### SERDP & ESTCP Webinar Series

# Hexavalent Chrome Elimination from Hard Chrome Surface Finishing

October 1, 2015



### SERDP & ESTCP Webinar Series

### Welcome and Introductions

Rula Deeb, Ph.D. Webinar Coordinator









# Agenda

Webinar Logistics

Dr. Rula A. Deeb

Geosyntec

(5 minutes)

Overview of SERDP and ESTCP

Dr. Robin Nissan

SERDP and ESTCP

(5 minutes)

Electrodeposited Nanostructured Alloys for Functional and Structural Applications

Dr. Jonathan McCrea

Integran Technologies

(25 minutes + Q&A)

 Electrodeposition of Nanocrystalline Cobalt-Phosphorus Alloy Coatings as an Alternative to Hard Chromium Electroplating Jack Benfer and Ruben Prado

Naval Air Systems Command

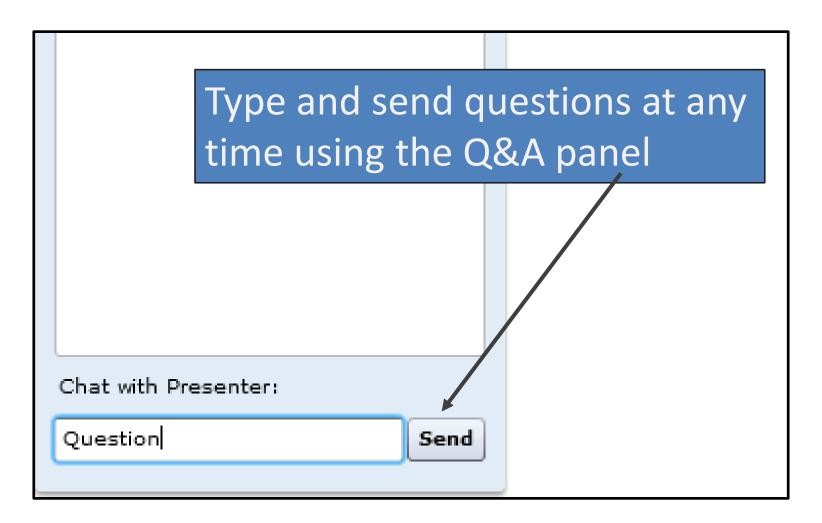
(25 minutes + Q&A)

Final Q&A session





### How to Ask Questions





### In Case of Technical Difficulties

- Delays in the broadcast audio
  - Click the mute/connect button
  - Wait 3-5 seconds
  - Click the mute/connect button again
  - If delays continue, call into the conference line
    - U.S./Canada: 1-877-776-3503
    - International: 330-871-6014
    - Required conference ID: 14046815
- Submit a question using the chat box

### SERDP & ESTCP Webinar Series

# SERDP and ESTCP Overview

Robin Nissan, Ph.D. Weapons Systems and Platforms Program Manager











### **SERDP**

- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management



### **ESTCP**

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

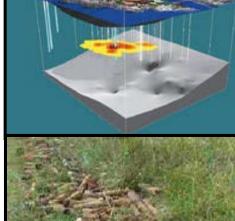




# **Program Areas**

- 1. Energy and Water
- 2. Environmental Restoration
- 3. Munitions Response
- 4. Resource Conservation and Climate Change
- 5. Weapons Systems and Platforms









## Weapons Systems and Platforms

- Major focus areas
  - Surface engineering and structural materials
  - Energetic materials and munitions
  - Noise and emissions
  - Waste reduction and treatment in DoD operations
  - Lead free electronics





### SERDP and ESTCP Webinar Series

DATE	Topics
October 15, 2015	LED-ing the Way: Sophisticated and Energy Efficient Exterior Lighting Systems for DoD Installations
October 29, 2015	Assessment and Treatment of Contaminated Sediments
November 12, 2015	Munitions Response: Land Based Program Closeout
December 3, 2015	Emerging Contaminants: DoD Overview and State of Knowledge on Fluorochemicals and 1,4-Dioxane
December 17, 2015	Watershed and Stormwater Management

### SERDP & ESTCP Webinar Series

### http://serdp-estcp.org/Tools-and-Training/Webinar-Series



### SERDP & ESTCP Webinar Series

### Electrodeposited Nanostructured Alloys for Functional and Structural Applications

Jonathan McCrea, Ph.D. Integran Technologies







# Agenda

- Problem statement
- Overview of nanostructured materials
- Nano CoP for hard chrome alternative
- Nano cobalt-alloys as an alternative to copper-beryllium high strength bushings
- Pulse plated ZnNi as an alternative to cadmium plating
- Conclusions



### **Problem Statement**

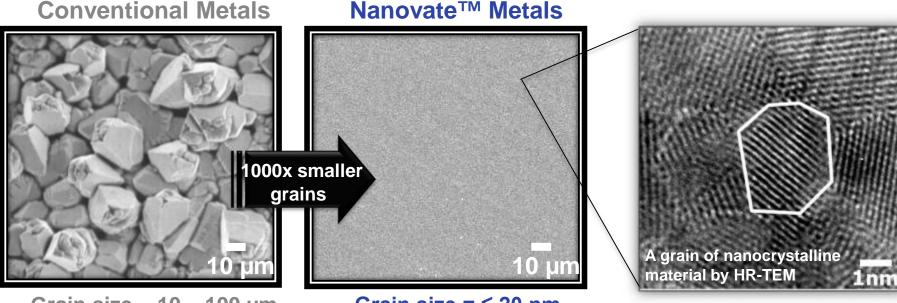
- Hexavalent chromium, copper-beryllium and cadmium continue to provide occupational health and safety concerns throughout the DoD
- Electrolytic Hard Chrome (EHC) coatings
  - Used for corrosion and wear protection of steel components (hydraulics, shocks, struts, etc.)
  - Process involves Cr<sup>6+</sup> → known carcinogen
- Copper beryllium
  - High strength, high resilience copper alloy used in spring contacts and anti-fretting, anti-galling bushings
  - Beryllium is a toxic substance
- Electrodeposited cadmium coatings
  - Used for sacrificial corrosion protection of steel components
  - Process and metal are toxic





