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ELECTRODEPOSITION OF NANOCRYSTALLINE COBALT ALLOY COATINGS AS A HARD CHROME ALTERNATIVE

Ruben A. Prado, CEF
Naval Air Systems Command (FRCSE)
Materials Engineering Laboratory, Code 4.3.4.6
Jacksonville, FL 32212-0016

Diana Facchini, Neil Mahalanobis, Francisco Gonzalez and Gino Palumbo
Integran Technologies, Inc.
1 Meridian Rd.
Toronto, Ontario, Canada
M9W 4Z6

ABSTRACT

Replacement of hard chromium (Cr) plating in aircraft manufacturing activities and maintenance depots is a high priority for the U.S. Department of Defense. Hard Cr plating is a critical process that is used extensively within military aircraft maintenance depots for applying wear and/or corrosion resistant coatings to various aircraft components and for general re-build of worn or corroded parts during repair and overhaul. However, chromium plating baths contain hexavalent chromium, a known carcinogen. Wastes generated from these plating operations must abide by strict EPA emissions standards and OSHA permissible exposure limits (PEL), which have recently been reduced from 52µg/m3 to 5µg/m3. The rule also includes provisions for employee protection such as: preferred methods for controlling exposure, respiratory protection, protective work clothing and equipment, hygiene areas and practices, medical surveillance, hazard communication, and record-keeping. Due to the expected increase in operational costs associated with compliance to the revised rules and the expected increased turnaround times for processing of components, there is increasing pressure to find an environmentally benign alternative to hard chrome. Electrodeposited nanocrystalline cobalt-phosphorus (nCoP) coatings have been developed as an environmental alternative to hard chrome deposits for both line of sight (LOS) and non-line-of-sight (NLOS) applications under the Strategic Environmental Research and Development Program (PP-1152), and are currently going through demonstration-validation testing in a project under the Environmental Security Technology Certification Program (WP-0411). Nanocrystalline Co-P coatings show great potential as an alternative coating to hard chrome plating due to: higher cathode efficiency, higher deposition rates, good sliding wear, and corrosion resistance properties.

Keywords: electrolytic hard chromium plating, carcinogen, hard chrome replacement, nanocrystalline cobalt-phosphorus, corrosion resistance, electrodeposition

INTRODUCTION

Hexavalent chrome plating has been used for decades in decorative and functional applications. Aircraft landing gear, hydraulic actuators, gas turbine engines, helicopter dynamic components and propeller hubs all make use of hard chromium coatings. Safety and environmental concerns surrounding hexavalent chrome plating stem mainly from the carcinogenic nature of vapor emissions produced during the process. Nanocrystalline cobalt-phosphorus (nCoP) has emerged as a viable alternative for both line-of-sight (LOS) and non-line-of-sight (NLOS) applications for several reasons: higher process efficiency with reduced energy consumption, higher deposition rates, large thicknesses deposited, no pitting, microcracks or pores, and lower environmental impact. The material properties reveal that nCoP has high hardness, enhanced ductility, lower wear rates, superior corrosion resistance, and no issues with hydrogen embrittlement after baking. The nCoP coatings are currently going through demonstration-validation testing in a project under the Environmental Security Technology Certification Program (WP-0411).

BACKGROUND

Electroplated engineering hard chromium (EHC) coatings (0.00025” to 0.010” thickness) are used extensively in critical aerospace applications. Utilized primarily for imparting wear resistance and for restoring worn or undersized parts, [1,2], EHC coatings possess intrinsically high hardness (600 – 1000 VHN) and a low coefficient of friction (<0.2) [3]. Hard chrome plating is an electrodeposition process which involves the use of an electrolyte containing chromic acid (CrO3) and sulfate ions operating at a temperature around 120 – 130°F. With the use of lead anodes and a DC power source, deposits are produced by immersing the part in the above electrolyte while making the part cathodic. A typical chromium electroplating setup indicating sources of Cr^{+6} contamination is shown in Figure 1.

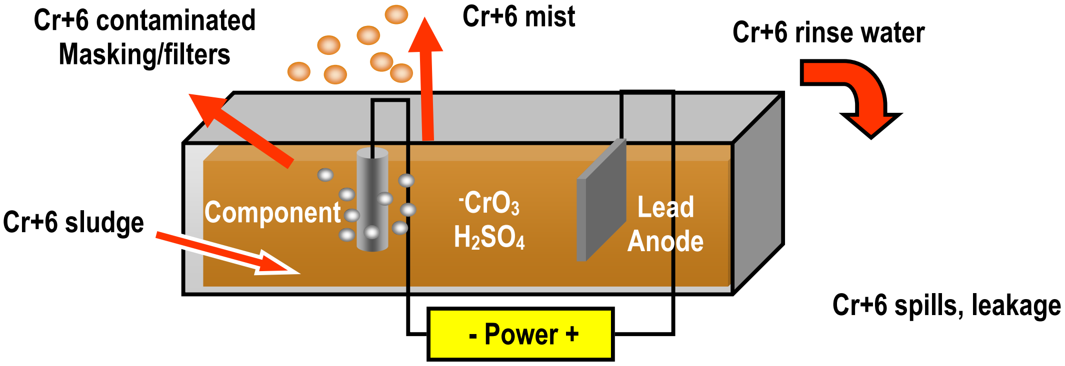


Figure 1: Typical EHC plating bath and sources of hexavalent Cr contamination.

