



# **Electrodeposited Nano Co-P: Coating Development and Technology Insertion at NADEP-JAX**

**Integran Technologies Inc.**

**HCAT Meeting, New Orleans – January 24<sup>th</sup>, 2007**

| Report Documentation Page                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                    |                                     |                                                           | Form Approved<br>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<br><b>24 JAN 2007</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                    | 2. REPORT TYPE                      |                                                           | 3. DATES COVERED<br><b>00-00-2007 to 00-00-2007</b> |                                 |
| 4. TITLE AND SUBTITLE<br><b>Electrodeposited Nano Co-P: Coating Development and Technology Insertion at NADEP-JAX</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                    |                                     |                                                           | 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)<br><b>Integran Technologies Inc.,1725 Washington Road, Suite 305,Pittsburgh,PA,15241-1209</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                    |                                     |                                                           | 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<br><b>Approved for public release; distribution unlimited</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                    |                                     |                                                           |                                                     |                                 |
| 13. SUPPLEMENTARY NOTES<br><b>27th Replacement of Hard Chrome and Cadmium Plating Program Review Meeting, January 23-25, 2007, New Orleans, LA. Sponsored by SERDP/ESTCP.</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                    |                                     |                                                           |                                                     |                                 |
| 14. ABSTRACT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                    |                                     |                                                           |                                                     |                                 |
| 15. SUBJECT TERMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                    |                                     |                                                           |                                                     |                                 |
| 16. SECURITY CLASSIFICATION OF:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                    |                                     | 17. LIMITATION OF ABSTRACT<br><b>Same as Report (SAR)</b> | 18. NUMBER OF PAGES<br><b>60</b>                    | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT<br><b>unclassified</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | b. ABSTRACT<br><b>unclassified</b> | c. THIS PAGE<br><b>unclassified</b> |                                                           |                                                     |                                 |

# Acknowledgements

---

## Team Members

- Program Manager - Bruce Sartwell
- Rowan Technologies – Keith Legg
- Integran Technologies
  - Francisco Gonzalez, Jon McCrea, Diana Facchini, Mike Uetz
- NADEP-JAX
  - Ruben Prato, John Devereaux, John Lamkin, Ernstine Lawson

## Support for the Program

- SERDP and ESTCP Program Office
- JSF Office
- Technology Partnerships Canada

## Collaborators

- Goodrich, Messier-Dowty, Pratt & Whitney Canada, Smiths Aerospace

Technology Partnerships Canada

# Overview

---

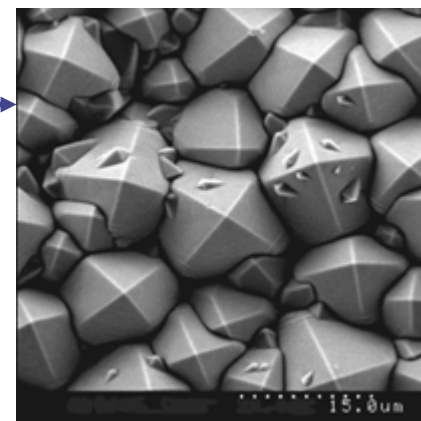
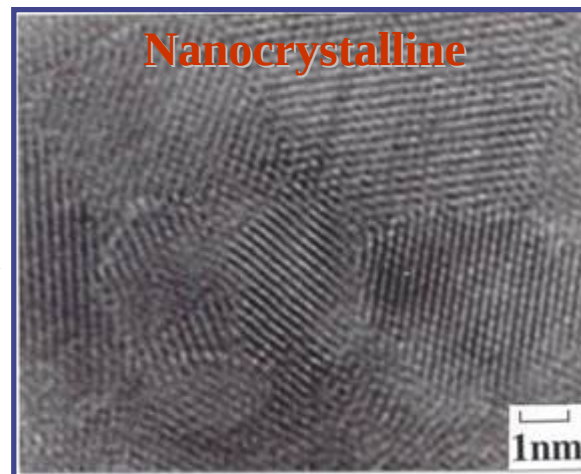
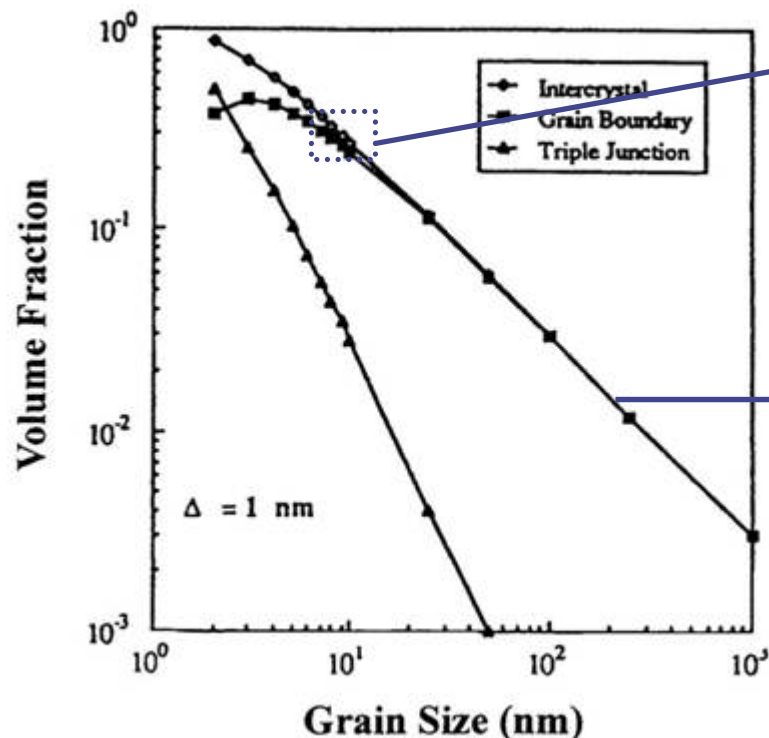
- **Nanocrystalline Materials**
- **History of the nCoP NLOS Cr-replacement Project**
- **Overview of nCoP Process and Properties**
- **Scale-up of Tank Process**
  - Installation at Integran
  - Installation at NADEP-JAX
  - Dem/Val Activities
- **Development of Selective Area (Brush) Plating**
- **Joint Test Protocol (JTP) – Sample Prep and Testing**
- **Thin Dense Chrome Development**
- **Application-specific Testing**
  - Smiths Aero
  - Messier Dowty
- **Summary**

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*

# Nanocrystalline Materials

A reduction in grain size below 100nm, **significantly increases** the intercrystalline content in the material, leading to many unique properties (high hardness/strength)



Need to understand the relationship between **Microstructure** and **Processing conditions**

# History of Cr-Replacement Project

---

**SERDP Project #PP-1152 – June 2000 to March 2003**

**Objectives: Develop an environmentally benign advanced nanocrystalline based coating technology that:**

- Can be applied to non-line-of-sight surfaces
- Is compatible with conventional electroplating infrastructure
- Will produce coatings that meet or exceed the overall performance of hard chrome (hardness, wear, corrosion, fatigue)

**Nano Co-P as EHC alternative was developed and demonstrated at the lab scale**

**ESTCP Project #PP-0411 – May 2003 to May 2006**

**Objectives:**

- Scale up to industrial production & move to depot (Integran/NADEP-JAX)
- Develop nano Co-P selective plating as repair
- Develop nano Co-P based TDC alternative
- Define and Execute JTP

**Cobalt alloy selection**

- Good mechanical properties, High plating efficiency
- No constituents on EPA or AFMC lists of hazardous materials
- Longer term view

Technology Partnerships Canada

# History of Cr-Replacement Project

## Progression of TRL / Timeframe

| Year | Project          | Roles                                                    | Steps to Transition                                             | DoD 5000 Series Technology Readiness Level (TRL)                                                                                                                                                                                                                                                                                                                                                                                           |
|------|------------------|----------------------------------------------------------|-----------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 2006 | ESTCP<br>PP-0411 | Technology Directorate<br>Acquisition Program Management | System Test, Launch and Operations System/Subsystem Development | 9. Actual system "flight proven" through successful mission operations (OT&E)<br>8. Actual system completed and "flight qualified" through test and demonstration (ground/flight) (DT&E)<br>7. Systems prototype demonstration in a flight/space environment (System Prototype Test in Operational Environment)<br>6. System/subsystem model or prototype demonstration in a relevant environment (Prototype Test in Relevant Environment) |
| 2003 |                  |                                                          | Technology Demonstration                                        | 5. Component and/or breadboard validation in a relevant environment (Breadboard Integration)                                                                                                                                                                                                                                                                                                                                               |
|      |                  |                                                          | Technology Development                                          | 4. Component and/or breadboard validation in laboratory environment (Breadboard Integration)                                                                                                                                                                                                                                                                                                                                               |
|      |                  |                                                          | Research to Prove Feasibility                                   | 3. Analytical and experiment critical function and/or characteristic proof of concept (Component Development)                                                                                                                                                                                                                                                                                                                              |
| 2000 | SERDP<br>PP-1152 |                                                          | Basic Technology Research                                       | 2. Technology concept and/or application formulated (Invention)<br>1. Basic principle observed/reported (Paper Study)                                                                                                                                                                                                                                                                                                                      |
|      |                  |                                                          |                                                                 |                                                                                                                                                                                                                                                                                                                                                                                                                                            |

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Technology Description

---

## Process

---

### Simply an electrodeposition process

- Parameters modified to yield deposits with average grain sizes below 100nm using pulse plating

### Plating Efficiency >90%

- High Deposition rates (2-8 mils/hr)
- 10x the plating rate of EHC at same power current density
- 1/10<sup>th</sup> the power consumption at the same plating rate

### Consumable & nonconsumable anode

- Cobalt Pieces in Ti basket, Graphite

### Phosphorus Content: 0 to 10wt%

- Controlled by solution chemistry and plating conditions

# Technology Description

---

## Solution Control and Maintenance

**Similar to that required for nickel-plating solutions:**

- **Filtration**
  - Control particles
- **pH monitoring**
  - Control deposit uniformity
- **Surface tension control**
- **Solution density monitoring**

## **Periodic maintenance procedures**

- **Activated carbon treatment**
  - Organics
- **Dummying (low current density plating)**
  - Remove various metallic impurities

