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Session J: Electroless Deposition II

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Electroless Deposition I
Session J

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J-1

Electroless Deposition II
Session J

Electroless Nickel Waste Treatment

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PAPER NOT RECEIVED IN TIME FOR PUBLICATION*

Electroless Nickel Waste Treatment

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Chemical waste treatment of spent electroless nickel baths is becoming increasingly important. This paper will investigate some of the common chemical and physical approaches to treatment, including precipitation, thermal destruction, liquid ion exchange, electrowinning, and ozonation. Cost data, chemical and equipment efficiencies, and strategies for reusing the nickel will be discussed.

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J-2

Electroless Deposition II
Session J

Factors Affecting Quality Electroless Nickel Plating of Thin Film Memory Disks

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FACTORS AFFECTING QUALITY ELECTROLESS NICKEL PLATING OF THIN FILM MEMORY DISKS

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Introduction

Electroless nickel has become the industry accepted standard as a base metal foundation for both plated and sputtered magnetic media on rigid aluminum computer disks. The increased information storage capacity (100 X the capacity of similar "floppy" disks), resistance to wear, increased speed of information capabilities for bulk manufacturing and improved reliability have made this technology ideal for today's booming business computer market.[1] However, due to the low flying heights (<10 micro-inches) of the recording heads and the high speeds used in the Winchester-type disk drives, great care must be taken in providing consistent high quality, low cost plating of aluminum memory disks. This paper will discuss the various factors that can affect the overall yields of high quality plating and finishing which in turn can affect the technological risks each company faces as it enters the making of thin film media for hard disk drives.

Discussion

Inherent properties of electroless nickel make this coating an obvious choice for rigid aluminum disks. These properties include uniform deposit thickness, diffusion barrier characteristics, corrosion resistance, non-magnetic nature of the deposit, and the ability to be polished to an optical finish.[2] To maintain consistency, certain parameters must be closely monitored in the plating operation. These parameters include smoothness of the as-plated surface, pitting, adhesion of the EN to the substrate, and of course certainly the non-magnetic nature of the deposits.

To control these parameters several factors must be followed closely. These factors, which can influence overall yields individually or in combination, are as follows:

1) Substrate, type and quality
2) Pretreatment
3) Electroless Nickel Bath
4) Polishing

Since the finished product must be essentially defect-free, variations such as the mineral content of the water can cause catastrophic problems. Hence, a complete understanding of every possible factor which can affect the overall quality of plating is essential.

Substrates

The aluminum substrate plated with the electroless nickel barrier coat has a profound affect on the quality of the final product. Among the important characteristics of the substrate are coefficient of expansion, moment of inertia, stiffness, residual stress and workability. Experience indicates 5000 series aluminum provides the core of plated disks, but other materials are prime candidates for future disk substrates such as glass, ceramics, and plastics.

At present aluminum alloys 5086 and 5586 are used mainly as the disk substrates. A summary of some of the aluminum alloys available from suppliers is found in Table I.

Table I

Aluminum Alloys by Supplier

Chemical Composition Limits/Ranges

Alloy	Fe	Si	Mn	Cu	Mg	Cr	Ti	Zn	Al
Alum.(5086) Assoc. Std.	0.40	0.50	.2-.7	0.10	3.5-4.5	.05-.25	.15		Balance
Kobe									
KS5086	0.5	0.4	.2-.7	0.1	"	"	"	.25	Balance
KS5186	0.16	0.1	.05	0.03	4.3-4.9	.05-.1	.03	.05	Balance
KS5586	0.16	0.1	.05	.05-.4	"	"	.03	.05-.4	Balance
NLM									
5086	.08	.05	.2-.3	.03	3.4-4.5	.05-.1	.03	--	Balance
T4M	.08	.05	--	.003	3.7-4.7	--	--	--	Balance
M4M	.06	comb.	--	.02-.1	3.7-4.7	--	--	--	Balance
Sumitomo									
486S	.5	.4	.2-.7	.1	3.5-4.5	.05-.25	.15	.25	Balance
XA334	.07	.07	.02	.02	"	.06	.01	.01	Balance
ZG50	.5	.4	.3	1.0-1.4	2.5-3.1	.13-.17	.2	4.6-5.4	Balance
Stolle									
5086	.4	.5	.2-.7	0.1	3.5-4.5	.05-.25	.15	.25	Balance
CW66	.08	.08	.2-.6	.02	3.5-4.5	.02-.1	.15	.25	Balance
CZ46	.08	.08	0.1	0.2	3.7-4.7	.1	--	.45	Balance

As seen in Table I, all substrates are predominantly magnesium alloys of aluminum. Hence, pretreatment must be specific for this type of substrate.

Upon further experimental investigation, it has been found that the relationship between intermetallic compound distribution and the grain size of the alloy can profoundly affect the defects of the Ni-P layer. Materials which are free from intermetallic compounds and/or are dense and homogeneous can improve the quality of the EN film (i.e., surface roughness and adhesion).[3] Figures 1 and 2 are photographs which depict the differences between the surface roughness of different alloys in the pretreatment and plating processes.

The differences of the EN film can be attributed to the differences of the zinc precipitates upon each alloy. The homogeneity of the zinc immersion layer has been found to be directly proportioned to the uniformity and grain size of the alloy itself.

Besides the quality of the alloy, there are two types of manufacturing techniques which provide distinct finishes of the substrate that the plater must cope with. These finishes are commonly referred to as diamond turned disks and matte finish or polished disks. Both finishes respond very differently to pretreatment methods and must be understood clearly in order to address the requirements of each.

Diamond turned disks are machined to a very flat, very smooth surface, to a typical finish of 0.0127 micrometers maximum arithmetic average deviation.[4] These disks have been rough cut from a stamped blank using a high carbon steel cutter. Since the first cut usually removes more material than the second cut, the first side can have much greater internal stress. This condition, concomitant with the fact that very high temperatures are produced in the cutting operation, may recrystallize the alloy and provide further differences between one side of the disk and the other. For example, greater levels of nodularity will manifest itself as a result, especially on the stressed side of the disks. Often this is perceived as a plating problem when it is not. Another consequence that can occur will be the difference in domain formation of the cobalt layer on one side of the disk versus the other. Different levels of nickel stress can affect the uniformity of the cobalt layer especially at the thin deposit ranges of 2-4 micro inches commonly used today.

Matte finishes are also constructed from a stamped blank. Unlike the diamond turned disks, these are ground to rough dimensions using large volumes of lubricant. Both sides are processed at the same time, hence surface stresses can be eliminated with this process.[5] Finished surfaces are achieved by proprietary polishing compounds. This method produces very flat disks with smooth surfaces which platers can easily activate, provided proper care is given to complete removal of polishing compounds in the pretreatment cycles.

Pretreatment

Pretreatment is crucial to developing consistent, reliable results in the production of high quality thin film disks and its importance cannot be overstated. In the past 10 years great strides have been made in the preparation of aluminum which have resulted in consistent plating yields of 99% or higher. A typical process cycle for various disk alloys is found in Table II.

Table II

General Pretreatment Process for Rigid Film Memory Disks

Process Step	Time	Temperature
1. Alkaline Soak Cleaner	2 - 8 minutes	130 - 160°F
2. DI Water Rinse		
3. Acid Etch/Conditioner	30 sec. - 2 minutes	R.T.- 150°F
4. DI Water Rinse		
5. 50% Nitric Acid Desmut	30 - 60 sec.	65 - 75°F
6. DI Water Rinse		
7. Dilute Alloy Zincate	30 - 60 sec.	65 - 75°F
8. DI Water Rinse		
9. 50% Nitric Acid	30 - 60 sec.	65 - 75°F
10. DI Water Rinse		
11. Dilute Alloy Zincate	20 - 30 sec.	65 - 75°F
12. DI Water Rinse		
13. EN Plate to Desired Thickness		
14. Dry		

Every step in the cycle is critical in order to obtain excellent performance and yields. Each step works in concert with the preceding and subsequent steps; hence a complete understanding of the mechanism of the pretreatment cycle is essential for successful plating of rigid disks.

Alkaline Soak Cleaner

The first step in the pretreatment cycle is the alkaline soak cleaner. Its job is simply to remove soils, lubricants and polishing compounds from the disks' surfaces by emulsification or dissolution. Pre-cleaning may be necessary to remove excess lubricants or polishing compounds which can cause dullness, pitting and/or nodularity. Some soak cleaners can actually etch aluminum causing voids which later appear as shallow spots. Careful control of time, temperature, pH, and concentrations of cleaner is essential for excellent yields. Silicated soak cleaners are most commonly used since they tend to be less aggressive towards aluminum and are excellent cleaners at elevated temperatures. However, when silicated cleaners are used, thorough rinsing is necessary following their use. Careless rinsing can lead to the formation of an insoluble silicate film which may lead to increased nodule formation as well as decreased adhesion of the EN to the aluminum substrate.

Acid Etch/Conditioner

One of the more critical steps in the preplate cycle is the acid/etch conditioner. Its primary function is to deoxidize the surface and remove the various alloying elements and inclusions from the aluminum surface. Most alloying constituents not removed can and will manifest themselves as sources for pits, nodules, blisters or cause poor adhesion for many reasons. Alloying elements such as magnesium, manganese, and copper found in 5086 and 5586 alloys will be removed in the acid etch. However, profilometer studies on acid etches indicate only modest changes of the surface from its original polished condition. Thus, removing the alloying elements at the surface and minimally attacking the aluminum rich surface of the memory disk substrate make acid etches the preferred etch in the process. For some applications acid conditioners have been used in place of acid etches. However, for diamond turned substrates the acid etch is preferred.

Nitric Desmut

The next step of the process involves the desmutting of the aluminum surface. The purpose of this step is to remove insoluble residues from the previous conditioning steps. Desmutting should leave a uniform, white, thinly oxidized aluminum-rich surface for the application of zincate. If the desmutting is incomplete and excess alloy segregations are left on the surface adhesion failures or nodules will become obvious.

Zinc Immersion Process

Following the desmutting of the surface comes the immersion process, commonly referred to as "zincating". Zincating continues to be the most reliable way to produce consistent adherent deposits of EN on aluminum. Aluminum has a natural affinity for oxygen, so there is always an oxide film present on the aluminum surface. This ever present oxide film interferes with the formation of metallic bonds of the EN to the aluminum. Consequently, the zincate immersion process was created simply to replace the oxide film with a thin metallic film of zinc which is resistant to oxidation. This process was first described by Hewitson in 1927[6] and modified later by Korpium[7] and Pernier.[8]

Within the last 5-7 years, alloy zincates have been found to be superior to the conventional alkaline zincates for many disks. Lashmore[9] reports that alloy zincates are superior in part to the alloying effects of the other metals. Immersion deposits from alloy zincates have been found to be thinner, more durable and highly uniform, which lead to improved adhesion and greater life of the EN bath. Deposits from these types of zincates leave thin "zinc rich zones" as described by Mallory.[10] These "zones" create excellent reproducible adherent EN deposits. Filtering of these solutions can be advantageous by the removal of zinc oxide which can be created at the air-solution interface. Nodules or poor adhesion will become noticeable by improper maintenance of these solutions.

Immersion times, concentration of the zincate, and temperature can affect the properties of the zincate. Constant attention to these parameters will provide consistent high quality deposits.

Finally, double zincating has been proven to yield more adherent, smoother EN deposits. The first zincate is removed in the dilute nitric acid followed by a second shorter immersion in a similar zincate. The mechanism of improved adhesion using double zincating is based on the fact that the first zincate provides porous incomplete coverage allowing potential sites for bad adhesion to occur. The nitric acid dip after the first zincate is important because it purifies the aluminum disk by removing exposed inclusions brought to the surface by the aggressive first zincate. The second zincate immerses much more densely and uniformly as a result and is noticeably thinner. Profilometer measurements clearly indicate the second zincate application is much more uniform and smoother than the first.[11]

Electroless Nickel Bath

One of the most important factors in providing high quality yields is the selection and control of the electroless nickel solution itself. Many different compositions of EN baths can give various results. For instance, the EN bath itself can directly be responsible for the following results:

1) Smoothness of the as-plated process
2) Non-magnetic nature of the deposit
3) Pitting of the deposit
4) Life on aluminum before blisters occur
5) Maintenance of rate over the life of the bath

All these factors are important to successful plating of rigid film disks and can substantially affect the overall yields.

The smoothness of the deposit is important in order to reduce polish cycles and allow for thinner deposits. Large cost savings can be realized by smoother as-plated deposits. Pits, even after polishing, can become evident if the EN deposit is crystalline in appearance masking over "shallow spots" areas. Figure 3 depicts EN deposits from two different formulations with DEKTAK traces of each.

The non-magnetic nature of the deposit is also a vitally important aspect of the EN bath. This non-magnetic quality is directly related to the amorphous structure of electroless nickels of high phosphorus content. Also, different types of chelation have been shown to affect the magnetic nature of the deposit.[12] It is imperative the EN bath be non-magnetic and amorphous since the coercivity of magnetic film overcoats are affected by the physical character of the surface upon which it is plated. If the crystallites of the magnetic layer should start non-uniformly, the squareness of the loop will suffer as will the noise ratio of the film.

Pitting of the EN deposit can be induced by the bath itself. Improper chelation, buffering, wetting agent selection, and stabilization are factors which can greatly exaggerate the phenomenon of pitting. Varied opinions have been voiced on the mechanism of pitting as it pertains to memory disk plating, but this topic goes beyond the scope of this paper and will be addressed in a future paper. Some of the pits experienced are pictured in Figure 4, 5 and 6.

The average life on aluminum for high phosphorus EN baths is 3-6 regenerations before adhesion failure occurs. Yarkosky and co-workers[13] claim the adhesion failure results from the increase in total acidity of the plating bath. Other investigators indicate that the adhesion of the coating to the substrate is influenced by the nature and magnitude of stress in the EN deposit.[14] Careful control of pH values and alkali used in pH adjustments can significantly prolong the useful life on aluminum disks. Bath formulations designed to prevent zinc contamination can further prolong the EN bath life on aluminum.

Maintaining the rate of the EN bath over the life of the bath can be useful and cost effective. By maintaining a consistent rate, high production volumes can be realized, reducing rejects due to low nickel thickness. Shorter bath times late in the EN bath life keep production time useful and profitable. Increased zinc contamination of the EN bath can suppress overall plating rates, so great care must be taken in rinsing after the last zincate to prolong the bath life of the EN.

Polishing

Since polishing is a major cost step in the process of thin film manufacturing, its economics of technique, materials, labor and yield have a great effect on the success of the enterprise. The character of polishing pads, laps, abrasives, and cutting fluids must be matched to the character of the EN, the type of machinery used, and the desired finish (Ra≤200 A).[15] These optimums can only be experienced at each facility and are usually kept confidential. However, pits after polishing are a common experience and some of the causes are described in Table III.

Table III

Causes of Pits After Polishing

1) Too much pressure in polishing
2) Too slow speed in polishing, get eddying effect
3) Pads too soft. Follows contours of substrate
4) Slurries too thin
5) Lapping action incorrect, must be perfectly parallel to the substrate

As indicated in Table III, many factors can cause pits after polishing. If too much pressure is present in polishing, nodules can be torn from the

surface and the broken nodule can scratch the data surface later in the polish sequence. These scratches can appear as irregular size pits. A typical case is diagrammed in Figure 7.

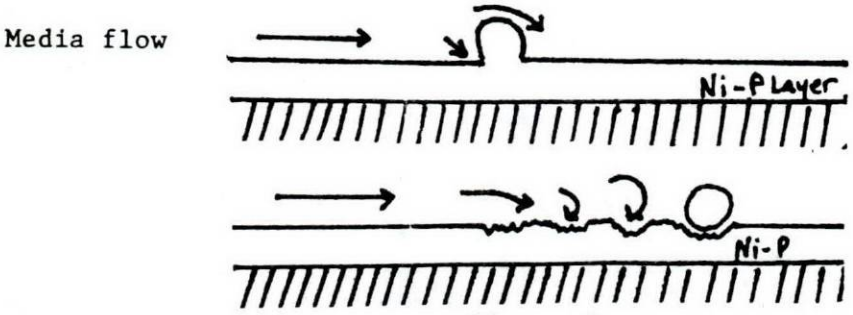

Figure 7

A too-slow speed in polishing can also contribute to pits after polishing. The slower speeds will not break away gross nodules as quickly and an eddying effect may take place immediately after the nodule. Figure 8 depicts this phenomenon.

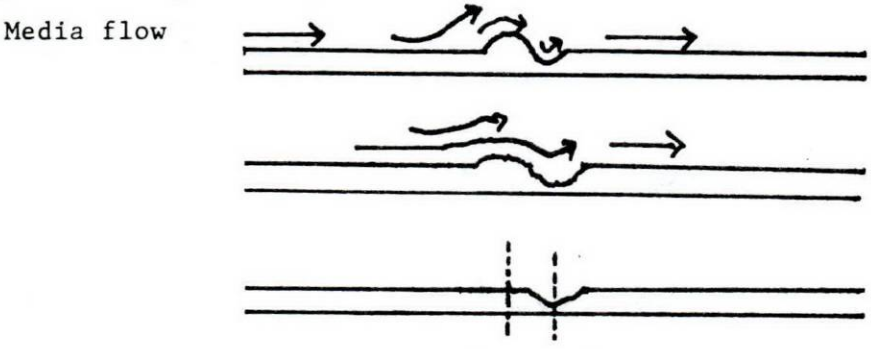

Figure 8

As can be seen, a pit will become evident immediately following the gross nodule. In a similar fashion, soft pads can also create the same phenomenon. Immediately after the gross nodule, soft pads can etch away the nickel more aggressively. The end result is similar to the slow speed polishing.

Slurries too thin can cause aggressive etching to occur. Smooth finishes and high yields will not be attainable if this should occur.

Finally, lapping action must be done very carefully and parallel to the substrate. Any discontinuity here will cause etching of the EN deposit and irregular scratches or pits will be created.

Summary

Herein it has been clearly demonstrated that many complex factors can affect the overall quality and yields of thin film memory disks. Obviously, to trouble-shoot problems in this industry can be difficult, time-consuming, and costly. Companies that have survived up to this point, however, are now attaining yields in the high 90's. This is a substantial increase from the

yields of <70% just a few years ago.

Substrates, pretreatments, EN baths and polishing techniques have significantly improved over the past few years. With continued refinement in all areas this industry will see continued expansion in the future. Further improvements, especially in the EN baths in terms of extended bath life, as-plated smoothness, and faster plating rates, can make EN a more viable choice over the ferric oxide based disks of today.

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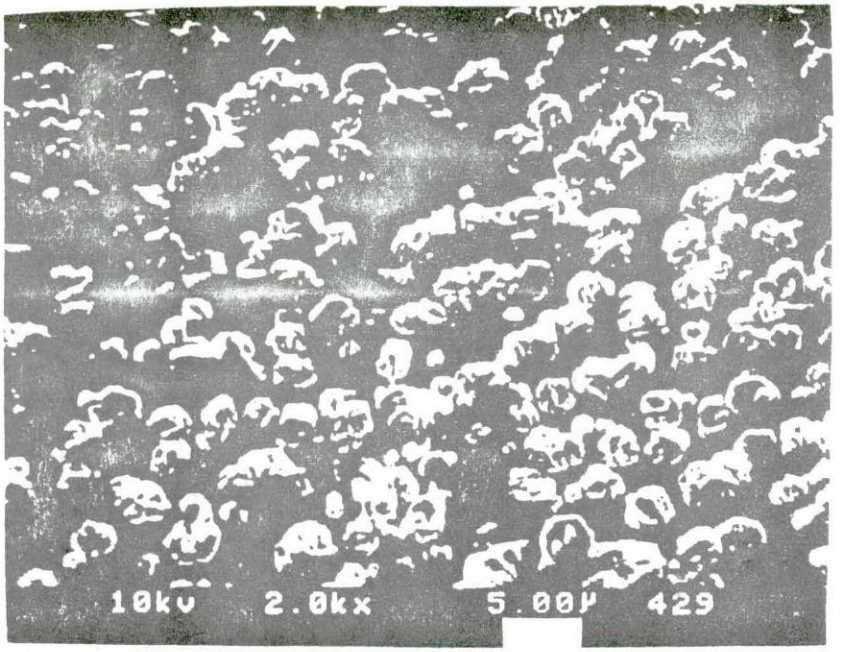
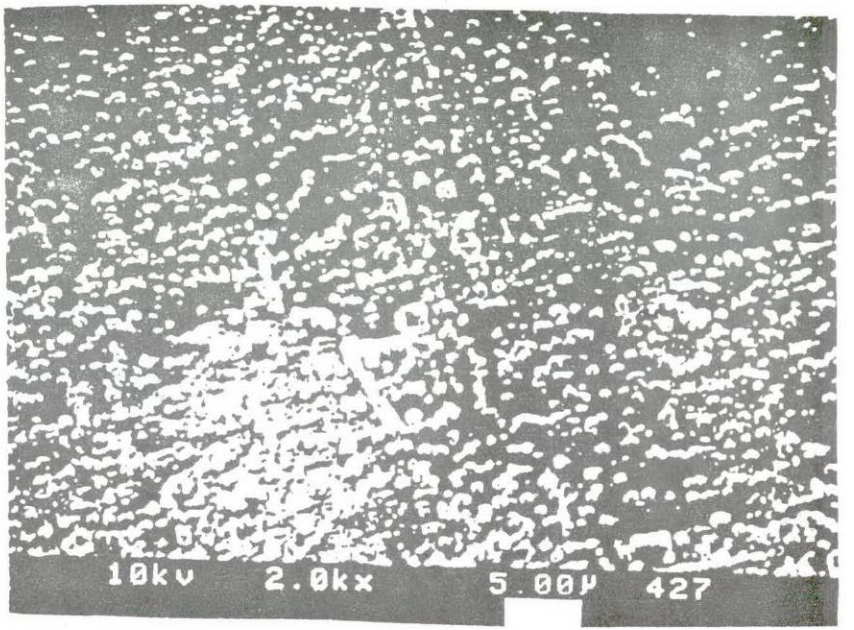
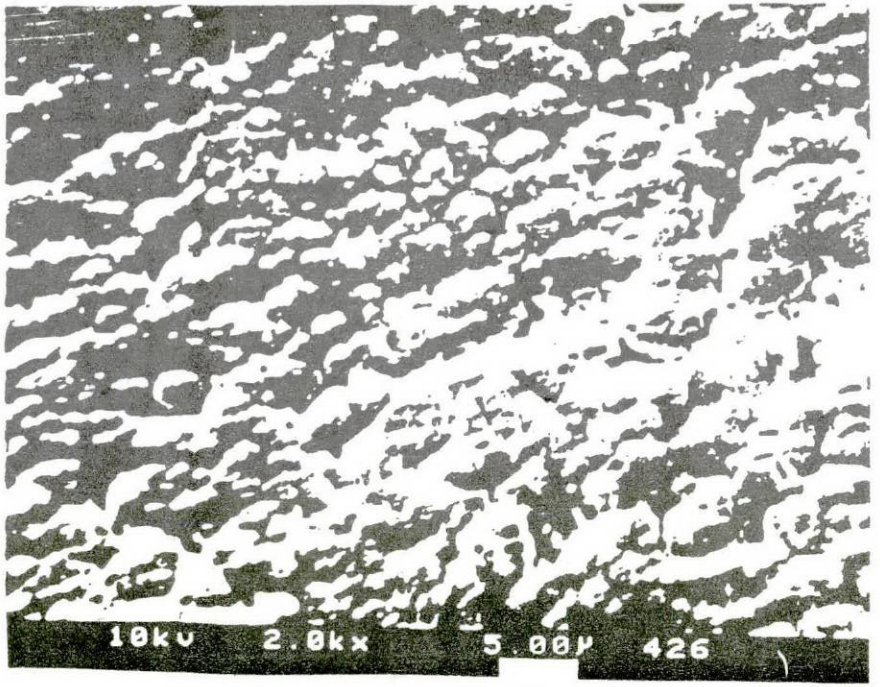


