Nanocrystalline Cobalt-Alloy Coatings for Non-Line-of-Sight Chrome Replacement Applications

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Electrodeposited nanocrystalline cobalt-alloy coatings have recently been developed as part of a U.S. Department of Defense pollution prevention program seeking an environmentally benign alternative to hard chrome for Non-Line-of-Sight (NLOS) applications. This paper, summarizes the process and properties of various nanocrystalline cobalt-alloy coatings in comparison to hard chrome, and outlines the broad areas of application for the various coatings. A brief review of the ongoing demonstration/validation program for the nanocrystalline coating currently being carried out at the Naval Ammunitions Depot (NADEP) in Jacksonville, Florida is also be presented.

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INTRODUCTION

As a result of its toxicity, exposure levels of chromate ions have been limited. The US Department of Labor's Occupational Safety and Health Administration (OSHA) recently reduced the permissible exposure limit (PEL) for hexavalent Cr and all hexavalent Cr compounds from 52μg/m^3 to 5μg/m^3 as an 8-hour time weighted average [[1]]. In addition to the reduction in the hexavalent Cr PEL, 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 proposed rule, there is tremendous 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.

The health risks associated with hexavalent Cr 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[2], plasma vapor deposition[2,3], and other Cr-free coatings applied by electrolytic or electroless plating techniques[4,5]. 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[6] and for other low-volume, high-added-value line-of-sight coating applications[2,7]. For coating applications requiring non-line-of-sight 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. 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 non-line-of-sight applications.

Over the last 7 years, electrodeposited nanocrystalline cobalt-phosphorus (nCoP) coatings have been developed as an alternative to hard chrome coatings for non-line-of-sight applications under the Department of Defense Strategic Environmental Research and Development Program (SERDP), and are currently going through demonstration-validation testing in a project under the

Environmental Security Technology Certification Program (ESTCP). In this paper, a general overview of nanocrystalline materials will be presented with particular emphasis on reviewing the process and properties of nCoP coatings as they pertain to hard Cr replacement. An overview of the ongoing ESTCP demonstration/validation testing will also be presented.

ELECTRODEPOSITED NANOSTRUCTURED MATERIALS

Nanotechnology is an exciting new field, which deals with the design of extremely small structures having critical length dimensions on the order of a few nanometers. One particular aspect of nanotechnology deals with nanostructured materials, i.e., materials with an ultra-fine average grain size (usually less than 100 nm), which were initially introduced as interfacial materials about two decades ago[8]. The main structural characteristic of these materials is the enhanced volume fraction of their interface component (the volume fraction of atoms associated with grain boundaries and triple junctions), which becomes significant when the average grain size decreases below 100 nm. As a result of having such a large fraction of atoms located at the interfacial defect structure, nanocrystalline materials show considerable changes in many mechanical, physical and chemical properties.

There are numerous early reports in the literature describing electrodeposits with ultra-fine structures[9]. The first systematic studies on the synthesis of nanocrystalline materials by electrodeposition, in an attempt to optimize certain properties by deliberately controlling the volume fractions of grain boundaries and triple junctions in the material, however, were only published in the late 1980's[10,11]. Since then, several different nanocrystalline alloys have been produced by electrodeposition, including pure metals (e.g., Ni[12,13], Co[14,15], Pd[16], Cu[14]), binary alloys (e.g., Ni-P[10,11], Ni-Fe[17,18,19], Zn-Ni[20,21,22], Pd-Fe[23], Co-W[24]) and ternary alloys (e.g., Ni-Fe-Cr[25,26,27]).

General Properties of Nanostructures

A critical assessment of the properties measured to date on electrodeposited nanocrystals indicated that the properties can be classified into two categories: (i) those that are strongly dependent on grain size and (ii) those that are relatively unaffected by grain-size. A detailed review of these properties is given in a recent publication[28]. Properties that have been found to vary with grain size include: strength, ductility, hardness, wear resistance and coefficient of friction, electrical resistivity, coercivity, hydrogen solubility and diffusivity, resistance to localized corrosion and intergranular stress corrosion cracking and thermal stability. Properties that have been found to be relatively unaffected by grain-size reduction to the nanocrystalline state include: bulk density, thermal expansion, Young's modulus, resistance to salt spray environment, and saturation magnetization.

