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Perspective On Plating For Precision Finishing

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PERSPECTIVE ON PLATING FOR PRECISION FINISHING

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Introduction

This paper is intended as an overview on platings for precision finishing operations. After a brief review of the two processes (polishing and precision machining) by which a coating on a part can be converted to a precision surface, the coatings which work successfully in these applications will be discussed. Then adhesion and stress aspects of deposits will be covered. Electroless nickel, which is a particularly attractive coating for precision finishing applications, will be discussed in some detail, from its early years as the "Kanigen" process to the present. Since microstructural changes in deposits are important for precision parts, this aspect will be covered for electroless nickel, copper and silver deposits. Lastly, some words will be directed at potential future electrodeposited coatings including nickel-phosphorus alloys, and various silver alloys.

Precision Finishing

There are two processes by which a coating on a part can be converted into an optical surface. These are conventional grinding and polishing and precision machining. While these processes are quite different the result of their application is the removal of physical irregularities on the coated surface, the generation of specific shape required, and the improvement of finish (reduction of surface roughness) to a level where any resultant scattered radiation is within tolerable limits.

Polishing

The removal of any material by polishing, be it glass or metal, is roughly a process of wear(1). Here a polishing or grinding lap base is coated with a deformable material (these vary greatly in compliance, viscosity and other

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material properties depending on the application). This lap is placed against the surface to be worked and continuously fed with a polishing compound, usually a fine, less than 3 μm diameter particle size metal oxide powder. The lap and workpiece are moved with respect to one another in a series of rotating and oscillating motions in a known way. The resultant energy imparted to the surface by the lap through a combination of mechanical abrasion, chemical attack, and thermal flow disrupt and remove the material. This process results in surfaces whose finish characteristics are small compared to the wavelength of light being applied and whose shape can be controlled to some extent(1).

The advantages of this process with respect to precision machining in general relate to the wide variety of materials that lend themselves to polishing and the relatively high quality finishes normally achieved. Optical polishing has been successfully applied to most all glasses, metals and crystals, as well as most all hard inorganic materials and semiconductors. It is a process that is insensitive to mechanical vibration, acoustic coupling, and in most cases, small variations in temperature(1).

Reflectance data for a number of coatings which had been diamond polished in silicon oil to 10Å RMS surface roughness or better ar shown in Figure 1 for the range between 0.40 and 2.5 μm wavelengths. Bright nickel and sulfamate nickel showed approximately 12% higher reflectivities than electroless nickel and tin-nickel. Although all four of thee coatings could be optically polished, only electroless nickel and tin-nickel deposits could be diamond turned without causing undue degradation of the diamond tool(2).

Precision Machining

Precision machining (also termed single point diamond turning or just diamond turning) is accomplished by combining the very hard and sharp edges obtained from certain crystalline (usually diamond) tools with extremely precise machine tools (either liquid or gas bearing) operating under closely controlled environmental conditions to produce finished or nearly finished optical surfaces. This technology removes some of the difficulties in forming optical surfaces encountered in conventional grinding and polishing, specifically for that family of materials both physically and chemically compatible with diamond tools. Because these tools are so hard and sharp, no cutting edge contact area is presented to the material. This promotes the cutting process by restricting it to a thin shear plane with a minimum of contact stress or friction and results in a process that minimizes material deformation. The result is a specular finish required for optical surfaces and a contour that is an exact copy of the tool path(1).

The materials that can be successfully diamond turned are limited in number. Table 1 lists those compatible with diamond tools and hence considered machinable. It is interesting to note that all of the metals listed in Table 1 except for beryllium-copper can be deposited from aqueous solutions or non-aqueous solutions (aluminum).

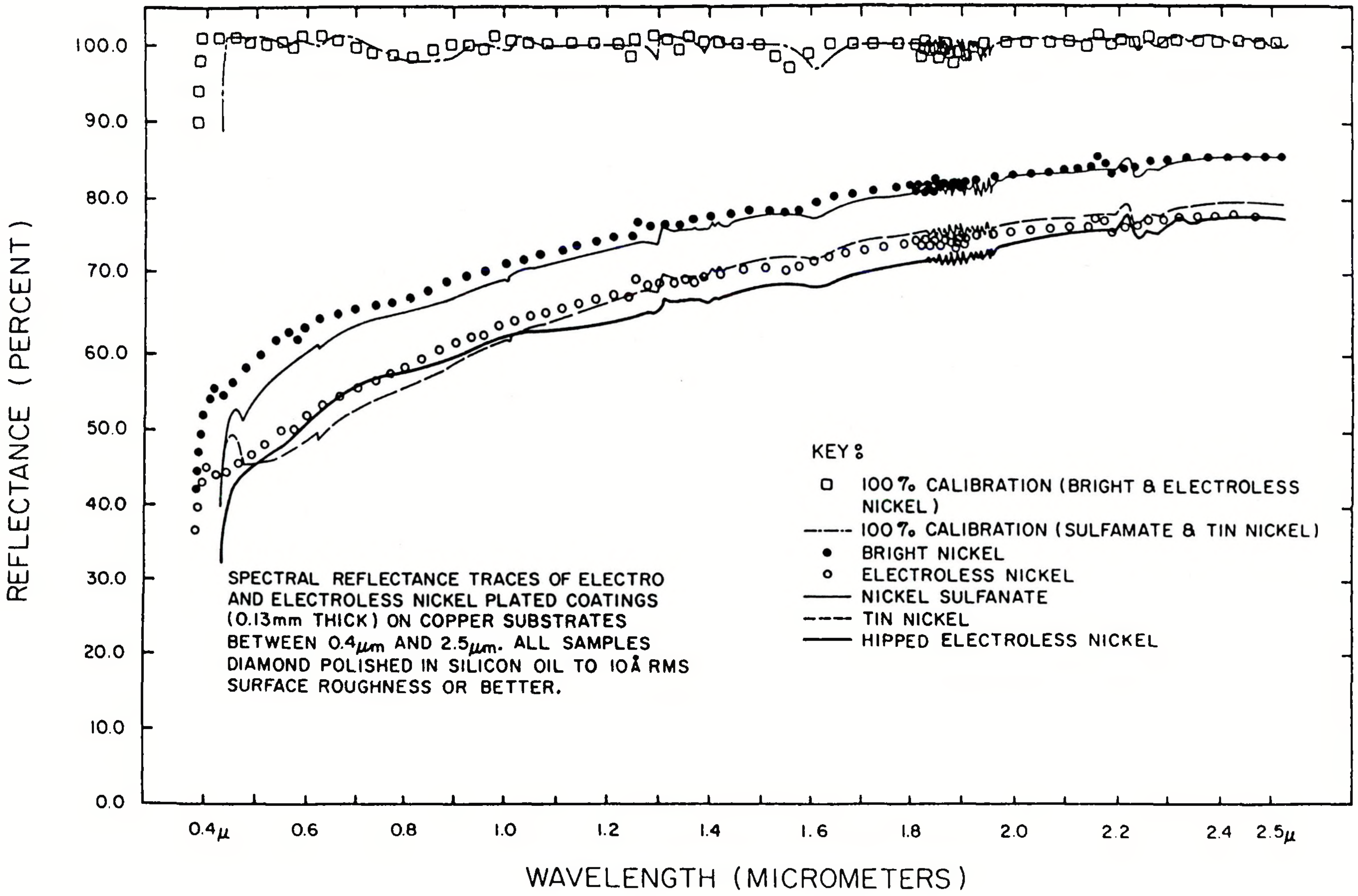


Figure 1 - Spectral reflectance traces of electrodeposited and electroless nickel plated coatings on copper substrates. From Reference 2.

