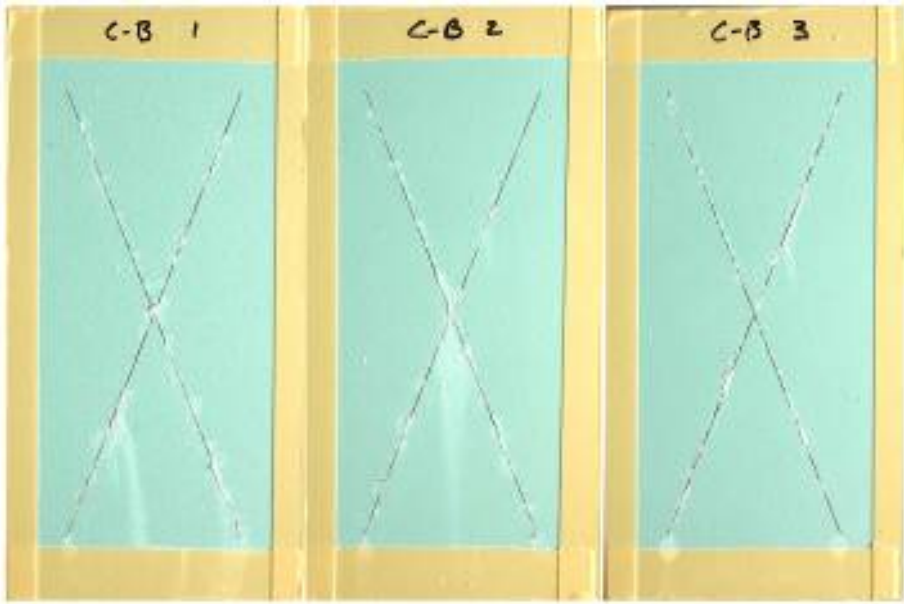
CeCC + Chromate
Deft Primer

Chromated primer performed well on all conversion coatings

Evaluation of Coating Systems

Round 5 Panels After 2000 Hours Salt Spray





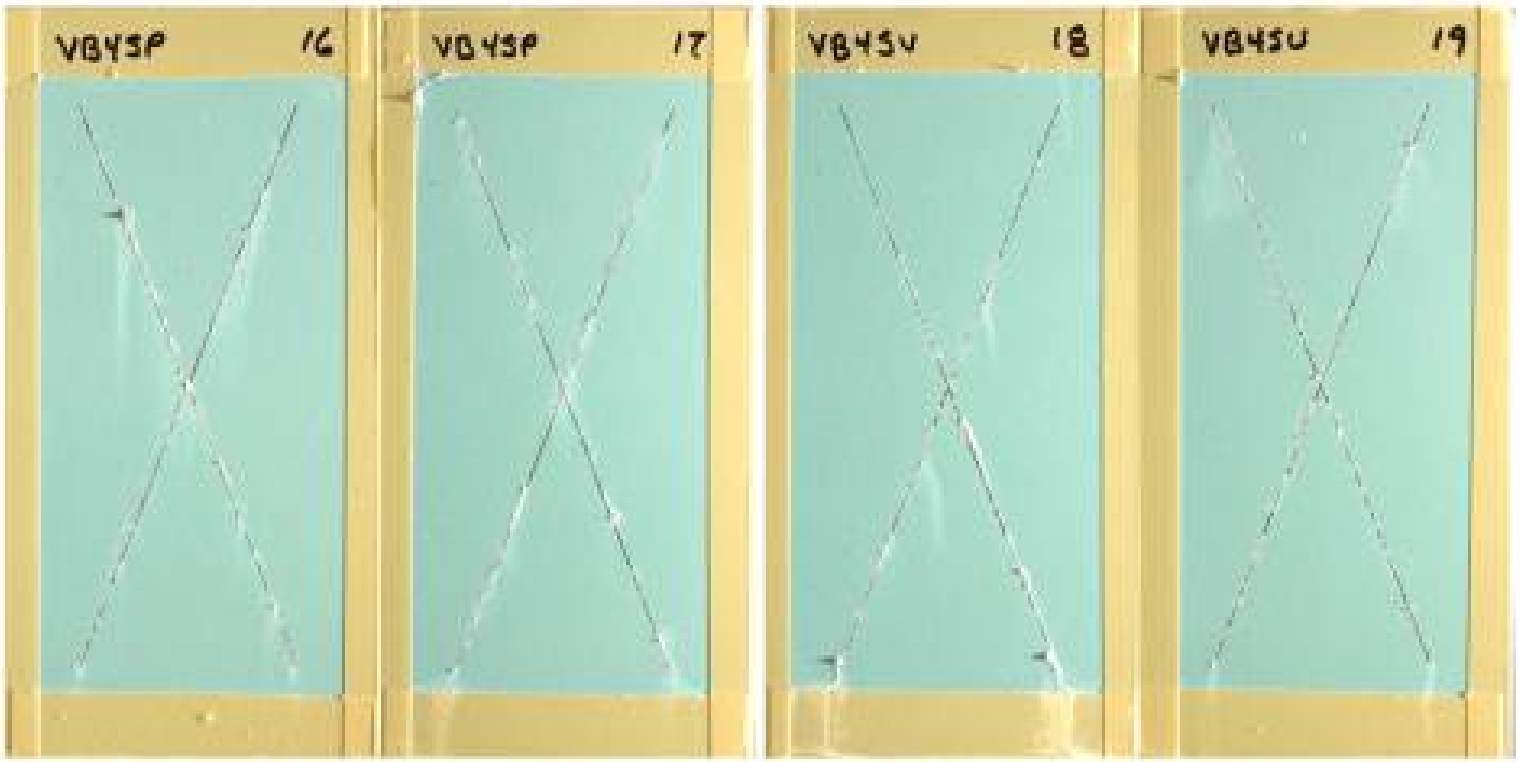
“Good” CrCC +
Non-Chromate Deft Primer

“Bad” CrCC +
Non-Chromate Deft Primer

More salting in scribe on “bad” CrCC panels

Evaluation of Coating Systems

Round 5 Panels After 2000 Hours Salt Spray



Unsealed (16, 17) and Sealed (18,19) CeCC + Non-Chromate Deft Primer

CeCC Summary

- Processes developed for CeCC deposition on high strength Al alloys
  - Spray and immersion
  - Deposition times are on the order of a few minutes
  - Coatings 200 nm to 500 nm thick
- Surface preparation is critical
  - More aggressive preparation needed for 2024-T3 than 7075-T6
- CeCCs on Al 2024-T3 and 7075-T6 can pass salt spray testing
  - No macroscopic corrosion pits or salt tails
  - Microscopic pits seen at higher magnification
  - Results imply coating scan tolerate damage/imperfections
- Spray deposition is accomplished with a few (5-10) spray-drain cycles
  - Spray for ~5 second, drain for ~35 seconds
  - The delay allows for chemical reaction
  - The thin film allows for reaction with air/oxygen

Primer Coating Summary

- Primer adhesion to CeCC was good in all cases
- Salt spray performance was studied
  - Non-chromate primer on CeCC generally inferior to controls
  - Comparable performance in a few cases
  - Non-chromate primer on CrCC
- Difficult to quantify trends
  - Sealed/unsealed CeCCs had about the same performance
  - Higher H_2O_2 content led to increased blistering
  - CeCCs with better stand-alone performance generally had better performance with a primer on top

