ELECTRODEPOSITION OF LOW STRESS NICKEL PHOSPHOROUS ALLOYS FOR PRECISION COMPONENT FABRICATION

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ABSTRACT

Nickel alloys are favored for electroforming precision components. Nickel phosphorous and nickel cobalt phosphorous are studied in this work. A completely new and innovative electrolytic process eliminates the fumes present in electroless processes and is suitable for electroforming nickel phosphorous and nickel cobalt phosphorous alloys to any desirable thickness, using soluble anodes, without stripping of tanks. Solutions show excellent performance for extended throughput. Properties include, cleaner low temperature operation (40 - 45° C), high Faradaic efficiency, low stress, Rockwell C 52 - 54 hardness and as much as 2000 N/mm^2 tensile strength. Performance is compared to nickel and nickel cobalt electroforming.

Keywords:

x-ray optics, electroformed optics, nickel alloy deposits, glassy nickel electroforms, electronic hydrodynamic stress monitor

Acknowledgments:

Introduction

In order to meet the goals of advanced space x-ray optical component fabrication, the use of new technology materials and methods of forming x-ray mirrors are being investigated. The mirrors are of the Wolter II design, that is a thin, nearly cylindrical shell with the optical surface on the inside. Future programs, however, demand much greater collecting areas achieved by nesting large numbers of successively larger shells. This in turn necessitates much lighter mirror shells to stay within cost limits and launch vehicle capabilities.

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.

It is required that the internal surface finish be nearly atomically smooth at about 1 – 4 Å rms and that the longitudinal and circularity form be extremely precise, on the order of one or two microns/meter. Further, the processing must be done reasonably near room temperature, as large temperature changes may alter the figure of the mandrel. In addition, the environment must not be corrosive or otherwise damaging to the mandrel during the processing.

The electrodeposited alloys of choice to date for this study are nickel cobalt phosphorus of about 16-18% Co: 9-11% P, balance nickel by weight, and nickel cobalt, 20-25% Co: balance Ni with traces of carbon and sulfur. The ratios may vary somewhat without serious consequence. These alloys have very high strength, with high plastic onset. These materials are also very hard. The phosphorous containing alloy can be readily machined with diamond

or other hard tools. Also the density of this alloy is about 10% lower than pure nickel, or nickel cobalt. Pure nickel electroform properties are compared here to demonstrate the improved qualities of the alloys. The results of the development program are presented.

High-Resolution Replicated Optics Require Advances in Adhesion Control and Shell Materials

Three dominant issues regarding deformation must be satisfied.

1) Internal stress in the deposited shell must be extremely low and uniform.
2) Adhesion must be minimized.
3) Material must be able to resist deformation due to applied stresses imparted during the separation and other stages of fabrication.

The relatively high density of nickel (8.9 g/cm^3) means that replicated shells must be extremely thin if they are to be light weight. While thin shells can be supported for handling and for testing with some difficulty, the most challenging aspect is to produce mirrors that are not deformed in the fabrication process. The deposition process will typically produce internal stress in the material as stored energy described elsewhere. During the separation of the electroformed shell from the mandrel, large enough stresses can be imposed on the mirror shell to cause plastic deformation. The separation stresses in the thin shells are dependent upon the level of adhesion of the mandrel to the shell and on the shell thickness. Therefore, the shell material must have a high yield strength and very low ductility.

For example the mirrors (shells) for the planned Constellation–X mission are to be 1/6 of the weight of presently electroformed shells made of pure nickel by the European Space Agency for the XMM and ABRIXUS missions.

To address these needs, shell technology development at MSFC has concentrated on reducing the internal stress, reducing the shell adhesion by suitable mandrel surface treatments and increasing the yield strength of the electroformed nickel through various alloying processes.

Electroformed Precision Optics

In order to fabricate the shell it is required to deposit the material onto a very highly polished substrate. This mandrel is made as follows:

1) Machine aluminum mandrel
2) Coat with electroless nickel phosphorus
3) Diamond machine to the final form and figure
4) Polish to the required optical finish
5) Passivate by an oxidation process
6) Evaporate gold to about 1000 Å.

The gold is deliberately very poorly bonded to the mandrel. The shell deposit is then applied with high adherence to the gold. The temperature of the mandrel and shell is lowered with LN2 until the difference in the thermal expansion separates the shell from the mandrel. The mandrel is then cleaned, inspected and returned to plating.

