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Electroformed Nanocrystalline Coatings An Advanced Alternative to Hard-Chrome Electroplating PP-1152

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Report Documentation Page

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Technical Objective



- ▶ **Develop an environmentally benign advanced nanocrystalline Co-based coating technology that:**
 - ▷ **Is compatible with conventional electroplating infrastructure**
 - ▷ **Will produce coatings that meet or exceed the overall performance of hard chrome (hardness, wear, fatigue, corrosion, and thermal stability)**
 - ▷ **Has costs similar to or less than life-cycle cost of existing hard chrome electroplating processes**
 - ▷ **Will be applied to non-line-of-sight surfaces**
- ▶ **Cobalt alloy selection**
 - ▷ **Mechanical properties**
 - ▷ **High plating efficiency**
 - ▷ **No constituents on EPA or AFMC lists of hazardous materials**
 - ▷ **Longer term view**





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Program Overview



Three Phases

- ▶ **Phase I Technology Viability Assessment**
 - ▷ **Completed**
- ▶ **Phase II Coating Optimization**
 - ▷ **Completed**
- ▶ **Phase III Extension to Complex ID Shapes**
 - ▷ **In Progress**





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Program Plan



	GFY00	GFY01	GFY02	GFY03
Phase I: Technological Viability Assessment				
1. Alloy Synthesis	◆ —◆			
2. Material Characterization	◆ —◆			
3. Impact Assessment		◆ —◆		
4. Reporting/Management/Go-No Go	◆ —◆			
Phase II: Coating Application Optimization				
5. Alloy Optimization		◆ —◆		
6. Mechanical Properties Testing			◆ —◆	
7A. Material Performance Testing			◆ —◆	
8. Reporting/Management/Go-No Go		◆ —◆		
Phase III: Extension to Complex Shapes				
7B. Material Performance Testing			◆ —◆	
9. Process Scale-up and Optimization			◆ —◆	
10. Mockup ID Applications and Evaluation				◆ —◆
11. Production Part Application and Evaluation				◆ —◆
12. Reporting/Management/Final Report			◆ —◆	





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Background



- ▶ **Synthesized Co-P, Co-Mo and Co-Fe nano alloys**
- ▶ **Synthesized and Optimized Co-Fe, Co-Fe-P, Co-Fe-Zn and Co-Fe-Zn-P nano alloys**
- ▶ **Optimized Co-P alloy**
 - ▷ **Cobalt chloride/ortho-phosphoric/phosphorous acid bath**
 - ▷ **Plating efficiency >90%**
 - ▷ **Grain size 12-15 nm**
 - ▷ **As-deposited hardness 700 VHN**
 - ▷ **Deposition rate 2-8 mills/hr**
 - ▷ **Precipitation hardenable**
 - ▷ **Good salt spray results**
 - ▷ **High Taber wear results (CS 17)**
 - ▷ **Good pin-on-disk results**



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Activities Since Toronto



- ▶ **Initial fatigue tests completed**
- ▶ **Initial hydrogen embrittlement tests completed**
- ▶ **Electrochemical tests completed**
- ▶ **Stripping study completed**
- ▶ **Representative ID geometry plated**



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Initial Fatigue Test Matrix



- 4340 HT (avg. ~46 Rc)
- R= -1, Air

Coating	Grit Blast	Peen	Final Ground Thickness (in)	No. Specimens
Bare	No	No	N/A	12*
Bare	No	Yes	N/A	12*
Nano Co 2-3% P	Yes	Yes	0.003	6+
Nano Co 4-5% P	Yes	Yes	0.003	6+
Nano Co	Yes	Yes	0.003	6+

* ksi/Hz 175 (5), 150 (5), 125 (10), 110 (10)

+ ksi/Hz 175 (5), 125 (10)



