Electrodeposited Nickel-Phosphorus

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Introduction

Nickel-phosphorus was electrodeposited first as a curiosity early in the last century. Deposits were also noted accumulating on the sides of containers when hypophosphite was added to a nickel solution at high temperature. Later studies by Dr. Abner Brenner and co-workers from the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST), led to the development of both electrolytic and electroless nickel-phosphorus plating processes. His famous book on electrodeposition of alloys cites several suitable electrolytic processes from work by others and by the NBS. In particular are some of the baths by NBS which produced strong sound alloys of 11-13 wt% Ni-P with cathodic efficiencies from 12 to 50%, based on the true alloy composition and assumed deposition parameters.

Early nickel-phosphorus electrodeposits did not find favorable acceptance. Numerous attempts to provide better solutions in the earlier years were abandoned in favor of the electroless processes. However, continuous deposition at lower temperature and higher efficiency is now possible. Modern Ni-P electroplating developments are described here which have improved their environmental impact and ability to plate to any desired thickness with exceptional properties, suitable for many applications. Additionally the electrolytic processes have no propensity to solution phase deposition "crash" and the phosphorus consumption is much less on a per unit deposit basis.

At least nine processes are described in recent literature as being in use. Numerous patents have issued since Dr. Brenner's first studies. Three processes are presently under patent protection and the others are apparently either not patented or have pending applications.[1-7]

Electroformed nickel and nickel-cobalt-phosphorus (Ni-P and Ni-Co-P)

The Ni-P plating process is unique to conventional nickel electroplating in many ways. An alloy of about 11 to 12 wt% phosphorus has about the same mass as the remaining amount of nickel would have as pure nickel metal. This is due to the expanded atomic structure of the metalloid obtained. The metalloid-metallic compound formed is nearly amorphous and possesses some properties much like glass. In other aspects however, it behaves more like a metal. It is sometimes called a "glassy metal." Although the occurrence of glassy metals is rare in thermally prepared alloys, several versions of deposited glassy metals are known. Nickel, iron or cobalt with >10% phosphorus, nickel-boron, tin-nickel, copper-bismuth and nickel-sulfur are the more common. Tin-nickel has been electrodeposited commercially for the exceptional corrosion resistance achieved. This alloy is not strong however. Nickel-phosphorus and/or boron compounds may be deposited by either electrolytic or catalytic methods. In general, cobalt may be substituted for all or part of the nickel in most of these processes, although the same properties are not necessarily achieved. Electrolytic and electroless deposition of nickel- and cobalt-phosphorus have been accomplished for more than 50 years since the initial work primarily by NBS (now NIST) and the development of the electroless (catalytic) nickel and cobalt plating processes.[1] Electrolytic deposition of iron-phosphorus has also been accomplished but has not found many applications.

Previous versions of electroplated nickel-phosphorus have had strict limitations and have not significantly replaced the electroless processes. These deposits tended to be highly stressed unless the deposition was carried out at very high plating temperatures and very low pH, typically from 0.5 to 1.0, which produced deposits only at low cathodic efficiency and mandated vigorous agitation.[8] Deposits were usually achieved with nickel anodes dissolving at high anodic efficiencies, presumably to avoid oxidation of the phosphorous acid used under these adverse conditions. Consequently, the nickel rapidly built up to unacceptable levels, periodically requiring decanting a portion of the bath.

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The former processes typically contain from 25 to 50% of nickel as nickel chloride to increase conductivity, making the solutions very corrosive to base metals and supporting equipment. With the high temperature, low plating efficiency, corrosive solution and control issues required there has been little incentive to use the prior art electrolytic Ni-P processes. An exception is that for the production of heavy deposits, the electrolytic processes have been used due to the non-existence of solution phase precipitation, which frequently occurs in the electroless processes limiting the plating time needed to achieve thick deposits.

A recently patented process[6] permits low stress operation at low temperature, 45 to 50°C, with soluble anodes to limit maintenance to pH control and infrequent adjustments between plating runs, similar to most other plating processes. A portion of the anode may be substituted with an inert anode to balance the use of the metal, leading to long life. Perhaps the most significant advantage of the new process for thick deposit applications is the control of stress. Also the process may be operated while covered with little operator intervention required other than periodic phosphorus and pH control and routine equipment checks for safety. Continued development of this category of material has led to improved glassy metal properties wherein the best attributes of glass and metal are sought. In particular, the material has exceptional microyield and strength properties. It appears that under optimum conditions, the Ni-Co-P material can be loaded to near failure at as much as 1.8 GPa without significant permanent deformation, compared to the engineering yield strength (defined as 2000 ppm yield) for conventional nickel. Conventional nickel plated from a standard sulfamate solution shows the first microyielding at less than 60 MPa. Thus significantly more than one order of magnitude improvement has been realized at room temperature.