### What is a Nanostructured Metal?

#### **Conventional Metals**



Grain size =  $10 - 100 \mu m$ 

Grain size =  $\leq 20 \text{ nm}$ 

A nanostructured metal is simple a metal with an average grain size in the nanometer range (10 - 100 nm) compared to >1 µm for a conventional metal

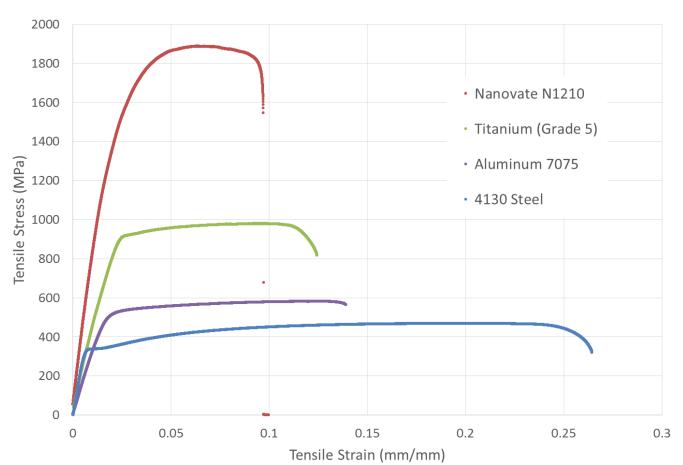
#### Decreasing Grain Size Dramatically Improves Hardness and Strength

Property	Units	Conventional Ni (20 µm)	Nanovate Ni (20 nm)
Yield Strength	MPa	100	900
Ult. Tensile Strength	MPa	400	1400
Vickers Hardness	kg/mm²	140	450



# Improved Properties Through Grain Refinement

Comparison of Nanostructured Ni-alloy strength with conventional structural materials

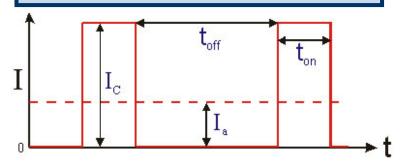


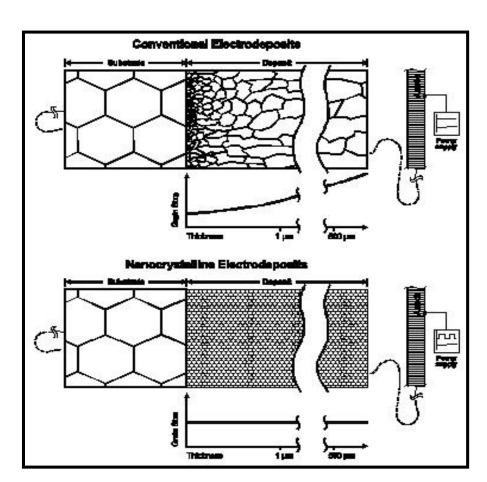


## How do we Achieve Unique Properties?

Microstructural control by pulsed electrodeposition

Pulse plating favors nucleation of new grains over growth of existing grains, resulting in an ultra-fine grain structure throughout the entire thickness of the coating, right from the substrate interface



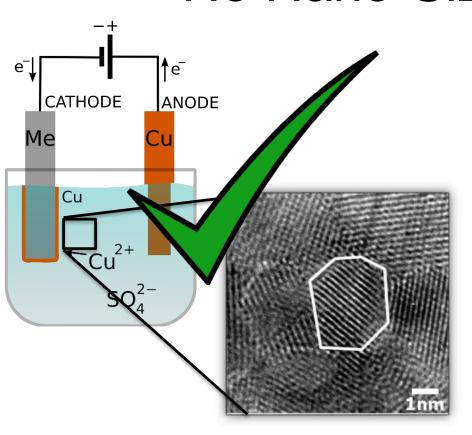


Pulsed electrodeposition from aqueous solutions results in the deposition of fully dense metal with a nanocrystalline grain size

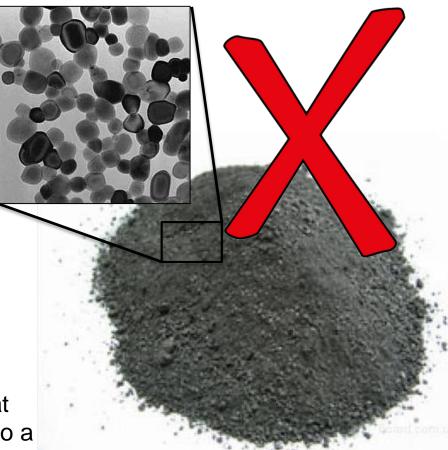




### No Nano-Sized Particles!



Metal ions (M<sup>2+</sup>) are reduced to solid metal at cathode during the process and arranged into a fully dense solid metallic "nanostructure". Particles are not used or produced in the process





### Several Nanovate™ Alloys Available

#### N1000 Series - Nickel

Good hardness, wear and corrosion resistance as well as good strength properties. Also used for erosion protection of composites