There are two primary uses of hard chromium plating within military applications. One is to provide wear and corrosion resistant coatings on original aircraft parts and components such as hydraulic and pneumatic actuators, landing gears, shaft journals and turbine engine components. The other and most common reason for which hard chromium plating is used within the military is for parts salvaging by reclaiming or rebuilding of worn and/or corroded parts back to their dimensional tolerances. These operations are routinely performed at repair depots and overhaul shops within DoD.

EHC Issues

Health risks posed by electrolytes containing hexavalent chromium (Cr^{6+}) have been well established and recognized since the early 1930s [4]. New legislation by the US Department of Labor’s Occupational Safety and Health Administration (OSHA) reduced the permissible exposure limit (PEL) for Cr^{6+} and all Cr^{6+} containing compounds from 52 μg/m^3 to 5 μg/m^3 as an 8-hour time weighted average [5]. Furthermore, provisions for employee protection such as: preferred methods for controlling exposure, respiratory protection, protective work clothing and equipment, hygiene areas and practices, medical surveillance, hazard communication, and record-keeping are also included in the new legislation. In addition to the above provisions, the Undersecretary of Defense recently released a policy to minimize the use of hexavalent chromium (Cr^{6+}) within DoD weapons systems and platforms due to associated environmental risks[6]. With the anticipated increase of operational costs associated with compliance to the proposed rules and recent DoD policy for maintenance operations, there is increasing pressure felt by the electroplating industry to find an environmentally benign alternative to hard chrome, as many believe these costs will be prohibitive thus resulting in numerous chrome plating shops shutting down or moving overseas.[7]

In addition to the health risks associated with Cr^{6+}, there are several other process and performance drawbacks to EHC coatings. As a result of the relatively low electrolytic efficiency of EHC plating processes, deposition (or build) rates are low compared to the plating of other metals and alloys (e.g., 0.0005”-0.001” per hour for EHC versus > 0.008” per hour for nickel (Ni)) [8]. Moreover, the intrinsic brittleness of EHC deposits (i.e., <0.1% tensile elongation [9]) invariably leads to micro- or macro-cracked deposits. These ‘cracks’, which do not compromise wear and erosion resistance, are wholly unsuitable for applications where corrosion resistance is required. In these applications, an electrodeposited underlayer of more ductile and corrosion resistant material (usually Ni) must be applied [9].

Current Alternatives

The health risks associated with Cr^{6+} have been known for some time, and as such, the chrome plating industry has been investigating potential alternative coatings for many years. Some coating technologies that have been considered as alternatives include: thermal spray [10], plasma vapor deposition [11], and other Cr-free coatings applied by electrolytic or electroless plating techniques [12]. Over the last 10 years, high velocity oxygen-fuel (HVOF) thermally sprayed WC-Co and WC-CoCr coatings have gone through extensive demonstration/validation testing as part of the Hard Chrome Alternatives Team (HCAT) program and have generally been accepted as suitable alternatives for hard Cr within the North American aerospace industry [13] and for other low-volume, high-added-value line-of-sight (LOS) coating applications [14]. For coating applications requiring non-line-of-sight (NLOS) deposition and/or high-volume, low-added-value production, however, it is generally believed that only electroplating technologies will be suitable and/or cost effective. For example, when plating certain internal diameters such as on landing gear components and hydraulic actuators, it is quite difficult to nearly impossible to coat these areas effectively with LOS technologies. Traditionally, most of the electroplated coating alternatives have been based on Ni alloys, including both electroless (Ni-P and Ni-B) and electrolytic (Ni-W, Ni-Co, Ni-Mo, etc) coatings. As Ni is listed by the Environmental Protection Agency (EPA) as a priority pollutant and is considered to be one of the 14 most toxic heavy metals, coatings containing Ni are considered to only represent a short-term solution. It is therefore evident that a non-Ni based electroplating technology would be ideal to provide an environmentally acceptable alternative for both LOS and NLOS applications.

ELECTRODEPOSITION OF NANOCRYSTALLINE MATERIALS

Nanocrystalline cobalt-phosphorus (nCoP) alloy coatings were evaluated under the Strategic Environmental Research and Development Program (SERDP) project #PP-1152 and scaled in the Environmental Security Technology Certification Program (ESTCP) project #WP-0411 as an alternative to hard chromium coatings. These projects showed that nCoP exhibits properties equivalent to (and in many ways better than) EHC. nCoP is an alternative to EHC processes on both LOS and NLOS applications, and can be viewed as part of an overall strategy to replace the currently used EHC processes and eliminate environmental and worker safety issues while significantly improving performance and reducing life-cycle costs.

The electrodeposition process for nCoP exhibits significant improvements over EHC as summarized in Table 1. Like EHC, nCoP is an aqueous bath process produced by electrodeposition. It therefore, represents a drop-in alternative technology that is fully compatible with the current hard chrome electroplating infrastructure, and renders nCoP well-suited for application to both LOS and NLOS surfaces. The nCoP process differs, however, in that it uses pulse plating technology for controlling and building fully dense, nano grain size deposits leading to improved material properties as compared to standard polycrystalline electro-deposited coatings. As the coating is built up, the coating remains fully dense and nanocrystalline in structure. The process uses no constituents on the EPA lists of hazardous materials, nor does it generate hazardous emissions or by-products. Significant reductions in energy consumption and increases in throughput can be achieved with the nCoP process as a result of higher overall plating efficiency (approx. 90% for nCoP compared to less than 35% for EHC). Further, nCoP has a high deposition rate ranging from 0.002” (50µm) to 0.008” (200µm) per hour depending on current density, in contrast to EHC which typically plates at 0.0005”-0.001” per hour.