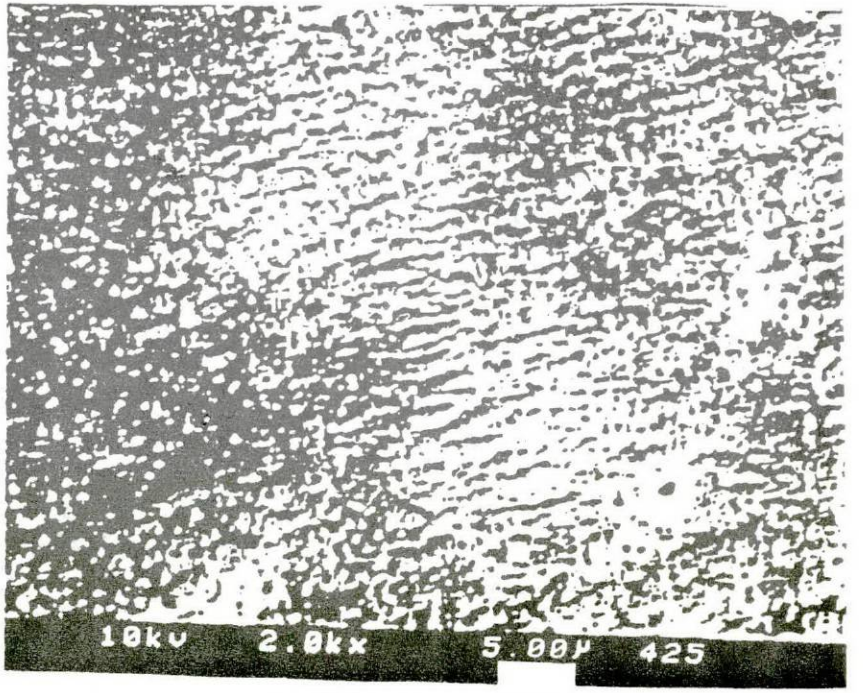
5086 FIRST ZINCATE



CZ46 FIRST ZINCATE

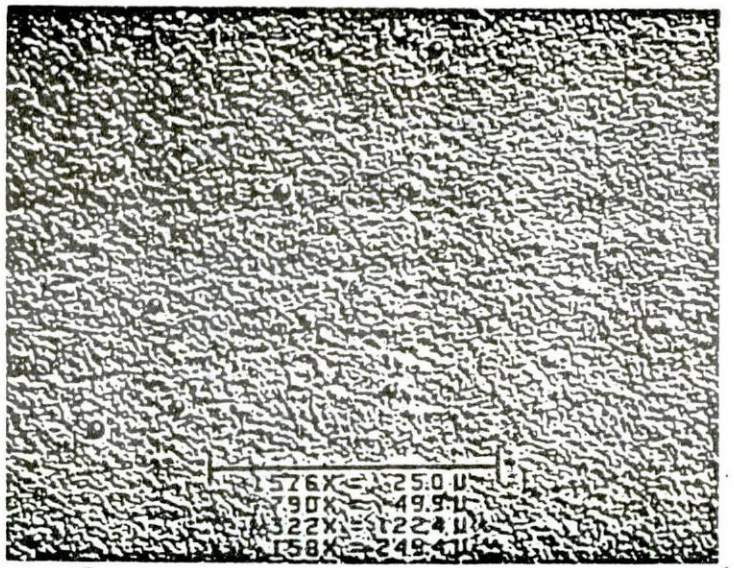


5086 SECOND ZINCATE

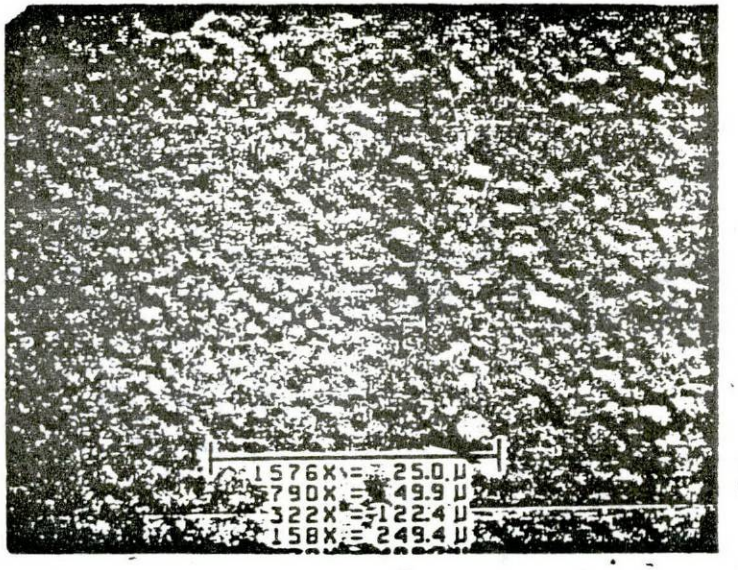


CZ46 SECOND ZINCATE

Figure I
Zincates on Different Substrates



ALLOY 5586 160X



ALLOY 5086 250X



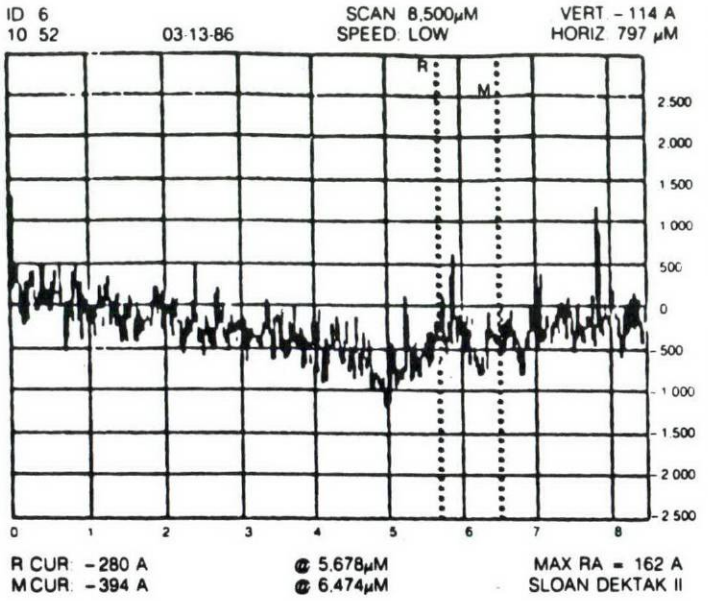
ALLOY CZ46 500X

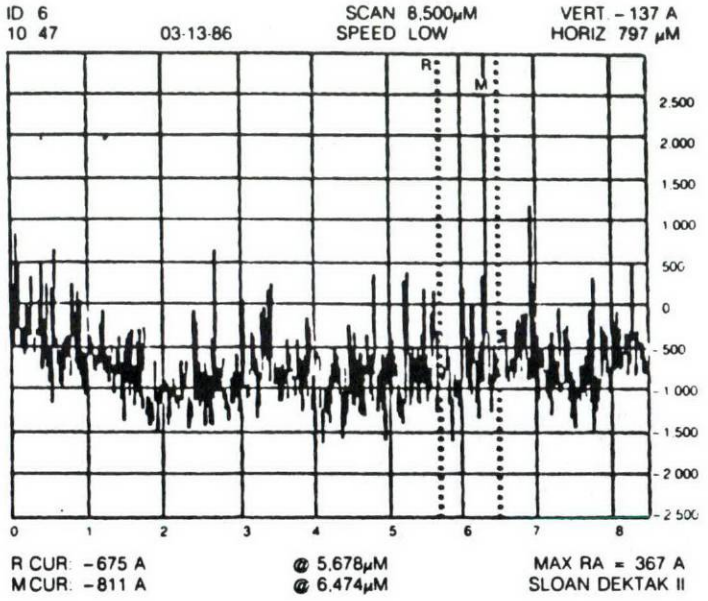


ALLOY CW66 500X

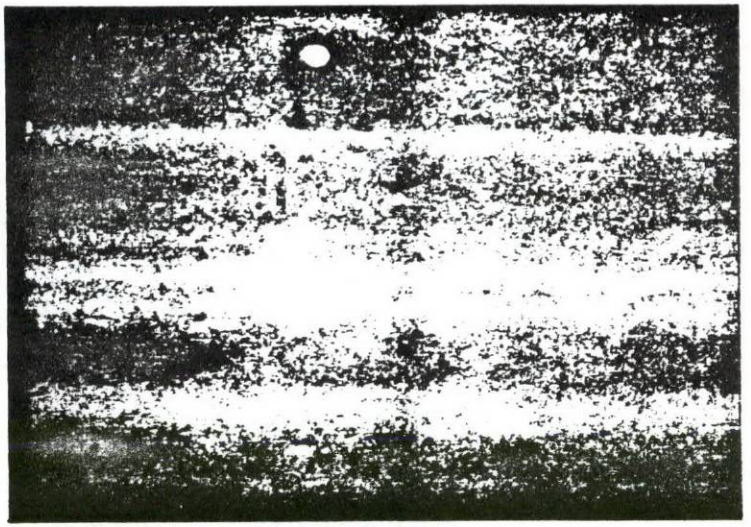
Figure 2
EN Deposit on Various Alloys

DEKTAK TRACES





507X AS PLATED

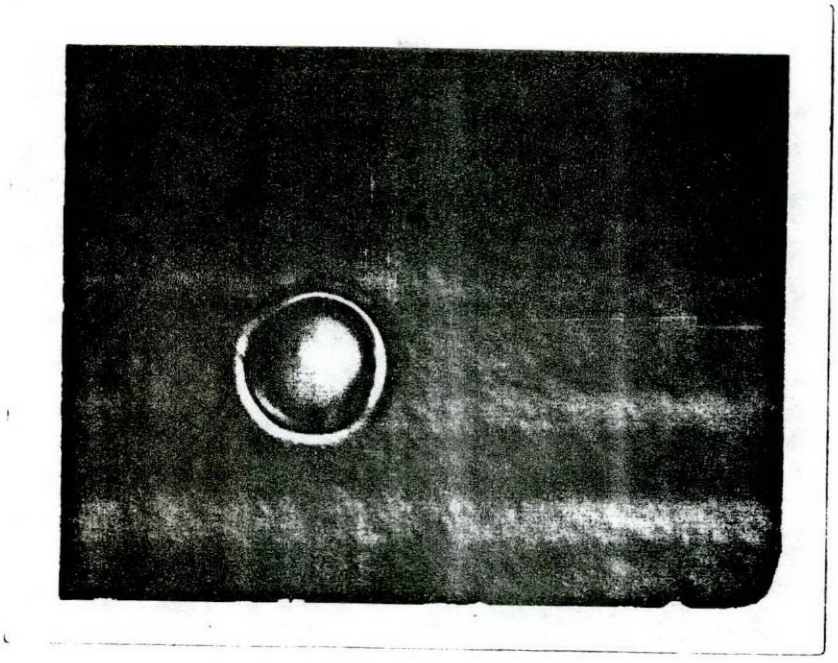


504X AS PLATED



Figure 3

Two Different EN Coatings on 5586 D.T.

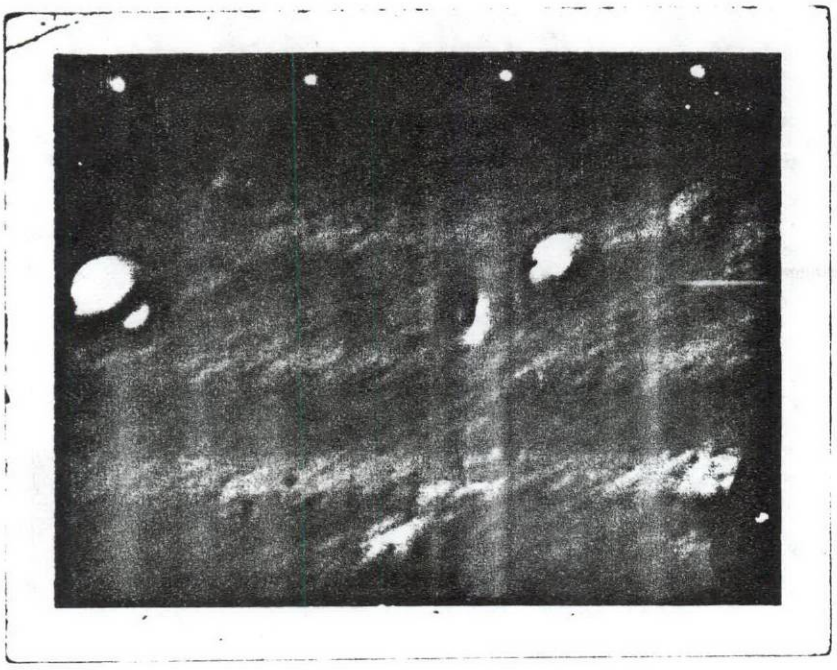


GAS PIT 500X

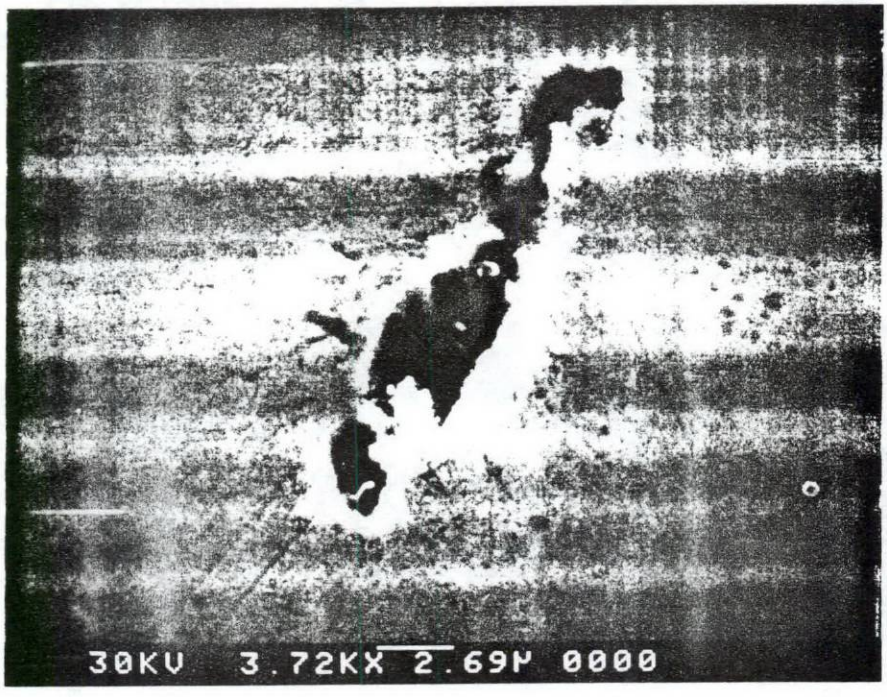


ORGANIC PARTICULATE 3760X

Figure 4

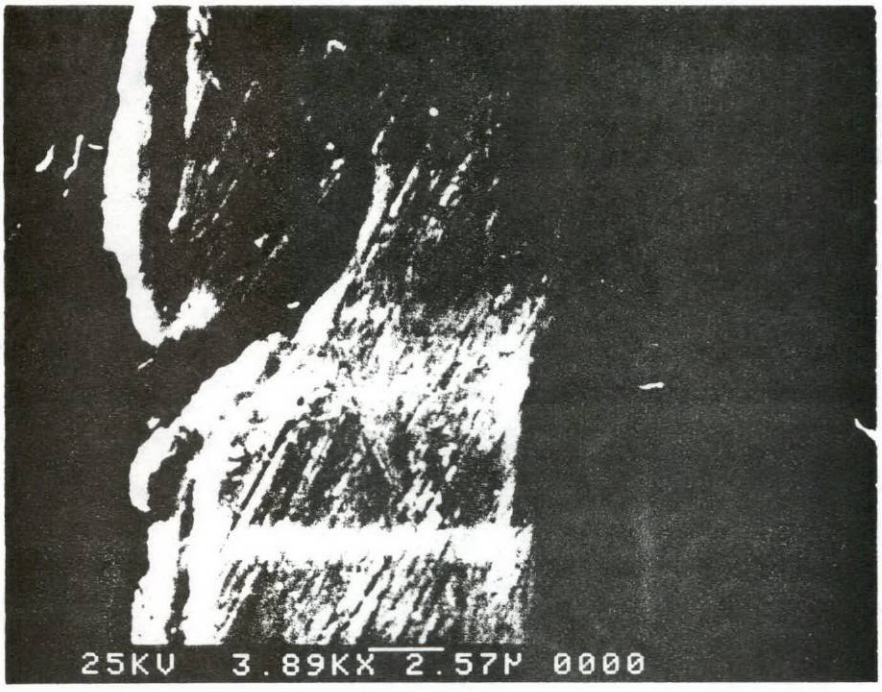


SHALLOW SPOTS 500X

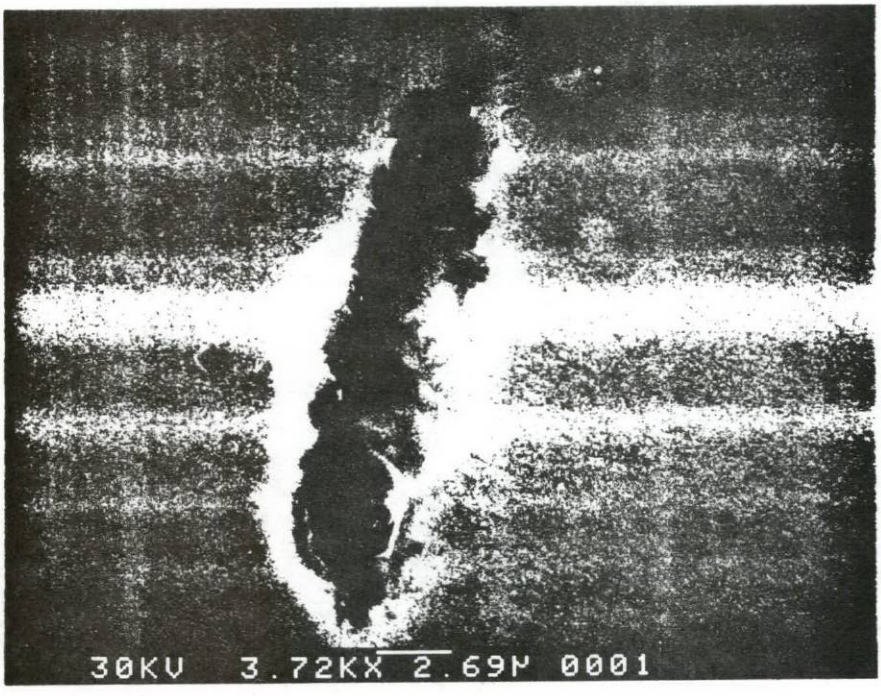


ORGANIC PIT 3720X

Figure 5



CROSS SECTION ORGANIC PIT 3890X



ORGANIC PIT 3720X

Figure 6

J-3

Electroless Deposition II
Session J

Sublayer Processing for Rigid Memory Disks

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Sublayer Processing for Rigid Memory Disks

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Introduction

Recently, rigid memory disks for high density magnetic recording have become a reality. After extensive laboratory development, many millions of disks are manufactured each year in modern production facilities throughout the world. The fast growth of thin-film recording media has opened new opportunities and established higher requirements for electroless plating processes.

Rigid memory disks (RMD) employed in high density recording (Winchester-type drives) consist of an aluminum substrate, a non-magnetic sublayer, a magnetic layer, and finally a protective overcoating. As both the magnetic layer and the overcoating are extremely thin films (approx. 500Å thick), properties of the sublayer become crucial to the overall performance of the disk. This layer must provide a hard durable surface with virtually zero defects (pits, nodules, etc.), while providing for adhesion both to the substrate and the magnetic layer. The crystalline structure of the sublayer can influence the properties of the magnetic layer and interfere with recording, so it must be amorphous and non-magnetic. The process described in this paper has been developed to satisfy all of the above requirements for the sublayer.

Experimental

Aluminum alloy (5086 series) 5.25" diameter (140mm outside diameter with 40mm inside diameter hole) diamond turned disks were used as the substrate in our study. The disks were pretreated and plated using rotating fixtures. Evaluation of each step in the process was done based on measurements of surface roughness (Dektak IID by Sloan Technology), adhesion (180° bend test, conical mandrel bend tester), deposit thickness and uniformity (X-ray Fluorescence Thickness Analyzer SFT-157 by Seiko Instruments and Electronics Ltd.).

Deposit magnetic properties were determined in the as plated condition and after heat treatment at various temperatures and times using a vibrating sample magnetometer (VSM 155, EG&G Princeton Applied Research).