The Ni-Co-P or Ni-P electrolytic processes clearly have superior properties and control mechanisms for many applications including optics. The preferred use of this material for other applications is obvious. For diamond machining such as in optics, and deposits of 0.05 mm or more, the electrolytic deposit may be more desirable. Indeed electroforms of more than 0.6-cm thickness are possible in one step with the new processes. Deposits of 0.5 mm are routinely electroplated for use as diamond-turned optics. Samples for material analysis are often plated to this thickness (See Figs. 4, 5, 7, 8 later in this article.).

From a conservation point of view the use of the electrolytic processes will save time, conserve energy and eliminate costly down time for cleaning and rejuvenating the electroless processes. For cases requiring a very uniform deposit into deep recesses, the electroless processes (EN) will still prevail, however. Table 1 is a comparison of the various plated materials discussed and Table 2 lists various applications.

From this data, it is obvious that the use of the electrodeposited nickel-phosphorus (or nickel-cobalt-phosphorus) has certain advantages over either the electroless nickel-phosphorus or the conventional electrolytic nickel or nickel-cobalt. This, in addition to the relative operational ease of the new electrolytic versions compared to the electroless process, makes the new processes attractive for many applications. Additional benefits in cost, downtime, health and safety and pollution control should add even more to the benefits of the new processes as less heat, water, replenishments and maintenance is required.

Control mechanism for Ni-P or Ni-Co-P alloy electroplating

Three kinetic processes prevail in the case of plating the Ni-Co-P alloy. The nickel is in sufficient supply to reduce according to Faraday's Law throughout the range of interest. The presence of the phosphorus will inhibit the nickel deposition at low current however, and acts as a self-stabilizing control. Decreased pH along with a complexant reduces the amount of nickel in the deposit for a given set of conditions. Increased current density from about 4 mA/cm^2 up to about 30 mA/cm^2 only slightly increases the nickel.

Table 1

Comparison of selected processes

Parameter	Nickel	Electroless Nickel	Electrolytic NiP and NiCoP
Plating Temperature, °C	38 - 50	82 - 90	40 - 60
Control Method	Soluble anode	Chemical replenishment	Soluble anode
Yield (0.2%), MPa	500	See UTS	See UTS
Microyield, MPa	70	500+	830+
UTS, MPa	800	850	1800 - 2150
Specific gravity	8.9	7.8 - 8.0	7.8 - 8.0
Stress control (Real time)	Yes (-10+10 MPa)	No (-5+30 MPa)	Yes (-10+10 MPa)
Hardness, Rockwell C	22 - 24	48 - 52	48 - 52
Diamond machining	No	Yes	Yes
Thick deposits	Yes (cm+)	0.25-mm Max (Typical)	Yes (0.5 cm+)

Table 2
Applications

- **NASA / UAH process used more than nine years**
- **Many variations are viable**
  - High-speed NiP plating, 50 microns/hr at 12% P
  - Non-Magnetic or magnetic deposits
  - "Free machining" alloy versions
  - Versatile: About any aspect of electroless Ni achieved
  - NiCoP with high hardness and low stress
  - Extremely high precision elastic limit (PEL)
  - Codeposition of solid powders (2001, 2003)
  - Decorative plating
  - Marine applications
- **Additional electroformed optical designs**
  - Normal incidence reflection
  - Post machined optics
  - Near-net free-standing forms
  - Coated optics

Beyond this, the phosphorus content falls off below the desired 12 wt% and internal stress increases.

The phosphorus deposition rate is limited by the reaction kinetics. At a given temperature and composition, the deposition rate of phosphorus will tend to be maximum for the lower current density. The phosphorus competes for reduction electrons by virtue of the relative potential and transference properties in competition with the nickel. Measured values of phosphorus in the deposit show that as long as sodium hypophosphite and/or phosphorous acid in solution is above 0.2M, the phosphorus in the deposit is generally above 10 wt% within the current density range of interest. As the agitation is increased, the available cobalt in the diffusion layer increases, replacing some of the nickel and lowering the stress if used. Thus at higher agitation levels and with the addition of cobalt, the current density may be increased significantly while maintaining low stress. Current densities as high as 150 mA/cm^2 have been achieved with suitable stress control. A typical stress response with moderate agitation is shown in Fig. 1.