Table 1
Comparison of nCoP and EHC Processes

	nCoP	**EHC**
Deposition Method	Electrodeposition	Electrodeposition
Applicable Part Geometries	LOS and NLOS	LOS and NLOS
Efficiency	85-95%	15-35%
Deposition Rate	0.002”-0.008” per hour	0.0005”-0.001” per hour
Appearance	Pit/Pore/Crack Free	Microcracked
Microstructure	Nanocrystalline (avg. grain size = 5-15nm)	-
Emission Analysis	Below OSHA limits	Cr^{+6}

MATERIAL PROPERTIES

Surface Morphology and Coating Integrity

Figure 2 (a) is an optical micrograph (500x magnification) of a nCoP coating showing the surface morphology typically observed in nanocrystalline materials. Visually, nCoP coatings are uniformly smooth and shiny, similar to EHC. Microscopically, nCoP has a fully dense structure, free from pits, pores and microcracks as shown in Figure 2(b).

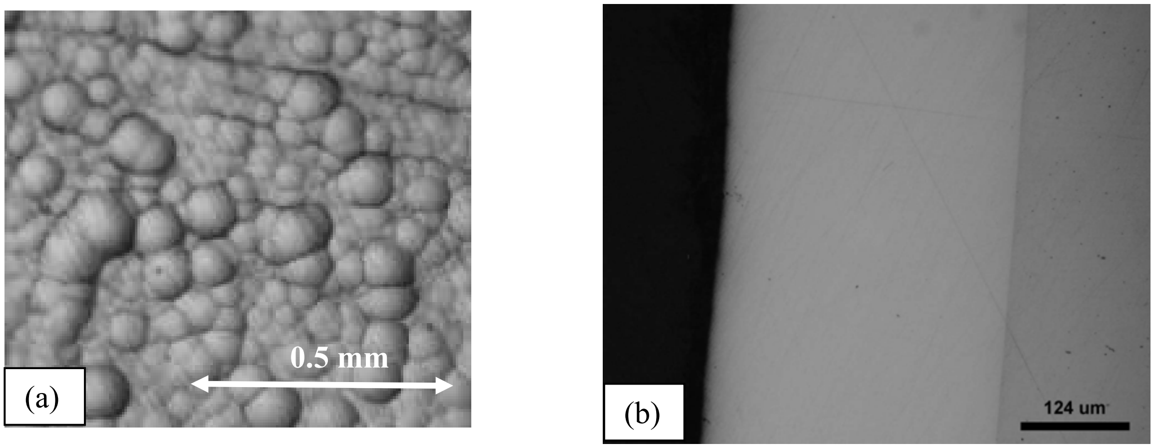


Figure 2: Optical micrographs of nCoP coatings showing (a) the as-deposited surface at 500x magnification and (b) the cross-section.

Nanocrystalline Microstructure

X-Ray diffraction (XRD) analysis was performed on polycrystalline, nanocrystalline and amorphous nCoP coatings as a means of determining the crystal structure, texture and for estimating the average grain size of the material [15]. Figure 3 shows a typical XRD pattern of a nanocrystalline cobalt phosphorous electrodeposit produced under the above SERDP project work. The XRD pattern shows that nCoP exhibits a hexagonal close-packed (HCP) crystal structure which is the equilibrium structure typically found in conventional cobalt at room temperature. Unlike conventional cobalt, however, nCoP exhibits a nanocrystalline microstructure, with an average grain size in the range of 5 to 15nm. An average grain size in this range gave the optimum combination of strength and ductility. Conventional deposits typically have a grain structure ranging from 10 – 100 µm.

