

ELECTRODEPOSITION OF HIGH QUALITY NICKEL PHOSPHOROUS ALLOYS FOR POLLUTION REDUCTION AND ENERGY CONSERVATION

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NASA and the University of Alabama in Huntsville have developed ecologically friendly, versatile nickel and nickel cobalt phosphorous electroplating processes. Solutions show excellent performance with high efficiency for vastly extended throughput. Properties include, clean, low temperature operation (40 - 60° C), high Faradaic efficiency, low stress and high hardness. A variety of alloy and plating speed options are easily achieved from the same chemistry using soluble anodes for metal replacement with only 25% of the phosphorous additions required for electroless nickel. Thick deposits are easily achieved unattended, for electroforming freestanding shapes without buildup of excess orthophosphate or stripping of equipment.

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1.0 Introduction:

1.1 Catalytic Deposition of Nickel Phosphorous Alloys

Historically, the deposition of nickel and phosphorus dates back to the 19th century when in 1844 Wurtz observed that nickel could be reduced from certain aqueous solutions by using hypophosphite anions. Typically only powders were obtained. By the early 20th century, Breteau and independently Roux were obtaining a bright deposit of nickel phosphorous. Their deposits, however would deposit spontaneously on the walls of the container as well as onto about anything in contact with the heated solution. Not until 1946, were the mechanisms well enough understood, to provide for suitable processes. Brenner and Riddel working for the National Bureau of Standards (Now NIST), developed processes and published papers describing proper conditions for sustained "electroless" or often "autocatalytic" plating of nickel phosphorous (Ni-P). The initial work by Brenner was with the electrolytic deposition of Ni-P. He observed that the Faradaic efficiency increased with the increase of temperature until at some point near boiling, the deposition rate exceeded 100% of predicted efficiency for pure nickel in the presence of hypophosphite ions. However the solutions were prone to spontaneous decomposition by solution phase reactions or at least solution containing particles would "bootstrap" the reaction by depositing nickel onto particles as they were created. ⁽¹⁾

For about ten years, the development of stable processes proceeded rapidly with the intention of eliminating the applied current in favor of more uniform plating over complex shapes achieved from the autocatalytic process. The processes have been studied extensively and have achieved very widespread use in the US as well as all major industrialized countries.

The principal benefits derived from electroless nickels (EN) are:

- 1) Uniform deposition over complex or recessed shapes
- 2) Good corrosion resistance in many media
- 3) May be machined with diamond tools for optical components
- 4) High phosphorous alloys are non-magnetic, useful in some applications
- 5) High hardness for wear resistance
- 6) Heat treatment improves hardness and restores ferromagnetism
- 7) Accepted specifications in place.

The principal objections to electroless nickel (EN) are:

- 1) Spontaneous decomposition still occurs all to frequently
- 2) EN processes consume about four to five times the phosphorous deposited
- 3) Operating temperature is very high, often near boiling water
- 4) Evaporation is high and misting of metal salts persists around equipment
- 5) Corrosion of equipment occurs if not specialty materials
- 6) Corrosion of test and monitoring equipment is high

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- 7) Continuous addition of metal, hypophosphite stabilizers, and pH control
- 8) Long plating times for thick deposits limit thickness achieved by most
- 9) Low plating rates for high phosphorous alloys
- 10) Short life of process without expensive recovery
- 11) High energy costs to maintain temperature and evaporation for additions
- 12) Safety requirements are more stringent than in most other nickel plating
- 13) Strict federal regulations applied in accordance to health and safety acts
- 14) Wastewater treatment and disposal often approaches initial solution costs
- 15) On-line purification to remove orthophosphite is expensive.

