
DEPOSITION OF AMORPHOUS ALUMINUM ALLOYS AS A REPLACEMENT FOR ALUMINUM CLADDING

US Army Corrosion Summit
February 3-5, 2009
Clearwater, FL

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This work sponsored by an Airforce STTR Phase II Contract No. FA 9550-U6-C-0077) under the
direction of Maj. Michelle Ewy (AFOSR)

Report Documentation Page

Form Approved
OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE FEB 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Deposition of Amorphous Aluminum Alloys as a Replacement for Aluminum Cladding				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) Enigmatics Inc.,9215 51st Avenue, No. 7,College Park,MD,20740				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					
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			

Presentation Outline

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- Future Work

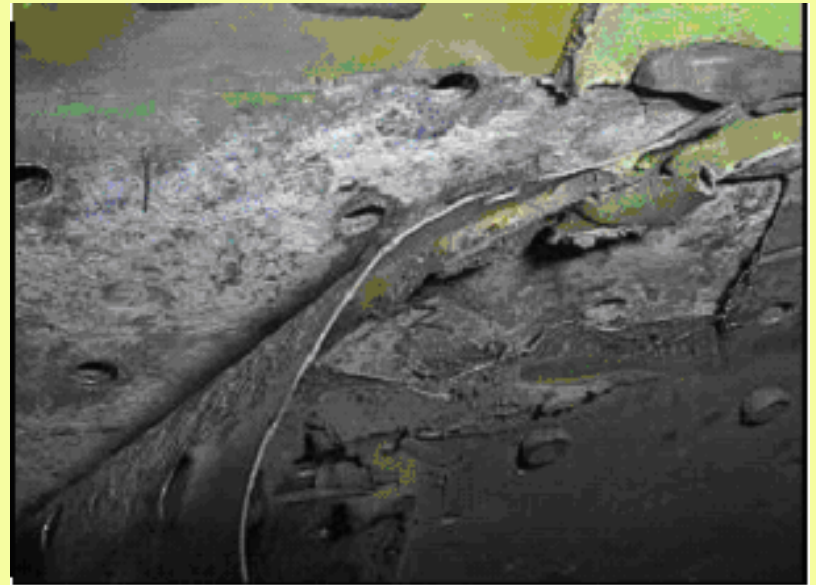


Photo from R. Kelly/D. Peeler/D. Kenzie
Corrosion concerns at lap-splice joint

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)

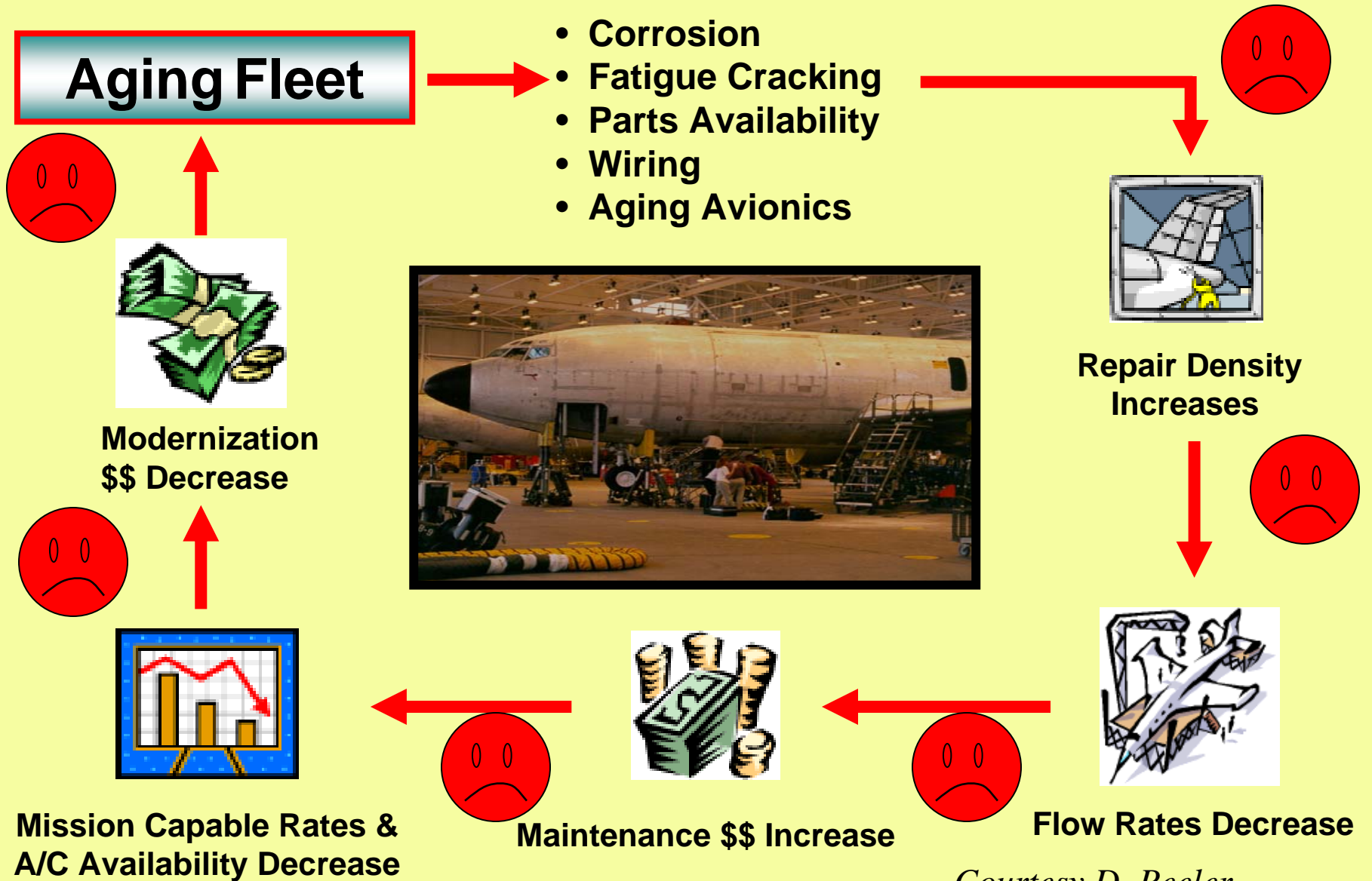
- Requires suitable coating technology
 - Form high-density coating
 - Retain desired amorphous or near-amorphous nanostructure