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# Properties Summary

|                          |                                | Nanocrystalline Co-P                                       | Hard Chrome                                                  |
|--------------------------|--------------------------------|------------------------------------------------------------|--------------------------------------------------------------|
| <b>Hardness</b>          | <i>As-Deposited</i>            | 600-700 VHN                                                | 800-1200 VHN                                                 |
|                          | <i>HT @ 250°C</i>              | 700-800 VHN                                                | -                                                            |
| <b>Ductility</b>         |                                | 2 – 7 % Elongation                                         | <.1%                                                         |
| <b>Thermal Stability</b> |                                | 400°C                                                      | 400°C                                                        |
| <b>Wear</b>              | <i>Adhesive</i>                | 5-6 x 10 <sup>-6</sup> mm <sup>3</sup> /Nm                 | 9-11 x 10 <sup>-6</sup> mm <sup>3</sup> /Nm                  |
|                          | <i>(Pin-on-disk)</i>           | (Alumina Ball on Nano Co-P Disk)                           | (Alumina Ball on Cr Disk)                                    |
|                          | <i>Coefficient of Friction</i> | 0.5                                                        | 0.7                                                          |
|                          | <i>Abrasive (Taber)</i>        | 18 mg / 1000 cycles (CS-17)<br>11 mg / 1000 cycles (CS-10) | 3.2 mg / 1000 cycles (CS-17)<br>1.0 mg / 1000 cycles (CS-10) |
| <b>Corrosion</b>         | Salt Spray                     | Protection Rating 7 @ 1000 hrs                             | Protection Rating 2 @ 1000 hrs                               |

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Scale up of Tank Process

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# Industrial Scale Up at Integran Technologies

## Integran Tank

- Dimensions (3'x5'x3')  
(~1300L)
- 1" Polypropylene
- Separate well to house pump and filter
- 3/4hp pump
- 1 $\mu$ m filter
- 60kw heaters (Ti) digitally controlled



Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Industrial Scale Up at Integran Technologies

---

## Dem/Val Studies

---

- **Integran 1300 L Bath** has been in operation for 26 months, >33,000 Amp-hrs, No major problems
- **Process Verification**
  - Scaled-up process produces acceptable nanostructured coatings on small and large test coupons
  - Verified on large test pieces (4" ID, 1' Length)
- **Operating Window Identification**
  - Optimal Bath chemistry and Pulse Conditions identified
  - Temperature, Current density and pH operating ranges identified
    - Based on hardness, grain size, composition, coating uniformity
- **Contaminant Study**
  - Completed a lab scale study of the effects of various metallic contaminants in the plating solution ( $\text{Cr}^{6+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Na}^+$ ,  $\text{F}^-$ , and  $\text{SO}_4^{2-}$ )
- **Developed activation procedures** for 4340, 4130, 300M, 15-5PH, Hy-Tuf, nCoP, Al
- **Developed alkaline dip stripping solution:** avg removal rate  $\sim 0.001''/\text{hr}$

**Operating Manual and Process transferred to NADEP-JAX**

Technology Partnerships Canada

# Technology Transfer to NADEP-JAX

## Milestone: Dem/Val Tank Setup at NADEP-JAX

- Dimensions
  - 47"x30"x48"
  - approx Vol. 290 gals
- Liner Type
  - Modified Vinyl based Terpolymer
  - 0.125" thick
- Ni Plated Copper Buss Bars
- In tank pump and filter
- ¾ hp pump
- 10 micron filter
- PVDF Steam Coil, new steam lines & regulator



290 gal Dem/Val plating tank

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Technology Transfer to NADEP-JAX

## Milestone: Chemistry Make-up at NADEP-JAX

- Operating Vol: 250 gals
- Proprietary Bath Chemistry
- Low pH
- High Temp
- Assisted by Integran



Building of new Nano Co-P Plating Bath  
Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Technology Transfer to NADEP-JAX

## Milestone: Pulse Rectifier Installed at NADEP-JAX

- Integrin's specifications
- Peak current 1500A
- Average current 500A
- Pulse timing (ton and toff)
  - 0-100ms,  $\Delta t=0.1\text{ms}$
- Remote Control Micro Touch Controller
- First verified at Integrin



Remote Controller



Pulse Rectifier

Technology Partnerships Canada

# Technology Transfer to NADEP-JAX

## Milestone: Initial Plating and Bath Optimization at NADEP-JAX

- 4130 Steel test coupons plated
- Initially dull, non-uniform deposits towards edges
  - Process parameters adjusted
- Subsequent deposits bright and uniform
- Plating rate: 5-6 mil/h



First 4130 panel plated



Dem/Val tank with Electrolyte and plating

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

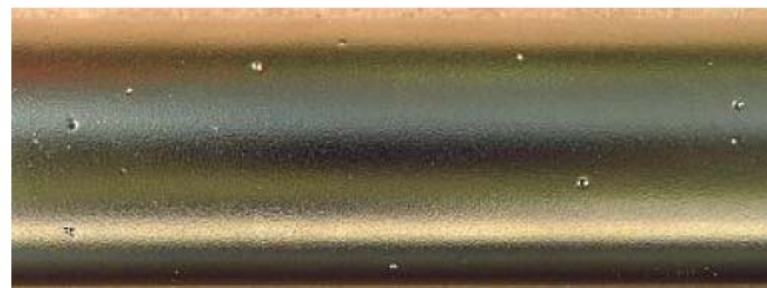
# Technology Transfer to NADEP-JAX

---

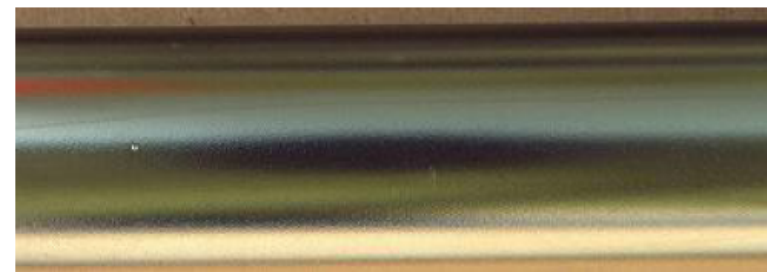
## Process Troubleshooting - Pitting

---

- Pitting of nano CoP observed at NADEP-JAX
  - All initially plated parts
  - Significant pitting present
- Caused by organic contamination
  - Leaching of newly installed liner from bath matrix and operating temperatures
- Carbon filtering significantly reduced pitting



Before carbon treatment

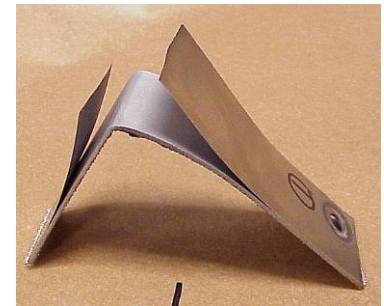


After carbon treatment

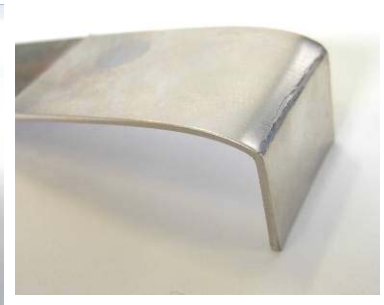
# Technology Transfer to NADEP-JAX

## Process Troubleshooting - Adhesion

- Adhesive failures of nano CoP observed at NADEP-JAX
  - 4130 flat coupons and IDs
  - Thought to be due to activation procedure
- Alternate activation procedure developed by Integran
  - Good adhesion demonstrated on 4130 flat coupons and IDs
  - Showed promise at NADEP-JAX
- Procedure to be implemented by NADEP-JAX
  - Activation tank setup in progress
  - Retrofit of existing nearby tank
  - Requires liner, buss bar & rectifier hook up



Adhesion failures  
Previously used activation



Good adhesion  
Newly developed activation

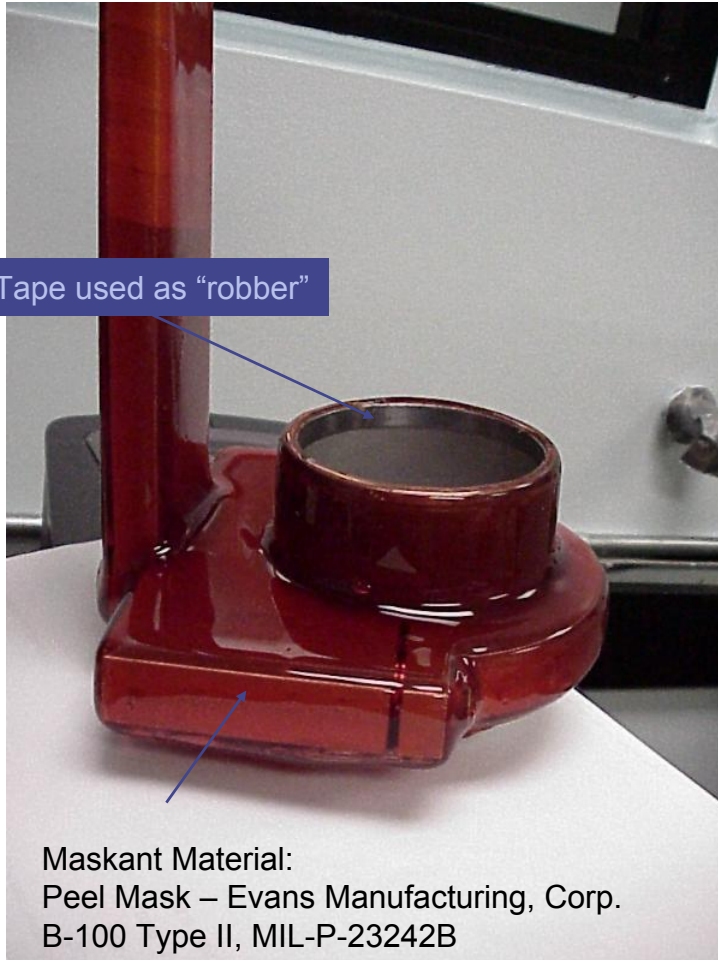
Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Component Plating Trials at NADEP-JAX

Demonstration with high temp maskant and titanium basket anode

Lead Tape used as "robber"



Maskant Material:  
Peel Mask – Evans Manufacturing, Corp.  
B-100 Type II, MIL-P-23242B