With the structure-property relationships for many nanocrystalline materials well defined, the main objective of the current study was to "engineer" the microstructure of electrodeposited Co-P coatings to optimize the relevant properties such that the performance of the coating met or exceeded that of hard Cr. In the following sections a review of the optimized process and properties of the nCoP coating will be presented and compared to hard Cr.

ELECTRODEPOSITION OF NANOCRYSTALLINE COBALT PHOSPHORUS

Process

Nanocrystalline Co-P electrodeposits, developed during the course this program, were produced from a plating solution containing: Co ions, Cl ions, a buffer, and a source of P. Electrodeposition parameters (e.g. bath composition, pH, temperature, overpotential, bath additives, etc.) were modified to optimize the microstructure of the coating for property enhancement (hardness, wear and corrosion resistance, etc). The overall plating efficiency of the process is approximately 90%, with a deposition rate ranging from 50μm (0.002") to 200μm (0.008") per hour, depending on current density. Both consumable and non-consumable anodes can be used for the deposition process, allowing for easy application to internal diameter surfaces.

Electroplating solution control and maintenance is similar to that required for Ni-plating solutions. Ongoing maintenance procedures should include filtration and monitoring various solution parameters such as: pH, surface tension, and solution density. Filtration is required to control the presence of particles in the bath that can lead to surface imperfections in the coating. Monitoring the pH is essential in order to maintain deposit uniformity. Periodic maintenance procedures that may be necessary include activated carbon treatment/filtration and dummying. Activated carbon treatment/filtration will remove any organic impurities that may have accrued during the life of the bath that may be detrimental to the deposition process. Dummying (low current density plating) may be required to remove various metallic impurities in the plating solution (eg. Cu, Sn).

Structure

Figure 1(a) is an optical micrograph of a Co 2-3wt%P coating showing the "cauliflower" surface morphology typically observed in electrodeposited nanocrystalline materials. It should be noted that each "bump" in the structure is not a grain but rather a collection of thousands of much smaller grains. From this image it is also clear that no pits, pores or microcracks are present in the coating. Figure 1(b) shows a cross-section of a Co 2-3wt%P coating on the ID of a 25 mm (1 in.) diameter pipe, showing a 330µm (0.013") thick coating free of pores and/or cracks with a relatively smooth coating.

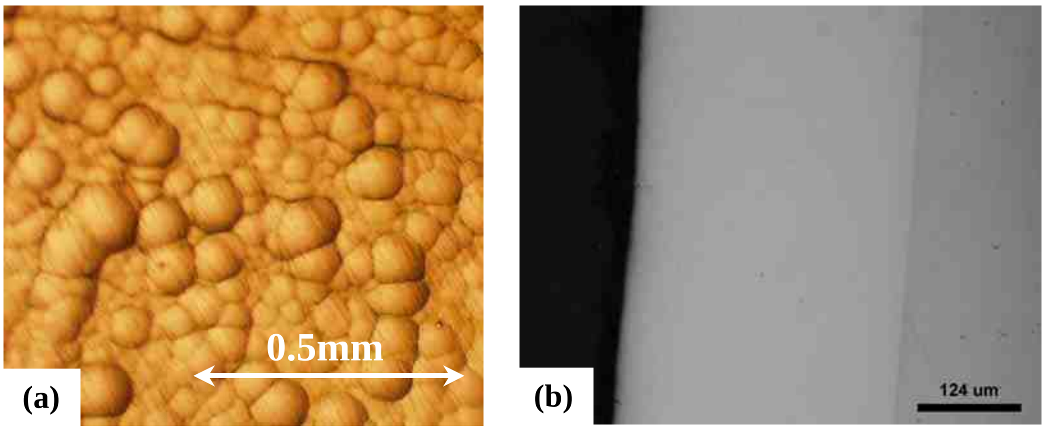

Figure 1 *Optical micrographs of Nanocrystalline Co 2-3wt%P coatings showing (a) the as-deposited surface and (b) the cross-section of a 330µm (0.013") thick coating on the ID of a 25 mm (1 in.) diameter pipe.*

