

E2S2 2011

May 10, 2011

Indium and Zinc Alloys as Cadmium Brush Plating Replacements



Elizabeth Berman, Ph.D.
Air Force Research Laboratory
Materials & Manufacturing Directorate

Natasha Voevodin, Ph.D.
University of Dayton Research Institute

Paul Brezovec
Melissa Klingenberg, Ph.D.
Eileen M. Schmura
Concurrent Technologies Corporation

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 10 MAY 2011		2. REPORT TYPE		3. DATES COVERED 00-00-2011 to 00-00-2011	
4. TITLE AND SUBTITLE Indium and Zinc Alloys as Cadmium Brush Plating Replacements				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, Materials & Manufacturing Directorate, 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 Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 9-12 May 2011 in New Orleans, LA.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 33	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			



Multi-Agency Team



- **Air Force Research Laboratory (AFRL)**
- **Hill Air Force Base**
- **Portsmouth Naval Shipyard (PNS)**
- **Concurrent Technologies Corporation (CTC)**
- **Boeing**
- **Northrop Grumman**
- **Harris Consulting**



Presentation Overview



- **Problem Statement**
- **Program Objective**
- **Technical Approach**
- **Current Status**
- **Summary**
- **Way Ahead**



Problem Statement



- Cadmium (Cd) plating is used on mating steel surfaces on Department of Defense (DoD) Weapon Systems
 - Federal regulations on Cd use have increased to protect human health and the environment
 - Rate of phase-out and cost have increased
- Maintenance, repair, and overhaul operations of a Cd-plated component has been transitioned to PNS that had previously eliminated Cd plating process as a standard operation
 - Obtained a waiver to enable the use of a Cd plating process
 - DoD facility requested that AFRL seek a “green” replacement



Program Objective



- Identify new material(s), develop, test, and optimize a brush-plated replacement
 - Meet SAE-AMS-QQ-P-416, Type I Class 2 Cd Specification
 - Must be electrically conductive throughout service life
 - Offer sacrificial corrosion protection to mild (10XX) steel
 - Must not produce voluminous corrosion products
 - Environmentally benign
- Transition process to DoD facility
 - Process must be straight forward to use
 - Process is similar to current processing
 - Design, fabricate and provide shielding for components that are not to be wetted during processing
 - Reduces the use of disposable rags and adsorbent industrial pads



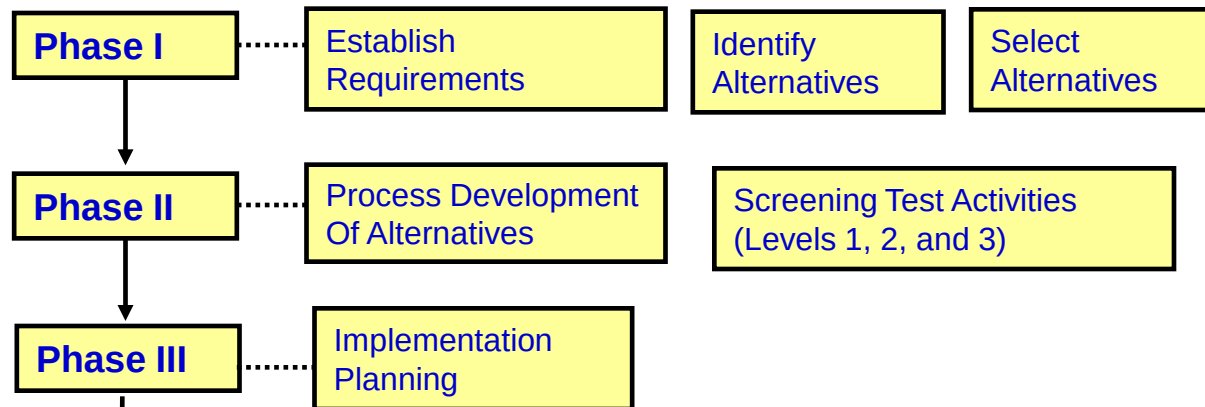
Commercial Cd Plating Setup



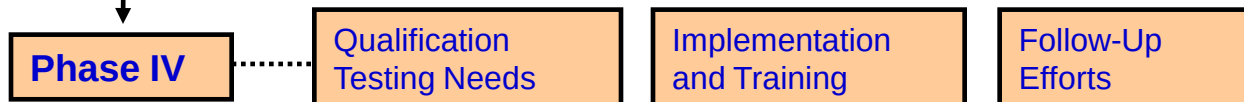
Approach



Assessment and Justification Phases



Production and Deployment Phase





Program Status: Overview



- Completed requirements analysis and technology assessment
 - Conducted comprehensive review in 2008 and 2010 to assess state-of-the-art technology
 - Selected and tested initial coating candidates (2009-2010)
 - Indium-tin (In-Sn), tin-zinc (Sn-Zn), and zinc-nickel (Zn-Ni)
 - In and Sn foils
 - Selected and currently testing follow-on candidates (2010 – present)
 - Indium-zinc (In-Zn) and different Zn-Ni chemistries
 - Considering other electrolytes for depositing current and previous chemistries
- Performing process development and testing
 - Completed full testing on In-Sn, Sn-Zn, and two Zn-Ni chemistries
 - Evaluated In-Zn foils to determine desired compositional range
 - Included standard brush-plated Zn-Ni chemistry and an immersion-plated Zn-Ni chemistry