Titanium anode basket with  
sleeve filled with Cobalt chips



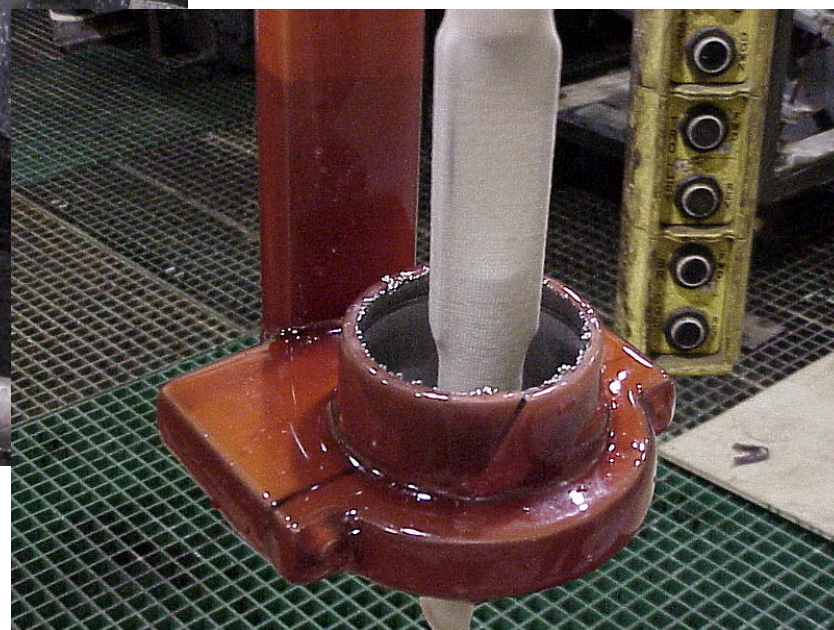
# Component Plating Trials at NADEP-JAX

Demonstration on an ID section of a P-3 MLG Actuating Cylinder



nCo-P Plating on ID:  
Section from P-3 MLG Actuating Cylinder

Plating Time: 4 hrs



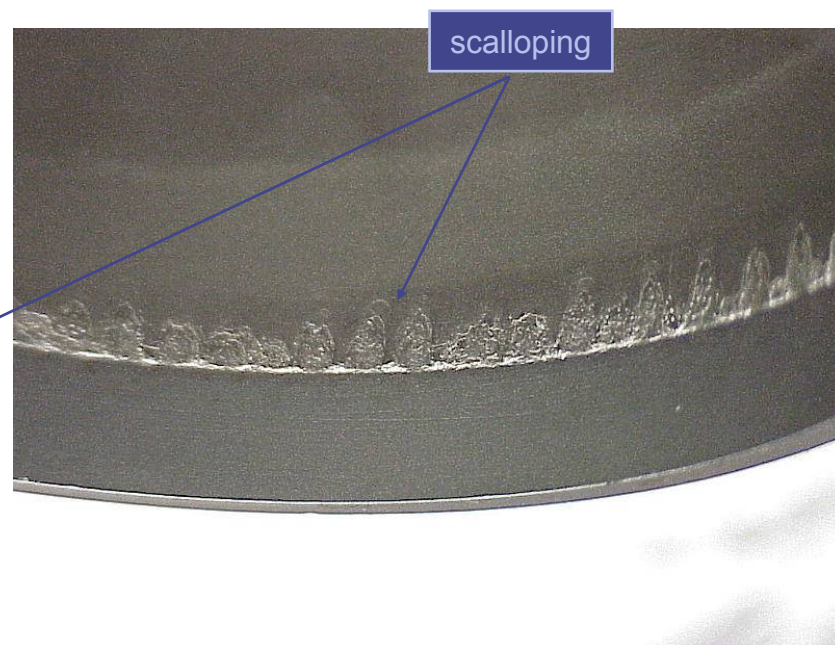
Rack Assy after plating:  
Section from P-3 MLG Actuating Cylinder

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Component Plating Trials at NADEP-JAX

Demonstration on an ID section of a P-3 MLG Actuating Cylinder



Part after de-masking:  
Section from P-3 MLG Actuating Cylinder

Appearance: Dull matt gray, few shallow pits  
Coating Thickness: 10.0 mils /side  
Deposition rate ~ 2.5 mil/hr

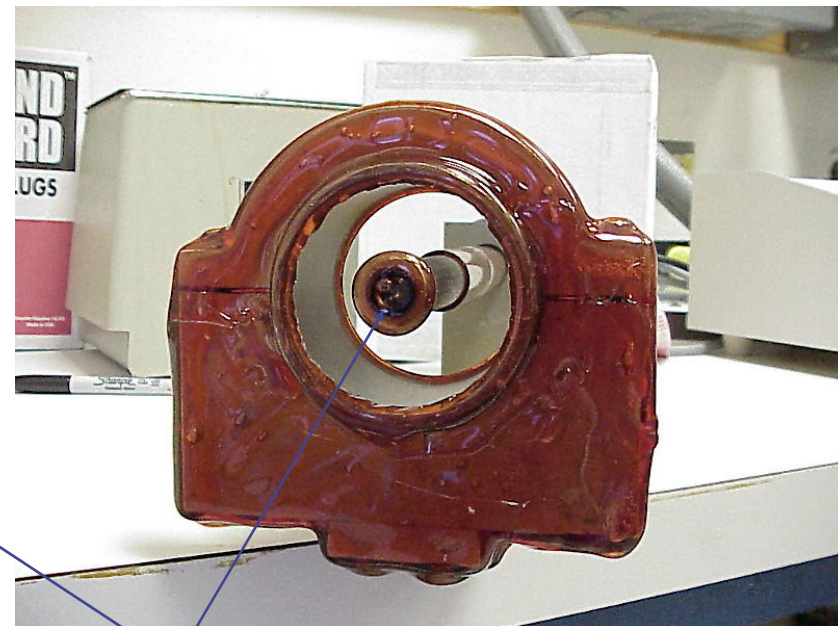
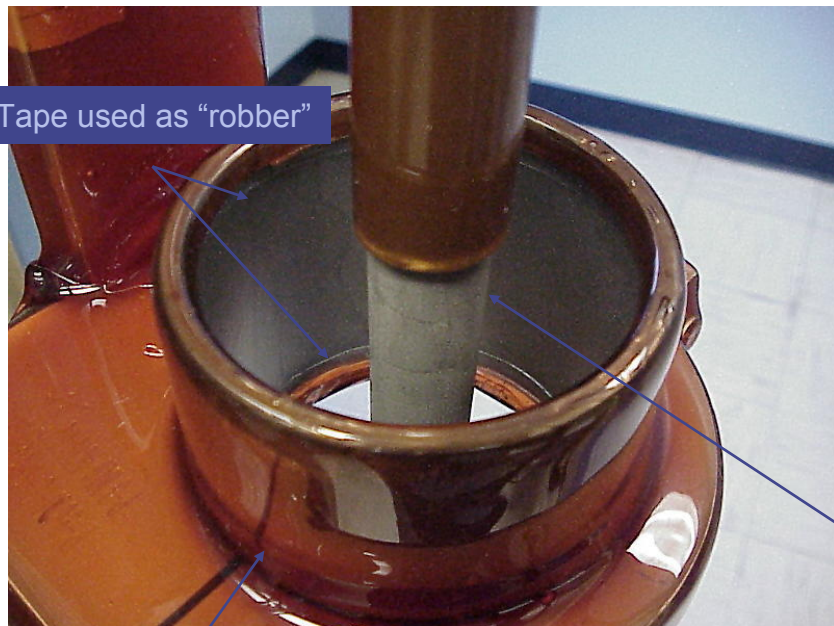
Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Component Plating Trials at NADEP-JAX

Demonstration with high temp maskant and Solid cobalt anode

Lead Tape used as "robber"



Cobalt Anode

Maskant Material:  
Peel Mask – Evans Manufacturing, Corp.  
B-100 Type II, MIL-P-23242B

Technology Partnerships Canada  
Section from a P-3 MLG Actuating Cylinder

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

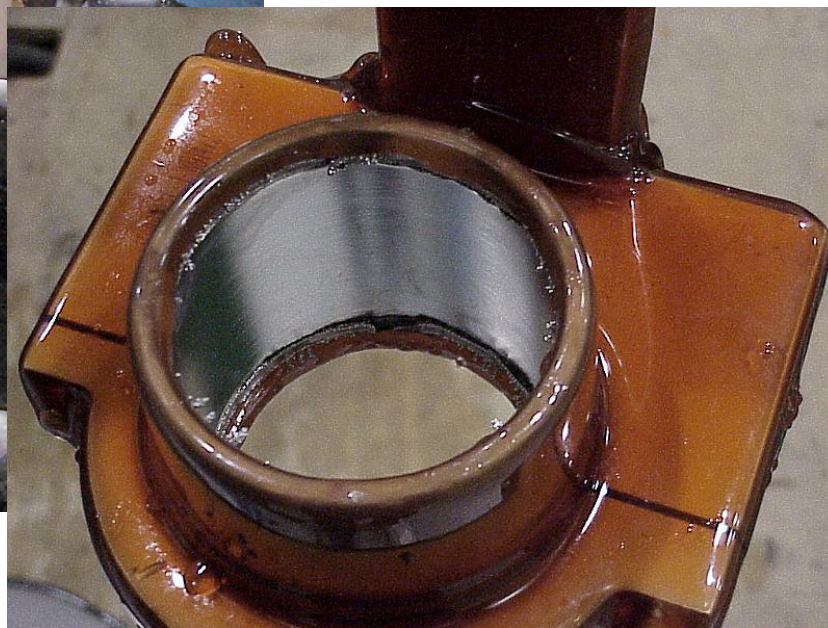
# Component Plating Trials at NADEP-JAX

Demonstration on an ID section of a P-3 MLG Actuating Cylinder



nCo-P Plating on ID:  
Section from P-3 MLG Actuating Cylinder

Plating Time: 2 hrs



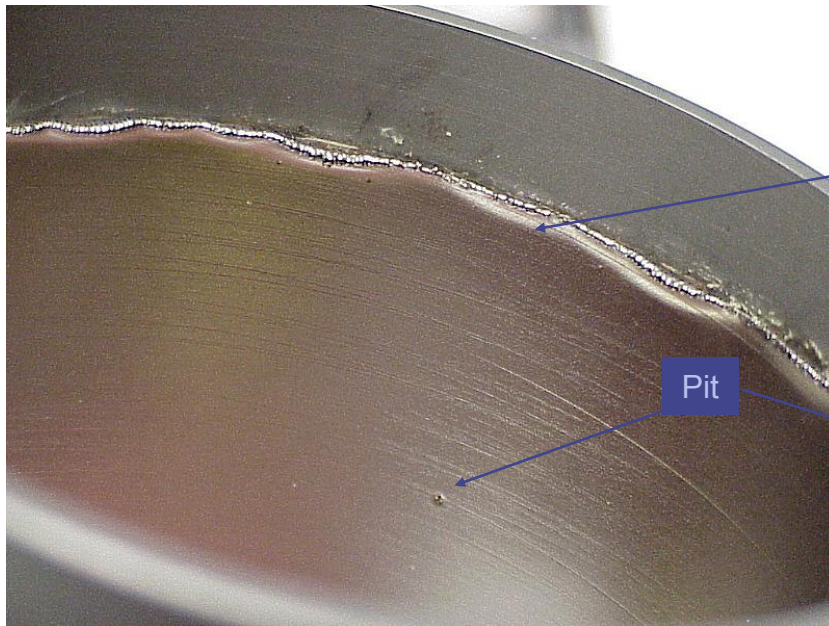
Rack Assy after plating:  
Section from P-3 MLG Actuating Cylinder