The crystalline structure of the deposit was analyzed by X-ray diffraction and Differential Scanning Calorimetry (DSC) techniques. In order to analyze defects which occurred during sublayer deposition, scanning electron microscopy (using an ISI-100B SEM) of the same area at each step of the process was done. The same evaluation was done for substrates prepared using a conventional pretreatment plating line (widely used by disk manufacturers at the present time) and served as the reference point in our study.

Results and Discussion:

Electroless nickel plating is an integral part of the disk manufacturing process. The quality of the electroless nickel deposit depends not only on the substrate material and its surface finish, but the chemical pretreatment process as well. It has a major effect on on subsequent process steps including mechanical polishing of the sublayer and deposition of the magnetic layer. Thus the quality of the electroless nickel deposit has a major impact on the ultimate performance of the memory disk.

Pretreatment process-In order to obtain a smooth, highly adherent nickel deposit on an aluminum alloy disk, several pretreatment steps are required. The disks must be cleaned (degreased but not etched) and then relieved of the tenacious oxide film which forms on aluminum when exposed to the atmosphere. By far the most popular method of removing this oxide film is based on the formation of an "immersion" zinc layer in alkaline solutions of zinc salts. It is commonly known as "zincating" (1). This layer provides a fresh, active surface for electroless nickel plating and assures adhesion of the deposit to the substrate.

We have developed a pretreatment process specifically for plating high density rigid memory disks. This process, combined with a proprietary electroless Ni-Cu-P alloy deposit, provides an extremely smooth, non-magnetic, bright sublayer coating. This proprietary pretreatment line features a very mild, non-etching alkaline cleaner, which is followed by a desmutter-conditioner and a unique acidic zincating solution. Details of process times and temperatures are given in Table 1.

Pretreatment Process For electroless Ni-Cu-P deposition on 5086 Al-alloy RMD.

Table 1

Process Step				Conditions
Proprietory Solutions		Concentration	Time(min.)	Temp.(°F)
1.	Alkaline cleaner	20%	5	135±5
2.	DI water rinse		2	70±2
3.	Conditioner	20%	45 sec.	70+2
4.	DI water rinse		2	70±2
5.	Acidic zincate	25%	2	70±2
6.	DI water rinse		2	70±2
7.	Nitric acid strip	50%	1	70±2
8.	DI water rinse		2	70±2
9.	Acidic zincate	25%	2	70+2
10.	DI water rinse		2	70±2

11. Electroless Ni-Cu-P Deposition at pH = 4.6 ± 0.5 T = 195±2°F, to 500 ± 50μ" thickness.

Disks prepared according to this process demonstrate very high adhesion of electroless nickel to the substrate. They pass 180° bend tests without any sign of deposit flaking on any part of the disk (no annealing was done prior to the test). As shown in Figures 1 and 2, the process provides a very fine , uniform zinc layer with low roughness. This assures rapid initiation of electroless nickel deposition and also results in an extremely smooth sublayer.

Electroless nickel bath- The proprietary electroless solution employed in this study produces an alloy deposit typically containing 86.5% Ni, 1.5% Cu, and12% P. The copper content of the deposit is largely responsible for its high brightness and smoothness. Presence of copper in the plating bath helps to assure stability. The phosphorus content of an electroless nickel deposit determines its crystalline structure and magnetic properties (2). Buildup of orthophosphite in the plating solution slows the rate of deposition and can eventually cause bath decomposition. Therefore, bath performance was evaluated here by measuring the deposition rate under various plating conditions (temperature, pH, number of cycles or bath metal turnovers) and determining the effect of these variables on the P and Cu contents of the deposit.

As with most electroless nickel solutions, the rate of deposition in this bath increased with increasing temperature and pH, while Cu and P content of the deposit decreased (Fig. 3,4) with increasing temperature and pH. Analysis of deposit properties showed that high Cu and low P content result in rough deposits. Such deposits can be slightly magnetic as plated and will recrystallize easily at elevated temperatures to become highly magnetic. In order to avoid degradation of magnetic properties while still maintaining a rather high rate of deposition (0.4 mil/hr.) this bath should be operated at 195°F and a pH of4.6±.5

The performance of this plating solution has been extensively studied by Dr. S. K. Doss (3). His results are in good agreement with this study. If operated at optimum conditions, the bath exhibits a slight decrease in the rate of deposition after 2.5 cycles. The Cu content in the deposit is very consistent, Figure 5. Consistency of performance that is independent of the number of plating cycles separates this bath from many other electroless nickel solutions presently used for rigid memory disks. It also makes possible complete automation of the plating line.

Deposit roughness- As has been demonstrated above, immersion zinc deposits from acidic zincating solutions are very thin, extremely fine, and uniform. Deposition of an electroless Ni-Cu-P alloy over the acidic zinc immersion coating produces a sublayer with an Ra (average surface

roughness) of 80 ± 5Å. This compares very favorably with an Ra of 180± 10Å for the surface finish achieved through conventional pretreatment processes. Such a low roughness of the Ni-Cu-P sublayer can be very beneficial to further disk processing. It allows the manufacturer to reduce sublayer polishing time or in some cases avoid it entirely.

Deposit crystallinity- The crystal structure of the sublayer can affect crystallinity and therefore the magnetic properties of the recording layer (4). In order to avoid such interference, the sublayer must be amorphous. X-ray diffraction and differential scanning calorimetric analysis (Fig. 6) shows that the Ni-Cu-P alloy produced in our process has no definite crystalline structure (i.e. was amorphous) in the as plated condition and after heat treatment at 250°C for one hour. No changes in structure occurred up to 325°C but strong recrystallization took place at that temperature leading to changes in deposit characteristics, especially the magnetic parameters.

Deposit magnetic properties-It is absolutely crucial to disk performance that the sublayer remain non-magnetic during the manufacturing process. A sublayer displaying ferromagnetic behavior can interfere with the read/write process by causing losses in signal amplitude, peak-shifts, and a decrease in resolution. Measurements of magnetic parameters of the deposit (magnetization-M_S, retentivity-B_r) showed that the deposit did not change the magnetic behavior of the Al-alloy substrate (Fig. 7). It stayed non-magnetic even after heat treatment at 250°C for up to five hours (Figure 8) or at 275°C for one hour (Figure 9).

Sublayer coating defects-Testing of the finished RMD showed a direct correlation between defects in the recording (missing or extra bit, low signal to noise ratio etc.) and the surface condition or defects in the sublayer (pits and nodules). A scanning electron microscope study of the nature of defects in the sublayer (5) showed that nodules and deposit roughness are mainly related to the plating solution formulation. However pitting, the most frequently encountered problem, depends on the substrate material and the pretreatment process. As the substrate contains intermetallic inclusions (Mg, Mn, Si) which can be easily etched out even in mild cleaners, some pits in the aluminum substrate are probably unavoidable. The task of the sublayer coating is to correct substrate defects caused by mechanical handling and chemical processing without introducing defects of its own. According to SEM study (Fig. 10) this can be achieved by using the proper pretreatment solutions which include a mild cleanerand an acidic zinc immersion coating applied under optimum conditions. The high rate of deposition and formulation of the Ni-Cu-P plating solution provides rapid fill-in of substrate defects. This

is practically complete during the first 5 minutes of plating and leads to a bright, uniformly smooth surface.

Summary

Standards for rigid memory disks used for high density magnetic recording demand that the sublayer meet very stringent requirements for surface finish and non-magnetic behavior. These requirements can be satisfied by the electroless deposition of a Ni-Cu-P alloy, combined with a unique pretreatment process designed specifically for applying the sublayer to RMD aluminum alloys. The sublayers produced in our study are amorphous alloys that are bright, smooth and non-magnetic. This alloy deposit retains all of its non-magnetic behavior even after heating at 250°C for 5 hours. The electroless bath used to apply this alloy deposit maintains a consistent deposit composition and plating rate up to at least 2.5 bath turnovers.

Acknowledgements

The author would like to thank Anthony J. Marczak and Howard A. MacKay for their help in collecting the data on the Ni-Cu-P plating parameters, deposit composition, and solution formulations. Special thanks to Gabrielle Bene for her expertise and valuable advice in the SEM study of the process. Also thanks to Rolf Krause and Gordon Fisher whose constant interest and participation in discussions made this paper possible.

References

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3. Saad K. Doss, "Electroless Nickel-Phosphorous-Copper Plating Bath Performance and Its Relation to Deposition Parameters", ECS Meeting, Honolulu, HA, Oct. 1987.

4. B.D. Cullity, Introduction to Magnetic Materials, Addison-Wesley, 1972.

5. Robert W. Dummer, "Magnetic Disk Substrate Overview", IRTC Papers, CDC, 1981.

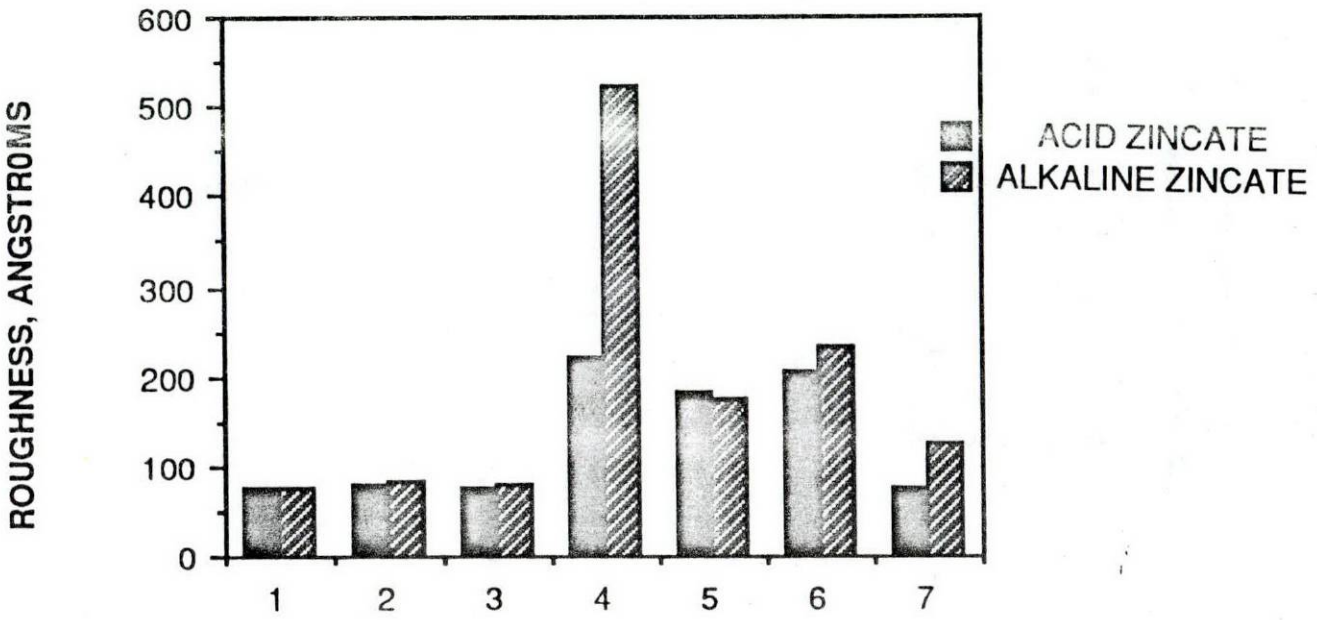


FIG. 1 COMPARISON OF SURFACE ROUGHNESS AT DIFFERENT STAGES OF SUBLAYER PROCESSING WHEN USING ACIDIC AND ALKALINE ZINCATE

1 - DIAMOND TURNED 5086-AL SUBSTRATE
2 - SAME SUBSTRATE AFTER CLEANING
3 - CLEANING / CONDITIONING
4 - FIRST ZINCATING
5 - NITRIC ACID STRIP
6 - SECOND ZINCATING
7 - ELECTROLESS NI-CU-P DEPOSIT (400μ")

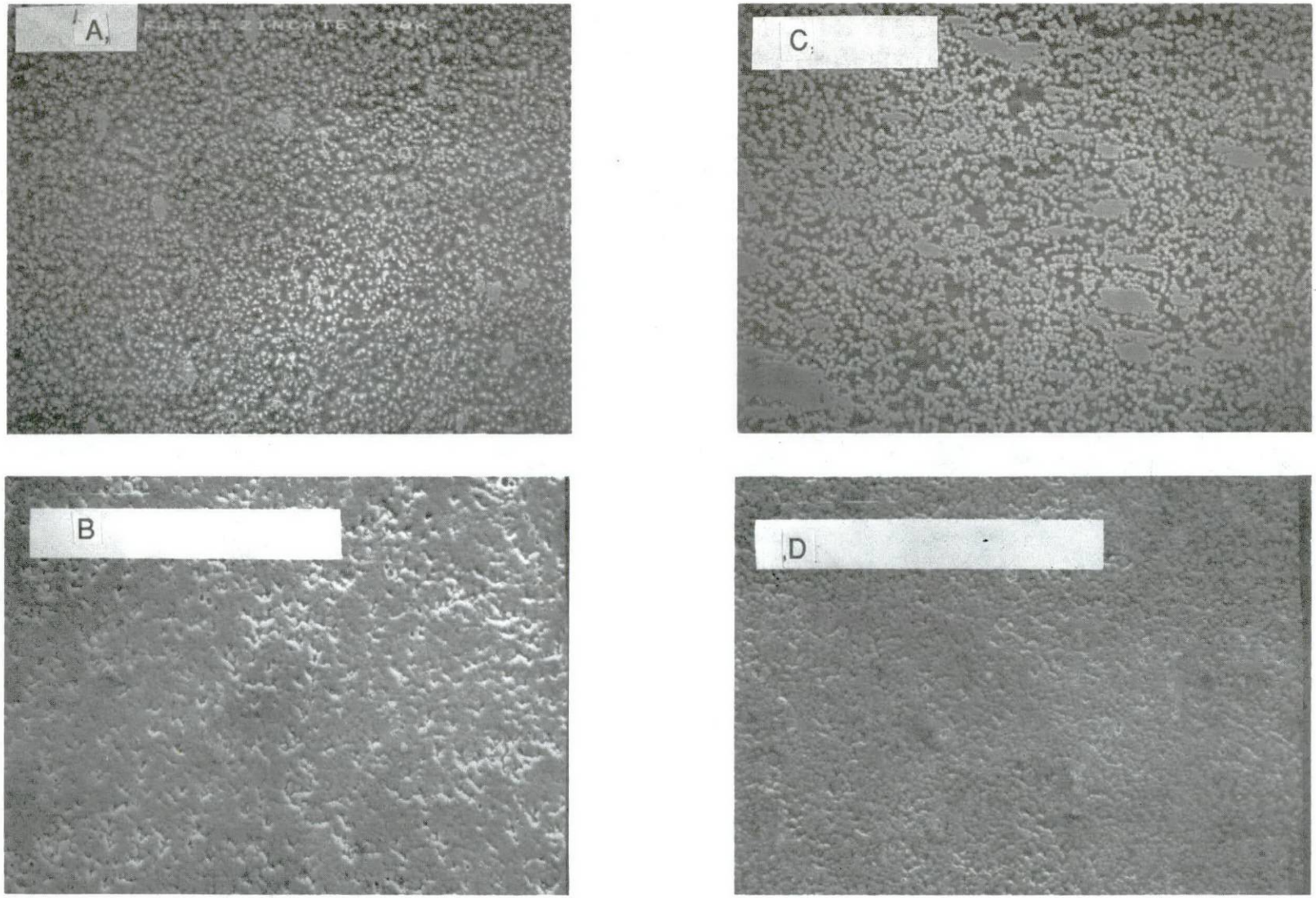


FIG.2 5086 AL-ALLOY DIAMOND TURNED SUBSTRATE AFTER FIRST AND SECOND ZINCATING STEPS CONVENTIONAL ALKALINE (C,D) SOLUTONS. SEM PICTURES, 750X

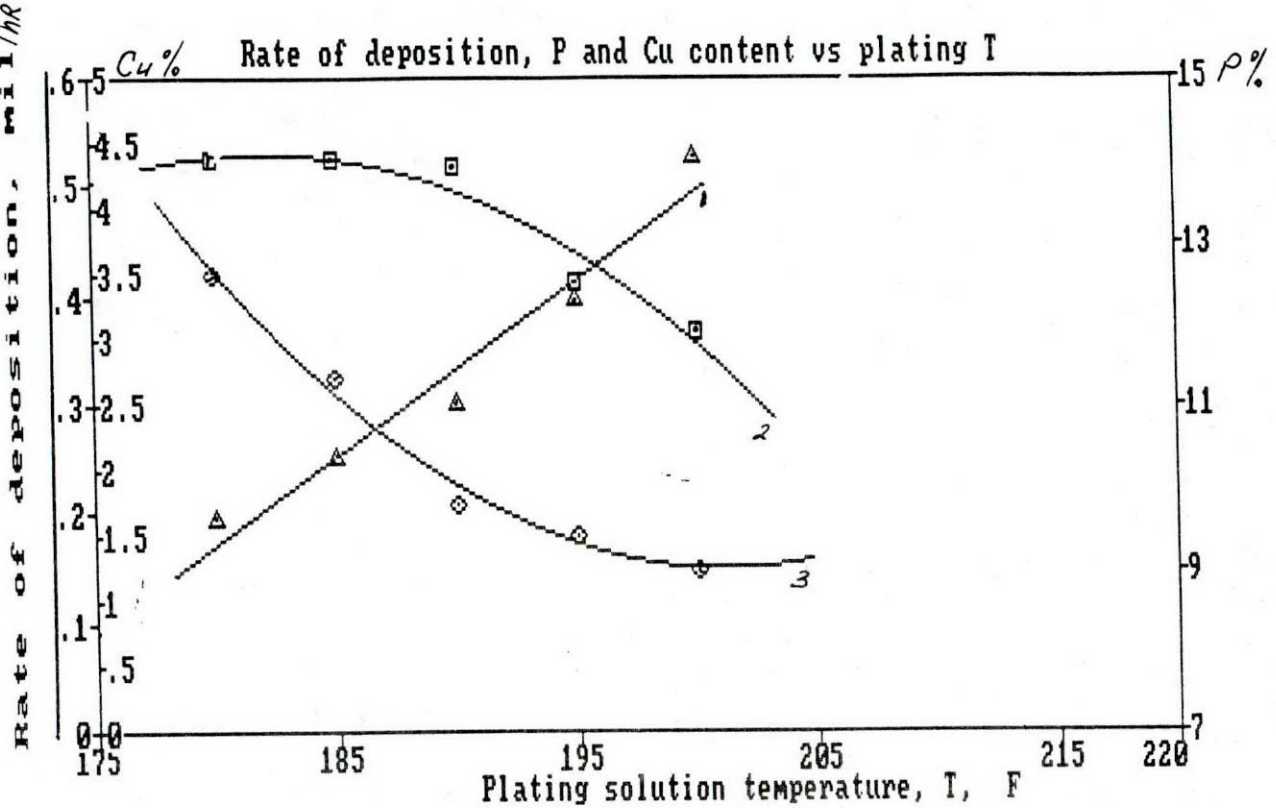


FIG. 3 EFFECT OF THE PLATING TEMPERATURE (T) ON THE RATE OF NI-CU-P DEPOSITION (R), PHOSPHOROUS (P) AND (CU) CONTENT IN THE DEPOSIT.