Program Status: Overview



- Performing process development and testing (cont'd)
 - Performing initial testing on two In-Zn and two Zn-Ni chemistries
 - Developing soluble anode deposition of In-Zn
 - Developing insoluble anode deposition of In-Zn
 - Developing Zn-Ni immersion chemistry into brush plating chemistry
 - Evaluating previously unavailable Zn-Ni brush plating chemistry
 - Using same Zn-Ni chemistry as being implemented at Odgen Air Logistics Center (OO-ALC) for landing gear



Technology Assessment Update



- Alloys of Zn and In show potential due to possible anodic protection
 - Dependent upon alloying element and whether a true alloy is achieved

Active (Anodic)

1. Magnesium
2. Manganese
3. Zinc (plated)
4. Aluminum
5. Cadmium (plated)
6. Indium
7. Tin (plated)
8. Steel 1010
9. Iron (cast)

10. Copper (plated)
11. Nickel (plated)
12. Cobalt
13. Bismuth
14. Tungsten
15. Titanium
16. Silver
17. Gold
18. Graphite

Noble (Less Anodic)



Attributes of Indium



Indium Foil



Indalloy #1 Wire
50% indium, 50% tin

- ✓ Not considered hazardous
- ✓ Commercial brush plating products can plate indium within thickness tolerances
- ✓ Sacrificial to mild steel (in sea water) and its couple to mild steel produces a potential <0.15 volts
- ✓ Electrically conductive, similar to Cd
- Metal “cold welds” to itself / Alloy
Avoids “cold weld” issue
- Metal subject to halide attack / Alloy unknown to halide attack



Attributes of Zinc



Zinc Foil

- ✓ Commercial brush plating products can plate zinc within thickness tolerances
- ✓ Sacrificial to mild steel (in sea water)
- ✓ Zinc oxide is 10X to 100X more electrically insulating than cadmium oxide
- ✓ No PEL currently established specifically for Zn
 - ✓ OSHA established PELs for zinc chloride and zinc oxide fumes, zinc oxide, and zinc stearate



Coatings



Coating	Target Composition	Status
Cd	100% Cd	N/A
Sn-Zn	70% Sn, 30% In	Failed to meet corrosion requirements, but met conductivity requirements
In-Sn	50% Sn, 50% In	Failed to meet corrosion requirements, but met conductivity requirements
Zn-Ni (I)	92-86% Zn, 8-14% Ni	Failed to provide adequate adhesion without Ni strike
Zn-Ni (II)	92-86% Zn, 8-14% Ni	Testing continues
Zn-Ni (III)	92-86% Zn, 8-14% Ni	Testing continues
In-Zn (I)	60-70% In, 30-40% Zn	Testing continues
In-Zn (II)	60-70% In, 30-40% Zn	Testing continues
In-Zn (III)	60-70% In, 30-40% Zn	In process-development

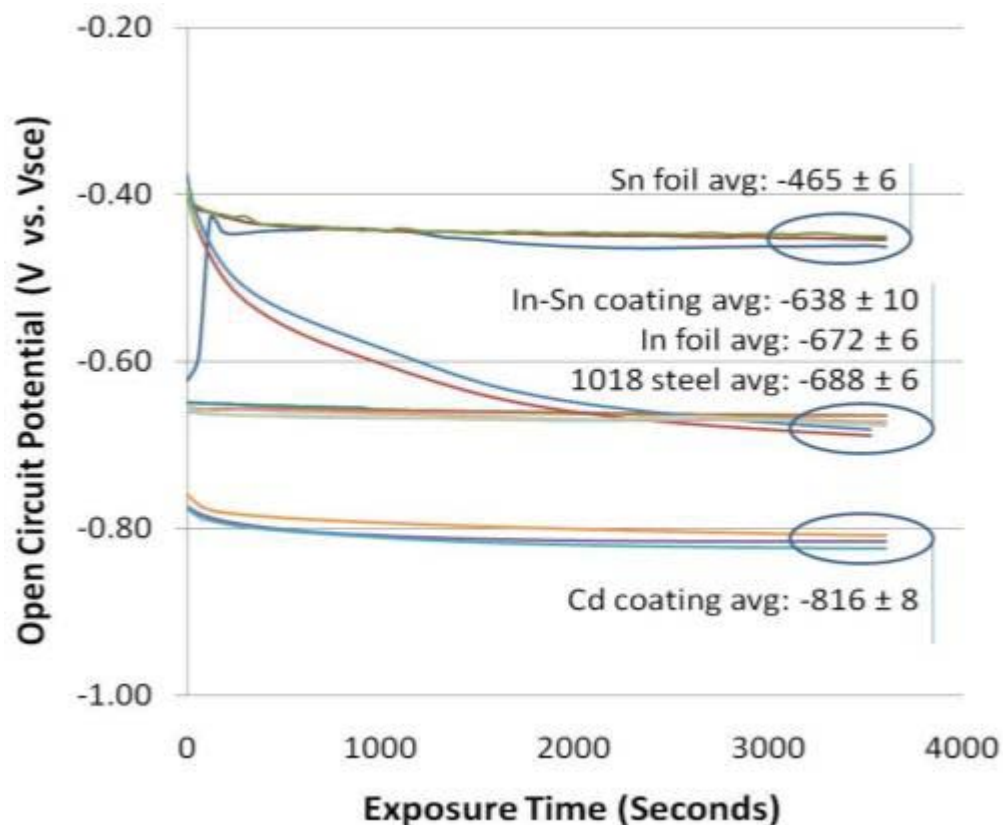


Electrochemical Testing: Open Circuit Potential (OCP)