Technology Partnerships Canada

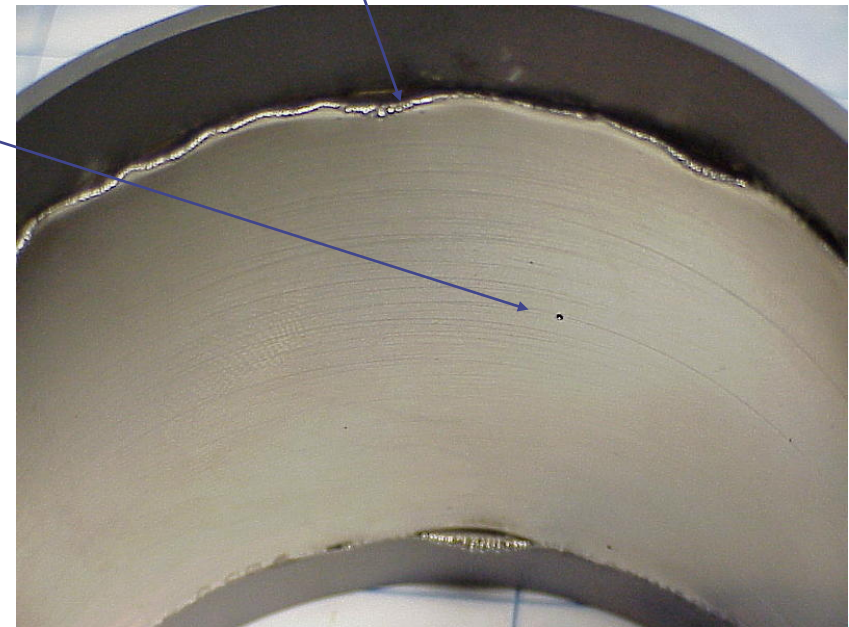
HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Component Plating Trials at NADEP-JAX

Demonstration on an ID section of a P-3 MLG Actuating Cylinder



Bridging of deposit over robber & maskant



Part after de-masking:  
Section from P-3 MLG Actuating Cylinder

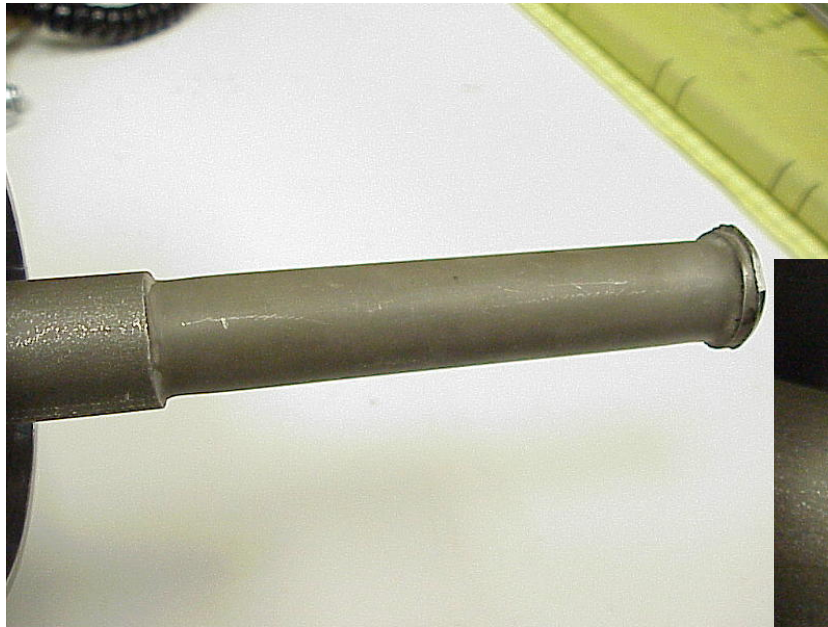
Appearance: Bright silver gray, 2 pits  
Coating Thickness: 12.0 mils /side  
Deposition rate ~ 6.0 mil/hr

Technology Partnerships Canada

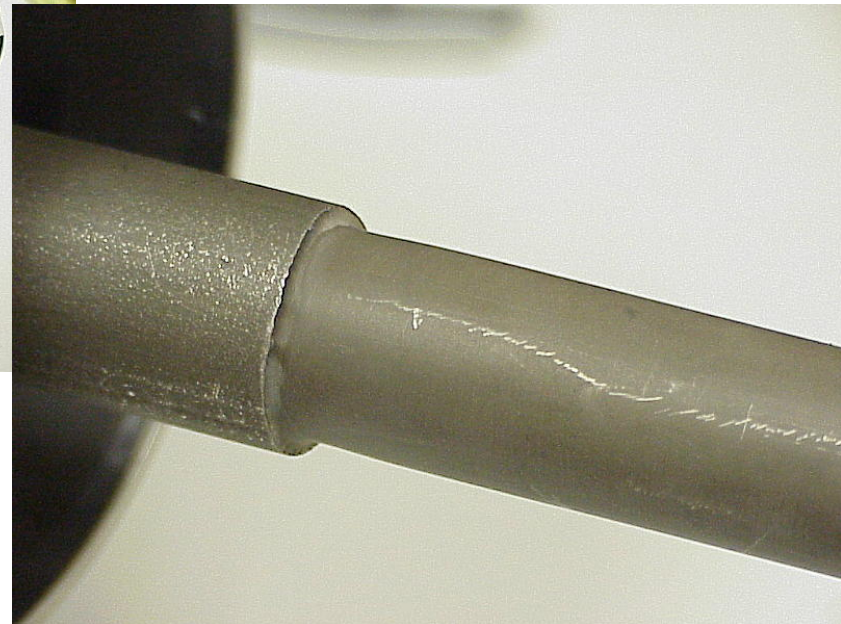
HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Component Plating Trials at NADEP-JAX

Demonstration on an ID section of a P-3 MLG Actuating Cylinder



Co Plated Anode Rod after Use



Cobalt anode after 2 Hrs of plating ID Section  
from P-3 MLG Actuating Cylinder

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Technology Transfer to NADEP-JAX

## Setup Considerations for ID Component Plating

### Masking

- Crucial step due to complex geometries
  - blind areas, pin holes, dissimilar metals, etc.
- Waxes used in Cr process not applicable due to high temp of solution
- Current "Peel Mask" maskant
  - small melting pot set up in the shop
  - not as forgiving as waxes with regards to trimming
  - degradation over time causing organic contamination
- Alternative masking method preferred - Platers Tape works, but difficult with complex geometries at JAX

### Anodes

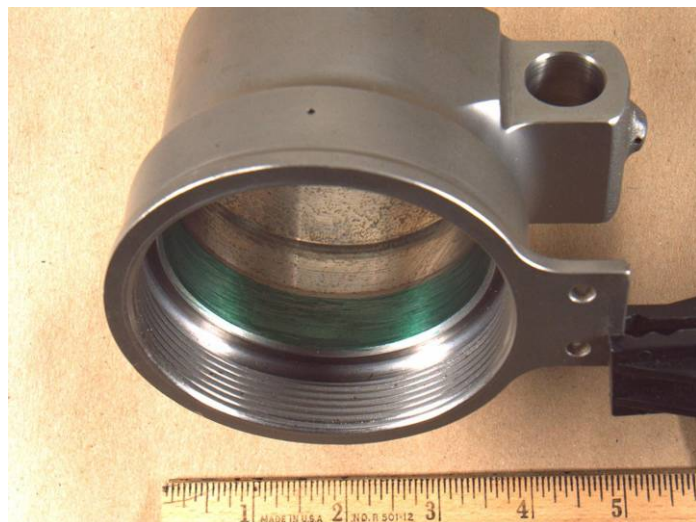
- Cobalt rods
  - best performance
  - consumed very quickly
- Ti baskets with cobalt chips
  - proper anode:cathode area and adequate flow must be maintained for proper deposit characteristics



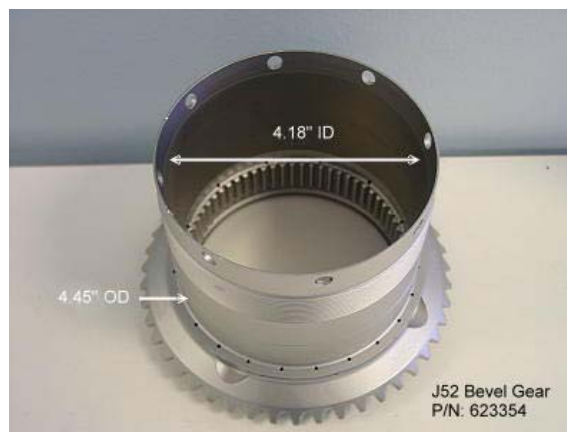
Rack Assembly of J52 Gear Spur

# Technology Transfer to NADEP-JAX

## Proposed Demo Parts to be Plated at NADEP-JAX



**P-3 MLG Actuating Cylinder**



**J52 Bevel Gear**



**P3 MLG Cylinder Section, Axle Journal**

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Selective Area (Brush) Plating Development