Metals which are carbide formers such as iron, pure nickel, molybdenum, tungsten and titanium are not amenable to single point diamond turning 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 single point diamond turning(3).

Table 1
Diamond-turned materials*

Nonferrous metals	Infrared-transmitting materials	Polymers
Aluminum[a]	Germanium[a]	Acrylic[a]
Brass[a]	Silicon[a]	Nylon[a]
Copper	Zinc sulfide[a]	Polycarbonate[a]
Beryllium-copper[a]	Zinc selenide[a]	Polystyrene[a]
Electroless nickel[a]	Alkali halide	Polysulfone
Gold	Lithium niobate	Acetal
Silver	Cedium iodide	Fluoroplastic
Tin	Potassium chloride	Silicone
Tin-nickel	Calcium fluoride	
Platinum	Cadmium telluride	
	Mercury cadmium telluride	

[a] Most common lens or mirror materials
* From Reference 3

Adhesion

A wide variety of substrates are used in the manufacture of precision parts. A number of these such as aluminum, beryllium, beryllium-copper, molybdenum and glass are not the easiest materials to coat with adherent deposits. Special processing is required to ensure adhesion of the coating to the substrate. When properly prepared for plating, adhesion can be quite good as revealed in Figure 2 which shows failure in 7075 aluminum which was overplated with thick nickel.

The origin of the problem for most difficult-to-plate substrates is typically a thin, naturally forming oxide film that is difficult to remove and that reforms quickly when a clean surface is exposed to air or water. Techniques that have been used by electroplaters to prepare difficult-to-plate substrates for coating include:

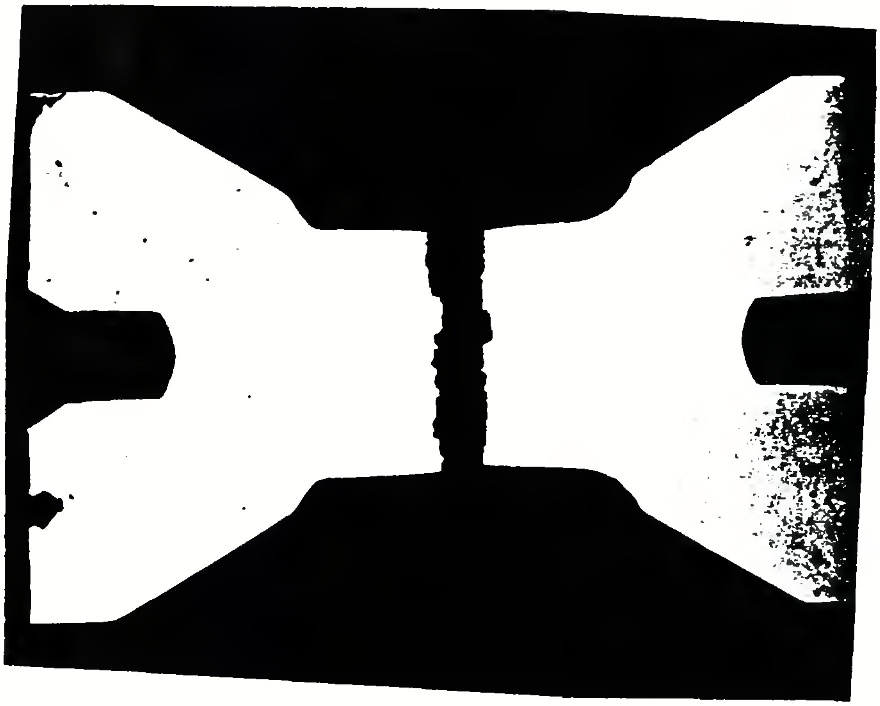


Figure 2. Cross-section of nickel plated 7075 aluminum conical head tensile specimen after testing (magnified 6X). Failure occurred in the aluminum at 83,000 psi (573 MPa).

etching to allow mechanical keying between the substrate and plated deposit, mechanical roughening such as glass bead or sand blasting to roughen the substrate surface, replacing the oxide film with a displacement coating, heating to allow for the interdiffusion between the substrate and coating, anodic oxidation of the substrate, and intermediate strike coatings to minimize coefficient of thermal expansion mismatches. With precision substrates many of these techniques are not very acceptable since they can noticeably alter the original surface. For example, chemical or mechanical etching can considerably change the surface finish and heating can induce distortion.

A relatively new approach that works very well and also eliminates the severe pickling, mechanical roughening or heating required of the processes just discussed is the use of augmented energy physical vapor deposition to provide an initial adherent coating and then electroplating over this to the required final thickness. Ion plating and hot hollow cathode deposition have been used successfully for providing the initial, adherent coating. Ring shear data (4) for three very difficult-to-plate metals, tungsten, molybdenum and titanium are presented in Table 2. In all cases, the adherence was considerably improved over that obtained without the use of PVD. Clearly, coupling augmented energy PVD processes with electroplating provides better adhesion than obtained with wet processes and also eliminates: 1) the need for roughening the surface chemically or mechanically, and 2) heating after coating.

Stress

Residual stresses which are inherent in deposition processes can result in distortion or be the cause of poor adherence of subsequently applied dielectric films (5-8). Some electroless nickel deposits on beryllium induce significant tensile stresses in the composite and these stresses can produce unacceptable distortions (5,8). Even room temperature relief of silver electroplating stresses can be a problem with optical parts. For example, a flat brass mirror plated with silver then diamond turned to better than 0.5 fringe deformed 9 fringes within 15 months after machining. Removing the silver by machining eliminated the distortion and essentially restored the original features (9). One technique used to minimize stress problems in these kinds of situations with silver and copper plated parts is to heat at 150°C prior to diamond turning. It is important to note, however, that with some electrodeposits this treatment could cause recrystallization and grain growth. For example, the grain size of silver deposited at 21.5 A/m^2 (2 asf) in a cyanide solution containing carbon disulfide increased from 2.36 to 3.22×10^{-6} cm during a three month storage period with a corresponding decrease in hardness from 148 to 130 VHN (10).

