Electrodeposited Nanocrystalline Cobalt-Phosphorus Alloys – An Advanced Alternative to Hard Chrome Plating for Non-Line of Sight Coating Applications

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Electrodeposited nanocrystalline cobalt-phosphorus alloys have been developed for non-line-of-sight (NLOS) coating applications as an alternative to hard chrome electroplating. Due to extreme grain refinement (3 to 100nm) and Hall-Petch strengthening, hard nanocrystalline coatings can be produced which meet or exceed the hardness and wear performance of current hard chromium plating technologies. In this paper the synthesis and properties of nanocrystalline cobalt-phosphorus coatings on NLOS surfaces will be outlined, focusing on key points such as: process efficiency, build-up rate, surface finish, hardness, wear and corrosion performance. Validation tests, such as fatigue and hydrogen embrittlement testing will also be discussed. The overall cost of the process in relation to current hard chrome plating as well as the effective recovery of cobalt from waste solutions will also be addressed.

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INTRODUCTION

Hard chromium coatings (0.25 to 20 mil thick) have been used extensively as wear and erosion resistant coatings for both industrial and military [1-4] applications for over 50 years. This is likely due to their intrinsic high hardness (600-1000 VHN) and low friction coefficient (<0.2) [5]. The most common (and most practical) means of depositing such hard chromium deposits has been through the use of solutions containing hexavalent chromium (Cr^{6+}), which is a known carcinogen. Although significant progress has been made in the development of less harmful 'trivalent Cr' plating processes [6], a reliable industrial process has yet to emerge.

In addition to the health risks associated with Cr^{6+}, there are several other process and performance drawbacks to hard chrome coatings. As a result of the relatively low electrolytic efficiency of Cr plating processes, deposition (or build) rates are relatively low compared to the plating of other metals and alloys (e.g., 1-2 mils per hour for Cr versus > 8 mils per hour for Nickel) [7]. Moreover, the intrinsic brittleness of hard chromium deposits (i.e., <0.1% tensile elongation [8]) 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 [8].

From the above summary, it is apparent that a need exists for an alternative technology that: (a) meets the hardness and low coefficient of friction of hard chromium coatings, (b) significantly reduces environmental and health risks, and (c) provides process and performance improvements such as: i) increased deposition rates, ii) enhanced ductility, and iii) improved spalling and corrosion resistance without the need of a nickel underlayer.

Electrodeposited nanocrystalline metal and alloy coatings, in addition to being fully compatible with current hard chromium plating infrastructure, have displayed properties that render them a superior alternative to hard chromium coating technology. In this light, this article describes the process and properties of electrodeposited nanocrystalline cobalt-phosphorus alloy coatings, which have been recently developed as an environmentally benign replacement for hard chrome electroplating for Non-line-of-sight (NLOS) applications.

PROCESS

Using a recently developed procedure [9,10], nanocrystalline cobalt-phosphorus alloys were produced using pulsed current electrodeposition. Electrodeposition parameters (e.g. bath composition, pH, temperature, overpotential, bath additives, etc.) were modified and optimized to yield deposits with average grain sizes between 5 and 15nm. The overall plating efficiency of the process is approximately 90%, with a deposition rate ranging from 2 to 8 mils/hour, depending on current density. Both consumable (cobalt pieces in a titanium basket) and non-consumable (graphite) anodes can be used for the deposition process, allowing for easy application to internal diameter surfaces.

PROPERTIES

Hardness

As a result of Hall-Petch strengthening, nanocrystalline materials display significant increases in hardness and strength relative to their coarser grained counterparts due to their ultrafine grain size. A further increase in hardness can be achieved through a solid solution hardening mechanism by alloying with phosphorus. The effect of phosphorus content on the hardness of nanocrystalline cobalt electrodeposits is shown in Figure 1. The figure shows a linear increase in the as-deposited hardness with increasing phosphorus content. The solid solubility of phosphorus in cobalt is negligible [11], however, a considerable extension of the solid solubility range has been observed in the present study, as Co-P solid solutions were obtained with phosphorus concentrations of more than 5wt%. Similar extended solubility ranges have been previously observed in other nanocrystalline alloys produced by electrodeposition, such as Ni-P [12-13], Co-W [14], Zn-Ni [15] and Ni-Mo [16]. As a result of this extended solubility range, the hardness was observed to increase from ~570 VHN, for pure nanocrystalline cobalt (grain size ~14nm), to ~820 VHN for nanocrystalline cobalt containing 5wt% phosphorus.