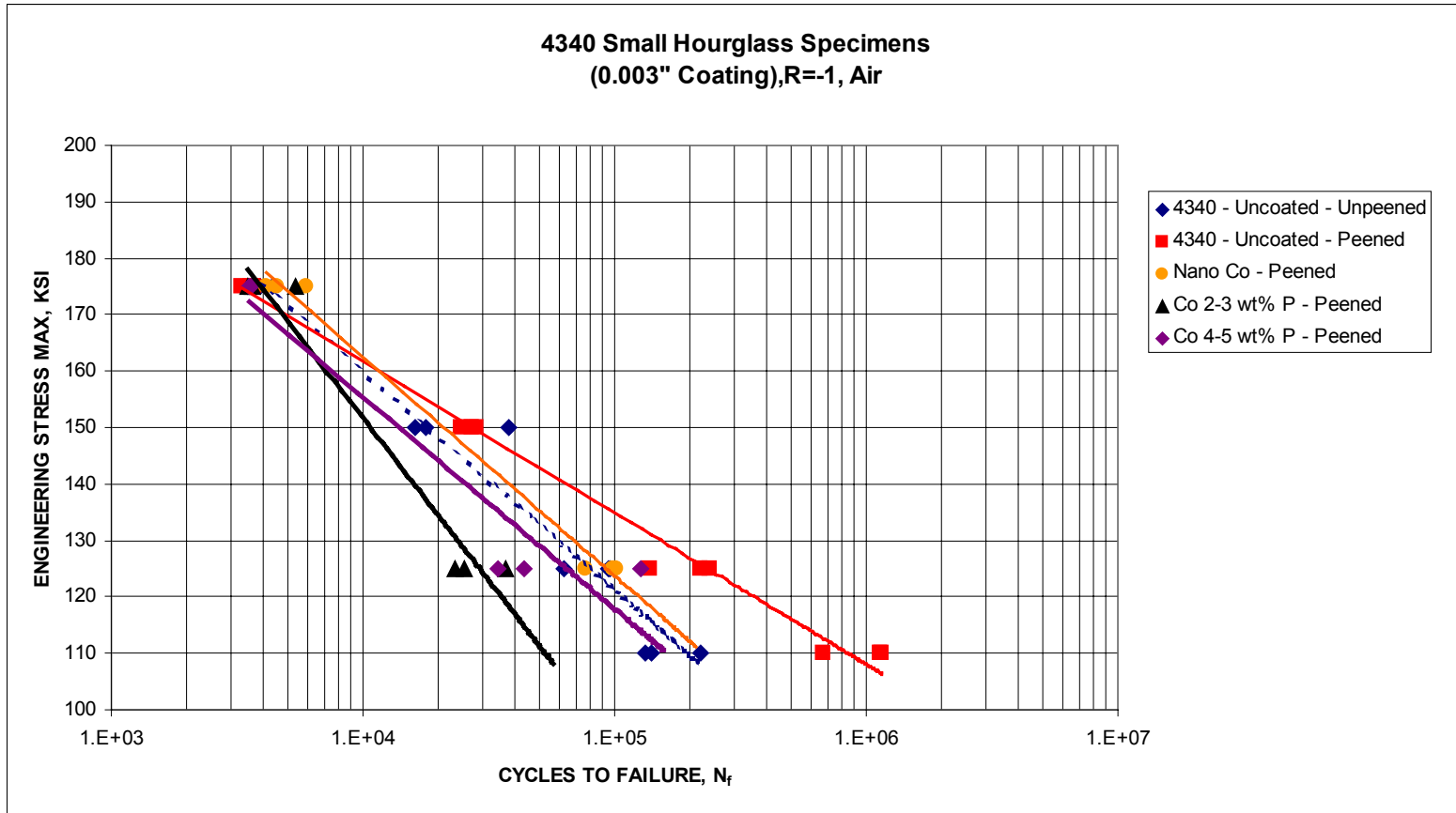


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Fatigue Test Results





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Fatigue Test Observations



- ▶ **Specimens were significantly softer than JTP criteria**
 - ▷ **Cannot compare with HCAT EHC results**

- ▶ **Debit evident for Co-P alloys**
 - ▷ **Failures initiate at coating to substrate interface**
 - ▷ **Does not appear to be adhesion problem**