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)

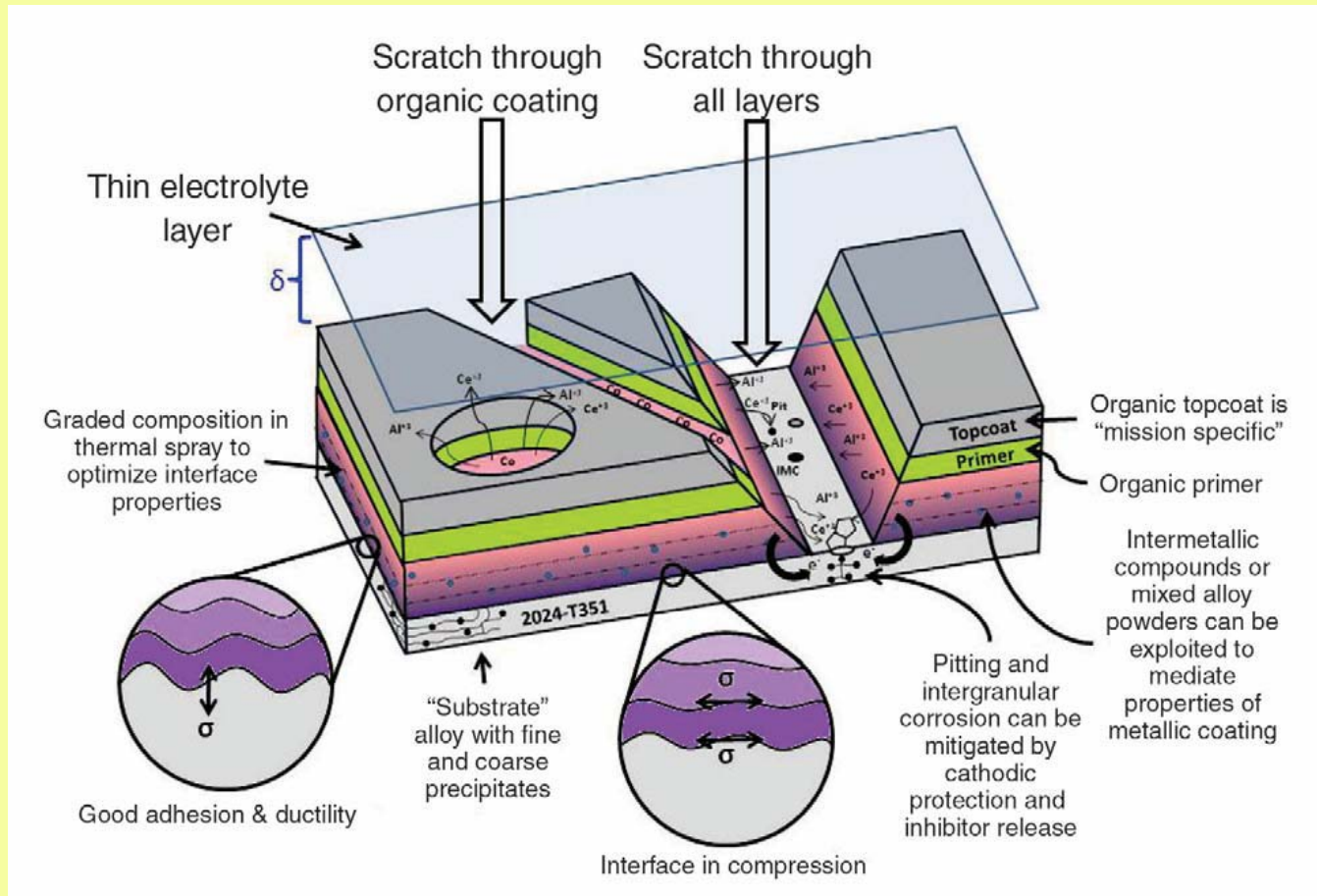


Aging Aircraft Challenge



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).

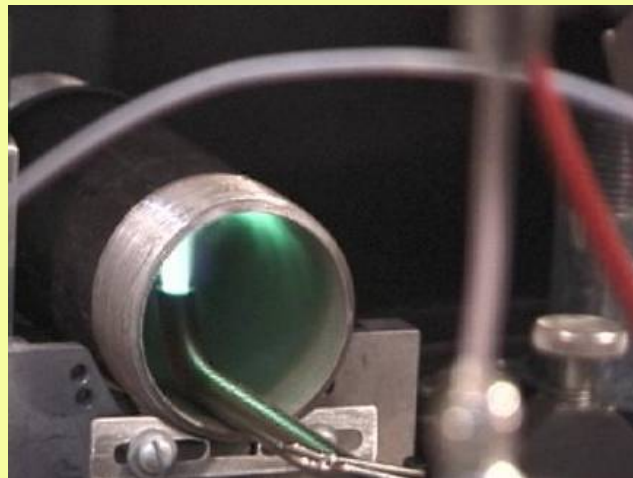
Desirable Coating Attributes

- **Barrier: Good Corrosion Resistance**
 - Defined by $E_{PIT}(\text{Alloy}) > E_{PIT}(\text{AA 2024-T351})$
 - 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 $E_{OCP}(\text{Alloy}) < E_{OCP}(\text{AA 2024-T351})$
 - 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, $\uparrow\downarrow\text{moles/cm}^2\text{-s}$
 - Alloy composition or chemical composition
 - Minimum oxide in coating
 - Does not need to be amorphous
 - Surface engineering to optimize release