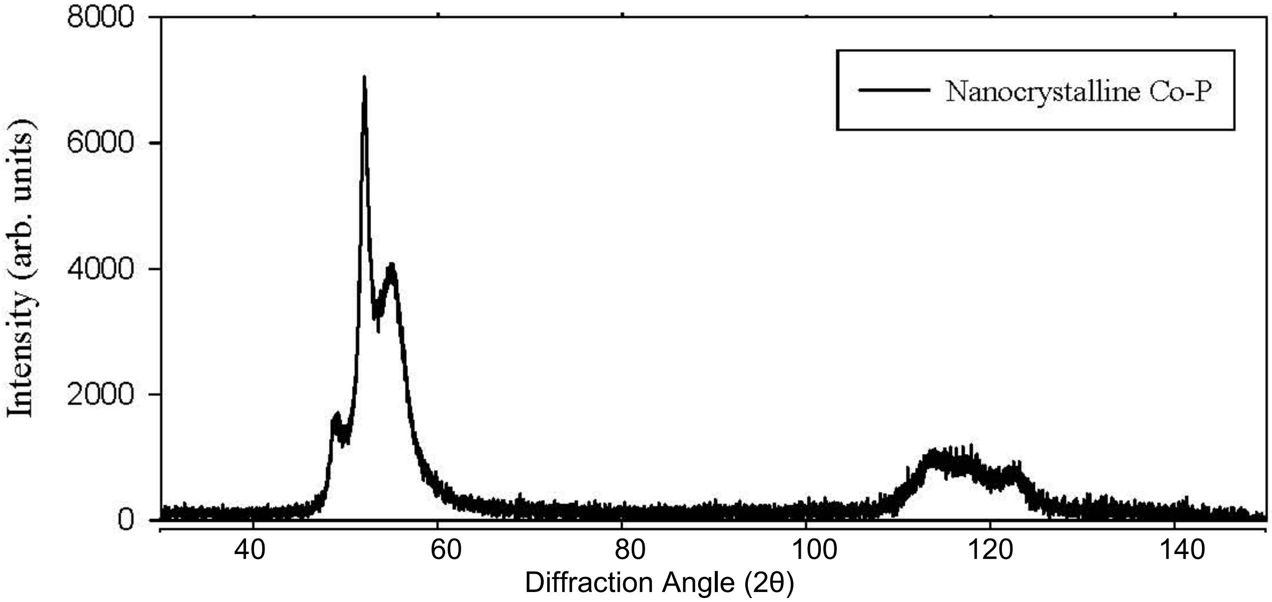


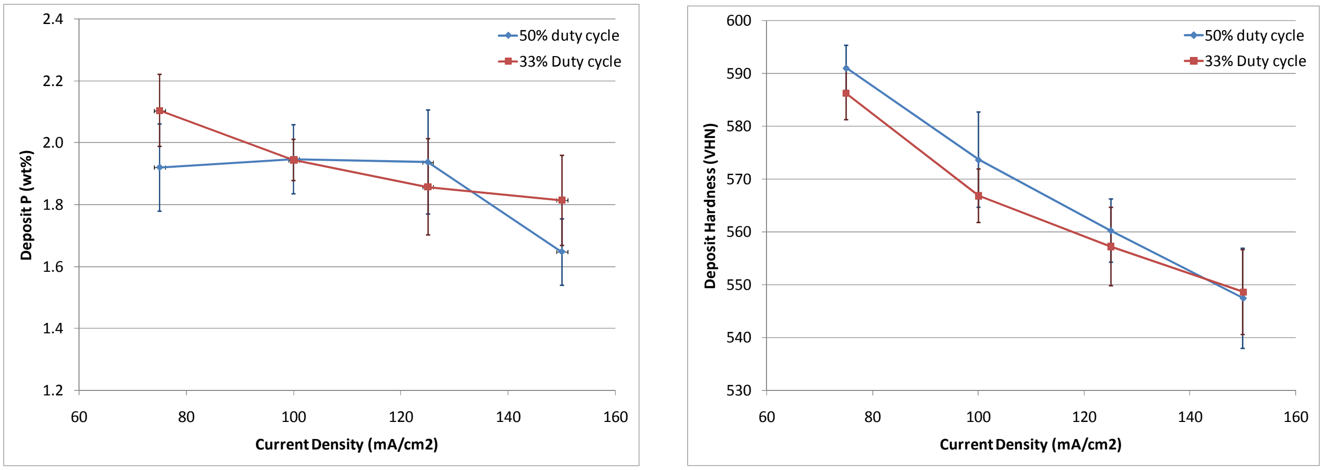
Figure 3: X-Ray diffraction pattern for nanocrystalline cobalt phosphorous electrodeposit

Hardness and Composition

As a result of Hall-Petch strengthening, nanocrystalline alloys like nCoP display significant increases in hardness and strength relative to their coarser grained counterparts due to their ultrafine grain size. Hardness of samples was determined using ASTM E384. Microindentation tests were completed using Clark Microhardness Tester CM-700AT with an applied load of 100g and sample thickness of 0.004”. All samples were prepared using traditional metallurgical techniques.

As-deposited nCoP exhibits a hardness in the range of 530-600 VHN. The phosphorous content in the deposit accounts mainly for the hardness levels achieved. A linear increase in the as-deposited hardness with increasing phosphorous content was shown under the SERDP project. Further evaluation for optimizing the parameters used in applying the coating was also established under ESTCP supplemental testing. Preliminary data shows the effects of operating conditions with deposit hardness (see Figure 4).

Through a precipitation hardening mechanism, a further increase in hardness can be obtained by annealing the as-deposited material to induce the precipitation of Co-phosphides from the supersaturated solid solution at elevated temperatures. The variation in hardness as a function of annealing time at and temperature are shown in Figure 5. Through this short heat treatment process, increases of over 150 VHN can be achieved.



(a) (b)

Figure 4: Effects of operating conditions on deposit phosphorous content (a) and deposit hardness (b).