Test Material	OCP at 1 hour (mV)
Ave Sn Foil (99.99% Sn)	-465 ± 6
Ave In Foil (99.99% In)	-672 ± 6
Brush-Plated In-Sn	-665 ± 3
Brush-Plated Cd	-816 ± 8
Bare 1018 Steel	-688 ± 6

Test solution: 3.5 % NaCl

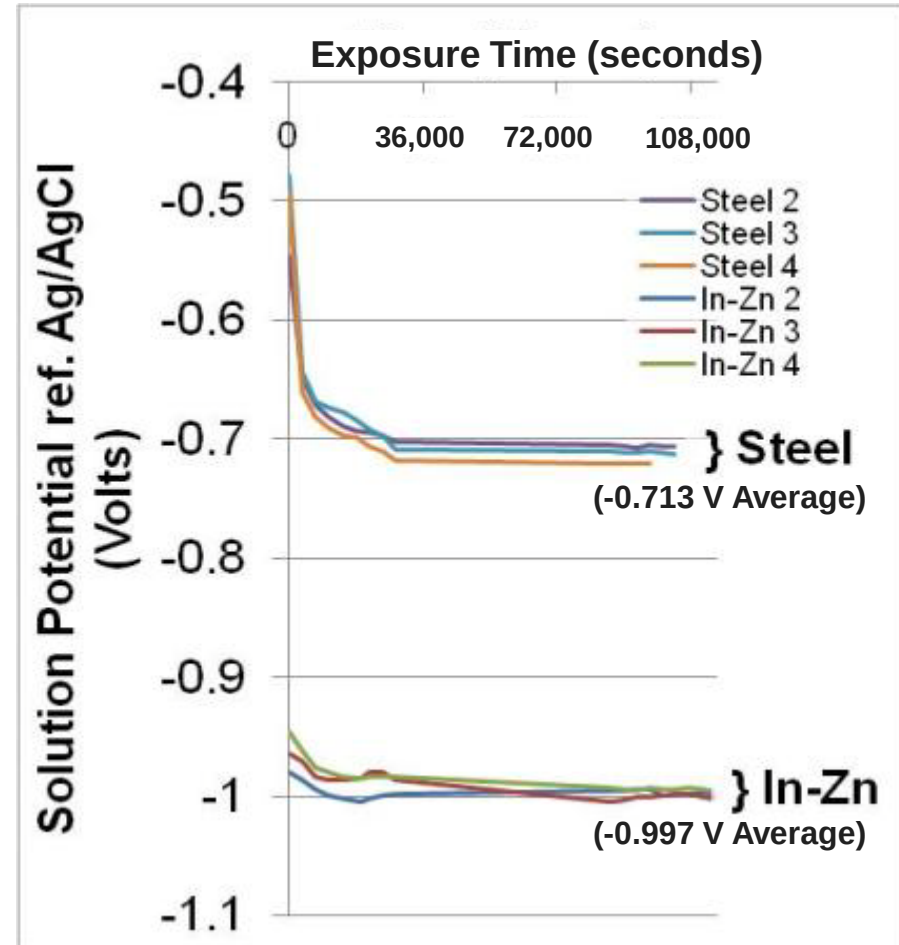




Solution Potential In-Zn & Steel



- Compositions Tested
 - Three bare steel panels
 - Three different In-Zn
 - InZn-2: 74 wt.% In: 26 wt.% Zn
 - InZn-3: 78 wt.% In: 22 wt.% Zn
 - InZn-4: 80 wt.% In: 20 wt.% Zn
- Results suggest In-Zn will provide sacrificial protection to the steel substrate under submerged saltwater conditions
 - Steady state reached at 4 readings ± 5 millivolts
 - In-Zn coating is more electronegative than steel