A further increase in hardness, via a precipitation hardening mechanism, can be obtained by annealing the as-deposited material to induce the precipitation of cobalt-phosphides from the supersaturated solid solution at elevated temperatures. Figure 2 shows the variation in hardness as a function of annealing time at 400°C for up to 30 minutes, for three cobalt-phosphorus deposits with different concentrations of phosphorus and a pure nanocrystalline cobalt deposit. The three cobalt-phosphorus deposits show an increase in hardness with annealing time passing through a maximum after around 10 minutes, followed by a slow decrease with increasing time. It should be emphasized at this point that through a short heat treatment process, presence of phosphorus in the deposit results in an additional increase in hardness to values close to those for the upper limit of hard chrome. A similar trend has also been observed for electrodeposited nanocrystalline nickel-phosphorus alloys [17]. The hardness of pure cobalt deposits, however, only decreases with increasing annealing time. The loss in hardness during the annealing of pure nanocrystalline cobalt is the result of grain growth occurring at this temperature.

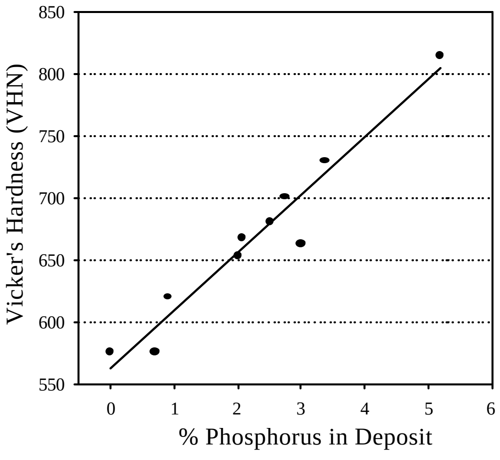

Figure 1 *Effect of phosphorus concentration on the hardness of nanocrystalline Co-P deposits.*

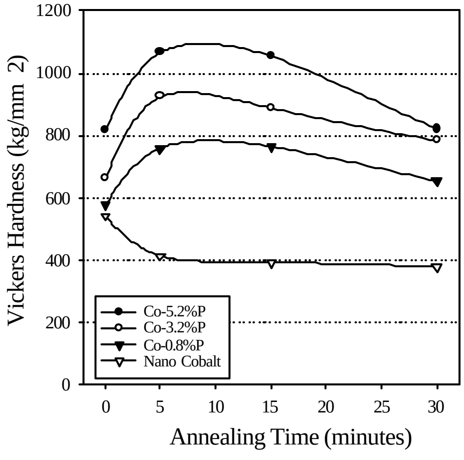

Figure 2 *Effect of annealing time on the hardness of nanocrystalline Co-P deposits annealed at 400°C.*

Strength and Ductility

In a recent study [18], the tensile properties of electrodeposited nanocrystalline cobalt (produced by the same process) were compared with that of a coarse grained polycrystalline counterpart (see table 1). Significant increases in strength were obtained while maintaining considerable ductility. The greater than two-fold increase in yield and tensile strength while maintaining considerable ductility is quite remarkable and an attractive property when compared to hard chrome coatings, which possess a tensile elongation of less than 0.1%.

Table 1 ***Tensile Properties of Nanocrystalline and Polycrystalline Cobalt[18].***

	Grain Size	**Yield Strength**	**Ultimate Tensile Strength**	**Ductility (% elongation)**
Nano Co	12 nm	1000-1100MPa	1750-1950MPa	4-8%
Poly Co	1µm	370-400MPa	760-860MPa	7-18%

Figure 3 show the results of ASTM B489 ductility bend tests on nanocrystalline Co-P deposits ranging from 0-6wt%P. The curve shows that the ductility of the coating decreases with increasing phosphorus concentration in the deposit, but that at 5-6wt%P a ductility of 2-3% is still obtained.