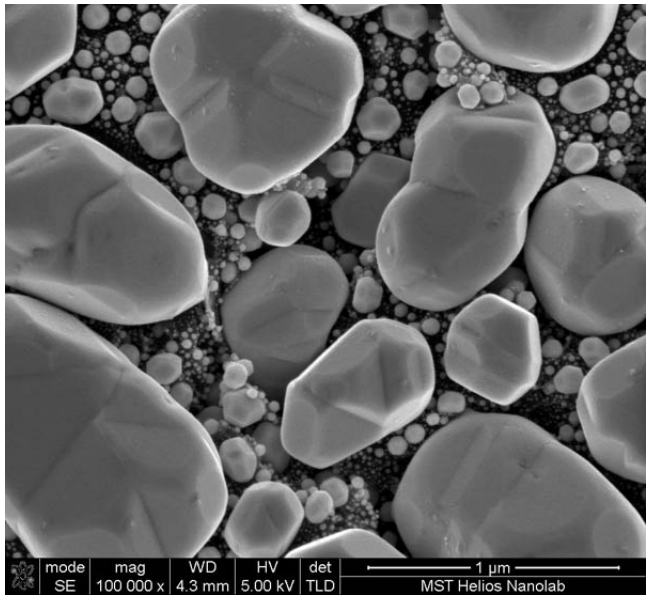
FIB Acquisition

- **Funding from CAMT and other sources**
  - **$900,000 CAMT**
  - **$500,000 NSF (Miller, Tsai, Switzer, Mormile, and O'Keefe)**
- **Acquisition of a Helios Nanolab 600 FIB/SEM**
  - **Potentially a benefit to all CAMT thrust areas**
- **Added significant capabilities**
  - **Imaging to 1,000,000X with 1 nm resolution**
  - **In-situ cross sectioning to reveal structure and interfaces**
  - **Rapid and precise TEM specimen preparation**
  - **3D renderings with nm resolution by serial sectioning/imaging**
- **Significant impacts**
  - **Only FIB in state of Missouri**
  - **Potential collaborations with academic institutions, industry, and government agencies**

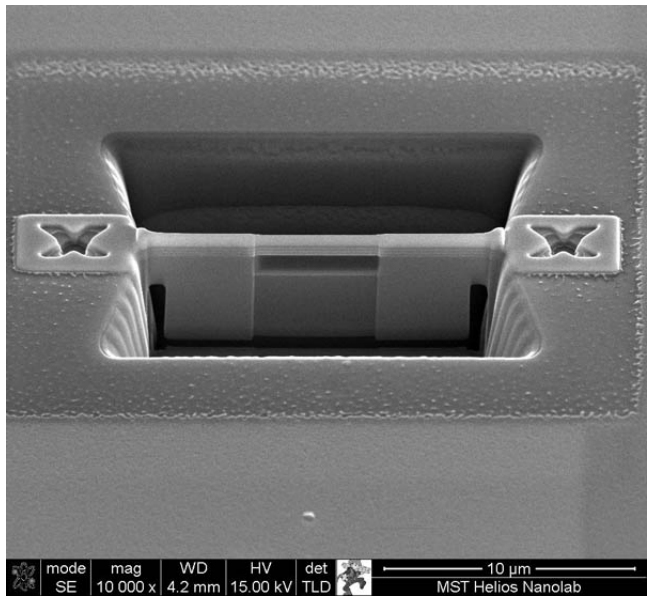
Helios Nanolab 600 FIB/SEM

- **Complements existing equipment**
  - **2 SEMS**
  - **EPMA**
  - **TEM**
- **Cutting edge technology**
  - **Undergraduate education**
  - **Graduate research**