Figure 2 shows typical x-ray diffraction patterns (XRD) of polycrystalline, nanocrystalline and amorphous Co-P deposits that have been produced in this project. The XRD patterns show that the crystal structure is hexagonal close packed (HCP) which is the equilibrium structure typically found in conventional cobalt at room temperature. Through pulse plating and modifications to the bath chemistry a nanocrystalline structure can be consistently obtained in the composition range from 0 to 6-wt% P. Above 6-wt% P an amorphous structure is typically observed. The average grain size of the optimized Co-P coatings was typically in the range of 5 to 15nm. An average grain size in this range gave the optimum combination of strength and ductility. For example, decreasing the grain size below 5nm results in significantly decreased ductility with no increase in hardness due to a breakdown in the Hall-Petch strengthening mechanism. Increasing the grain size above 15 nm results in a decrease in hardness.

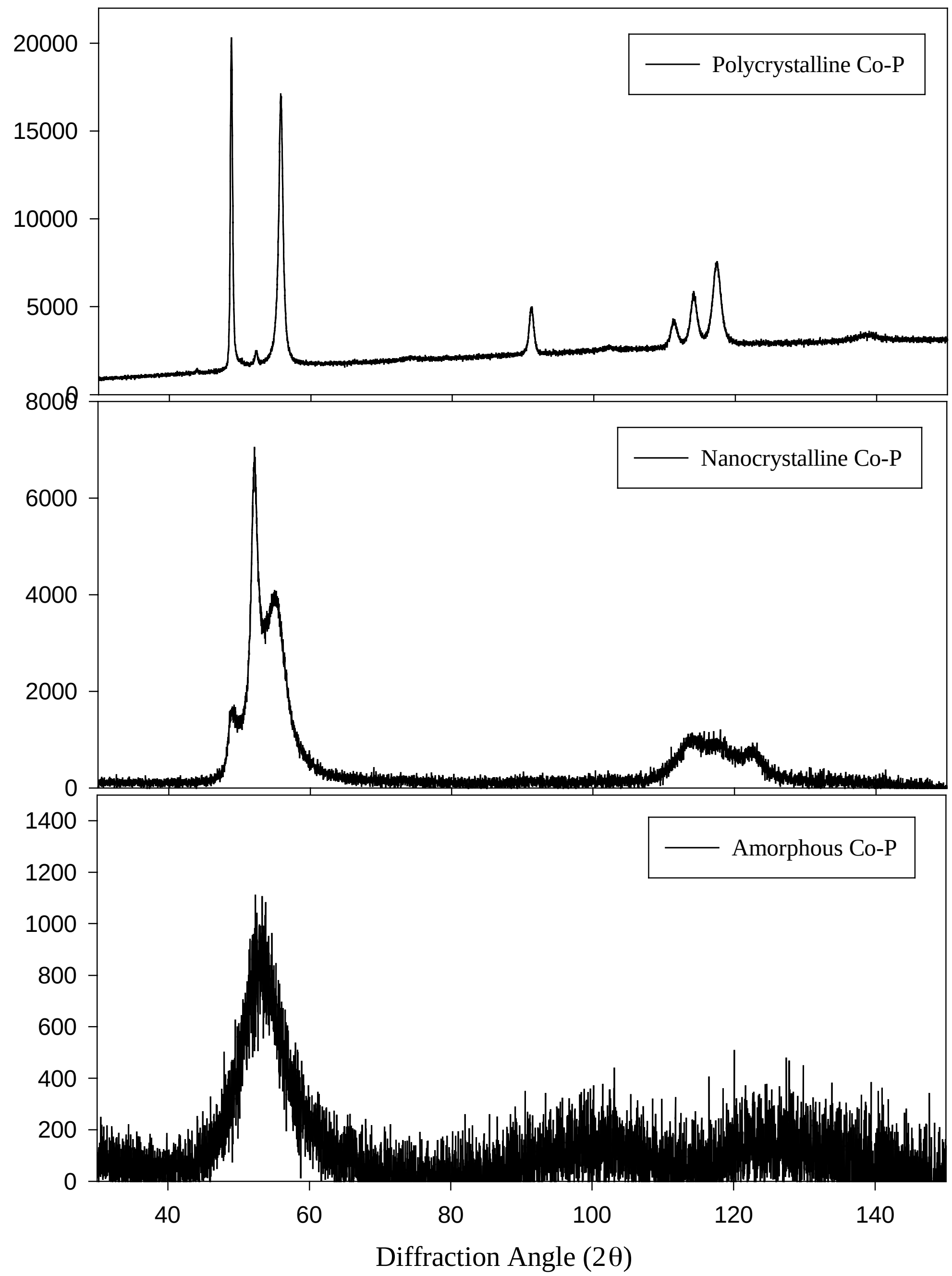

Figure 2 *X-Ray diffraction patterns for polycrystalline, nanocrystalline and amorphous Co-P electrodeposits*