1-RATE OF DEPOSITION

2-P CONTENT IN THE NI-CU-P ALLOY

3-CU CONTENT IN THE NI-CU-P ALLOY

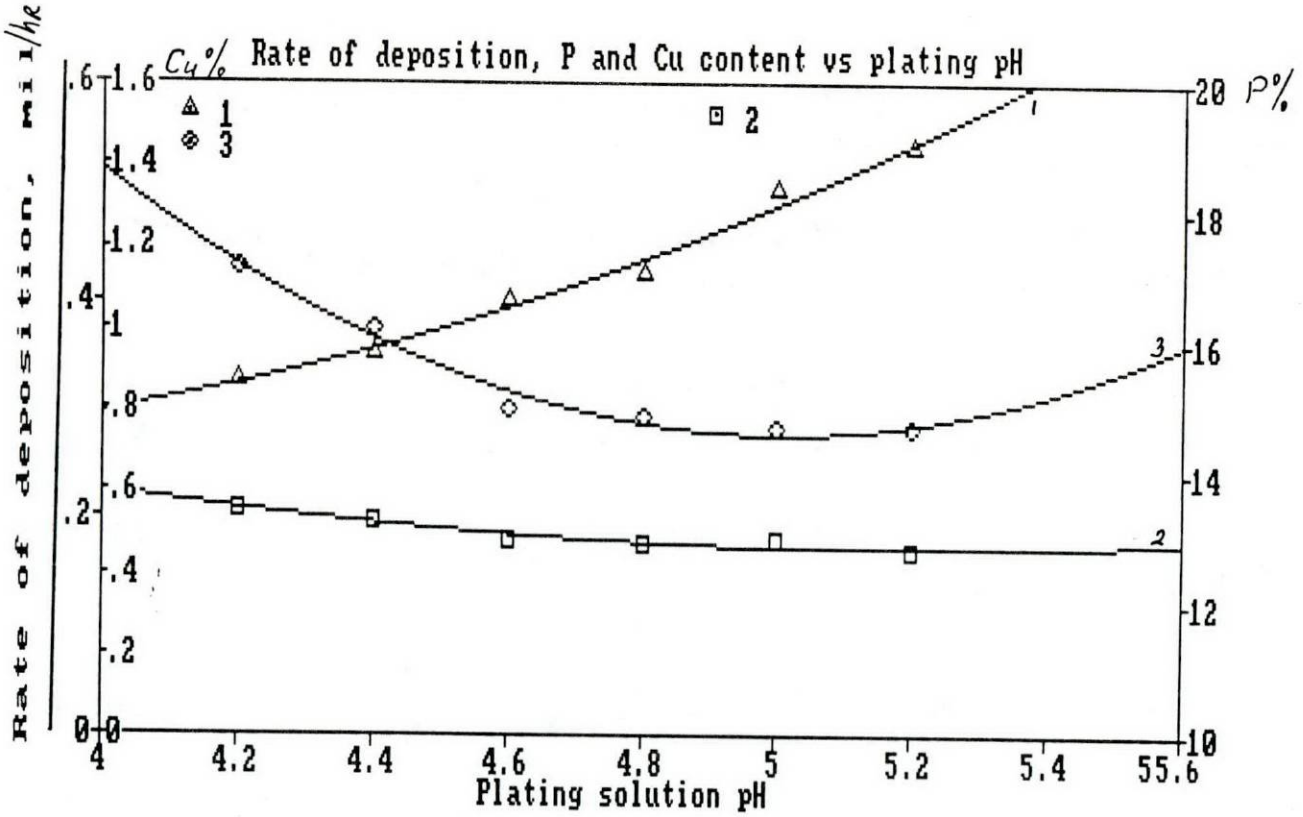


FIG. 4 EFFECT OF THE PLATING SOLUTION PH ON THE RATE OF NI-CU-P ALLOY DEPOSITION (R), PHOSPHOROUS (P) AND COPPER (CU) CONTENT IN THE DEPOSIT

1-RATE OF DEPOSITION

2-P CONTENT IN THE NI-CU-P ALLOY

3-CU CONTENT IN THE NI-CU-P ALLOY

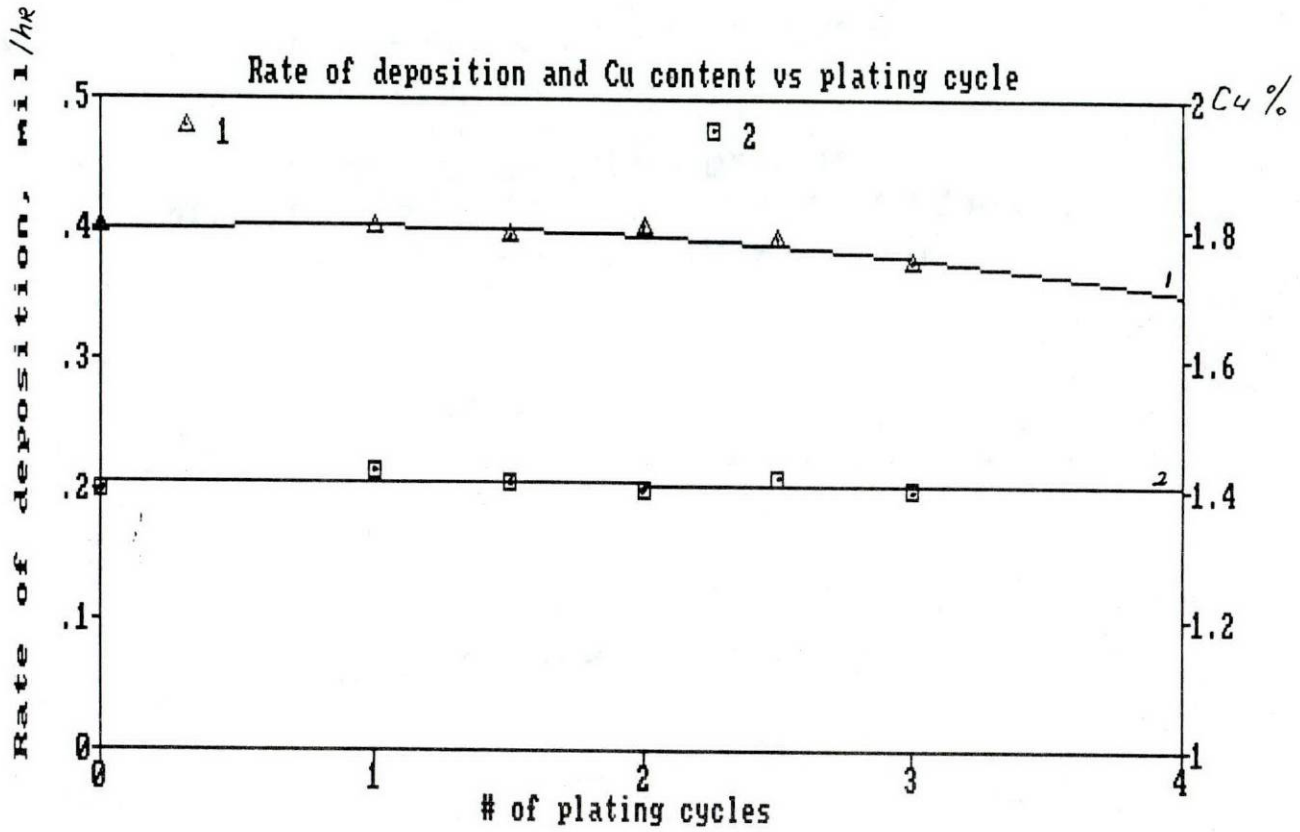


FIG . 5 DEPENDENCY OF THE RATE OF DEPOSITION (R) AND COPPER CONTENT (CU) IN THE DEPOSIT ON THE NUMBER OF THE PLATING CYCLES.

1- RATE OF DEPOSITION

2- CU CONTENT IN THE DEPOSIT

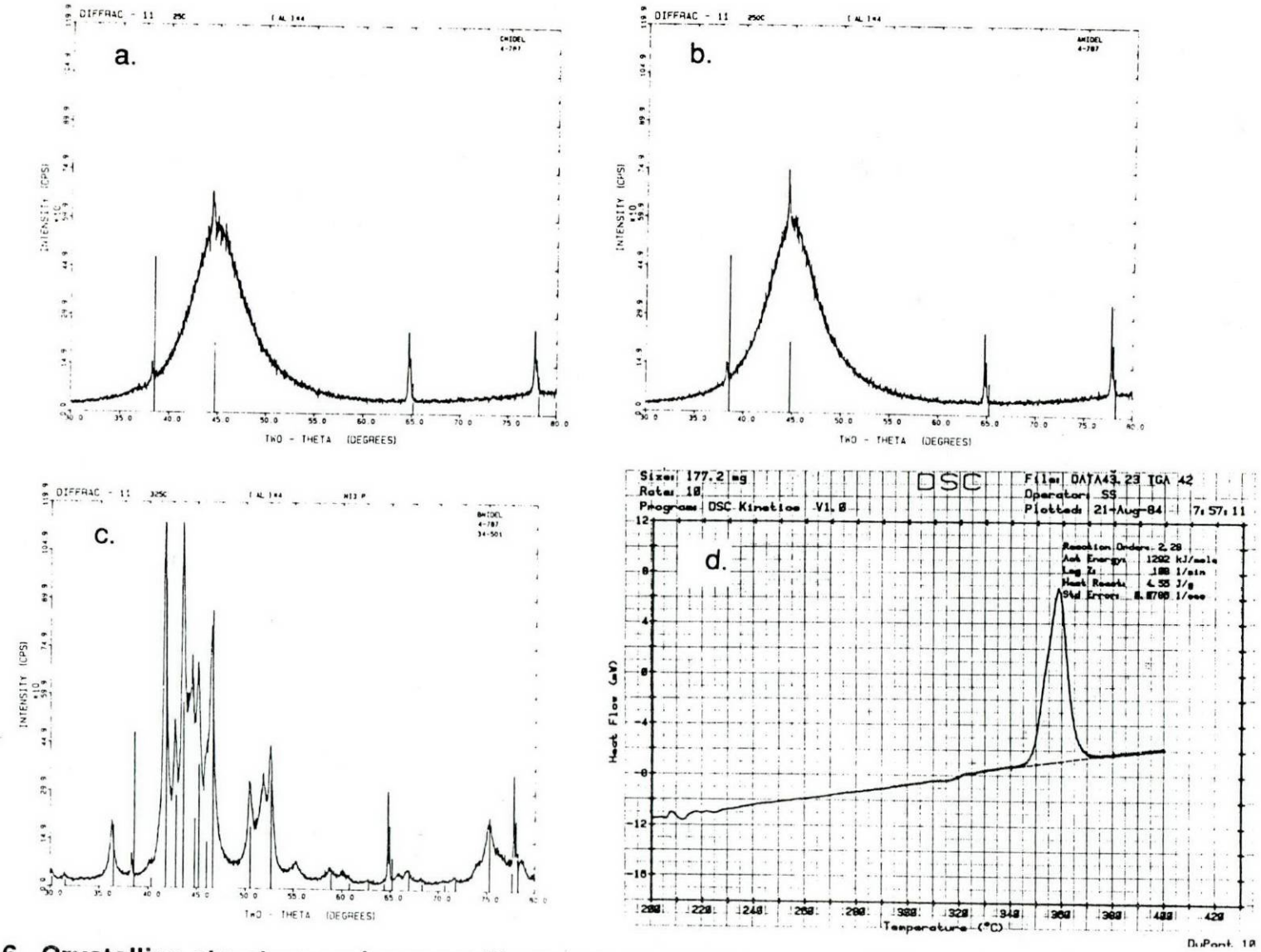
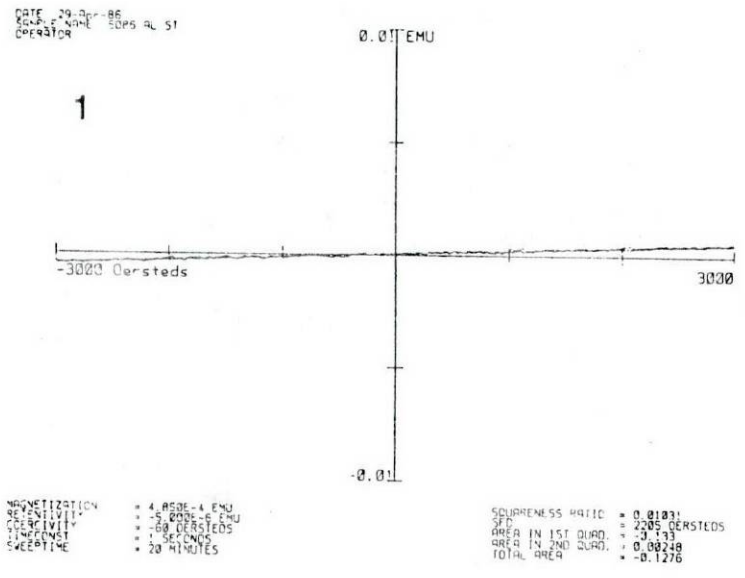
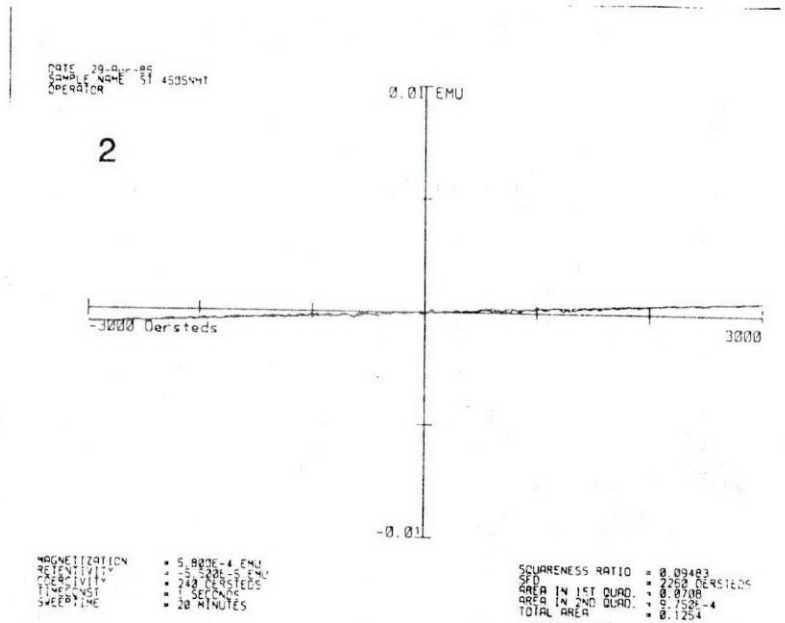


Fig. 6 Crystalline structure and recrystallization temperature range of electrolessly deposited Ni-Cu-P alloy.

a. X-ray diffraction of as plated sample b. X-ray diffraction of heat treated sample at 250°C for 1 hour.

c. X-ray diffraction of heat treated sample at 325°C for 1 hour. d. Recrystallization range via DSC analysis.





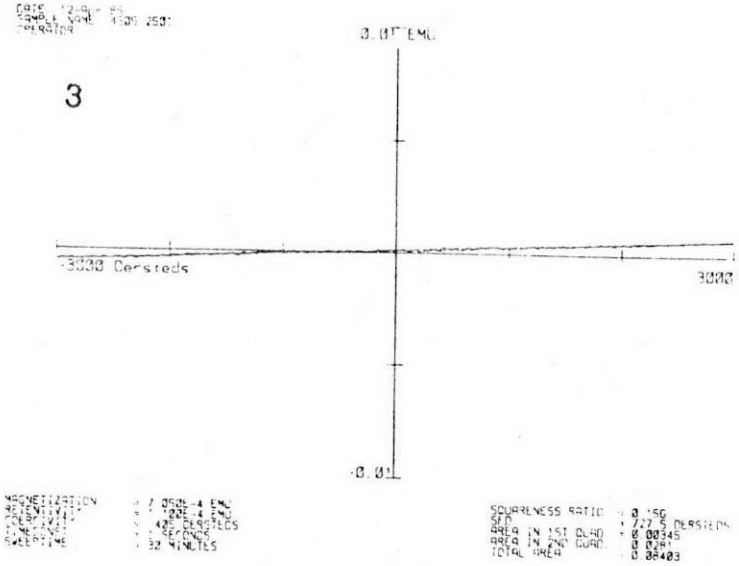


Fig. 7 Magnetic parameters of the electrolessly deposited Ni-Cu-P alloy (500μ" thick)

1- VSM chart of 5086 Al-alloy substrate (reference).
2- VSM chart of "as plated" Ni-Cu-P deposit (500μ" thick) over the same substrate.
3- 250° / 1 hr. heat treatment.

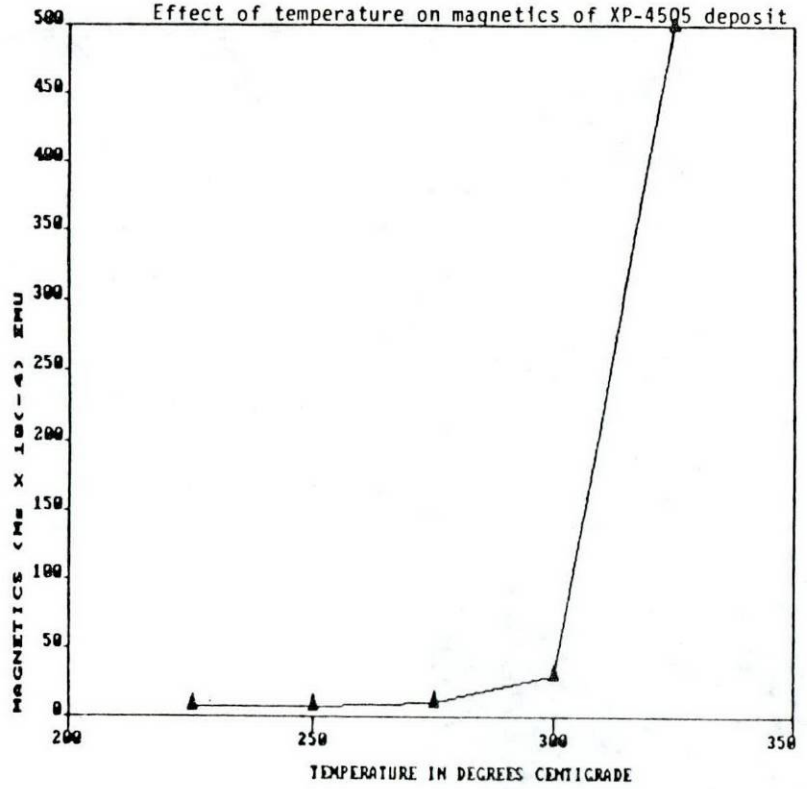


Fig. 8 Effect of the heat treatment temperature on the Ni-Cu-P deposit's magnetic parameters (M_S).

Magnification (M_S) vs. T° applied for 1 hour

Sample size : 0.25x0.25"; 500μ" deposit thickness on each sample side.

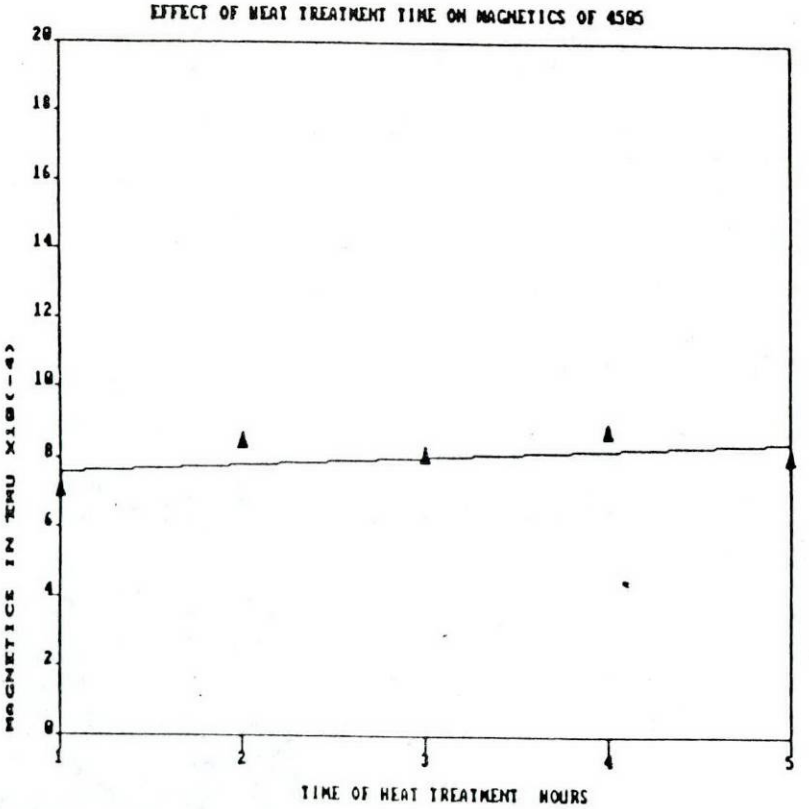
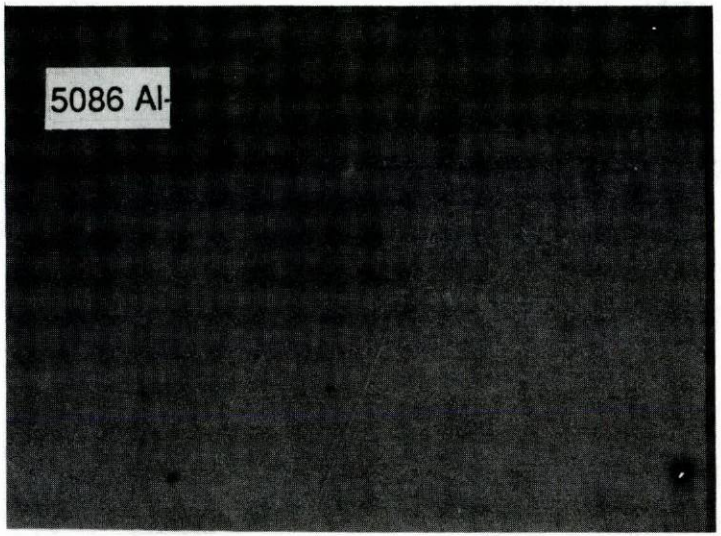


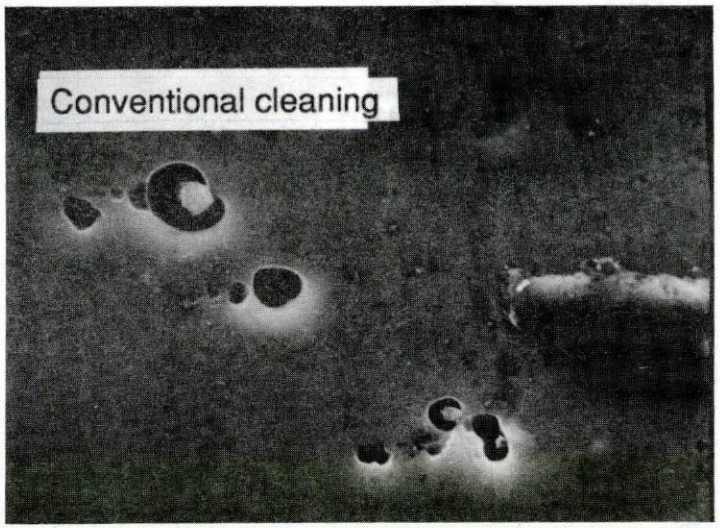
Fig. 9 Effect of the heat treatment time on the Ni-Cu-P deposit's magnetic parameters (M_S)

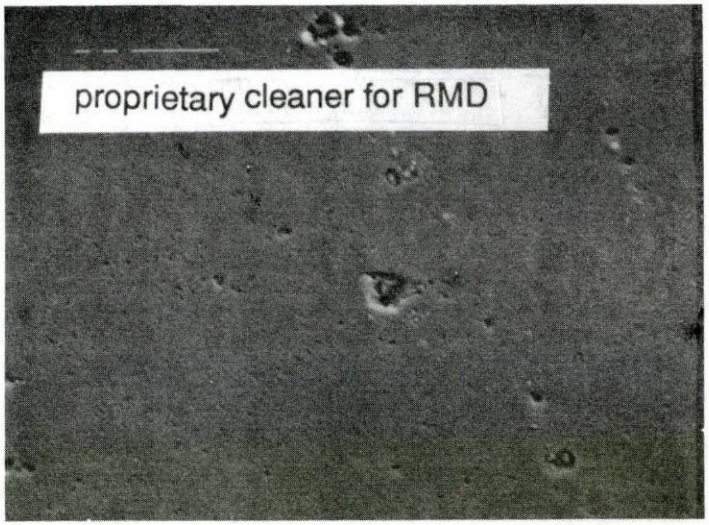
Heat treatment was done at 250°C for each period of time. Sample size: 0.25 x 0.25", 500μ" deposit thickness on each sample size.

SEM study of the defects nature and correction through electroless sublayer deposition.