Grafalloy Epic<sup>™</sup> golf shaft - graphite/epoxy coated with Nanovate<sup>™</sup> N1010



#### N2000 Series – Nickel Alloy

Higher strength than the N1000 series. Some compositions also offer magnetic shielding properties, increased resilience or decreased CTE

EMI shielded cell phone casing

HE Nand

Metallix™\_\_\_\_ HEAD racquet with\_ Nanovate™ N2015 foil

#### R3000 Series - Cobalt

Superior hardness, wear and corrosion resistance; it has been validated as an environmentally friendly alternative to hard chrome. Also has excellent structural properties

Nanovate<sup>™</sup> R3010 for hydraulic actuators



#### C4000 Series – Copper

Strong and hard, fine grained Cu being developed for electronics, high strength wires, anti-microbial and defense applications

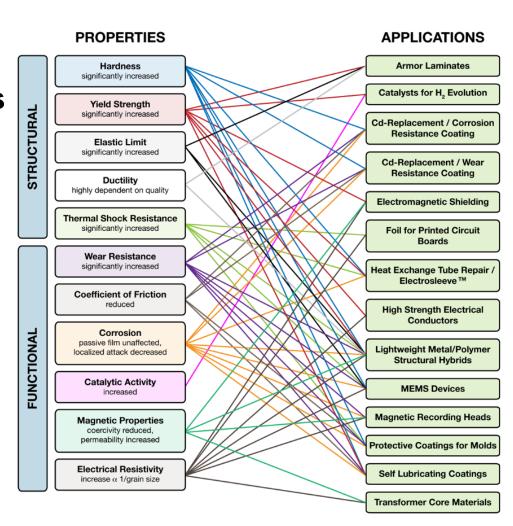
Nanovate<sup>™</sup> C4010 shape charge liner





### Multifunctional Materials

- Due to their ultrafine grain size, electrodeposited nanostructured materials possess an interesting combination of both structural and functional properties
- Used as either coatings and freestanding electroforms allows for numerous potential applications
- Can nanostructured materials be used as alternatives to toxic Cr, Cd and Be containing materials/processes?





# SERDP/ESTCP Projects

- Nanostructured materials have been investigated in various SERDP and ESTCP projects as possible alternatives to toxic processes and materials commonly used in DoD repair and overhaul sites
  - Nano CoP for Hard Chrome Alternative (PP-1152)
    - Corrosion/wear protection of steel hydraulics, shocks, struts, etc.
  - Nano cobalt-alloys for CuBe alternative (WP-2137)
    - High strength, anti-fretting, anti-galling bushings
  - Pulse plated alkaline ZnNi for Cd alternative (WP-1616)
    - Sacrificial corrosion protection of steel components



### Nanovate CR as Hard Chrome Alternative

#### SERDP

- Initial development program investigating various nanostructured alloys in 2000
- Cobalt selected as best fit for properties and environmental acceptability
- Positive results moved the technology to demonstration, validation and commercialization

#### ESTCP

- Entered into program in 2004
- Deployed with US Navy Depot, Jacksonville in 2006
- Validation for aerospace specifications
  - Hard chrome
  - Thin dense chrome
- Addresses all configurations, suitable for non line-of-sight-applications

#### Commercial use

Licensed to Enduro Industries in 2007



### Nanovate CR as Hard Chrome Alternative

#### Nanovate CoP advantages

- High deposition rate: 5x faster than chrome, shorter cycle/increased throughput
- High current efficiency: Reduced power consumption (up to 20 times less process power)
- Drop-in technology: Aqueous bath electroplating, reuse of equipment and minor training
- Bath stability: Bath maintenance basic and impurities can be removed

PROCESS COMPARISON			
	Nanovate CoP	Hard Chrome	
Efficiency	85-95%	15-25%	
Deposition Rate	Up to 200 µm/h (0.008"/hour)	Up to 40 µm/h (0.0016"/hour)	
Power Consumption	Low – Highly efficient process	High due to inefficient process	
Anode	Co Anode	Lead Anode	



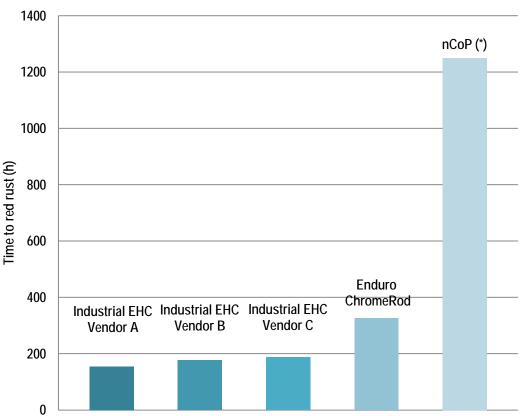
Drop In Processing Time Significantly Improves Productivity







# nCoP vs. EHC - Corrosion (B117)



Nanovate CoP vs. hard chrome (HEEF) and other competitive coatings on steel bars at similar thickness (\*) Test was stopped after 1200 hours with no corrosion present on Nanovate CoP samples



Nanovate CoP
Pit, pore and crack-free







### WP-2137 Problem Statement

#### Benefits of copper beryllium

- Cu-Be is the hardest and strongest of any copper alloy
- The high yield strength and high stiffness make it an ideal material for components under repeated stress and strain (spring wire, load cells, bushings, etc.)
- Other advantageous properties include good conductivity, low friction, non-galling, non-sparking, nonmagnetic, good high temperature and corrosion resistance

