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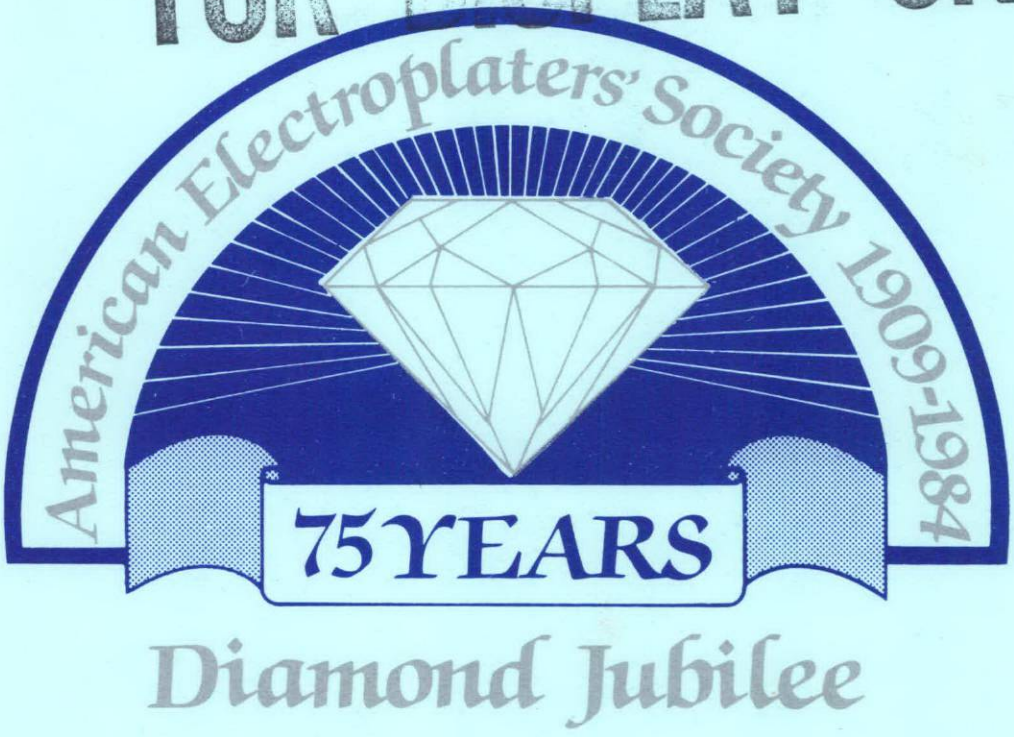

July 16-19, 1984
New York Hilton
New York, NY

Session H - Optics

AMERICAN ELECTROPLATERS' SOCIETY, INC.

71ST ANNUAL TECHNICAL CONFERENCE - NEW YORK CITY

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Techniques of Electroforming as Applied to Optical Replication

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TECHNIQUES OF ELECTROFORMING AS APPLIED TO OPTICAL REPLICATION

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Electroless Nickel in the Optics Industry

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ELECTROLESS NICKEL IN THE OPTICS INDUSTRY

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Electroless nickel is required for the producibility of many of the sophisticated components used in reflective optical systems. A major reason for using electroless nickel on a substrate material, which has a good strength to weight ratio, is the ease of optically surfacing the nickel. Nickel can be surfaced using standard polishing methods, diamond turning methods or a combination of both. Substrate materials most commonly used are as follows: aluminum, beryllium, stainless steel, brass, copper and kovar.

Some of the difficulties with electroless nickel plating are the thickness and environmental requirements that need to be met. Most specifications for optical components require .004 to .006" of void free plating and an adherence that would need to pass some very hostile environments. One such case is demonstrated as follows: a system consisting of three optical components made of beryllium, plated with .005" of nickel, allowing no voids on the optical surface of more than .002" diameter and numbering no more than two per ten inch diameter or allowing any cracks or lifting of the nickel plating. All of the afore-mentioned criteria had to be met after the plating was subjected to environmental testing of -470°F to +250°F numerous times.

Components are of various geometrical and mechanical shapes. Some component plating may require that only one surface be plated (the other surfaces are masked). Much emphasis is placed on cleanliness of the surface prior to masking because the masking must withstand temperatures of 200°F for a minimum of ten hours. Any leakage could be cause for rejection and replating of the part. The need for one surface plating is due to stresses that may be induced and the additional weight added to the component if plated all over.

Components that require nickel plating may be valued in the thousands of dollars prior to plating. One such prevalent component is a machined beryllium mirror, approximately 18" in diameter, worth $60,000.

Plating requirements have specifics that will add to the costs. One such specific was mentioned earlier - one side plated and masking of all other surfaces. Another is a stress free plating expressed as "low stress" plating. Low stress is the matching of the coefficients of expansion of the electroless nickel and the base material. One of the best matches to electroless nickel is on the material beryllium. This can be done by adjusting the phosphorous content to match thermal coefficients. Low stress nickel is used on mirrors that will be used for space-borne missions, satellite telescopes and cryogenic test systems. Needless to say, the cost of such a plating would be expensive. A high risk is also introduced because of the difficulty in plating beryllium and the cost of the beryllium substrate.

Another specific that adds to cost is the ability to have "void free" surfaces and pass environmental requirements as specified in the military

specifications. Aluminum with electroless nickel plating is a combination most commonly used for optical systems in the less severe environments. Such environments range from -70°F to +160°F. These systems are used in tank fire control systems, rifle and automatic weapons aiming systems and missile seeker systems utilizing infrared technology.

Electroless nickel is a precipitation hardened alloy of nickel and phosphorous and ranges from an as plated hardness of 50 Rockwell C to a heat treated hardness of 62 Rockwell C. Excessive hardening can cause a crystaline structure and should be avoided.

Electroless nickel containing approximately 1% copper can be applied to surfaces in a relatively magnetic free state.

Nickel is under compression on materials that have higher thermal coefficients of expansion when cooled. Materials that are relatively close or less in coefficients will put the nickel into tensile stress at lower temperatures creating cracking if certain precautions are not taken.

Nickel is also a good medium for other coatings including evaporative coatings such as silver, aluminum, evaporated gold and multi-layer coatings.

Higher degrees of success have been noted in the diamond turning of nickel compared to some of the substrate materials. Iron based materials, pressed materials such as beryllium and molybdenum, are not readily diamond turned to produce optical surfaces and need to be nickel plated.

More emphasis should be directed in the utilization of nickel as the molds for plastic lenses. A significant advantage is the smooth surface that is created when diamond turned and polished. Because of the amorphous condition of the nickel, very fine surfaces in the order of 5 to 10 angstroms have been achieved.

Because of it's corrosion resistance and it's versatility, high quality electroless nickel has found special applications in areas of high technology such as computer memory discs, high accuracy metal optics and molding tools. I feel that a large potential also exists in the new technology of robotics and could be a market of the future.

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Aspects of Electroless Nickel Plating on Molybdenum

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ASPECTS OF ELECTROLESS NICKEL PLATING ON MOLYBDENUM

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Operated by Union Carbide Corporation, Nuclear Division
for the U.S. Department of Energy
under contract W-7405 eng 26

ABSTRACT

A process for depositing an adherent coating of an electroless nickel-phosphorus alloy on molybdenum was developed at the Oak Ridge Gaseous Diffusion Plant at Oak Ridge. Tennessee. The required pretreatment processes included an anodic etch in a chromic acid-nitric acid solution, an anodic etch in a phosphonic acid solution, and an oxide stripping step in a chromic acid-nitric acid solution. Initiation of the electroless nickel plating was accomplished through a series of strikes in the nickel bath. Scale-up from laboratory parts to large components involved optimization of parameters such as pretreat time, current density, anode-to-cathode ratio and strike time.

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INTRODUCTION

The process described in this paper was the outgrowth of a need for the deposition of a nickel-phosphorus alloy on highly pure, large molybdenum components. A method was developed, for which a patent was granted,* which directly deposits an adherent coating of a nickel-phosphorus alloy on molybdenum. This was accomplished by means of a unique pretreatment process and subsequent conventional catalytic chemical plating, i.e., electroless nickel plating. The project required that several full-size molybdenum components, ranging in size from 1 to 6 ft^2 be coated with an electroless nickel-phosphorus alloy containing approximately 11- to 12-wt % phosphorus. In addition, each coating was to be 10-mils thick and be pit- and blemish-free. The 10-mil-thick coatings were eventually machined to meet the specified dimensional requirements. The principles of this patent are discussed along with the necessary modifications and adjustments required to apply the process to full-size components.

PROCESS DEVELOPMENT

Development studies were carried out on arc-cast and sintered molybdenum coupons approximately 4 $in.^2$ in surface area. Initially, conventional etching techniques, utilizing common laboratory reagents, were evaluated. The method of application varied from immersion to electroetching processes such as direct current, alternating current superimposed on direct current, and anodic-cathodic arrangements. Numerous solutions evaluated were successful at etching the molybdenum and exposing the underlying grain structure. However, subsequent plating with an electroless nickel-phosphorus alloy resulted in coatings that exhibited poor bond quality with the substrate.

It was felt that, although the etch treatments were exposing a fresh surface for bonding, the type of etch was inadequate for forming tenacious bonds between the electroless nickel coating and molybdenum substrate.

The method ultimately developed for producing adherent coatings of electroless nickel on molybdenum relied on successive anodic etches in acidic solutions. The steps of this pretreatment process are listed in Table 1 and include a chromic acid-nitric acid anodic etch, a phosphonic acid anodization, an oxide film removal step, and an electrostrike.

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*U.S. Patent 4,212,907, Pretreatment for Molybdenum or Molybdenum-Rich Alloy Articles to be Plated, Ralph R. Wright, Oak Ridge, Tennessee, July 15, 1980.

