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# Nanocrystalline Co-P for Cr- Replacement

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# Outline

- **Nano Co-P Summary**
- **Background**
- **Industrial scale-up and move EHC nanoCo-P alternative to depots**
- **Development of selective plating of nano coatings for repair**
- **Development of Nano Co-P based as Thin Dense Chrome alternative**



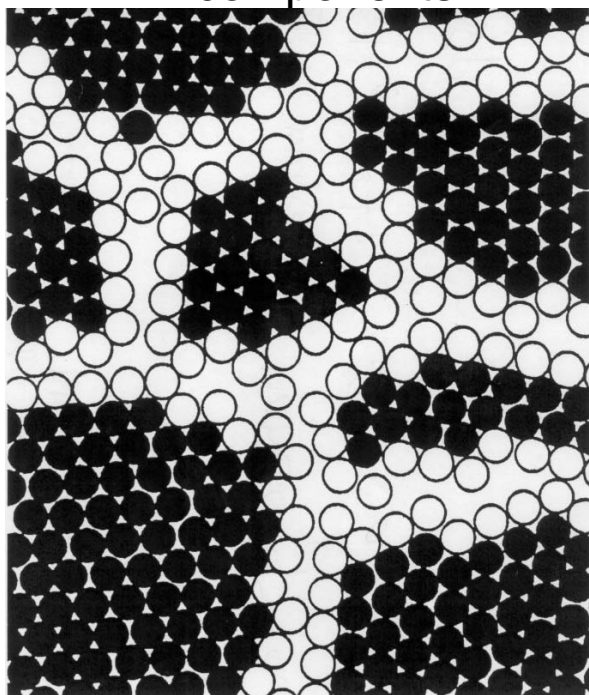
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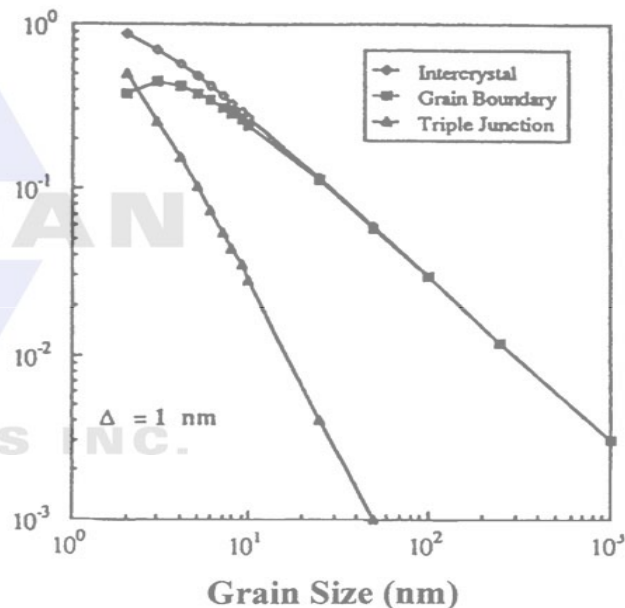
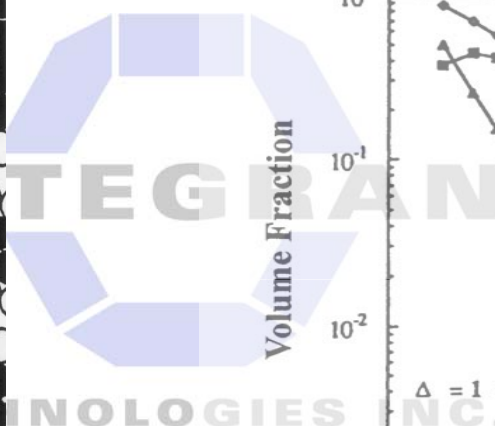
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# Nanocrystalline Materials