#### Drawbacks of beryllium copper

- Exposure to Be results in a range of diseases including lung cancer and Chronic Beryllium Disease (CBD)
- DoD employees are exposed to Be dust and fumes as a result of the wearing of Be-containing alloys during operation and during machining and other fabrication operations
- An environmentally benign alternative is required for worker health and safety









# Nano Co-Alloy High Load Bushings

- Cu-Be alloys still represent the best combination of strength, wear properties and cost for highly loaded bushing applications
- Integran recently tested and evaluated an electroformed Co-alloy as an alternative to Cu-Be as part of US DoD SERDP Project WP-2137 and revealedthe following regarding Nanovate electroformed cobalt bushings
  - Significantly higher tensile and compressive yield strength than CuBe
  - Low coefficient of friction against various 'pin" materials
  - Possess high galling resistance
  - Have superior performance in highly-loaded subscale bushing test





### Nano Co-Alloy Mechanical Properties

 Nanostructured cobalt-based alloy has much higher compressive and tensile strength than conventional bushing materials

Material	Compression Strength ksi (MPa)	Tensile Yield Strength ksi (MPa)	Tensile Ultimate Strength ksi (MPa)	Tensile Modulus of Elasticity (GPa)
Nanostructured	285 ksi	225 ksi	290 ksi	18855 ksi
Cobalt Alloy	(1967 MPa)	(1550 MPa)	(2000 MPa)	(130 GPa)
Copper Beryllium (C17200-TH04)	142 ksi (973 MPa)	172 ksi (1185 MPa)	190 ksi (1310 MPa)	18855 ksi (130 GPa)
Nickel Aluminum	110 ksi	68 ksi	110 ksi	16700 ksi
Bronze (C63000)	(760 MPa)	(470 MPa)	(760 MPa)	(115 GPa)



# Electroformed Nanometal Bushings

- Near net shape manufacturing process with high 'buy-to-fly' ratio
- Cost effective due to less material waste during machining

Step 1 Electroform desired thickness (~0.25") onto temporary mandrel	<b>Step 2</b> Remove mandrel	Step 3 Machine Bushings

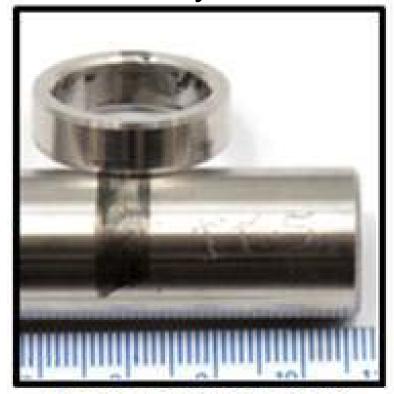


# Sub-scale Bushing Performance

Nanovate bushings perform favorably to CuBe



Cu-Be Bushing: MP 35N Pin 1725 cycles total 125 cycles at 10,000 lbs



Nano Co-alloy Bushing: 440C Pin 2000 cycles total 400 cycles at 10,000 lbs





# High Load Bushings

Nanovate bushings samples; diameter range from 0.5" to
 6" fabricated to date





# Pulse-Plated Alkaline ZnNi for Cadmium Alternative

- SERDP program WP1616, found that Integran's pulse electroplating technology could be used with Dipsol's commercial alkaline ZnNi IZ-C17+LHE system in order to further improve its performance
- Specifically, pulse plating achieved the following
  - Helped refine grain size (and thereby improve hardness, corrosion resistance, friction coefficient, and appearance)
  - Provided a coating with low porosity and uniform coating composition, thereby leading to good corrosion resistance
  - Consistently passed hydrogen re-embrittlement (a.k.a., in-service embrittlement) testing, a critical requirement for general implementation, whereas conventional DC plating (DC-ZnNi) did not
- PP-ZnNi would be viewed as part of an overall strategy to replace the currently used Cd processes and eliminate environmental and worker safety issues, while significantly improving performance and reducing life-cycle costs





### PP-ZnNi Microstructure Comparison

 Following the work in SERDP Project WP-1616, a number of key properties were improved in the PP-ZnNi when compared to Cd or DC-ZnNi

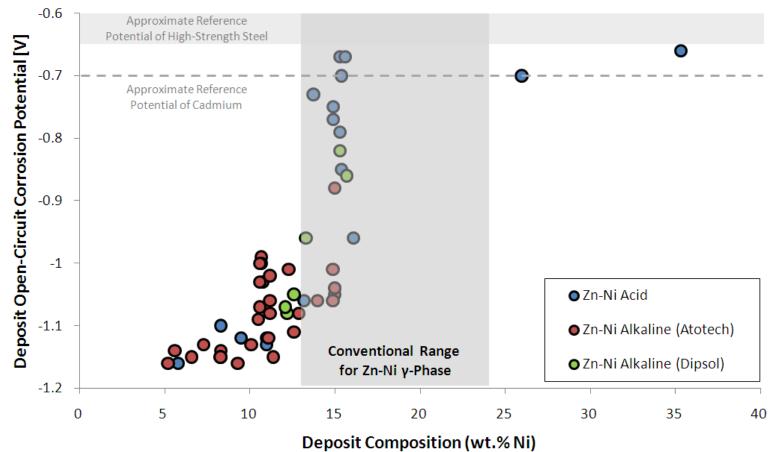
Property	PP-ZnNi	DC-ZnNi	Cadmium
Macroscopic	Uniform, shiny	Uniform, dull	Uniform, dull
Surface Morphology	Smooth, dense	Rough, porous	Rough, porous
Cross Section			and the