Table 2
Ring Shear Data Show the Value of Combining PVD with Electroplating for Coating Difficult-to-Plate Metals

Metal	Ring Shear Adhesion (MPa)	
	Electroplating	PVD & Electroplating
Tungsten	48[a](Cu)[b]	173[c](Cu)
Molybdenum	125[d](Au)	216[e](Cu)
Titanium	145[f](Ni)	252[g](Cu)

a) This process included etching in 3 parts HF, 1 part HNO_3, and 4 parts H_2O for 5 min. at 22°C followed by anodic treatment (1076 A/m^2) in 300 g/l KOH at 50°C for 5 min. prior to plating.

b) Metal in parenthesis was that used for building up the thick ring (1.5mm) required for ring shear testing.

c) The magnetron ion plating process included sputter etching in vacuum, magnetron ion plating with 6µm of copper and then electroplating to final thickness. Base pressure of the system was 5 x 10^{-6} Pa (10^{-8} Torr), etch power was 0.5 watts/cm^2, and bias power was 0.078 watts/cm^2 (but tapered to zero after deposition of about 20,000Å of copper).

d) This process included degreasing in perchlorethylene, firing in dry hydrogen (<2ppm H_2O) for 10 min., immersing in a solution containing four parts NH_4OH (28%) and one part H_2O_2 (30%) for 8 to 10 seconds at room temperature, rinsing in distilled water, gold striking to deposit 0.15 to 0.63 mg/cm^2 (0.08 to 0.32 µm), rinsing in distilled water, firing in dry hydrogen at 1000°C for 10 min., and then electroplating to final thickness.

e) The magnetron ion plating process included sputter etching in vacuum, magnetron ion plating with 6µ of copper and then electroplating to final thickness. Base pressure of the system was 5 x 10^{-6} Pa (10^{-8} Torr), etch power was 0.5 watts/cm^2 and bias power was 0.078 watts/cm^2 throughout the coating run.

f) This process included abrasive blasting, cleaning in hot alkaline solution, pickling in HCl, bright dipping in a solution containing 10% by vol. of HF (70%), 1% HNO_3 and balance water, followed by anodic etching for 6 min. at 162Å/m^2 in a 40°C solution containing 13% by vol HF (70%), 83% acetic acid and 4% water. Then 25 µm of Ni was plated in a sulfamate solution at 48°C. Specimens were heated at 480°C for 2 hours and then plated with approximately 1.5 mm of nickel.

g) This process included coating with 10 µm of copper by hot hollow cathode deposition and then electroplating to final thickness. Conditions for the etch cycle included a source power/rate of 10Å/sec, substrate voltage of 2 KV and pressure of 3 x 10^{-4} Torr. Conditions for the coating cycle were a source power/rate of 100 Å/sec, and a pressure of 3 x 10^{-4} Torr.

By judicious choice of plating operating conditions (e.g., current density, pH, solution composition, and additive content) it is possible to deposit coatings that are in a stress-free state. For example, Figure 3 shows deposit stress as a function of current density for a plating solution used to deposit up to 1 mm of copper on glass. This plot defines the current density to use to produce zero stress in the deposit and this information was utilized to coat neutral density glass substrates (15 cm by 15 cm) with 1 mm of copper and pyrex optics (22 cm diameter) with 0.4 mm of copper. This deposit was capable of withstanding single point diamond turning to provide an optical surface (Figure 4). it was also able to withstand heating at 250°C for four hours without degradation of the metal-glass bond (11).

One technique utilized to provide for real time control of stress that has been used in the electroforming of optical components is plating on a strain gage simultaneously with the actual part (Figure 5). As the plated surface of the gage bends in response to compressive or tensile forces, an analog is produced. The strain signals are analyzed by computer programs which vary the output of the power supply up or down to compressive or tensile bending of the plated surface. Stress control with this method is reported to have been held sufficiently close to zero so that dimensional accuracy in optical nickel electroforms was 0.15 µm (12).

If one has the chance to provide input on the substrate material at the design stage, this can considerably help in minimizing stress problems with subsequent coatings. An example is Figure 6, which shows the stress in electroless nickel deposits as a function of phosphorus content for aluminum and brass which have high expansion coefficients, and steel, beryllium and titanium, which have low expansion coefficients. Besides showing that the substrate has a very distinct influence on stress, the curves also show that for each metal, a deposit with zero stress can be obtained by controlling the amount of phosphorus in the coating (13).

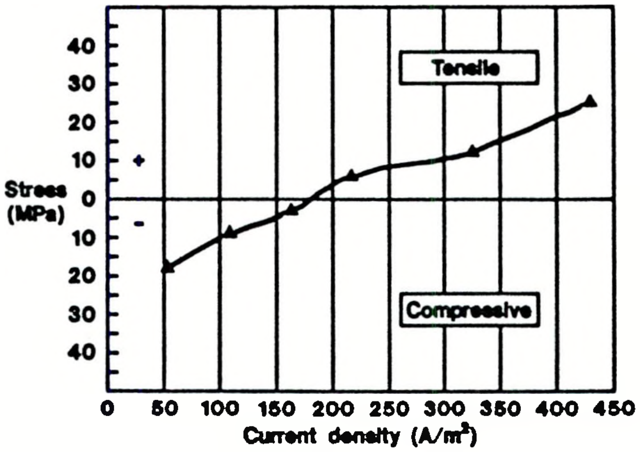


Figure 3 - Deposit stress as a function of current density for a high copper/low sulfuric acid solution containing a proprietary brightener. From reference 11.

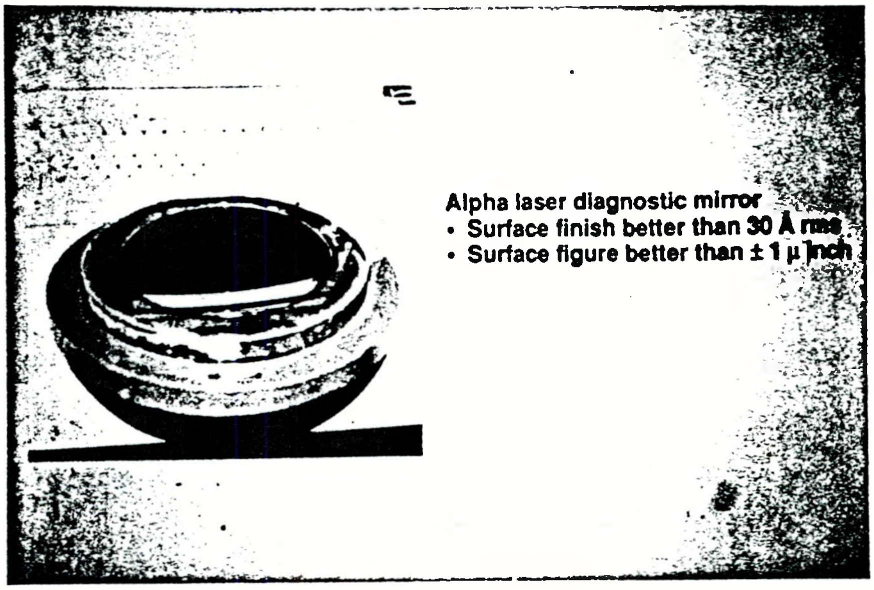


Figure 4 - Diamond machined electrodeposited copper on a glass substrate.