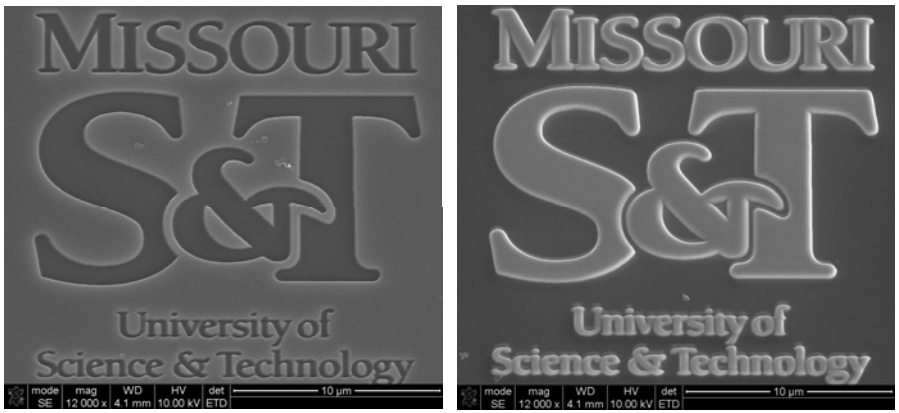
Examples of FIB Results



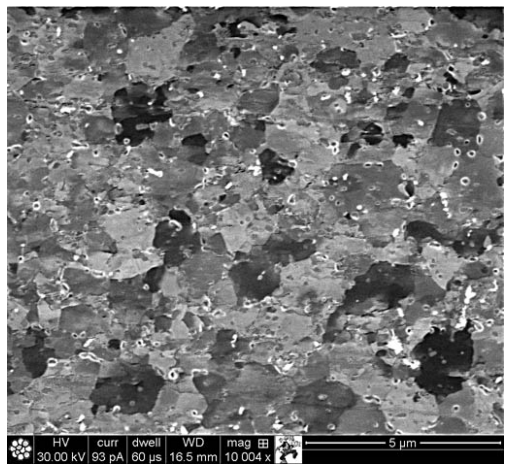
High Resolution electron imaging (gold crystals on carbon)



TEM lift-out sample of multilayers on SiO_2/Si substrate



Site-specific ion milling and Pt deposition



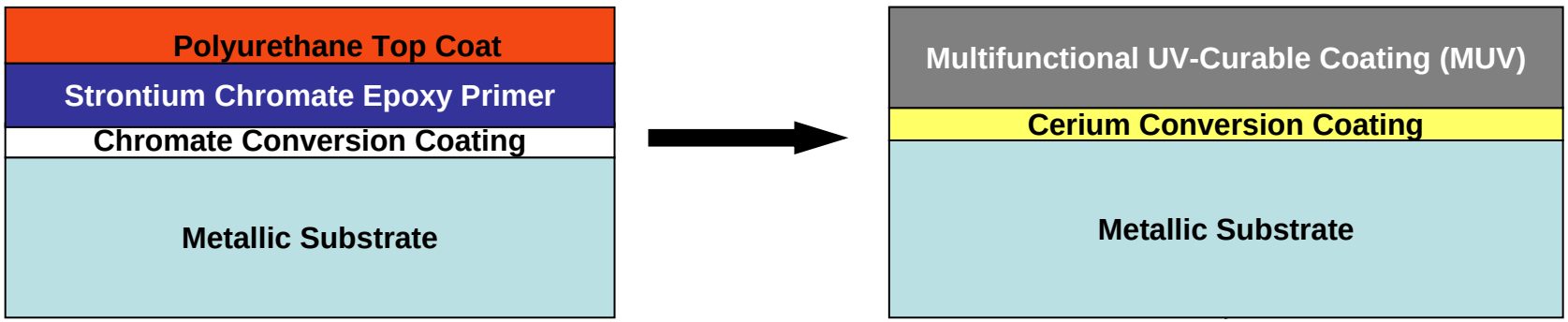
Ion channeling images reveal sub-micron grains in a friction stir welded Al alloy

Relevant Research Capabilities

- **Conversion coating deposition**
  - **Electrolytic, spray, and immersion coating processes**
- **Corrosion testing**
  - **2 salt spray chambers running ASTM B117 protocol**
- **Electrochemical characterization**
  - **Electrochemical impedance spectroscopy and polarization**
  - **Dynamic open circuit potential**
- **Analytical characterization**
  - **Hi resolution optical microscopy still images and videos**
  - **Scanning and transmission electron microscopy**
  - **Focused ion beam/SEM dual beam system (acquired in Task 7.2)**
  - **X-ray photoelectron spectroscopy**
  - **Auger electron spectroscopy depth profiling**
  - **Full suite of materials characterization available at MRC**
- **Leveraging of results from center funding**
  - **Two follow on projects**
  - **Commercialization of university technology**