# Influence of Composition

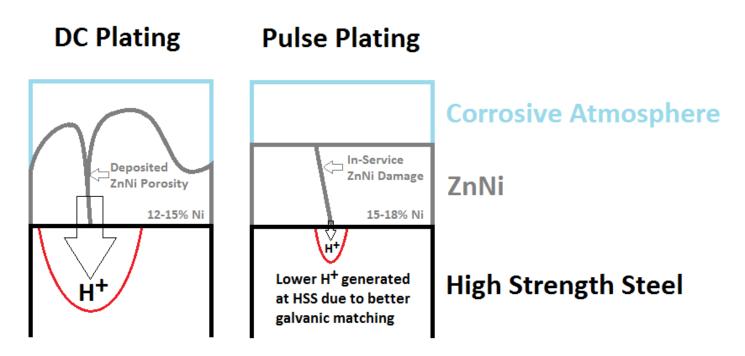
 SERDP test data showed ZnNi coating composition had a significant effect on the OCP of the coating, thereby effecting the galvanic couple to HSS





# Influence of Coating Porosity

 In addition, pulse plating leads to a ZnNi coating that is more (i) hard, (ii) wear resistant, (iii) lubricious, among other characteristics







# PP-ZnNi Property Comparison

Property	PP-ZnNi	DC-ZnNi	Cadmium <sup>2</sup>
Hardness (VHN)	490 ± 19	350-450 <sup>1</sup>	60
Time to Red Rust (hrs) <sup>3</sup>	>1,000	>1,000	>1,000
Friction Coefficient <sup>4</sup>	0.16	0.30	0.12
Embrittlement <sup>5</sup>	PASS	PASS	PASS
Re-Embrittlement <sup>5</sup>	PASS	Marginal Pass/Fail	Marginal Pass (2/4)

- 1. Values from Dipsol of America technical data sheet for IZ-C17-LHE. Assumes plating current density of 50 mA/cm<sup>2</sup>
- 2. Assumes plating current density of 50 mA/cm<sup>2</sup>
- 3. Measured using salt spray corrosion testing (ASTM B117)
- 4. Measured using torque tension/lubricity friction, after HSS JTP, 07/31/2003 (The Boeing Company, Seattle, WA)
- 5. Measured using ASTM F519 using type 1a.1 notched bars. Embrittlement was loaded to 75% NFS; a full pass is considered 4 our of 4 bars held to 200 hour duration. Re-embrittlement was loaded to 45% NFS and held in 3.5 wt.% NaCl solution; a full pass is considered 4 out of 4 bars held to 150 hour duration



## Conclusions

- Nanostructured materials have been shown to meet and/or exceed the properties of Hard chrome, Copper-Beryllium and Cadmium, with numerous additional advantages for select applications
- Implementation of the various technologies throughout DoD sites can help reduce occupational health and safety concerns due to worker exposure to Hexavalent Chromium, Beryllium and Cadmium.



# **Next Steps**

- EHC Alternative / Nanovate CR → Mil-spec released. Currently available for licensing from Enduro Industries, or from Integran for low volume manufacturing
- CuBe Bushing Alt / Nano Cobalt Bushings →
   Proof-of-concept established, proposal submitted
   to ESTCP to move to Dem/Val technology at
   Depot Level
- Cd Alternative / Pulse Plated Alkaline ZnNi
   Applicable to standard Alkaline ZnNi
   electrodeposition processes. Final report available

#### For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Weapons-Systemsand-Platforms/Surface-Engineering-and-Structural-Materials/Composites-Alloys-and-Ceramics/WP-2137 https://www.serdp-estcp.org/Program-Areas/Weapons-Systemsand-Platforms/Surface-Engineering-and-Structural-Materials/Coatings/WP-1616

#### **Speaker Contact Information**

mccrea@integran.com; 416-675-6266 (x235)



## **Q&A Session 1**



Electrodeposition of Nanocrystalline Cobalt-Phosphorus Alloy Coatings as an Alternative to Hard Chromium Electroplating



Jack Benfer and Ruben Prado Naval Air Systems Command











# Agenda

- Hexavalent chromium
- Technical objectives
- Plating process
- Performance testing
- Field demonstrations
- Technology transfer
- Future work

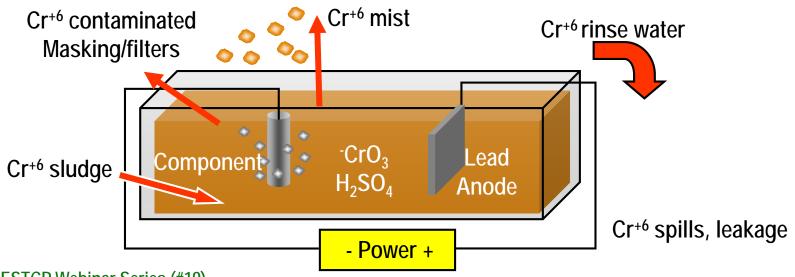




## **Hexavalent Chromium**

- Hard chrome plating environmental and health hazards
  - Hard chrome plating utilizes chromium in the hexavalent state, Cr(VI)
  - Cr(VI) is a known carcinogen and poses a health risk to operators
  - OSHA lowered the Cr(VI) PEL from 52 μg/m³ to 5 μg/m³
- 8 Apr 09, Memorandum, DoD Directive
  - Hexavalent Chromium Management Policy