Table 1

PROCESS DEVELOPED FOR ELECTROLESS NICKEL PLATING OF MOLYBDENUM COUPONS

1. Degrease	
2. Scrub with pumice	
3. Rinse	
4. Anodic etch, 1 min, R.T.	
CrO_3	10 wt %
71% HNO_3	10 vol %
Direct current density of 1 amp/in.^{2}	
5. Rinse	
6. Anodization, 4 min, R.T.	
Phosphonic acid	25 vol %
Direct current density of 1 amp/in.^{2}	
7. Rinse	
8. Oxide film removal, 1 min, R.T.	
CrO_3	10 wt %
71% HNO_3	10 vol %
9. Rinse	
10. Electroless nickel plate:	
Electrostrike, 5 volts, 15 sec	
Plate to thickness	

Chromic Acid-Nitric Acid Anodic Etch

After a preliminary cleaning the molybdenum was anodically etched in a solution of 10-wt % chromic acid plus 10-vol % nitric acid (reagent grade). During this process (step 4 of Table 1) the usual surface films were removed, the surface finish was broken, and foreign materials such as mill slag were removed. The electron micrographs in Figures 1 and 2 depict the polished molybdenum surface prior to anodic treatment and the micrographs in Figures 3 and 4 show the effects of the anodic etch. The formation of a matte finish indicated that the proper degree of etching had been achieved. Good results were obtained with chromic acid concentrations ranging from 5 to 15 wt % and nitric acid concentrations ranging from 5 to 20 vol % at current densities between 0.5 and 1.5 amp/in^2.

Phosphonic Acid Anodization

The next step in the pretreatment process (step 6 of Table 1) was the anodization of the molybdenum surface in a solution of 25-wt % phosphonic acid. The key to this step was the preferential etching of the crystal boundaries while avoiding electropolishing. The formation of a uniform grey oxide film on the molybdenum surface indicated that sufficient etching had occurred. The micrographs in Figures 5 and 6 show the surface after anodization. It was felt that the etching of the crystal boundaries during this step was responsible for the subsequent formation of a tenacious bond between the nickel coating and molybdenum substrate. However, the application of too high a current density resulted in an electropolishing of the substrate. This was indicated by the formation of a dark blue-to-black oxide film. When this occurred, the nickel coating did not bond to the molybdenum substrate. Preferably, the current density was maintained between 0.5 and 1.5 amp/in.^{2} and the acid concentration was varied from 15 to 35 vol %.

Oxide Film Removal

Removal of the anodized film (step 8 of Table 1) was accomplished by immersion in a fresh solution consisting of 10- wt % chromic acid and 10-vol % nitric acid (reagent grade). A fresh solution was specified, rather than utilizing the solution from the initial anodic step, to prevent the redeposition of contaminants on the molybdenum surface. The stripping process required vigorous agitation for one min. Electron micrographs in Figures 7 and 8 reveal the fresh molybdenum surface with the grain boundaries properly etched.

Electrostrike

Finally, the electrodeposition of a minute layer of nickel, based on applied voltage, rendered the surface catalytic. With the rectifier on and set at 5 volts, the part was immersed in the nickel bath and an electrostrike was applied for 10 to 15 sec. When the surface was activated the deposition process became self-sustaining and the part was plated to the desired thickness. Figure 11 shows the cross-section of a 2.5-mil deposit of an electroless nickel-phosphorus alloy on molybdenum, as processed according to the method described in Table 1.

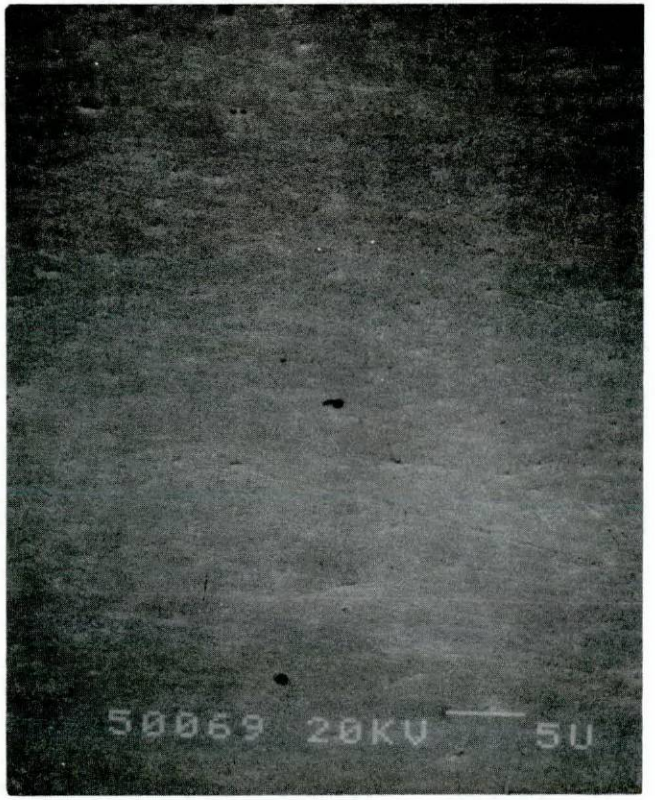

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Figure 1. Polished molybdenum surface.

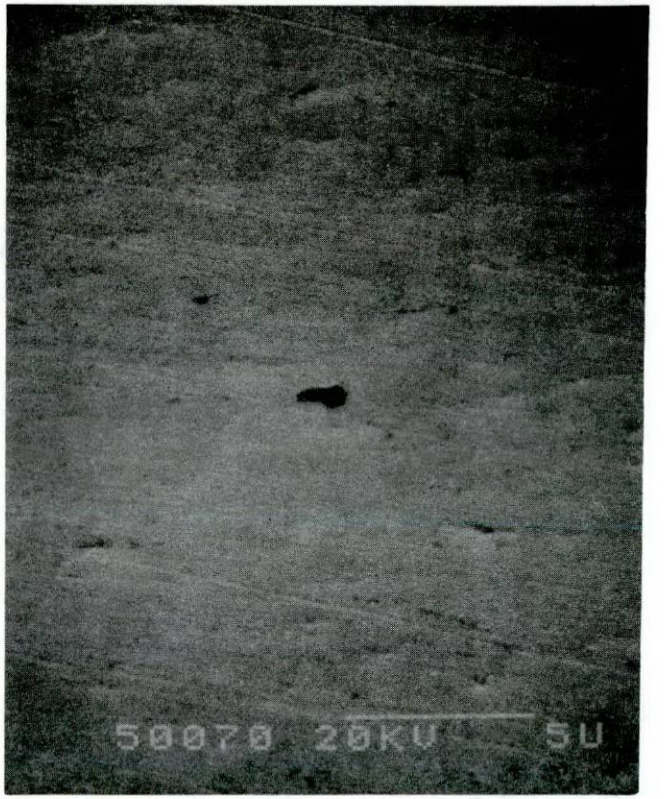

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Figure 2. Polished molybdenum surface.

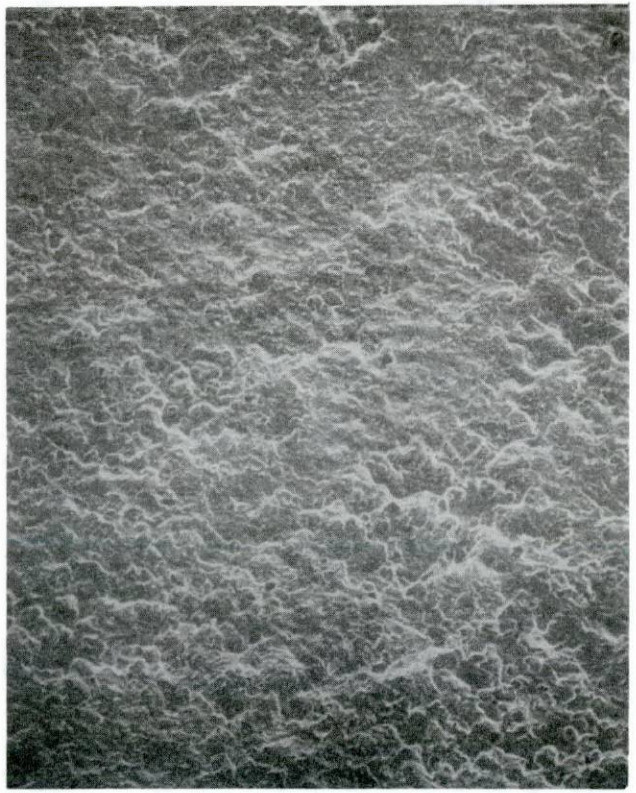

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Figure 3. Molybdenum surface after anodic etch in 10-wt % CrO_3 + 10-vol % HNO_3.

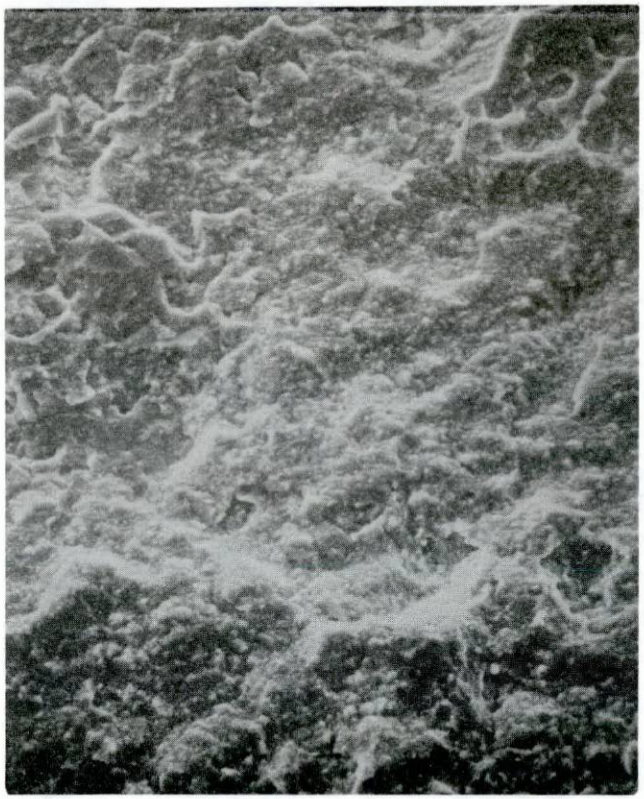

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Figure 4. Molybdenum surface after anodic etch in 10-wt % CrO_3 + 10-vol % HNO_3.