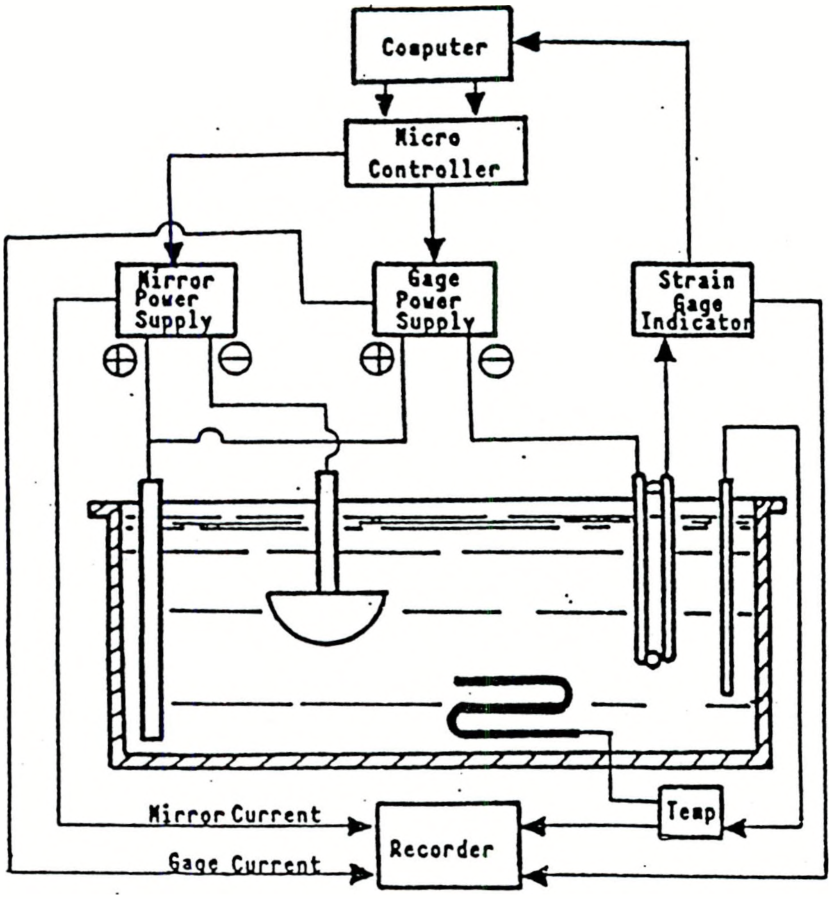


Figure 5 - Strain gage technique for measuring stress in electrodeposits. From reference 12.

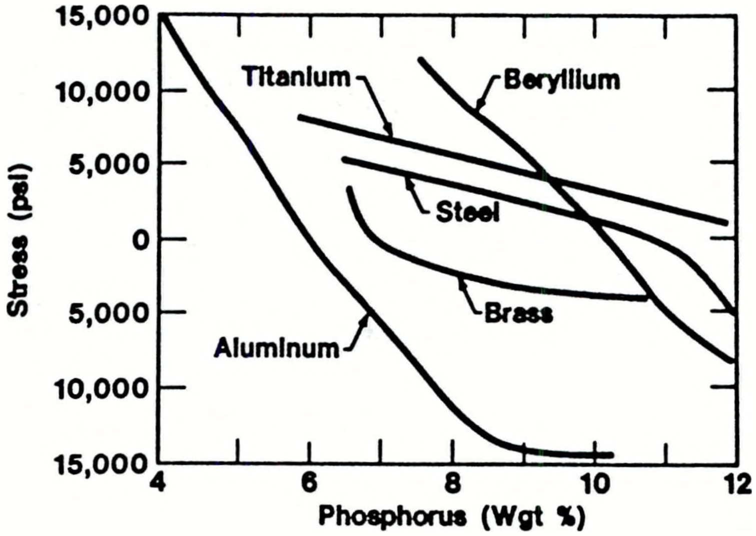


Figure 6 - Stress in electroless nickel as a function of phosphorus content for metals with a high expansion coefficient (aluminum and brass) and a low expansion coefficient (steel, beryllium, and titanium). From reference 13.

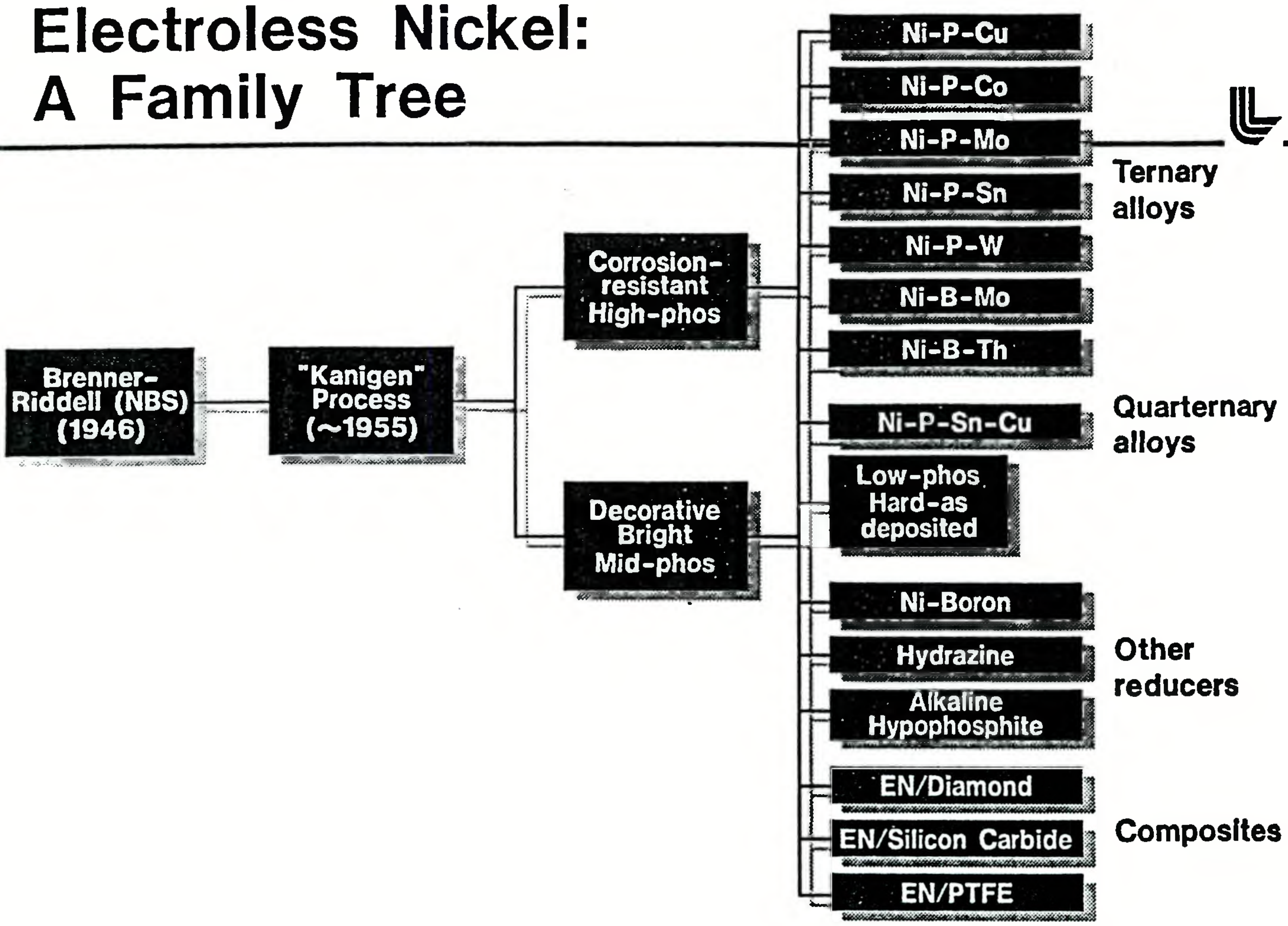
Electroless Nickel - A Brief History

Abner Brenner and Grace Riddell of the National Bureau of Standards are typically credited with starting electroless nickel on the road to commercialization (14). Their work, with solutions containing glycolate and hypophosphite and first reported in 1946, had been preceded by Wurtz in 1844 who reported that nickel metal could be produced from a solution containing nickel salts and hypophosphite (15) and the first patented report of thick, adherent nickel deposits in a hypophosphite solution by Roux in 1916 (16). General American Transportation Company in the mid 1950's established the first commercially feasible electroless nickel process, known as the "Kanigen" process utilizing solutions containing lactate and hypophosphite (17). They developed stabilizers which prevented dissociation of the solution by masking catalytically active nuclei (18). Small amounts of lead, tin, arsenic, molybdenum, or thiourea were effective in stabilizing the solution and this led the way to effective commercialization of the process.