# Technical Objectives

- Demonstrate/validate pulsed electrodeposition of Nanocrystalline Cobalt-Phosphorous (nCoP) alloy coatings as a Electrolytic Hard Chrome (EHC) electroplating alternative for DoD manufacturing and repair
- Fully define deposition parameters and properties
  - Establish production plating processes
  - Demonstrate/validate performance
  - Develop Eng Tech Data Packages
  - Initiate NAVAIR approval process



**Demo Site: FRC JAX** 



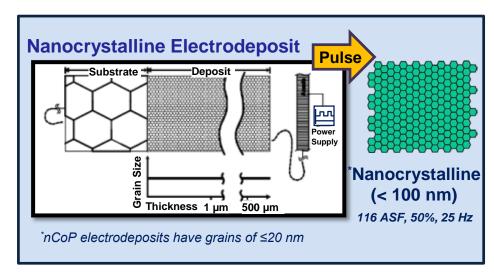


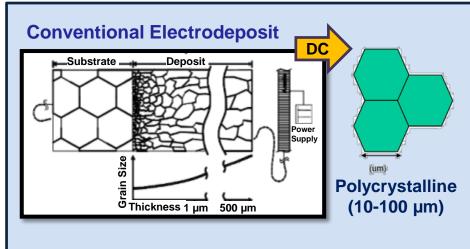
# **Technology Description**

 Coating applied by pulsed current waveform



- Nucleation versus growth Uniform and fine grain structure
- Leads to unique properties
  - Yield Strength, wear, ultimate tensile strength
  - ↓ Coefficient of friction









# **Process Comparison**

Parameter	Nanovate R3010	EHC
Deposition method	Electrodeposition (Pulse)	Electrodeposition (DC)
Part geometries	*LOS and **NLOS	*LOS and **NLOS
Efficiency	85-95%	15-35%
Deposition rate	0.002" - 0.008"/hr	0.0005" - 0.001"/hr
Emission analysis	Below OSHA limits	Cr <sup>+6</sup>
Bath temperature	185°F	140°F

<sup>\*</sup> Line of sight

- At least 5X faster than chrome plating
- Increased throughput
- Can replace several hard chrome tanks
- Bath is stable

<sup>\*\*</sup> Non-line of sight





# **Technology Integration**

- NAVAIR Fleet Readiness Center Jacksonville
  - Dem/Val line in operation since 2006
  - 250 gallon plating tank
  - Pulse power supply
  - Activation tank used for most all alloys



Plating Tank



Plating Pulse Power Supply



**Activation Tank Power Supply** 





## Joint Test Protocol

#### 24 Core Tests Defined in JTP

1.	Appearance 🗸	13.	Corrosion	(OCP)	V
					/

2. Thickness ✓ 14. Adhesion ✓

3. Porosity ✓ 15. HE ✓

4. Hardness 🗸 💮 16. HE (No Bake) 🗸

5. Grain Size 🗸 💮 17. Fluid Compatibility 🗸

6. Ductility ✓ 18. HRE ✓

7. Stress ✓ 19. Wear – Taber ✓

9. Coating Integrity 🗸 💎 21. Wear – Endurance Rig 🔻

10. Corrosion (B117) ✓ 22. Wear – Falex ✓

11. Corrosion (SO2) ✓ 23. Wear – Gravelometry ✓

12. Corrosion (Beach) ✓ 24. Wear – SATEC ✓

Completed tests

#### 3 Dem/Vals



T45 Pivot Installed: Mar 2012



Lifting Arm Pin Installed: Jul 2013

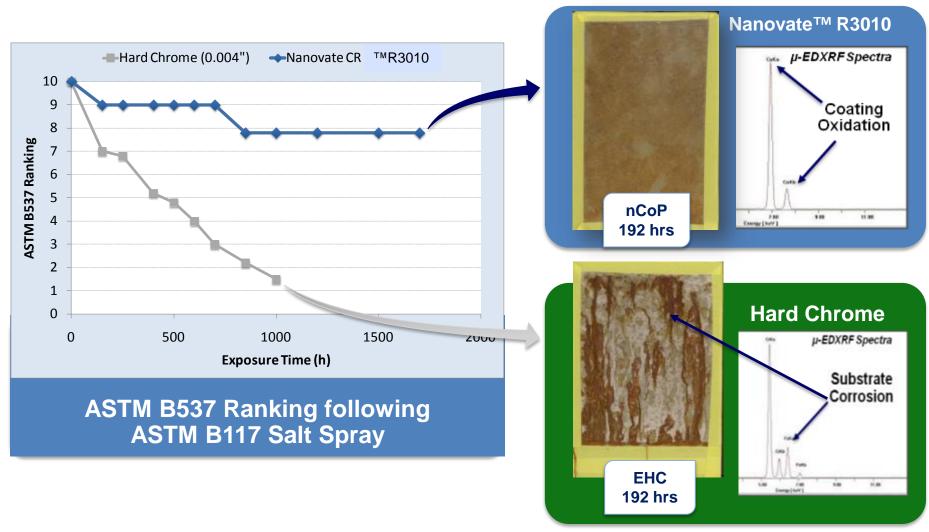


M9ACE
Cylinder
Installed: Mar 2014





## **ASTM B-117 Corrosion Test**



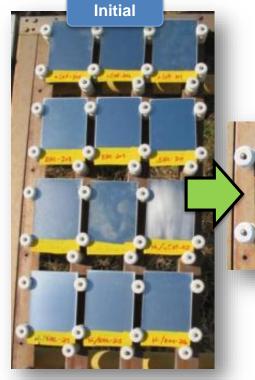




# Beach Exposure Corrosion Test

- Test facility, NASA KSC
- EHC exhibits red rust
- Surface tarnish of nCoP









EHC 12 months nCoP 12 months



# Cycling Corrosion/Seal Wear

#### Cycling corrosion/seal wear

- Cylinder testing cycle (1 mil coating)
  - 1. Cylinder cycling 1000 cycles
  - 2. ASTM B117 10 days