The regulatory rulings include, but may not be limited to the following:

- 1) Environmental Protection Agency (EPA)
- 2) Occupational Safety and Health Act (OSHA)
- 3) Clean Air Act (CAA)
- 4) Resource Conservation and Recovery Act (RCRA)
- 5) Comprehensive Environmental Response Compensation and Liability Act
- 6) (CERCLA)
- 7) Hazard Communication Standard (29 CFR 1910.1200)
- 8) Respiratory Protection Standard (29CFR 1910.134)
- 9) Local Standards for a given community
- 10) County Standards
- 11) State compliance
- 12) Internal safety and environmental standards
- 13) Individual response to the airborne fumes.
- 1.2 Electrolytic deposition of Nickel Phosphorous Alloys

Electrolytic deposition of the alloys of nickel with phosphorous as well as many other elements, dates to the 19th century as well. Suitable processes were hindered by poor material choices for construction of plating tanks and impurity of available chemicals. Thomas Edison and others studied the magnetic properties of nickel alloys and powders, obtained electrolytically, used in telephone microphones and receivers.

The deposition of a non-metal with a metal remained more of a novelty than practice until the work of Dr. Abner Brenner and his colleagues. Along with the advances in autocatalytic deposition of nickel phosphorous, he developed usable methods of depositing nickel phosphorous electrolytically. However the operating parameters were about as stringent as for the electroless processes. Instead of using a reducing agent such as hypophosphite, electrolytic deposition of NiP was obtained from acids such as phosphoric acid and phosphorous acids and nickel salts. The temperature for deposition was very high and the use of nickel anodes would lead to rapid build-up of metal in solution due to the spontaneous corrosion and the very low efficiency of the processes. The pH was lowered and the temperature and current density was

raised until the nickel deposition potential was near that of hydrogen and co-deposition of hydrogen, Ni and P occurred. This process will permit deposition of thick deposits without cracking under close control. The utility over electroless nickel is marginal due to the operational conditions and as such the "Brenner Electrolytic NiP Process" has not gained high popularity. Several later processes were introduced but due to the similarity in operating requirements to those of electroless nickel, have not gained popularity either.

More recently the use of ligands for shifting the potential of the nickel and phosphorous closer together have provided for more amenable NiP electrolytic processes. The benefits are essentially the inverse of the electrolytic detriments. The regulatory requirements remain the same for all plating pursuant to 40 CFR 413 and 40 CFR 433. Compliance is much more amenable to the lower operating temperature and ease of control for the new electrolytic processes.

2.0 Comparison of newer electrolytic NiP processes to prior electroless processes

The essential differences in the new electrolytic processes and the earlier work by Dr. Brenner that has prevailed for many years now are in the operating temperature and the efficiency. By reducing the temperature to below 60 C (140 F) it is possible to use conventional plating techniques as for most other electrolytic nickel plating operations.

	Nickel	Nickel-Cobal	t EN	Ni or NiCo 11%P
Plating Temp (°C)	38 - 50	38 - 50	82 - 90	43 - 55
Ni Control Method	Sol Anode	Sol Anode	Chemical Replenish	Sol Anode
Phosphorous control	NA	NA	Chem. Repl. 5:1	Chem. Repl. 1:1
Phosphorous analysis	NA	NA	Frequent Titration	Amp Hour or Wt.
Yield (0.2%) (kg.mm ²⁾	50	80	See UTS	See UTS
Microyield (kg/mm ²)	7.1	21	50 +	85 +
UTS Max (kg/mm ²)	80	150 - 200	86 - 100	180 - 215
Hardness (R-C)	22-24	45-50	48-52	48-52
Specific Gravity	8.9	8.9	7.8 - 8.0	7.8 - 8.0
Stress Control (Real Time	e) Yes	Yes	No	Yes
Diamond Machining	No	No	Yes	Yes
Machining (Steel, WC)	Yes Difficult	Yes Difficult	No	Yes Easily
Thick Deposits	Yes	Yes	No	Yes
Typical Rates (µm/Hr)	12 - 200	12 - 50	5 - 18	5 - 100
Metal Turnovers/recover	NA	NA	6 - 8	200 +
Spontaneous Deposition	No	No	Occasionally	No
Strip Equipment	No	No	Yes Periodically	No
Form Replicates	Yes	Yes	Very Difficult	Yes
Uniformity	Moderate	Good	Excellent	Very Good

Table 1. Comparison of some of nickel-plating parameters demonstrates these advantages:

2.1 Discussion:

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. The physical properties of electroless nickel are achieved with nearly the ease of regular electrolytic nickel plating with the electrolytic NiP process. This makes the new electrolytic nickel phosphorous processes attractive for many applications. Additional benefits in cost, no downtime, health & safety and pollution control add more benefits to the new processes. Facilities that commonly turn down electroless nickel are able to compete for some of the electroless nickel work.