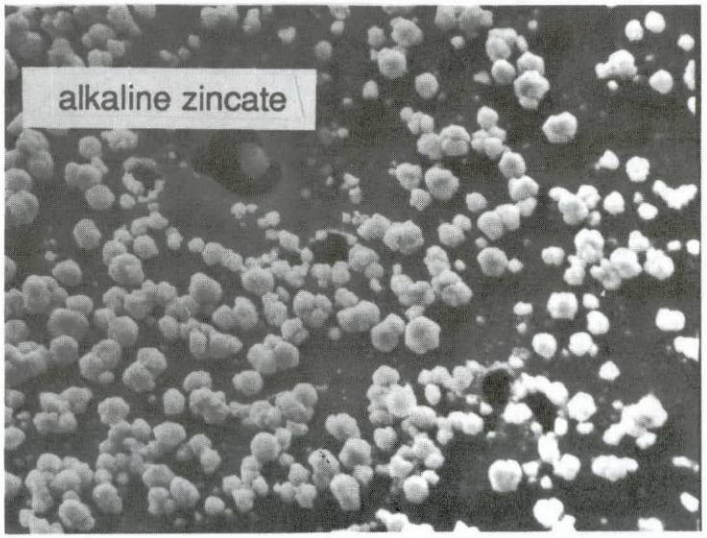
Diamond-turned 5086 Al-alloy substrate prior to processing 1500 X

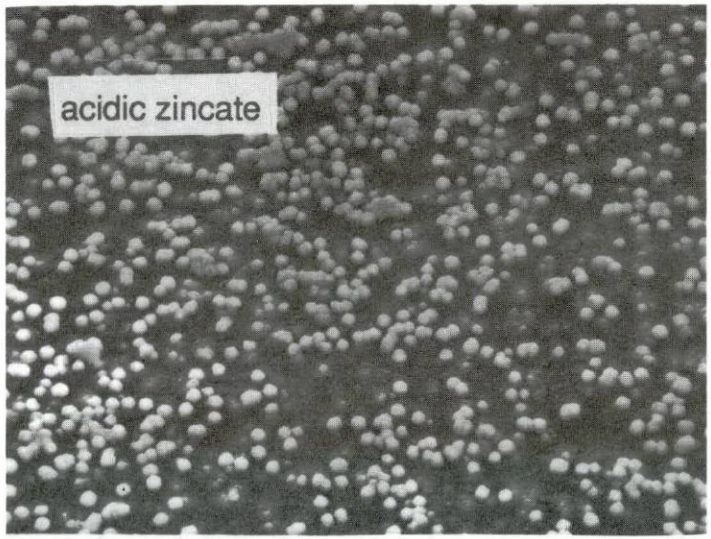




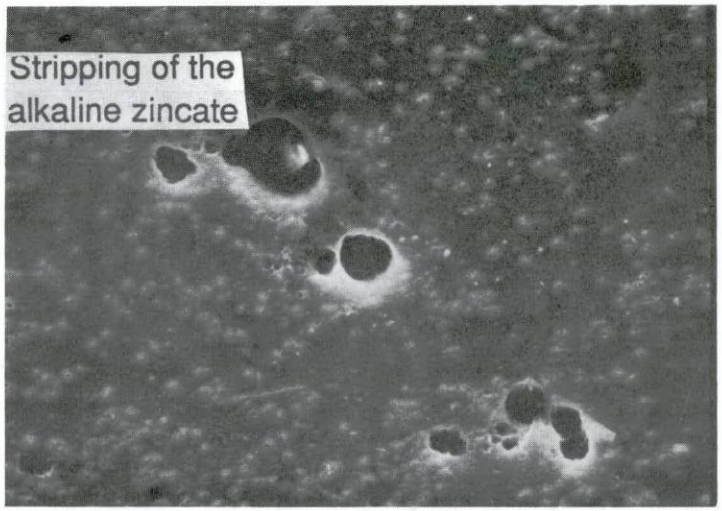
Same substrate after cleaning-degreasing at optimized conditions.

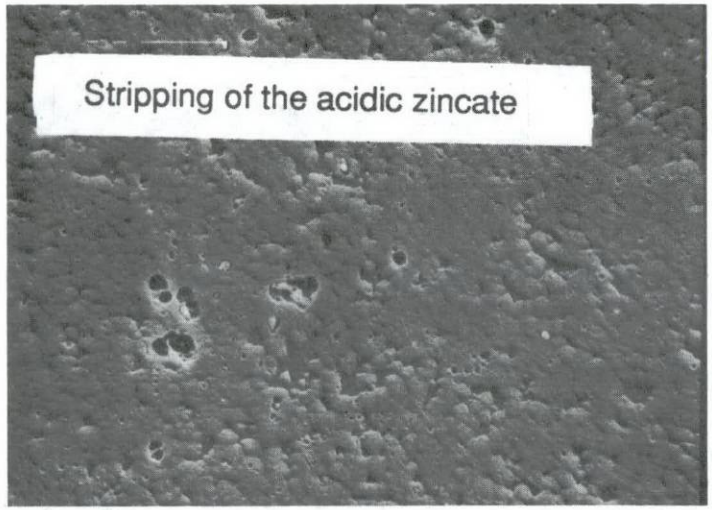
Same substrate after 1st. zincating step at optimum conditions.



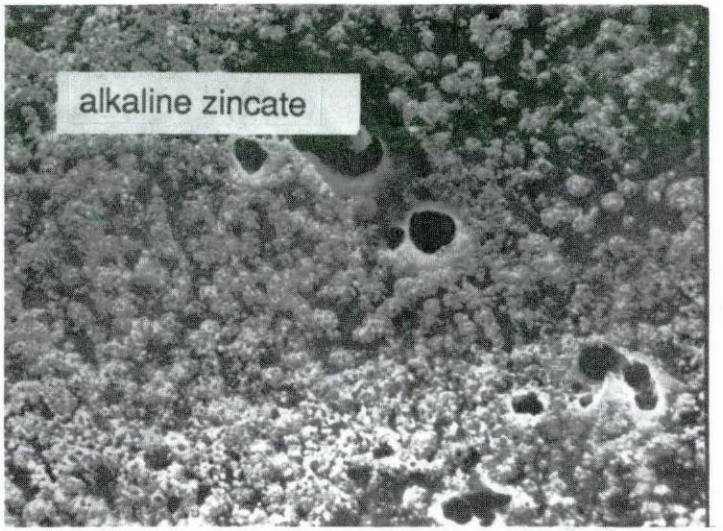


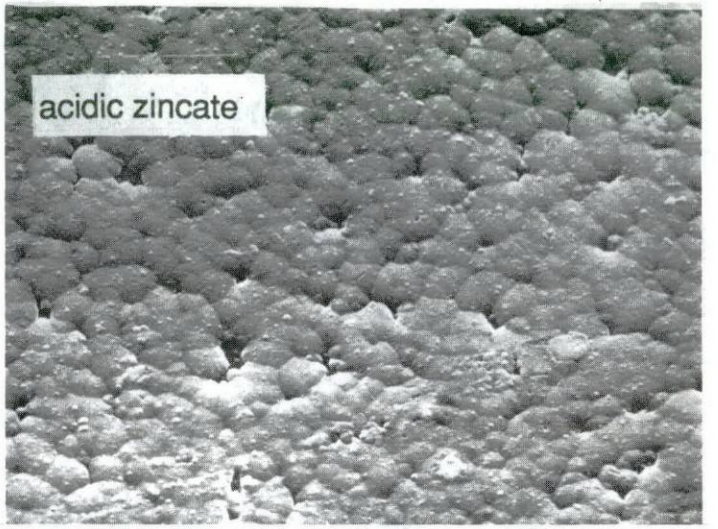
Same substrate after nitric strip following first zincating.



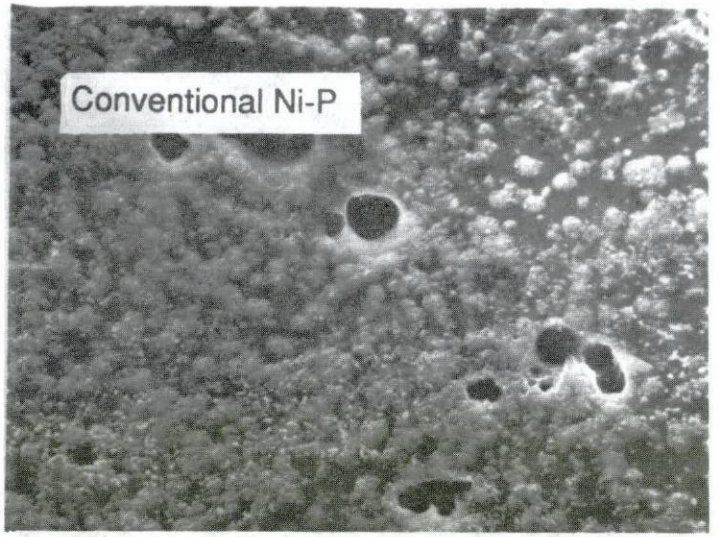


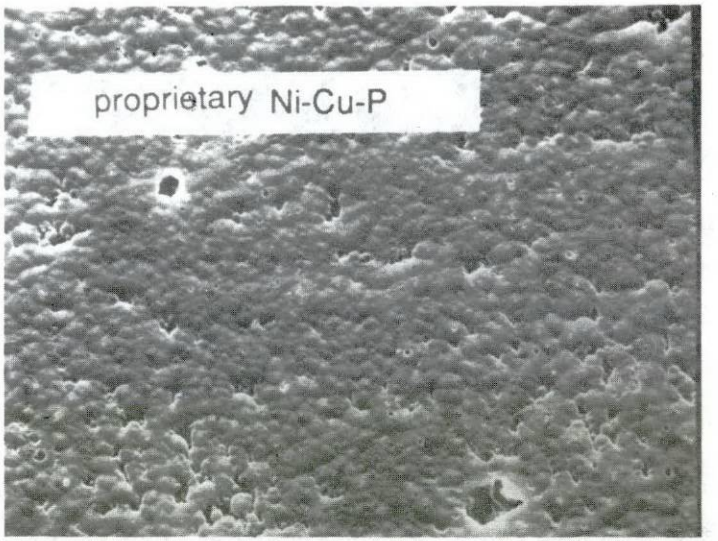
Same substrate after second zincating at optimum conditions



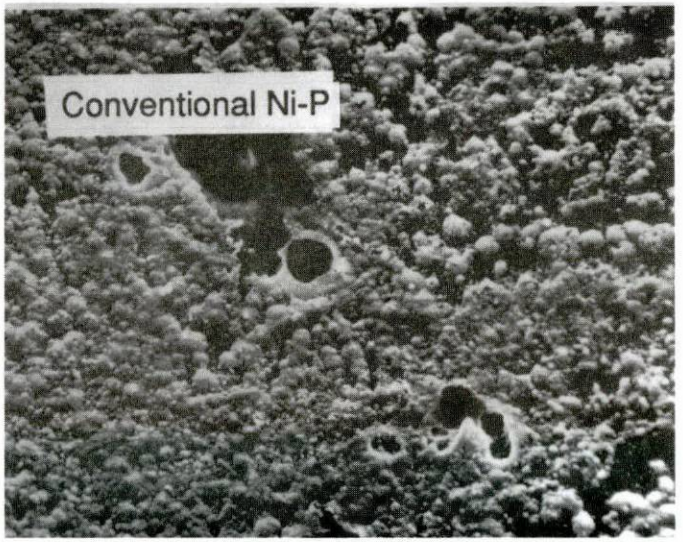


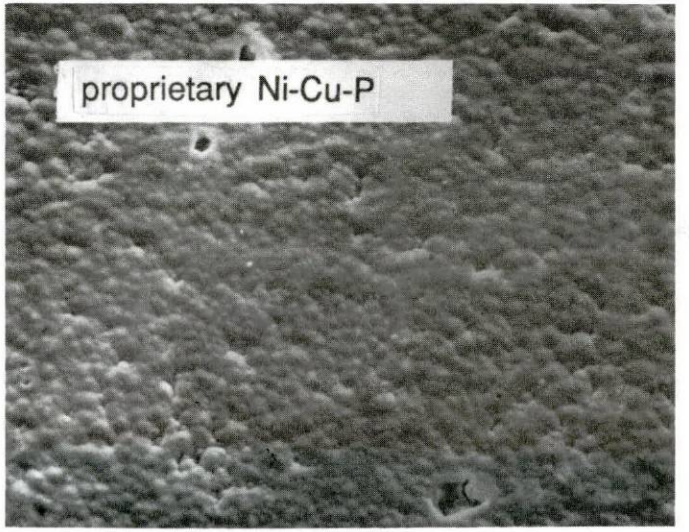
Same substrate during electroless nickel deposition for 20 sec,



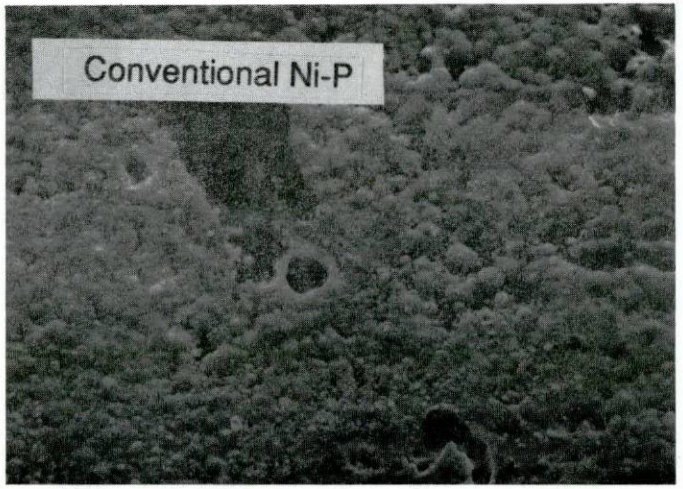


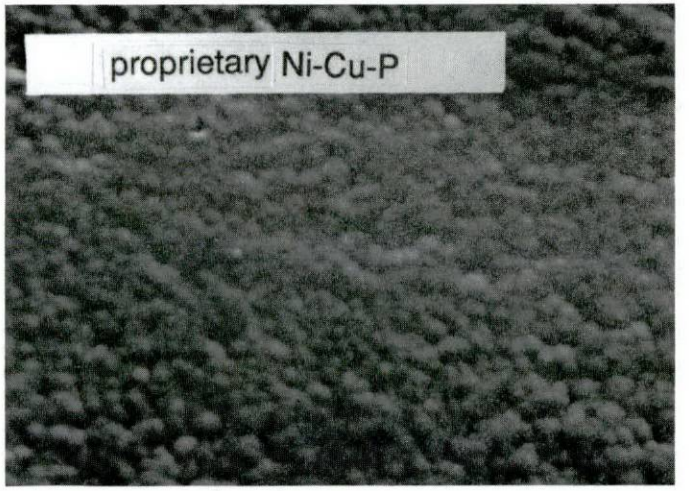
Same substrate during electroless nickel deposition for 1 min.





Same substrate during electroless nickel deposition for 5 min.





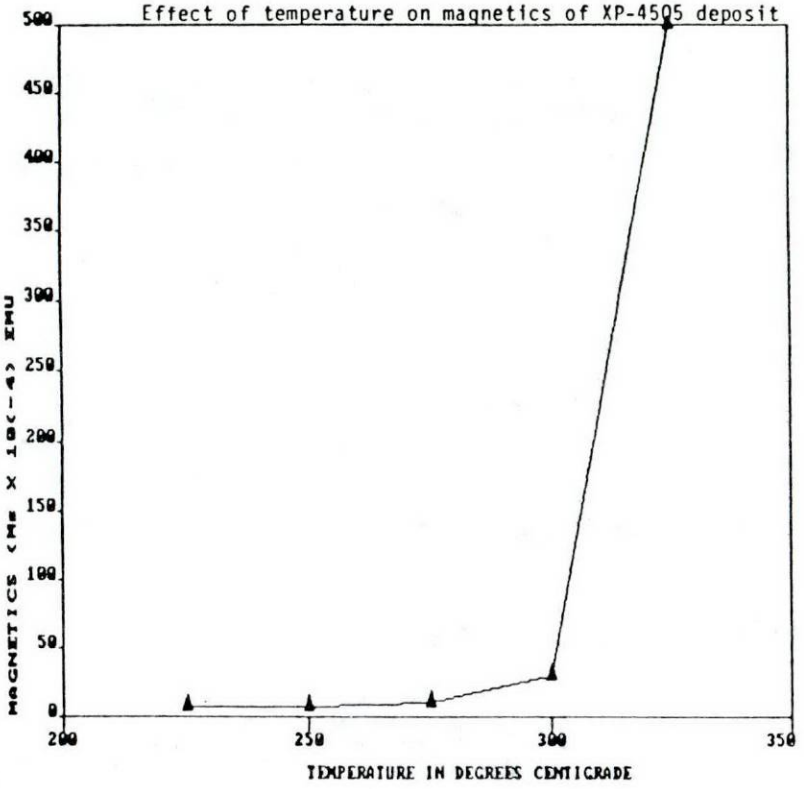


Fig. 8 Effect of the heat treatment temperature on the Ni-Cu-P deposit's magnetic parameters (M_S).

Magnification (M_S) vs. T° applied for 1 hour

Sample size : 0.25x0.25"; 500µ" deposit thickness on each sample side.

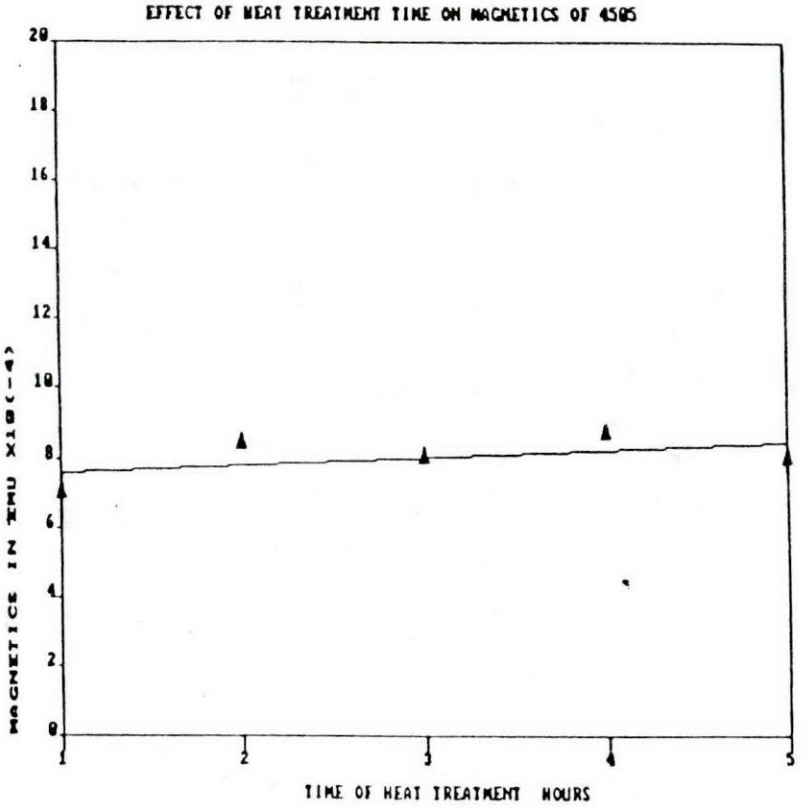


Fig. 9 Effect of the heat treatment time on the Ni-Cu-P deposit's magnetic parameters (M_S)

Heat treatment was done at 250°C for each period of time. Sample size: 0.25 x 0.25", 500µ" deposit thickness on each sample size.

J-4

Electroless Deposition II
Session J

Mechanism of Electroless Nickel Deposition: A Review

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MECHANISM OF ELECTROLESS NICKEL DEPOSITION: A REVIEW

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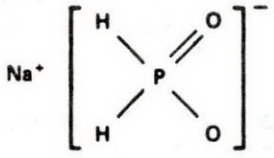
INTRODUCTION

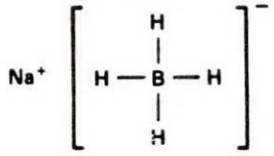
Four reducing agents are used in the chemical reduction of nickel from aqueous solutions:

Sodium Hypophosphite



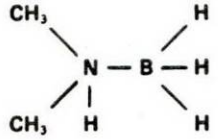
$NaH_2PO_2 \cdot H_2O$

Sodium Borohydride



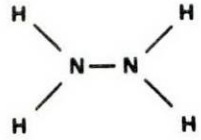
$NaBH_4$

Dimethylamine Borane (DMAB)



$(CH_3)_2NHBH_3$

Hydrazine



$N_2H_4 \cdot H_2O$

The four reducing agents are structurally similar in that each contains two or more reactive hydrogens, and nickel reduction is said to result from the catalytic dehydrogenation of the reducing agent.

Electroless nickel deposition can be viewed, in a very elementary manner, as the sum of two chemical reactions occurring in an electrochemical cell — an oxidation reaction that liberates electrons, and a reduction reaction that consumes electrons:

Oxidation of reducing agent:

$$Red \longrightarrow Ox + ne$$

Reduction of nickel ion:

$$mNi^{+2} + 2me^{-} \longrightarrow mNi^{0} \quad , 2m = n$$

With the overall or sum reaction:

$$mNi^{+2} + Red \longrightarrow mNi^{0} + Ox$$

The sum equation is a schematic illustration of the type of stoichiometric reactions usually written to describe the chemical reduction of nickel by a reducing agent. However, these overall reactions do not account for all of the phenomena that are observed during plating. Experimentally detected reaction characteristics indicate that the course of the reaction is considerably more complex than described by simple stoichiometric equations. Hence, it is necessary to attempt to ascertain the mechanism of the nickel reduction by the various reducing species.

An explicit understanding of the reaction mechanisms that govern electroless nickel deposition is necessary from both theoretical and practical viewpoints. Knowledge of the mechanisms of the reaction of a reducing agent with nickel ions can lead to the solution of a series of problems; development of methods to increase the plating rate, for enhancing hypophosphite efficiency, and for regulating the phosphorus or boron content of the deposit. It must be emphasized that an understanding of the course of the reaction, especially as it relates to the reduction of phosphorus or boron, is extremely important. It is the inclusion of P or B in the respective nickel alloys (Ni-P and Ni-B) that determines the properties of each alloy.

Before discussing the individual reducing agents, and the proposed mechanisms of their reactions with nickel, it might be informative to recall certain characteristics of the process that the mechanism must explain:

a) The reduction of nickel is always accompanied by the evolution of hydrogen gas;
b) The deposit is not pure nickel but contains either phosphorus or boron depending on the reducing media used;
c) The reduction reaction takes place only on the surface of certain metals;
d) The generation of hydrogen ions is a by-product of the reduction reaction;
e) The utilization of the reducing agent is considerably less than 100 percent; and
f) The molar ratio of nickel deposited to reducing agent consumed is usually equal to or less than 1.