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Figure 5. Molybdenum surface after anodization in 25-vol % phosphonic acid

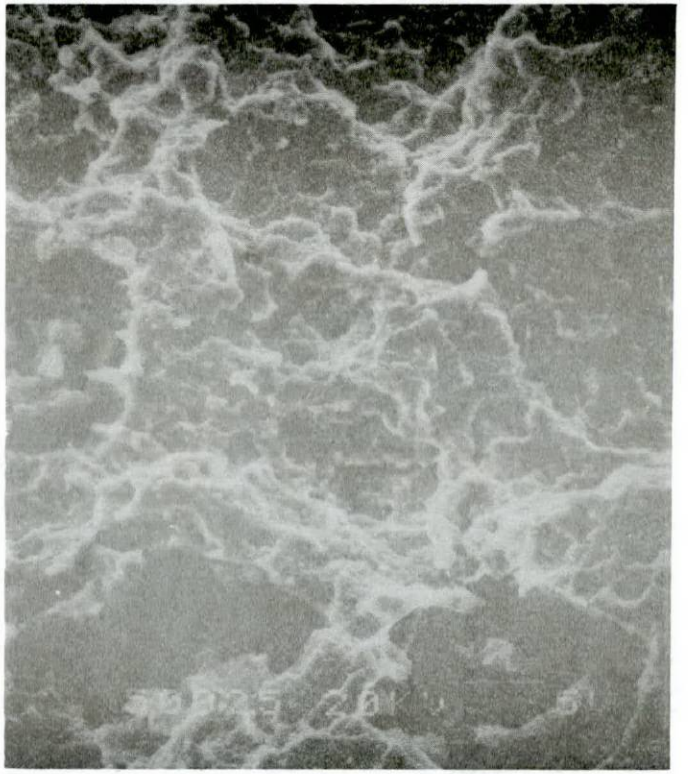

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Figure 6. Molybdenum surface after anodization in 25-vol % phosphonic acid.



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Figure 7. Molybdenum surface after oxide film removal.

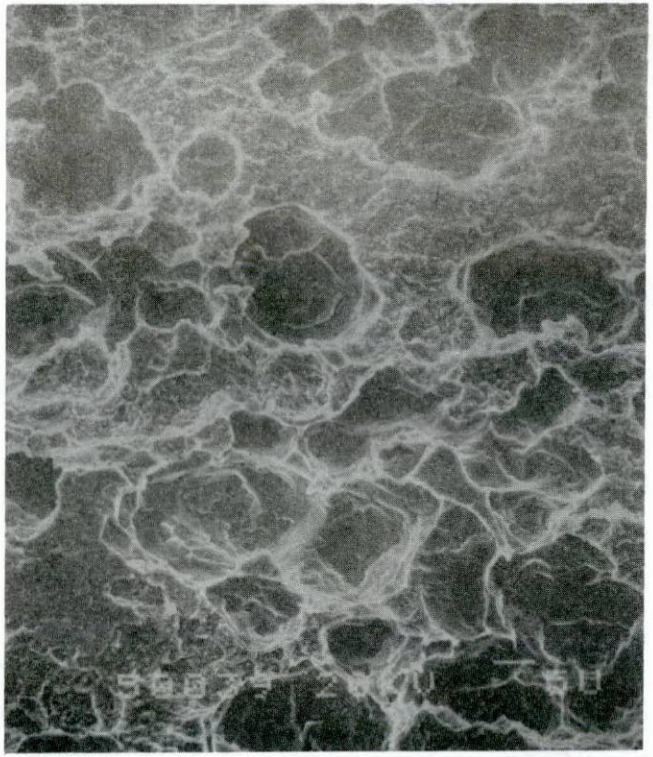

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Figure 8. Molybdenum surface after oxide film removal.

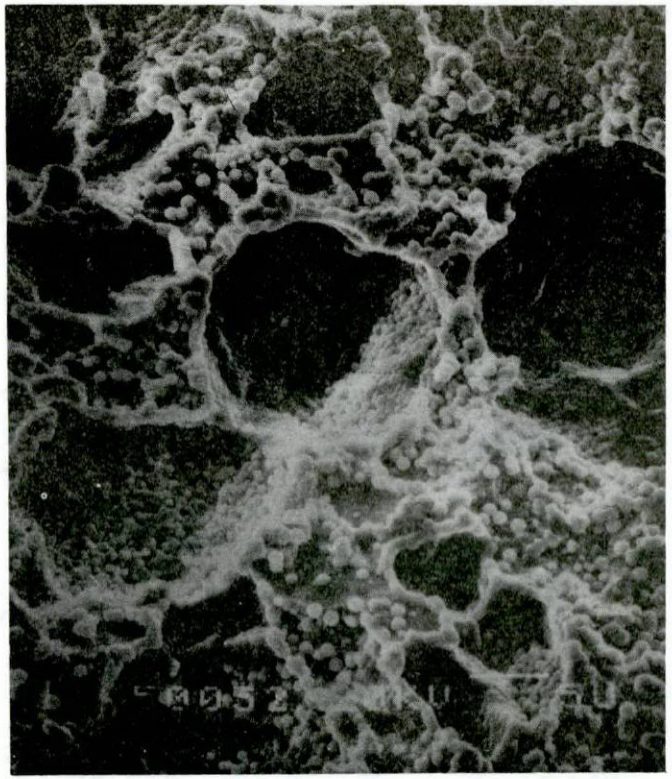

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Figure 9. Molybdenum surface after 10-sec electrostrike in electroless nickel bath.

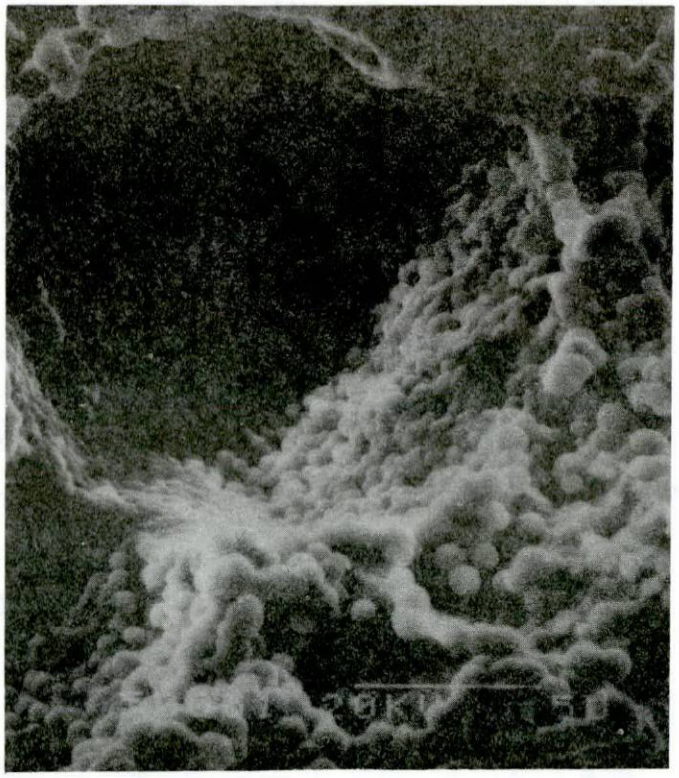

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Figure 10. Molybdenum surface after 10-sec electrostrike in electroless nickel bath.

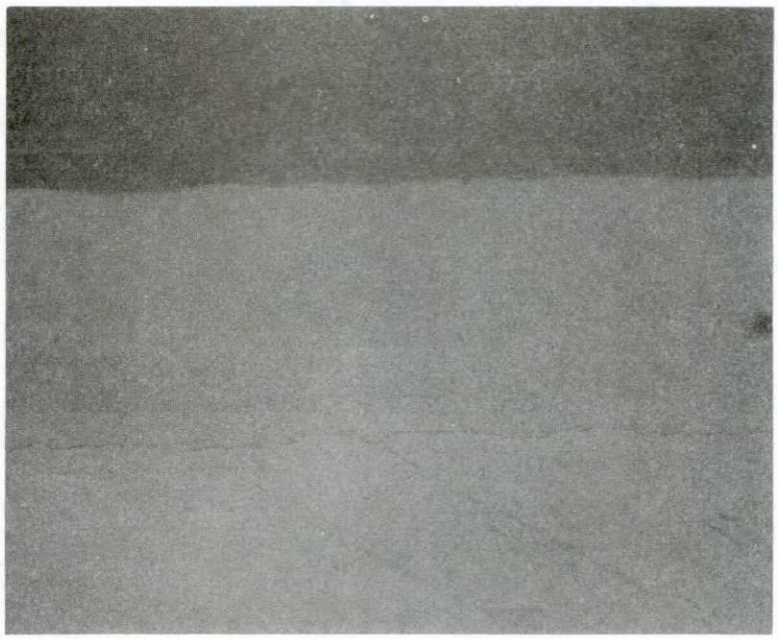

Figure 11. Cross-section of 2.5-mil electroless nickel-phosphorus alloy on molybdenum.

ADHESION EVALUATION

Plated molybdenum coupons with a 1-mil deposit of an electroless nickel-phosphorus alloy were evaluated for adhesion using the following methods:

- Punch Test - Indentations were made to the plated surface with sufficient force to penetrate the molybdenum. Examination of the nickel plating around the punch marks showed no evidence of flaking or lifting (Figure 12).

- Bend Test - The coated coupons were subjected to a 65°-bend at a 1-in. radius; the coupons fractured during the test. There was no evidence of cracking or lifting of the deposit from the substrate at the fractured surfaces of the coupon. The plating could not be chipped or flaked from the fracture surfaces (Figure 12).