One common misunderstanding is that since the uniformity of EN over irregular shapes is superior to electrolytic nickel plating, then electrolytic is not suitable. This is not the case however for the electrolytic NiP. We have noted that for many common shapes of pieces such as cylinders, flat disks, concave and convex shapes, we can achieve very satisfactory uniformity by simple shielding concepts. Furthermore for thinner deposits of $10 - 40 \mu m$ it is often not possible to differentiate the two. The conduction in the electrolytic NiP alloys is not limited to electron transport in the metal ions but is more like in a "high throw" copper or gold bath. The supporting electrolyte provides for a very good distribution of the field and as such the metal, with minimal effort. The solution conducts with as much as 0.8 S/cm conductivity. Electroless nickel is superior for deep recesses but again we have had very satisfactory results in this regard for most parts. For reasonable size part runs it is very economical to use a simple shield to produce uniform deposits much like in high throw copper sulfate solutions using low metal and high acid concentration. Software is available to assist with the shielding design. ⁽²⁾

2.2 Experience to date:

NASA Marshall Space Flight Center (MSFC) and the University of Alabama in Huntsville (UAH) have developed the NiP and NiCoP electroplating processes. We have received US patent 6,406,611, "Nickel cobalt phosphorous low stress plating" which describes the process for low stress plating of NiP and NiCoP at low temperature.

A considerable effort was invested in the endeavor since it was our goal to develop a process for producing ultra-high quality x-ray optics with superior strength and especially an exceptionally high precision elastic limit. Precise analytical methods were used to determine the material composition, the solution make-up and control and the properties of the deposited materials.

The process of electroforming nickel x-ray mirror shells from superpolished mandrels has been widely used. The recently launched XMM mission by the European Space Agency (ESA) is an excellent example, containing 174 such mirror shells of diameters ranging from 0.3 - 0.7 meters and with a thickness range of 0.47 - 1.07 mm. To continue to utilize this technique for the next generation of x-ray observatories, where larger collecting areas will be required within

the constraints of tight weight budgets, demands new alloys must be developed. This is so that the mirrors can withstand the large stresses imposed on very thin shells by the replication, handling and launch processes.

Towards this end, we began a development program in late 1997 to produce a high-strength alloy suitable for electroforming very thin high-resolution x-ray optics for the Constellation project. Requirements for this task are quite severe, not only must the electroformed deposit be very strong, it must also have very low residual stresses to prevent serious figure distortions in large thin-walled shells. Further, the processing must be done reasonably near room temperature, as large temperature changes will modify the figure of the mandrel. Also the environment must not be corrosive or otherwise damaging to the mandrel during the processing. The results of the development program are presented elsewhere ^(3,4), showing the evolution of the plating processes and materials through to the present "glassy" nickel phosphorous and low stress nickel cobalt alloys.

The maximum stress in the shell during this critical operation is related to the thickness of the deposit and the adhesion of the gold interfacial layer to the passivated mandrel surface. This stress and the subsequent stresses due to handling must not plastically deform the shell.

The figure of merit of the material for the lightweight electroformed optic is the microyield (permanent yield of 1 ppm), referred to also as the Precision Elastic Limit (PEL) with a tolerance on the acceptable deformation. This is the measure of the permanent strain, allowed for optics to be only a few microstrain units (parts per million), residual after an applied stress.

2.3 Internal Stress Considerations in X-ray Optics

While the internal (or intrinsic) stress does vary with plating conditions, it is possible to adjust the temperature, agitation and current density to optimize a particular nickel alloy chemistry for low stress over a reasonable range of current density. The internal stress of pure nickel can be controlled within certain limits using prior knowledge. Typically $\pm 5*10^3$ kPa is considered very good control for most applications. For the larger shells we must have control to about $\pm 5*10^2$ kPa. Note that the stress is manifested as bending stress and not typically uniaxial or biaxial tensile or compressive stress. For the alloys considered the control methods for the stress had to be developed.