10,000 cycles/ 100 Days
No Failures





4000 cycles/ 40 Days EHC-2 Failed









# Shafting Application

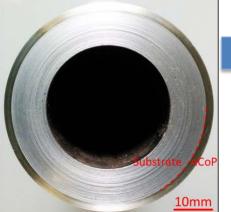
- Journal wear testing completed
  - nCoP demonstrated as a viable alternative for Navy propulsion shafting applications
  - Wear testing showed no measurable mass loss
  - Demonstrated bond integrity on Inconel 625, 70/30 CuNi and low alloy steels



**Wear Test Equipment** 

#### Nanovate™ R3010 Plating on Navy Shaft Geometries/Materials





nCoP ~78 mils thick

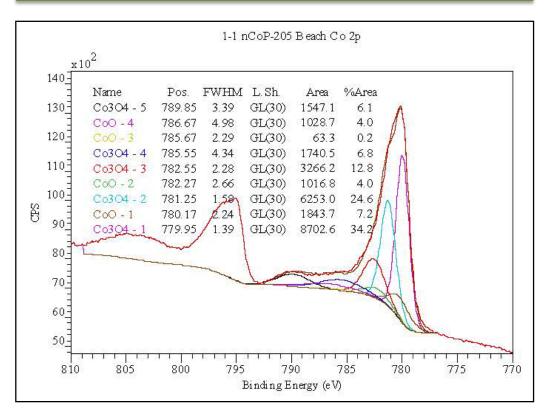
(b)





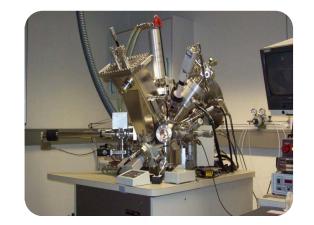
## Oxide Characterization

X-ray photoelectron spectroscopy (XPS) analysis determined Co oxide (Co<sub>3</sub>O<sub>4</sub>) and CoO on surface (NO IRON PRESENT)





nCoP Coupon (Nanovate R3010)







# **Endurance Rig Testing**

Test developed by Messier-Dowty



• 20,000 Cycles

 Observe effect of surface finish, seal types and hardening condition





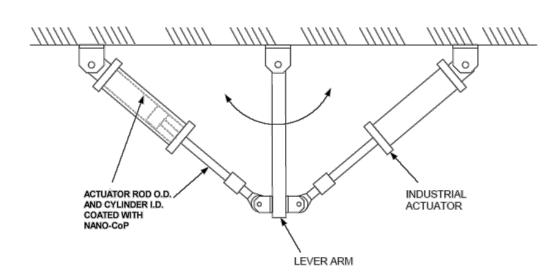
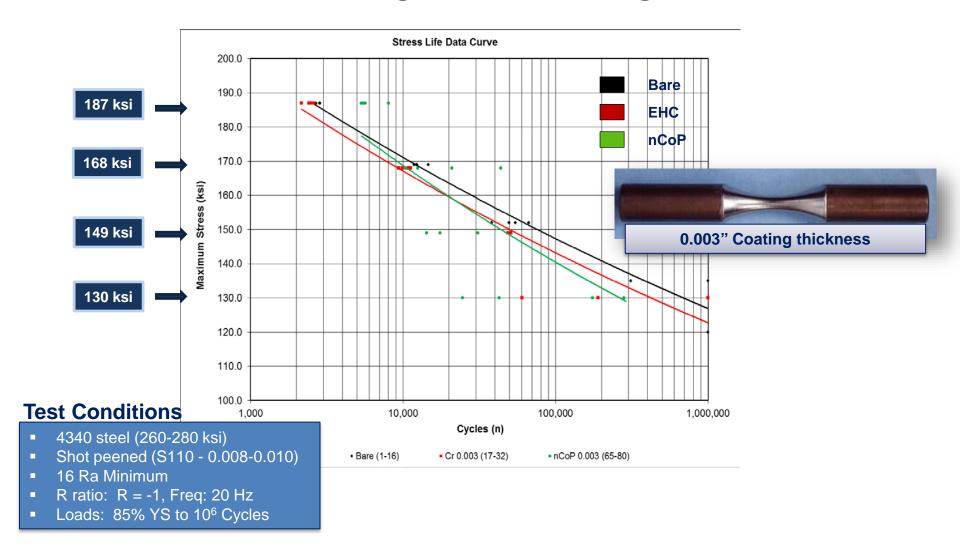


FIGURE 1 – ILLUSTRATION OF TEST SETUP





# **Fatigue Testing**







## Field Demonstrations



NAVAIR JAX Plating Dem/Val

#### nCoP Plating of T-45 Arresting Hook Pivot





nCoP Plate









## Field Demonstrations



#### **Dem/Val Component Field Inspection**

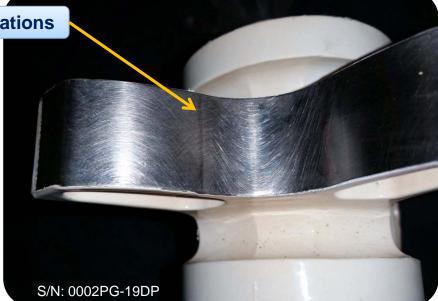
#### Field Performance: T-45 Arresting Hook Pivot