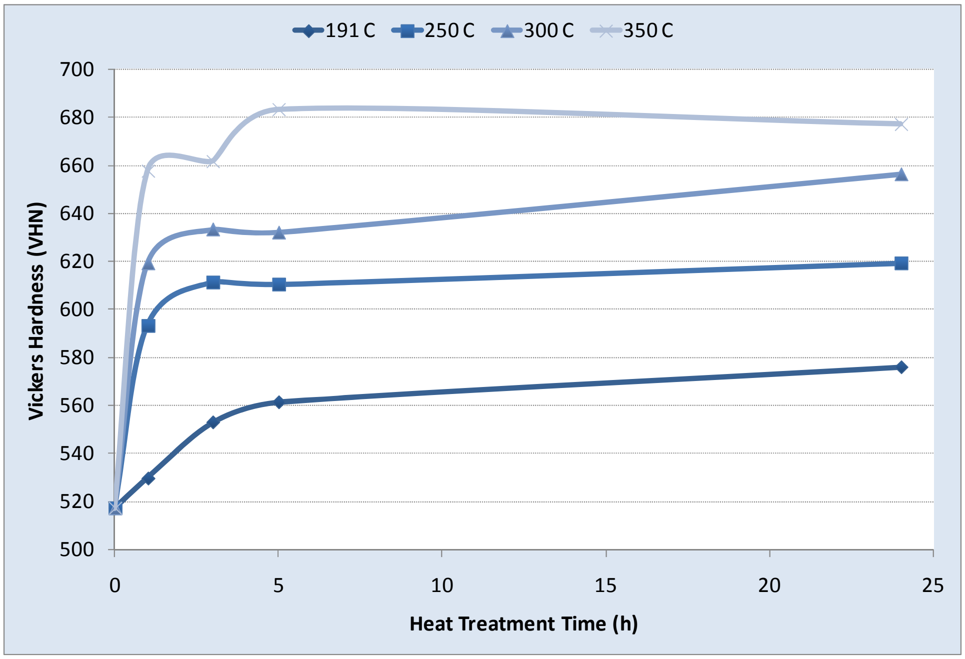


Figure 5: Hardening behavior of nCoP through the application of heat treatments.

Corrosion Resistance

Salt Spray Testing. nCoP has exhibited superior corrosion resistance to EHC. Salt spray corrosion testing was conducted according to the requirements of ASTM B117, "Standard Practice for Operating Salt Spray (fog) Apparatus". nCoP (0.002") or EHC (0.004") deposits were applied to mild steel panels. Exposed areas of the substrate were masked. Coated panels were placed in the salt spray cabinet oriented longitudinally with the plated surface inclined 15° from the vertical, and then exposed to the environment of a salt spray cabinet to determine corrosion resistance after various exposure times.

Panels were rated by comparing them with Figure X2.2 of ASTM B537 (Standard Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure). The Protection Rating refers to crater rusting, pinhole rusting, rust stain, blisters and any other defects that involve basis metal corrosion. Figure 6 shows the ASTM B537 Protection Rating as a function of exposure time for nCoP and EHC. nCoP performed very well, decreasing to only a protection/appearance rating of 8 after 1000 hours exposure time, compared to a rating of less 2 for EHC after the same exposure time [16]. Note that the nCoP coating was 50% thinner than the EHC coating.

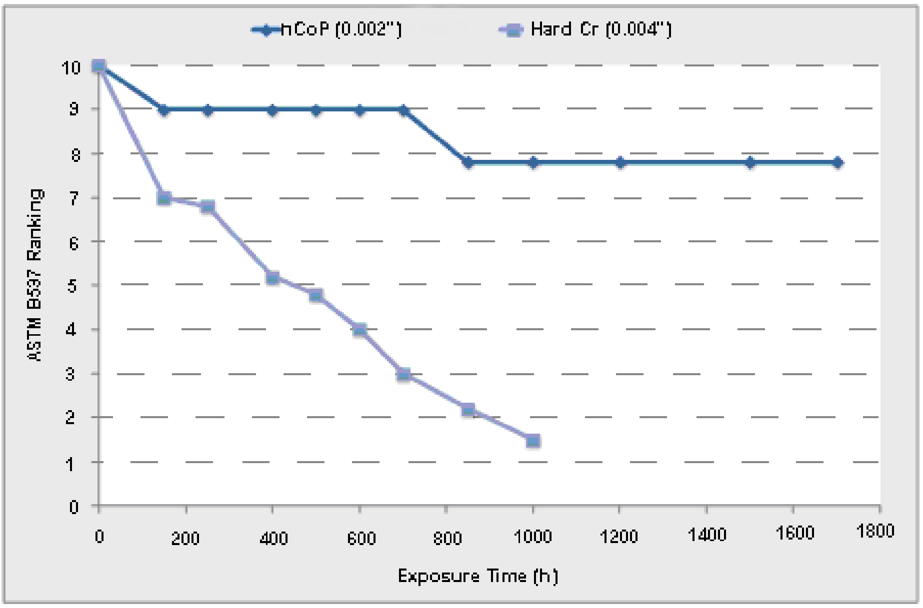


Figure 6: ASTM B537 ranking as a function of exposure time for nCoP and EHC coatings.

Potentiodynamic Polarization Testing. Electrochemical potentiodynamic corrosion testing provides further insight into corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. This test was carried out per ASTM G61 (Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys) where Linear polarization resistance (LPR) scans were used with a 3.56 wt% NaCl solution to determine the difference between polycrystalline Cobalt, electrolytic hard Chrome, as well as nanocrystalline Cobalt and nCoP.

Figure 7 shows the corrosion rate for the various materials tested as a function of test time. Generally the corrosion rate is relatively stable versus testing time. EHC was found to have the lowest corrosion rate of all the materials due to the formation of its stable oxide film (Cr_2O_3). Polycrystalline cobalt had the highest corrosion, at approximately 2 millimeters per year (mpy). It can be seen that a decrease in grain size improves the corrosion resistance of the material (seen from the improvement in corrosion rate of nanocrystalline cobalt over polycrystalline cobalt). Also, the addition of small amounts of phosphorus to nanocrystalline cobalt results in a further decrease in corrosion rate.