Control mechanism for Ni-P and Ni-Co-P alloy electroplating

If cobalt is used, at a fixed temperature and modest agitation, when the current density is increased from about 5 to 12 mA/cm^2 the stress decreases while the deposited cobalt concentration increases. This is in contrast to a conventional nickel-cobalt process without phosphorus where the cobalt decreases due to limited concentration and accordingly the stress decreases for increasing current density. From 12 to 40 mA/cm^2, the stress behaves in a more conventional manner and increases. Thus, as seen in Fig. 2, the stress initially decreases, crossing zero at the low end at about 6 to 10 mA/cm^2, reaches a minimum at 10 to 12 mA/cm^2, then increases and crosses zero again at about 17 to 20 mA/cm^2. If vigorous agitation is applied, presumably approaching turbulent flow, *i.e.*, Re >2000, then the stress remains compressive beyond 120 mA/cm^2, at 45 to 50°C. The pH may be operated higher in the Ni-Co-P than in the Ni-P solution. Throughout the entire range the stress is acceptable for all but the most critical operations such as freestanding optics for which the zero stress point is utilized.

Ni-P and Ni-Co-P solution operating life

Two factors control the solution life span. First, we have the electrolytic aging effect, which is primarily due to an imbalance of material removed by electrolysis versus what is required to maintain the process. Second are the reactions that may occur outside of the required reduction of nickel, phosphorus and cobalt by electrolysis. Hypophosphite initially used for the supply of

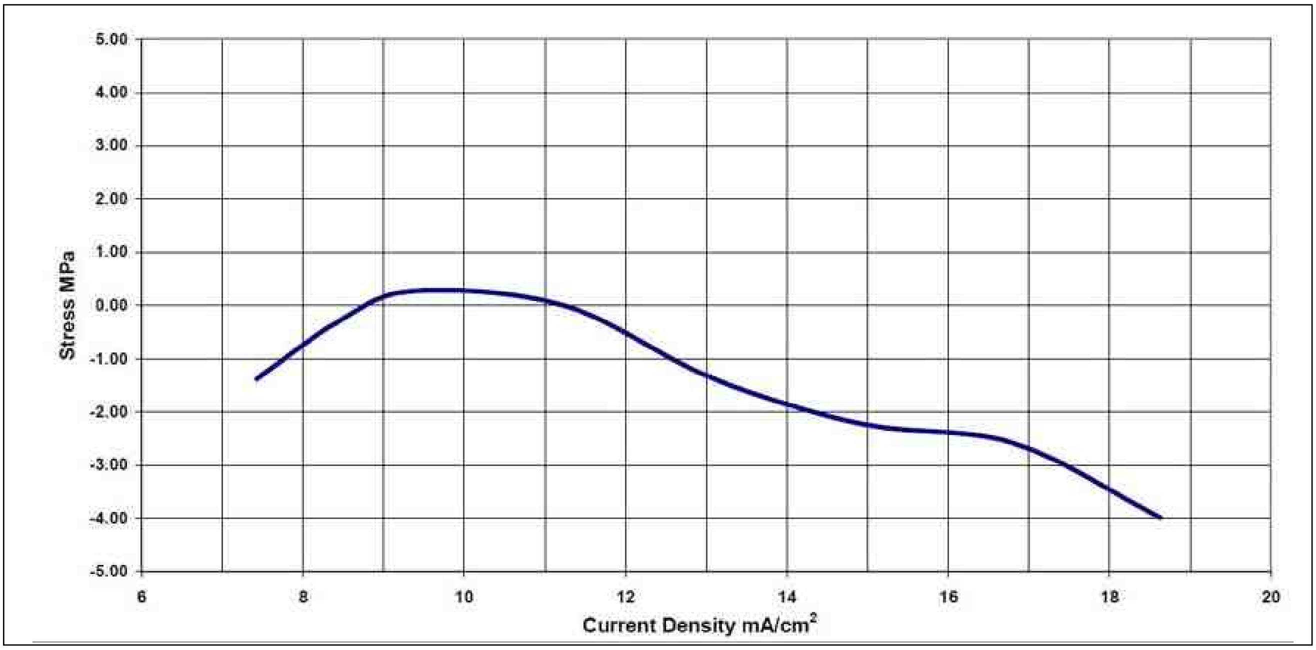

Figure 1—Stress versus current density for NiP at 50°C.

