DEPOSITION OF AMORPHOUS ALUMINUM ALLOYS AS A REPLACEMENT FOR ALUMINUM CLADDING

US Army Corrosion Summit
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Report Documentation Page

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Prescribed by ANSI Std Z39-18

Presentation Outline

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- Future Work

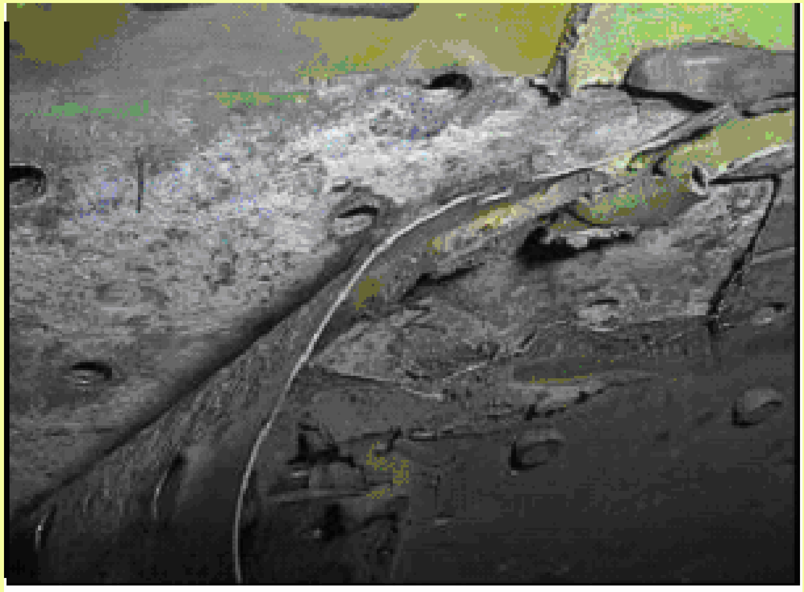


Photo from R. Kelly/D. Peeler/D. Kenzie

Corrosion concerns at lap-splice joint

Basis of STTR Collaboration

UVA developed promising family of amorphous-forming aluminum alloys

- Multi-functional corrosion protection (AFOSR MURI)
- Demonstrated on melt-spun ribbons (AFOSR MURI)
- Computationally-guided alloy coating design (AFOSR MURI)

To be demonstrated: Alloy applied in a functional form (coated)

- Requires suitable coating technology
  - Form high-density coating
  - Retain desired amorphous or near-amorphous nanostructure

Pulsed Thermal Spray coating system developed by Enigmatics/SAIC

- High quench rates
- Short particle residence time
- Low substrate thermal loading
- Capability of using relatively small-size feedstock material (<20 micron)

University of Virginia

SAIC

Aging Aircraft Challenge

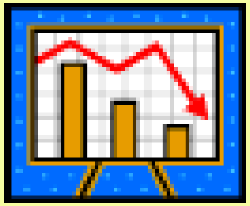
Aging Fleet

- **Corrosion**
- **Fatigue Cracking**
- **Parts Availability**
- **Wiring**
- **Aging Avionics**