Hypophosphite, H_2PO_2

Nickel deposition by hypophosphite is usually represented by the following equations:

$$Ni^{+2} + H_2PO_2^- + H_2O \longrightarrow Ni^0 + H_2PO_3^- + 2H^+ \quad (1)$$

$$H_2PO_2^- + H_2O \xrightarrow{Cat.} H_3PO_3^- + H_2 \quad (2)$$

overall,

$$Ni^{+2} + 2H_2PO_2^- + 2H_2O \longrightarrow Ni^0 + 2H_3PO_3^- + 2H^+ + H_2 \quad (3)$$

The product of nickel plating with hypophosphite are alloys of nickel and phosphorus; however, equations 1, 2, and 3 completely fail to account for the phosphorus component of the alloy. Further, if the plating reaction took place in accordance with the above equations, the rate of deposition would be proportional to the concentrations of the reactants. Experimental data shows that in acid plating solutions, pH $\geq$ 3.0. The plating rate is dependent on the hypophosphite concentration over a very wide concentration range, and dependent on the nickel concentration over a very small concentration range; the rate is independent of nickel concentration beyond about 0.075M Ni^{++}[1]. In alkaline solution, the rate is dependent only on the hypophosphite concentration.

Scholder and Heckel[2] were the first to observe that the products of the homogeneous reduction of nickel salts by hypophosphite was a mixture of metallic nickel and nickel phosphides. According to these researchers, the reduction of nickel salts by hypophosphite in alkaline solutions yields metallic nickel and several nickel phosphides, whereas in acid solutions only a mixture of different nickel phosphides is obtained. Scholder and Heckel explained the formation of metallic nickel and nickel phosphide by the following equations:

$$NiO + H_3PO_2 \longrightarrow Ni^0 + H_3PO_3 \quad (4)$$

$$3H_3PO_2 \longrightarrow H_3PO_3 + 2P + 3H_2O \quad (5)$$

$$2Ni + P \longrightarrow Ni_2P \quad (6)$$

They postulated that reactions 4 and 5 occur simultaneously, followed by the formation of Ni_2P according to reaction 6. They based their assumption on the fact that in nickel-free solutions, the disproportionation reaction (equation 5) yields hydrogen phosphide instead of phosphorus. The authors also assumed that hydrogen gas evolution was a consequence of the formation of metallic nickel, which then catalyzed the decomposition of hypophosphite; they made no connection between nickel reduction and hydrogen gas evolution. It must be remembered that the interest of these investigators was directed mainly to the study of the composition of the powders obtained as the products of nickel and/or cobalt reduction with hypophosphite.

Since the publication in 1946 of the paper by Brenner and Riddell[3], four principal reaction mechanisms have been proposed to explain electroless nickel deposition, which is incompletely represented by the stoichiometric reactions in equations 1,2 and 3. These reaction schemes attempt to explain nickel reduction by hypophosphite in both acid and alkaline media. To account for the phosphorus in the deposit, the proposed mechanisms involve a secondary reaction of hypophosphite to elemental phosphorus.

Appropriately, the first chemical nickel reaction proposed was advanced by Brenner and Riddell[3]. They postulated that the actual nickel reductant is atomic hydrogen, which acts by heterogeneous catalysis at the catalytic surface. The atomic hydrogen, generated by the reaction of water with hypophosphite, is absorbed at the catalytic surface, that is:

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H_{ad} \quad (7)$$

The absorbed atomic hydrogen reduces nickel ions at the catalytic surface:

$$Ni^{+2} + 2H_{ad} \longrightarrow (Ni^{+2} + 2H^+ + 2e) \longrightarrow Ni^0 + 2H^+ \quad (8)$$

The evolution of hydrogen gas, which always accompanies catalytic nickel reduction, was ascribed to the recombination of two atomic hydrogen atoms:

$$2H_{ad} \longrightarrow (H + H) \longrightarrow H_2 \quad (9)$$

Gutzeit[1] essentially agrees with the Brenner-Riddell atomic hydrogen concept of nickel reduction. However, Gutzeit[1] attributes the formation of atomic hydrogen to the dehydrogenation of the hypophosphite ion during formation of the metaphosphite ion:

$$H_2PO_2^- \xrightarrow{Cat.} PO_2^- + 2H$$

followed by the formation of O-phosphate molecule and a hydrogen ion according to:

$$PO_2^- + H_2O \longrightarrow HPO_3^{-2} + H^+ \quad (10)$$

A secondary reaction between hypophosphite and atomic hydrogen results in the formation of elemental phosphorus:

$$H_2PO_2^- + H \longrightarrow P + OH^- + H_2O \quad (11)$$

Although the atomic hydrogen mechanism, which has received the support of several authors, sustains the observed results, it fails to explain certain other phenomena. The scheme does not account for the simultaneous reduction of nickel and hydrogen, nor does it explain why the utilization of hypophosphite is always less than 50 percent.

The second mechanism, known as the "hydride transfer mechanism," was first suggested by Hersch[4], who claimed that the behavior of hypophosphite is analogous to the reduction of nickel ions by borohydride ions. That is, Hersch assumed that hypophosphite acts as the donor of hydride ions. Hersch's proposed mechanism was later modified by Lukes[5].

In acid solution, the primary step in the mechanism involves the reaction of water with hypophosphite at the catalytic surface, and may be described by the following equation:

$$2H_2PO_2^- + 2H_2O \xrightarrow{Cat.} 2H_2PO_3^- + 2H^+ + 2H^- \quad (12)$$

The corresponding reaction in alkaline solution is given by:

$$2H_2PO_2^- + 6OH^- \xrightarrow{Cat.} 2H_2PO_3^- + 2H_2O + 2H^- \quad (13)$$

The reduction of nickel ion in this mechanism proceeds as follows:

$$Ni^{+2} + 2H^- \longrightarrow (Ni^{+2} + 2e^- + 2H) \longrightarrow Ni^0 + H_2 \quad (14)$$

The hydride ion can also react with water or a hydrogen ion:

$$\text{Acid: } H^+ + H^- \longrightarrow H_2 \quad (15)$$

$$\text{Alkaline: } H_2O + H^- \longrightarrow H_2 + OH^-$$

According to Lukes, the hydrogen that appears as hydride ion was originally bonded to phosphorus in the hypophosphite. If equation 11 is included in this scheme, the co-deposition of phosphorus is also accounted for. The hydride mechanism presents a satisfactory explanation for the coupled reduction of nickel and hydrogen.

The third mechanism is the so-called electrochemical mechanism originally proposed by Brenner and Riddell and later modified by others. This theory can be represented as follows:

(i) An anodic reaction where electrons are formed by the reaction between water and hypophosphite:

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^- \quad (16)$$

(ii) Cathodic reactions that utilize the electrons generated in equation 16:

$$Ni^{+2} + 2e \longrightarrow Ni^0 \quad (17)$$

$$2H^+ + 2e \longrightarrow H_2 \quad (18)$$

$$H_2PO_2^- + 2H^+ + e \longrightarrow P + 2H_2O \quad (19)$$

According to this mechanism, the evolution of hydrogen gas that takes place during nickel deposition is due to the secondary reaction represented in equation 18. The electrochemical mechanism implies that the nickel ion concentration should have a significant effect on the rate of deposition; however, the converse is the case.

The fourth mechanism involves the coordination of hydroxyl ions with hexaquonickel ion. This mechanism was proposed by P. Cavallotti and G. Salvago[6], and later supported by the results of calorimetric studies on electroless nickel plating by J.P. Randin and H.E. Hintermann[7]. The chemical reduction of nickel at a catalytic surface can be represented by the following reactions:

Decomposition of water:

$$2H_2O \longrightarrow 2H^+ + 2OH^- \quad (20)$$

Coordination of hydroxyl ions to solvated nickel ion:

$$Ni(H_2O)_6^{+2} + 2OH^- \left[\begin{matrix} & OH \\ Ni\ (aq) & \\ & OH \end{matrix} \right] + 2H_2O \quad (21)$$

Reactions of hydrolyzed nickel species with hypophosphite:

$$\left[\begin{matrix} & OH \\ Ni\ (aq) & \\ & OH \end{matrix} \right] + H_2PO_2^- \longrightarrow NiOH_{ads} + H_2PO_3^- + H \quad (22)$$

$$NiOH_{ads} + H_2PO_2^- \longrightarrow Ni^0 + H_2PO_3^- + H \quad (23)$$

Where $NiOH_{ads}$ represents a hydrolyzed Ni^{+1} species adsorbed at the catalytic surface. The two atoms of atomic hydrogen can react and evolve as hydrogen gas:

$$H + H \longrightarrow H_2 \quad (24)$$

and it can reduce hypophosphite to phosphorus:

$$H_2PO_2^- + H_{ads} \longrightarrow P + H_2O + OH^- \quad (25)$$

The reaction of hypophosphite with water must also be included in the reaction scheme:

$$H_2PO_2^- + H_2O \longrightarrow HPO_3^{-2} + H^+ + H_2 \quad (26)$$

$\left[\begin{matrix} & OH \\ Ni\ (aq) & \\ & OH \end{matrix} \right]$ is a schematic representation of the reacting species formed by loosely bonded OH^- ion in the coordination sphere of partially solvated $Ni(H_2O)_4^{+2}$ ions, and not nickel hydroxide. Cavallotti and Salvago, in fact, point out that when nickel hydroxide precipitates, inhibition phenomena are evident. If the hydroxyl ions are bonded too tightly to the nickel, they will not react with the hypophosphite ion. The adsorption of the hydrolyzed species on the active surface probably influences the lability of the coordination bonds.

Among the four proposed reaction mechanisms, only the hydride transfer and hydrolyzed nickel mechanisms account for the observed values for the ratio of moles of nickel deposited to the moles of hypophosphite consumed during deposition. The data obtained in the studies of Franke and Moench[8] and later Sutyagina, Gorbunova, and Glazunov[9] concerning the origin of the hydrogen gas evolved from the interaction between water and hypophosphite ion can be explained by either of these two mechanisms.

Each of the heterogeneous reaction mechanisms outlined above requires a catalytic surface on which the reaction sequence will proceed. Hence, electroless nickel plating occurs only on specific surfaces. The reduction reaction begins spontaneously on certain metals; almost all metals of Group VIII of the Periodic Table in active form.

Metals that are more electropositive than nickel, such as iron or aluminum, will displace nickel from a solution of its ions as follows:

$$Fe^0 + Ni^{+2} \longrightarrow Fe^{+2} + Ni^0_{Cat.} \quad (27)$$

or

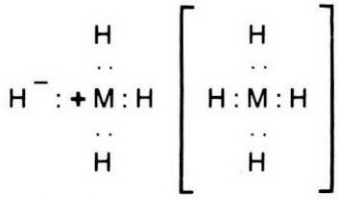
$$2Al + 3Ni^{+2} \longrightarrow 2Al^{+3} + 3Ni^0_{Cat.} \quad (28)$$

forming the catalytic surface. It is ironic to note that when steel or aluminum, the most commonly plated substrates, are electroless nickel plated, the initial phase in the deposition process is the displacement reaction.

If the substrate metal is more electronegative than nickel, it can be made catalytic by electrolytically depositing a thin nickel deposit on its surface. This can also be accomplished by providing contact, in the solution, between the substrate and a more electropositive metal, thereby forming an internal galvanic cell. For example, copper and its alloys are usually plated with either of these techniques.

The Borohydride Ion, BH_4

The only complex hydrides of non-transition elements known at the present time are formed by boron, aluminum, and gallium. They occur as salts of hydride ions, that is, $NaBH_4$, Li (AlH_4), etc. The MX_3 group behaves as an electron acceptor and the hydride ion as an electron donor:



, where M = B, Al, or Ga

The thermal and chemical stabilities of the three anions vary relative to the ability of the MH_3 group to act as an electron acceptor, the order being:

$$B > Al > G$$

BH_4^- is stable in water, while AlH_4^- and GaH_4^- are rapidly and sometimes explosively hydrolyzed by water:

$$MH_4^- + 4H_2O \longrightarrow M(OH)_4^- + 4H_2$$

and acid hydrolysis,

$$MH_4^- + H^+ \longrightarrow MH_3 + H_2$$

The alkali metal salts of MH_4^- anion are very powerful reducing agents; however, only the salts of BH_4^-, such as $NaBH_4$, can be utilized in aqueous solutions.

In the 40 or so years since the discovery of "electroless" nickel plating by Brenner and Riddell, hundreds of papers describing the process and the resulting deposits have been published. Although other electroless systems are covered, the vast majority of these publications (papers and patents) are concerned with nickel- or cobalt-phosphorus alloys and the plating solutions that produce them.

Attempts to develop alternative reducing agents led several workers to investigate the boron containing reducing agents; in particular, the borohydrides and amine boranes. Subsequently, several patents were issued covering electroless plating processes and the resulting deposits.

The deposits obtained from electroless systems using boron containing reducing agents are nickel-boron alloys. Depending on the solution operating conditions, the composition of the deposit can vary in the range of 90 - 99.9 percent nickel with varying amounts of reaction products. In some cases, the metallic stabilizer will be incorporated in the deposit during the plating reaction.

As is the case with nickel-phosphorus alloys, nickel-boron deposits are characterized by their unique chemical and physical properties.

The borohydride reducing agent may consist of any water soluble borohydride compound. Sodium borohydride is generally preferred because of its availability. Substituted borohydrides in which not more than three of the hydrogen atoms of the borohydride ion have been replaced can also be used; sodium trimethoxyborohydride ($NaB(OCH_3)_3H$) is an example of this type of compound.

The borohydride ion is a powerful reducing agent. The redox potential of BH_4^- is calculated to be $E^0_{ca} = 1.24V$. In basic solutions, the decomposition of the BH_4^- unit yields eight electrons for the reduction reaction:

$$BH_4^- + 8OH^- \longrightarrow B(OH)_4^- + 4H_2O + 8e^- \quad (29)$$

Then, each borohydride ion can theoretically reduce four nickel ions. That is, adding equation 29 to:

$$4NI^{+2} + 8e^- \longrightarrow 4Ni^0 \quad (30)$$

gives the overall reaction,

$$4Ni^{+2} + BH_4^- + 8OH^- \longrightarrow B(OH)_4^- + Ni^0 + 4H_2O \quad (31)$$

However, it has been found experimentally that one mole of borohydride reduces approximately one mole of nickel.

There are only a few published articles that are concerned with the mechanism of nickel deposition with borohydride, and most of the proposed schemes are not supported by experimental data. In spite of the experimental evidence to the contrary, several authors still assume that each borohydride ion reduces four nickel ions, that is:

$$4Ni^{+2} + BH_4^- + 8OH^- \longrightarrow 4Ni^0 + BO_2^- + 6H_2O \quad (32)$$

Although the authors of three separate mechanisms agree that nickel reduction proceeds as expressed in equation 32, the reduction of boron is approached differently in each case.

Case 1[10]. Here the author assumes that only three hydride ions are oxidized to protons; the fourth hydride is oxidized to a hydrogen atom, which leads to the formation of a molecule of evolved hydrogen gas:

$$4Ni^{+2} + 2BH_4 + 6OH^- \longrightarrow 2Ni_2B + 6H_2O + H_2 \quad (33)$$

Case 2[11]. In this instance, it is assumed that all hydride ions are oxidized to protons, so that:

$$5Ni^{+2} + 2BH_4 + 8OH^- \longrightarrow 5Ni^0 + 2B + 8H_2O \quad (34)$$

Case 3[12]. Boron reduction is, as assumed by these authors, the catalytic decomposition of borohydride to elemental boron that takes place independently of nickel reduction:

$$2BH_4^- + 2H_2O \longrightarrow 2B + 2OH^- + 5H_2O$$

K.M. Gorbunova, M.F. Ivanov, and V.P. Moiseev[13] raised an objection to the three above hypotheses. They argue, that based on data relating to the reduction reactions by hypophosphite, it is doubtful that the hydrogen atoms, formed during the oxidation of the hydride ions of BH_4, are intermediate products that can take part in either nickel or boron reduction.

Data obtained from mass-spectrometric measurements of the isotope composition of hydrogen gas evolved during electroless Ni-B deposition experiments using heavy water (D_2O), led Gorbunova and co-workers to propose a mechanism that more nearly fits the results of their studies. Their experiments were carried out using plating solutions prepared with D_2O, and also containing NaOD. It should be noted that calculations based on previously proposed schemes yielded results that deviated by almost 200% from the experimental data obtained in isotope experiments.

The proposed scheme of Gorbunova et al. for the reaction mechanism of nickel-boron plating consists of three main steps:

(1) Reduction of nickel:

$$BH_4^- + 4H_2O \longrightarrow B(OH)_4^- + 4H + 4H^+ + 4e^- \quad (35)$$

$$2Ni^{+2} + 4e^- \longrightarrow 2Ni^0 \quad (36)$$

$$(35) + (36) \quad BH_4^- + 2Ni^{+2} + 4H_2O \longrightarrow 2Ni^0 + B(OH)_4^- + 2H_2 + 4H^+ \quad (37)$$

(2) Reduction of boron:

$$BH_4^- + H^+ \longrightarrow BH_3 + H_2 \longrightarrow B + \frac{5}{2} H_2 \quad (38)$$

(3) Hydrolysis of borohydride:

$$BH_4^- + 4H_2O \longrightarrow + B(OH)_4^- + 4H + 4H^+ + 4e^- \longrightarrow B(OH)_4^- + 4H_2 \quad (39)$$

G.O. Mallory has also investigated the reduction of nickel ions by borohydride and amine boranes[14]. On the basis of experimental data, the author suggests that the hydrolyzed nickel mechanism of Cavallotti and Salvago, proposed to explain nickel reduction with hypophosphite, can be adapted to explain nickel reduction with borohydride or amine boranes. The modified hydrolyzed nickel mechanism with borohydride can be represented by the following sequence of reactions:

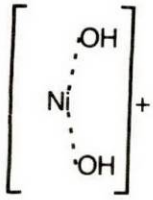
(1) Decomposition of water:

$$4H_2O \longrightarrow 4H^+ + 4OH^- \quad (40)$$

(2) Coordination of hydroxyl ions to solvated nickel ion:

$$2Ni(H_2O)_6^{+2} + 4OH^- \longrightarrow 2 \left[\begin{matrix} & OH \\ Ni(aq) & \\ & OH \end{matrix} \right] + 4H_2O \quad (41)$$

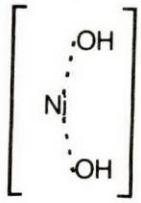
(3) Reaction of hydrolyzed nickel species with borohydride ion:



$$+ BH_4^- \longrightarrow NiOH_{ads} + BH_3OH^- + H \quad (42)$$

$$NiOH_{ads} + BH_3OH^- \longrightarrow Ni^0 + BH_2(OH)_2^- + H \quad (43)$$

The $BH_2(OH)_2^-$ species reacts with the second hydrolyzed nickel ion in a similar manner:



$$+ BH_2(OH)_2^- \longrightarrow NiOH_{ads} + BH(OH)_3^- + H \quad (44)$$

$$NiOH_{ads} + BH(OH)_3^- \longrightarrow Ni^0 + B(OH)_4^- + H \quad (45)$$

(4) The four atoms of atomic hydrogen react to form hydrogen gas:

$$2H + 2H \longrightarrow 2H_2 \quad (46)$$

Thus, equations 40 through 46 can be represented by the overall reaction:

$$2Ni^{+2} + 4H_2O + BH_4^- \longrightarrow 2Ni^0 + B(OH)_4^- + 2H_2 + 4H^+ \quad (47)$$

The reduction of boron is accounted for in the reaction of BH_4^- with a hydrogen ion:

$$BH_4^- + H^+ \longrightarrow BH_3 + H_2 \longrightarrow B + \frac{5}{2}H_2 \quad (48)$$

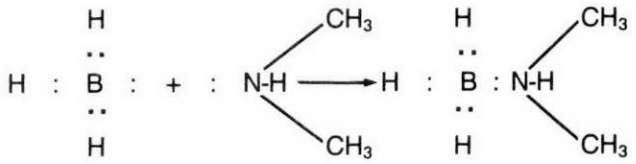
Equations 47 and 48 can be combined to obtain:

$$2Ni^{+2} + 2BH_4^- + 4H_2O \longrightarrow 2Ni^0 + B + B(OH)_4^- + 3H^+ + \frac{9}{2}H_2 \quad (49)$$

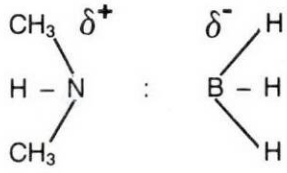
The mechanism proposed by Gorbunova et al. and the modified Cavallotti and Salvago proposal lead to the same overall reaction. Also, in both schemes, the increase in acidity observed in the process is due to hydrogen ions that originate from water molecules only. Finally, the two mechanisms indicate that the mole ratio of nickel reduced to borohydride consumed is 1:1, which is supported by experimental evidence.

The Amine Boranes

In the BH_3 molecule the boron octet is incomplete, that is, boron has a low-lying orbital that it does not use in bonding owing to a shortage of electrons. As a consequence of the incomplete octet, BH_3 can behave as an electron acceptor (Lewis acid). Thus, electron pair donors (Lewis bases), such as amines, form 1:1 complexes with BH_3 and thereby satisfy the incomplete octet of boron. The linkage between BH_3 and dimethylamine is illustrated by the following:



The amine boranes are covalent compounds, whereas borohydrides such as $NaBH_4$ are completely ionic; that is, $NaBH_4 = Na^+ + BH_4^-$. Although the amine boranes do not ionize like other molecules with heteronuclear covalent bonds, one of the atoms will, in general, have a greater affinity for the electrons than the other and the bond will therefore be polar, i.e.:



In this case, the electrons are displaced toward the boron atom giving the boron atom excess negative character; whereas, the nitrogen atom displays excess positive charge. The electrical polarity of a molecule, expressed as its dipole moment, plays an important role in the reactions of covalent compounds.