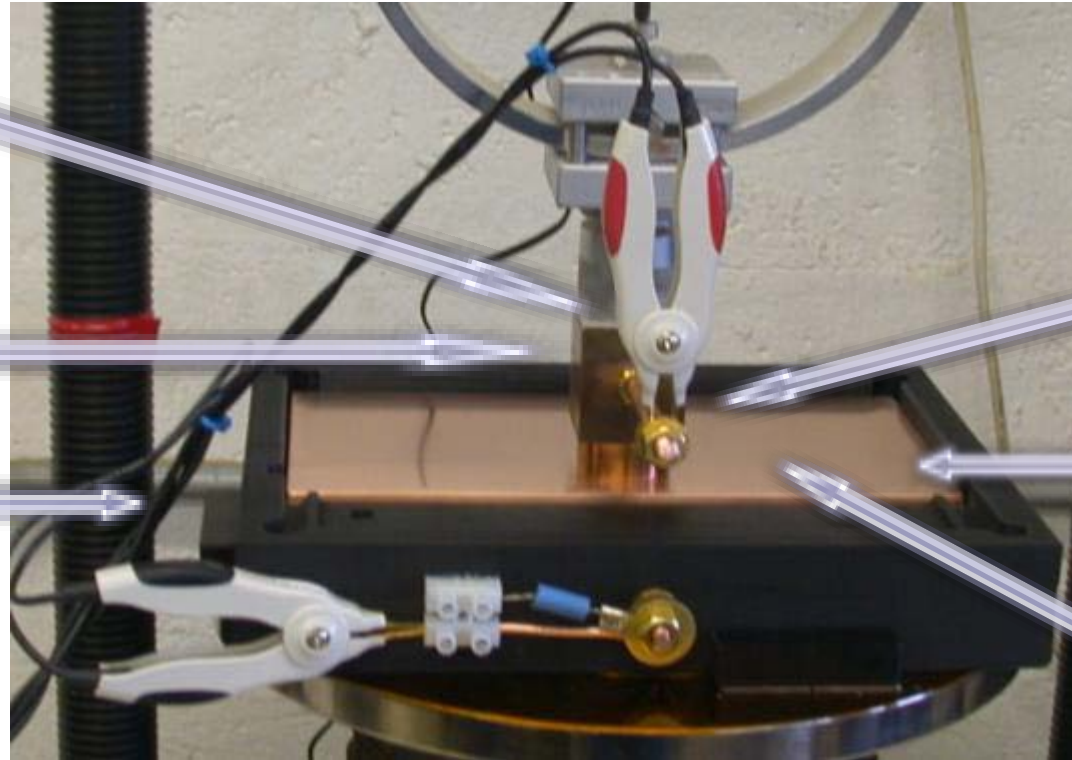
Electrical Resistance



Electrical
Isolation
(Kapton® Tape)

Upper Electrode
(1-inch² Area)

To 4-Wire
Low Contact
Resistance Meter



Load (200-
pounds/inch²)

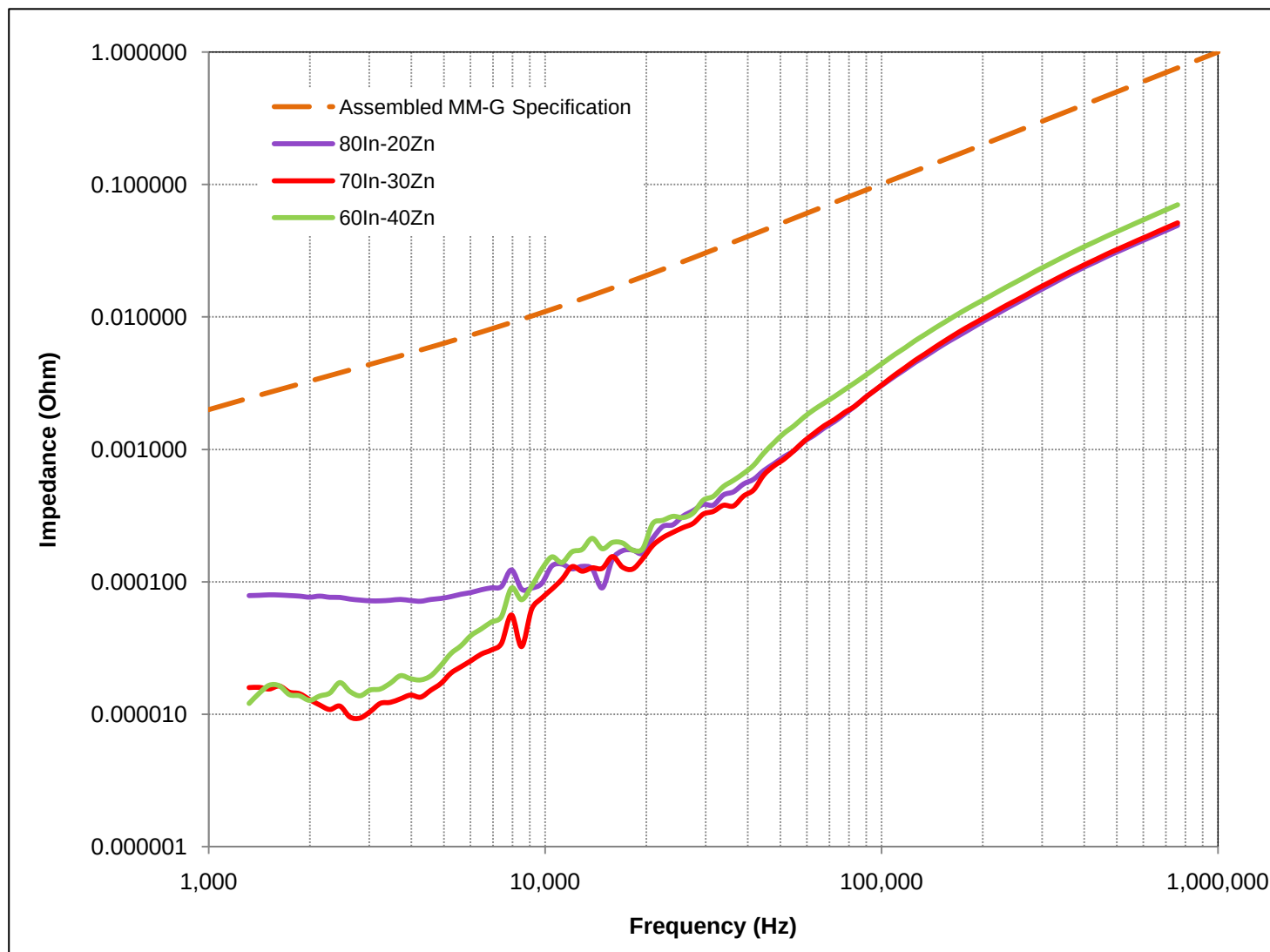
Lower Electrode
(= Panel Area)