Non-Chromate, Zero VOC Coating System

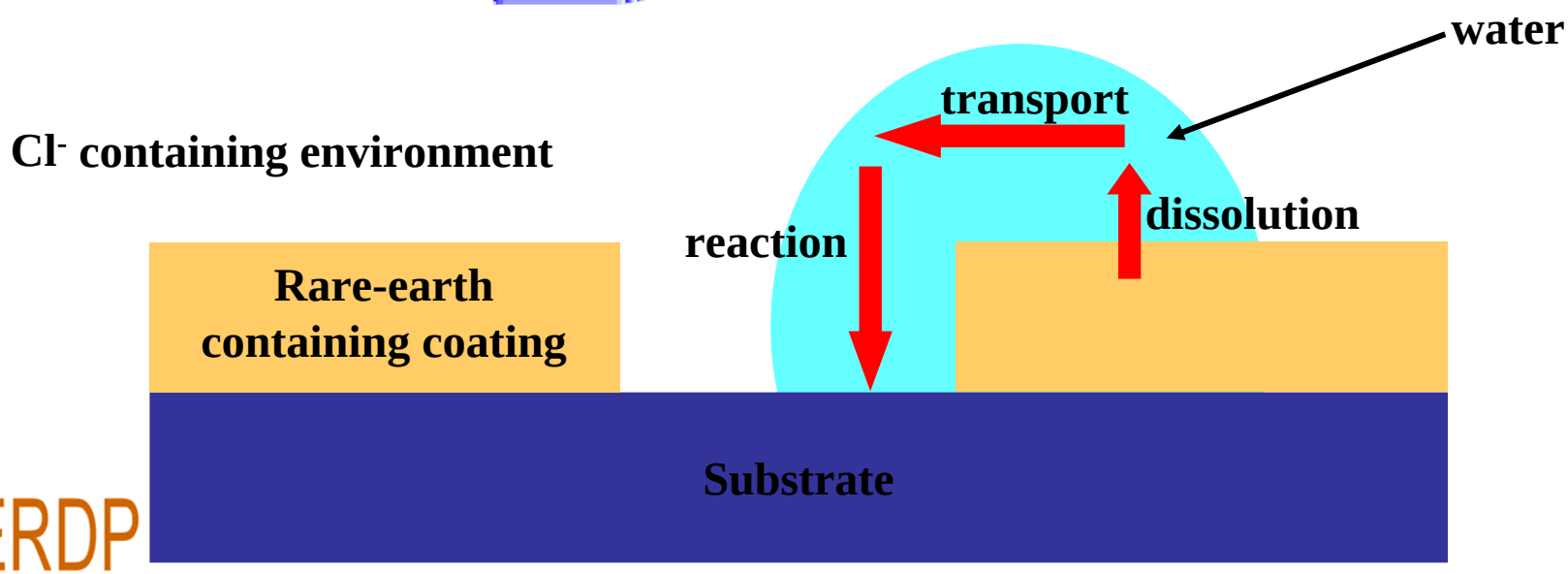
- **Goals:** Develop non-chromate, zero VOC, HAP-free coating system
- **Approach:** Combine CeCC with UV curable multi-functional coating
  Missouri S&T: CeCC development
  Boeing/LCC: MUV and performance testing
- **Partners:** Boeing-St. Louis
  Light Curable Coatings



SERDP
Strategic Environmental Research and Development Program

Rare-Earth Coating Protection Mechanisms

- **Goal:** Develop mechanistic models for protection mechanisms
  - Cerium-based conversion coatings
  - Deft commercial non-chromate primers
- **Approach:** Characterize coatings before, during, and after corrosion
  Use electrochemical methods to identify transport methods
- **Partner:** Deft, Inc.



DoD EPA DOE SERDP
Strategic Environmental Research and Development Program

Non-Chromate Corrosion Inhibitor

- **Based on university researched funded through AFRL**
  - **Patent application has been published**
- **Technology licensed and commercialized by Deft**
  - **Solvent-based and water borne non-chromate primers**
  - **In use in manufacturing and re-painting operations**
  - **Qualified to military specifications**

F-15 coated with Deft 02GN084 non-chromate primer that uses a Pr-based inhibitor

Technician coating an Apache fuselage with Deft non-chrome primer

MISSOURI S&T