Properties

Vickers Hardness

As a result of Hall-Petch strengthening, nanocrystalline Co alloys display significant increases in hardness and strength relative to their coarser grained counterparts due to their ultrafine grain size. Through a solid solution hardening mechanism, a further increase in hardness can be achieved by alloying with P. This effect is demonstrated in Figure 3, which shows a linear increase in the as-deposited hardness with increasing P content.

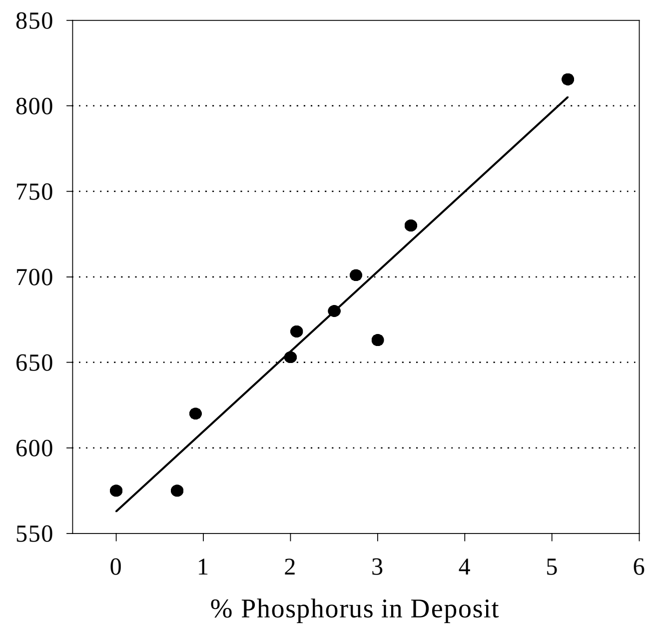

Figure 3 *Effect of phosphorus concentration on the hardness of nCoP deposits.*

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 400°C (750°F) is shown in Figure 4 for Co-P deposits with different P concentrations. Through this short heat treatment process, the additional increase in hardness brings it close to the upper limit of hard Cr. A similar trend has also been observed for electrodeposited nanocrystalline Ni-P alloys[29].

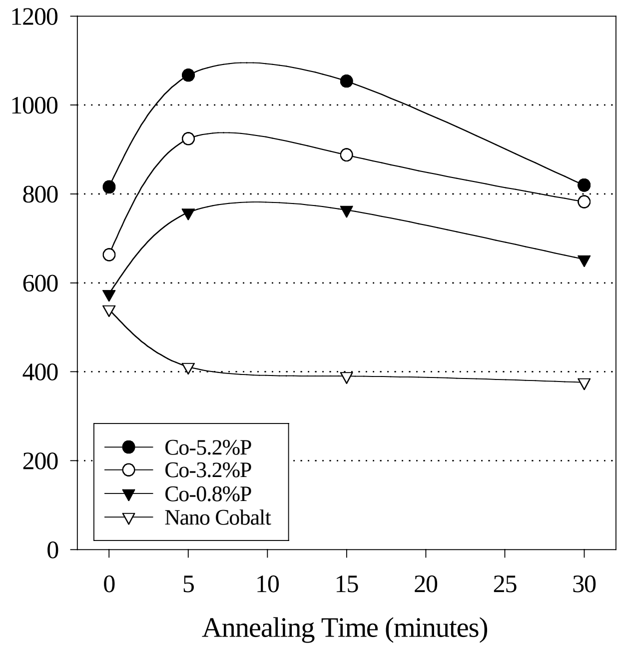

Figure 4 *Effect of annealing time on the hardness of nCoP deposits annealed at 400°C (750°F).*