- Passed inspections & reinstalled on aircraft
- 147 arrestments w/ 1,055 flight hours (Feb 2015)





nCoP: After 72 arrestments, 705  $\pm$  10 Flight Hrs



nCoP: After 97 arrestments, 825 ± 15 Flight Hrs





## Field Demonstrations



#### M9 ACE Cylinder Dem/Val

- Assembled/pressure tested at Marine Corp Depot, Albany, GA
- Installed on vehicle, Mar 2014
- Field tested at Panama City



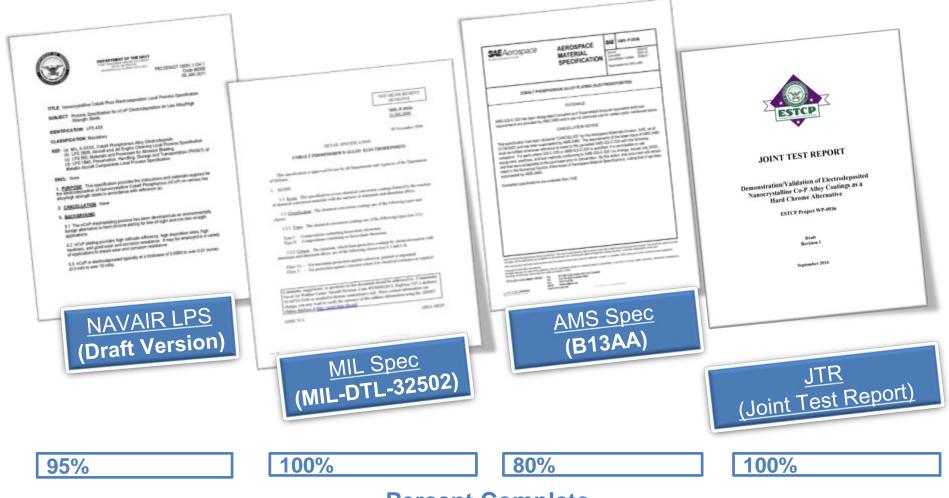








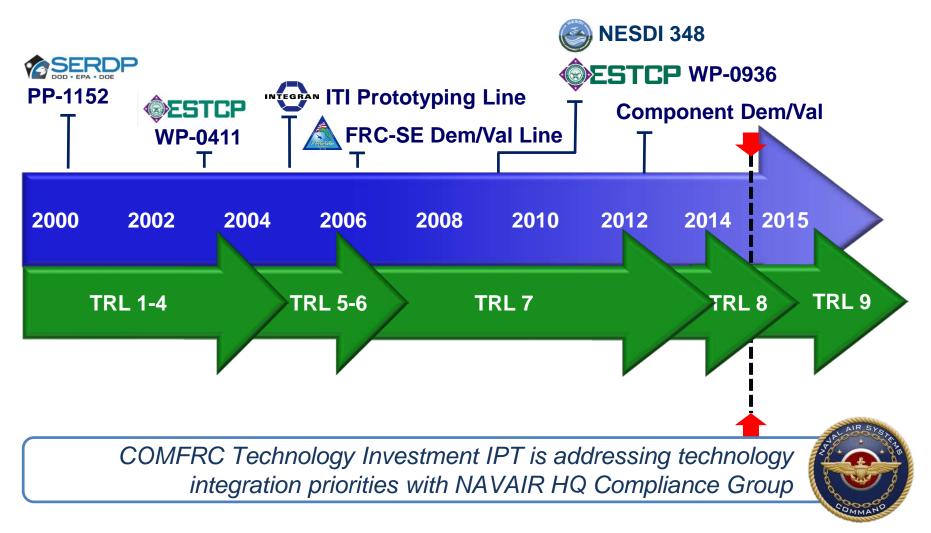
# Technology Transfer







# Technology Readiness Level







## **Future Work**

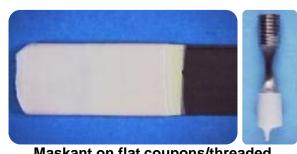
- Evaluating non-solvent based High Temp Wax (Darent Wax Company LTD)
  - Compatible with nCoP plating Bath
  - Initial evaluation on small mock-up samples/pieces
    - Melting point >100 °C (212 °F)
    - Rapid solidification
    - Ease of use



Traditional electroplaters tape (L) and custom electrical tape (R)



Thermal analysis of wax



Maskant on flat coupons/threaded items evaluated at 130°C (266°F)





## **Future Work**

#### Electroformed Nanostructured Cobalt Alloy Bushings

(Raw Material Stock Obtained via Electroforming)

Step 1 - Electroform desired thickness (~0.25") onto temporary mandrel	Step 2 - Remove mandrel	Step 3 - Machine bushings	





## nCoP Conclusions

- Eliminates the usage of hexavalent chromium
- Plating rates are 5x to10x more rapid than EHC
- Corrosion performance exceeds EHC
- Hydraulic actuators performance exceeds EHC
- Mixed results with fatigue testing based upon loading
- High temperature wax maskants require development for improved ease-of-use

## For additional information, please visit

https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Surface-Engineering-and-Structural-Materials/Coatings/WP-200936

## **Speaker Contact Information**

John.Benfer@navy.mil; 904-790-6405 Ruben.Prado@navy.mil; 904-790-6381





## Q&A Session 2



# The next webinar is on October 15, 2015

LED-ing the Way: Sophisticated and Energy Efficient Exterior Lighting Systems for DoD Installations



# Survey Reminder

Please take a moment to complete the survey that will pop up on your screen when the webinar ends