Project Overview

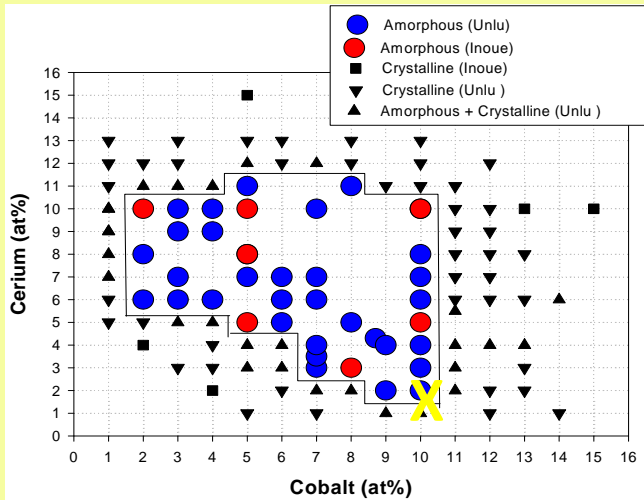
Develop practical PTS-applied corrosion protective coating

- ❑ 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



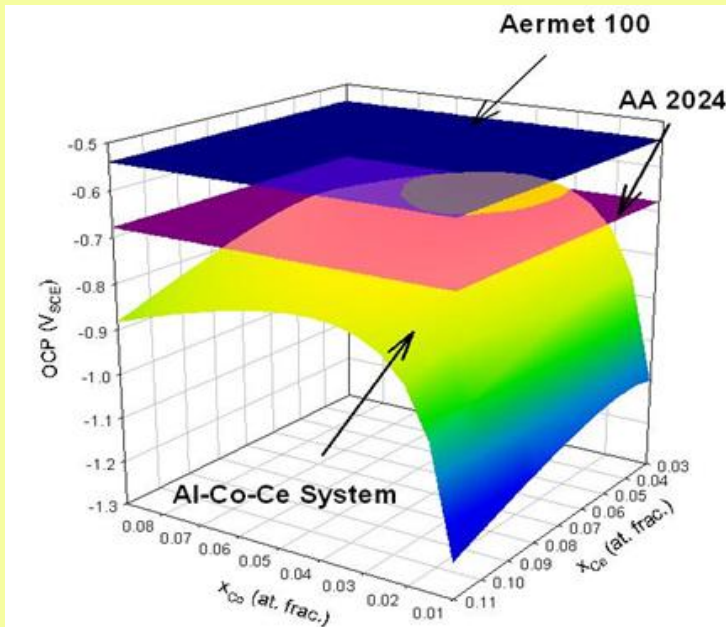
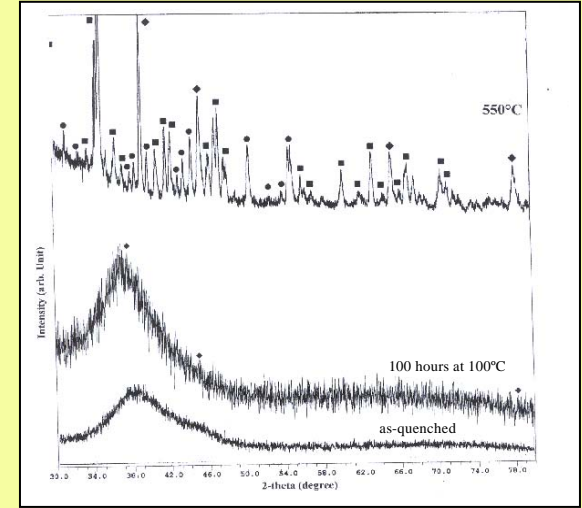
PTS system showing small ID coating capability

Alloy Development



Glass-forming composition identified

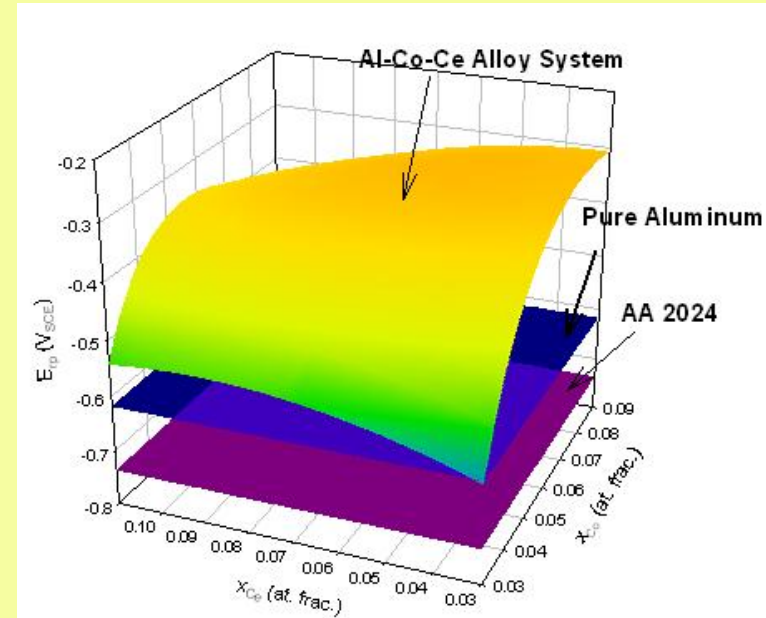
Stable amorphous state at 100° C (alloy stable to higher temperatures than 2024)