Internal Stress Considerations in X-ray Optics

The internal (or intrinsic) stress varies with plating conditions. It is possible to adjust the current density, temperature, and agitation to optimize a particular chemistry for low stress over a reasonable range of current density for the processes studied. The internal stress of pure nickel can be controlled within certain limits using prior knowledge. Typically ± 5 MPa is considered very good control for most applications. For the larger shells we must have control to about ± 0.5 MPa. 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. This approach has been extended to include variable flow input and is used to measure the hydrodynamic effect of the transport phenomena on internal stress. 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 in the stress must be held to an absolute minimum for the large thin shells of concern.

To control the uniformity of the deposit, shielding of the electric field is required. A commercial electrochemical boundary element program [T] was used to develop the shielding for each configuration of mandrel and process configuration tested. This has helped to achieve a thickness uniformity of the electrodeposited shell to within a few percentile. This in turn provides nearly uniform stress along the optical profile if uniform agitation of the plating solution to part surface, is also achieved.

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. Analysis shows 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.

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The internal stress gradient along the length of the shell is a function of plating variables, particularly in real time, the current density and the agitation of the solution. A gradient of 0.75 MPa 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.

Plating Stress and Hooks Law:

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

Where E = The elastic modulus, epsilon is the strain in x and y and μ 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 causes the change in the angular accuracy of the shell over the length considered. See Figure 1.

Separation Stress:

The strain applied to the shell during the separation process is related to the (CTE Aluminum – CTE Shell) * Delta Temperature. The stress is then found from geometric and Hook's law principles from the applied biaxial strain. The strain is assumed biaxial due to the thin shell. Since the shell is in compression for this operation, any permanent deformation would be in the form of buckling. It is found that about 25 MPa is applied for each 10° C drop in temperature. The stress applied is a function of shell thickness with the thinner shells subjected to more stress in order to overcome the adhesion. Very large stresses can be imparted in thin materials by even a modest amount of adhesion. For example, a 0.25-mm-thick shell would experience a stress of around 10^2 MPa when being thermally released from a solid mandrel at a low adhesion of 7 10^5 Pa, independent of diameter. To achieve stable and low adhesion, we have experimented with many types of surface treatments and coatings these

past few years, all designed to give low adhesion in a uniform and controlled manner without degrading the mandrel's superpolished surface. The most promising of these approaches, and the one we are currently using, results from applying a metal-oxide coating immediately prior to gold-plating the mandrel. Tests with polished flats (5 A rms surface) showed no measurable (<1A) increase in surface roughness, and test separations confirmed low uniform gold adhesion at the desired 7 10^5 Pa level.

At this level of adhesion, the stress in our example 0.25-mm thick shell would be around 10^8 Pa - comfortably below the yield strength of ordinary nickel (~4*10^8 Pa). However, this yield strength represents a permanent strain of 2000 parts per million (ppm). Of concern here, is a permanent change at the parts per million level, termed microyield, or precision elastic limit (PEL) and in pure nickel this is evident at loading significantly below the yield stress.

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 at sufficiently low temperature. 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

The UAH speckle interferometry system developed by Dr. Vikram was used for measuring the microyield of candidate electroplated test samples. The technique uses laser speckle interferometry to record changes in a sample's length after a load has

been applied and then released. Gradually increasing the applied load generates a set of data showing permanent strain as a function of applied stress. Performing these tests on pure demonstrate that the above-quoted stress of 10^8 Pa would produce a permanent (and unacceptable) strain at the level of 70 ppm.

Clearly, pure nickel is not a viable material if very-light-weight, and hence very-thin, optics are required. We therefore developed low-temperature, low-stress plating processes for much higher strength nickel-based materials. Pure nickel, with the addition of certain organic compounds to give much finer grain structure, and nickel/cobalt alloys, were all found to have microyields two to three times higher than the pure nickel. Nickel phosphorous and nickel cobalt phosphorous demonstrate "glassy" behavior. Although an electronic conducting metal, this material shows little evidence of crystalline structure and behaves much more like a ceramic, exhibiting essentially no ductility when stressed at room temperature. See figure 2.