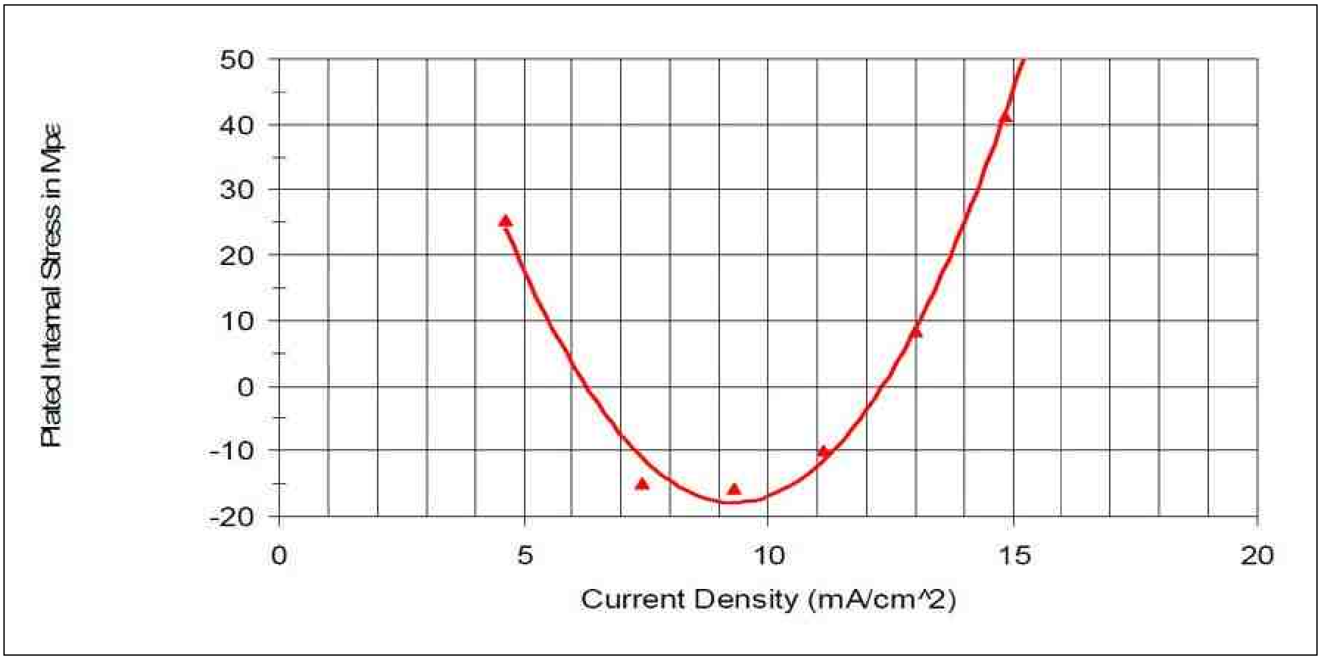

Figure 2—Stress versus current density for NiCoP at 50°C.

phosphorus converts exponentially to orthophosphate minus the electrolytically deposited phosphorus in the alloy. It is interesting to note that, during the course of this oxidation state change, there is very little change in the deposited alloy appearance, efficiency or properties. However, after the hypophosphite has converted at 1.0 to 2.0 A-hr/L, the phosphorus falls off in the deposit. Beyond this point it appears that the phosphorus can be added, one-to-one, as sodium hypophosphite or phosphorous acid to maintain a constant alloy[9-10] with little difference noted in properties.

Thus as the plating of parts consumes phosphorus at 11% of the weight of the deposit as a whole, this amount as phosphorus is replaced using sodium hypophosphite or phosphorous acid, H_3PO_3. This 1:1 phosphorus consumption ratio is in sharp contrast to a conventional electroless nickel process wherein the solution maintenance consumption of phosphorus as hypophosphite is typically five times the equivalent deposited phosphorus. This consumption leads to an early saturation of an electroless nickel bath with sodium products and orthophosphate, necessitating replacement or treatment. A direct relationship for the extended life of the electrolytic process has not yet been established. This is however far beyond the typical six to eight "metal turnovers," *i.e.*, 36 to 48 g/L of nickel consumed, since the addition is nearly 1:1 with the consumption, and no detrimental phosphorus compounds accumulate with increased use of the electrolytic process (Fig. 3).