Test Panel
Placement Area

Fixture made of ABS Plastic



Electrical Resistance: In-Zn Foils

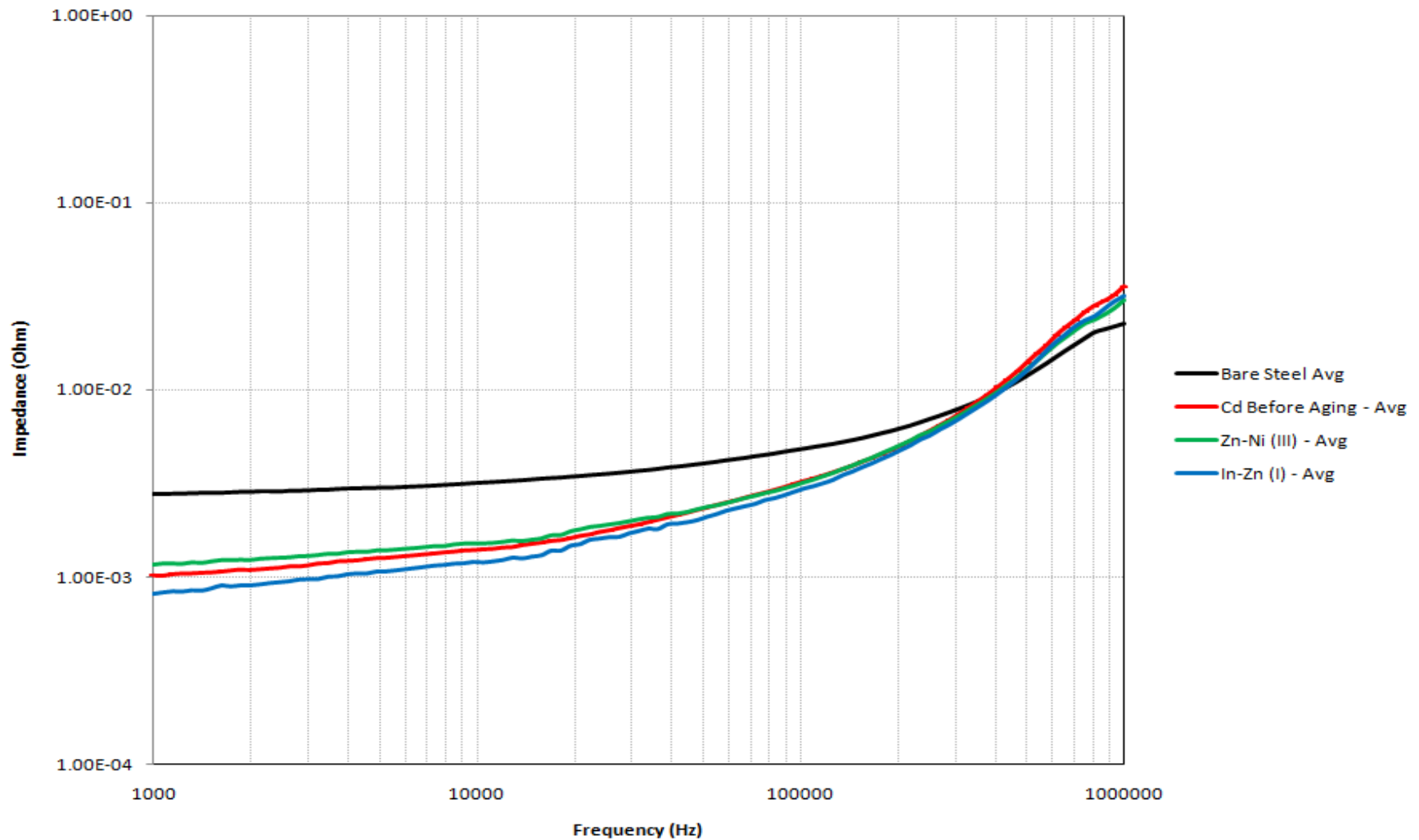




Electrical Resistance: As-plated



Averages of All Panels Per Coating





Salt Fog Corrosion Resistance



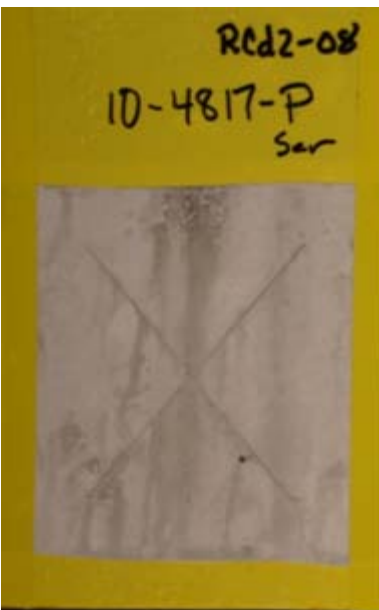
- Testing per ASTM B 117
- Cd, Zn-Ni (II), and In-Zn (II) are complete
- Zn-Ni (III) and In-Zn (I) are in progress
- In-Zn (III) not tested since it is in process development