Tunable Properties

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)

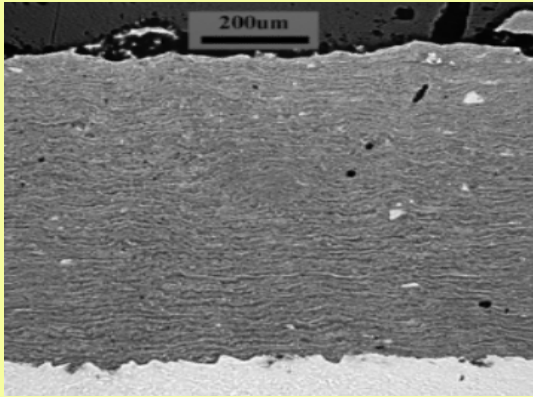
2. **Reduced substrate thermal loading**

- Substrate maintained under 100° C to prevent overaging & recrystallization
- Use of small feedstock particles (<20 microns) over a cold (<100° C) substrate leads to 10⁶ K/s cooling rates and formation of amorphous or nanocrystalline coatings

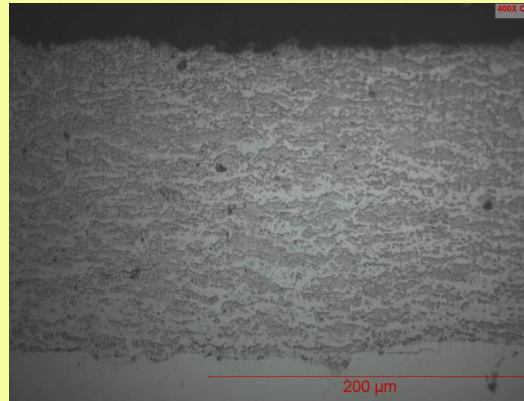
3. **Minimal substrate standoff (¼-1”)**