- ▶ **Retest**
 - ▷ **Ensure Specimens meet hardness criteria**
 - ▷ **Include EHC specimens in retest matrix**
 - ▷ **Evaluate effect of reducing internal stress**





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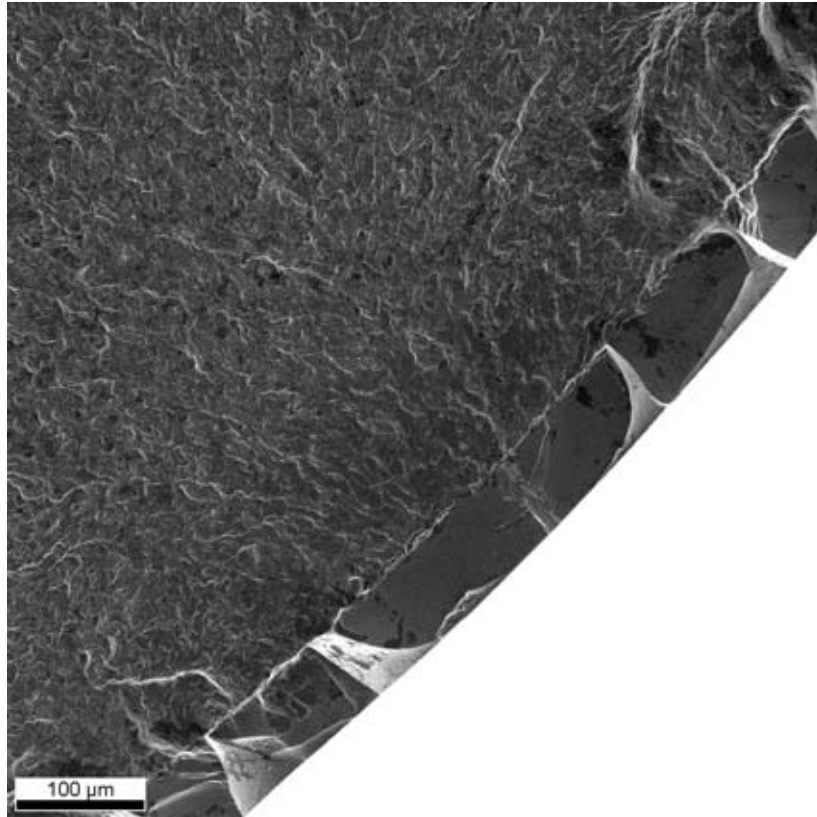
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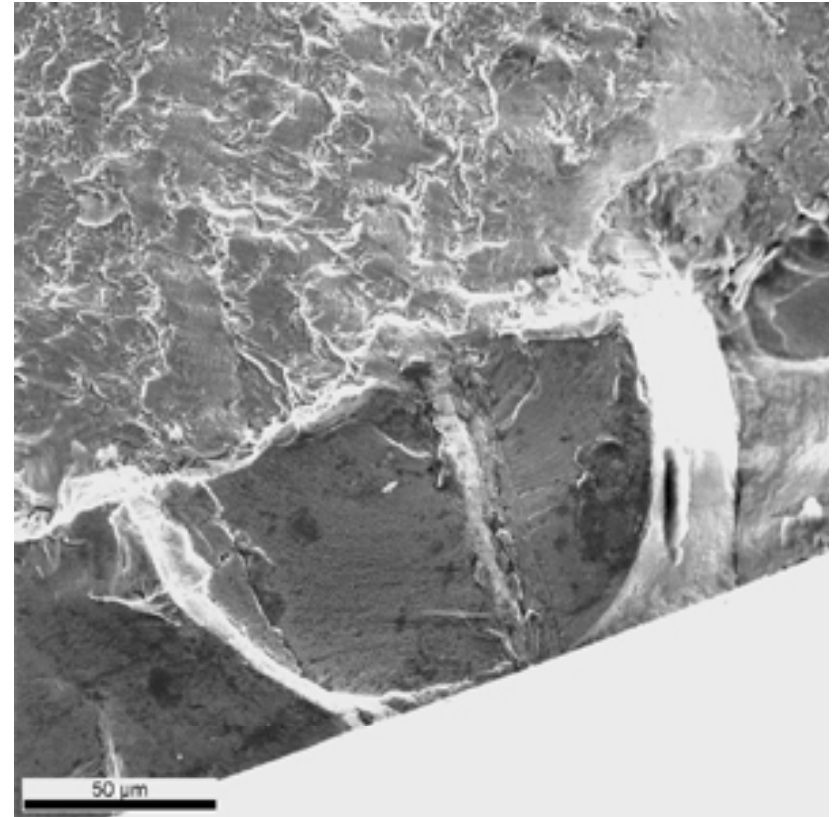
Fatigue Results