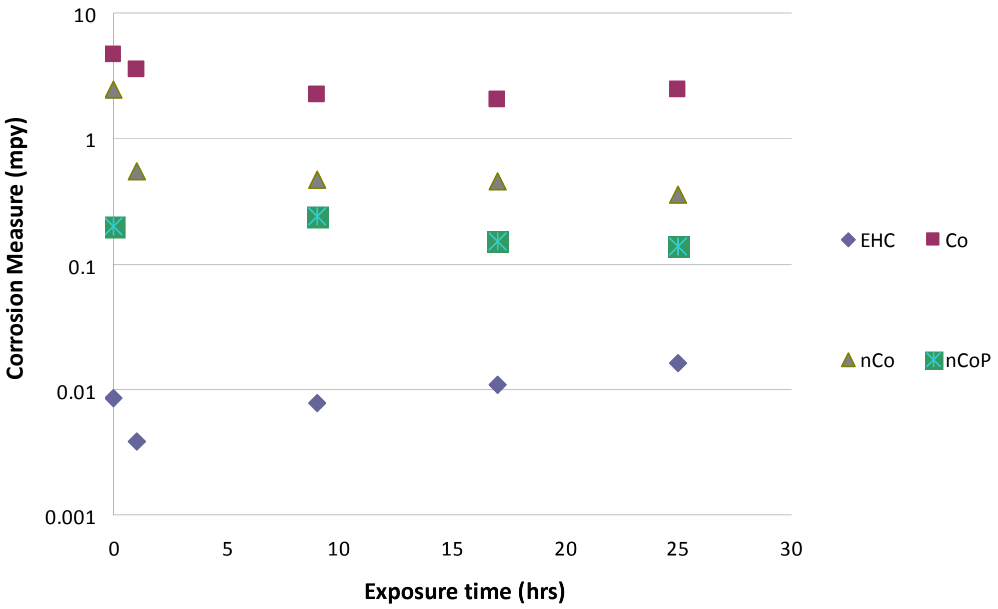


Figure 7: Electrochemical corrosion rate of nCoP, nanocrystalline Co (nCo), polycrystalline Co, and EHC as a function of testing time

Wear Resistance and Lubricity

As shown in Table 3, pin-on-disc sliding wear testing indicates that nCoP exhibits less wear loss than EHC. Further, the wear loss of the mating material is significantly less severe. nCoP has a lower coefficient of friction than EHC, resulting in enhanced lubricity.