Technology Partnerships Canada

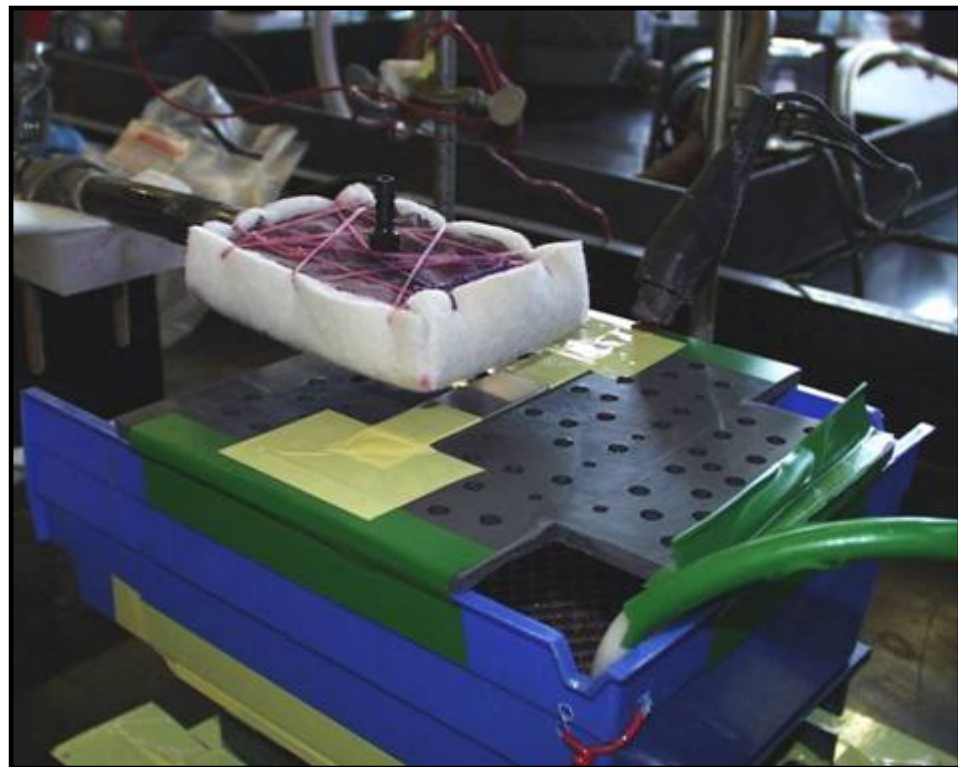
*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# Selective Area (Brush) Plating Development

## Overview

- Method to electrodeposit metal without tanks for localized coating
- Well characterized industrial process
- Moving anode – static cathode
- Can be easily field-implemented
- Can be applied manually, semiautomatic and automatic



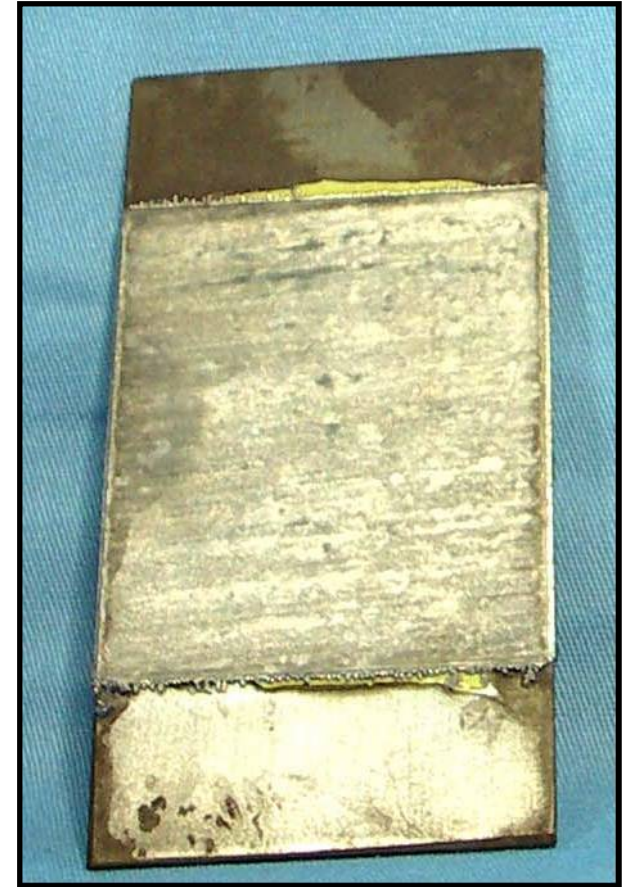
Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Selective Area (Brush) Plating Development

## Status

- Nano CoP brush plating procedure established
  - Optimized bath chemistry
    - Efficiency: > 90%
    - Deposition rate: 6mil/hr
    - High hardness: 600-700 VHN
    - Uniform composition
  - Good adhesion (ASTM B571)
  - Good tribological properties
  - Lower Coefficient of Friction
  - Adhesion on mild steel passes ASTM B571
- Process adapted for various geometries
  - cylindrical samples
  - large plates
  - thick deposits
- Samples being produced for JTP



Technology Partnerships Canada

# Joint Test Protocol (JTP) Sample Prep and Testing

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# Joint Test Protocol (JTP)

---

## JTP Summary\*

---

- **Demonstrate adhesion on various substrates**
  - 4340, 15-5PH, Aermet 100, Al 7075 and Ti 10-2-3
- **Pre-Test Grinding Study**
- **Performance Testing (Tank plating)**
  - Corrosion (ASTM B117 & G85)
  - Rod-Seal Wear
  - Fluid Immersion
  - Hydrogen Embrittlement (ASTM F519)
  - Axial Fatigue (ASTM E466-96)
- **Performance Testing (Brush Plating)**
  - Axial Fatigue (ASTM E466-96)
  - Hydrogen Embrittlement (ASTM F519)
  - Corrosion (ASTM B117)

**\*Copy of JTP can be found on the HCAT website**

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# Pre-Test Grinding Study

## Motivation

- Determine a set of reasonable (but not necessarily optimum) grinding conditions for nano CoP

## Sample Preparation

- Piston Rods (1" diameter) coated with ~0.010" nano CoP at Integrin
- Pre-Grinding study
  - 4 x 4130 (2 As-dep'd / 2 HT @ 191°C for 24h)
  - 2 x 15-5PH (As-dep'd)
- Final Grinding Study
  - 4340 HT to 260-280ksi
    - most susceptible or sensitive to grinding burns
    - 3 x As-dep'd
    - 3 x HT at 191°C for 24hrs
    - 3 x HT at 300°C for 1-3hrs



Four 4130 and two 15-5PH rods used for pre-grinding study

# Pre-Test Grinding Study

---

## Results

- Rods ground to ~ 0.001" at NADEP-JAX
  - Followed Mil-Std-866 using standard Al<sub>2</sub>O<sub>3</sub> abrasives
  - Rod was easily finished to a 2-3µin roughness
  - No problems, ground very similar to chrome
- Ground coating stripped at Integran
  - Using alkaline chemical dip solution
- Stripped parts subjected to Nital Etch at NADEP-JAX
  - No evidence of any grinding burns was present

Mil-Std-866 Acceptable for nCoP

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*

# Corrosion

## Sample Preparation

- Substrates
  - 4340
  - 15-5PH
  - 7075Al
- Nano CoP coating
  - 0.006"
  - 0.013"
- Post-plate grinding
  - final dimensions
    - 0.003"
    - 0.010"
  - Final surface finishes
    - 12-16  $\mu$ " Ra grind
    - <4  $\mu$ " Ra superfinish

4340



0.006" nano CoP



0.013" nano CoP

15-5PH



0.006" nano CoP



0.013" nano CoP

7075 Al



0.006" nano CoP



0.013" nano CoP

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# Corrosion

---

## Testing details

- ASTM B117-9 salt fog
  - Solution: 5% NaCl
  - pH: 6.5-7.2
  - Temperature: of 35°C (95°F)
  - Test duration: 1000 h, inspect every 168 h
- ASTM G85, SO<sub>2</sub> salt fog
  - Solution: add SO<sub>2</sub>
  - Test duration: 336 h, inspect at 100, 200 and 336 h
- Nano CoP to be compared to EHC of comparable thickness and surface finish (EHC samples prepared at NADEP-JAX)

## Status

- Sample preparation complete
- Samples currently being ground

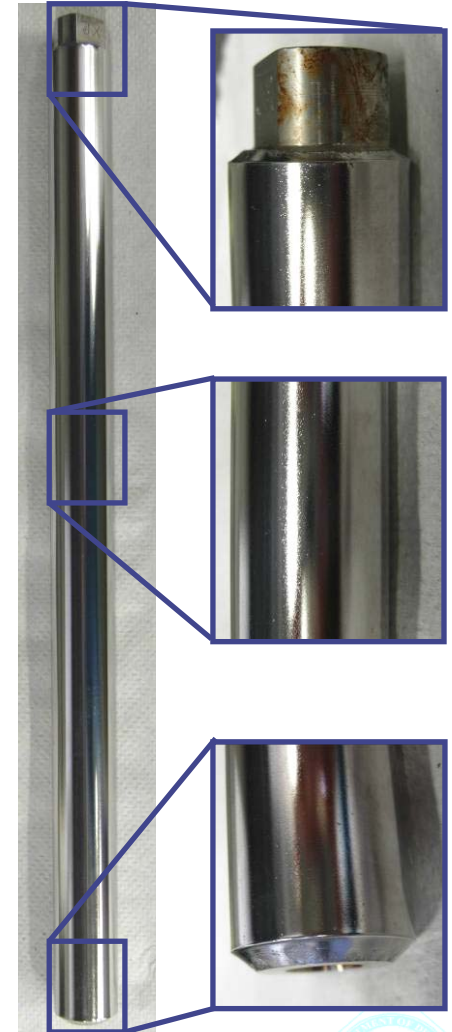
# Rod-Seal Wear

## Purpose

- Wear under simulated actuator service conditions
  - Compare performance of nano CoP to EHC
  - Determine optimum surface finishes on nano to minimize seal wear