The Kanigen patents have long since expired and today there are many dozens of suppliers who market formulations for electroless nickel plating. For that matter, there are any number of electroless nickel deposits that can be commercially deposited, including the engineering types with high phosphorus content, the more decorative middle phosphorus deposits and the recent low phosphorus deposits for improved wear resistance. Also, other metals or compounds can be incorporated in the deposit for enhanced properties in specialized applications. As Stevenson recently stated, "Today, electroless nickel truly is a family of coatings:" (19), and this is shown in Figure 7.

Figure 7

Electroless Nickel: A Family Tree



Brenner-Riddell (NBS) (1946)

"Kanigen" Process (~1955)

Corrosion-resistant High-phos

Decorative Bright Mid-phos

Ni-P-Cu
Ni-P-Co
Ni-P-Mo
Ni-P-Sn
Ni-P-W
Ni-B-Mo
Ni-B-Th

Ternary alloys

Ni-P-Sn-Cu

Quarternary alloys

Low-phos Hard-as deposited

Ni-Boron
Hydrazine
Alkaline Hypophosphite

Other reducers

EN/Diamond
EN/Silicon Carbide
EN/PTFE

Composites

Electroless Nickel-Influence of Phosphorus Content

Electroless nickel deposits for single point diamond turning should contain at least 11% (wgt) phosphorus to minimize tool damage (Figure 8). A stress relief treatment at 200°C for 2 hours even further enhances the cutting characteristics of deposits containing greater than 11% phosphorus (20).

Electroless Nickel-Pitting

A general requirement for electroless nickel for optical use is that it have no porosity since porosity on the finished surface would result in a void on a mirror surface or a "pip" in the molded surface. Both of these are degrading to optical performance (21).

Typically, with precision parts, the plater does not have the luxury of an endless supply of parts or for that matter sometimes even one practice part that could be used for characterizing the deposition process. This means that occasionally parts have to be stripped and re-plated because of defects such as pits in the coating. Obviously, this is not an ideal situation. What clearly is needed is some manner of characterizing the plating operation so that when the actual part is coated, the chance for defects is minimized to the highest degree possible. A methodology for handling this type of situation is one of the goals of the organizers of this conference.

In the thin film rigid memory disk industry where electroless nickel plays an important part, much effort has been directed at understanding the cause and influence of defects (22). Microscopic examination of both as-plated and lightly polished electroless nickel surfaces has revealed that the surface defects that contributed to yield and magnetic performance problems were pits which could be classified into two groups. The first type (class A) were small (2-10 µm) circular pits of varying depths. The second type (class B) were considerably larger (10-30 µm) and irregularly shaped. Class A pits were found to be the most frequent in number and process related due to chemical imbalance in the plating solution. Class B pits were often only one or two per surface and related to prior physical handling damage in the aluminum substrate and particulate matter in the electroless plating solution.

Another example is random micropits on the surface of computer discs that were driving electroless platers "buggy". They had prepared solutions carefully, using deionized water, clean room conditions, carefully cleaned discs, and effective filters. Still pits of very small size were causing about six percent of the computer discs to be rejected, with one or more random pits on the surface (23). After much analysis it was finally discovered that the pits were caused by a micro-organism that was able to live in the plating solution. Once this discovery was made, the platers checked the system and found organisms in the deionized water. These nematodes were originally in the "raw" water. As the water went through the ion exchanger they multiplied and remained in the carbon filters, eventually escaping into the deionized water. By irradiating the water with UV light, the platers were able to kill the organisms and eliminate pitting of the discs (23,24).

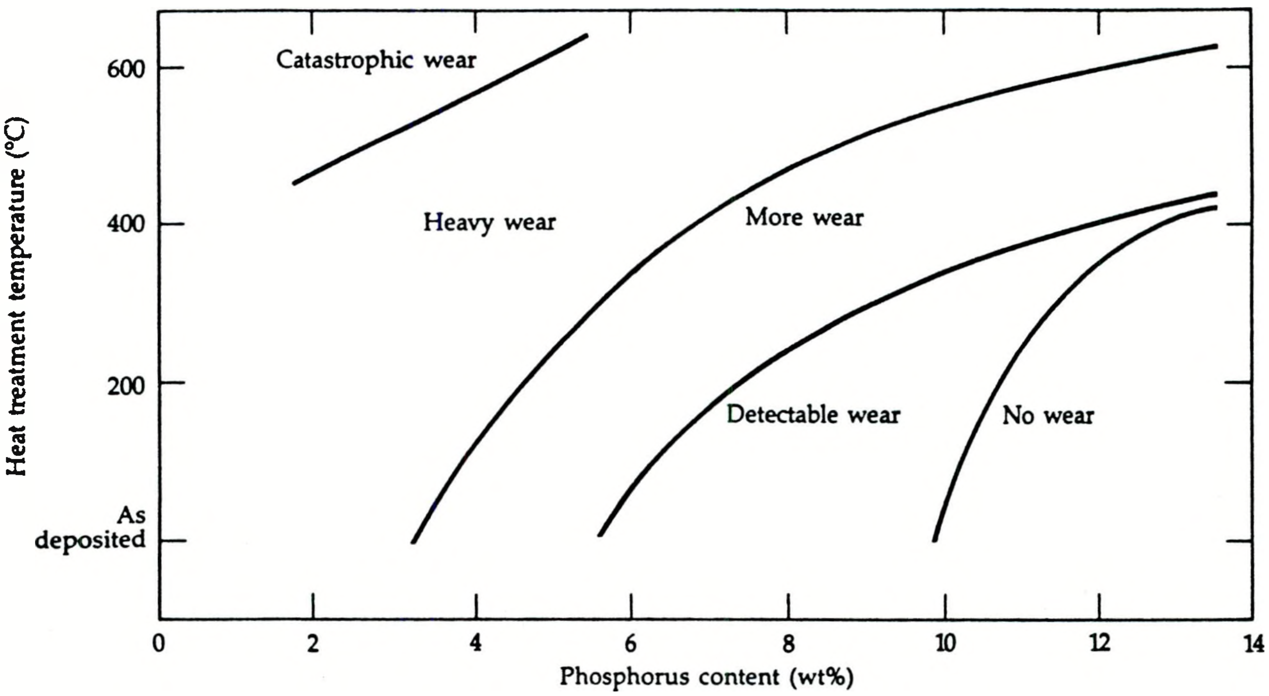


Figure 8 - Map of diamond tool flank-face wear and damage vs. electroless nickel phosphorus content and heat treatment conditions, based on scanning electron microscopy. From reference 20.

Recently, American Metaseal Corporation of Maryland discovered that in its area of the country (mid-Atlantic region) electroless nickel plating on aluminum required DI water. Hard water left mineral deposits in the solution that caused pitting and roughness on parts (25).

The purpose of the above discussion on pitting is to show the insidious nature of the problem. It can be a very complex issue and require a considerable amount of time and effort to understand and control.