Repair Density Increases

Flow Rates Decrease

Maintenance $$ Increase

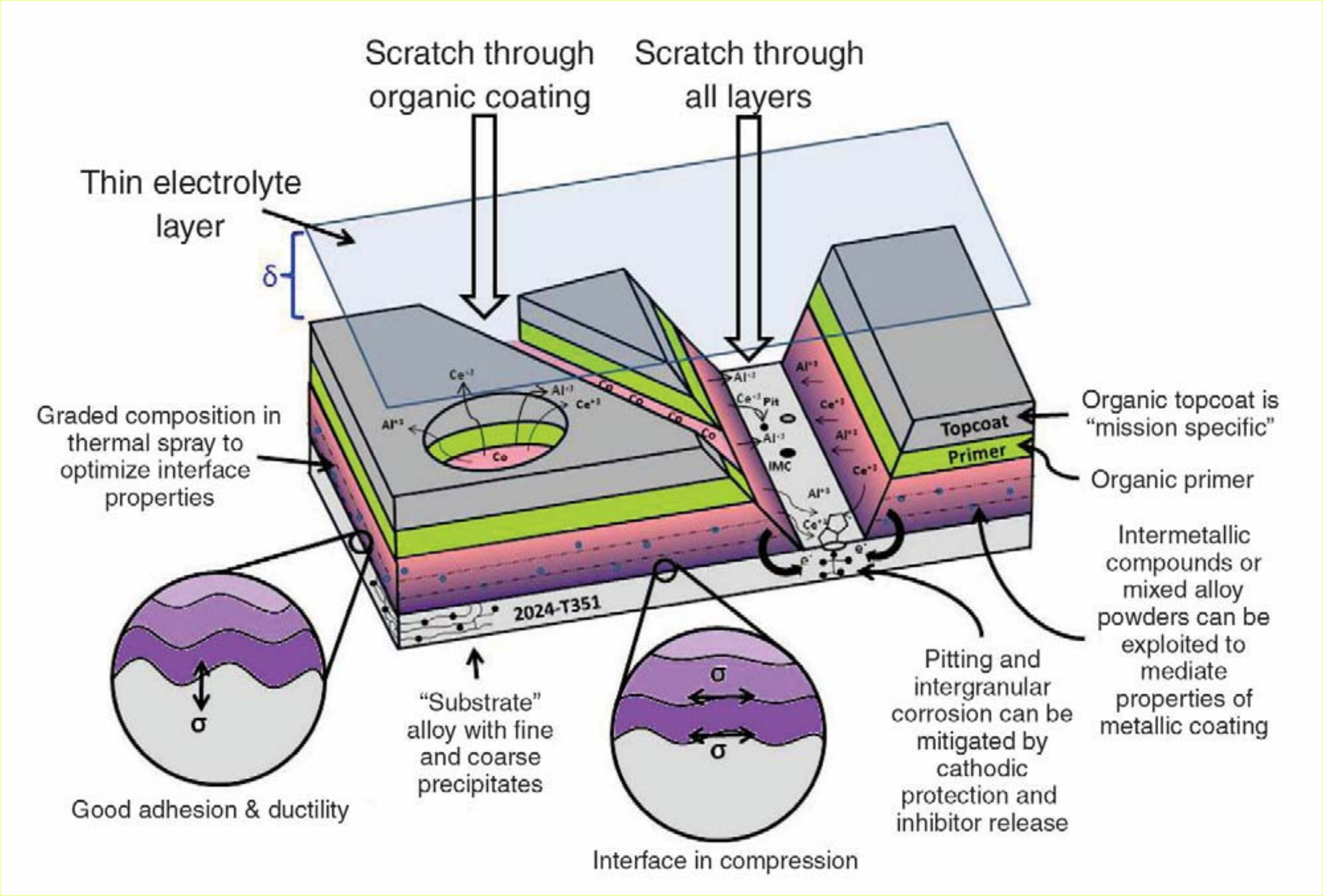


Mission Capable Rates & A/C Availability Decrease

Modernization $$ Decrease

Courtesy D. Peeler

Multi-functional Coating for AA 2024



Goal: Design metal coating with better/more potent corrosion protection functions than existing aerospace cladding (i.e., provide sacrificial protection, active inhibition, and local corrosion barrier properties).

Scully Group, Materials Today 2008.

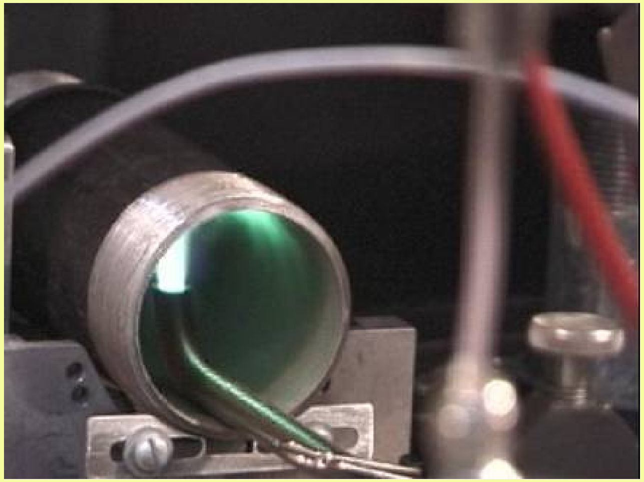
Desirable Coating Attributes

- Barrier: Good Corrosion Resistance
  - Defined by E_{PIT} (Alloy) > E_{PIT} (AA 2024-T351)
  - Low porosity
  - Strong coating-substrate adhesion
  - Alloy composition controls E_{PIT}
  - May desire amorphous to improve corrosion barrier
- Sacrificial Anode: Good Sacrificial Anode
  - Defined by E_{OCP} (Alloy) < E_{OCP} (AA 2024-T351)
  - Alloy composition or mixed powders
  - Minimum oxide in coating composition
  - May not want to be amorphous if crystalline phases depress OCP
- Inhibitor: Release Capability- (Optimize Storage/Release)
  - Defined by on-demand release rates, ↑↓moles/cm^2-s
  - Alloy composition or chemical composition
  - Minimum oxide in coating
  - Does not need to be amorphous
  - Surface engineering to optimize release

Project Overview

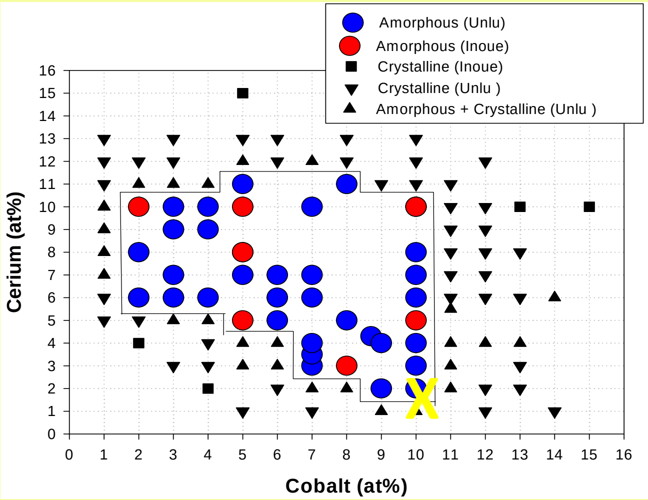
Develop practical PTS-applied corrosion protective coating

- Replacement/repair option for aluminum cladding
- Exploit tri-functional protection capabilities of Al-Co-Ce family of alloys
- Exploit unique advantages of PTS system
  - PTS coating method produces nanocrystalline coatings
  - Electrochemical properties show potential for high corrosion resistance
  - Application-relevant corrosion experiments
  - Salt spray
  - Demonstrate attractive capabilities suitable for corrosion application.
  - Repair capability