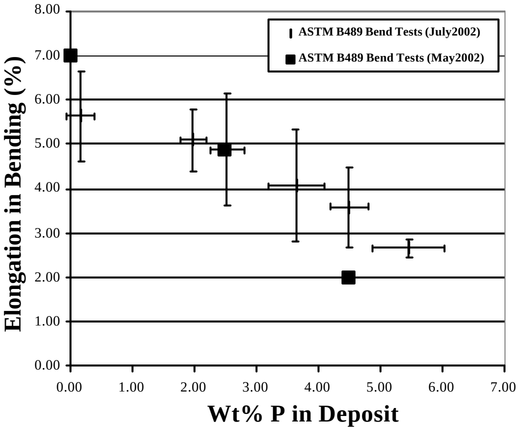

Figure 3 *Ductility (in bending) of nanocrystalline Co-P deposits as a function of phosphorus concentration.*

Thermal Stability

Due to the ultra-fine grain size in nanocrystalline materials, there is a large driving force for grain growth due to the stored energy at the grain boundaries. As a result, nanocrystalline materials have definitive thermal stability limit, as seen by the loss in hardness in the pure cobalt deposit after an annealing treatment at 400°C for 30 minutes (figure 2). Another consequence of their ultra-fine grain size is an increased electrical resistivity over polycrystalline materials due to their high volume fraction of grain boundaries. By measuring the electrical resistivity at elevated temperatures, the point at which the material is no longer thermally stable can be determined by a sharp decrease in the electrical resistivity arising from the onset of grain growth. Figure 4 shows the electrical resistivity as a function of temperature from 25°C to 700°C for two nanocrystalline cobalt-phosphorus samples and a pure nanocrystalline cobalt sample.

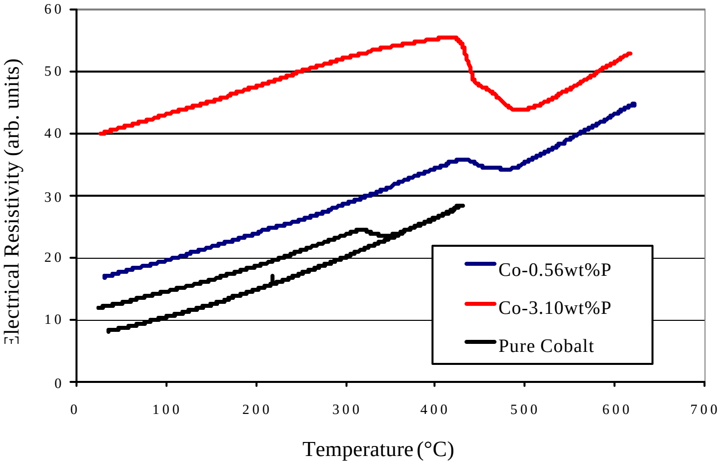

Figure 4 *Electrical Resistivity as a function of temperature for three nanocrystalline Co-P Alloys.*

The figure shows that the onset of grain growth (as indicated by the large drop in resistivity) increases from 350°C for pure nanocrystalline cobalt to 475°C and 485°C for nanocrystalline Co-0.56%P and Co-3.10%P, respectively. Therefore, the presence of phosphorus in the deposit creates a stabilizing effect on the nanocrystalline grain structure.

PERFORMANCE

Sliding Wear

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 2 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 2wt% phosphorus to pure cobalt sample, but little improvement was seen after 2wt%, even though the composition of phosphorus in the test samples varied from 2 and 10wt%. A nanocrystalline Co~4wt%P was tested after hardening by a heat treatment at 400°C for 10minutes, and although the hardness increased by 35%, no significant improvement in the wear resistance was observed.

Table 2
Hardness and sliding wear data for various standard and nanocrystalline materials.

Material	*Hardness (VHN)*	*Coefficient of Friction*	*Wear Volume Loss (mm3/Nm) x 10^{-6}*
Standard Samples			
Mild Steel	150	0.73	18.2
Tool Steel	250	0.75	13.1
Hard Chrome	1200	0.70	11.9
Nanocrystalline Samples			
Nano Cobalt	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
Nano Co~10%P	720	0.50	6.2

Hydrogen Embrittlement

Hydrogen embrittlement tests were performed according to ASTM F519, “Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating Processes and Service Environments,” on Standard F-519 Type 1a notched bar specimen. The test specimens were 4340 steel heat-treated to achieve R_c hardness of 51-53. Test samples were plated with 4 mils of nanocrystalline Co 2-3wt%P and tested in the as-plated condition and after baking at 191°C for 24 hours. Four samples were tested at each condition.

Figure 5 shows cross sections of a typical hydrogen embrittlement specimen plated with nanocrystalline Co 2-3wt%P. The thickness of the coating was approximately 25µm at the base of the notch (0.001”) and 80µm on the edge (0.0032”), given a ratio of notch thickness to edge thickness of approximately 1/3rd.