2-3wt% P



125ksi



175ksi





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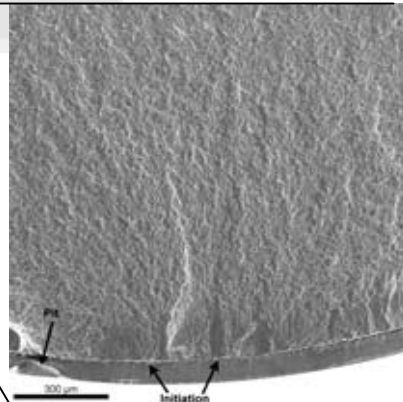
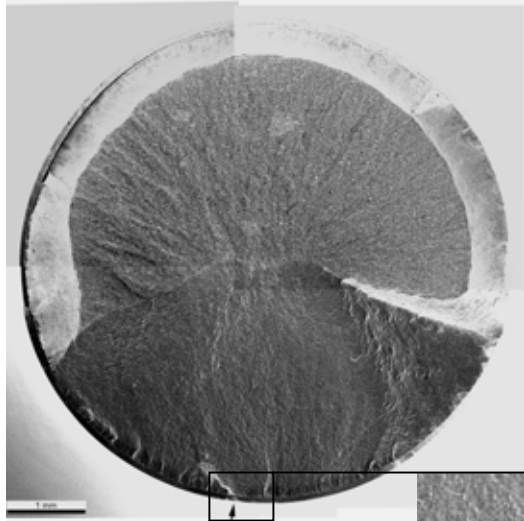
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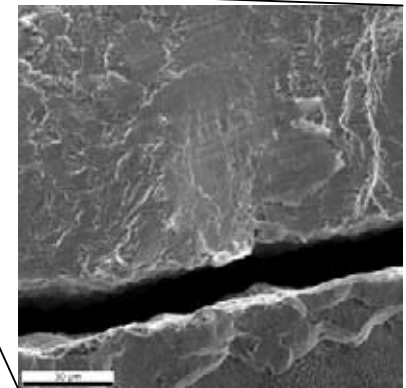
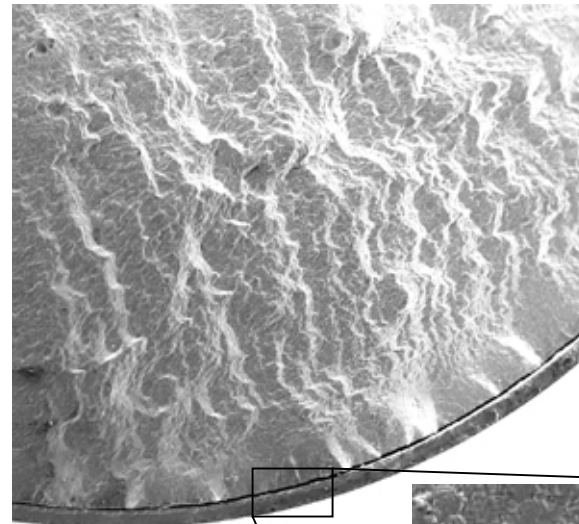
Fatigue Results