Small 35-L nickel-cobalt-phosphorus solutions prepared for testing have been operated with cobalt anode current equivalent to the cobalt usage and the balance of current on a nickel anode, leading to a gradual slight increase in nickel content. This has had no adverse effect after about 200 A-hr/L (equivalent to about 180 g/L as metal.) This is equivalent to about five times the normal life of an electroless process. During this extended period, no solution phase precipitation has been observed while plating. Later, the solution was replaced once for experimental reasons although the original solution was still functional. The anodes have been in place for about 48 months with no sign of process degradation. It was observed that the pH should be maintained at no more than 4.0 to avoid possible cobalt salt formation at the anodes. If no cobalt is used, the pH must be less than 3.5. Additional metal chips are added to the anode baskets as they are consumed by the plating. Subsequently platinized titanium anodes were used to offset partially the increase in nickel and have been in use since. The use of H_3PO_3 avoids buildup of sodium, and it has been shown that at least the equivalent of 100 metal turnovers (800 g/L) is possible for the equivalent life of at least ten electroless nickel baths without replacement or major replenishment.

Samples for hardness and machining tests were electroplated more than 0.6 cm thick, and appear perfectly sound. One of a series of 4-L test solutions of Ni-P operating at 60 to 65°C (without cobalt) produced sound deposits after 200 A-hr/L of operation with a nickel anode. Figures 4 and 5 show examples of heavy deposits obtained 0.3 to 0.6-cm thicknesses.

Appearance and corrosion resistance

The electrolytic deposits obtained without organic additives are substantially sounder than those with organic additives. For our applications using the deposit both for diamond-turned and highly polished mandrels as well as free-standing replicated optics, no additives were used for leveling. The deposits are fully white bright without additives at about any thickness up to 0.5 cm, if the starting substrate is smooth, and have the identical appearance to electroless Ni-P, as seen in Figs. 4, 7 and 8. If the substrate is coarse, the deposit assumes about the same finish and becomes slightly smoother with increased thickness. Organic additives may be added to level the deposit and choices are similar to those of ordinary nickel or electroless nickel. Pulsed plating offers some advantage, but for our applications, it was deemed unnecessary.

