Electrodeposited Nickel Phosphorus

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Nickel phosphorus was deposited first as a curiosity early in the last century. Deposits were 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 National Institute of Standards Technology (NIST) led to the development of both electrolytic and electroless nickel phosphorus plating processes. In particular his famous book on electrodeposition of alloys cites several suitable electrolytic processes from work by others and by NBS. In particular some of the baths by NBS produced strong sound alloys of 11-13%wt NiP with cathodic efficiencies from 12 to 50% based on the true alloy composition and assumed deposition parameters.

These early solutions have not found favorable acceptance. Numerous attempts to provide better solutions in the earlier years were abandoned in favor of the electroless processes however deposition at lower temperature and higher efficiency is now possible.

Modern NiP electroplating developments are described which have improved the environmental impact and ability to plate 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 are presently under patent protection and the others are apparently either not patented or have pending applications. See Ref.[1-6].

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1.0 Electroformed Nickel and Nickel Cobalt Phosphorus (NiP or NiCoP)

The NiP plating process is unique to electroplating in many ways. An alloy of about 11 to 12 weight percent phosphorus has about the same density, as the remaining amount of nickel would be 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 “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 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 has been accomplished for more than 50 years now since initial work primarily by NBS (now NIST) and the development of the electroless or catalytic nickel and cobalt plating processes [1]. Electrolytic deposition of iron phosphorus has also been accomplished but has not found much favor.

Previous electroplated versions of nickel phosphorus have had strict limitations and have not replaced the electroless processes in any significant proportion. These deposits tended to be highly stressed unless the deposition was carried out at very high plating temperatures. The stress control required low very low pH typically from 0.5 to 1.0 which produced deposits only at low cathodic efficiency and mandated vigorous agitation[7]. Due to the need to use nickel anodes at high anodic efficiencies, presumably to avoid oxidation of the phosphorous acid used under these conditions, the nickel rapidly built up to unacceptable levels requiring decanting a portion of the bath periodically.

The former processes typically contain from 25% to 50% of 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 NiP 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 to achieve thick deposits.

A present patented process permits low stress operation at low temperature, 45° - 50C, 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 for extended periods with little operator intervention required other than periodic phosphorus and pH control and routine equipment checks for safety. Continued development of this category 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 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 more than one order of magnitude improvement has been realized in PEL.

The NiCoP or NiP 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 any situation requiring diamond machining such as in optics, and heavy deposits of 0.05 mm or more, the electrolytic deposit may be more desirable. Indeed electroformed shapes of more than 0.6 centimeter thickness are possible in one step with the new processes.

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. The use of cobalt can be eliminated for all but the most critical hardware. 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:

Table 1. Comparison of Selected Processes:

Parameter	**Nickel**	**Electroless Nickel**	**NiP & NiCoP (Electrolytic)**
Plating Temp ºC	**38 – 50**	**82 – 90**	**40 – 60**
Control Method	**Soluble Anode**	**Chemical Replenish**	**Soluble Anode**
Yield (0.2%) (MPa)	**500**	**See UTS**	**See UTS**
MicroYield (MPa)	**70**	**500 +**	**830 +**
UTS Max (MPa)	**800**	**850**	**1800 – 2150**
Specific Gravity	**8.9**	**7.8 – 8.0**	**7.8 – 8.0**
Stress Control (Real Time)	**Yes**	**No**	**Yes**
Hardness (Rockwell C)	**22 – 24**	**48 – 52**	**48 – 52**
Diamond Machining	**No**	**Yes**	**Yes**
Thick Deposits	**Yes**	**No**	**Yes**

From these material 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 should make 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 and maintenance is required.

2.0 Control Mechanism for NiP Alloy Electroplating

Three kinetic processes prevail in the case of plating the NiP 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, beyond this the phosphorus content falls off below the desired 12% and internal stress increases.

The phosphorus deposition rate is limited by the reaction kinetics. At a given temperature 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 or phosphorous acid in solution is above 20 grams/liter, the phosphorus in the deposit is generally above 10% by weight 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 density as high as 150 mA/cm^2 has been achieved with suitable stress control. See Figure 1 for typical stress response.