4-5wt% P



125ksi



175ksi



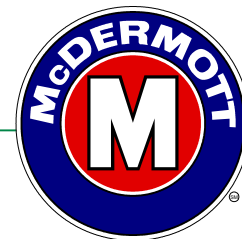


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Initial H₂ Embrittlement Test



- ASTM Type 1a Specimens -.003” coating thickness
- Acceptance criteria: 4 > 200 hrs @ 75% NFS or 3 > 90% NFS for 1 hr
- Notch failure except as indicated

Coating Composition	Hours (NFS)		
	No Bake	191 °C/ 12 hours	191 °C/ 12 hours
Bare	10 for NFS	-	-
Nano Co 2-3 wt%P	150 (75) 215 (83) 239 (82) 200 (80)	110 (75) BHF 162 (75) BHF 110 (75) BHF 215 (84)	180 (75) 233 (80) 233 (78) 233 (80)
Nano Co 4-5 wt%P	-	<18 (75) <18 (75) <64 (75) <64 (75)	216 (84) 216 (84) 216 (82) <46 (75)

BHF = Button Head Failure





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H₂ Embrittlement Retest



- ▶ **Nano Co 2-3 wt% P**
- ▶ **Careful NDE of test specimens before plating**
- ▶ **Bake at 8 and 16 hours**
- ▶ **Include stripped, re-coated and baked specimens**



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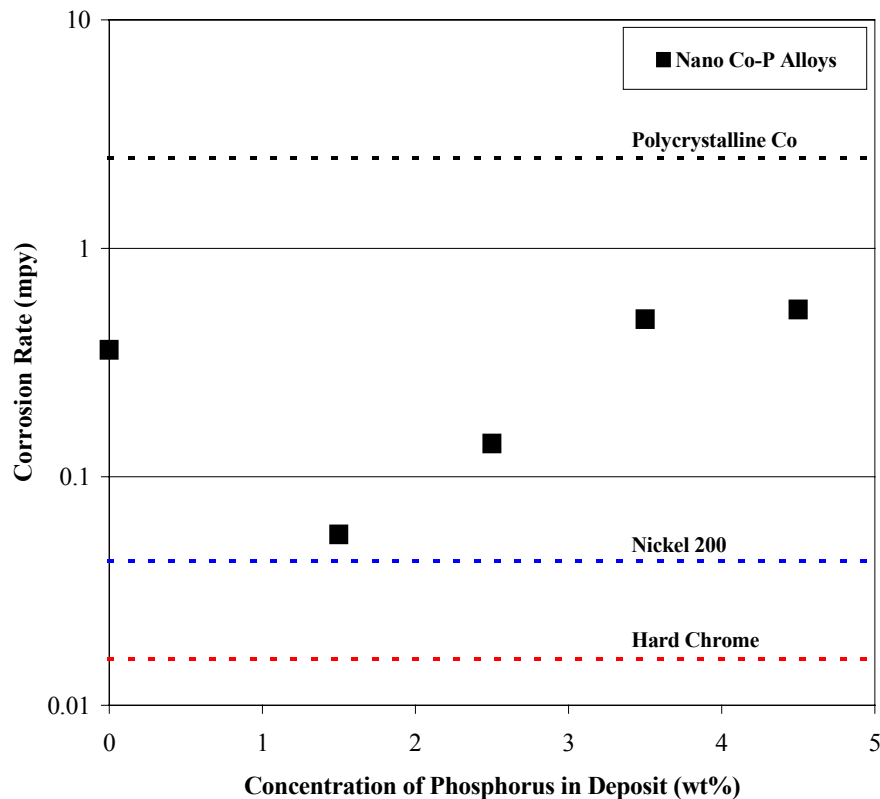
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Electrochemical Testing



- ▶ **Linear polarization resistance scan (LRP) per ASTM G61**
- ▶ **3.56 wt% NaCl, room temperature**