PROCESS SCALE-UP

Scale-up in this project involved shifting from molybdenum coupons of relatively small surface area to large molybdenum components, ranging from 1 to 6 ft^2 in area. Application of the process as described in Table 1 to these large molybdenum components resulted in poor quality plating with areas displaying excessive pitting and a "shag bark" appearance (alternating streaks of adherent plating and bare molybdenum). It was apparent that the process and the parameters involved would have to be reevaluated. The lack of a full-size molybdenum component, suitable for testing, prevented the implementation of a full-scale development program. Instead, adjustments of key parameters were made during actual processing runs. Defective coatings from these runs were removed from the molybdenum components by machining. Table 2 lists the variables and equipment that required optimization in order to implement the process on large components.

Table 2

AREAS REQUIRING MODIFICATION FOR SCALE-UP TO LARGE MOLYBDENUM COMPONENTS

1. Anode design
2. Part fixturing
3. Current density and process time
4. Electroless nickel strike process
5. Agitation

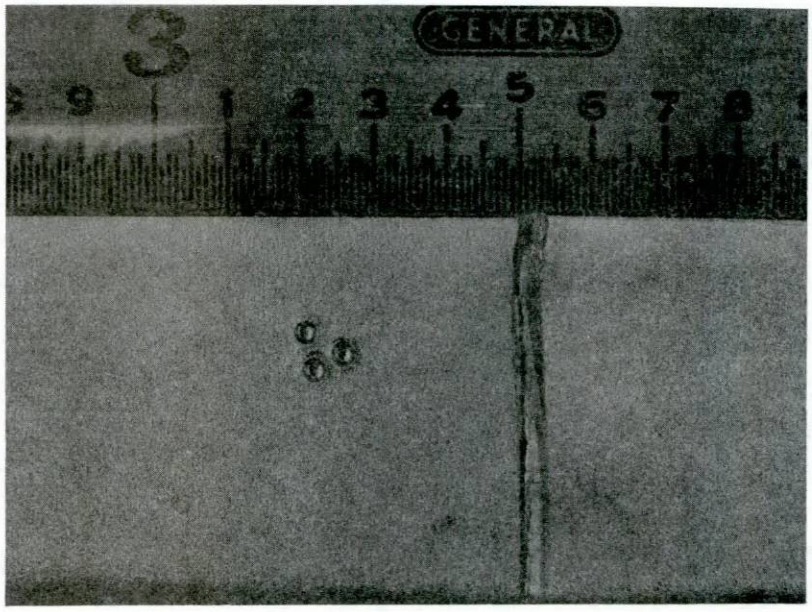

Figure 12. Adhesion tests for electroless nickel-phosphorus deposit on molybdenum.

1. Anode Design

During processing of the large components the varied etch pattern of the substrate indicated that the current density on the part was not sufficient and uniform. Therefore, it was necessary to fabricate anodes which were more uniformly tailored to each particular component. Anodes constructed from 304-L stainless steel were preferred because of the high-corrosion resistance of this steel and its ability to be passivated. This enabled long-term immersion of the anodes in the various solutions. However, due to the low electrical conductance of stainless steel, a greater anode-to-cathode surface area ratio was required. Each anode was designed to contain approximately four times the surface area of the molybdenum component. These measures enhanced the current distribution between the part and the anode.

2. Part Fixturing

Relatively pure molybdenum is hard and brittle and can be chipped or shattered quite easily. The large molybdenum components that were coated in this project weighed approximately 300 to 400 lb. Great care had to be taken to avoid damaging the parts during movement to each processing station. Therefore, it was necessary to use specially designed mounting and lifting fixtures to ensure safe handling of the parts.

3. Current Density and Process Time

Current density and process times were modified somewhat for each anodic pretreatment step. The large components required up to 5 min of anodic treatment at 1 amp/in.^{2} in the chromic acid-nitric acid solution (instead of 1 min) to develop the proper grain structure and matte finish. Three min were required to form the characteristic grey oxide film during anodization with phosphonic acid and the anodization process could be achieved between 0.25- and 0.50-amp/in.^{2}. These changes in the process parameters were attributed to the geometry of the large components and the anode-to-cathode spacing, conformity, and area ratio.

4. Electroless Nickel Strike Process

Several major changes in the process were made to make the molybdenum catalytic in the electroless nickel bath. Instead of utilizing a brief electrostrike, based on the voltage applied to the part, the molybdenum surface was cathodically treated with a series of strikes and current surges based on current density. A current density of 0.27 amp/in.^{2} applied for 15 sec, followed by a surge of 0.53 amp/in.^{2} for 3 sec, constituted one cycle of the electrostrike. This process was repeated six times. During the electrostrike the molybdenum part was rotated while the anode remained fixed. The timing of the rotation was such that the part was exposed to a

different section of the anode during each surge. This was done to minimize any areas of high or low current density which ensured a uniform distribution of the current. During the electrostrike process the surface of the molybdenum part reached a sufficient temperature to sustain the autocatalytic electroless nickel reaction once the current was removed at the end of the sixth cycle.

5. Agitation

Elimination of the pitting problems, associated with hydrogen gas clinging to the plated surface, was accomplished through the use of an agitation sequence. After completion of the electrostrike process, the component was agitated vigorously for 5 min, rapidly for 15 min, moderately for 15 min and finally reduced slightly for the remainder of the run. The types of part agitation utilized were rotational, horizontal, vertical, and linear. Effective results were obtained when rotational agitation was combined with either vertical, horizontal, or linear agitation. Essentially pit-free coatings approximately 10-mils thick were obtained utilizing this type of agitation along with that provided by the solution pumping system.

CONCLUSION

A process was developed for depositing an adherent coating of electroless nickel on molybdenum components, which was essentially pit- and blemish-free. The unique pretreatment process involved successive anodic etches in a chromic acid-nitric acid solution and a phosphonic acid solution. This process exposed the grain structure and preferentially etched the crystal boundaries, which likely was the key to producing a good adhesive bond between the nickel coating and molybdenum substrate.

Table 3 presents the process used to plate an adherent coating of an electroless nickel-phosphorus alloy onto large molybdenum components. Scale-up from laboratory-size development coupons to full-size molybdenum components required modifications to the process and the parameters. Greater detail to anode conformity was essential when processing the large parts. Further, the time of processing and the current density used to etch each part had to be optimized for each particular component. The process used to activate the large molybdenum parts in the electroless nickel bath was based on an electrostrike consisting of a series of strikes and current surges. This method relied on applied current density rather than voltage (as in the coupon development process) as a measure of electrical input.

This process was optimized to plate an adherent coating of electroless nickel onto specific molybdenum components. Application of this procedure to other full-size molybdenum components may require some experimentation, with anode design and conformity, anode-to-cathode surface area ratio, treatment time, and current density in order to optimize the process conditions.

Table 3

PROCESS FOR ELECTROLESS NICKEL PLATING LARGE COMPONENTS

1. Degrease
2. Scrub with pumice
3. Rinse
4. Anodic etch, 5 min max, R.T.
   CrO_3 10 wt %
   71% HNO_3 10 vol %

   DC current density of 1.0 amp/in.^{2}
5. Rinse
6. Anodization, 3 min max, R.T.
   Phosphonic acid 25 vol %
   DC current density 0.25 - 0.50 amp/in.^{2}
7. Rinse
8. Oxide film removal, 1 min, R.T.
   CrO_3 10 wt %
   71% HNO_3 10 vol %
9. Rinse
10. Enter plating bath at 5 volts idle, initiate electroless sequence:
    (a) 0.27 amp/in.^{2}, 15 sec
    (b) 0.53 amp/in.^{2}, 3 sec

    Repeat six times
11. Remove leads and plate to thickness

H-4

Optics
Session H

Electroless Nickel Coating for Diamond Turning Applications

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Hughes Optical Products, Inc.
Chicago, IL

ELECTROLESS NICKEL COATING FOR DIAMOND TURNING APPLICATIONS

Eric Ulph
Hughes Optical Products, Inc.
Chicago, IL

Diamond Turning

Direct generation of optical surfaces via diamond turning has been the subject of many papers and as such we only touch briefly on the subject. As the name implies diamond turning employs a gem quality natural diamond to remove material to generate an optical surface. The diamond is mounted in a tool holder and is positioned by a highly accurate drive mechanism. The work piece is mounted to an air bearing spindle so that rotation is true to better than 5 microinches. Typical two axis generating machines have positional accuracies of 2 microinches when using laser feedback control.

The surface generated by diamond turning looks, under magnification, like a phonograph record. The grooved surface acts as a diffraction grating and thus limits the use of diamond turned surfaces in the visible region, but in the infrared region, where the wave length of energy is longer, no such limitation exists. Therefore, the use of diamond turned optics in the IR region is increasing, due not only to improved optical performance but also for cost reduction, by the use of aspheric lenses.

Materials that are currently diamond turnable are:

Germanium
Silicon
Zinc Sulfide
Zinc Selenide
Lithium Niobate
Potassim Dihydrogen Phosphate (KDP)
AMTIR
Aluminum
Brass
Copper
Beryllium Copper
Gold
Silver
Platinum
Electroless Nickel
Many plastics

Mold Tooling Using Electroless Nickel

The first application for discussion of diamond turning electroless nickel is for the injection molding of plastic optics. The mold consists of a mold base, a pair of holder blocks, and stainless steel mold inserts, Figure 1. The mold inserts are used to form the optical surface. The beauty of injection molded plastic optics is that once the tooling has been fabricated and the molding process established, the part repeatability is excellent. With this in mind, and without going into a treatise on optical design, let me say that it is often useful to have a lens with an aspheric, nonspherical, surface in an optical system. Once the moldinsert has been fabricated with the proper aspheric surface the molding process really doesn't care what the shape of the surface is; aspheric lenses can be molded as easily as spherical lenses. Testing aspheric lenses is more difficult than spherical lenses.