We have put considerable effort into developing and understanding this material, which has an ultimate tensile strength of $\sim 2*10^9$ Pa and a PEL of *at least* 5.10^8 Pa at room temperature for moderate time, which is the limit of our test. Due to its glass-like behavior, the microyield may well approach the ultimate tensile strength - at which point the metal shatters, glass-like, into many tiny pieces. Figure 2, curve-5, shows the microyield data obtained for our new material. The limiting resolution of the test method, due to sample flexing under load, is between 5 and 10 ppm, so curve-5 is consistent with *no permanent strain* under the experimental conditions. Use of the glassy nickel material will permit much thinner shells to be plated, down to thicknesses of 0.15 mm, if cryogenic separation temperatures are used. Use at higher than room temperature will require more study.

Electroformed Nickel Alloys

Numerous electrodeposited alloys including composites of nickel with various ceramic or other powders incorporated (electrocomposites) have been reported with improved mechanical properties over pure nickel. For almost as long as nickel has been used for forming freestanding shapes, the search for improved properties has been pursued. Notably, improvements have been well established by the use of cobalt as an alloying constituent. Also the addition of organic additives has led to control of the stress and improved hardness. The hardness is a first measure, in most materials, of the yield properties.

Nickel Alloy Considerations

Our first attempts at improving the material properties were centered on nickel cobalt and organic additives for the nickel or nickel cobalt. By adding a small amount of cobalt to a highly concentrated commercial nickel sulfamate solution (3% of the nickel total) about 15% to 30 % cobalt will be obtained in the deposit. This in turn increases the internal stress to an unacceptable level for the present needs. Therefore, the addition of organic additives to the nickel cobalt was optimized to balance the stress over a wide range of current density, providing a harder, stronger deposit with significantly improved PEL. This approach has permitted the development of very uniformly low stress alloy plating with significantly improved PEL.

Addition of the organic additives to the nickel alone required that some form of stress offset in the opposite (tensile) direction be used since the use of the common "hardeners" imparts a compressive stress value. For this, the addition of several ions other than cobalt were made in small amounts. Chloride, iron, zinc, manganese and lead were tested one at a time. Typically the stress could be offset however the offset was such that the stress versus current density was very sensitive due to the differences in the potential of preferred reduction of nickel with respect to each ion tested. This in turn creates problems for the fabrication process since it is difficult to control the current density to be absolutely uniform over the x-ray mandrel while plating. As such cobalt was used as the choice of alloying metals due to the similarities with nickel in deposition properties and the uniform stress vs. current density achieved with the other additives. A third alloy approach was for the refinement of nickel phosphorus

(NiP) or other "glassy" nickel alloy deposition at low temperature and with controlled low stress.

Combined Property Requirements:

Therefore the limitation on the thickness of the shells is related to the adhesion and the first onset of yield of the shell material. This in turn dictates a high PEL for the material in order to assure no distortion after separation.

The interfacial surface tension is given by:

ΔT $(\alpha_{Al} - \alpha_{Ni})$ * E_{Ni}* Thickness Shell = Applied Surface Tension along an imaginary line of unit length. Omitting detail on the thickness of the aluminum mandrel and the thickness of the electroless coating on the mandrel, the radial adhesion stress is:

ΔT $(\alpha_{Al} - \alpha_{Ni})$ * R_1 *E_{Ni} $/((R_1^{2})$ * $((1/\text{thickness}) - \mu/(2*\text{thickness}))) = \sigma$ Adhesion

And the hoop stress is approximated by:
σ Adhesion * $R_1 /$ thickness = σ Hoop

From which the stress in the shell is approximately:
$\text{SQRT}(\sigma \text{ Hoop}^{2} + \sigma \text{ Adhesion}^{2})$

Figure 3 is a family of curves showing the relationship of the minimum thickness of a given cylindrical shell versus the accepted PEL for different adhesion levels. Note that the adhesion is expressed in terms of surface tension in this chart.

Electroformed Nickel and Nickel Cobalt Phosphorus (NiP or NiCoP) Plating Process

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 some-

times 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. This frequently occurs in the electroless processes, mandating frequent stripping of the process tanks and equipment.