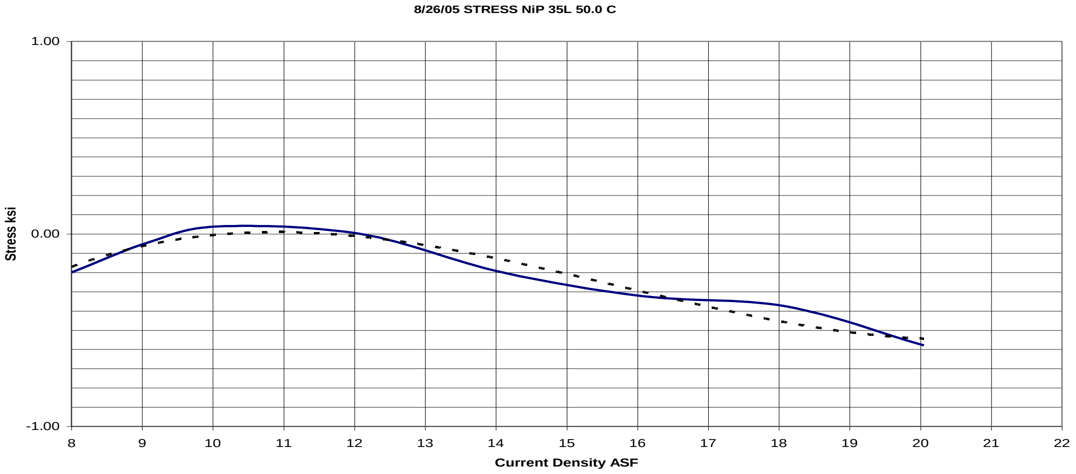

Figure 1 Stress vs. Current Density NiP 50 C

3.0 Control Mechanism for NiCoP Alloy Electroplating

If cobalt is used, at a fixed temperature and agitation, when the current density is increased from about 5 – 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 mA/cm^2 to 40 mA/cm^2, the stress behaves in a more conventional manner and increases. Thus the stress initially decreases, crossing zero at the low end at about 6-10 mA/cm^2, reaches a minimum at 10 – 12 mA/cm^2, then increases and crosses zero again at about 17 – 20 mA/cm^2. If vigorous agitation is applied, presumably approaching turbulent flow, i.e. Re > 2000, then the stress remains compressive beyond 30 mA/cm^2 at 45°C. The pH may be operated higher in the NiCoP than in the NiP solutions. 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. See Fig. 2.