Wear Resistance

Sliding wear measurements were performed on various standard and nanocrystalline materials in accordance with the ASTM G99 Standard (Standard Test Method for Wear Testing with a Pin-on-Disk Apparatus). Table 1 shows the hardness and sliding wear data for the various materials tested. In general, the sliding wear volume losses for the nanocrystalline alloys were found to be lower than the reference materials, including mild steel, tool steel and hard chrome. A significant drop in wear rate was observed with the addition of 2-wt% P to pure Co sample, but little improvement was seen after 2-wt%, even though the composition of P in the test samples varied from 2 and 6-wt%. A nanocrystalline Co~4-wt%P was tested after hardening by a heat treatment at 400°C for 10 minutes, and although the hardness increased by 35%, no significant improvement in the wear resistance was observed.

Table 1 *Hardness and sliding wear data for various standard and nanocrystalline materials.*

Material	***Hardness (VHN)***	***Coefficient of Friction***	***Wear Volume Loss (mm^3/Nm) x 10^{-6}***
Standard Samples			
Mild Steel	150	0.73	18.2
Tool Steel	250	0.75	13.1
Hard Cr	1200	0.70	11.9
Nanocrystalline Samples			
Nano Co	500	0.35	10.7
Nano Co~2%P	730	0.53	5.5
Nano Co~4%P	745	0.48	6.4
Nano Co~4%P (HT)	1010	0.44	5.3
Nano Co~6%P	730	0.45	7.1

Corrosion Resistance

Nanocrystalline Co-P deposits (50 μm (0.002") thick) were electroplated onto mild steel test panels and exposed to the environment of a salt spray cabinet operated according to the requirements of ASTM B117-97, "Standard Practice for Operating Salt Spray (fog) Apparatus". Figure 5 shows the ASTM B537 protection rating as a function of exposure time for nCoP and for other hardfacing materials after being exposed to a salt spray environment for up to 1000 hours. The nCoP test samples performed very well, decreasing to only a protection/appearance rating of 8 after 1000 hours exposure time, compared to ratings of less than 5 for HVOF WC-Co and Tribaloy 400 and less than 2 for hard Cr after the same exposure time.

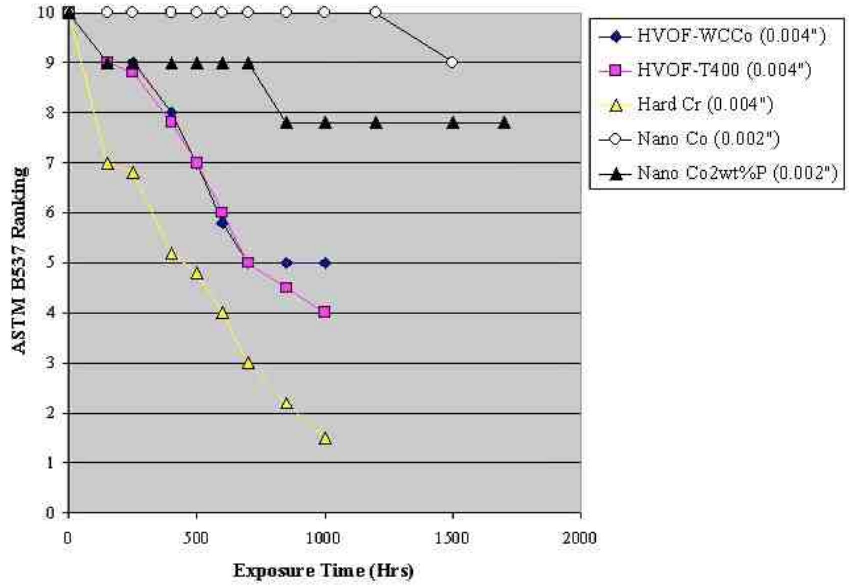

Figure 5 *ASTM B537 ranking as a function of exposure time for various nanocrystalline cobalt-alloy coatings along with Hard Cr and HVOF coatings*

Tables 2 and 3 summarize the process and properties, respectively, of nCoP in comparison to those of hard chrome.