Test results showed that at each condition one sample failed before 200 hours at 75% of the notch fracture strength (NFS) while the remaining three lasted over 200 hours. The remaining three, however, were step loaded and failed before 90% of the NFS, thus indicated embrittlement. Metallurgical examination of the samples, however, revealed the presence of pre-existing cracks, therefore the samples are currently being retested.

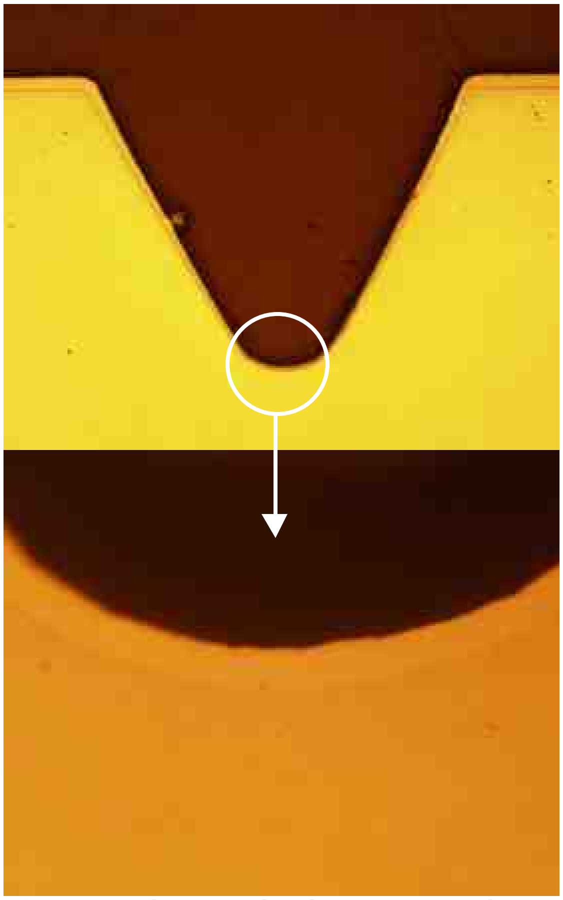

Figure 5 *Hydrogen Embrittlement test sample*

Fatigue

Fatigue testing of the 4340 steel test specimens coated with 3 mils of nanocrystalline Co-P was conducted according to the ASTM Standard E466, “Force Controlled Fatigue” at room temperature in lab air. Figure 6 shows typical test specimens after coating with Co 2-3wt%P. Testing was conducted on Co-P samples with 0%, 2-3wt% and 4-5wt%P as well on both peened and unpeened uncoated samples for reference. All testing was conducted at an R-Ratio of –1 at stress levels of 175ksi and 125ksi.

Preliminary test results for samples tested at the high stress level (175ksi) revealed that there was no significant difference in fatigue life between the coated and the uncoated samples, indicating that the presence of the coating did not introduce a fatigue debit as is commonly seen for chrome plated samples. Samples are currently being tested at the lower stress conditions. Figure 7 shows an SEM micrograph of a fatigue sample (Nano Co2-3wt%P tested at 175ksi) showing beach marks initiating at the surface of the substrate, which then radiate into the coating.

Figure 6 *Photograph of the 43040 wear samples coated with nanocrystalline Co 2-3wt% P.*

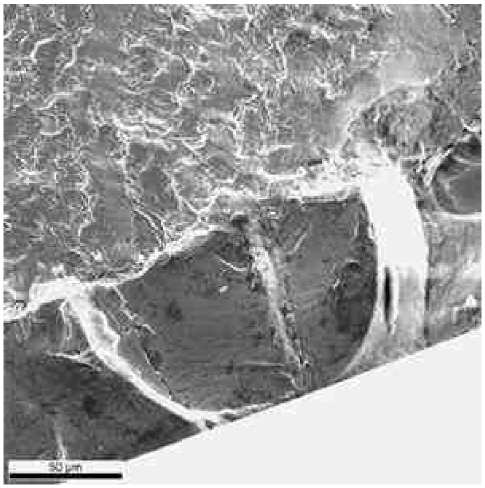

Figure 7 *SEM Micrograph of a fatigue sample (Nano Co2-3wt%P / 175ksi) showing beach marks initiating at the surface of the substrate, which radiate into the coating.*

Electrochemical Corrosion

Electrochemical potentiodynamic corrosion testing (per ATSM G61) was performed on three (3) standard materials: metallurgical prepared polycrystalline cobalt, nickel 200 and electrolytic hard chrome, as well as on three electrodeposited nanocrystalline alloys: cobalt, cobalt 2-3wt% phosphorus and cobalt 4-5wt% phosphorus. Linear polarization resistance scans (LPR) were performed in 3.56wt% NaCl solution at room temperature. From these measurements the corrosion rate was determined.