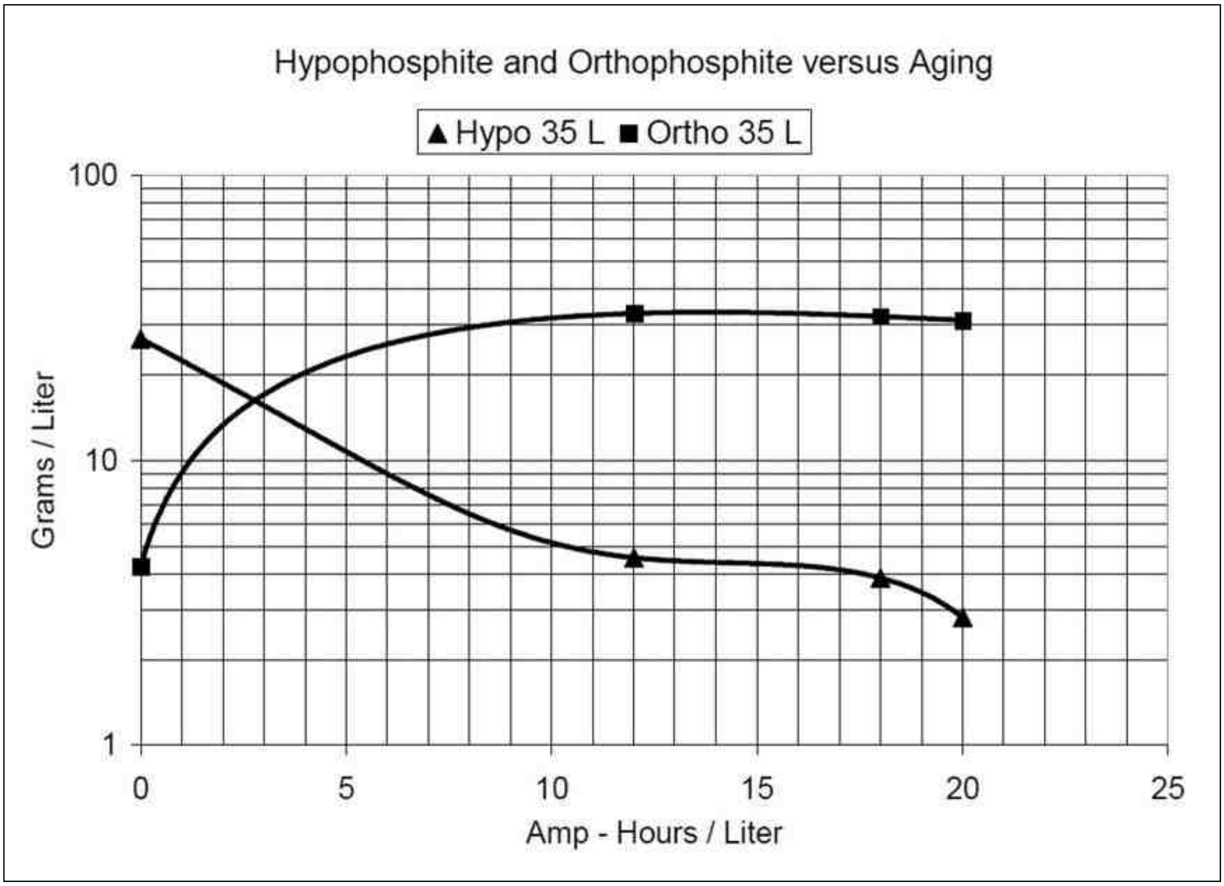

Figure 3—Oxidation of hypophosphite.

Figure 4—Electroplated NiP and NiCoP samples including a 0.6-cm thick electroform.

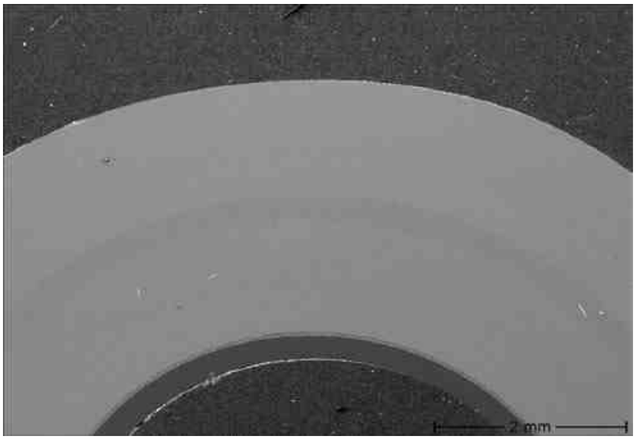

Figure 5—A 0.3-cm (3-mm) thick NiCoP electrodeposit: Hardness ($HV_{0.1}$) - 550, 560, 580, 540, 580, 590, 580 (inside to outside).

Corrosion and passivation of electrolytic Ni-P for electroforming are identical to that for electroless nickel of the same alloy composition. ASTM B117 salt spray testing was conducted on samples of 11 wt% wt electroless and electrolytic Ni-P with no observed difference over six months. All alloys tested were non-magnetic with 10 wt% or more phosphorus. Lower alloys were of course obtained at lower P/Ni ratios, but these have not been pursued for our applications. Since electroless Ni-P is used extensively for the ultimate in uniform deposit in deep recesses, samples were prepared on drilled circuit boards with a very small pointed drill (Fig. 6). The deposits were about 12 mils thick and appear exceptionally uniform (Fig. 7). A 0.25-mm thick, 15-cm diameter electroplated Ni-P mandrel for electroforming x-ray mirror shells is shown to have excellent uniformity even in the gasket grooves (Fig. 8). A 0.5-m Ni-Co-P x-ray mirror was the largest electroformed (Fig. 9).

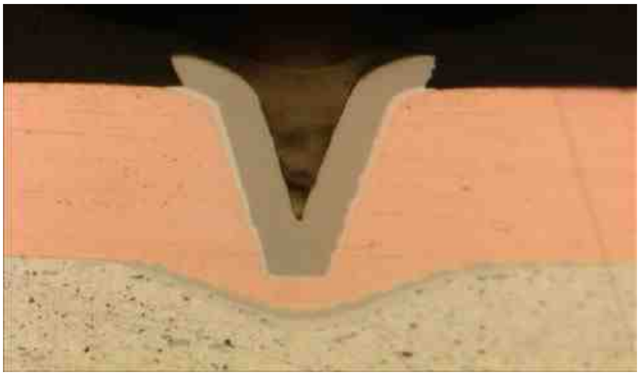

Figure 6—NiP electroplated in a 0.25-mm drilled taper hole.