Table 2 Nanocrystalline cobalt-phosphorus process summary compared with that of hard chrome.

PROCESS DATA SUMMARY		
	Nanocrystalline Co-P Alloy	**Hard Chrome**
Bath Chemistry	Co 2-3wt%P (Co^{2+})	Cr ($CrO3$ / SO_4^{2-})
Efficiency	85-95%	15-35%
Deposition Rate	Up to 200µm (0.008") per hour	Up to 40µm (0.0016") per hour
Thickness	Demonstrated up to 1000µm (0.040")	Typically <500µm (0.020")
As-Deposited Appearance	Pit / Pore Free	Microcracked
Microstructure	Nanocrystalline (avg. grain size=8-15nm)	-
Relative Process Cost	Comparable	-
Emission Analysis	Below OSHA limits	Cr^{+6}

Table 3 *Nanocrystalline cobalt-phosphorus property summary compared with that of hard chrome.*

PROPERTY DATA SUMMARY			
		Nanocrystalline Co-P	**Hard Chrome**
Hardness	*As-Deposited*	600-700 VHN	800-1200 VHN
	HT @ 250°C*	700-800 VHN	-
	*HT** @ 400°C*	1000-1200 VHN	-
Ductility		2-7% Elongation	<0.1%
Thermal Stability		400°C	-
Wear	*Abrasive (Taber)*	18 mg/1000cycles (CS-17)	3.2 mg/1000cycles (CS-17)
		11 mg/1000cycles (CS-10)	1.0 mg/1000cycles (CS-10)
	Adhesive (Pin-on-disk)	5-6 x 10^{-6} mm^3/Nm (Alumina ball on nCo-P disk)	9-11 x 10^{-6} mm^3/Nm (Alumina ball on Cr disk)
Corrosion	*Salt Spray*	Protection Rating 7 @ 1000 hours	Protection Rating 2 @ 1000 hours
Internal Stress		10-15 ksi (Tensile)	Cracked – Exceeds cohesive strength

*Heat treated for 3 hours
**Heat treated for 10 minutes

DEMONSTRATION VALIDATION TESTING (ESTCP PROGRAM)

Industrial Scale-Up

The main objective of the on-going ESTCP program is to demonstrate and validate the nCoP deposition process on an industrial/production scale. The demonstration sites for the project are Integran Technologies Inc. in Toronto Ontario and the Naval Aviation Depot in Jacksonville, Florida (NADEP-JAX). A 1200 L (~300 gal) nCo-P-plating tank has been installed at Integran and a 1500 L (~400 gal) plating tank (previously used for hard Cr plating) has been retrofitted at NADEP-JAX for nC-P plating. Figures 6 and 7 show pictures of the plating tanks installed at Integran and NADEP-JAX, respectively. Experiments have been performed to validate that the process works on the larger scale. The optimal operating conditions have been determined and were found to be very similar to those used during laboratory scale testing.

Figure 6 *1200 L (~300 gal) nCoP Plating tank installed at Integran Technologies.*

Figure 7 *1500 L (~400 gal) nCoP Plating tank installed at NADEP-JAX.*

As the process uses pulse plating, a high capacity pulse plating power supply was designed and built to the specifications required for deposition. The output capacity of the power supply was determined based on current requirements needed for the largest parts that NADEP-JAX intends to coat with, namely the P3 nose landing gear cylinder. A pulsed power supply capable of supplying a 1500 Amp peak and 500 Amp average current was acquired. As high capacity pulse power supplies are relatively uncommon, it was subjected to thorough testing to ensure adequate performance.

Selective Plating Repair Technology

The development of the nCoP process for selective (Brush) plating is also being performed as part of this project. Brush plating is commonly used for field-level repair since it permits repairs to be made without stripping and recoating the entire part, but it has not often been used for Air Force landing gear. nCoP brush plating is an option for field repair of chips on hard Cr coatings on landing gear, eliminating the cost of removing the gear and sending it for repair (also, of course, eliminating the waste streams associated with chrome stripping and replating). Through modifications to the conventional nCoP tank bath chemistry, the brush plating process has been used to deposit high quality nCoP deposits with current efficiencies as high as 90% and deposition rates as high as 450µm/hr (~0.018"/hr), using standard brush plating equipment. Figure 8 shows a cross-section of a relatively thick nCoP coating on a mild steel substrate applied by brush plating.