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Chemical Stripping



- ▶ **4130 substrate - .005” Co 2-3 wt%P coating**
- ▶ **Evaluated HVOF Rochelle salt solution with anodic polarization**
 - ▷ **Low removal rate (<1gm/hr) at pH ~10**
 - ▷ **Faster removal rate (2-3 gm/hr) at higher carbonate concentration - substrate pitting noted**
- ▶ **Evaluated concentrated nitric acid**
 - ▷ **Fast removal rate (4-8 gm/hr)**
 - ▷ **Little substrate impact (.13% weight loss after 20 hour immersion)**



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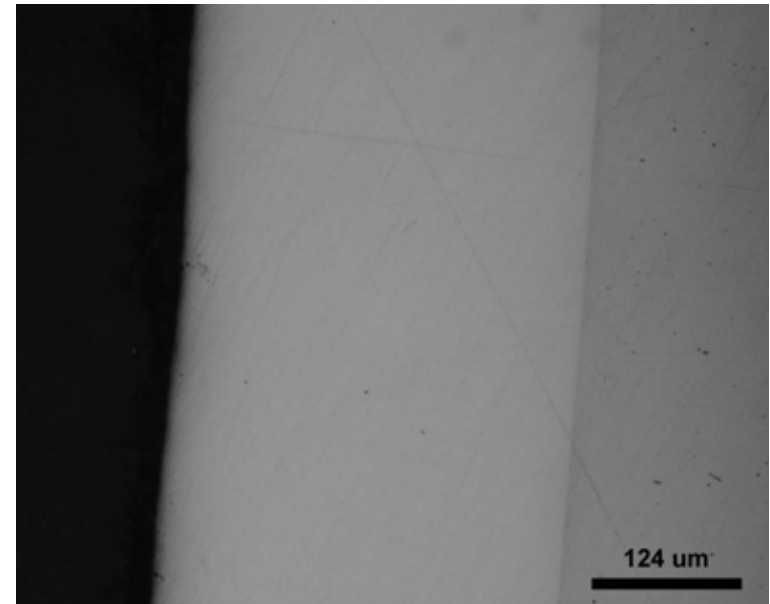
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Application to ID Surfaces



- ▶ **Mockups utilized**
 - ▷ **Blind and through cylinders**
 - ▷ **Pins**
 - ▷ **External lugs**
- ▶ **Anode design study**
 - ▷ **Small ID surfaces**
 - ▷ **Non-consumable graphite anode**
 - ▷ **Large ID surfaces**
 - ▷ **Consumable Co anode**



**Optical Micrograph - 13 mil Nano
Co 2-3wt%P coating on 1" ID**

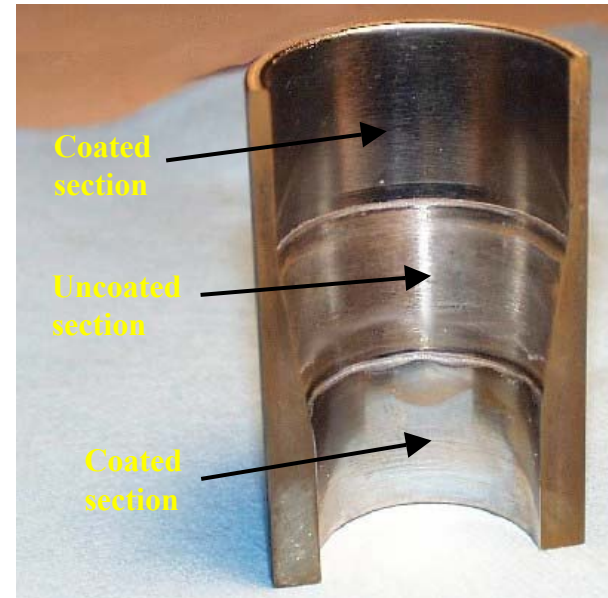
Small ID Surfaces



Stepped ID



- Stepped graphite anode
- Plastic plug used to mask uncoated section, with holes to allow for flow