- Two Phase Material
  - Crystalline and intercrystalline components



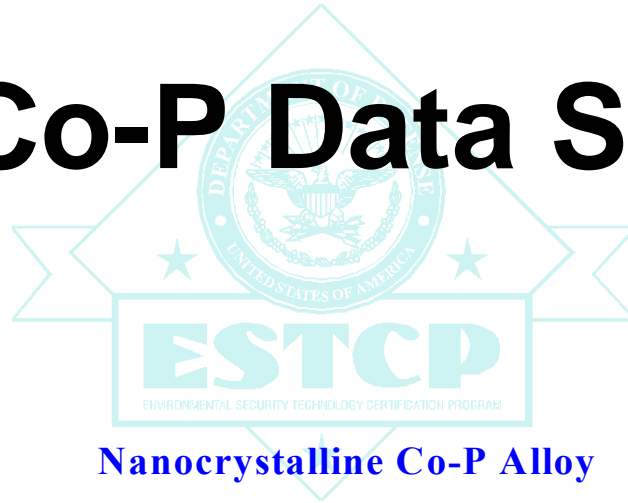
A reduction in grain size below 100nm, significantly increases the intercrystalline content in the material, leading to many unique properties.



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Technical Objectives

- **Develop an environmentally benign nanocrystalline Co-based coating**
  - Compatible with existing electroplating infrastructure
  - Can meet or exceed EHC (hardness, wear, fatigue, corrosion, and thermal stability)
  - Costs compatible with life-cycle cost of EHC
  - Can be applied to NLOS
- **Why Co?**
  - Mechanical properties
  - High plating efficiency
  - No on EPA or AFMC lists of hazardous materials
  - Longer term view

# Nano Co-P Data Summary



## Nanocrystalline Co-P Alloy

## Hard Chrome

**Bath Chemistry**

Co 2-5wt% P  
(Chloride Based)

Cr  
(Chromic Acid)

**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**

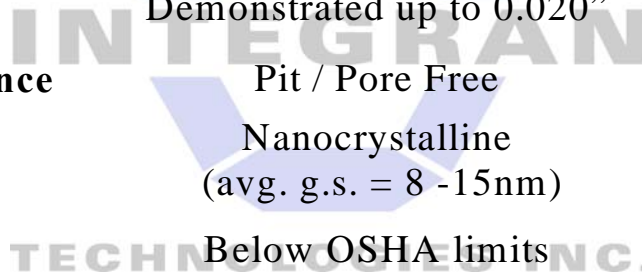
Nanocrystalline  
(avg. g.s. = 8 -15nm)

-

**Emission Analysis**

Below OSHA limits

Cr<sup>6+</sup>



# Nano Co-P Data Summary

	<b>Nanocrystalline Co-P</b>	<b>Hard Chrome</b>
<b>Hardness</b>	<i>As-Deposited</i> 600-700 VHN <i>HT @ 250°C</i> 700-800 VHN <i>HT @ 400°C</i> 1000-1200 VHN	800-1200 VHN - -
<b>Ductility</b>	2 – 7 % Elongation	<.1%
<b>Thermal Stability</b>	400°C	-
<b>Wear</b>	<i>Adhesive (Pin-on-disk)</i> 5-6 x 10 <sup>-6</sup> mm <sup>3</sup> /Nm (Alumina Ball on Nano Co-P Disk)  <i>Coefficient of Friction</i> 0.5  <i>Abrasive (Taber)</i> 27 mg / 1000 cycles (CS-17) 11 mg / 1000 cycles (CS-10)	9-11 x 10 <sup>-6</sup> mm <sup>3</sup> /Nm (Alumina Ball on Cr Disk)  0.7  3.2 mg / 1000 cycles (CS-17) 1.0 mg / 1000 cycles (CS-10)
<b>Corrosion</b>	Salt Spray Protection Rating 7 @ 1000 hrs	Protection Rating 2 @ 1000 hrs
<b>Hydrogen Embrittlement</b>	No – No Bake Required	Yes – min bake 14 hrs

# Background

- Development originally supported by SERDP PP-1152
- Nano Co-P as EHC alternative was developed
- Dem-Val project supported by ESTCP and TPC
  - Scale up to industrial production & move to depots
  - Develop nano Co-P selective plating as repair
  - Develop nano Co-P based TDC alternative