In the development of a lens mold the inverse of the desired optical surface is generated in the mold insert, the mold is assembled and run. The resulting optical elements are evaluated for optical parameters, and the mold inserts are changed accordingly. This process is fairly easy with spherical surfaces since the grinding and polishing of the steel is straight forward, via conventional optical methods. On the other hand the generation of an aspheric surface is not quite so easy.

In the early phases of the development of plastic aspheric technology the aspheric curve was generated in the steel with a grinding wheel mounted on an aspheric generator. The aspheric generator was the forerunner of today's diamond turning machines, with the grinder mounted where the diamond is. The ground surface was then polished to obtain a specular surface. During the polishing cycle it is imperative the polishing rate be uniform for if it is not, and this is usually the case, the shape of the ground aspheric curve is changed. After the aspheric insert is polished, we continue as in the case of the spherical element, and assemble the mold and mold parts for evaluation. Again, as in the case of the spherical optic, the insert shape is modified to give the correct finished lens shape. Since this iterative process is generally a number of steps, the initial cost of developing the mold for the aspheric is very high.

In an In an attempt to reduce the cost of fabricating the aspheric insert an alternative method of generating the aspheric curve was sought. Remembering that a surface generated in the proper material with a diamond tool gives a specular surface, albeit with minute groves, it was determined to investigate the possibility of using an electroless nickel coating on the steel insert.

The concerns with using an electroless nickel plating on the insert were two-fold. Would the plating withstand the molding temperature cycle, and would the plating withstand the wear of the molding process? The molding temperature cycle is as follows; the mold is maintained at a constant temperature of about 200°F. The plastic material is injected into the cavity at a temperature of 400°F. The plastic material cools to between 250° and 300°, and then the mold opens to ambient, 70°F.

The wear of the plated insert is related to the fact that the plastic material impinges on the face of the insert, and the insert moves during the ejection process.

It was determined that a plating program should be initiated to determine the suitability of electroless nickel as a mold insert surface. Since the plating was to be done on a small scale, and the inserts themselves are small, a laboratory type setup was made.

A general requirement for the electroless nickel coating for optical use is that it have no porosity and be as low in internal stress as possible. The reason for the former is the fact that porosity on the finished surface would result in a void on a mirror surface or a "pip" in the molded surface, both of which are degrading to optical performance. The desire for low stress is due to the fact that the diamond turned surfaces see wide temperature variations which might cause crazing of a highly stressed coating.

Because it is generally desired to use a spherical surface on the substrate a fairly thick, 0.005 inch, coating is to be applied to accommodate the aspheric shape.

Our plating operation is rather small, consisting of 3 and 4 liter beakers in a laboratory environment. The small size of the operation is very much a drawback as far as the stability of both the plating bath temperature and pH level. It also creates a problem in the quantity of product that can be plated at any time.

The plating process we finally used was for stainless steel only and fairly straightforward. The parts to be plated were mounted on a fairly stiff copper lead, and appropriately masked. The masking was done using Enthone Stop Off. The part was then electrocleaned and given a nickel chloride strike. The part was then electroless nickel plated using Enthone 419 at a deposition rate of 0.0005 inch per hour. The temperature of the plating bath was maintained between 175° and 180°F and the pH between 4.5 to 5.0 with the gcal of maintaining 4.7 to 4.5. A magnetic stirrer was used in the bottom of the 4 liter beaker and air agitation was used around the sides. The biggest problem, as mentioned before, was maintaining the proper pH in

such a small volume. After plating the coated part was heat-treated at 750°F for one hour. There is no concern that these coatings be bright, since they were to be diamond turned afterwards.

Enthone recommends continuous filtration through a 15 micron filter during the plating process to obtain a smooth surface, and if this is not possible, to cool the plating solution at the end of a plating run and then filter the solution through a 3 micron filter. We used the latter method with varying degrees of success. More than half of the time we achieved a coating that was smooth and could be directly diamond turned. Other times we found that the surface had developed small nodules and quite often the bulk of them could be rubbed off. In these cases, since the nodules were only a surface phenomenon, we took a light surface cut with a carbide or cubic boron nitride tool prior to diamond turning.

After the plating cycle the inserts were diamond turned to achieve the desired aspheric curve. The insert with an "as turned" surface was assembled into the mold and plastic optical elements were molded for optical figure evaluation.

The plastic lens has a spherical surface and an aspheric surface. The spherical surface is formed by an insert surface directly polished into stainless steel. During the molding cycle the optical figure of both surfaces is affected by the molding parameters, so while the molding cycle is being developed both surfaces must be monitored as well as the mechanical properties of the lens, i.e., outside diameter, center thickness, flange thickness etc. Once a molding "window" has been found where the molding process is stable, the optical figure of the surface is measured. The inserts are now modified to correct any error in surface figure. The spherical surface is modified by repolishing the stainless steel insert, and the aspheric surface by diamond turning the electroless nickel coated insert. This iterative process is repeated until the plastic element is to the desired configuration.

As indicated earlier, a diamond turned surface is not usable in the visible region of the spectrum, and since the molded plastic lens replicates the insert surface, the electroless nickel must now be polished. The polishing must only remove the diamond turning grooves and not change the optical figure or the surface.

Polishing is done using Engis Corporation Hyprez diamond polishing paste, in conjunction with a felt lap. The felt lap is formal to figure on the part by mounting the felt to dental impression wax substrate and then heating the wax in boiling water and pressing the wax/felt polishing pad against the part to be polished. The polishing pad is scalloped to achieve

even material removal at the edge of the part being polished.

Typically the first stage of polishing requires the use of 3 micron diamond polishing paste. The polishing time is adjusted to remove only the diamond turning grooves. Once the grooves have been removed the final polishing is done using 1 micron diamond paste.

During the polishing stage the optical figure of the insert is checked to determine that there is not too much material being removed from localized areas. If there is an uneven removal rate, the shape of the scallops on the polishing felt is altered to reduce the effective polishing effect in the high removal rate area.

When the polishing is finished the mold insert is assembled into the mold and the plastic optics molded and checked.

Mold inserts fabricated in this fashion have been in use for over four years and have proven very durable. There was some initial concern about wear on the side of the insert during the ejection process but this has proven unfounded.

Electroless Nickel for Missile Mirror

Another application of the electroless nickel process for diamond turning is in the direct generation of an optical surface for a missile guidance system. (Sidewinder)

Here a stainless steel substance is bonded to an Alnico substrate. Here again the material we wish to be the optical surface is the stainless steel.

At first glance it appeared that our biggest problem would be masking the piece prior to plating, and then establishing electrical contact with the surface to be plated during the electrocleaning process.

The first problem was solved by generating a nylon plug that fit inside the bore of the Alnico donut which was retained in the bore by a combination of 3M plating tape and either Microflex M-0011 or Enthone Stop Off.

The next problem was solved by modifying an alligator clip to go from edge to edge across the narrow width of the mirror. There was concern that the footprint of the alligator clip would lead to incomplete cleaning of the surface to be plated but this fear proved unfounded.

Since we had such success with the process previously described, we followed the same procedure. All went well until we finished the plating process and examined the surface. The

plated surface exhibited a phenomenom we had not seen before. The surface showed a well defined pattern that did not have any relationship to shape or the part. While we were trying to determine what was causing this effect we plated a second piece. This second piece did not show the same effect. It was clear that something must have been wrong with the first piece. The part was stripped and replated, but again the surface pattern appeared.

About this time someone noticed that the unit that showed the unusual surface effect could be used to pick up razor blades and other light metallic objects, whereas the one that took the plating with no problem would not. The partially magnetized unit was stripped, de-magnetized and replated with no other problems. After the successful plating the electroless nickel surface was diamond turned with no other difficulty.

Electroless Nickel Mirror for Space Environment

The third and last application I would like to describe was the use of an electroless nickel coating for an aluminum mirror. As was mentioned earlier aluminum is directly diamond turnable, but in this case it was desired that the optical surface be polished after diamond turning so that the system could be used in the visible spectrum for system alignment, although the ultimate application was for the I.R.

I shall not describe the plating process since we didn't do it, feeling it to be beyond our limited capability, and instead had it done by O.S.T.I. Bedford Ma., but we did specify a high density, low stress coating.