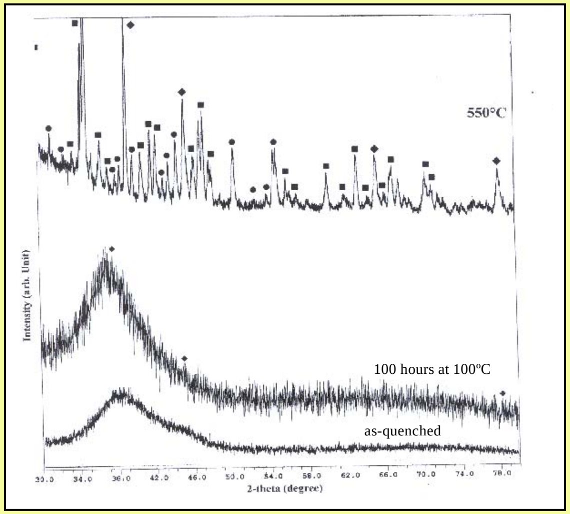
PTS system showing small ID coating capability

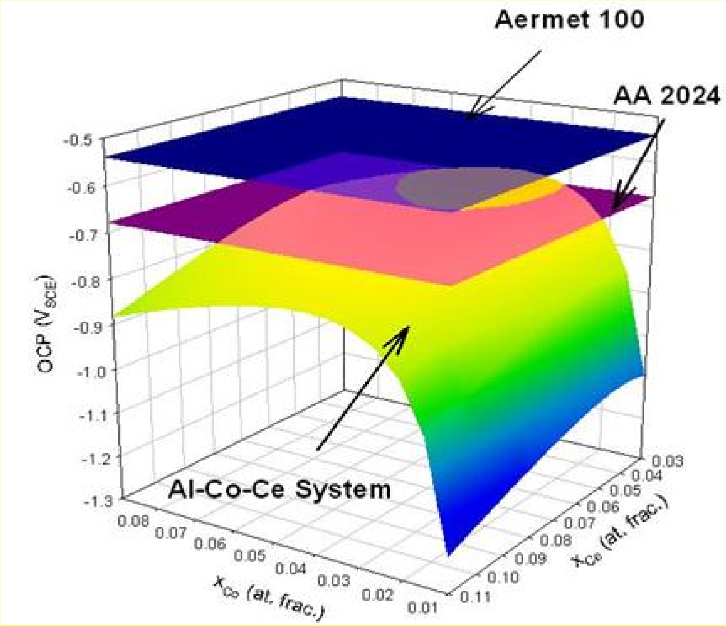
Alloy Development



Glass-forming composition identified

Stable amorphous state at 100° C (alloy stable to higher temperatures than 2024)

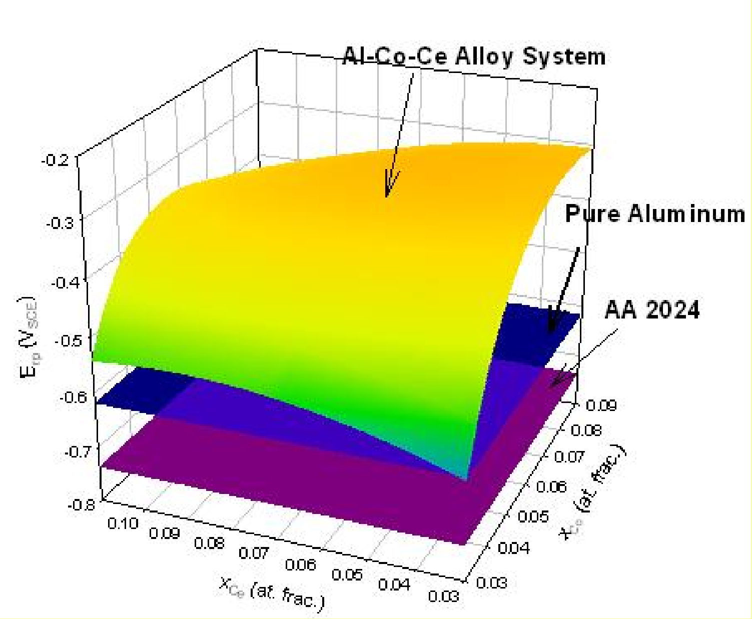




<u>Tunable Properties</u>

OCP

E_{pit}



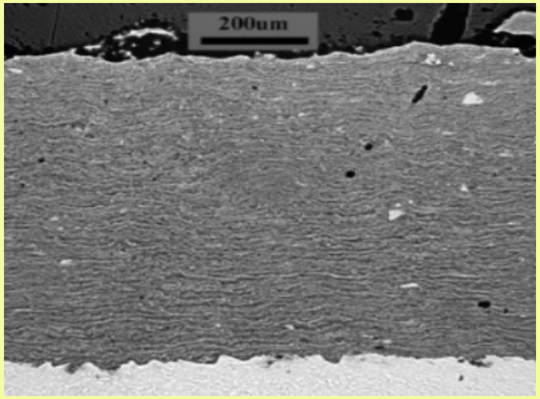
M. Gao, N. Unlu, et al. 2007.
M. Goldman, et al. 2005.
M. Goldman Thesis 2005.