Microstructural Stability of Electroless Nickel, Copper and Silver Deposits

A potential problem in using coatings for precision finishing applications is metallurgical instability. Electroless nickel, copper and silver deposits all have the possibility of undergoing changes that could seriously affect precision parts.

As-deposited electroless nickel is metastable and undergoes a crystalline transition at moderate temperature (240 to 400°C). This change causes a rapid increase in the hardness and wear resistance of the coating while reducing the corrosion resistance and ductility (26,27). The transition also causes an increase in density and accordingly a decrease in volume. This volume change, which can vary from 0.1% to 1.3% (28-30), coupled with differential thermal expansion is the cause for cracking or fissuring often found in deposits after heat treatment (30). The extent of the crystalline transition is a complex function of a number of factors including: 1) temperature and time at temperature, 2) heating rate, 3) previous temperature history, and 4) phosphorus content (31). Figure 9 provides a time/temperature profile which illustrates the transition from an amorphous to a crystalline structure for electroless nickel containing 11% phosphorus. If thermal exposure is maintained in the time/temperature envelope below the dotted curve, then the electroless nickel will remain entirely amorphous. However, if exposure conditions fall above this curve, then partial or complete crystallization will occur(31).

Copper deposits have been shown to markedly soften after storage at room temperature for 30 days (32). Interferometric tests on copper mirrors revealed a change in the optical surfaces over a period of six months. Metallographic analysis revealed that recrystallization had occurred in the copper, accompanied by a shifting of the surface along individual grain boundaries(33). 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. Figures 10 and 11 show the roughening of a single point diamond turned copper electrodeposit as a result of recrystallization. The problem is caused by the high density of defects in the electroplated copper, often much higher than that achieved by cold working. Differential scanning calorimetry (DSC) showed that copper plated at 5 asf had a very high recovery energy exotherm of 1.97 J/g at 148.5°C and a much lower recrystallization energy exotherm of 0.529 J/g at 283.8°C (Figure 12). 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 (Figure 13). To

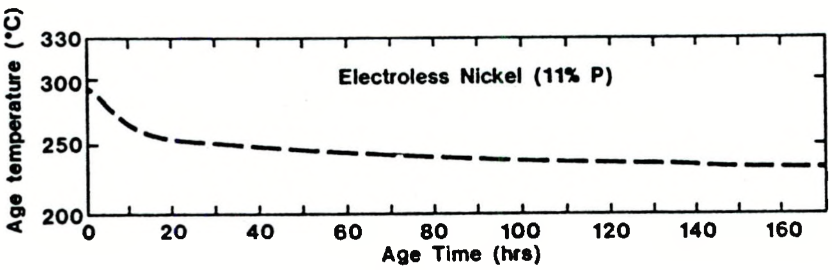


Figure 9 - Time/temperature profile illustrating the transition from an amorphous to a crystalline structure for electroless nickel containing 11% phosphorus. From reference 31.

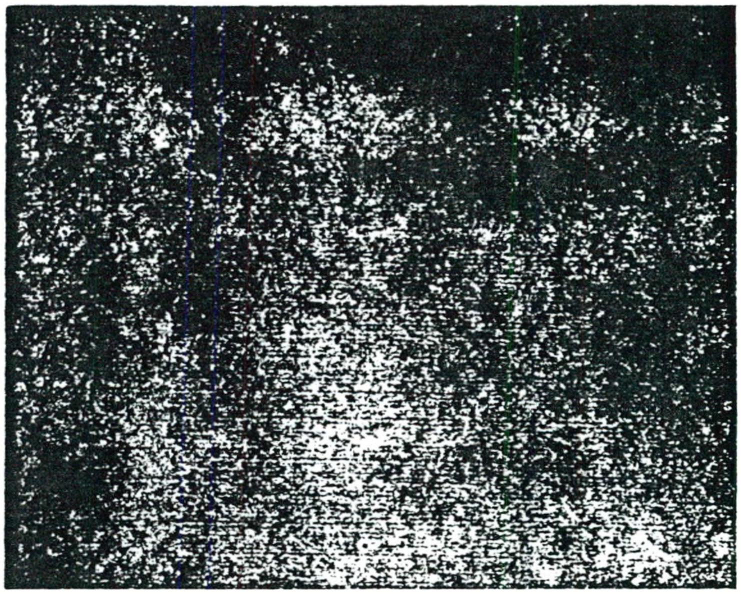


Figure 10 - Nomarski micrograph of a diamond turned copper surface before recrystallization (100X). From reference 33.

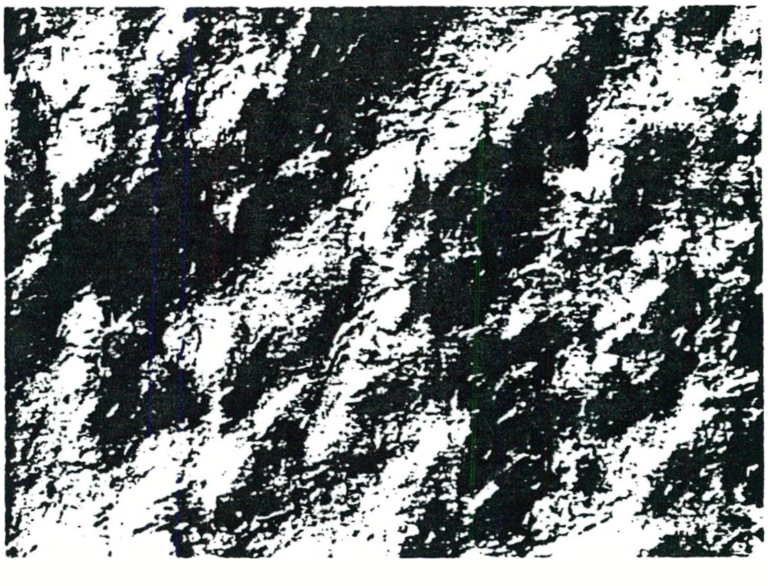


Figure 11 - Nomarski micrograph of a diamond turned copper surface after recrystallization (100X). From reference 33.