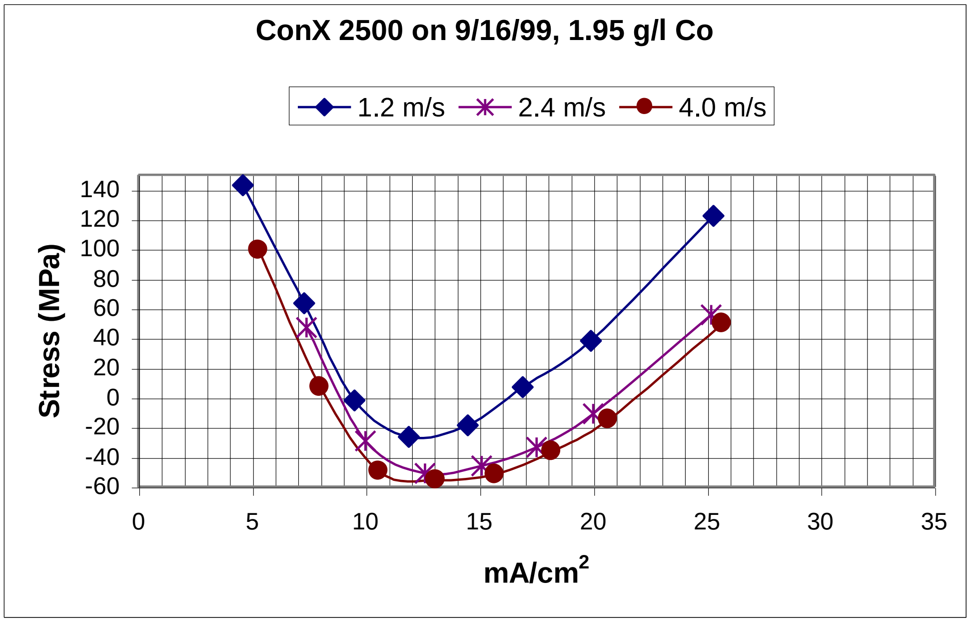

Figure 2. Typical Effect of Agitation on Stress for NiCoP

4.0 NiP and NiCoP Solution Operating Life

Two factors control the solution life span. First the electrolytic aging effect, primarily due to an imbalance of material removed by electrolysis versus what is required to maintain the process. Second are reactions that may occur outside of the required reduction of the nickel, phosphorus and cobalt by electrolysis. Hypophosphite initially used for the supply of phosphorus converts exponentially to orthphosphite 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, efficiency or properties. However after the hypophosphite has converted (@ 1 to 2 amp-hours/liter) the phosphorus falls off in the deposit. Beyond this point it appears that the phosphorus can be added, 1 to 1, as sodium hypophosphite or phosphorus acid to maintain a constant alloy [8].

Thus as the plating of a part consumes phosphorus at 11% of the weight of the deposit as a whole, this amount as phosphorus is replaced using sodium hypophosphite. 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 orthophosphite. A direct relationship for the extended life of the electrolytic process has not yet been established. This should be well beyond the typical 5 or 6 "metal turnovers" i.e. 30 grams/liter nickel consumed, since only 1/5 of the additional sodium and no additional phosphorous compounds accumulate with increased use of the electrolytic process. See Fig.3.

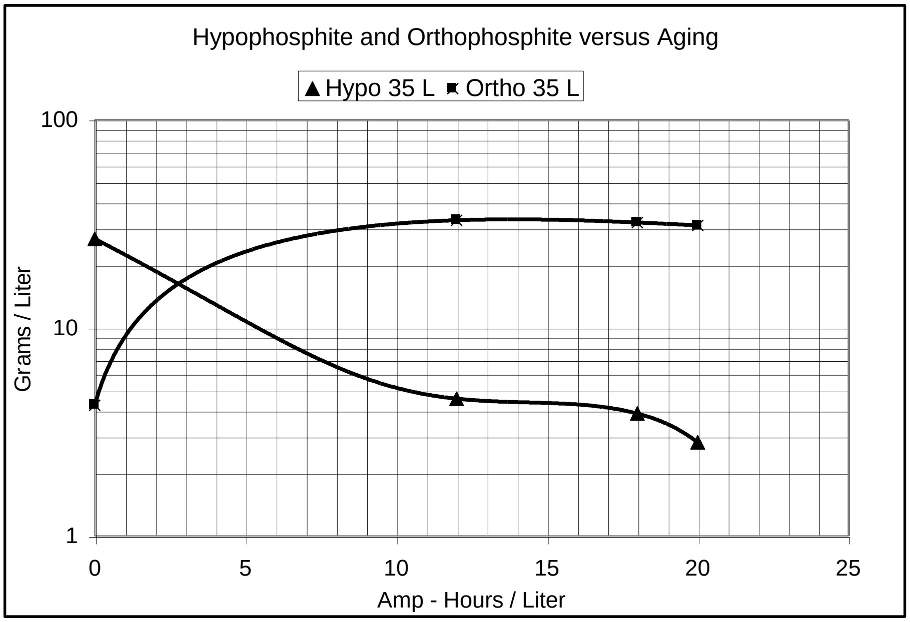

Figure 3. Oxidation of Hypophosphite

Small 35-liter 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 amp-hours/liter (equivalent to about 180 grams/liter as metal.) This is equivalent to about 6 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 twenty four months with no sign of degradation of the process. It was observed that the pH should be maintained at no more than 4.0 to avoid possible cobalt salt formation at the anodes. Additional metal chips are added to the anode baskets as they are consumed by the plating. Subsequently platinized titanium anodes were used to partially offset the increase in nickel and have been in use since and it has been shown that at least the equivalent of 100 metal turnovers is possible for the equivalent life of at least 15 electroless baths at 6 -8 turnovers of 6 g/l without refurbishment or replacement.