Coating	Condition	First Sign of White Rust	First Sign of Red Rust	Noticeable Propagation of Red Rust
Cd	Scribe	16 hours	121 hours	600 hours
	Un-Scribe	16 hours	262 hours	935 hours
Zn-Ni (II)	Scribe	21 hours	116 hours	445 hours
	Un-Scribe	21 hours	116 hours	445 hours
Zn-Ni (III)	Scribe	22 hours	120 hours	505 hours
	Un-Scribe	22 hours	71 hours	702 hours
In-Zn (I)	Scribe	22 hours	120 hours	505 hours
	Un-Scribe	22 hours	173 hours	505 hours
In-Zn (II)	Scribe	16 hours	262 hours	600 hours
	Un-Scribe	16 hours	121 hours	935 hours



First Sign of White Rust (Scribed)



Cd
(16 hrs)



Zn-Ni (II)
(21 hrs)



Zn-Ni (III)
(22 hrs)



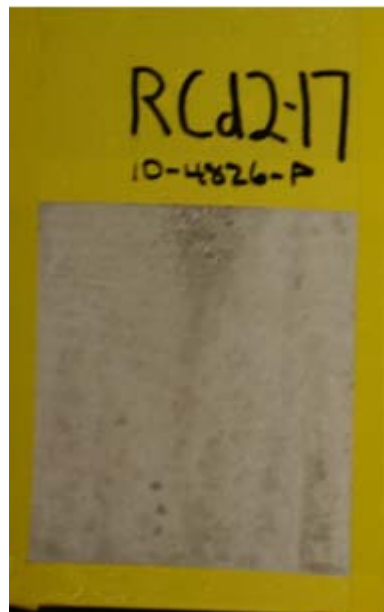
In-Zn (I)
(22 hrs)



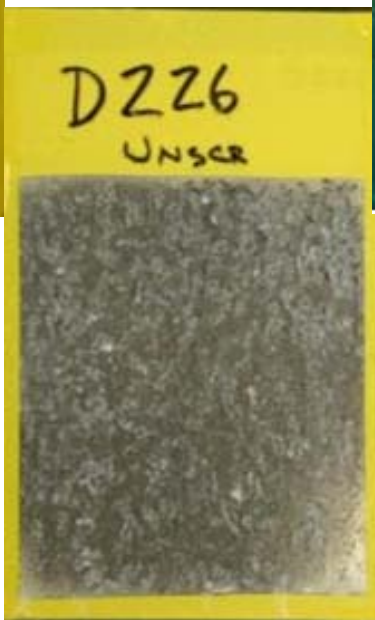
In-Zn (II)
(16 hrs)



First Sign of White Rust (Un-scribed)



Cd
(16 hrs)



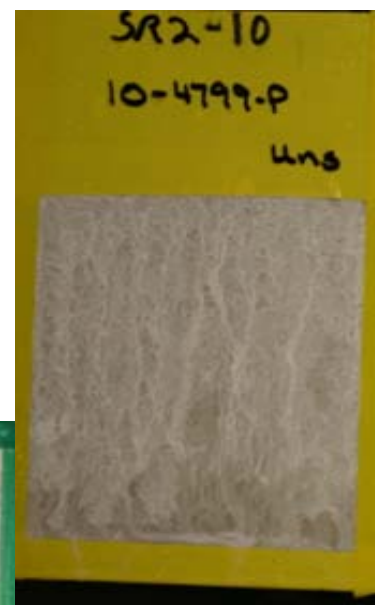
Zn-Ni (II)
(21 hrs)



Zn-Ni (III)
(22 hrs)



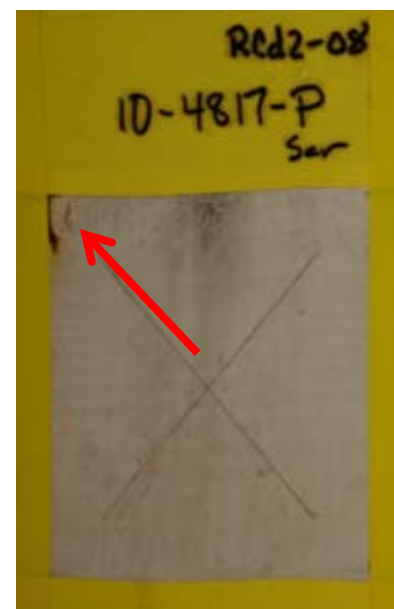
In-Zn (I)
(22 hrs)



In-Zn (II)
(16 hrs)



First Sign of Red Rust (Scribed)



Cd
(121 hrs)



Zn-Ni (II)
(116 hrs)



Zn-Ni (III)
(120 hrs)



In-Zn (I)
(120 hrs)