The present Constellation-X NiCoP process permits low stress operation at low temperature, 45° C, with soluble anodes to limit maintenance to pH control and infrequent adjustments between plating runs similar to most other plating processes. Perhaps the most significant advantage of the new process for

this or other optical applications is the real-time 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 within the past two years, to improved glassy metal properties wherein the best attributes of glass and metal are sought. In particular for this application is the fact that the material must have exceptionally low microyield at room temperature or below. This is 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 this material up to about $8*10^5$ kPa at room temperature. 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. This 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 microyielding at less than $6*10^4$ kPa. Thus more than one order of magnitude improvement has been realized in PEL.

The NiCoP or NiP electrolytic processes appear to 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 and has been demonstrated.

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.

From this 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. For cases requiring deposition of a very uniform deposit into deep recesses, the electroless processes will prevail.

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/cm^2 up to about 20 mA/cm^2 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 and higher agitation. 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 while reducing the phosphorous concentration.

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 $5 - 12$ 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/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. 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 4.

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 charge transfer balance for reduction of the nickel, phosphorus and cobalt by electrolysis.

Hypophosphite initially used for the supply of phosphorus converts exponentially to orthophosphite 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 in the deposit. Beyond this point the phosphorus can be added as sodium hypophosphite. 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 orthophosphite. See Fig. 5.

To date small 35-liter nickel cobalt phosphorus solutions prepared for testing have been operated with 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. No solution phase precipitation has been observed while plating 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 without cobalt operated at 60 - 65 degrees Centigrade was producing sound deposits after 200 amp-hour/liter of operation with a nickel anode.

The chemistry of the 2500-liter process solution used to form the large mirrors, appears to be quite stable and has not given indication of deleterious changes. The electrolysis raised the nickel slightly, converted a portion of the initial hypophosphite to orthophosphite, and required pH maintenance.

Summary:

All three of our fabrication goals appear to have been achieved, low internal plating stress, low adhesion and high microyield electroformed thin wall shells. Separation of thin shells has been accomplished without distortion from high forces due to high adhesion. Stable, low stress NiCo, NiP and NiCoP electroplating processes are established. Soluble anodes have been used for about twenty four months with no sign of degradation of the NiP and NiCoP process. Capillary electrophoresis has been used to maintain this process. Anode chips are replaced as they are consumed by the plating. See figures 6 and 7.
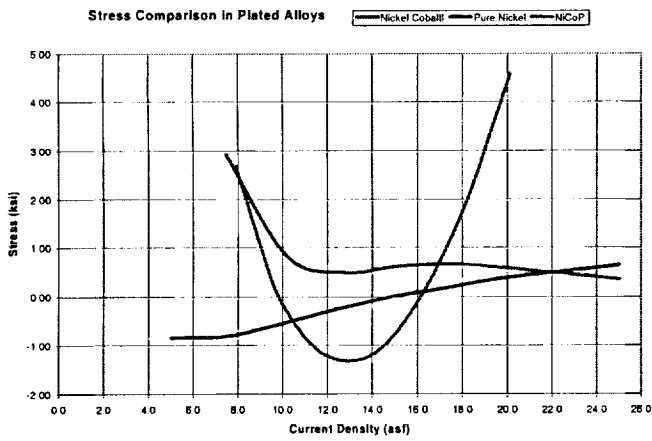
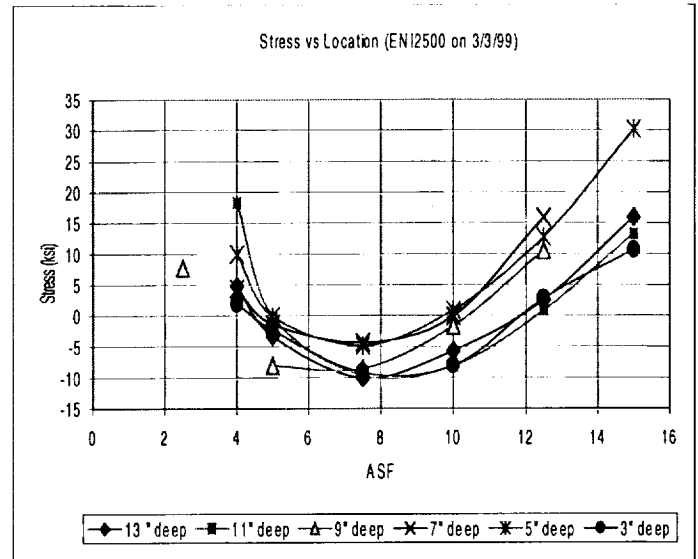**Figure 1**
Comparison of Internal Plating Stress