# Industrial Scale up and Technology Transfer to Depots

- **Purchase equipment**
- **Set up equipment at Integran. Qualify**
- **Move to depot**
  - Nano Co-P to JAX
  - Selective plating repair to Ogden
  - Other depots
- **Stakeholders kick off meeting in May**
- **Stakeholders JTP**

# Industrial Scale up and Technology Transfer to Depots

- **Power supply**
  - Integran's specifications
  - Peak current 1500A
  - Average current 500A
  - Pulse timing ( $t_{on}$  and  $t_{off}$ ), 0-100ms,  $\Delta t=0.1ms$

# Industrial Scale up and Technology Transfer to Depots

- **Tank**

- **Dimensions (3'x5'x3') (~1000L)**
- **1" Polypropylene**
- **Separate well to house pump and filter**
- **3/4hp pump**
- **1 $\mu$ m filter**
- **60kw heaters (Ti) digitally controlled`**

# Selective Plating

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

# Selective Plating

- Properties
  - Excellent adhesion
  - High build-up rates
  - Low (or none) H embrittlement
  - No post-machining (precision build-up)
  - No heat distortion
  - High deposit density (no porosity)

# Selective Plating

- Requirements
  - Specially designed power pack,
  - Assortment of working tools (styluses)
  - Accessories and auxiliary equipment to provide solution flow and stylus or part motion

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# Selective Plating

- **Initial work results**
  - **Nano Co-P was produced (proof of concept)**
  - **Surface morphology and hardness**
  - **High density (no pits or porosity)**
  - **Good adhesion**

# Selective Plating

- **Future work**
  - **Anode wrapping material**
  - **Solution concentration**
  - **pH control**
  - **[wt%P] in the deposit as a function of thickness**
  - **Characterization of the structure of the deposit (surface and cross-section for integrity check)**
  - **Deposit surface roughness vs. thickness**
  - **X-Ray Diffraction (crystal structure and grain size)**
  - **Vicker's Microhardness (VHN) vs composition**
  - **Adhesion and ductility tests**

# Properties of TDC

- **Excellent adhesion**
  - No flaking, chipping, spalling or peeling off in ASTM B489-85
- **High hardness**
  - > 850VHN
- **Wear and Friction**
  - Nodular surface – low friction
  - AMS 2438 Spec requires TWI or 2.4 or lower with CS-10 wheels
- **Corrosion**
  - Non-microcracked surface
  - Most specs require 50 hours in ASTM B117
- **Good electroplating precision**
  - Uniform thickness, no excess built-up at edges
  - Low surface roughness

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# Disadvantages of TDC

- **Same health and environmental issues exist for TDC as for Electrolytic Hard Chrome**
- **Process difficult to maintain**
  - **Reliable suppliers difficult to find**
  - **Difficult meeting specifications**

# Nano Co-P for TDC Applications

Nanocrystalline Co-P alloy coatings show promise for TDC Applications:

- **Good adhesion (ASTM B571)**
- **High Hardness**
  - 600-800 VHN As Deposited
  - >1000 VHN Heat Treated
- **Good Tribological Properties**
  - Low Coefficient of Friction
  - Good Sliding Wear (ASTM G99)
- **Excellent Salt Spray Corrosion (ASTM B117)**
  - ASTM B537 ranking >7/10 after 1000hrs for 0.002” thickness

# Focus of Development Efforts

- The thickness of the nano Co-P alloy coatings developed in the SERDP program were much thicker (0.002” – 0.010”) than that required for TDC applications (0.00005” – 0.001”)
- Further development of the nano Co-P process is needed to optimize the properties for TDC thickness range.
- Process development efforts will focus on:
  - **Obtaining a uniform, continuous nodular surface that is free from cracks, spalling, chipping, flaking or other imperfections**
  - **Maximizing the throwing power of the solution**
  - **Maximizing hardness**
  - **Maximizing tribological properties**
  - **Optimizing phosphorus concentration**
  - **Providing a highly reliable solution which requires minimal maintenance**