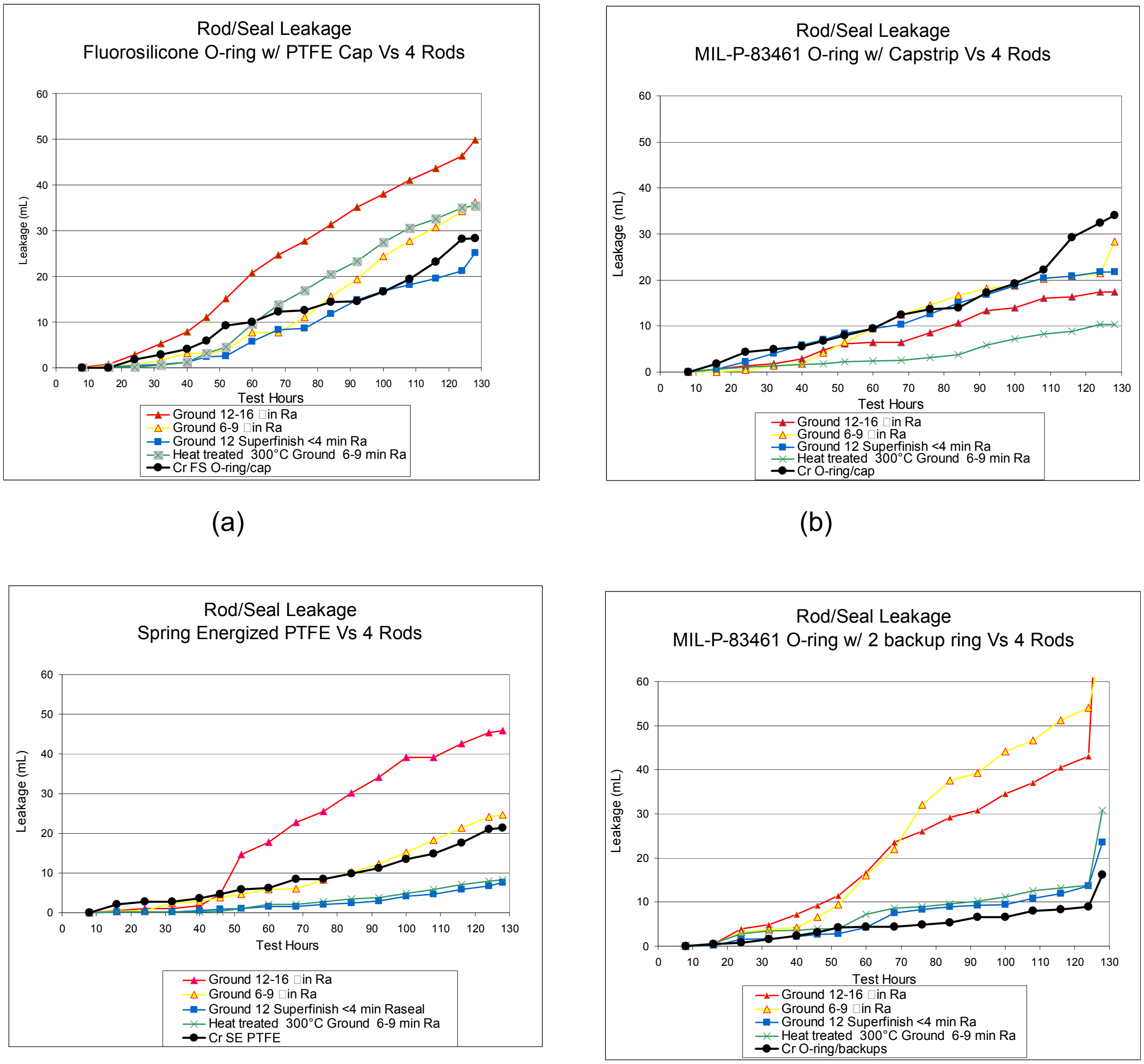
Table 3

Sliding wear properties of nCoP compared to EHC (against Al_2O_3 ball)

	nCoP	**EHC**
Wear volume loss	6-7 x 10^{-6} mm^3/Nm	9-11 x 10^{-6} mm^3/Nm
Coefficient of friction	0.4 - 0.5	0.7
Pin Wear	Mild	Severe

In addition to the above wear test, the Hard Chrome Alternatives Team (HCAT) funded Naval Air Systems Command (NAVAIR) to perform Phase III endurance testing of various seal configurations and a rod coated with nCoP. Previously performed tests included High Velocity Oxygen Fuel (HVOF) coated rods with various seal configurations to evaluate wear resistance and leakage. The objective of the Phase III testing was to compare the wear resistance and leakage of one Nanocrystalline-Cobolt-Phosphorus material with the results from Phase I and II of the above effort.

Each rod was tested for accumulated leakage using four seal configurations; including two cap-strips, one o-ring, and one Polytetrafluoroethylene (PTFE) metal spring energized seal. Figure 8 shows preliminary data obtained from this study as compared to EHC baseline deposits. Test showed nCoP deposits comparable to EHC. Like HVOF coatings in previous HCAT studies, lowest leakages were seen with surfaces superfinished to <4 micro inches and spring energized PTFE seals.



(a) (b)

(c) (d)

Figure 8: Accumulated leakage of: (a) Fluorosilicone O-ring w/ PTFE Cap, (b) MIL-P-83461 O-ring w/ Capstrip, (c) Spring Energized PTFE , and (d) MIL-P-83461 O-ring w/ 2 backup rings

Hydrogen Embrittlement

The high plating efficiency of the nCoP process leads to significantly less hydrogen generation at the cathode compared to EHC processes, thus minimizing the likelihood of hydrogen uptake and subsequent embrittlement of susceptible materials (i.e., high-strength steels). Hydrogen embrittlement tests conducted in accordance with ASTM F519 indicate that the standard hydrogen embrittlement relief baking procedures for EHC can be applied to the nCoP to fully eliminate the risk of embrittlement.

DEMONSTRATION/VALIDATION

Industrial Scale-up and Technology Demonstration at FRC Jacksonville

Scale up and demonstration/validation of the nCoP technology is currently being performed at the Fleet Readiness Center (FRC) in Jacksonville as part of a project under the Environmental Security Technology Certification Program (WP-0411).

An existing process tank at FRC Jacksonville (see Figure 9) was modified for demonstrating & validating the new Nanocrystalline Co-P plating process. The 250 gal tank was equipped with new busbars/electrical cables, new tank liner (constructed of 0.125" thick Modified Vinyl based Terpolymer), a ¾ hp in-tank filter pump with 3 micron size filters and educator system for solution agitation. For heating and maintaining the bath to its operating temperature of around 185°F, a Poly Vinylidene Fluoride (PVDF) steam coil with new steam lines and temperature regulator was installed. Titanium anode (auxiliary) baskets sleeved with anode bags, holding soluble electrolytic cobalt pieces, were used as the anodes. Once the chemistry was built and adjusted, it was not long before coupons and select demo components were successfully coated.