## Sample Preparation

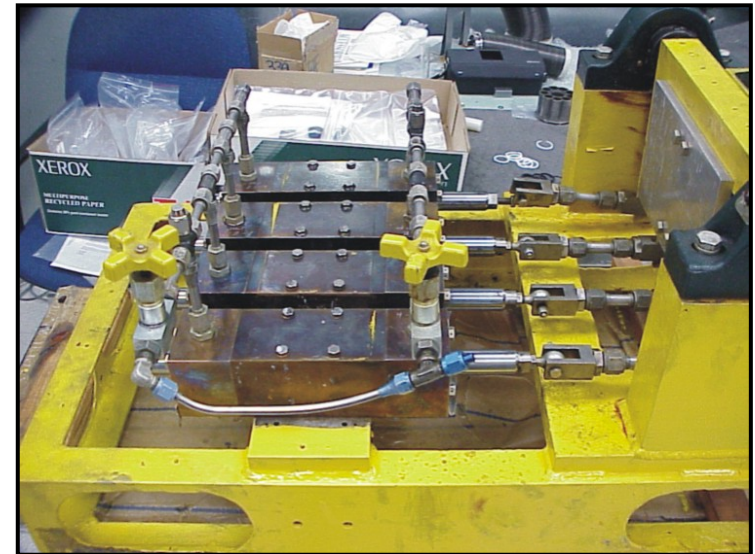
- Four hydraulic actuator rods
  - PH 13-8Mo, 16" long, 1" diameter
  - plated with 0.006-0.008" nano CoP
- Post-plating finishing
  - Rod #1: Hydrogen bake (375°F, 23h), ground to Ra 12-16  $\mu$ inch
  - Rod #2: Hydrogen bake, ground to Ra 6-9  $\mu$ inch
  - Rod #3: Hydrogen bake, superfinished to Ra < 4  $\mu$ inch
  - Rod #4: Heat treat (300°C, 6 h), ground to Ra 6-9  $\mu$ inch



# Rod-Seal Wear

## Testing details

- Hydraulic cylinder rod wear test
  - similar conditions to ID cylinder wear - wear against seals
  - master hydraulic piston drives four test rods
  - each rod passes through two blocks
- Two seal types to be tested per rod
  - standard MIL-P-83461 O-ring/Cap
  - Spring Energized PTFE
- Performance metrics
  - meet or exceed performance of hard chrome with a standard 12-15 $\mu$ " Ra ground finish
- Testing to be conducted at NAVAIR Patuxent River



Rod-Seal Wear Test Apparatus  
Consisting of Four Rods Passing  
Through Blocks Containing Seals

# Fluid Immersion

## Sample Preparation

- 34 x 1" diameter 4340 discs
- Coated with 0.003" nano CoP

## Testing Details

- Testing conducted at ARINC
- Coated discs submerged in various fluids
  - service conditions and overhaul fluids
- Specimens weighed before and after immersion
- Appearance of each specimen subsequent to immersion compared to that obtained prior to immersion



4340 discs  
No coating



4340 discs  
0.003" Nano CoP coating

# Fluid Immersion

## Preliminary Results – Visual Examination

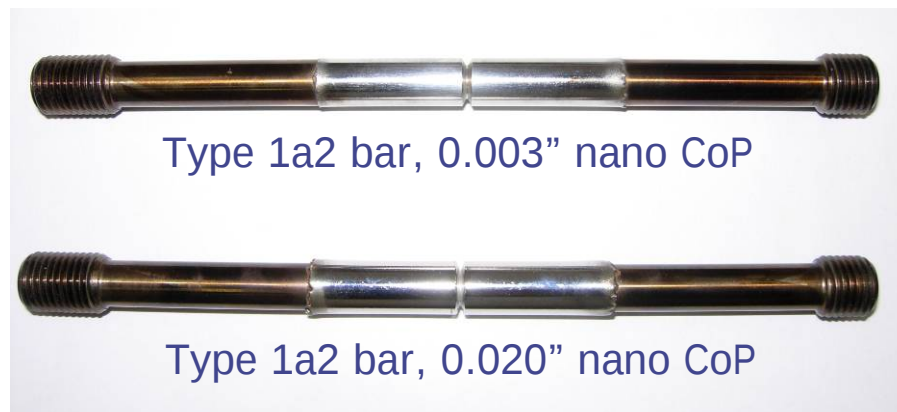
- Visual examination of specimens after immersion
- Mass changes to be examined

|                                                                                                                                                                                                                                                                                            |                                                                                                                                                                                                             |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p><b><u>No effect</u></b></p> <ul style="list-style-type: none"> <li>• fluorescent penetrant (for NDI)</li> <li>• MIL-C-87937 (aviation cleaner)</li> <li>• propylene glycol (de-icer)</li> <li>• Cee-Bee J-84A (heavy duty soak clean)</li> <li>• Cimstar 40 (grinding fluid)</li> </ul> | <p><b><u>Discoloration</u></b></p> <ul style="list-style-type: none"> <li>• Nital (grind burn etch)</li> <li>• Oakite 90 (alkaline cleaner)</li> <li>• Turco Vitro-Klene (Heavy duty soak clean)</li> </ul> |
| <p><b><u>Degradation</u></b></p> <ul style="list-style-type: none"> <li>• ammonium persulfate (grind burn etch)</li> <li>• Bleach</li> <li>• Turco scale Gon (descaling)</li> <li>• Sodium hydroxide (Cr strip)</li> <li>• 35% Nitric acid</li> </ul>                                      | <p><b><u>Not available</u></b></p> <ul style="list-style-type: none"> <li>• Cd plating solution (inconclusive)</li> <li>• Hydraulic fluids (TBD)</li> </ul>                                                 |

# Hydrogen Embrittlement (ASTM F519)

## Sample preparation

- Type 1a2 bar (4340, long bar)
- plated with 0.003" or 0.020" nano CoP
- Hydrogen baked at 375°F for 24h or not baked



## Testing details

- Constant load testing
  - Constant load 75% of Notch Tensile Strength (NTS)

| Thick. | Stress (%NTS) | Hydrogen bake | Qty const load | Results #bars >200hrs |
|--------|---------------|---------------|----------------|-----------------------|
| 0.003" | 75%           | No            | 4              | 0/4                   |
| 0.020" | 75%           | No            | 4              | 0/4                   |
| 0.003" | 75%           | Yes           | 4*             | 2/4                   |
| 0.020" | 75%           | Yes           | 4*             | 0/4                   |

## Results

- Both baked and unbaked samples failed ASTM F519

# Hydrogen Embrittlement - Results

## ESTCP JTP and Previous Results

| Test           | Coating Thickness | Plating Parameters | Bar Type    | Heat Treatment           | Result       |
|----------------|-------------------|--------------------|-------------|--------------------------|--------------|
| SERDP          | 0.003"            | A                  | 1a.2        | None                     | PASS         |
| Goodrich       | 0.005"            | B                  | 1a.1        | None<br>375F/12hrs       | FAIL<br>PASS |
| In-House       | 0.005"            | A                  | 1a.2        | None<br>375F/12hrs       | FAIL<br>PASS |
| Ext Customer 1 | 0.004"            | B                  | 1a.1        | 375F/24hrs               | PASS         |
| Ext Customer 2 | 0.005"            | A                  | 1a.1        | None<br>375F/24hrs       | PASS<br>PASS |
| <b>ESTCP</b>   | <b>0.003"</b>     | <b>B</b>           | <b>1a.2</b> | <b>None / 375F/24hrs</b> | <b>FAIL</b>  |
| <b>ESTCP</b>   | <b>0.020"</b>     | <b>B</b>           | <b>1a.2</b> | <b>None / 375F/24hrs</b> | <b>FAIL</b>  |
| ESTCP(RETEST)  | 0.003"            | A                  | 1a.2        | 375F/24hrs               | PASS         |

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans



# Hydrogen Embrittlement Questions

---

## Summary

- JTP HE results first instance of failure on thin coatings ( $< 0.005''$ ) after baking, all previous tests passed with bake
- First tests of thick ( $0.020''$ ) nano CoP coatings
- Type 1a.2 bars (long) are more sensitive than 1a.1 (short)
- While change in operating parameters did not have significant effect on coating properties (structure, composition, hardness) it did have large effect on HE

## Questions:

- Did change in operating parameters:
  - Somehow change deposit characteristics to let Hydrogen escape during bakeout?
  - Prevent hydrogen from getting in?
  - Does the fully dense coating prevent hydrogen from escaping?
  - How does nCoP compare to Ni / other dense non-chrome electroplated coatings?

Follow up Studies Being Conducted to Address these Questions

# Axial Fatigue

## Sample Preparation

- Peened fatigue smooth bars
  - 4340, 15-5PH or 7075 Al
- Coated with nano CoP
  - 0.006", 0.013" or 0.018" as-deposited
  - 0.003", 0.010" or 0.015" ground, Ra of 12-16 uinch



4340 fatigue bar coated with Nano CoP (as-dep'd)



15-5PH fatigue bar with Nano CoP (as-dep'd)