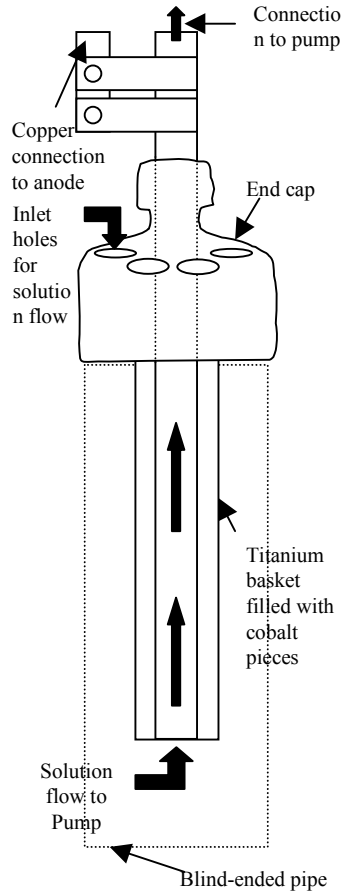


- Uniform coating thickness on the two ID surfaces

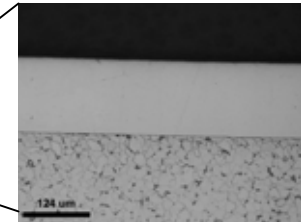
Large ID Blind Hole



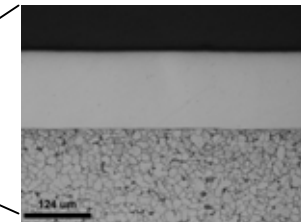
Plating Assembly



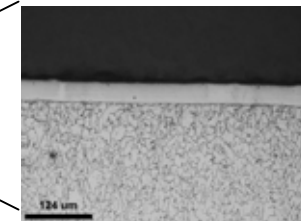
Top



Middle



Bottom





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Process Data Summary



Nanocrystalline Co-P Alloy

Hard Chrome

Bath Chemsitry

Co 2-5wt%P
(CoCl₂ / H₃PO₄ / H₃PO₃)

Cr
(CrO₃ / SO₄²⁻)

Efficiency

85-95%

15-35%

Deposition Rate

Up to 8 mil per hour

Up to 1.6 mil per hour

Thickness

Demonstrated up to 0.020"

Typically < .005"

As-Deposited Appearance

Pit / Pore Free

Microcracked

Microstructure

Nanocrystalline
(avg. g.s. = 8 -15nm)

-

Relative Process Cost

1.3

1.0

Emission Analysis

Below OSHA limits

Cr⁶⁺





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Property Data Summary



Nanocrystalline Co-P

Hard Chrome

Hardness	<i>As-Deposited</i>	600-700 VHN	800-1200 VHN
	<i>HT @ 250°C</i>	700-800 VHN	-
	<i>HT @ 400°C</i>	1000-1200 VHN	-
Ductility		2 – 7 % Elongation	<.1%
Thermal Stability		400°C	-
Wear	<i>Abrasive (Taber)</i>	27 mg / 1000 cycles (CS-17)	3.2 mg / 1000 cycles (CS-17)
		11 mg / 1000 cycles (CS-10)	1.0 mg / 1000 cycles (CS-10)
	<i>Adhesive (Pin-on-disk)</i>	5-6 x 10 ⁻⁶ mm ³ /Nm (Alumina Ball on Nano Co-P Disk)	9-11 x 10 ⁻⁶ mm ³ /Nm (Alumina Ball on Cr Disk)
		<i>Coefficient of Friction</i>	0.5
Corrosion	Salt Spray	Protection Rating 7 @ 1000 hrs	Protection Rating 2 @ 1000 hrs
	Poteniodynamic	.07 - .15 mpy	.02 mpy
Internal Stress		10-15 ksi (Tensile)	Cracked – Exceeds cohesive strength
Hydrogen Embrittlement		Additional tests planned	Yes – min bake 14 hrs
Fatigue		Additional tests planned	Fatigue Debit



Remaining Actions



- ▶ **Conduct final material tests**
- ▶ **Complete ID application demonstrations**
- ▶ **Submit final report**
- ▶ **Submit ESTCP white paper proposal**