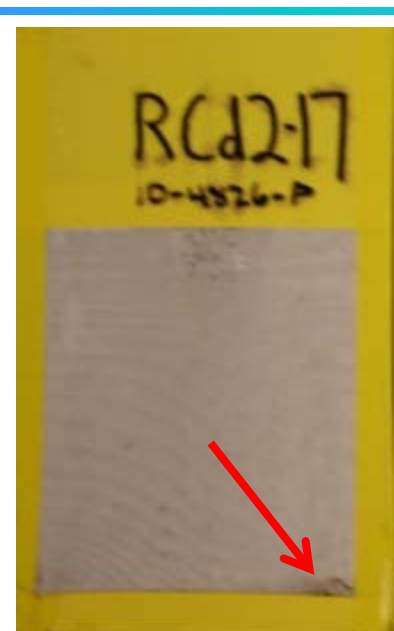


In-Zn (II)
(262 hrs)

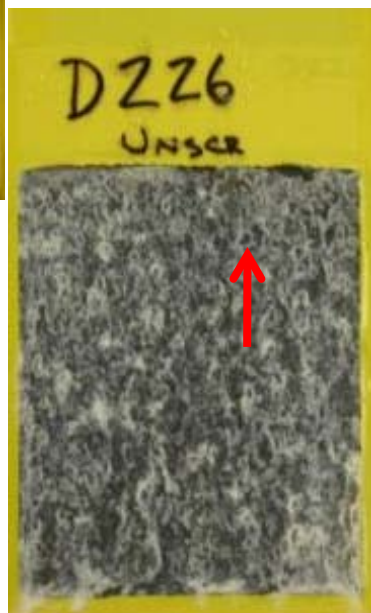
Red Rust
indicated by
Red Arrow



First Sign of Red Rust (Un-scribed)



Cd
(262 hrs)



Zn-Ni (II)
(116 hrs)



Zn-Ni (III)
(71 hrs)



In-Zn (I)
(173 hrs)

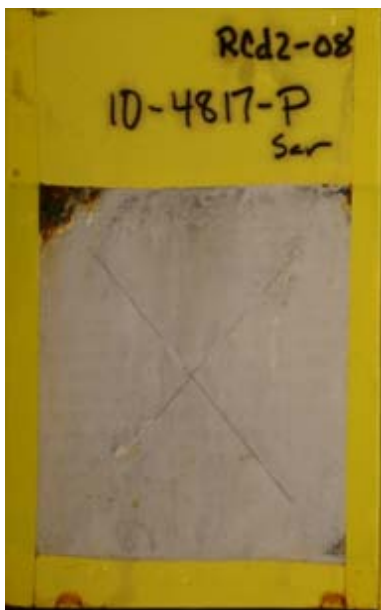


In-Zn (II)
(121 hrs)

Red Rust
indicated by
Red Arrow



Noticeable Propagation of Red Rust- (Scribed)



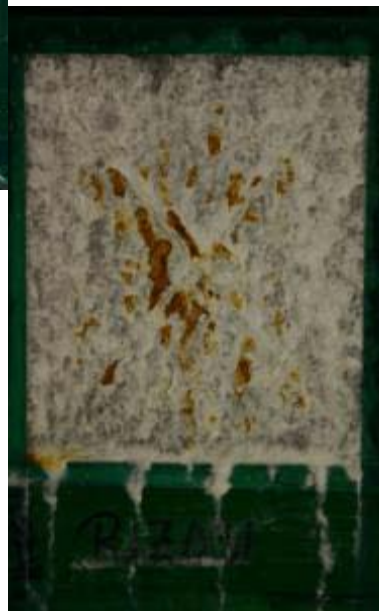
Cd
(600 hrs)



Zn-Ni (II)
(445 hrs)



Zn-Ni (III)
(505 hrs)



In-Zn (I)
(505 hrs)



In-Zn (II)
(600 hrs)



Noticeable Propagation of Red Rust (Un-scribed)



RCd2-17
10-4826-P
Unscr



Cd
(935 hrs)

DZZ6
Unscr



Zn-Ni (II)
(445 hrs)



SZN-12
Zn-Ni (III)
(702 hrs)



RI-030
In-Zn (I)
(505 hrs)

SR2-10
10-4799-P
Unscr



In-Zn (II)
(935 hrs)



Summary



- **Performed electrochemical testing on In and Sn foils and In-Sn coatings**
 - In-Sn is not sacrificial to steel - no further testing was conducted
- **Preliminary results showed success using an immersion-plated Zn-Ni**
 - Partnered with Zn-Ni vendor to modify the process chemistry for brush plating (shown as Zn-Ni II)
 - Continued development and testing
- **Identified a new/pre-commercial brush-plating Zn-Ni**
 - Currently testing product as Zn-Ni III



Summary



- **In-Zn Plating Testing**
 - OCP data indicates In-Zn will provide sacrificial protection to steel substrate under submerged saltwater conditions
 - Developing two systems for this program
 - Working with chemical suppliers on an insoluble anode (In-Zn I) system and a soluble anode system (In-Zn II)



Way Ahead



- Continue process screening and optimization testing of additional candidates
 - Finalize development of Zn-Ni brush plating parameters
 - Finalize plating activities for In-Zn and Zn-Ni brush plating
- Complete verification testing
- Implement identified alternative(s)
- Seeking non-aqueous deposition techniques of alternative(s)



Laboratory Brush-Plating Set-up



Acknowledgements



- **This work was conducted under tasking by the Air Force Research Laboratory.**
- **The authors would like to recognize the beneficial contributions of**
 - Dr. Elizabeth Berman, AFRL
 - Dr. Natasha Voevodin, University of Dayton Research Laboratory (UDRI)
 - Hill Air Force Base
 - PNS
 - Harris Consulting
 - Matco Services Inc.