## Testing Details

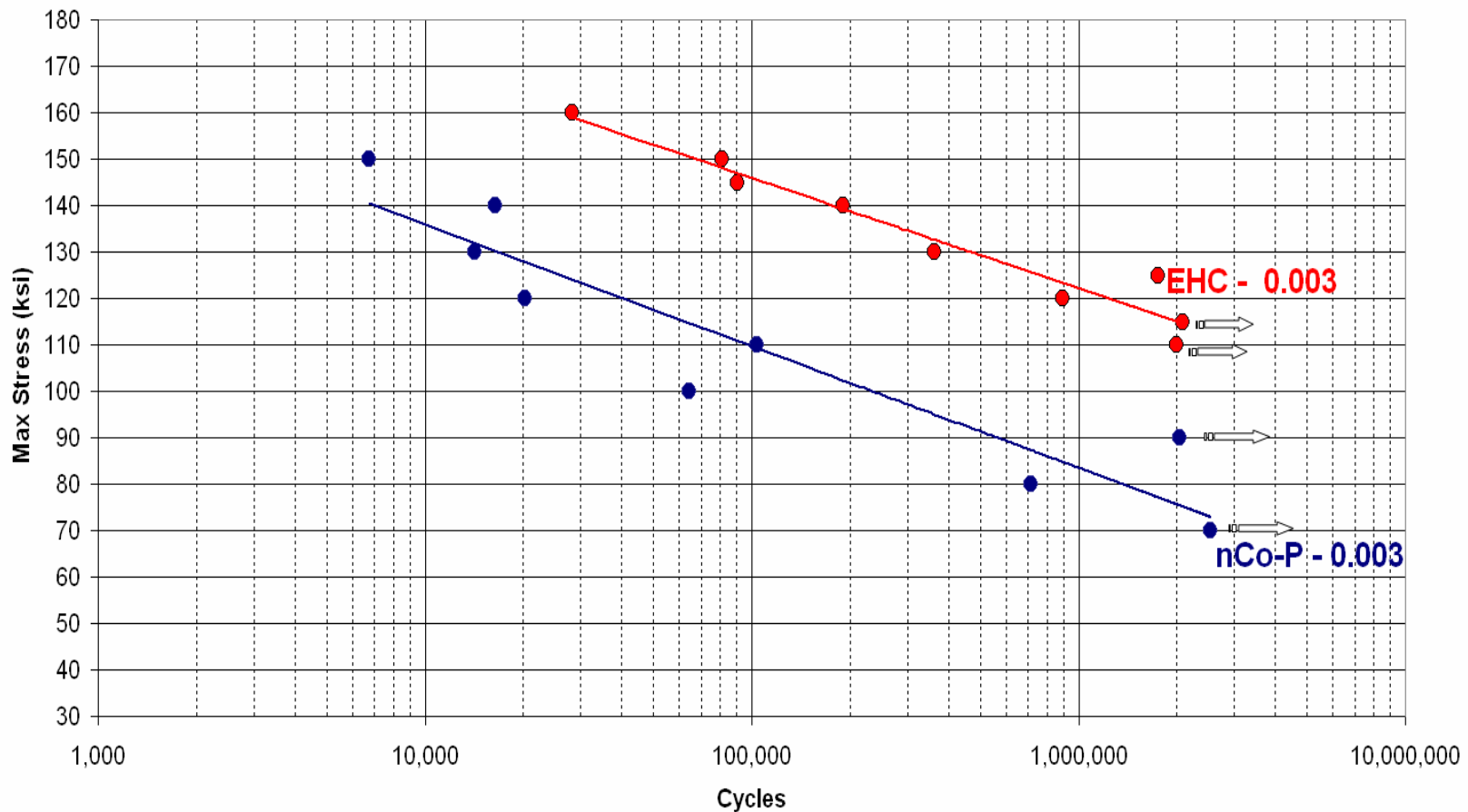
- Load-controlled constant amplitude axial fatigue testing (ASTM E466-96)
- Loads spread between high and low loads
  - High load – 85% of  $F_{ty}$  (yield)
  - Low load – uncoated specimen fatigue life is approximately  $10^6$  cycles (runout)
  - maximum four points per load
- R ratio:  $R = -1$
- Compare S-N curve to EHC coated samples of similar thickness

Technology Partnerships Canada

# Axial Fatigue

## Results – 4340 Substrate

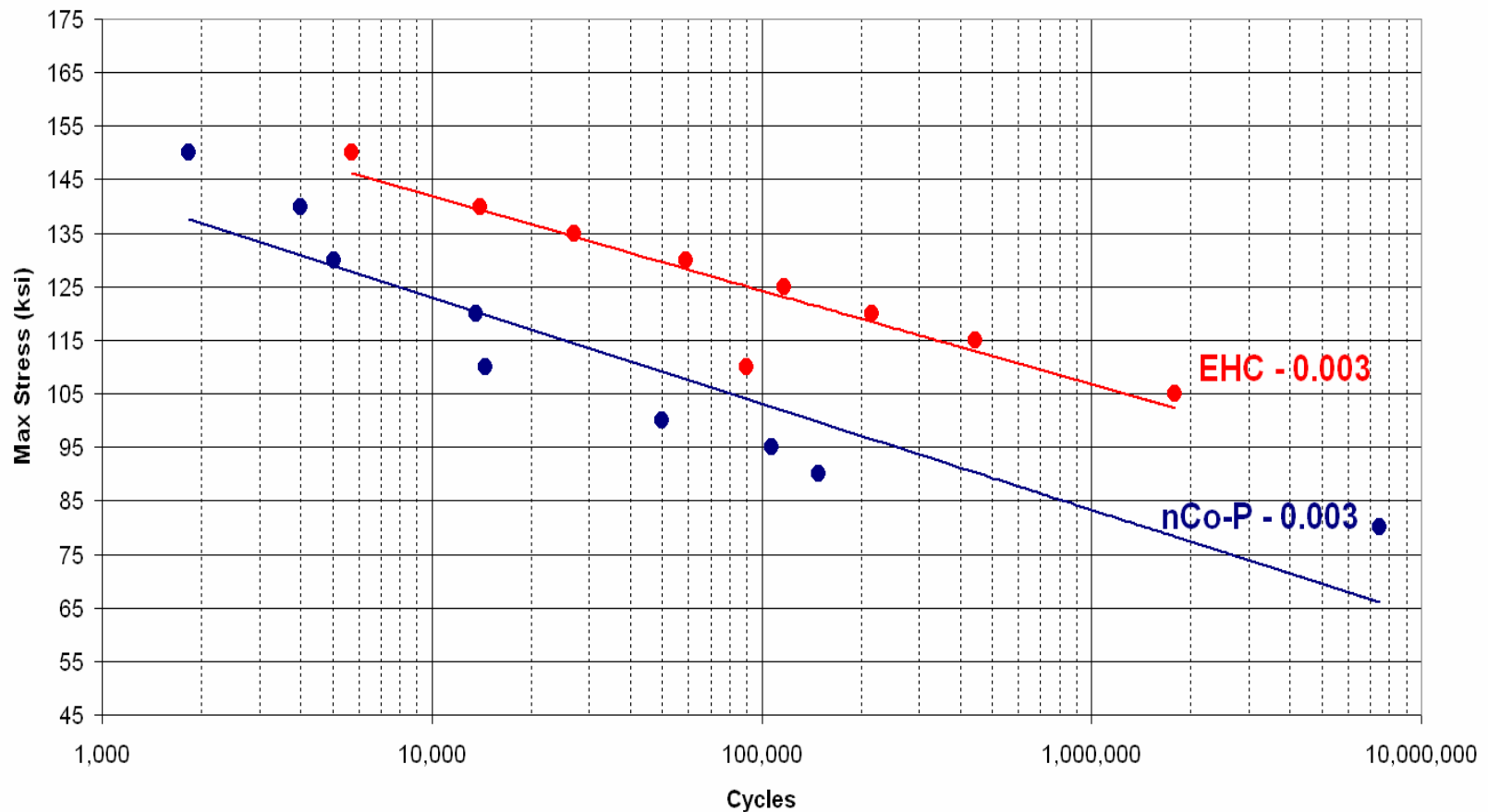
- Nano CoP shows fatigue debit compared to EHC at 0.003" and 0.010"
- Possible effects of hydrogen embrittlement?



# Axial Fatigue

## Results – 15-5PH Substrate

- Nano CoP shows fatigue debit compared to EHC at 0.003" and 0.010"
- Possible effects of hydrogen embrittlement?



# Brush Plating Performance Testing

## Testing to date - Hydrogen Embrittlement

### Sample Preparation

- 8 Type 1a1 notched tensile bars (short bars)
  - brush plated with 0.003" nano CoP
  - 4 bars hydrogen baked at 375°F for 24h
  - 4 bars not baked

### Testing Details

- 75% of Notch Tensile Strength (NTS)

### Results

- Hydrogen baked - **PASS**
  - 1 of 4 fractured < 200h
  - Remaining bars step-loaded to >95% NTS
- Not hydrogen baked – **PASS**
  - 1 of 4 fractured < 200h
  - Remaining bars step-loaded to >95% NTS



No hydrogen bake



Hydrogen bake

Technology Partnerships Canada

# Brush Plating Performance Testing

---

## On-going Sample Preparation

- Corrosion
  - 4"x6" peened 4340 and 15-5PH test panels
  - 0.003" and 0.010" nano CoP
- Hydrogen Embrittlement
  - Type 1a1 notched bars (short bars)
  - 0.010" nano CoP
  - With and without hydrogen bake at 375°F for 24h
- Axial Fatigue
  - Peened 4340 and 15-5PH smooth bars
  - 0.010" nano CoP (0.013" as-deposited)

# Thin Dense Chrome (TDC) Development

Technology Partnerships Canada

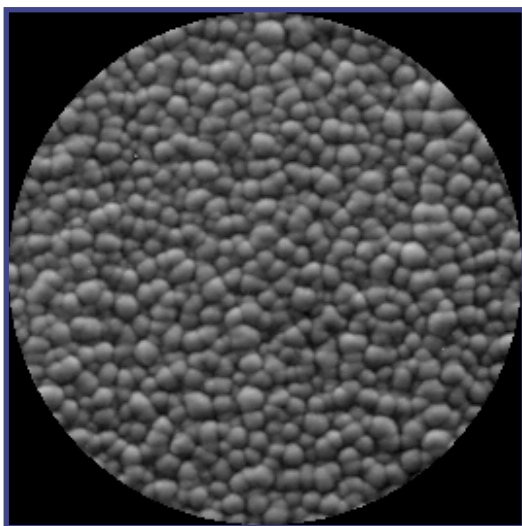
*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# TDC Alternative Development

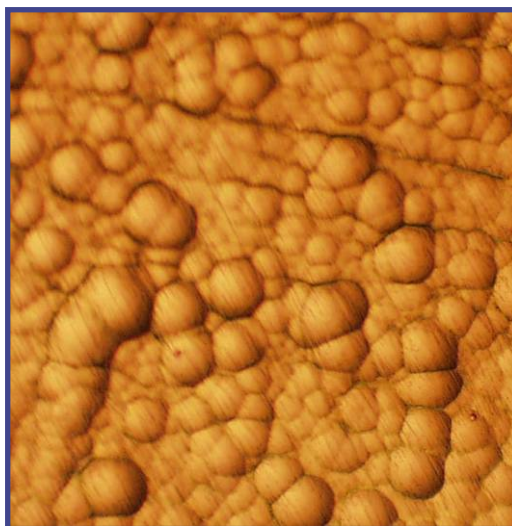
**Investigated Range of CoP Alloys (0-12wt%P) and tested for:**  
**Thickness Uniformity, Surface Finish, Morphology, Adhesion, Ductility, Corrosion,**  
**Hardness, Sliding and Abrasive Wear Testing**  
 (Benchmark comparison made against TDC (AMS 2438A))