- Capable of tracing complex surface features
- Allows ID coating capability

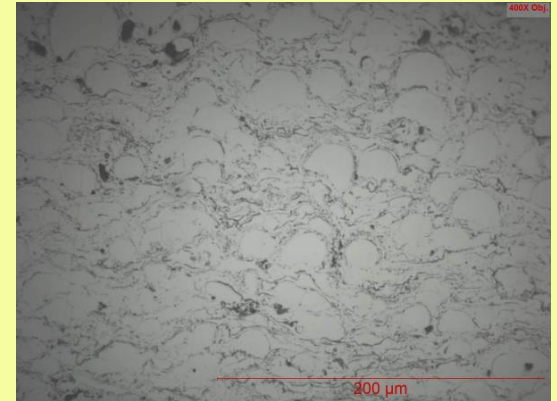
Pulsed Thermal Spray



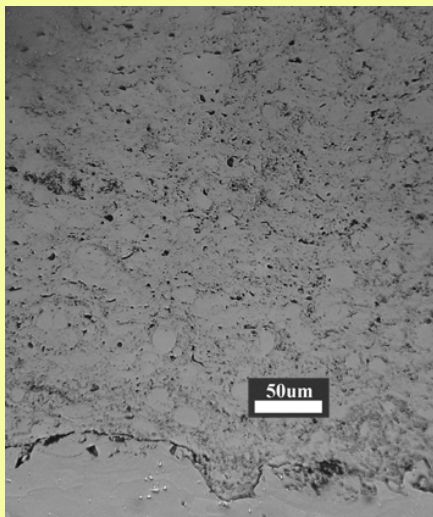
Tantalum for gun barrel applications



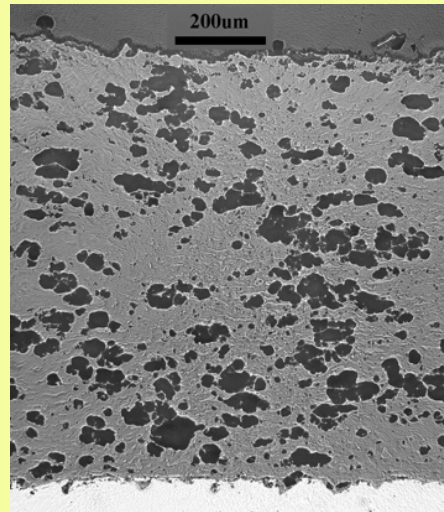
WC-Co-Cr for landing gear ID



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



Pure aluminum for Cd replacement

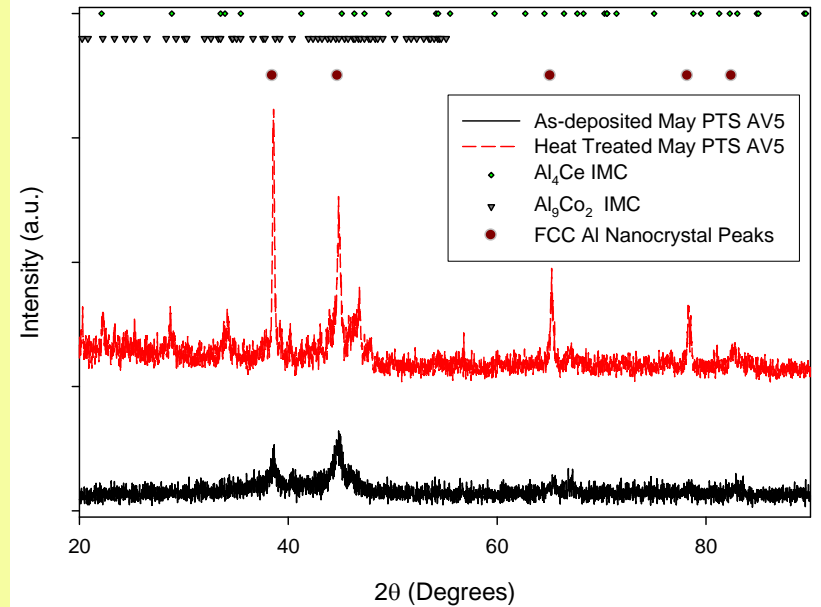
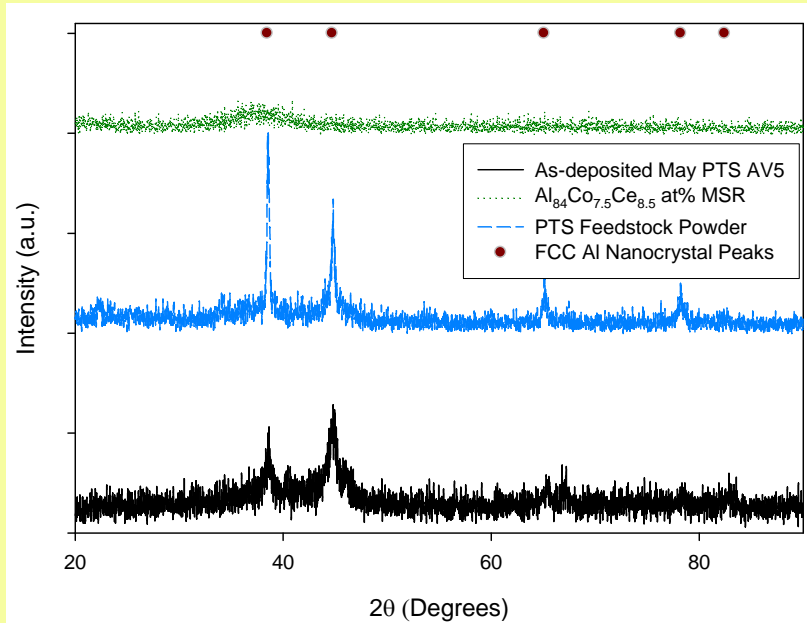


Porous Y-ZrO₂ for thermal barrier system

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.

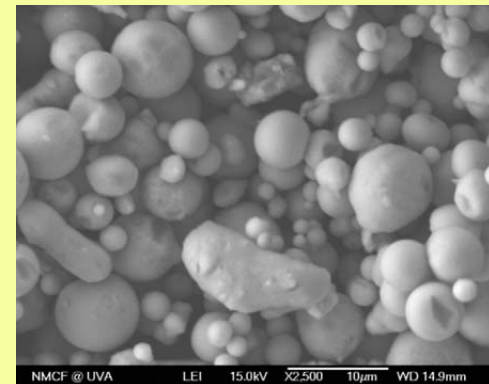
Nanostructured Al-Co-Ce



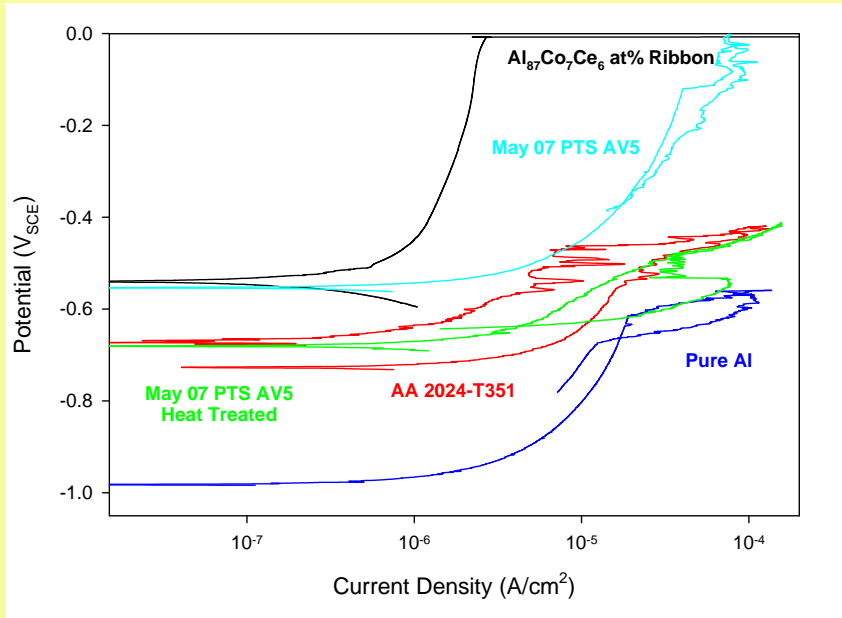
- Composition of feedstock powder and PTS is $\text{Al}_{88}\text{Co}_{10}\text{Ce}_2$ at%, MSR is $\text{Al}_{87}\text{Co}_7\text{Ce}_6$ at%
- Sample heat treated at 275 °C for 6 hrs and 285 °C for 3 hrs

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 .