Fig 2
Elastic Behavior of Nickel Alloys

Figure 3
Minimum Shell Thickness Based on Micro-yield

Figure 4
Effect of Agitation on Stress for NiCoP

Figure 5
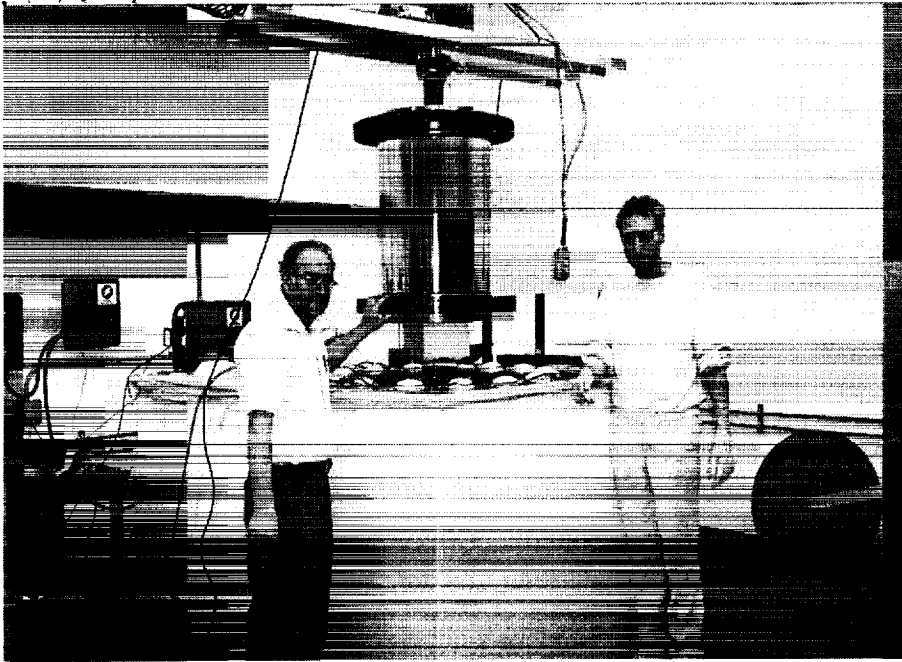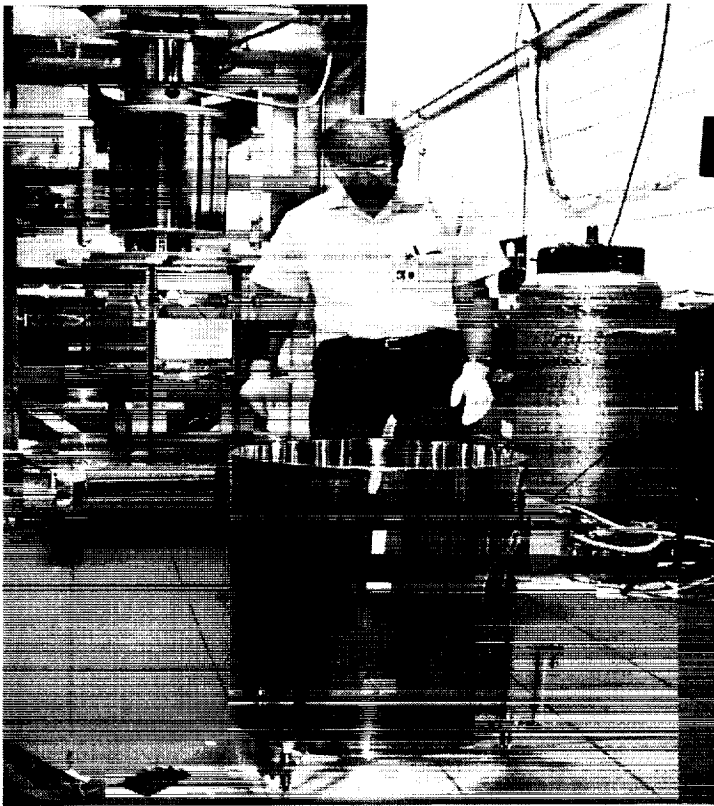**Oxidation of Hypophosphite**

Fig 6
50-cm Mandrel Above Glassy Metal Plating Bath

Figure 7
Glassy Nickel Shell, 0.25 Millimeter Thick