Pulsed Thermal Spray

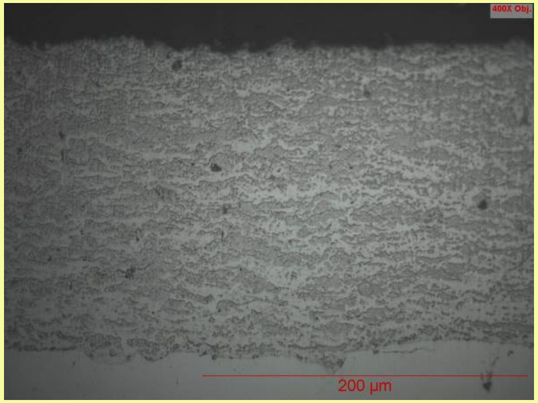
An intermittent thermal spray process ideally suited for forming amorphous or near-amorphous coatings. Key attributes of PTS include:

1. **Rapid heating and particle acceleration**
   - Reduced residence time allows for use of smaller feedstock materials
   - Oxidation is minimized
   - High velocities are obtained (800 m/s typical)
2. **Reduced substrate thermal loading**
   - Substrate maintained under 100° C to prevent overaging & recrystallization
   - Use of small feedstock particles (<20 microns) over a cold (<100° C) substrate leads to 10^6 K/s cooling rates and formation of amorphous or nanocrystalline coatings
3. **Minimal substrate standoff (¼-1")**
   - Capable of tracing complex surface features
   - Allows ID coating capability