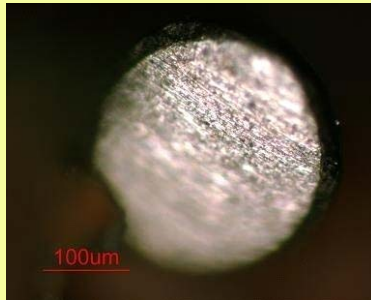
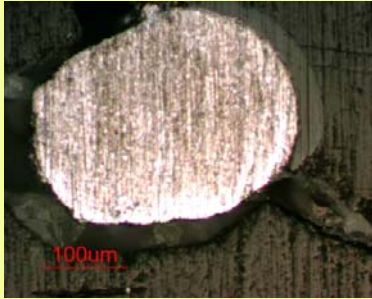
Heat treated sample treated at 275 C (527 F) for 6 hours followed by 285 C (545 F) for 3 hours. Grain growth and observation of intermetallics were noted in XRD (previous slide).

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

Sacrificial Anode and Inhibitor Release Capability

Pretest

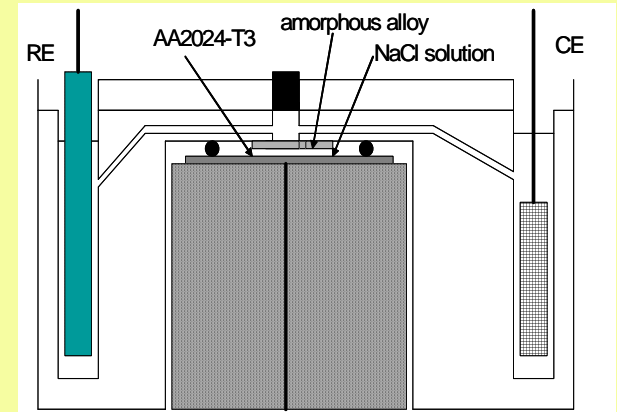
Alone



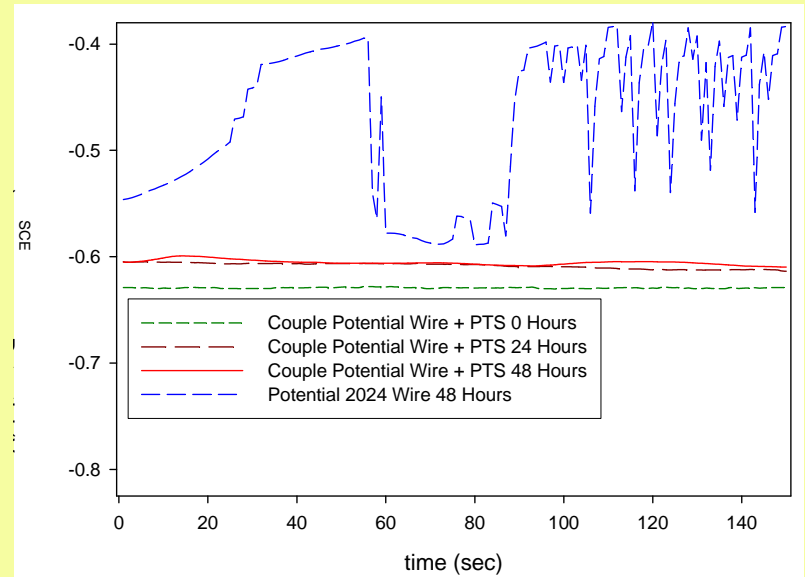
Coupled to MSR

Coupled to PTS

- All cells exposed to pH 2, 10 mM NaCl for 48 hrs
- (Above) area of PTS 0.15 cm² testing over 48 hrs



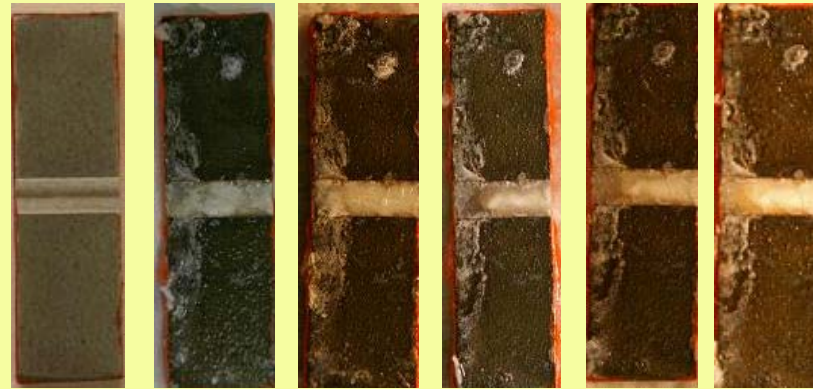
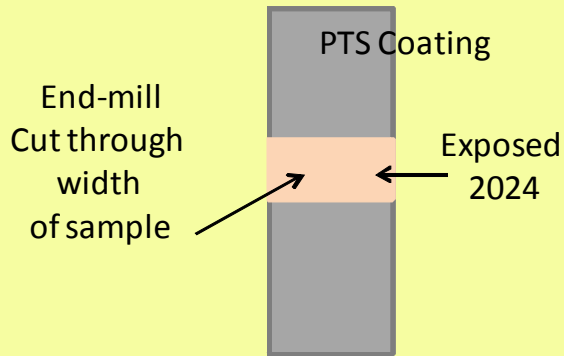
Potential, V_{SCE}