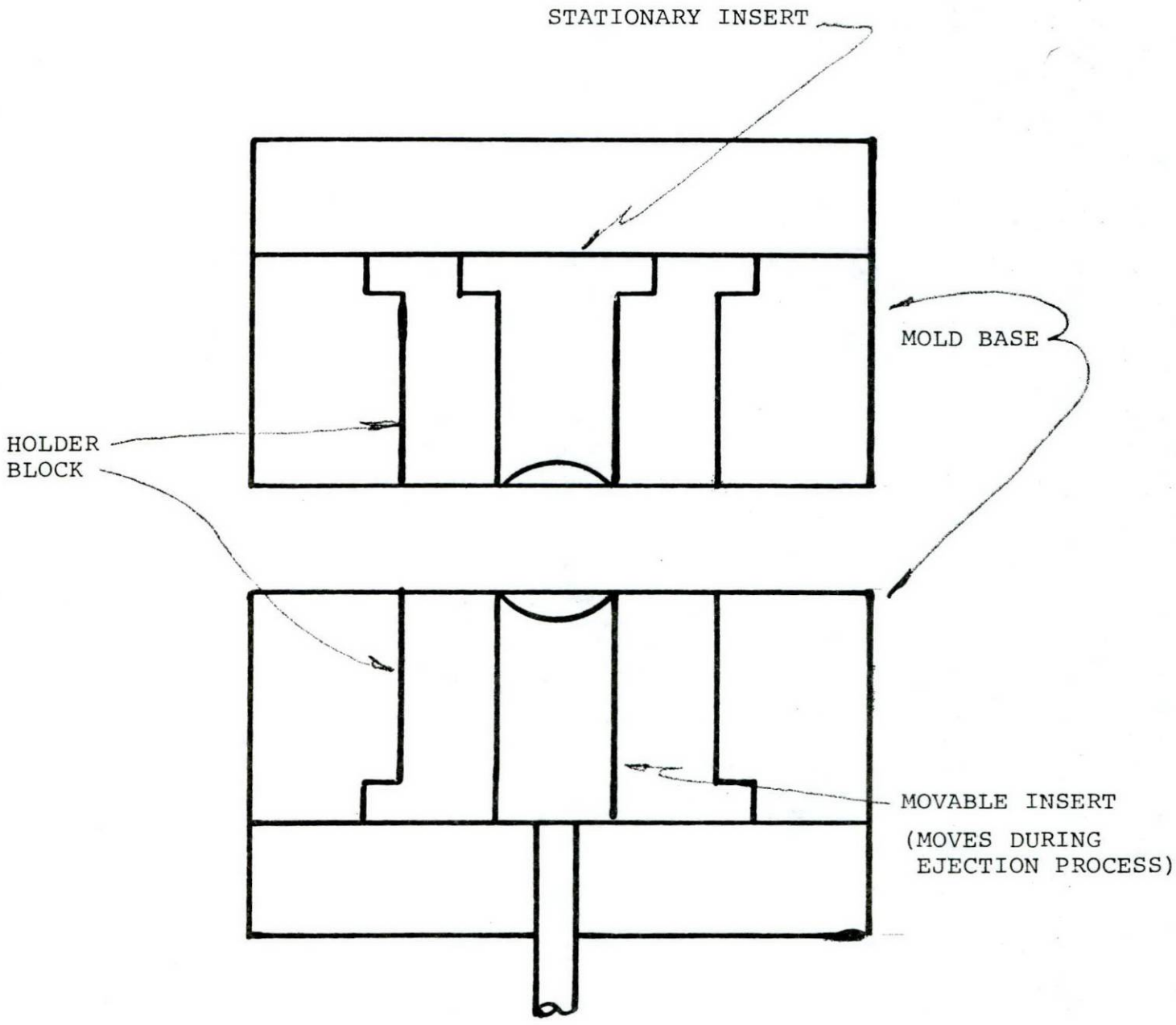
The main reason for mentioning the application is to point out the need to consider the environment in which the finished product will function.

In this case the mirror was to be used in an outer space environment and as such it has to withstand extreme cold without changing shape. The coefficient of thermal expansion of electroless nickel is 13-14 x $10^{-6}/C^{o}$ whereas that of 6061 aluminum is 23-24 x $10^{-6}/C^{o}$.

To minimize the effect of the differential expansion of the base material and the plating, two steps were taken. The first was to make the part rotationally symmetric and the second and most important was to plate the back of the mirror substrate as well as the optical surface. This has the effect of creating a restraining force on the back of the mirror to prevent deformation of the front surface.

The mirror substrate was machined in a conventional manner and aspheric surface was roughed in. In this case since we wanted to keep the final machined coating thickness as uniform as possible, the aspheric was cut to the final shape prior to coating, with a carbide tool. The mirror was coated with 0.004" to 0.005" electroless nickel. Prior to diamond machining the mirror surface, the back surface of the substrate was diamond turned to obtain an accurate mechanical reference. The substrate was then removed and the diamond turned reference surface mounted to a diamond turned faceplate and the final mirror surface diamond turned. The finished mirror has functioned well in a space environment.

These are just a few applications of electroless nickel plating where the ease of application and the ability to diamond turn and polish make it uniquely suited for use in an optical product.



PLASTIC OPTICS MOLD

FIGURE 1

H-5

Optics
Session H

Microstructural Stability of Copper Electroplate

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MICROSTRUCTURAL STABILITY OF COPPER ELECTROPLATE

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This article was based on work sponsored by the Department of Energy on Contract W-7405-ENG-36 and DARPA Contract 29601-80-C-0040.

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Introduction

Single point diamond turning (SPDT) machines can produce high quality optics with complex configurations. The success of machining the optics is dependent on the compatibility of the diamond tool with the substrate material, the quality of the material and the long term microstructural stability of the material. Surface roughnesses of 40A Ra and less have been produced with SPDT. In order to maintain the quality of finish on the entire machined surface, the diamond tool must survive the entire cutting operation without degrading. Experience has shown that metals which are carbide formers, such as iron, pure nickel, molybdenum, tungsten and titanium are not amenable to SPDT because they cause rapid deterioration of the diamond tool. Metals with which carbon has very low or no solubility, such as aluminum, copper, gold, silver and tin lend themselves well to SPDT. Electroless nickel, which is a nickel - phosphorous alloy, has also been successfully diamond turned. The quality of the substrate is also extremely important to the success of SPDT. A fine grained substrate, free of inclusions and impurities, is necessary to produce a high quality SPDT optic. The remaining necessary condition for a high quality SPDT optic is long term microstructural stability. Tests performed by Wiesner and Frey indicated that copper electroplate from an acid copper solution markedly softened after room temperature storage for 30 days[1]. If the substrate material undergoes recrystallization after being diamond turned, the optical surface is roughened and the optical quality is degraded.

Discussion

Electroplated copper from a copper sulfate-sulfuric acid electrolyte meets the requirements for a high purity, fine grained structure necessary to produce a high quality SPDT optic. A typical electroplating solution used for producing mirror quality copper electroplate is shown below in Table I.

Table I. Copper Electroplating Bath

Composition	Concentration Range
Copper Sulfate ($CuSO_4 \cdot 5H_2O$)	180-210 g/L
Sulfuric Acid (H_2SO_4)	60-75 g/L
$CuSO_4$ to H_2SO_4 Ratio	3.5:1
Chloride ion (CL)	30-80 mg/L (PPM)
Equivalent to 30-80 cc conc HCL/100 gal	
Addition Agent	0.175 to 0.225% vol

In addition to the copper electroplate having properties suitable for SPDT, copper has other properties which are desirable for optics. Among these properties are high thermal conductivity, optical efficiency and economy. Relatively high mechanical properties and hardness also make the copper electroplate an attractive selection for optical substrates. Typical

mechanical properties and hardness are presented in Table II.

Table II - Mechanical Properties of Copper From Acid Copper Electrolyte

Yield Strength (0.2% Offset)	30-60 KSI
Ultimate Tensile Strength	40-100 KSI
Hardness (KHN)	110-200
% Elongation	9-30

A serious drawback in using electroplated copper as an optical substrate has been found to be metallurgical instability. Interferometric tests on copper mirrors for the Antares Laser system at Los Alamos National Laboratory revealed a change in the optical surfaces over a period of six months. Metallographic analysis indicated that recrystallization had occurred in the electroplated copper layer, accompanied by a shifting of the surface along individual grain boundaries. In the most extreme cases this was visible to the eye as an orange-peel effect which scattered the laser beam and degraded reflectance measurements. The roughening of the SPDT surface after recrystallization is illustrated in Figures 1 and 2.

Recovery/recrystallization is a time-temperature function with the rate following an Arrhenius-type equation [2]

$$1/t = A \exp - Q/RT$$

Where t = time, A = constant, T = temperature, Q = Activation energy, R = universal gas constant

For wrought metals, activation energy appears to be a function of strain hardening where the increased strain hardening and accompanying higher defect densities appear to lower the activation energy, thus permitting recovery/recrystallization to occur at lower temperatures and/or shorter times. For most wrought metals short term recrystallization takes place at approximately 1/2 the melting temperature (K). For pure copper this temperature is approximately 400C. At temperatures below 400C, vacancy and dislocation movement become very slow, and recrystallization takes a considerable amount of time (i.e. a number of years at room temperature).

The situation with recrystallization in electroplated metals is somewhat different. It is possible to achieve a much higher density of defects through electroplating than can be achieved by deformation. Increasing the defect density of a metal increases the free energy, no matter whether the defects are the result of deformation or electroplating. In either case the effect is the same; the free energy is increased by an amount approximately equal to the stored strain energy.[3] Under certain circumstances a metal lattice with a

high free energy may begin to soften spontaneously. This softening, or releasing of the stored energy, does not usually occur by a single, simple reaction. There are more likely a number of different reactions most involving some sort of atom or vacancy movement. The realignment of atoms into crystals with a lower free energy is called recrystallization. An entirely new set of essentially defect free crystals grows at the expense of the original crystals.[4] The amount of time necessary, as well as the temperature at which recrystallization will occur, both vary with the amount of stored energy.[5] The difference in recrystallization temperatures is related to the higher density of defects in the electrodeposit than is normally found in strain hardened copper. In electroplating, these defects may be produced by the speed with which the ions are deposited. In general, an increase in the depositional rate also increases the defect density. A more effective way to increase the number of defects is to add something to the electrolyte which interferes with the ionic deposition. This may be done to increase strength or hardness, add brightness or refine the grain size.[6]

Investigations of copper plated at various current densities indicated that low current densities (i.e. less than 20 ASF) caused considerable strain energy to be stored in the electrodeposit. Differential scanning calorimetry (DSC) showed that copper plated at 5 ASF had a very high recovery energy exotherm of 1.97 J/g at 148.5C, and a much lower recrystallization energy exotherm of 0.529 J/g at 283.8 C (see Figure 3). A DSC of copper plated at 15 ASF appeared to have a joined recovery/recrystallization energy exotherm of 1.27 J/g at 306.2°C, see Figure 4. Copper plating performed at 36 ASF did not show a recovery energy exotherm and the recrystallization energy exotherm occurred at approximately 320C, see Figure 5. To eliminate the problem of recrystallization at room temperature, the low current density copper was given a low temperature heat treat (1 hour @ 250C) to remove the recovery energy without causing recrystallization and grain growth. The DSC of low current density copper which had been heat treated did not have any retained recovery energy and the recrystallization energy also appeared to be reduced, see Figure 6.