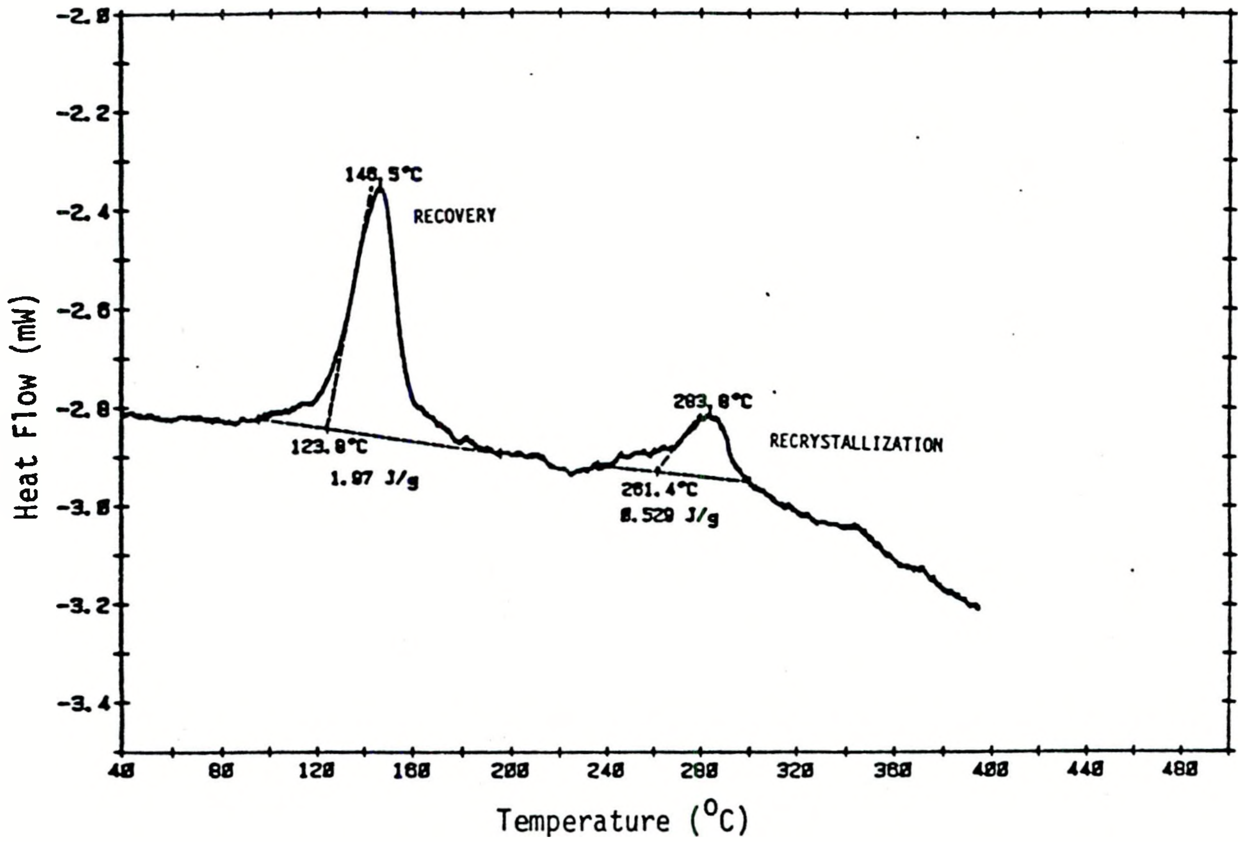


Figure 12 - DSC showing exotherm at 148.5°C and 283.8°C for copper plated at 5 asf. From reference 33.

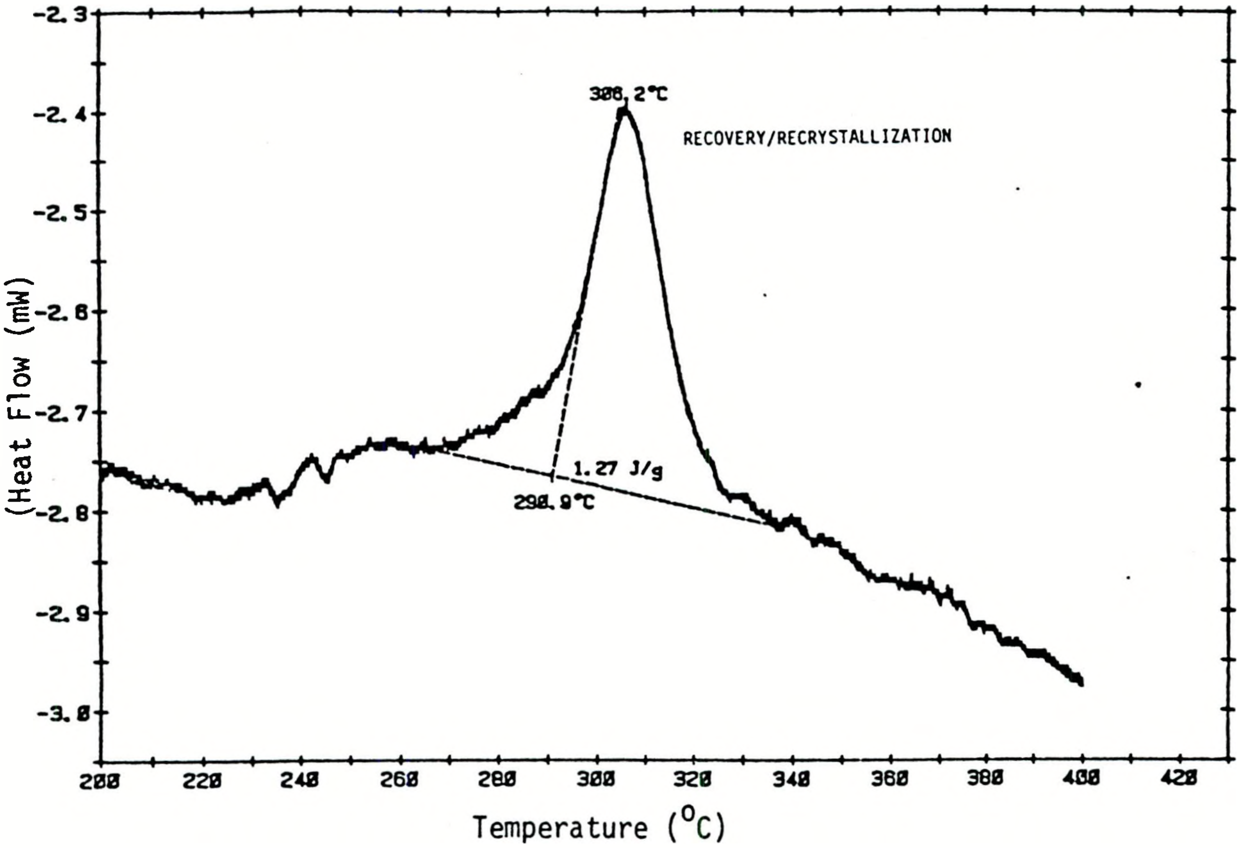


Figure 13 - DSC showing energy release at 306.2°C for copper plated at 15 asf. From reference 33.