KEY FINDINGS

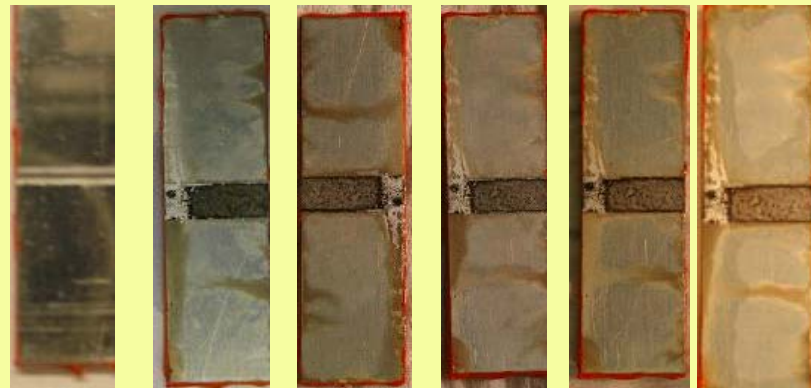
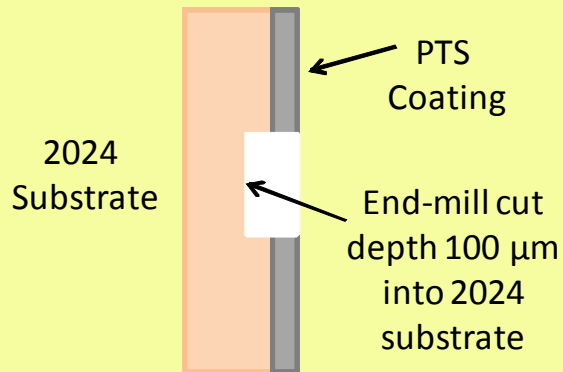
PTS demonstrates enhanced sacrificial anodic protection (compared to melt-spun ribbon). When coupled to PTS, pitting events on AA 2024 stop.

ASTM B-117 Salt Fog



PTS 5 mm

0 288 432 600 786 1000 hrs



Alclad™
5 mm

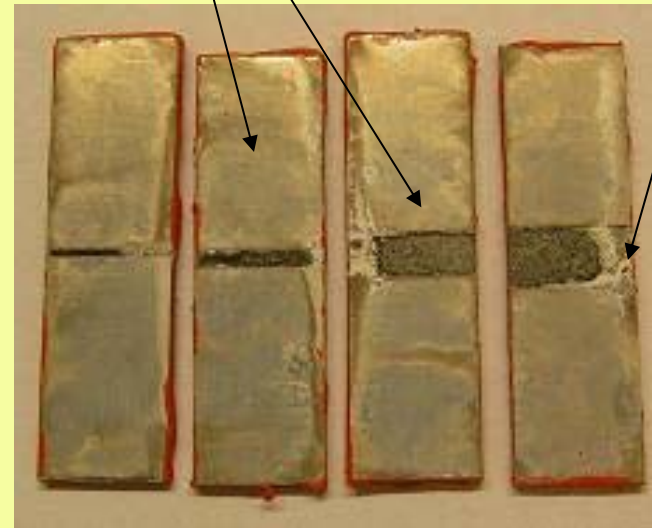
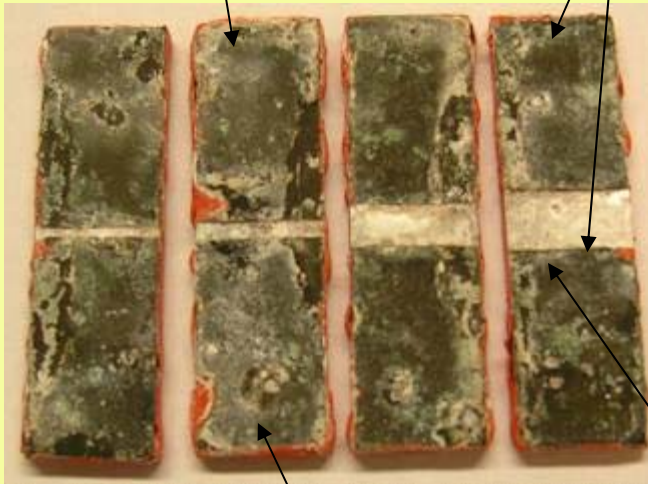
Salt Fog Results (cont)

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)



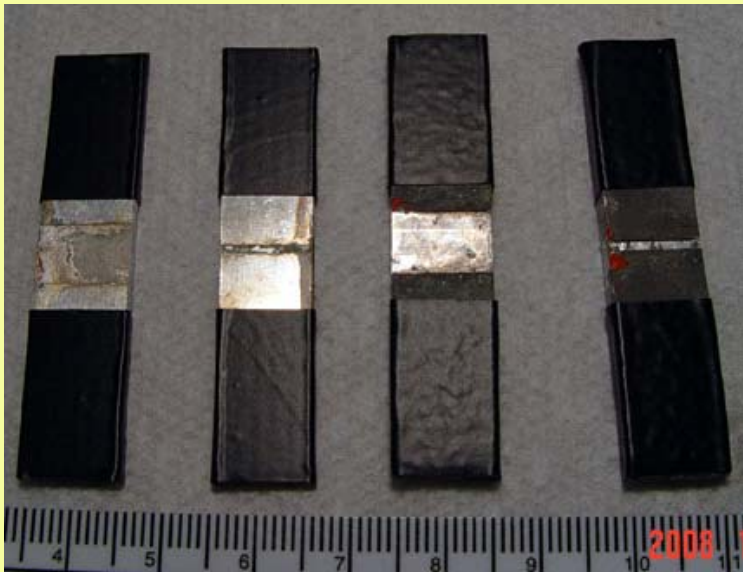
Corrosion pits seen
Pits may penetrate
coating, but stop at 2024
(cathodic protection)