In order to determine the effect of various heat treatments on the electroplated copper, x-ray diffraction, mechanical property and hardness tests were conducted. X-ray diffraction tests showed that heat treatments at temperatures of 250C and lower for 1 hour appeared to cause ordering to take place, but heat treatments at temperatures of 350C and higher for 1 hour appeared to cause recrystallization and grain growth, see Figure 7. Mechanical property tests indicated that low strength copper plated at 36 ASF had only a small drop in tensile properties after the 1 hour at 250C heat treat. An additional exposure of 166 hours at 150C caused only a 2.1 ksi drop in yield strength indicating that the copper was metallurgically stable (See Table III). Also shown in Table III is high strength copper plating produced using high additive levels. The high strength copper showed a considerable drop in tensile strength after 1 hour at 150C (103.1 ksi to 51.7 ksi). The vendor for the copper electroplating bath indicated that low current densities caused higher concentrations of the additive to be occluded in the deposit. Abnormally high levels of the additives had a similar effect. Hardness tests seemed to substantiate the vendors claim. (See Table IV).

TABLE III

MECHANICAL PROPERTIES OF COPPER PLATING

TYPE	CONDITIONING	ULTIMATE TENSILE STRENGTH (KSI)	YIELD STRENGTH 0.2% OFF SET (KSI)	% ELON-GATION
36 ASF Low Strength	As Plated	50.0	38.4	23
	1 hour @ 150°C	47.0	35.6	29
	1 hour @ 250°C	46.7	34.5	30
	1 hour @ 350°C	43.2	26.5	37
	1 hour @ 450°C	40.8	21.9	41
	1 hour @ 250°C + 166 hours @ 150°C	45.7	32.4	34
36 ASF High Strength	As Plated	103.1	66.1	24
	1 hour @ 150°C	51.7	46.7	19
	1 hour @ 250°C	50.7	43.3	21

Modulus of Elasticity (E) ~16 x 10^6 psi.

TABLE IV

HARDNESS OF COPPER PLATINGS (KHN)

SOLUTION/CURRENT DENSITY	AS PLATED	CONDITIONED (1 hour @ °C)			
		150	250	350	450
Solution #1/ 36 ASF	118	117	109	92	83
Solution #2/ 36 ASF	143	133	134	120	112
High Strength/ 36 ASF	225	145	153	113	91
Solution #1/ 5 ASF	219	231	206	121	58
Solution #1/ 15 ASF	228	151	135	123	103

Metallographic examination of copper platings showed that room temperature recrystallization could result in a mixed metallurgical structure. Some grains have recrystallized and are softer and adjacent grains can have the original as plated structure which is much harder, see Figure 8. Original plated structure has a columnar structure and has small diamond indentations, and the recrystallized grains are larger and also, have larger diamond indentations. The columnar structure shown is typical of copper deposited at 15 ASF. Copper deposited at even lower current density of 5 ASF had a laminar type structure and the higher current density of 25 ASF had a desirable fine grain structure, see Figure 9.

Summary

In summary, electrodeposited metals can spontaneously recrystallize over shorter time periods and at lower temperatures than wrought metals because they may contain a significantly higher defect density. The plating parameters which lead to high defect densities in acid copper electrodeposits appear to be low current densities (below 20 ASF) and/or abnormally high additive levels. Recrystallization after diamond turning can significantly degrade optical surfaces. However, modest heat treatments prior to diamond turning can remove the stored energy and lessen the tendency toward recrystallization.

Acknowledgements

The authors of this paper acknowledge the contributions of W. Doty, W. Reichet, N. R. Borch, and J. Gray of Los Alamos National Laboratory and R. B. Simonson of TRW.

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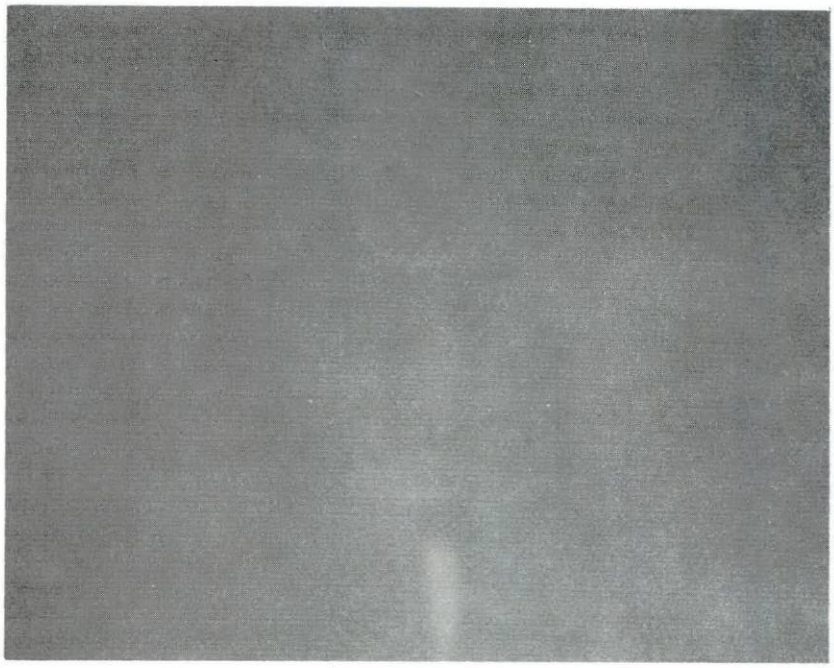

Figure 1. Nomarski micrograph of a diamond-turned copper surface before recrystallization, approx. 100 X.



Figure 2. Nomarski micrograph of a diamond-turned copper surface after recrystallization, approx. 100 X.

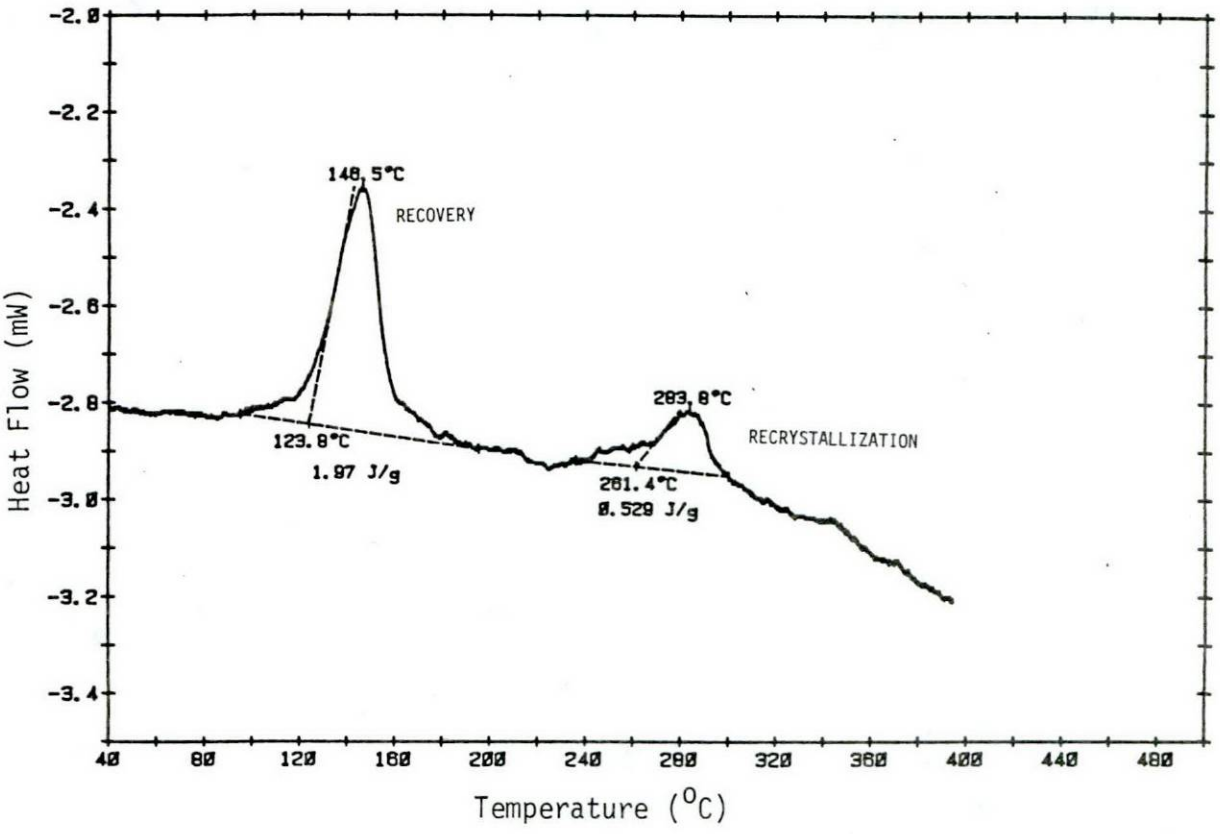

Figure 3. DSC showing exotherm at 146.5°C and 283.8°C for copper plated at 5 ASF.