In order to accurately and expediently observe the stress in the deposits we use three methods. First the use of an electronic monitor with a recorder or computer data acquisition is the primary instrument for data acquisition and also real-time control. In order to observe the effects of the plating variables on thick deposits, an arrangement with cylindrical rings was plated. Then the rings were cut to reveal the bending stresses by either opening or closing of the gap. The gap change of the ring was used to calculate the residual stress. This method was extended to evaluate the stress in the shells as well. For the deviation in a given shell due to internal stress, a long trace profilometer is used to correlate the figure of the shell to that of the

original mandrel. If the stress varies with current density and the current density varies over the part, then the stress varies over the part of course. This gradient stress must be held to an absolute minimum for the large thin shells. To control the uniformity of the deposit to the required precision, shielding of the electric field is required.

The deformation due to internal stress in the x-ray mirror can be approximated by segments of discontinuous hoop stresses along the length of the shell. This gives a modest overestimation since the stress is actually coupled and at least biaxial, but is very useful for determining the actual distortion. By knowing the stress at a given current density and also the plating rate for the given current density it is then possible to measure the thickness profile and estimate the stress profile and by these approximations, estimate the deformation. For the tensile case the circumference of the optic will tend to be less by the strain induced for relaxation of the stress using simple Hook's law principles. Likewise for the compressive case, the shell will tend to be larger in diameter. If the stress is uniform along the length of the optic (within small limits) the entire shell will tend to be only slightly larger or smaller overall, changing the focal point with respect to the end of the shell slightly. Finite element and more rigorous analysis show that there is also a longitudinal deformation due to the bending nature of the internal stresses. This stress increases the deformation slightly at the ends, if extreme.

The internal stress gradient along the length of the shell is a function of plating variables, particularly the current density and the agitation of the solution. A gradient of 0.2 kg/mm^2 distributed over half the length of the part will deform the optical path beyond use for the larger parts while perhaps remaining acceptable for the smaller sizes. It is imperative to maintain constant conditions on the current density and any variables affecting this gradient.

Hooks Law has the stress for any planar shape as;

Stress = $\sigma_x = E (\varepsilon_x + \mu \varepsilon_y)/(1 - \mu^2)$

Where E = The elastic modulus, epsilon is the strain in x and y and mu is the Poisson's ratio.

From this the Stress is the product of about 1.4 * Elastic Modulus * Strain.

The optical distortion is the change of Circumference / 2π due to the strain, measured as the change in radius for each increment considered. This then is the change in the angular accuracy of the shell over the length considered.

For a 0.5 meter diameter optic, the distortion becomes unacceptable for a stress gradient of about $0.4 \text{kg}/\text{mm}^2$ / meter. For the same stress in a smaller 0.05 meter diameter optic this may be acceptable.



Figure 1 Minimum shell thickness vs microyield of material



Permanent Micro Strain Versus Stress for Nickel, NiP & NiCoP

Figure 2. Precision Elastic Limit (PEL)

Precision Elastic Limit

A speckle interferrometric procedure and also a dual strain gauge method were used independently to determine the PEL of the different materials considered. In this process the microstrain was determined after loading a tensile test (ASTM E8) to a particular level and then returning to a fixed low starting point. This is known as a "ratchet" test and if the sample returns to virtually the same strain level then the microstrain is zero. However, as the load is incrementally increased and the sample is measured, the plastic deformation begins to appear for more ductile materials. For glassy materials such as ceramic or about any glass, the return from any load below fracture does not produce permanent deformation. Key to performance of a brittle material is the magnitude of the failure level. Most ceramic materials fail below about $8*10^5$ kPa. Glassy nickel has been deposited with about 2 to 3 times this ultimate strength.