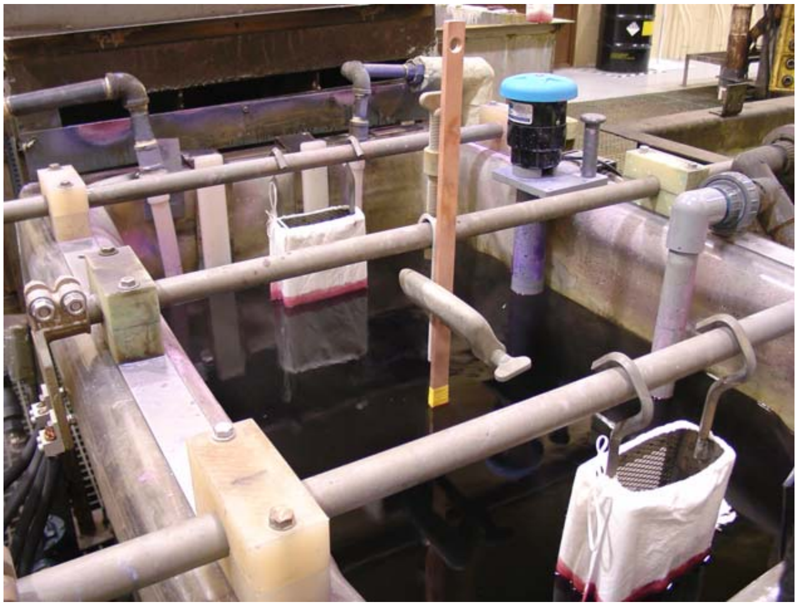


Figure 9: 250 gallon nCoP dem/val plating tank at FRC-SE

The plating process works similarly to that of many electrodeposition processes in that parts still go through a cleaning and an activation process to ensure optimal conditions for plating. The difference is in the plating step itself. All present-day depot (and most commercial) electroplating uses direct current (DC) between the cathode and anode to build the coating. The nCoP technology uses pulse plating to control the nucleation and growth of the coating material and create a nanocrystalline grain structure. Pulse control allows the optimal ratio of grain nucleation and growth, which determines the final grain size of the material. The pulse plating process is achieved by the use of a high capacity pulse plating power supply designed and built to deliver 1500 Amp peak and 500 Amp average current (see Figure 10) using a particular set of pulse conditions. Figure 11 shows a wall mounted remote controller that is used to control the power supply or rectifier for delivering the proper current and pulse conditions to the process tank/work load.

Figure 10: Pulse Power Supply

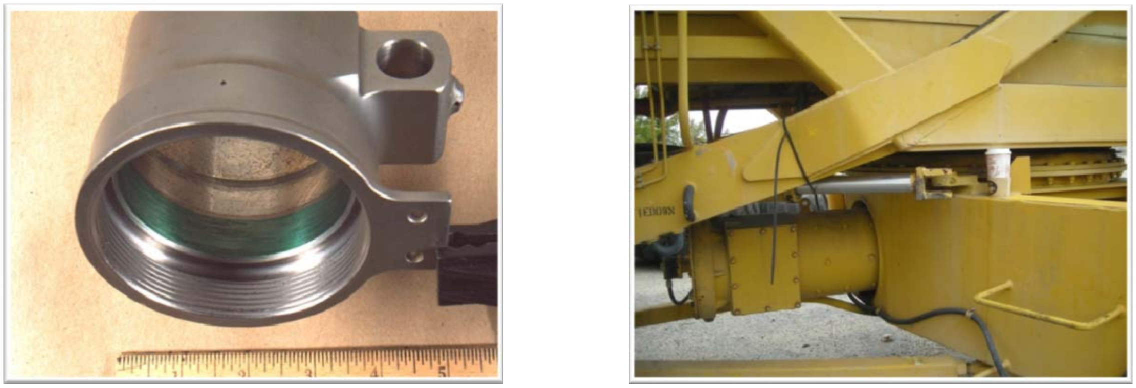
Figure 11: Remote Controller

To date, process validation is underway at FRC Jacksonville. A large portion of the validation and producibility testing will involve electrodeposition of various material substrates and components with different sizes and complex geometries to better understand the capabilities and limitations of the technology. Much of this focus will include looking at best configuration for anodes, the use of thieves, masking/demaksing, activation and plating of different alloys, non-destructive testing, coating thickness uniformity and appearance, grinding, and plating bath stability just to mention a few. Initial coupon trials have already been conducted on flat plates and internal diameter (ID) surfaces (see Figure 12).

Component plating trials have also been initiated (see Figure 13) for demonstrating ID plating of areas where HVOF deposits are difficult to apply. Plating of ID journals was demonstrated by using cobalt plated titanium anode rods as well as titanium basket anodes filled with cobalt pieces. Additional proposed classes of demo components include a P-3 MLG Actuating Cylinder ID Section and Crash Crane Hydraulic cylinder (see Figure 14). In addition to aircraft components chosen from workloads at FRC Jacksonville, ground support equipment (GSE) chosen from NAVAIR Lakehurst will be targeted since these are non safety-critical and will facilitate a more rapid technology transition.

Figure 12: Coupon trials (flat plates and IDs) for process validation

Figure 13: Component plating trials for process validation



(a) (b)

Figure 14: Proposed classes of demo components: (a) P-3 MLG Actuating Cylinder Section and (b) Crash Crane Hydraulic Cylinder

CONCLUSIONS

Due to the health concerns and costs associated with complying with federal regulations regarding exposure to Cr^{6+}, there is a large driving force to find an alternative to EHC coatings. An electrodeposited nanocrystalline cobalt-based (nCoP) coating, in addition to being fully compatible with current hard chromium plating infrastructure, has displayed properties that may render it a superior alternative to EHC. Such properties include: higher cathode efficiency, higher deposition rates, high hardness and superior sliding wear and corrosion resistance. nCoP is currently being demonstrated and validated for military use as an EHC alternative at FRC-SE. Upon successful evaluation and field testing obtained from this program, the above technology will be considered for transition across all navy sites. NAVAIR Lakehurst ground support equipment and certain non safety critical NAVSEA Systems will be considered first for technology transition due to lower risk implementation issues.

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