The commercial use of amine boranes in electroless nickel plating has, in general, been limited to dimethylamine borane (DMAB), $(CH_3)NHBH_3$. DMAB has only three active hydrogens bonded to the boron atom and, therefore, should theoretically reduce three nickel ions for each DMAB molecule consumed (each borohydride ion will theoretically reduce four nickel ions). The reduction of nickel ions with DMAB is described by the following equations:

$$3Ni^{+2} + (CH_3)_2NHBH_3 + 3H_2O \longrightarrow Ni^0 + (CH_3)_2NH_2^+ + H_3BO_3 + 5H^+ \quad (50)$$

$$2[(CH_3)_2NHBH_3] + 4Ni^{+2} + 3H_20 \longrightarrow Ni_2B + 2Ni^0 + 2[(CH_3)_2NH_2^+] + H_3BO_3 + \tfrac{1}{2}H_2 + 6H^+ \quad (51)$$

In addition to the above useful reactions, DMAB can be consumed by wasteful hydrolysis:

$$\text{Acid: } (CH_3)_2 + NHBH_3 + 3H_2O + H^+ \longrightarrow (CH_3)_2NH_2^+ + H_3BO_3 + 3H_2 \quad (52)$$

$$\text{Alkaline: } (CH_3)_2NHBH_3 + OH^- \longrightarrow (CH_3)_2NH + BH_3(OH)^- \quad (53)$$

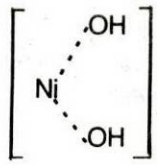
However, the theoretical expressions for nickel reduction are not supported by experimental findings. The results of studies on chemical nickel plating with DMAB indicates that the molar ratio of nickel ions reduced to DMAB molecules consumed is approximately 1:1[14]. A modified hydrolyzed nickel mechanism satisfactorily accomodates the experimental data.

Based on his studies, M. Lelental[15] suggests that nickel deposition with DMAB is dependent on the adsorption of the reducing media on the catalyst surface followed by cleavage of the N-B bond of the adsorbed amine borane. The adsorption step is consistent with the polar nature of the DMAB molecule. The mechanism can be illustrated as follows:

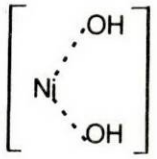
(1) N-B bond cleavage:

$$2R_2NHBH_3 \xrightarrow{\text{Cat.}} 2R_2NH + 2BH_{3ads} \quad (54)$$

(2) Reduction of hydrolyzed nickel with BH_{3ads}:

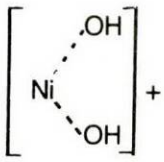


$$+ BH_{3ads} \longrightarrow Ni^0 + BH(OH)_{2ads} + 2H \quad (55)$$



$$+ BH(OH)_{2ads} \longrightarrow NiOH_{ads} + B(OH)_3 + H \quad (56)$$

$$NiOH_{ads} + BH_{3ads} \longrightarrow Ni^0 + BH_2OH + H \quad (57)$$



$$+ BH_2OH \longrightarrow Ni^0 + B(OH)_3 + H \quad (58)$$

The sums of the above equations, including the decomposition of water, is given by:

$$3Ni^{+2} + 2R_2NHBH_3 + 6H_2O \longrightarrow 3Ni^0 + 2R_2NH_2^+ + 2B(OH)_3 + 3H_2 + 4H^+ \quad (59)$$

(3) Boron reduction:

$$R_2NHBH_3 \xrightarrow{Cat.} R_2NH + BH_3 + H_2 + H^+ \longrightarrow R_2NH_2^+ + B + \frac{5}{2} H_2 \quad (60)$$

Equations 59 and 60 can be combined to give:

$$3Ni^{+2} + 3R_2NHBH_3 + 6H_2O \longrightarrow 3Ni^0 + B + 3R_2NH_2^+ + 2B(OH)_3 + \frac{9}{2}H_2 + 3H^+ \quad (61)$$

Hydrazine

Soon after Brenner and Riddell published their findings on nickel reduction with hypophosphite, L. Pessel[16], in 1947, was issued a patent claiming the use of hydrazine as a metal reductant. During the succeeding 16 years many papers and patents were published detailing electroless nickel-phosphorus deposition. However, it was not until 1963, when D.J. Levy[17] reported the results of his investigations, was any information forthcoming on electroless nickel plating with hydrazine. Later, Dini and Coronado described several electroless nickel-hydrazine plating baths and the properties of the deposits obtained form ther solutions.[18]

Hydrazine is a powerful reducing agent in aqueous alkaline solutions:

$$N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^-, E_B^0 = 1.16V$$

Levy proposed the following reduction reaction for nickel ions with hydrazine in an alkaline solution:

$$2Ni^{+2} + N_2H_4 + 4OH^- \longrightarrow 2Ni^0 + N_2 + 4H_2O \quad (62)$$

CONCLUSION

Of the four mechanisms proposed to explain the chemical reduction of Ni-P and Ni-B alloys, the so-called hydrolyzed nickel theory of Cavalloti and Salvago is the one that is supported by experimental evidence. The hydrolyzed nickel theory can also be considered a universal mechanism since it can also be used to characterize the reduction processes with borohydride and amineboranes as well as with sodium hypophosphite.

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Electroless Deposition II
Session J

Electronic Applications of Electroless Nickel, New or Unusual

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ELECTRONIC APPLICATIONS OF ELECTROLESS NICKEL, NEW OR UNUSUAL

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Electroless nickel deposits provide functional characteristics that are useful for many electronic devices. Deposit characteristics such as electrical conductance/resistance, magnetic properties, hardness, and amorphous/partially crystalline structure can be varied by using different plating solution compositions and operating conditions. Good brazing, soldering, laser welding, and wire and die bonding can be achieved using special bath formulations. This paper discusses some of the specific applications which take advantage of the unique properties of various electroless nickel plating systems.

Ceramic Microballoons

Electronic circuits often require protection from electromagnetic interference (EMI), particularly at radio frequencies (RF interference). One common method of providing EMI shielding is by depositing a layer of electroless copper followed by a layer of electroless nickel onto the plastic cases that house the electronics. The electroless nickel must exhibit reasonably good conductivity, such as a low-phosphorus nickel or a nickel-boron alloy. Much has been written about this type of shielding.[1,2,3] Electroless nickel can also be applied by other methods to provide EMI and RF shielding. One significant example is a coating of electrically conductive "microballoons" (Figs. 1 and 2)†[4,5]

These microballoons (microspheres) are hollow spheres of fired ceramic with a typical outer diameter of 50 microns and wall thickness of near 10 microns, and are coated with a thin layer of metal to provide a conductive surface. Since RF energy is only conducted on the outer surface (about one microinch thick) of a solid conductor — the "skin effect" — the microballoons provide the same shielding and conductivity as plated metal deposits or paints containing solid metal particles, yet provide significant cost savings and weight reduction due to the lower amount of metal used. They are structurally strong yet lightweight, with a density of about 0.7 and a crush strength of about 4,000 psi isostatic. Their spherical shape is ideal since it has maximum volume per surface area, thus using the least amount of metal to fill any unit volume. Spherical particles spray easily when applied with coating resins, are isotropic to RF energy, and have a dense continuous packing arrangement, filling about 70% of the coating volume.

Spheres can be made slightly magnetic by including magnetite into the ceramic or using a magnetic electroless nickel deposit. Magnetic attraction between the spheres promotes dense packing and uniform properties. It also increases the shield effectiveness due to hysteresis losses. This improves the low impedance EMI shielding effectiveness. Ferrite is added to the ceramic as a strong absorber of RF energy. "With these additions a particle is created with superb conductivity which absorbs strongly any induced fields."[4,5]

Noble metals such as silver, gold, platinum, palladium, iridium, and osmium provide greater long-term conductivity than metals such as copper that oxidize with age, increasing contact resistance. The least expensive of these metals is silver. Coatings containing silver are excellent conductors and shields, and the basic chemistry of silver deposition is well known.

Electroless nickel plated onto the microballoons followed by a very thin silver immersion deposit reduces the amount of silver used, and therefore the cost of production, without sacrificing shielding effectiveness. Highly conductive electroless nickel deposits may eliminate the need for silver in some applications. Deposit conductance is enhanced by using a reducing agent that produces nearly pure nickel, such as a boron agent (boron content of deposit less than 0.3%) or hydrazine (caution — hydrazine is highly toxic and explosive).

Gindrup† discusses the shielding performance of silver coated magnetic ceramic microballoons (SCMCM) on Norel™ plastic:

"A typical coating on NOREL appears as a very smooth light tan paint. It has a dry weight of 0.04 g. to 0.05 g. per square inch. This coating contains one half by weight SCMCM or 0.02 g. to 0.025 g. per inch square. The film gives a conductance between 0.1 and 0.2 ohms per square. The shielding effectiveness will exceed -40 dB from zero to one Gigahertz with very little change due to frequency. Reflection of EMI by a conductive surface is caused by an impedance mismatch. RF currents are induced into the shield and are attenuated as they pass through the shield. RF energy reaching the back of the shield is partially reflected back into the shield and partially radiated into the enclosure. A solid metal shield mainly attentuates the induced currents by only ohmic losses which are small in a solid metal wall, allowing considerable energy to reach the backside. In comparison, the silver coated microballoons cause great attenuation because each microballoon creates six impedance mismatches. This results in large amounts of energy being dissipated by multiple internal reflections and destructive interference. The absorption is enhanced by the multiple conductive paths."

Electroless nickel solutions used for this application are generally more concentrated than for other applications. The surface area-to-solution volume ratio is extremely large compared to normal plating situations. For example, each 100 grams of microballoon material has a surface area of 8-10 square meters, resulting in bath loading of over 100 square feet per gallon. In comparison, typical bath loading is about 0.5 to 1 square foot per gallon when plating ordinary devices. Depending on the particle size being coated, the nickel coating will range from 10% to 20% by weight. The plating temperature is from 25-35 C with a plating time of 30-45 minutes.

Typical preparation consists of a dilute palladium chloride solution rinse and immersion in an alkaline formaldehyde solution to reduce the palladium to the metal. Careful rinsing follows, then electroless nickel plating.

Other applications include ablative laser shields, electrically conductive liquids, radar scattering and absorption, electrostatic capacitors, electrostatic generators, ultra-high speed projectiles, and ultra-light aerospace composites.[4,5,6]

Electroless nickel plated fibers have also been plated for similar applications.

Via Hole Filling

Integrated circuit (I.C.) designers constantly strive to increase the operating speed and decrease the cost of complex circuits by squeezing more circuit elements onto smaller areas of silicon chip "real estate". Today's very large scale integrated circuits (VLSI) use multilevel circuit interconnections to provide high density and reliability in a compact structure.

During fabrication, a layer of metallization is deposited on the silicon wafer, and conductors are etch-defined. A layer of dielectric is then deposited, and windows ("via holes") are etched through to connection points on the metallization. The next layer of metallized conductors is then applied to form interconnections.

It is important to have a flat (planar) surface topography at all stages of production, or stress, etching irregularities, and serious problems in lithographic patterning can result. However, the upper level of metallization is not completely planar because of the depth of the via holes (Fig. 3)[7]; and this problem is compounded when additional layers are required to complete all interconnections. Therefore, it is essential to fill the via holes with a conductor before metallization to produce high-reliability interconnections (Fig. 4)[7]. Vacuum deposition methods have been studied extensively, but fall short of the results of electroless nickel plating. Electroless processes are simple, low cost, and easy to implement.

Ting, Paunovic and Chiu† [8,9,10] report the following process:
"Substrates with one micron Al-Si layer deposited by a standard sputtering process. The dielectric layer over Al is 1.0-1.5 micron thick undoped oxide deposited by an LTO process. Via holes of 1.5 micron nominal size are formed by the usual photolithography and plasma etching process." The aluminum conductor is first activated by using a light etch to remove surface oxides, a deionized water rinse follows, then immersion in a palladium activation solution ($PdCl_2$, HCl and water) at about 40 C. The wafers are rinsed and immersed in an electroless nickel-boron plating solution, pH about 6, temperature 55 C; the plating rate was slowed to 2.8 microns/hr. (by the lower temperatures) to minimize nodule formation.

For plating onto the silicon surfaces, palladium activation is not necessary. The silicon is first etched lightly in a nitric acid-fluoride salt or hydrofluoric acid-water mixture. The pH of the electroless nickel -boron solution is raised to about pH 8. Plating proceeds when the wafer is immersed in the plating bath at 55 C.

Harada, Fushimi, Madakoro, Sawai and Ushio[11] report via hole filling by electroless nickel onto aluminum conductors patterned on 4 in. silicon substrates with 600 nm thickness of phosphosilicate glass (PSG) films deposited on the Al patterns for interlayer insulation. Via holes of 2,3, and 4 micrometers in diameter were formed using reactive ion etching (RIE), and activated with palladium chloride, followed by electroless nickel-boron plating. Two methods of activation were reported. The "wet" method where the bottom of the hole was activated, and the "lift off" method where palladium is vacuum deposited selectively in the holes coating the walls as well as the bottom. The wet method resulted in a flat, smooth (planar) surface with 100% process yield (Fig. 5)[11].

Ceramic-to-Metal Joining †††

Bonding metals to ceramic substrates to produce high strength joining has long been a problem. Differences in the thermal expansion characteristics of metals and ceramics account for much of the problem. Irregularities including bumps and micro-fissures in the ceramic surface result in stresses which can lead to joint failure. Preparation of the ceramic surface to produce a smooth but sufficiently porous surface to allow adhesion has been difficult.

Methods have been developed which produce joints sufficiently strong for engineering applications such as bearings, seals, turbochargers, gas turbine engines, and diesel engines, as well as electronic applications such as producing circuits directly on ceramic substrates (without metallization by metal pastes such as molybdenum manganese), joining two or more ceramic devices, and producing multilayer ceramic devices. The preparation steps involve machining of the ceramic component to remove surface irregularities which could

lead to stress, and chemical surface preparation in mixed acid/fluoride treatment. "It alters the grain boundry to matrix structure and provides a more regular surface with reduced flaws."[12]

The prepared ceramic is catalyzed and plated in an electroless nickel-boron plating bath. Direct bonding is achieved. Part configuration is not a limiting factor since deposit distribution is uniform over all surfaces to be plated. Joining is accomplished by brazing. Test results show as high as 450 MPa tensile force (ASTM Std. F692) is necessary to separate the metal layer. Nickel-boron plating is chosen because it will withstand thermal excursions without cracking. It does not alter structure due to formation of intermetallic compounds as is the case with nickel-phosphorus. It is also easily soldered and wire and die bonded, making it suitable for a varity of applications.

"Ceramics to which metals have been bonded include alumina, silicon carbide, lithium aluminum silicate, mullite, steatite, sintered silicon nitride and partially stabilized zirconia."[12]

Additional Applications

Electroless nickel deposits are used in an increasing number of electronic devices too numerous to discuss in detail in the this paper. Additional examples are:

"Air-bridges" used to connect circuit elements on wafers and other substrates for integrated circuits and microhybrid circuits. An air bridge is produced by masking the conductor to be transversed, electroless nickel plating to form a bridge conductor, and then removing the mask.

Medical devices such as pacemakers utilize electroless nickel plating on piezoelectric ceramic which is joined to metal to form a sensor.

Solder bumps are used to join flip chip devices to the electronic package. An electroless nickel layer prior to forming the solder bumps provides high reliability to the device.

Multi-layer flexible circuits utilize electroless nickel layer to promote bonding of copper conductor layer to polyimide substrate material. Copper-clad polyimide sheet is produced by one supplier utilizing a thin electroless nickel-boron bonding layer followed by copper plating. This technique results in an extremely thin laminate since it eliminates the adhesive bonding layers, allowing a larger number of layers in a multilayer circuit.

Electroless nickel baths are readily adaptable to modification by alloying other metals to produce specific properties to suit many electronic device requirements. Some examples are: nickel-iron-boron to produce a highly permiable soft magnetic deposit; nickel-cobalt-phosphorus and cobalt-phosphorus deposits to produce a hard magnetic deposit, nickle-tungsten-boron deposits for good solderability and high temperature resistance; and cobalt-boron and cobalt-nickel-boron alloys which produce special soft magnetic deposits. Many other alloys are possible to achieve specific characteristics, and new applications continue to unfold as technology advances.

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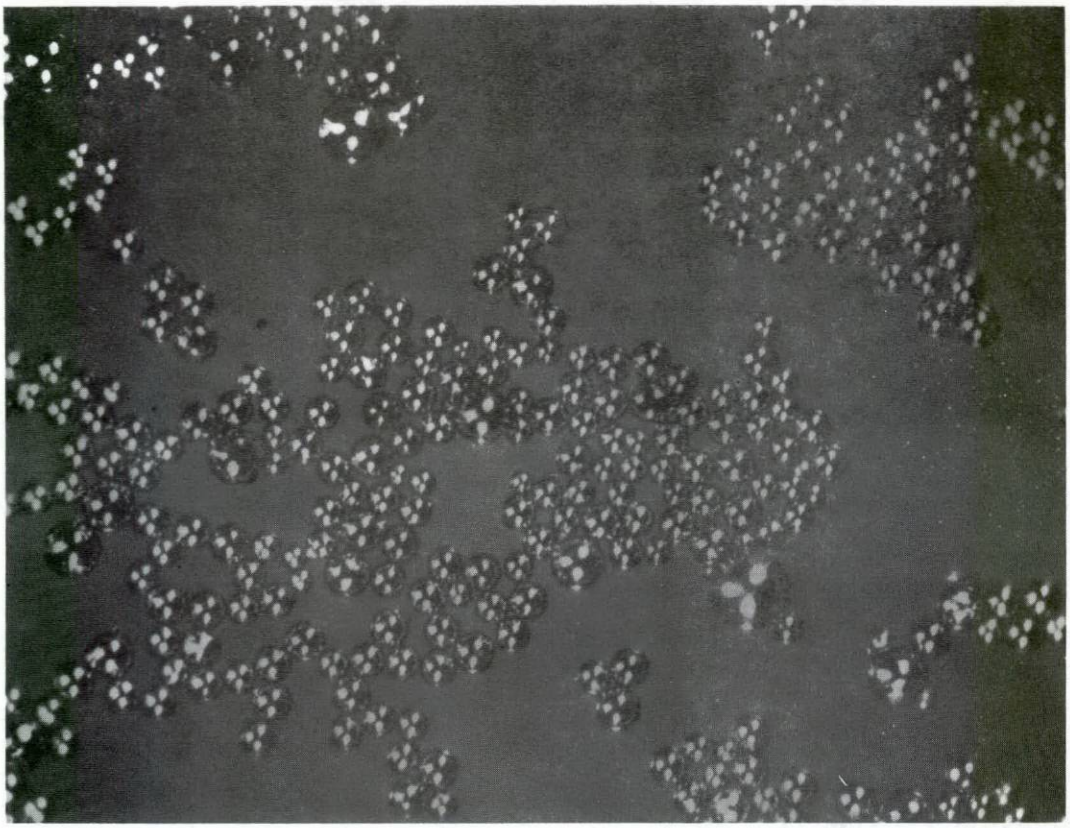


Figure 1. 100X Photomicrograph of nickel-coated magnetic ceramic microspheres (15% by weight nickel-phosphorus)

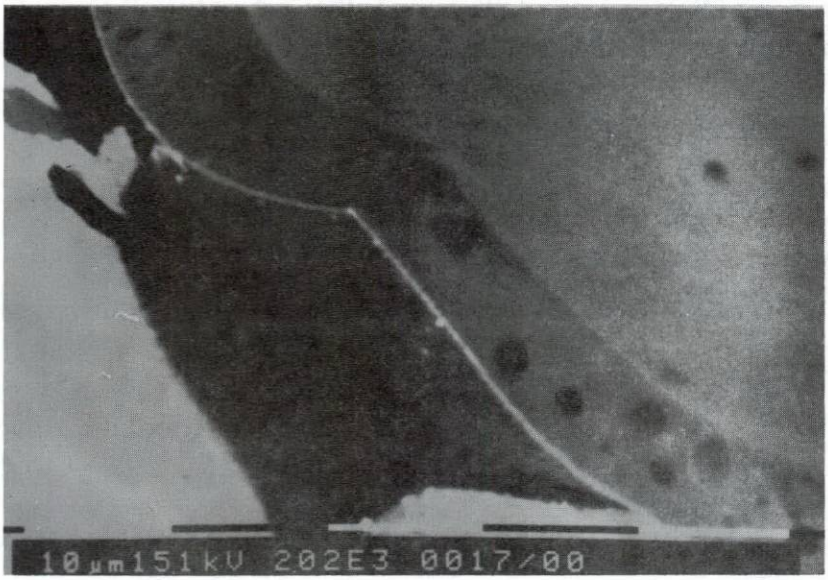


Figure 2. SEM showing cross-section of broken metal-coated microsphere

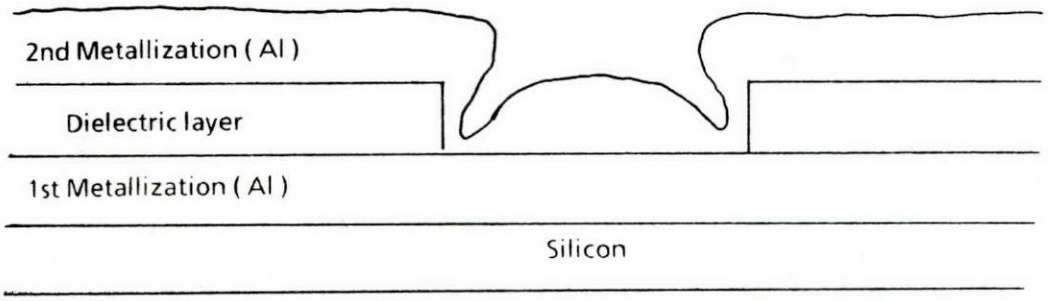


Figure 3. Poor step coverage on non-planar topological metallization

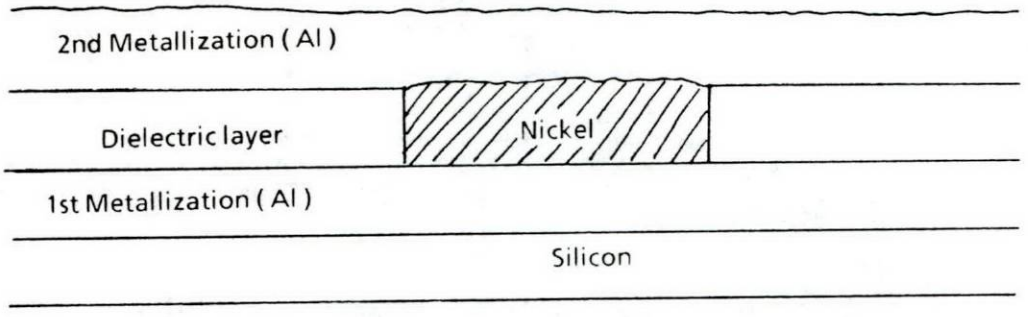
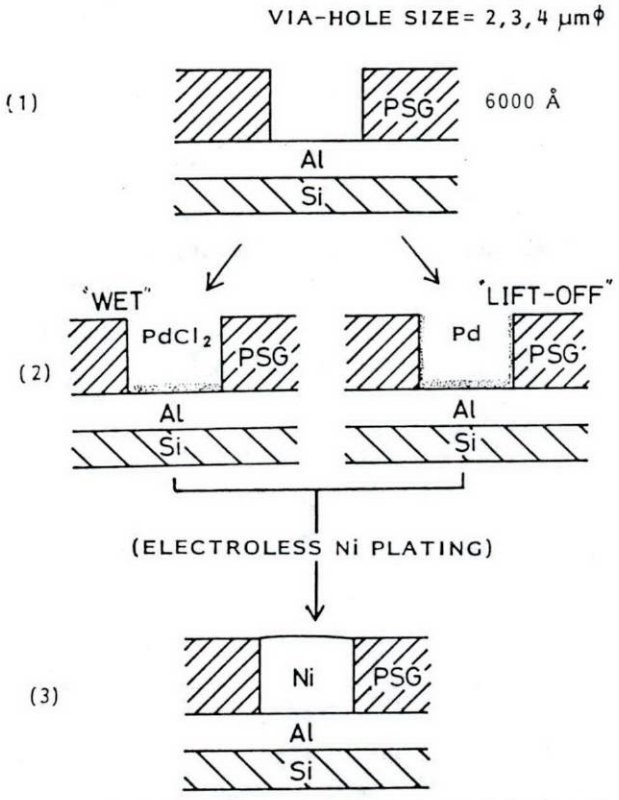


Figure 4. Planarization of metallization by via hole filling with electroless nickel plate



Via-hole filling process flow. (1), After via-holes formation using a reactive ion etching method. (2), After selective activation into via-holes. (3), After completion of via-filling using electroless Ni plating method.