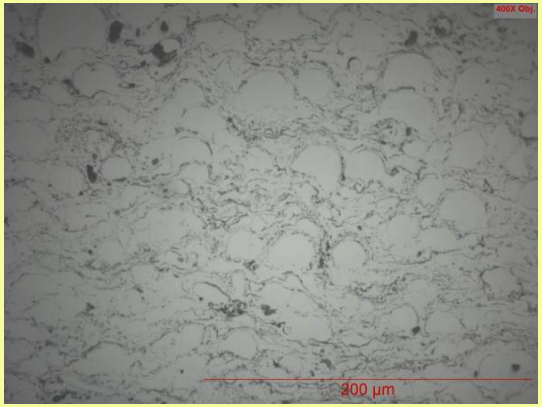
Pulsed Thermal Spray



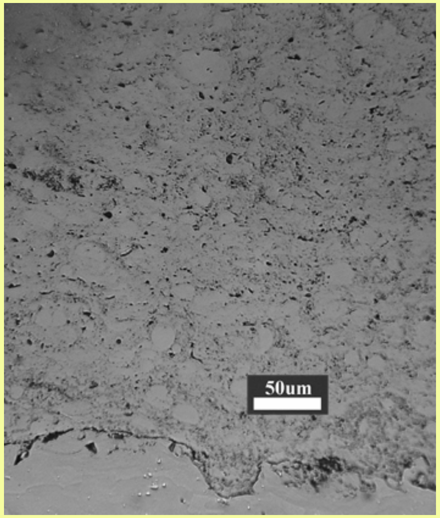
Tantalum for gun barrel applications



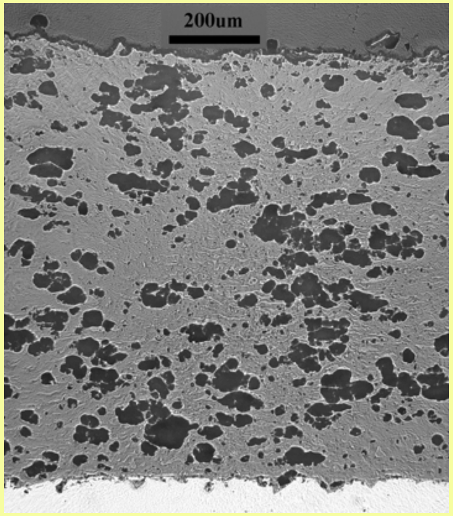
WC-Co-Cr for landing gear ID



Co-Cr-Al-Y bond coat for thermal barrier system



Pure aluminum for Cd replacement

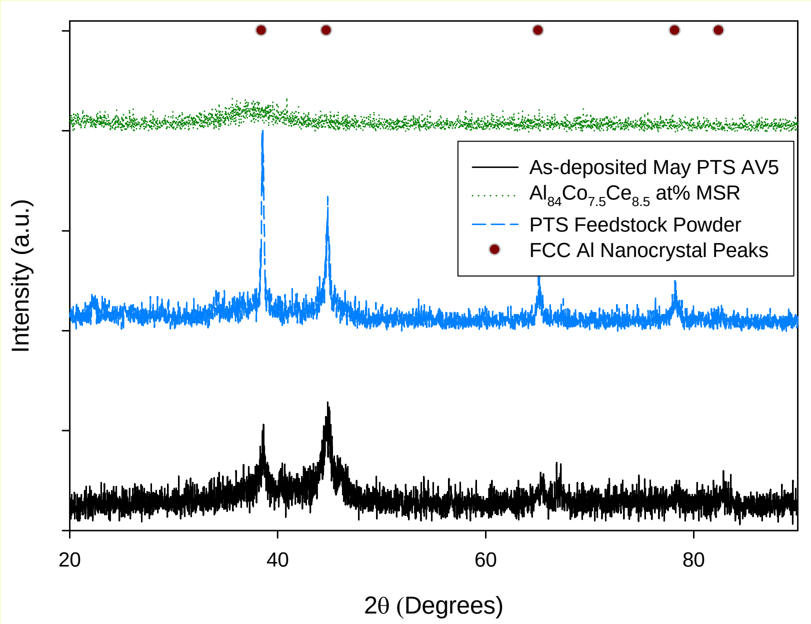


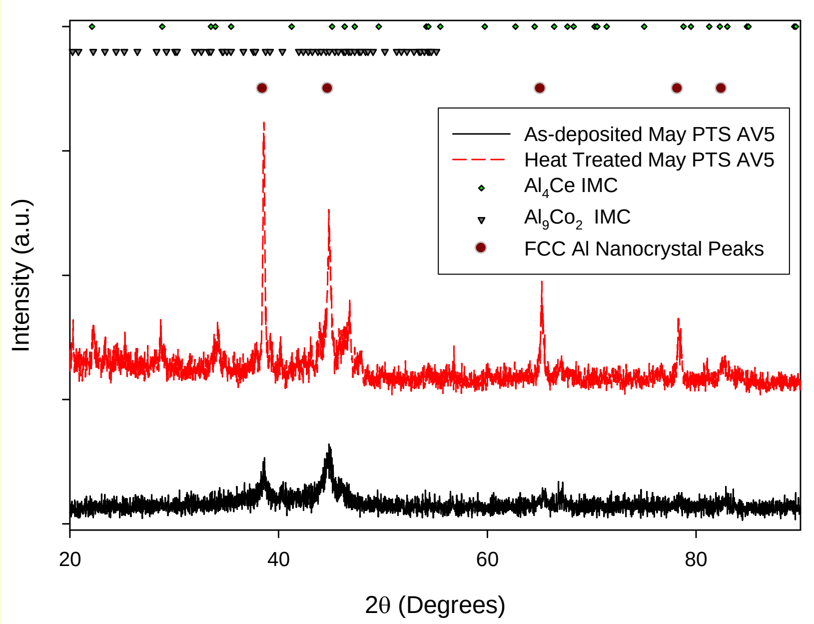
Porous Y-ZrO2 for thermal barrier system

A versatile system capable of coating a wide range of materials including:

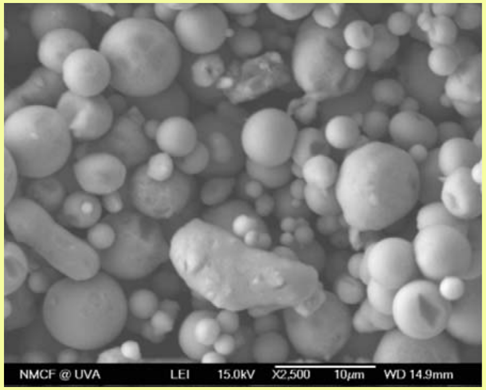
- Pure metals (Al, Fe, Mo, Ta, etc.)
- Oxides (Titania, Y-ZrO2, etc.)
- Carbides, Inconels, etc.

Nanostructured Al-Co-Ce





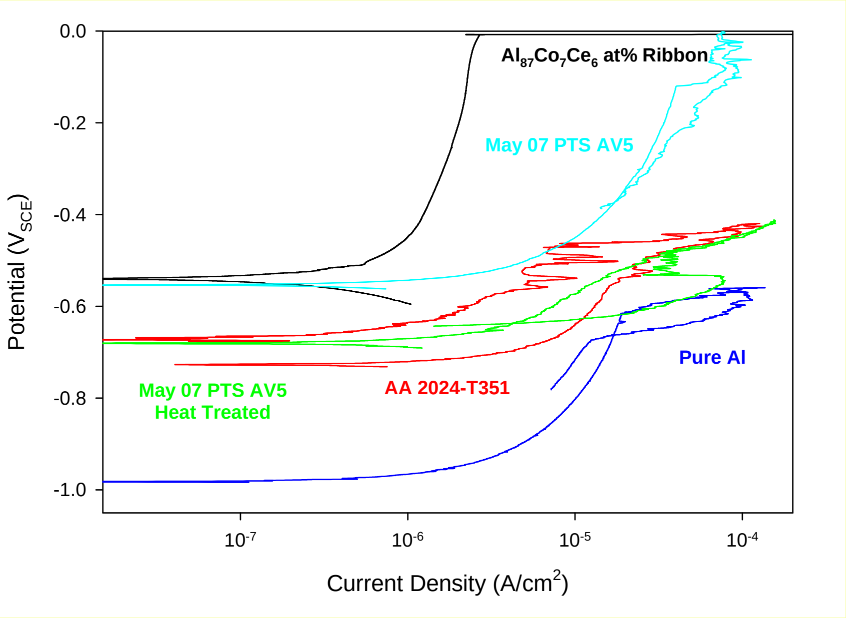
- Composition of feedstock powder and PTS is $Al_{88}Co_{10}Ce_2$ at%, MSR is $Al_{87}Co_7Ce_6$ at%
- Sample heat treated at 275 °C for 6 hrs and 285 °C for 3 hrs



KEY FINDINGS

As-sprayed PTS coatings are amorphous with fcc-Al nanocrystals. Intermetallic compounds develop after heat treatment.

Cyclic Polarization



E-log(i) polarization curves of:
1) as-deposited PTS coating May 07 AV5,
2) Heat-treated AV5
3) Melt Spun Ribbon
4) pure Al
5) AA 2024-T351.