Surface morphology is **nodular** (similar to that of Thin Dense Chrome)



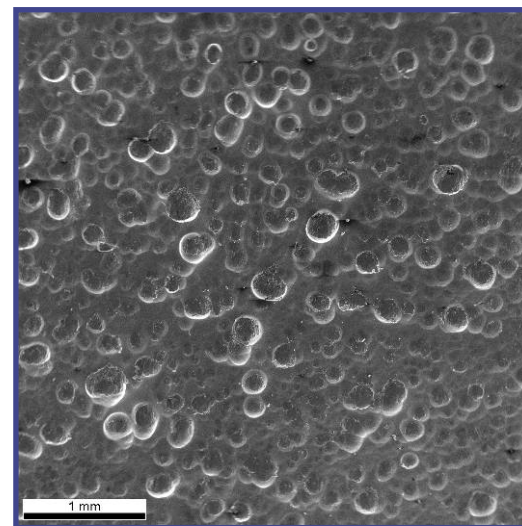
**Thin Dense Chrome**

Hardness  
 >900VHN



**Co 2-3wt% P**

Hardness  
 ~600-650VHN As-Dep



**Co 11wt% P**

Hardness  
 ~700VHN As-Dep

Technology Partnerships Canada

HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans

# TDC Alternative Summary

## Two Classes of Coatings Recommended

|                             | <b>Class 1</b><br>nCoP 2-3wt%P<br>HT 191°C – 24hrs                             | <b>Class 2</b><br>nCoP 11-12wt%P<br>HT 300°C – 6hrs                                |
|-----------------------------|--------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| <b>Application Types</b>    | When corrosion resistance is required and the substrates cannot be HT to 250°C | When corrosion resistance is not required and the substrates can be HT above 250°C |
| <b>Thickness Uniformity</b> | Need proper masking/shielding to achieve required thickness                    |                                                                                    |
| <b>Surface Finish</b>       | Surface roughness unaltered after coating to 0.0005"                           |                                                                                    |
| <b>Adhesion</b>             | Pass                                                                           | Pass                                                                               |
| <b>Ductility</b>            | 4-5%                                                                           | ~1%                                                                                |
| <b>Corrosion Salt Spray</b> | Pass                                                                           | Fail                                                                               |
| <b>Hardness</b>             | 650 VHN                                                                        | 1100 VHN                                                                           |
| <b>Wear (Sliding)</b>       | Good                                                                           | Good                                                                               |
| <b>Wear (Abrasive)</b>      | Good<br>~18mg/1000cycles                                                       | Very Good<br>~7.7mg/1000cycles                                                     |

Technology Partnerships Canada

# Application-Specific Testing

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# TDC Alternative Dem/Val

## Motivation

- Part of Dem/Val to qualify nano CoP as TDC alternative

## Objectives

- Demonstrate nano CoP for use as TDC alternative in actuator cylinder

## Methods

- Actuator cylinder IDs coated with 0.0003" nano CoP
- Endurance testing and evaluation at Smiths Aerospace
  - Compared to Armoloy NTDC in a side by side rig test

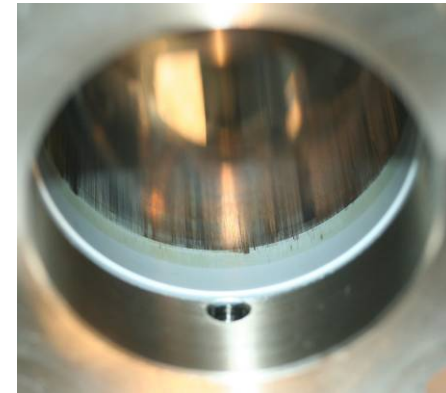


# TDC Alternative Dem/Val

---

## Preliminary results

- **Endurance testing and evaluation**
  - Nano Co-P showed similar behaviour and performance to Armoloy NTDC
  - Considered equivalent in this application
- **Future Work**
  - More extensive testing of nano CoP required for this application
  - Commercial details
    - Local suppliers of this process?
    - Would like more information of production quantity processing costs from a more dedicated, production facility



TDC-coated actuator  
Post-test



nano CoP-coated actuator  
Post-test

Technology Partnerships Canada

# Endurance Testing

## Motivation

- TDC alternative for NLOS applications in landing gear manufacturing

## Objectives

- Demonstrate adhesion on base metal substrates
- Design and fabricate plating anodes for plating 1" ID cylinders
- Assess performance of nano CoP coatings in utility actuator application

## Methods

- Nano CoP (0.0005") applied to
  - OD surface of actuator piston rods
  - ID surface of actuator cylinders
- Endurance testing at Messier Dowty
  - 20,000 cycles
  - simulates a scheduled commercial overhaul inspection

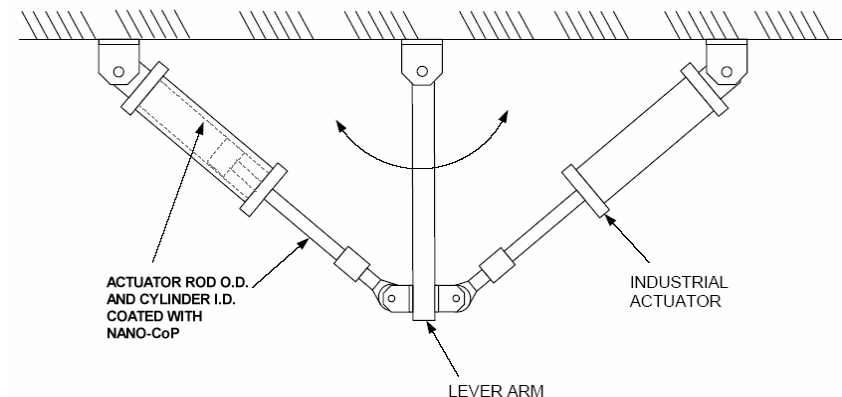


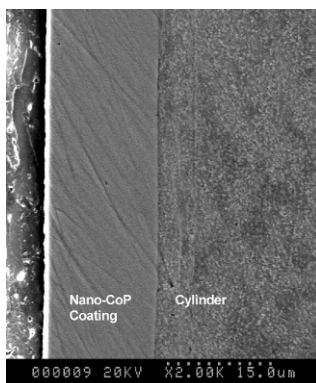
FIGURE 1 – ILLUSTRATION OF TEST SETUP

# Endurance Testing

## Performance Testing and Results

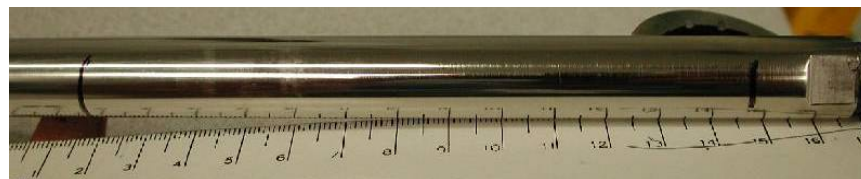
### nano CoP coating

- conformed to substrate surface
- no change in surface roughness ( $R_a = 0.06$ )



- 1 of 3 cylinders showed delamination during sectioning
  - caused by activation procedure
  - corrective actions implemented

### Endurance testing



- Minor wear/scoring (discoloration)
  - localized areas of piston and cylinder
  - sub-micron depth scoring (negligible wear)
- Acceptable leakage performance
  - <1 drop of hydraulic fluid in 25 cycles



- tests successful in meeting performance goals
- coating under consideration for the A 380 nose landing gear design team

Technology Partnerships Canada

# Summary

---

- **Industrial scale-up of nCoP process successful to date**
- **NADEP-JAX Dem/Val**
  - Tank installation complete
  - Technology transfer underway
  - Some growing pains incurred (i.e. issues with Pitting/Adhesion/Anode Set-up)
  - Issues have been addressed Dem/Val process continues
- **JTP Testing**
  - Sample preparation and testing well underway
  - Initial hydrogen embrittlement issues seem to be resolved
  - Additional studies being performed to get to root of HE Problem
  - Fatigue testing to be repeated
- **TDC Alternative Development**
  - Preliminary testing complete
  - Application-specific testing ongoing
- **Application-specific testing**
  - Actuator rig testing reveals good results against polymeric/rubber seals

Technology Partnerships Canada

# The End

---

THANK YOU FOR LISTENING!

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# History of Cobalt Use

---

**Cobalt is widely used in industry for years:**

- **Pigments**
  - Cobalt coloring of ceramics has been known for well over 2,000 years in Persia and Egypt
- **Metallurgical**
  - Superalloys, Hastalloy, Stellite, Thermal Spray Alloys, Co-WC
- **Electronics**
  - Samarium cobalt hard magnets
  - Magnetic particle recording
  - Perpendicular recording with Co-Cr
- **Catalysts**
- **Medicine**
  - Co-Cr alloys in prosthetics
  - Cobalt 60 used in food and medical sterilisation
- **Agriculture**
  - Animal feed to increase vitamin B12 in meat
- **Plating**

Technology Partnerships Canada

*HCAT Meeting – Jan 24<sup>th</sup>, 2007 – New Orleans*



# Cobalt Health Concerns?

**Cobalt in small amounts is essential to many living organisms, including humans**

- Cobalt is a central component of the vitamin cobalamin, or vitamin B-12.
- Having 0.13 to 0.30 mg/kg of cobalt in soils markedly improves the health of grazing animals.

## **Health Studies**

- Co(II) added to a brand of beer in the 1960, increased rate of cardiomyopathy (later attributed to poor diet combined with Co ingestion)
- Diamond polishers exposed to Co, WC, etc metal dust developed chronic fibrotic lung disease, however workers exposed to cobalt in strictly Co-refining showed no evidence of lung fibrosis
- No human case studies have indicated Co alone to be potential carcinogen

## **American Cancer Society Has Four Categories of Carcinogens:**

### **1. "Known to Be Human Carcinogens"**

- Cadmium and cadmium compounds
- Chromium [VI] compounds
- Nickel compounds

### **2. "Probably Carcinogenic to Humans"**

### **3. "Reasonably Anticipated to Be Human Carcinogens"**

- Cobalt Sulfate

**No chemicals used in Nano CoP Process on the ACS list of Carcinogens**