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

The NiP plating process is unique to electroplating in many ways. The introduction of phosphorus into a nickel deposit is not new but it does represent an interesting aspect of electrochemical behavior. 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 phosphorus, nickel boron, tin nickel 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.

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.

Previous electroplated versions of nickel phosphorus have had strict limitations and have not replaced the electroless processes in any significant proportion. The former methods for electrodepositing nickel or cobalt phosphorus alloys required high temperature plating to control the internal stress of the deposit, and proceeded with very low efficiency. In addition, the pH of the past processes was very low (acid) making the solution very corrosive to base metals and supporting equipment. As such there were no soluble anodes used, requiring frequent addition of chemicals much like in the electroless processes. With the high temperature, low plating efficiency, corrosive solution and constant chemical additions required there has been little incentive to use the prior art electrolytic NiP process. An exception is that for the production of heavy deposits, the electrolytic processes have been used due to the decreased formation of solution phase precipitation, which frequently occurs in the electroless processes. This mandates frequent stripping of the electroless nickel process tanks and equipment.

The present NiP and NiCoP processes permits low stress operation as low as 45° C, with soluble anodes to limit maintenance to pH control and infrequent adjustments between plating runs similar to most other plating processes. The processes may be covered completely to

conserve energy and purified water. 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 within the past four years, to improved glassy metal properties wherein the best attributes of glass and metal are sought. In particular for free-standing shapes is the fact that the material must have exceptional microvield and low stress in order to sustain removal from the mandrel and additional handling steps when shells are of extremely low aspect ratio with respect to the ratio of diameter to thickness. At the same time, the strength must be very high compared to glass, to allow for handing and manufacturing steps. There is no appreciable permanent strain or hysteresis in the material up to about 8×10^5 kPa. It appears that under optimum conditions, the material can be loaded to near failure at as much as $1.8*10^6$ kPa without significant permanent deformation compared to the engineering yield strength defined as 2000 ppm yield. represents an incredible improvement in yield strength properties over most metal forming processes and all other known electroforming processes. Conventional nickel plated from a standard sulfamate solution shows the first microvielding at less than $6*10^4$ kPa. Thus more than one order of magnitude improvement has been realized in PEL.

A 2500-liter process was used for about three years. The process was in use since 1999 until completion of the contract in 2002. Scaling up to plating of large mirrors (1.1 square meter) from small 35-liter process solutions has been accomplished. 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 deposition of a very uniform deposit into deep recesses or uniformity around sharp corners, the electroless processes will prevail.

2.5 Control Mechanism for NiCoP Alloy Electroplating

Three kinetic processes prevail in the case of plating the NiCoP alloy. The nickel is in sufficient supply to reduce according to Faraday's Law throughout the range of interest. The cobalt is added at about 5 to 10 % of the nickel concentration and mandates a lower limiting current density. The presence of the phosphorus will inhibit the cobalt deposition at low current however, and acts as a self-stabilizing control. Thus increased pH along with a complexant reduces the amount of cobalt in the deposit for a given set of conditions. Increased current density actually increases the cobalt from about 4 mA/cm² up to about 20 mA/cm² where the cobalt reaches about the same concentration as the nickel in the alloy. Beyond this the phosphorus content falls off 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 cobalt. Measured values of phosphorus in the deposit show that as long as the sodium hypophosphite in solution is above 1.5 or 2.0 grams/liter, the phosphorus in the deposit is generally above 11% 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. Thus at higher agitation levels the current density may be increased while maintaining low stress.

At a fixed temperature and agitation, when the current density is increased, the very interesting and unusual effect is that from the lower acceptable current density from about $5 - 12 \text{ mA/cm}^2$ the stress decreases while the cobalt 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. From this point on 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/cm², reaches a minimum at $10 - 12 \text{ mA/cm}^2$, then increases and crosses zero again at about $17 - 20 \text{ mA/cm}^2$. If vigorous agitation is applied, presumably approaching turbulent flow, i.e. Re > 2000, then the stress remains compressive beyond 30 mA/cm² at 45°C. Throughout the entire range the stress is acceptable for all but the most critical operations such as freestanding optics wherein the zero stress point is sought. See figure (3). Figure (4) demonstrates the uniformity of the alloy in a thick deposit. Figure (5) shows the stress in a cobalt free process vs. temperature.