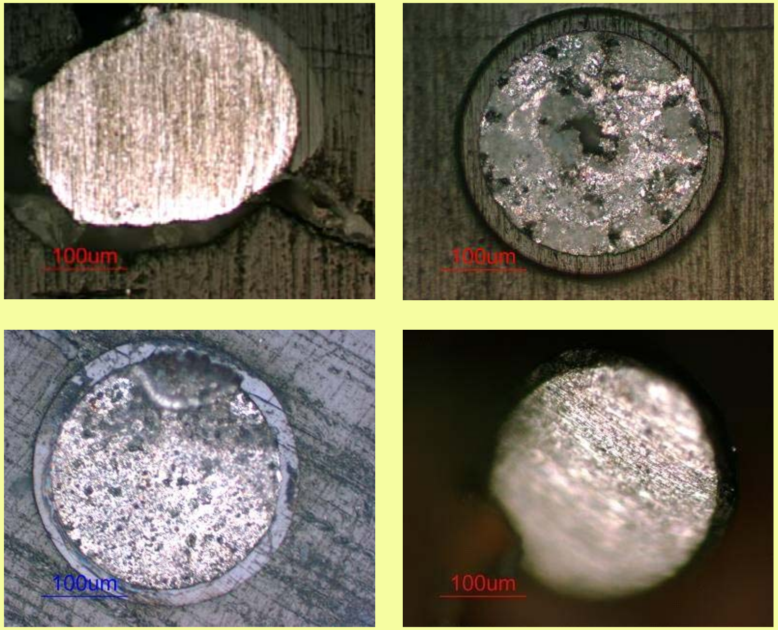
All tested in de-aerated, 6 mM NaCl, after a 5-minute hold at OCP. The thickness of the coating was ~100 µm.

Heat treated sample treated at 275 C (527 F) for 6 hours followed by 285 C (545 F) for 3 hours. Grain growth and observation of intermetallics were noted in XRD (previous slide).

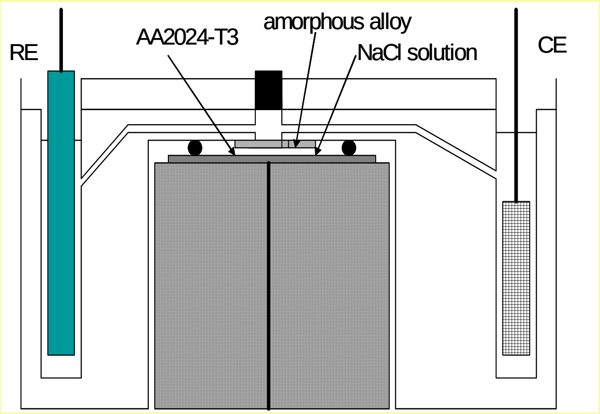
Nano/amorphous structure preserves desirable barrier properties. Intermetallic development suppresses them.

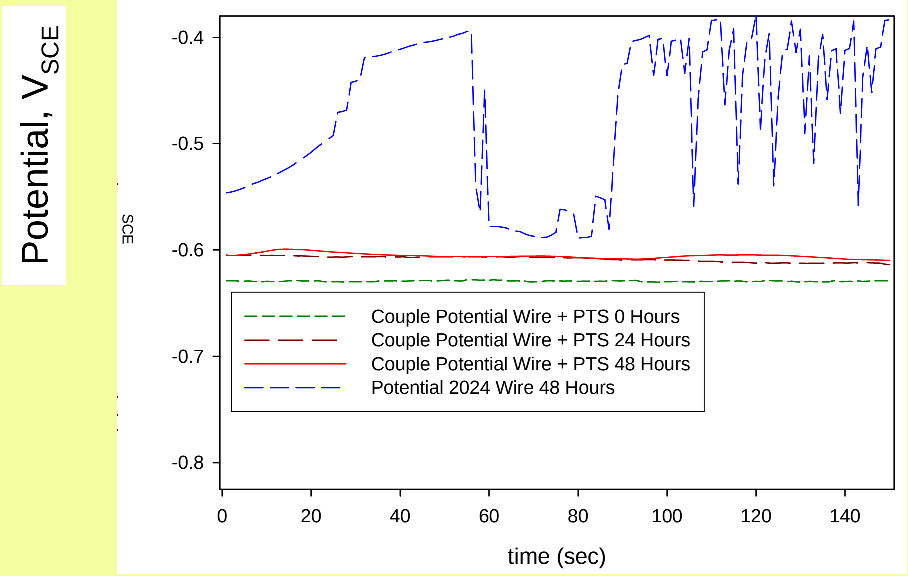
Sacrificial Anode and Inhibitor Release Capability

Pretest | Alone



Coupled to MSR | Coupled to PTS



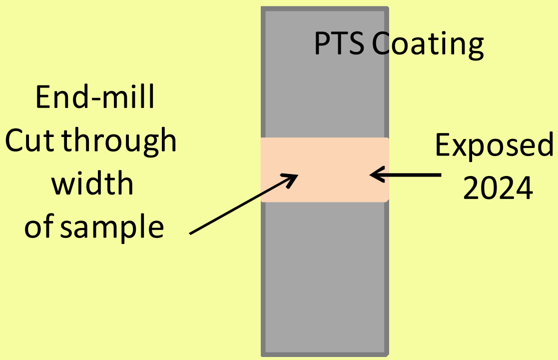


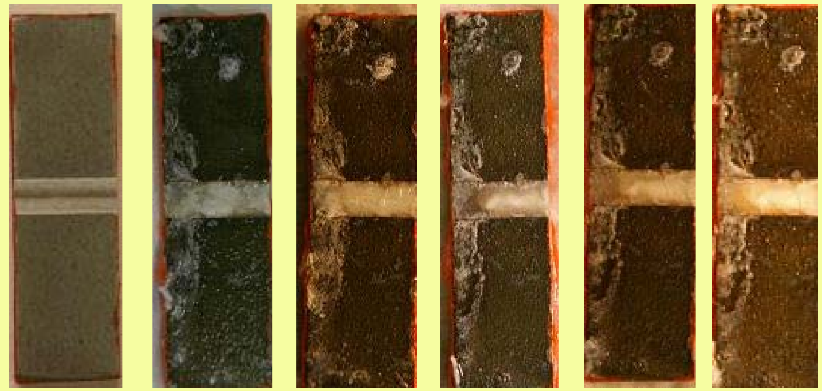
- All cells exposed to pH 2, 10 mM NaCl for 48 hrs
- (Above) area of PTS 0.15 cm^{2}, testing over 48 hrs

KEY FINDINGS

PTS demonstrates enhanced sacrificial anodic protection (compared to melt-spun ribbon). When coupled to PTS, pitting events on AA 2024 stop.