Back Up Slides



OCP of In-Zn



- Three In-Zn coated coupons
 - Tested as-received
 - Composition
 - “InZn-2,” 74 wt.% In: 26 wt.% Zn
 - “InZn-3,” 78 wt.% In: 22 wt.% Zn
 - “InZn-4,” 80 wt.% In: 20 wt.% Zn
 - Appeared chalky white
- Three bare mild steel coupons
 - Wet-sanded with 600 grit silicon carbide (SiC) paper and washed with deionized water to provide a fresh surface for testing



In-Zn Coated Coupons



**Steel Substrate Coupon (typical)
[shown are the backsides of the
In-Zn coated coupons]**



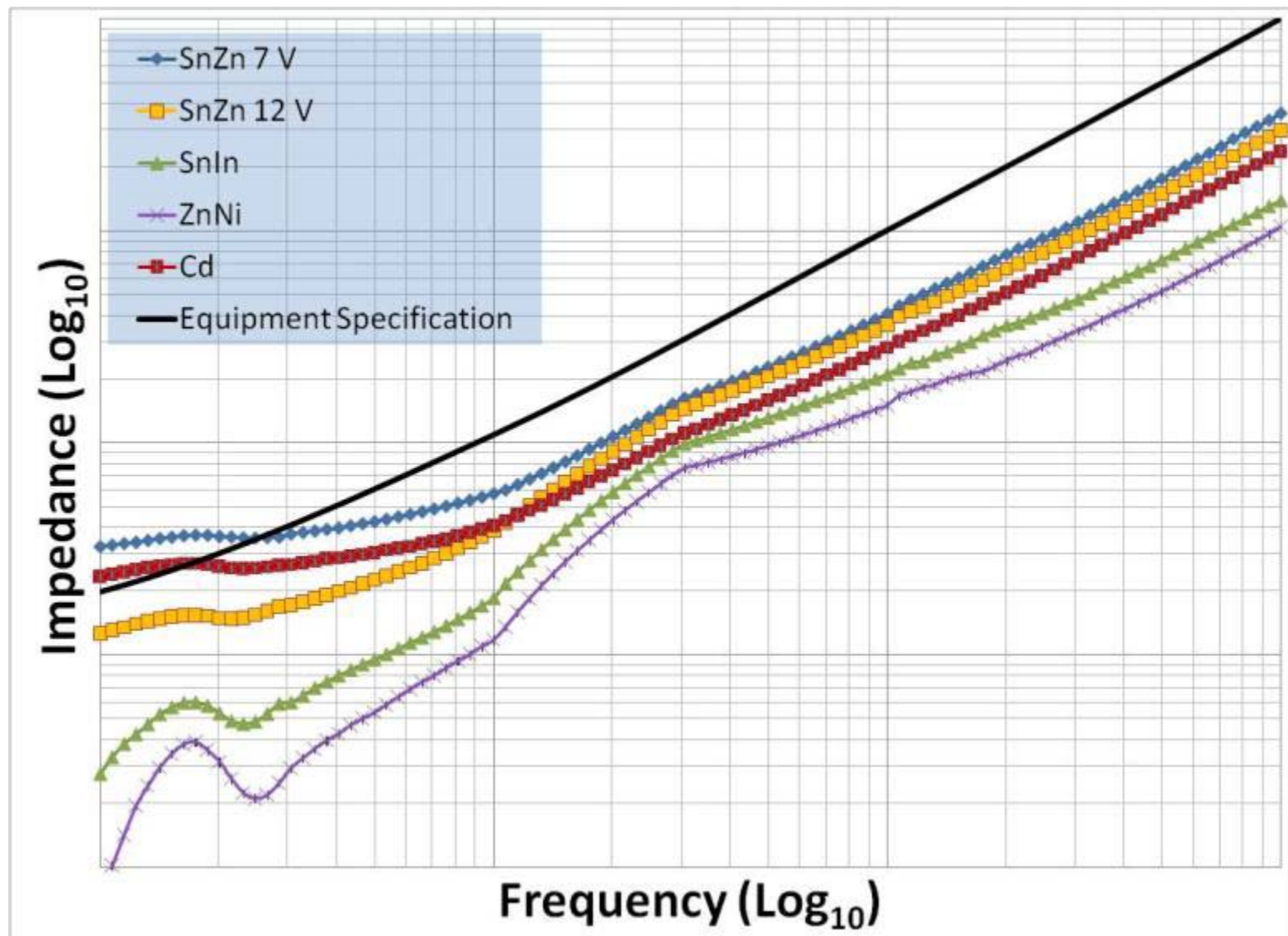
Caveats of Indium Alloys



1. Low temperature eutectic:
 - The Sn-In system eutectic is 244°F at ~48.3 weight % Sn
 - Cd-In-Sn system eutectic is ~199°F
 - Good for a solder
2. Greater hardness than both Cd and In:
 - Less deformable on the mating surfaces
 - Potentially reduces the contact between these surfaces and electrical conduction
3. Relatively expensive; therefore, conduct a review of its cost/benefit to adopt indium alloy plating



Electrical Resistance- As-plated





Electrical Resistance- Aged