Figure 3

Effect of agitation on stress for NiCoP



Figure 4. EDX microprobe of alloy in cross section



Figure 5. Stress in NiP vs Temperature (65 C Red, 55 C Black, 45 C Blue)

2.6 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. Secondly 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 less the electrolytically deposited phosphorus in the alloy. It is extremely 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 (ca 1 to 2 amp-hours/liter) the phosphorus falls off slightly in the deposit. Beyond this point it appears that the phosphorus can be maintained as sodium hypophosphite

The non-cobalt solution can be operated similarly with a small amount of sodium hypophosphite. Maintenance of either is simplified by either amp-hour tally or by the weight of the deposit to provide the amount of phosphorous added.

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 hypophosphite is typically five times the equivalent deposited phosphorus. This consumption leads to an early saturation of an electroless nickel bath with orthophosphate. The appropriate method for controlling the concentration of orthophosphate is to simply add it to a new solution. This is extremely interesting since this would be exactly counter to what would be good practice in an electroless process. This strongly suggests that a spent electroless bath made from the same chemistry could be converted to essentially a "new" electrolytic bath.

A direct relationship for the extended life of the electrolytic process has not yet been established. This is 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. More than 200 equivalent "turnovers" have been accomplished from test solutions with no sign of precipitation. See Fig. 6.



Figure 6. Oxidation of Hypophosphite

3.0 Examples:

NiCoP

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/l 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. A large (2500 liter) process was used in place for about three years without any downtime.

NiP

The nickel phosphorous solutions have the phosphorus maintained at 1:1 addition to consumption. This was measured by using Capillary Zone Electrophoresis and amp hour considerations for comparison. The phosphorous is deposited at about the same rate so long as the maintenance is about 1:1. Electroless nickel requires about 4 to 5 addition to 1 consumed phosphorous equivalent by comparison and leads to rapid destruction of the solution by adding orthophosphite which causes undue stress and low plating rates in the electroless nickel phosphorous deposit. Many samples and prototypes were plated and the uniformity has been compared to high throw copper. Mandrels have been plated which have grooves for the gaskets of about 6 mm deep and 3 mm wide. The plating is observed to cover very uniformly within these grooves. The material is readily diamond machined.

Analysis is simplified for the electrolytic process as only amp hours or deposit weight need be recorded in order to adjust the phosphorous content. The pH is maintained about the same as normal nickel plating with acid instead of alkaline adjustments, so that no precipitation of NiOH takes place.



Figure 7. Mandrel placed into NiCoP Bath



Figure 8. Electroformed NiCoP x-ray mirror

4.0 Summary:

Nickel and nickel cobalt phosphorous alloys are now electroplated with much the same ease as pure nickel or nickel cobalt. The deposits have virtually the same properties as equivalent alloys of electroless deposits. The process requirements and environmental aspects are far less stringent than those for electroless (autocatalytic) EN processes. The lower temperature, 1:1 phosphorous consumption, extended life of the solution and comparable initial cost for solution will bring much relief to the metal deposition industry. The energy costs are reduced dramatically as are the continuing costs for chemicals, operation and maintenance. The extended life eliminates the need for frequent purification or disposal. The 2500 liter NiCoP process was fully covered and the tank insulated. Once the process was at a temperature of 43°C a 1000 watt 110 VAC heater and controller was used to maintain constant temperature. The duty cycle was about 0.8 or about 880 watts. By comparison an electroless nickel process of 250 liters was operated at 88°C with the top open to permit enough evaporation for additions and required 3kw heaters at a duty cycle of about 0.8 or about 2400 watts. Also the EN process required copious ventilation while the electrolytic process was operated with only the ongoing room ventilation. The electroless process was used to produce 0.25 mm thick deposits and required constant attention either by operator or controller. Similar NiCoP and NiP processes have been left unattended for days at a time producing deposits as thick as 0.6 cm with no problems.

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