Samples for hardness and machining tests were electroplated more than 0.6 centimeter thick, and appear perfectly sound. One of a series of 4-liter test solutions of NiP operating at 60-65 degrees Centigrade (without cobalt) was producing sound deposits after 200 amp-hour/liter of operation with a nickel anode. See Figure 4, 5 for examples of heavy deposits obtained to1 centimeter thickness.

Figure 4 Electroplated NiP and NiCoP Samples Including 0.6 cm Thick Electroform

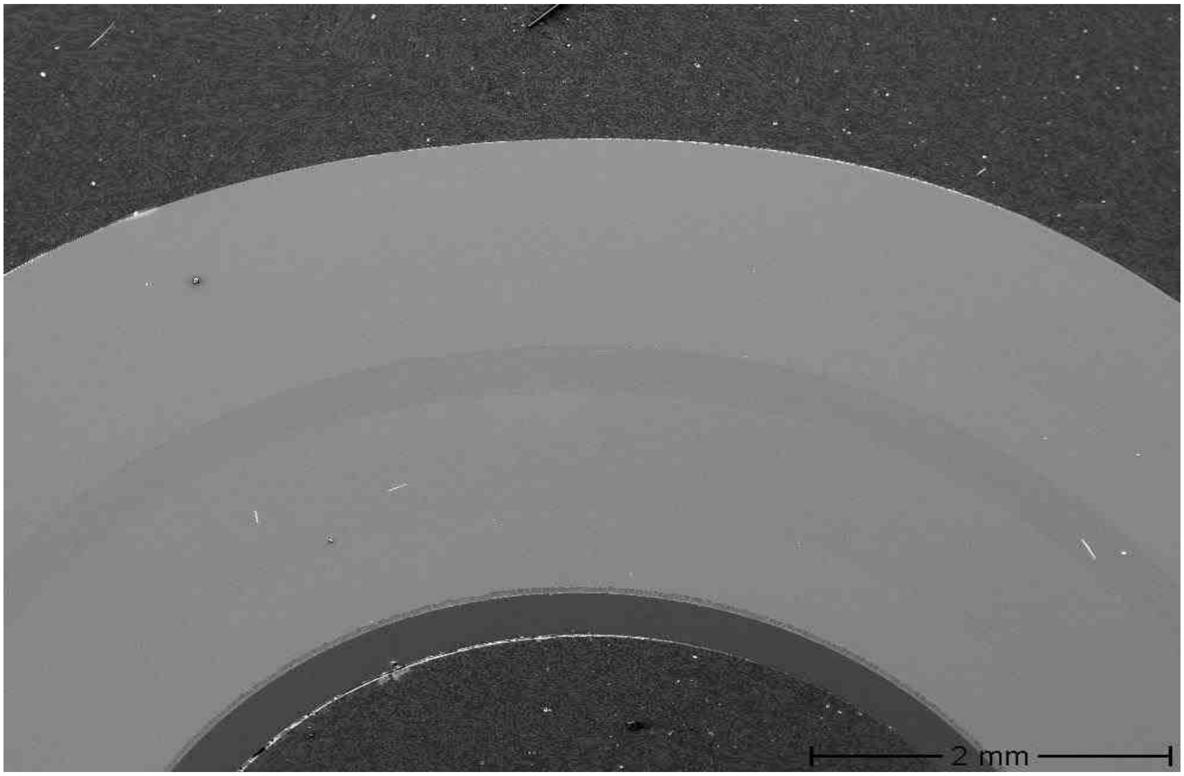

Figure 5 NiCoP Sample 1 cm thick electrodeposit

5.0 References

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