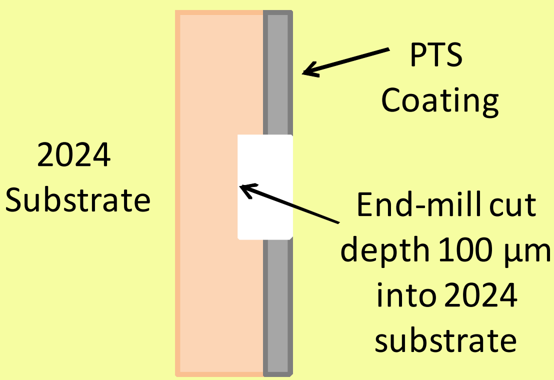
ASTM B-117 Salt Fog





PTS 5 mm

0 288 432 600 786 1000 hrs



Alclad™
5 mm

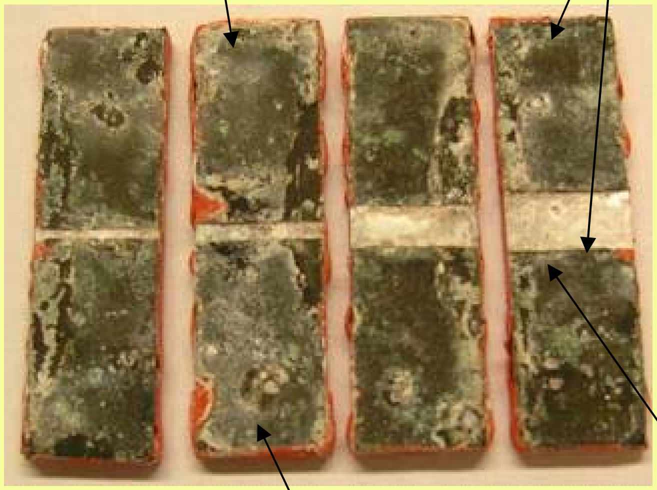
Salt Fog Results (cont)

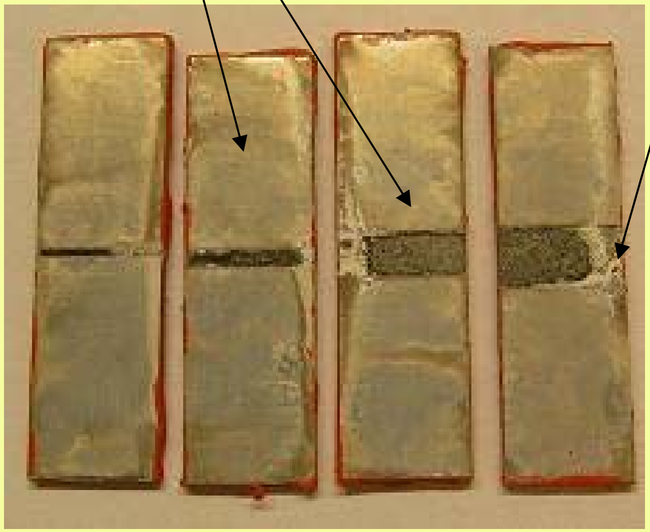
$CaCo_3$, $Mg(OH)_2$ from synthetic seawater (common for cathodically polarized surfaces)

No Cu detected on PTS samples

Cu detected (evidence of 2024 corrosion)

2024 not protected by Alclad™ *(black spots are pits)*





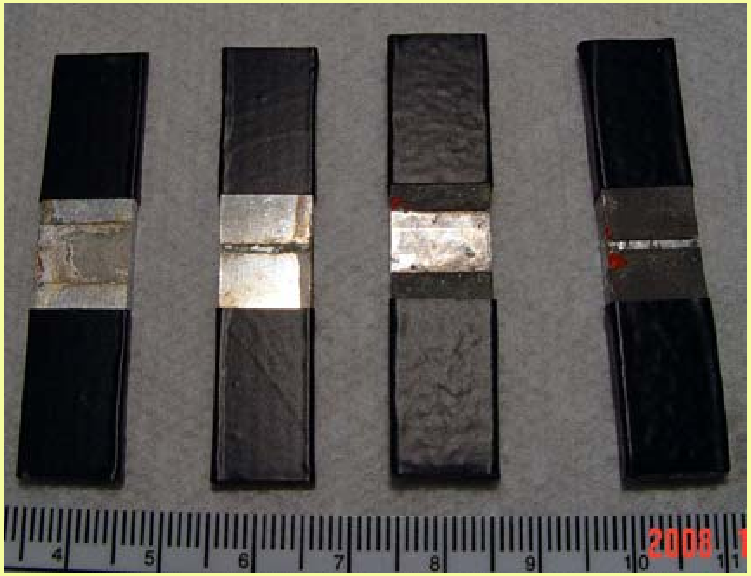
Corrosion pits seen
Pits may penetrate coating, but stop at 2024 (cathodic protection)