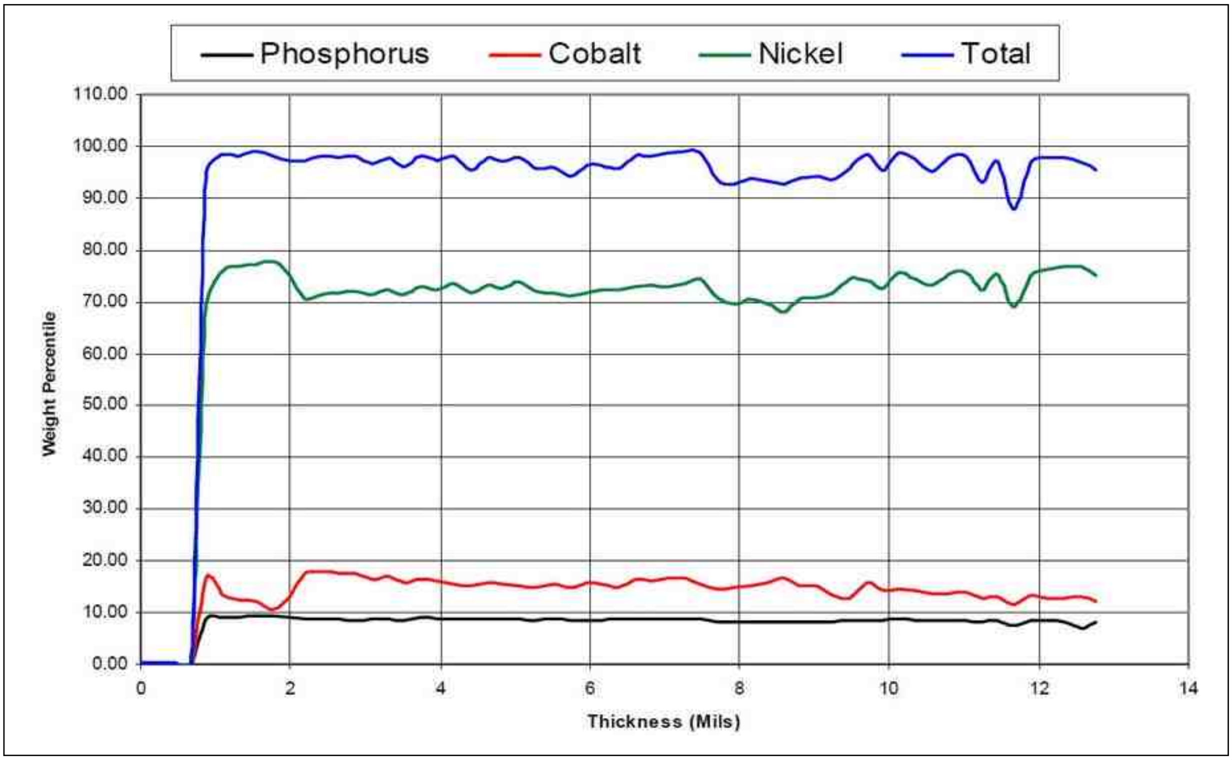

Figure 7—Composition of an NiCoP alloy cross-section.

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Figure 8—An as-plated 0.25-mm thick NiP electrodeposit on a 15-cm diameter mandrel.

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About the author

Darell Engelhaupt is a Senior Research Scientist at the University of Alabama in Huntsville with more than 30 years experience in fabricating high tolerance components using electroforming processes. He has 15 patents as author or co-author in metal finishing and in instrumentation design. Mr. Engelhaupt is a staff member of the UAH Center for Applied Optics where he is currently developing manufacturing processes for NASA's Space Science x-ray optics programs. His education includes a B.S. in General Engineering/Physics at the University of Missouri - Kansas City (UMKC) and graduate studies in Mechanical Engineering/Physics at the University of Kansas. He is a long-standing member of NASF (AESF), SPIE and ECS.

Figure 9—A 0.25-mm thick NiCoP electroformed x-ray mirror with a gold inner surface.