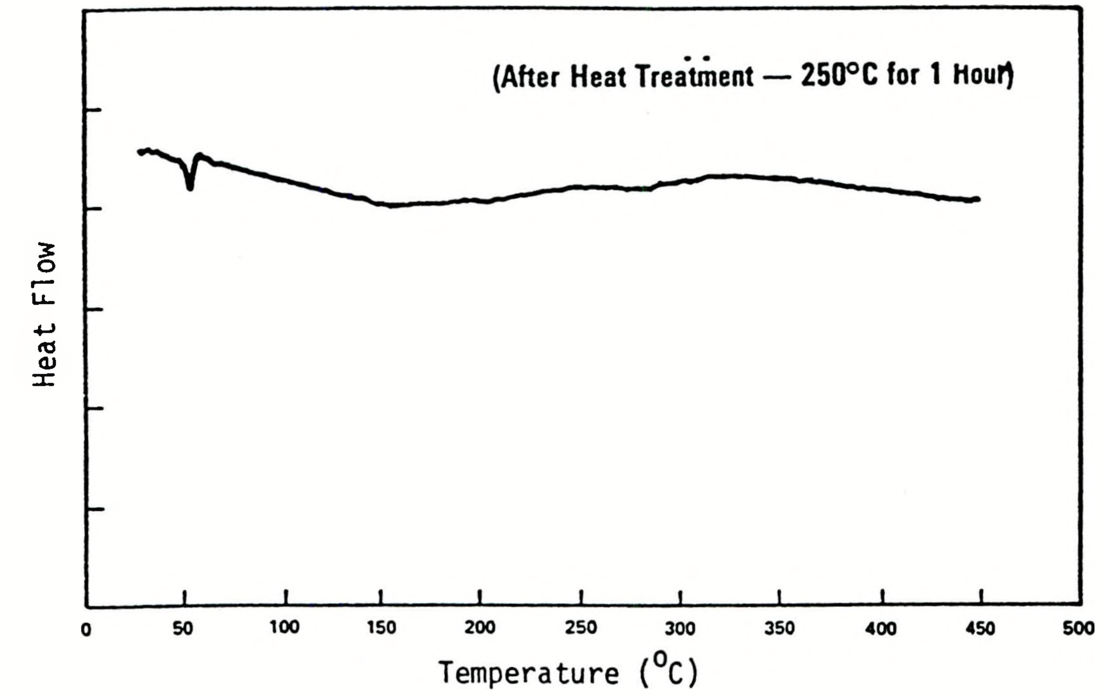


Figure 14 - DSC of copper which had been plated at 5 asf and then heat treated. From reference 33.

eliminate the problem of recrystallization at room temperature, the low current density copper is given a low temperature heat treatment (1 hour at 250°C) to remove the recovery energy without causing recrystallization and grain growth (33). 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 (Figure 14).

Silver deposits have also gone through changes on precision parts. This was discussed earlier in this paper in the section on stress in coatings.

Potential Future Coatings

Electrodeposited Nickel-Phosphorus Alloys

Recently, increased attention has been directed at electrodeposition as an alternate to electroless deposition for producing Ni-P alloys. The electrodeposition process offers a number of potential advantages:

1) alloys with 14-15% P which is higher than that obtainable with electroless nickel are possible, and as shown in Figure 8, higher P means less tool wear.

2) an order of magnitude greater deposition thickness can be produced.

3) noticeably less expensive than electroless deposition since electrodeposition is not a batch process.

4) the possibility of reduced porosity

Preliminary work at three different establishments has shown the viability of substituting electrodeposition for electroless deposition of Ni-P alloys. At LLNL an electrodeposited Ni-14P coating compared quite favorably with electroless nickel coatings even after a cutting distance of 25 km (15.3 miles). Figure 15 shows a collection of surface roughness profiles, 500 microinches in length at cutting distances from 15 to 60,000 ft. for electroless Ni-13P, illustrating the variety of profile shapes and amplitudes that occur. Figure 16 shows a similar measurement for electrodeposited Ni-14P at the end of the test after a cutting distance of 81,000 ft. Comparison of the two figures reveals that for the tools used in these studies, the electrodeposited Ni-P was not as damaging to the tool as the electroless Ni-P. With electrodeposited Ni-P, rms roughness after cutting 81,000 ft was 15.7 Å versus 83.2 Å for electroless nickel after 60,000 ft of cutting (34).

Researchers at NIST also reported good results with electrodeposited Ni-15P. After 40 km (24.8 miles) of machining, no change in surface finish was noted (35). Recent results published in Australia also suggest that electrodeposited Ni-P is a viable alternative to electroless Ni-P in the high quality finishing of mirrors (36).

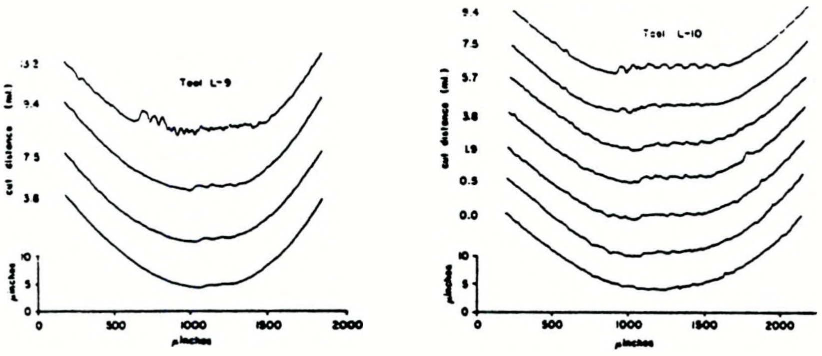


Figure 15 - Talystep profiles of replication grooves for electroless nickel labeled with cutting distance in miles. The leading edge of the tool is toward the left. From reference 34.

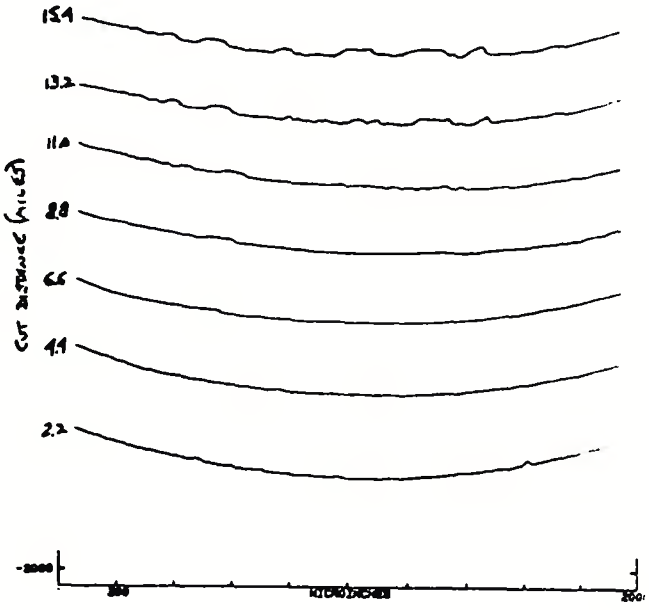


Figure 16 - Talystep profiles of replication grooves for electrodeposited Ni-P with cutting distance in miles. The leading edge of the tool is toward the left. From reference 34.

Lastly, Lashmore and co-workers have reported that pulse plated Ni-P alloys can contain greater than 20% P with a layer spacing that is much finer and more uniform in appearance than that in the dc alloy (37,38). This would be an intersting material to evaluate for diamond turning applications.

Electrodeposited Silver Alloys

Silver, which surpasses other metals in terms of reflectivity in the spectral region from 15 to 0.4 μm, is widely used in optical instrument manufacture as a mirror coating. However, silver coatings must be protected in order to prevent a loss of their reflectivity in air. Some Russian researchers have reported that it is possible to electroplate alloys of silver-antimony (2.7%) which are about 2 times harder than pure silver and 10-15 times more abrasion resistant. Tests under natural climatic conditions for two months with ambient relative humidities of 65 ± 15% and temperatures of 25 ± 10°C showed that silver was covered with a continuous black film after a month, while the silver-antimony coating suffered practically no change (39). Some work directed at determining the practicality of depositing silver-antimony alloys and also determining if these alloys are diamond turnable might prove fruitful.

Silver alloys containing 10 to 27% tin also are worth some consideration. Alloys containing 10% tin reportedly exhibit good ductility and solderability and have a low coefficient of friction. They also exhibit considerably improved tarnish resistance when compared with pure silver (40). Another potential coating is the intermetallic Ag_3Sn (73 Ag-27 Sn). Electrodeposited coatings of this alloy could be polished to high luster and were more resistant to tarnish in sulfide mixtures than pure silver (41).

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