Exposed 2024 protected by Al-Co-Ce coating

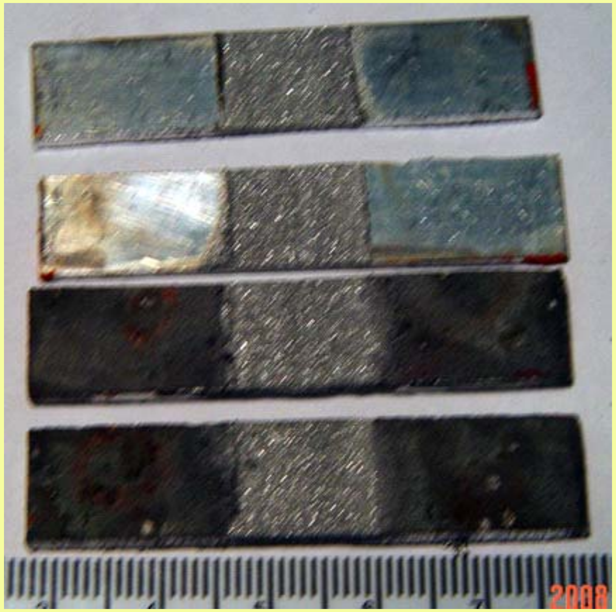
1, 2, 5 and 7 mm in width scratches in PTS coating (left) and Alclad™ (right) after 1000 hours

Repairing Damaged Samples

Alclad™ and PTS coated samples with 1 mm and 7 mm scratches after 1000 hours of B117



After acetone cleaning.
Target repair areas around scratches.
(electrical tape masks remainder)



After gritblast preparation.
(masking removed)

PTS Repair

PTS coating 1 mm scratch

PTS coating 7 mm scratch

Damaged

Recoated (unpolished)

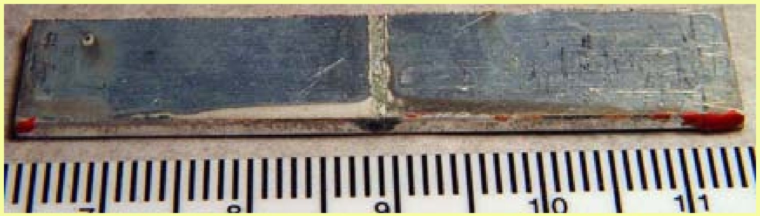
Repaired

What is preferred surface for PTS coating? More surface area enables higher inhibitor release rates. Smoother coatings preferred for many applications. OEM may prefer “as-sprayed” for process simplicity. For this study, polished samples highlight continuity between repair and original.

Alclad Repair

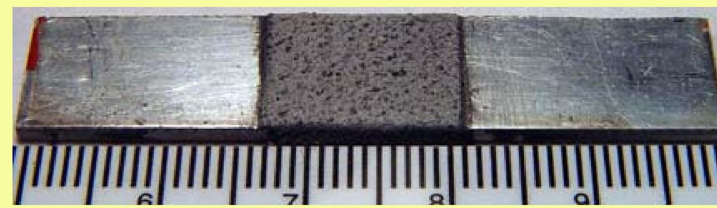
Alclad™ 1 mm scratch

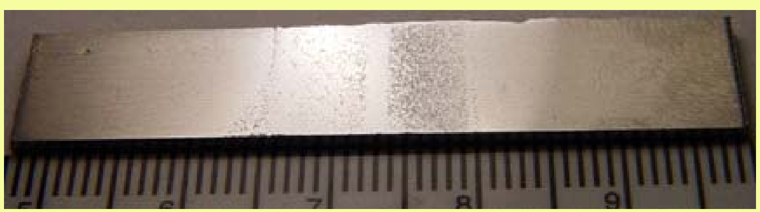
Alclad™ 7 mm scratch



Damaged

Recoated (unpolished)





Repaired

For repair of locally damaged areas, polishing of surface will not significantly affect cost/repair time. Using PTS for repair of existing Alclad™ surfaces may be easier commercialization route than incorporating PTS coatings into an OEM spec.

Summary

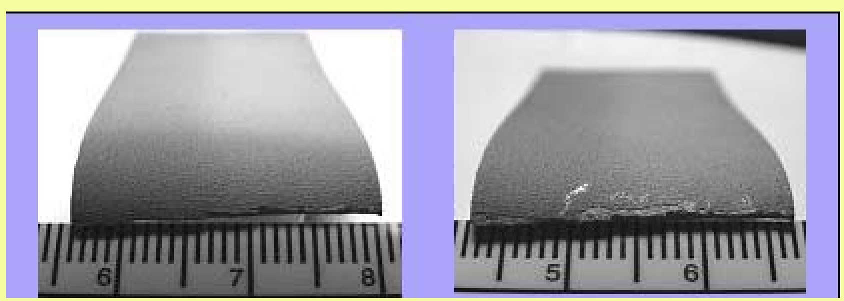
- PTS-sprayed Al-Co-Ce results in a dense, nanocrystalline/amorphous coating
- The coating has been demonstrated to act as:
  1) Barrier to general and local corrosion
  2) Sacrificial anode
  3) Source of corrosion inhibitor ions
- Salt spray testing has confirmed the ability of the coating to protect damaged areas
- Process is suitable for in-field repair of both its own coatings and legacy cladding

Future Work

- Fatigue testing
- Continued focus on improving as-sprayed surface finish
- More environmental testing
- Further optimization of repair process
- Assessment of commercial market, development of commercialization plan

Would like to establish relationship with Air Force end-user to:

Help determine application requirements
Focus in on a few target applications
Provide guidance for in-field repair capabilities/limitations



Any Questions?