Figure 8 shows the preliminary results from the experiment showing the corrosion rates of nanocrystalline Co-P alloys as a function of phosphorus concentration along with the corrosion rates of Hard Chrome, Ni200 and metallurgically prepared polycrystalline cobalt. As expected, hard chrome had the lowest corrosion rate of all the materials tested due to the formation of its stable oxide film (Cr_2O_3). Polycrystalline cobalt had the highest corrosion rate of all the materials tested, at approximately 2 millimetres per year (mpy). The corrosion rate of nanocrystalline Co-P alloys was found to initially decrease with increasing phosphorus concentration, to approximately 1-2wt%P, and was then found to increase with increasing phosphorus concentration. At 1-2wt%P, the corrosion rate was only slightly higher than that of Nickel 200. From these results a few conclusions can be made: (i) 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), (ii) the addition of small amounts of phosphorus (1-2wt%) to nanocrystalline cobalt results in a further decrease in corrosion rate, and (iii) the corrosion rate of nanocrystalline Co 1-2wt%P is similar to that of Nickel 200.

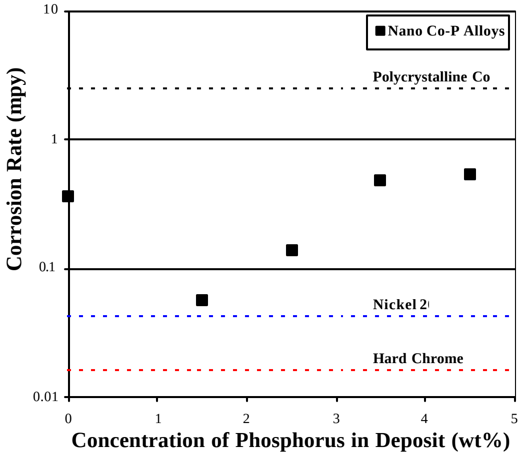

Figure 8 *Corrosion Rate of various materials as a function of exposure time.*

APPLICATION TO INTERNAL DIAMETER SURFACES

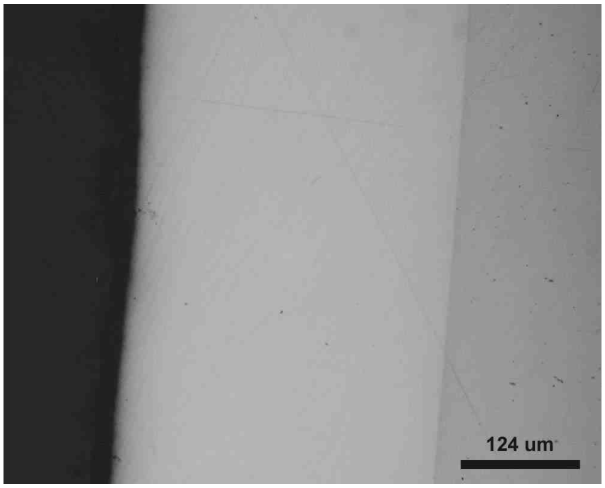

Figure 8 *Nanocrystalline Co 2-3wt%P coating on the ID of a 1 inch pipe (~13mil thickness).*

Figure 8 shows an optical micrograph of a cross-section of a nanocrystalline Co 2-3wt%P coating on the internal diameter of a 1-inch pipe. The coating was plated using a graphite anode to a thickness of approximately 13 mils. The coating was found to be free from pits, porosity and/or cracking and was plated at a rate of approximately 5 mils/hour.

PROCESS COST

An estimate of the cost to electrodeposit various nanocrystalline Co-P alloys was performed using the hard chrome deposition process as a benchmark comparison. The cost was broken into two parts, the base metal cost and the power cost associated with the DC electrodeposition currents needed. As the hard chrome electrodeposition process uses a non-consumable anode, the base metal cost was estimated from the price of chromic acid. For the case of conventional nickel and nanocrystalline cobalt alloys, consumable anodes are used, thus the base metal price was estimated simply from the alloy composition. For the case of the phosphorus containing alloys, however, the cost of the hypo/phosphorous acid was included in the estimate. The cost analysis is given in Table 3.