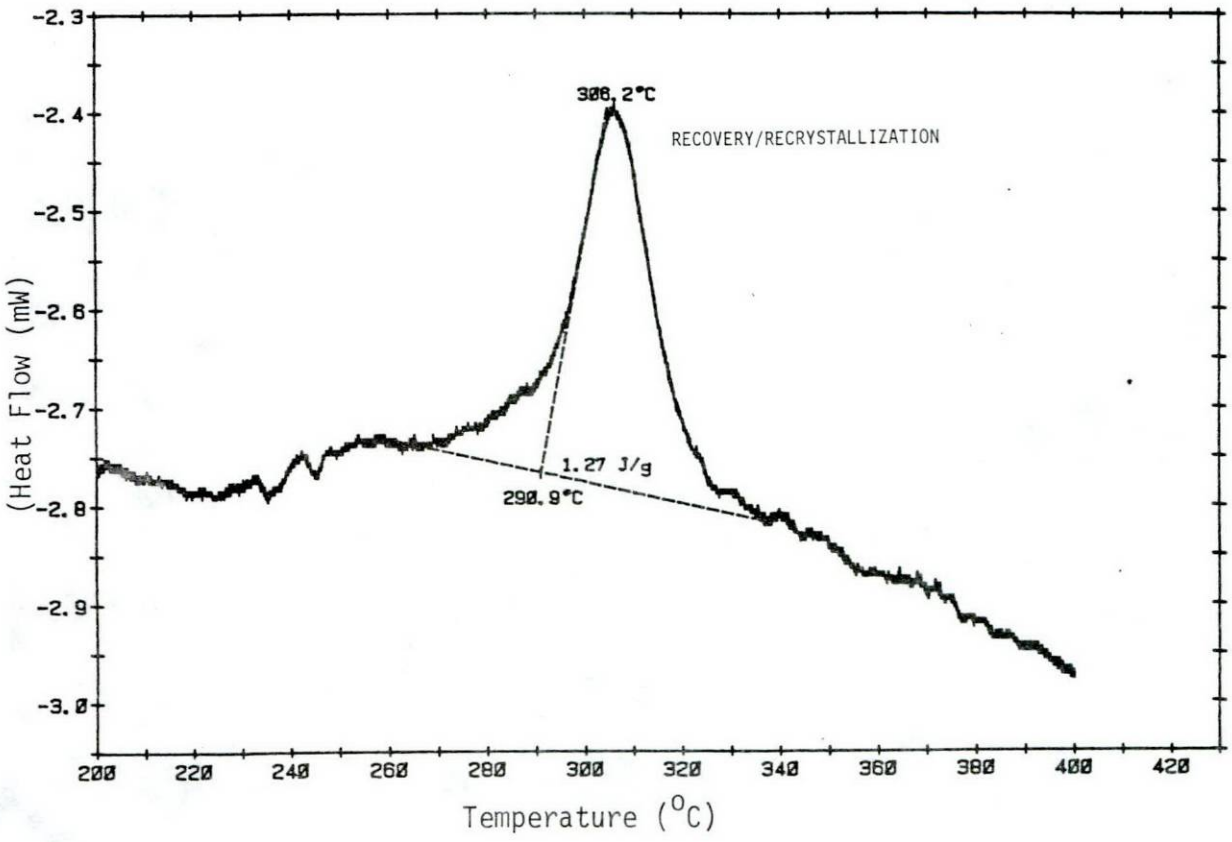

Figure 4. DSC showing energy release at 306.2°C for copper plated at 15 ASF

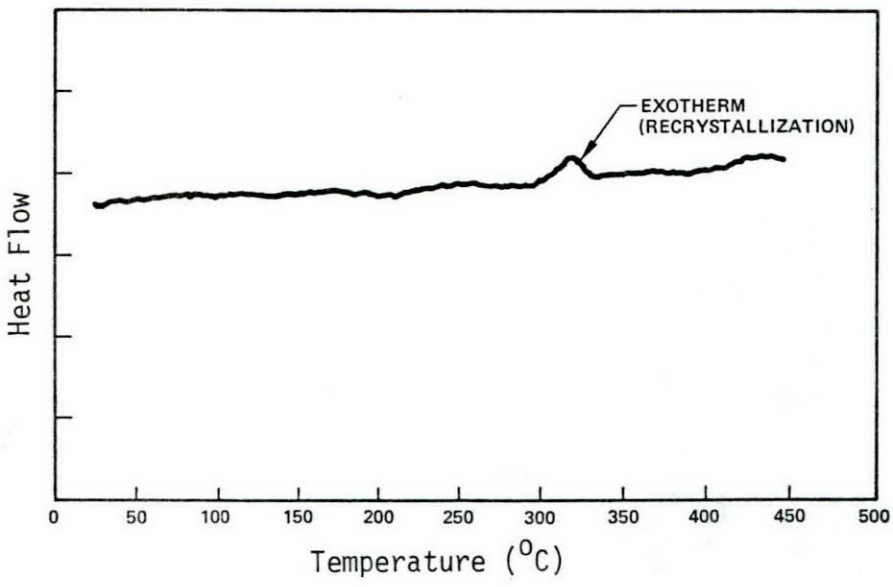

Figure 5. DSC showing recrystallization exotherm without a recovery exotherm of copper plated at 36 ASF.

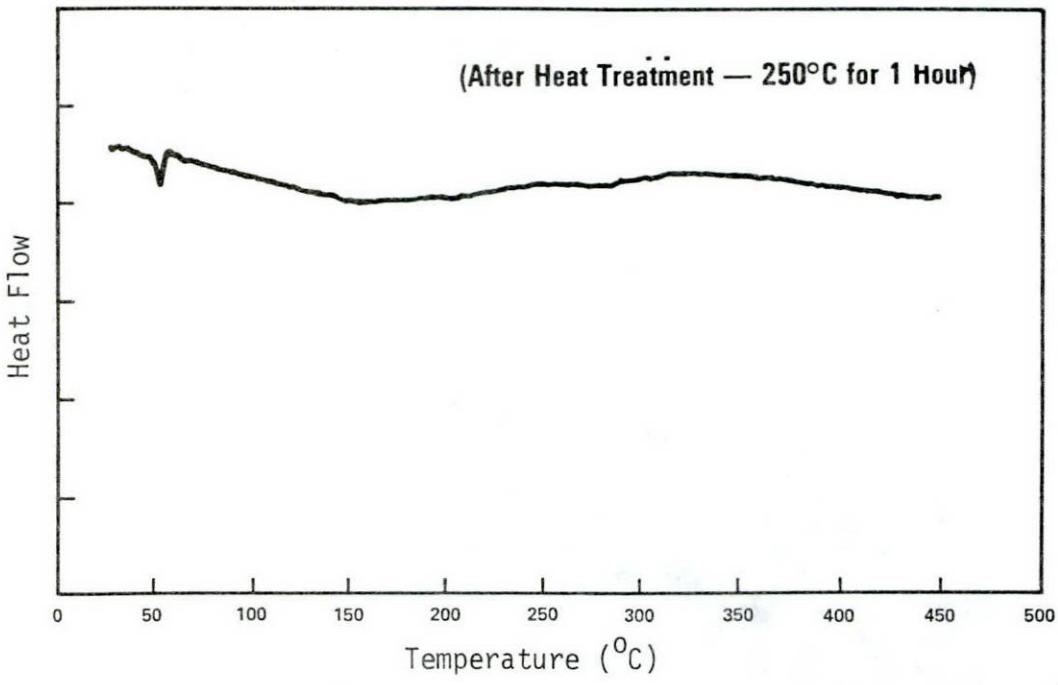

Figure 6. DSC of copper plated at 5 ASF after being heat treated.

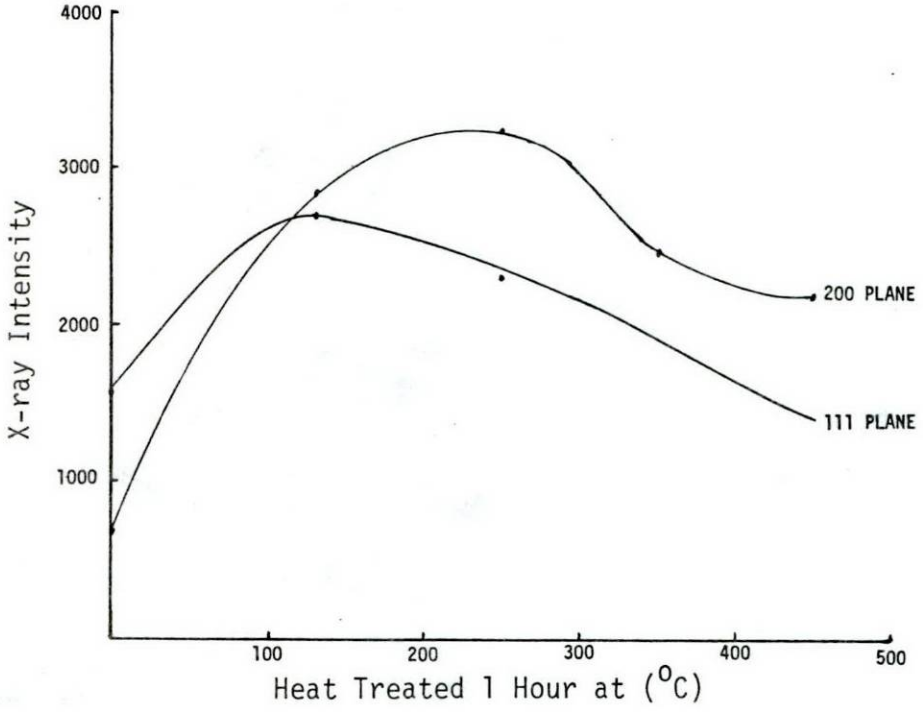

Figure 7. X-ray intensity after various heat treatments.



Figure 8. Nomarski micrograph of partially recrystallized copper with hardness indentations, approx. 200X.

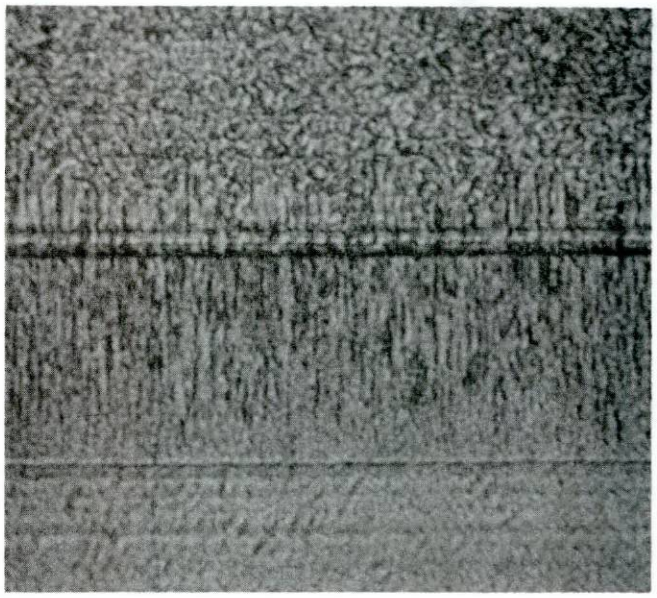

Figure 9. Photomicrograph showing microstructure of copper plating at various current densities, 400X.


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