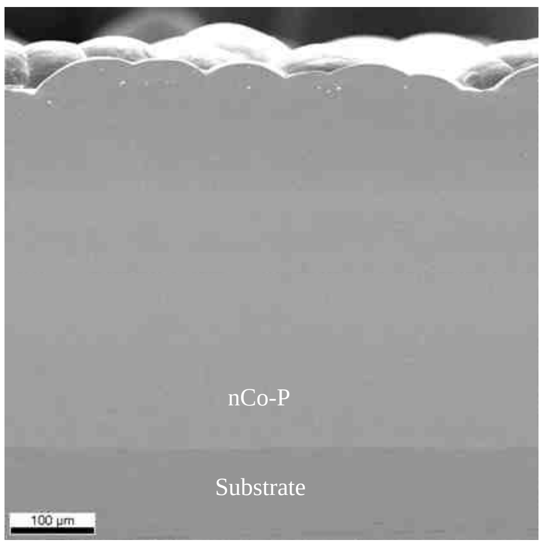

Figure 8 *Cross-section of a nCoP coating on a mild steel substrate applied by brush plating.*

Performance Testing

With input from many stakeholders, a Joint Test-Protocol has been drafted which specifies the specific substrates of interest and the main performance tests that are relevant for hard chrome coatings within the aerospace sector. The main substrates of interest are: 4340, PH15-5, Aermet 100 and 7075 Al. The main performance tests scheduled to be performed on tank plated and brush plated nCoP coatings, alongside hard Cr for comparison, include: axial fatigue (ASTM

E466-96), corrosion (ASTM B117), fluid immersion, hydrogen embrittlement (ASTM F519) and rod-seal. Testing is in progress, however the following preliminary results are available.

Fluid Immersion

The thirty-four 1” diameter, 4340 disks were plated with 0.003” nCo-P and were submerged in various fluids at different temperatures and for different times to simulate service conditions and overhaul fluids. Two samples were immersed in each fluid. The specimens were weighed before and after immersion. The appearance of each specimen subsequent to immersion was compared to that obtained prior to immersion.

The results of fluid immersion testing are summarized in Figure 4. In most cases, the fluids exhibited a slight or moderate effect on the nCoP coating, in the form of mild discoloration or weight change. However, bleach and 35% nitric acid were found to cause significant degradation of the nCoP coating.

Figure 4 Effects of various service and overhaul fluids on nCo-P

Fluid	***Purpose***	***Fluid Temp. (^oC)***	***Time (hr)***	***Result****
MIL-PRF-83282	Hydraulic	70	500	1
Skydrol AS1241 Type 4	Hydraulic	70	500	1
Fluorescent penetrant	NDI	Standard	1	1
Propylene glycol	De-icer	20	1	1
Nital	Grind burn etch	Standard	0.1	1
Ammonium persulfate	Grind burn etch	standard	0.1	2
MIL-C-87937	Cleaning	50	6	1
Oakite 90	Cleaning	50	6	2
Cimstar 40	Grinding fluid	20	6	2
Cee-Bee J-84A	Heavy duty soak clean	50	6	1
Turco Vitro-Klene	Heavy duty soak clean	50	6	2
Turco ScalGon	Descaling	50	6	2
Bleach				3
Cd plating solution		standard	1	2
35% Nitric acid	15-5 passivation	Per AMS QQ-P-35	1	3
Sodium hydroxide	Cr strip	standard	1	2

* 1 – little to no effect; 2 – mild to moderate effect; 3 – significant effect

SUMMARY

Due to the health concerns and costs associated with complying with federal regulations regarding exposure to hexavalent Cr, there is a large driving force to find an alternative to it. Nanocrystalline Co-P coatings show great potential as an alternative coating to hard chrome for non-line of sight applications due to: higher cathode efficiency, higher deposition rates, high hardness and good sliding wear and corrosion resistance. Originally developed on the laboratory scale, the nCoP deposition process is currently going through demonstration/validation testing as part of a US Department of Defense funded ESTCP program. To date the process has been scaled up to the industrial/production scale and is undergoing performance testing.

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