# Development Plan

- **Process variables**
  - **Solution composition**
  - **Temperature**
  - **Pulse current parameters**
  - **Current density**
  - **Additives**
  - **Additional particles for increased functionality**

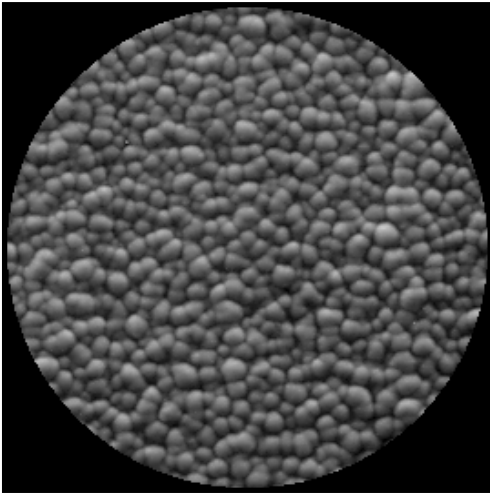
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# Development Plan

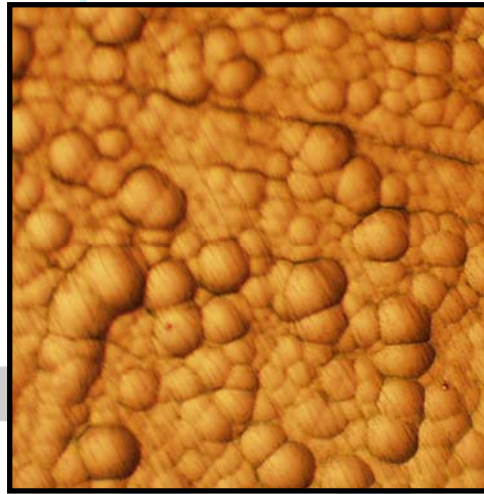
- **Thin nano Co-P within the 2-12% P range**
- **Initial characterization includes**
  - **Surface Morphology (Optical / Scanning Electron Microscopy)**
  - **Thickness uniformity throughout the coating (destructive/metallographic)**
  - **Surface Roughness (Stylus Profilometry)**
  - **Adhesion (ASTM B571 and B489-85)**
  - **Salt Spray Corrosion (ASTM B117)**
  - **Vicker's Microhardness**
  - **Wear**
    - **Pin-on-disk (ASTM G99)**
    - **Taber (CS-10 wheels)**

# Surface Morphology and Hardness

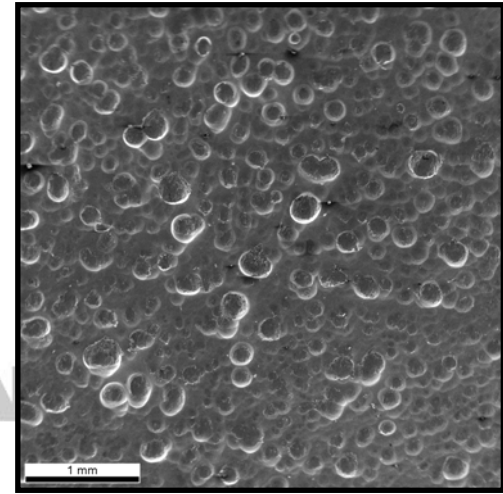
Surface morphology is **nodular** (similar to that of Thin Dense Chrome) and free of pits, pores and/or microcracks. Hardness is close, but needs HT to bring to TDC level.



**Thin Dense Chrome**  
Thickness ~0.0005"  
Hardness >900VHN



**Co 2-3wt% P**  
Thickness ~0.002"  
Hardness ~600-650VHN



**Co 11wt% P**  
Thickness ~0.002"  
Hardness ~700VHN As-Dep  
~1000VHN HT 1hr 300°C

# Other Testing

- **Solution**

- Reliability

- Reproducibility

- Qualification

- **H<sub>2</sub> embrittlement**

- **Fatigue**