The relative consumable cost for the nanocrystalline alloys is slightly higher than that for chrome due to the relatively high price of cobalt (~7US$/lb) and/or phosphorus. The relative power cost for the production of the nanocrystalline alloys, however, is far below that for chrome. This is due to two factors. First, hexavalent chrome ions need 6 electrons to be reduced to a metallic state at the cathode whereas both cobalt and iron only need 2 electrons. Therefore the chrome process requires 3 times as much electricity than the cobalt process. Secondly, the efficiency of the chrome process is significantly below that of the nanocrystalline alloy processes, further increasing the power cost. Therefore, estimating the cost of electricity at 0.1$/kWhr, the total relative process cost for the production of nanocrystalline Co and Co-3%P is 1.09 and 1.31, respectively, when compared to the hard chrome process. An additional factor that was not considered in the above cost analysis is the environmental costs associated with wastes generated during the process.

Table 3 ***Cost analysis for the production of electrodeposited nanocrystalline cobalt and cobalt-3%phosphorus compared to conventional nickel and hard chrome.***

Plating Process	Nominal Plating Efficiency (%)	Consumables	Relative Plating Cost (by weight)	Relative Power Cost (by weight)	Total Relative Process Cost
Chrome(VI)	25	Cr_2O_3	1.00	1.00	1.00
Conventional Ni	90	Ni	0.70	0.08	0.44
Nano Co	>90	Co	1.83	0.08	1.09
Nano Co-3%P	>90	Co H_3PO_3	2.21	0.08	1.31

ENVIRONMENTAL IMPACT

With regard to potential environmental impact, it is anticipated that waste stream volumes will be, for all intents and purposes, identical to those currently experienced with hard chrome plating processes on a per tonne metal plated basis. However, the environmental impact of the wastes associated with the nanoscale deposition will be significantly reduced as none of the chemical constituents required for nanoscale cobalt-alloy deposition are presently on EPA and AFMC lists of hazardous materials. Moreover, the high plating efficiencies typically observed with nanoscale electrodeposition, are expected to significantly reduce overall electrical power requirements relative to that of chrome plating operations.

The potential impact on workplace safety was investigated by sampling the laboratory air directly above the plating tanks. The airborne emissions from three-nanocrystalline plating electrolytes (Co, Co-P and Co-Fe-P) were measured by sampling 30L of air over a 5 hour period during the electrodeposition process. A sampling line was placed about 1 inch from the surface of the plating solution and air was sampled at approximately 100mL/min. The vials were then analyzed for any traces of cobalt, iron, chloride, sulphate, and for two additives. A summary of the emission results is given in Table 4. The toxicity level given in the first column is that set by OSHA. In all cases the measured emissions were far below the toxicity level. For the case of the two additives, no emissions were measured above the background.

Table 4 *Results from the emission analysis measurements for cobalt, cobalt-phosphorus and cobalt-iron-phosphorus bath chemistries.*

Element/Compound	**Toxicity Level**[1] *(mg/m^3)*	**Bath#1 Cobalt** *(mg/m^3)*	**Bath#2 Co-P** *(mg/m^3)*	**Bath#3 Co-Fe-P** *(mg/m^3)*
Cobalt	0.05	0.0039	<0.0005	<0.0005
Iron	1.0	<0.0005	<0.0005	<0.0005
Chloride	N/A	0.216	0.043	0.053
Sulphate	N/A	0.258	0.014	0.29
Additive#1	N/A	N.A.B.	N.A.B.	N.A.B.
Additive#2	N/A	N.A.B.	N.A.B.	N.A.B.

[1] OSHA Time Weighted 8 Hr Avg, N.A.B. = Not Above Background

SUMMARY

Nanocrystalline cobalt-phosphorus alloys have been described as a replacement for hard chrome coatings, specifically for non-line-of-sight (NLOS) applications. The plating process has high efficiency (>90%), provides fast plating rates (2-8mils/hour), yields deposits free of porosity and/or cracking, and using no chemicals currently on the EPA or AFMC lists of hazardous materials. Property tests have shown that nanocrystalline Co-P coating meet the hardness criteria of hard chrome while maintaining considerable ductility. Performance tests have shown that the sliding wear resistance is superior to chrome, the corrosion rate is similar to Ni 200 and that the coating does not cause a fatigue debit on high strength steel (4340, Rc=52) when tested at high stress (175ksi) under full reversed conditions. The overall cost of the process was found to be only slightly higher than that of hard chrome plating, before considering environmental costs associated with the generated wastes.

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