Exposed 2024 protected
by Al-Co-Ce coating

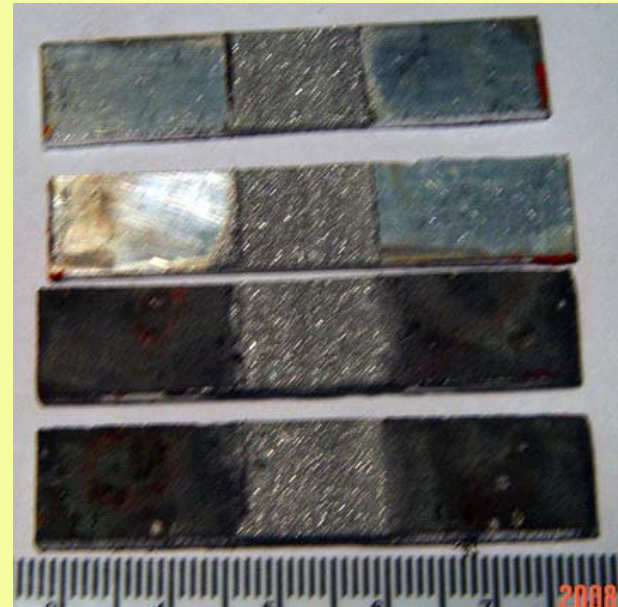
1, 2, 5 and 7 mm in width scratches in PTS coating (left) and Alclad™ (right) after 1000 hours

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



Damaged

PTS coating 7 mm scratch



Recoated
(unpolished)



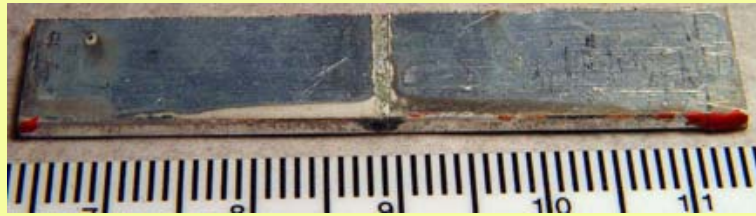
Repaired



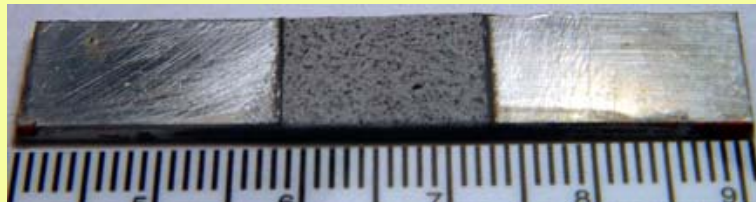
What is preferred surface for PTS coating? More surface area enables higher inhibitor release rates. Smoother coatings preferred for many applications. OEM may prefer “as-sprayed” for process simplicity. For this study, polished samples highlight continuity between repair and original.

Alclad Repair

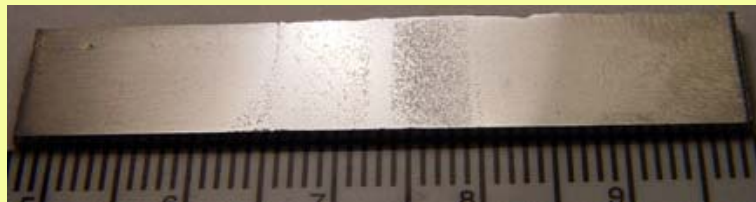
Alclad™ 1 mm scratch



Damaged

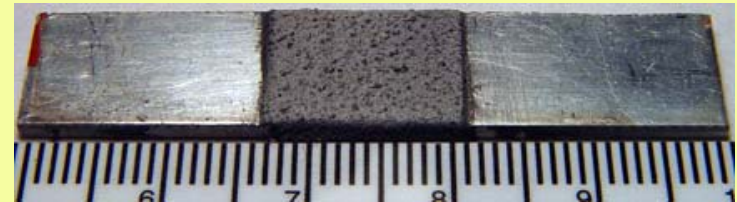
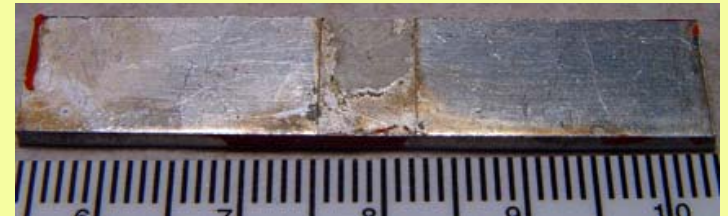


Recoated
(unpolished)



Repaired

Alclad™ 7 mm scratch



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

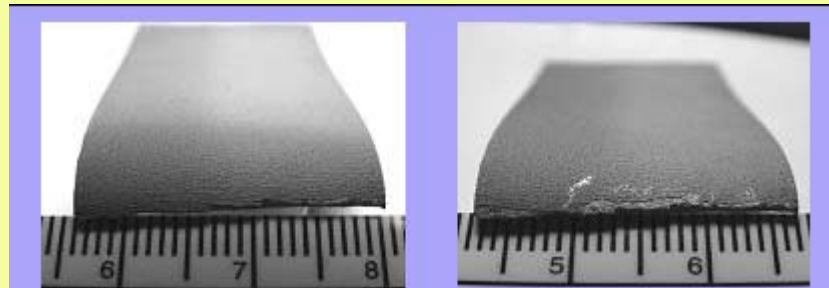
- Fatigue testing
- Continued focus on improving as-sprayed surface finish
- More environmental testing
- Further optimization of repair process
- Assessment of commercial market, development of commercialization plan

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?