Figure 5. Process for via hole filling using electroless nickel

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Electroless Deposition II
Session J

Optimizing the Manufacturing Economics of Electroless Nickel Bath Operation

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OPTIMIZING THE MANUFACTURING ECONOMICS OF ELECTROLESS NICKEL BATH OPERATION

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In the world marketplace, with product quality being equal, the price of manufactured goods dictates acquisition of market share via cost leadership. The goal associated with reducing manufacturing cost is to maintain competitive prices. Various methods of reducing manufacturing cost have been implemented including the use of relatively low cost labor in the Pacific Rim countries and Mexico. Another strategy which has proven to be successful in maintaining competitive prices is to focus attention to manufacturing detail aiming at the reduction of direct materials consumption in the manufacturing process [1]. Electroless nickel (EN) plated surfaces are a direct material cost in numerous industrial sectors. These EN plated products range from valves, drilling machinery and chemical processing equipment to aerospace and electronics/computer components with applications seemingly limited only by the imagination[2,3]. One method of reducing manufacturing cost in the industrial sectors which utilize EN as a direct material is to optimize the manufacturing economics of electroless nickel bath operation.

Various process parameters contribute to the costs associated with the application of EN plated surfaces. A portion of the cost of these process parameters is related to the EN bath composition and the reducing chemistry of the bath. The reducing chemicals in the bath supply the electrochemical energy required to reduce the nickel in solution to metallic nickel. Several different reducing chemicals such as sodium hypophosphite, sodium borohydride, dimethylamine borane and hydrazine have been successfully used in EN plating baths [4]. The majority of commercially available EN bath formulations incorporate either sodium hypophosphite or dimethylamine borane as reducing agents. The EN bath composition formulated with sodium hypophosphite is abbreviated as EN-P and the EN bath composition formulated with dimethylamine borane is abbreviated EN-B. The EN-P formulation selected in this economic analysis is a commercially available product [5]. The EN-B formulation used in this economic analysis is also a commercially available product[5]. The EN plating bath which is chosen by the consumer (either EN-P or EN-B) is selected based upon the amenability of the nickel plate finish to the consumer's application and compliance with specifications.

The process parameters which contribute to EN plating cost can be separated into the general categories of: 1) optimum chemical consumption, 2) minimizing extraneous EN bath plate-out, and 3) maintaining a homogeneous bath. These process parameters are generally independent of the type of EN bath be it EN-P or EN-B. However, a portion of the cost of operating an EN bath is related solely to the reducing chemistry. The scope of this presentation does not include the EN plating cost related to the specific reducing chemistries.

Optimum Chemical Consumption

Optimum chemical consumption is designated as the minimum quantity of chemical cost required to EN plate a surface in compliance with a

specification or requirement. Compliance of an EN surface to grade, specification or requirement is usually designated in terms of a minimum plating thickness with coverage over all required surfaces[6]. Other parameters include: corrosion resistance, different basis metals, hardness, adhesion, lack of discoloration, appearance of surface finish, solderability, high temperature resistance, uniform thickness, fretting resistance and wire bondability. The economic consideration associated with plating thickness is the unnecessary expenditure for chemicals used in EN plating for excessive thickness and the cost of scrap generated by adhesion defects related to excessive nickel thickness[7,8].

On any given part which is EN plated, there is an average cost which can be calculated empirically for each mil of plating thickness over the surface of one foot of area requiring EN plating. For example, if the actual thickness of EN plate exceeds the specified thickness range for a compliant part by 25%, the average EN plating cost per unit will be 125% of required cost. There is no need to waste the money associated with excessive thickness and the cost of scrap generated by adhesion defects related to excessive nickel thickness. The EN plating thickness can be readily controlled in-process by the use of a thickness measuring device. The thickness of a nickel plated surface can be non-destructively measured using beta-back scatter or x-ray fluorescent spectrometry[9,10,11]. A statistically reliable sample quantity must be used in order for the thickness measurements to be reliable. The parts subjected to non-destructive thickness analysis should be randomly drawn from the group in accordance with MIL-STD 105 or in accordance with MIL-C-26074 C[6].

A comparison of the thickness measuring methods of beta backscatter (BB) and x-ray fluorescence (XRF) within a high volume manufacturing facility designates that XRF retains distinct advantages. The advantages of XRF nickel thickness measuring methods include: accuracy associated with product geometry, time required to complete the analysis, separation of input signals from metals with close atomic numbers[12], non-contact with components and operation without consideration to barometric pressure, temperature, humidity, light, or other environmental influences[13]. Following is a short summary of the operational details associated with nickel thickness measurements by x-ray fluorescent spectrometry.

X-ray fluorescence is an emission of x-ray photons which is resultant of the displacement of a low energy electron within an atom caused by an incident photon of energy. When the incident photon of energy releases a low energy electron within an atom, the higher energy electrons in the outer electron shells move to the lower energy positions and the extra energy is emitted[14]. The fluorescent x-rays which are emitted are characteristic for each element[15]. The thickness measurements are conducted electronically by comparing known fluorescent emission values which are stored in a computer versus the actual emission data. The known values consist of the quantity of x-rays emitted at a specific energy level generated by a known thickness. The thickness measurement includes emissions from both the surface material and the base material. See Figure 1.

The typical XRF thickness gauge contains: an x-ray source with a constant incident beam energy, a

collimator which controls the sample area which is exposed to the incident x-rays, a stage upon which the sample is placed at a constant focal length, a filter which is required on occasion to separate fluorescent x-rays, a proportional counter which amplifies signals and a multichannel analyzer which classifies signals regarding the quantity of signals (counts per minute) and the energy of the signals [14]. See Figure 2. In the case of nickel thickness measurement, the 7.48 KeV energy emission is monitored [15]. The quantity of signals at the 7.48 KeV energy level is proportional to the nickel thickness. The nickel thickness measurements are affected by: variation in alloy composition, counting statistics relative to collimator area, beam-to-part angular alignment, x-ray target plus window specifications and software designed to correct for drift and intensity. The nickel thickness measurements are also affected by: composition (absorption, enhancement, spectral overlap, and phosphorous content in EN-P plus boron content in EN-B) effects, surface smoothness, angular part to beam relationships and sample porosity inclusive of impurities [14]. The standards used to calibrate an XRF thickness instrument should be as close in deposit characteristics to the sample as possible.

Spectral overlap limits the use of beta backscatter when measuring the thickness of nickel over metals which have an atomic number near 28 [12]. The thickness of nickel (atomic #28) over copper (atomic #29) can be measured by XRF instrumentation which incorporates either a cobalt secondary filter or software which is capable of digital filtration[a]. Figure 3 specifies the benefit available when using mechanical filtration with a cobalt filter. Digital filtration is the term which describes the software which conducts a computerized spectral deconvolution of a thickness curve for two overlapping spectra into two component curves. See Figure 4. Digital filtration can also be used to deconvolute overlapping curves from nickel over iron, nickel over alloy 42 and nickel over kovar [15]. The currently available XRF thickness measuring instrumentation also retains the capability to measure: single layer coatings, double layer coatings, triple layer coatings, binary alloy composition, elemental qualifications and metal content analysis of nickel plating solution [16].

Control of Plating Thickness

A short calculation can be made utilizing the data from the XRF thickness gauge measurements to control in-process EN plating thickness. While maintaining the operational parameters of the EN bath (pH, bath activity, temperature, nickel concentration), plating two groups of the same parts for equal periods of time will provide results for nickel thickness within a demonstrated range. The range (R) of nickel thickness can be calculated by subtracting the lowest demonstrated thickness value from the highest demonstrated thickness value. The optimum plating time (t2) can be calculated by multiplying the original plating time (t1) by the ratio of the desired thickness (N2) to the difference of the average demonstrated nickel plated thickness minus one half of the range (R).

(See calculation on following page).

[a]SFT-7000. Seiko Instruments, Torrence, CA.

$$t_2 = \frac{N_2}{N_1 - 0.5R} \times t_1$$

where: t_1 = plating time to achieve demonstrated thickness
t_2 = projected plating time to obtain desired average thickness
R = range of demonstrated nickel thickness (high-low)
N_1 = demonstrated average nickel thickness
N_2 = desired average nickel thickness

This calculation is based on empirical data and the actual thickness gauge measurements which are used include R and N1. Since the calculation is based upon empirical data, compensation is made for subtle variations which may be present including: different lots of material, varying lots of parts, slightly different process parameters, and normal in-plant variations. This in-process thickness control calculation can be used numerous times to project the optimum plating time for the next group of parts. By conducting this calculation on each processed group of parts, the actual average plating thickness per group will fluctuate in a range whose average is within R of the desired thickness. It should be noted that only data from the preceding group (R and N1) of the same type of parts should be used to project the plating time for the next group of parts. This calculation to project the plating time of the next group of parts is not necessarily applicable if part quantities change.

Modeling the Cost of EN Bath Operation

In order to optimize the manufacturing economics of EN bath operation, a baseline cost should first be defined. Once this baseline is established, the improvement phase can begin and progress can be monitored in actual dollars by which cost is reduced. A typical EN bath contains: nickel salts, chelating agents, stabilizers, pH regulators, exhaltants, buffering agents and reducing agents[17]. The EN bath constituents which are consumed during plating or plate-out consist primarily of nickel salts, pH regulators, and reducing agents. The cost per unit (CPU) associated with the operation of an EN bath can be calculated by summing the cost of chemicals consumed divided by the total number of parts processed. The cost of EN bath operation includes the cost of make up chemicals (C1), the cost of replenishment chemicals (C2) and the cost of pH controlling chemicals (C3).

$$\text{Cost Per Unit (CPU)} = \frac{C_1 + C_2 + C_3}{\text{Number of Units}}$$

where: C_1 = cost of make up chemicals
C_2 = cost of replenishment chemicals
C_3 = cost of pH control chemicals

The CPU can be calculated to establish baseline cost. The CPU can be calculated after changes have been implemented and the difference in the CPU is equal to the cost improvement or increased cost associated with the change.

Following are models that can be used to calculate the cost of operating an EN bath. Bath make up is the first chemical cost encountered. Per the specification sheet for the EN-P process[5], make up of the alkaline solution includes the use of 15% by volume of the component which contains nickel salts and other required make up chemicals plus the use of 8% by volume of the component

which contains the hypophosphite reducer[b]. The pH adjusting solutions are either 1:1 ammonium hydroxide which raises the pH or 25% sulfuric acid to lower the pH. All solutions are mixed to 100% volume using distilled water. The specification sheet for the EN-B process , designates that 15% by volume of the component which contains nickel salts and other required chemicals be mixed with 5% by volume of the component which contains the borane reducer[c]. The pH adjusting solutions are either concentrated ammonium hydroxide which raises the pH or 50% acetic acid to lower the pH. All solutions are mixed to 100% volume using distilled water. The cost of bath make up can be calculated as follows:

$$C_1 = V_1 M_1 + V_2 M_2 + V_3 M_3$$

where: C_1 = cost of make up chemicals
V_1 = volume of nickel make up solution
M_1 = cost of nickel make up solution per volume
V_2 = volume of reducer
M_2 = cost of reducer per per volume
V_3 = volume of pH adjusting solution
M_3 = cost of pH adjusting solution per volume

The calculation for the cost of EN bath make up (C1) will change if more or less components are required in bath make up.

Bath replenishment is the second EN bath cost which is encountered. The replenishment chemicals which are used in the EN-P process[5], are: the solution which is used to maintain nickel concentration, the solution which is used to maintain hypophosphite reducer concentration and the solution which is used to replace materials lost by normal drag-out. The replenishment chemicals which are used in the EN-B process[5], are: the solution which is used to maintain nickel concentration and the solution which is used to maintain borane reducer concentration. The cost of replenishment chemicals can be calculated as follows:

$$C_2 = V_4 M_4 + V_5 M_5 + V_6 M_6$$

Where C_2 = cost of replenishment chemicals
V_4 = volume of nickel replenishment solution
M_4 = cost of nickel replenishment solution per volume
V_5 = volume of reducer replenishment
M_5 = cost of reducer replenishment per volume
V_6 = volume of other solutions
M_6 = cost of other solutions per volume

The calculation for the cost of EN bath replenishment (C2) will change if more or less components are required in bath replenishment.

The pH control chemicals for the EN-P bath and the EN-B bath are different as previously mentioned in the discussion of solution make up. Per the specification sheet for the EN-P alkaline solution[5], the pH is adjusted up using 1:1 ammonium hydroxide or the pH is lowered with 25% sulfuric acid. Per the specification sheet for the EN-B solution[5], the pH is raised using concentrated

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[b] Niklad 776, Allied-Kelite, Melrose Park, Illinois
[c] Niklad 752, Allied-Kelite, Melrose Park, Illinois

ammonium hydroxide and the pH is lowered with 50% acetic acid. The pH of EN plating solution can be adjusted after make up, during replenishment or alone. The cost of pH adjustment chemicals can be calculated as follows:

$$C_3 = V_7 M_7 + V_8 M_8$$

Where: C_3 = cost of pH control chemicals
V_7 = volume of pH elevating solution
M_7 = cost of pH elevating solution per volume
V_8 = volume of pH lowering solution
M_8 = cost of pH lowering solution per volume

The calculation for the cost of EN bath pH adjustment (C3) will change if more or less components are required in bath pH adjustment.

Minimizing Extraneous Bath Plate-Out

Extraneous bath plate-out is a major economic consideration in EN bath operation within a manufacturing facility. Extraneous bath plate-out is defined here as any nickel deposition and chemical depletion that takes place which is not associated with nickel deposition and chemical depletion on predesigned surfaces and desired locations. Once the baseline CPU for an EN plated product has been established, various avenues can be investigated which have the potential to decrease the CPU by minimizing extraneous bath plate-out. One of the major causes of extraneous bath plate-out is improper bath activation. Substrate metal surfaces such as: aluminum, cobalt, gold, iron, nickel, palladium, rhodium, and steel are catalytically active substrates which initiate electroless nickel deposition[4,17,18]. Whenever products containing these inherently catalytic surfaces are EN plated, the potential exists for metallic fines or dusts to enter the plating bath and cause extraneous plating[17,19]. These catalytic particles serve as nucleation sites for improper activation and increase the cost associated with the CPU. Remedial action which can be taken to minimize this improper activation is to either completely clean the parts of fines and dusts or continuously filter the bath solution to remove this source of improper EN bath activation.

Another major cause of extraneous plating is improper activation of components. Substrate surfaces such as brass, ceramic, copper, molybdenum, molybdenum-manganese, molybdenum-manganese-silica, plastic, tungsten, tungsten-manganese-silica, and silver are noncatalytic for an electroless nickel bath and require activation[4,20,21]. These noncatalytic surfaces can be activated by immersion plating with a catalytically active metal as mentioned above, galvanically plated by contacting an actively plating surface[20], immersed in palladium chloride[4,8,21], or cathodically activated with nickel[4]. Wherever parts are activated, the potential exists for excessive activation on the parts. Although extraneous activation will not always be visible prior to EN plating, extraneous activation is definitely visible after EN plating. Extraneous bath plating in the form of excessively activated parts can be monitored by inspecting and documenting the quantity of parts which retain excessive plating. Once the magnitude of an excessive plating problem has been specified, corrective steps can be taken in the activation cycle to decrease extraneous plating. Remedial action aimed at reducing extraneous

plating and the baseline CPU includes: decreased time for immersion activation, reduced concentration of immersion activation chemistry, reduced contact time for galvanic plating, a modified ratio of parts to galvanic media used in galvanic activation, reduced palladium concentration in palladium activation, reduced activation time in palladium, improved rinsing of palladium after activation and optimization of parameters associated with cathodic activation.

Extraneous bath plating in the form of catalytically activated handling equipment such as racks or barrels can also increase the CPU. Remedial action focussing on the reduction of costs associated with the plating of handling equipment includes: changing of racks or barrels between activation and plating, nickel stripping after the plating cycle or resurfacing of original surfaces with noncatalytic materials.

Extraneous bath plating in the form of plated tank walls, plated heaters, plated racks, plated barrels, plated filters, etc. can be caused by excessive heating or hot spots[17,19]. Excessive heat alone will cause spontaneous deposition of an EN bath resulting in the plating of nonactivated surfaces. Heat induced extraneous plating can be minimized by using derated heaters with a maximum density of 20 watts per square inch, the use of a double boiler system to evenly distribute heat and circulation of plating solution to provide homogeneous bath temperature without hot spots. Reduction of the baseline CPU aiming at heat related extraneous EN bath plating can be accomplished by proper heat design, the use of heater output commensurate with needs wherein heaters are operational in excess of 70% of production time, only heating the bath when production needs exist and controlling bath temperature.

Extraneous bath plating in the form of plated tank walls, plated heaters, plated racks, plated barrels, plated filters, etc. can be caused by extended exposure to EN plating solution. Although a surface is not catalytically activated or subjected to excess heat within an EN bath, the nickel particulate within the solution may activate the surface. Although this particulate is filtered, removal from solution does not eliminate the potential for catalytic activation. Whenever a tank or other equipment is unacceptably plated with nickel, this nickel can be stripped. However the use of liners has been considered as a means to reduce tank wall plate-out[17,22]. Plate-out on tank walls is reduced by periodically changing the liner to present a new, nonactivated surface to the bath solution. Since liners are available in different materials and costs vary, an analysis of the CPU with and without the use of a liner should be conducted to insure that cost savings justify the use of liners.

The presence of palladium in the form of a dissolved ion will cause spontaneous decomposition of an EN bath resulting in greatly reduced bath longevity and an undesirably increased CPU. The drag-in of such contaminating chemicals will cause irreversible bath problems[17]. When a palladium activation cycle is used[4,18,21], extensive control of rinses should be monitored to insure that the parts entering the bath are free from dissolved palladium[23]. The monitoring of rinse water quality after activation can be accomplished by the use of: resistivity meters, pH monitoring of rinse water or maintaining proper rinse flow rate.

Maintaining a Homogeneous Bath

An Electroless nickel bath is composed of a variety of chemicals. An EN bath contains a balance of nickel salts, chelating agents, pH regulators, stabilizers, exhaltants, buffering agents and reducing agents [17]. The chemical parameters which generally required control include: nickel concentration, concentration of reducer and pH control. The cost of operating an EN bath will increase as the quantity of chemicals used in replenishment is increased or as bath longevity is decreased. An imbalance in the chemical control of the bath will cause the excessive generation of one type of by-product while the bath is deficient in other components. An imbalance in the pH control can induce precipitation of compounds in the EN solution and increase replenishment requirements and ultimately the cost of an EN bath. This imbalance can lead to premature catastrophic decomposition of the bath or increased chemical requirements such as reducer. Both of the activities of increased replenishment requirements and catastrophic decomposition lead to increased bath costs. Maintaining a homogeneous bath will minimize the possibility of bath imbalance and reduce the increased cost associated with a bath which is out of control.

The frequency of additions is another criteria which should be evaluated in perspective to the economics of EN bath operation. When the frequency of analysis and additions is such that process controls and limits cannot be maintained without making adjustments within a 20 minute period, then there may be a design problem. A complete EN bath analysis for pH, nickel concentration and concentration of reducer requires approximately 20 minutes. If the parameters which are monitored undergo a change to a concentration outside specification within 20 minutes, actual bath control is non-existent. When the monitored parameters undergo an excursion beyond process controls and limits, this imbalance leads to premature catastrophic decomposition of the bath or increased chemical requirements such as reducer. The proper frequency of additions promotes the maintenance of a homogeneous bath and this control allows operations to decrease chemical costs. The maintenance of a homogeneous bath is further promoted by minimizing the volume of each chemical addition.

The design problem associated with maintaining proper frequency of additions is the proper ratio of tank volume versus product throughput. Each load of parts which enters an EN plating bath will consume a certain quantity of chemicals per minute. If the tank volume is too small, then a replenishment will be required in less than 20 minutes. In order to compensate for insufficient tank volume, the quantity of parts must be reduced or the rate of plating must be reduced to decrease the quantity of chemical consumed per minute. Under limitations of capacity and throughput, the tank should be sized to accommodate requirements or a continuous feed rate of chemicals should be used. A tank which is too small can induce a chemical excursion outside of proper operating limits and cause a solution imbalance increasing the EN operating cost.

The opposite is also true in that an oversized EN plating tank will increase plating costs. When an EN bath is at operating temperature, the reducer is being consumed by thermal decomposition independent of the quantity of parts being plated. When the bath loading (square feet

of plating surface per gallon of solution) is very low, excessive reducer is consumed because the quantity of reducer consumed by thermal decomposition exceeds the quantity of reducer consumed in plating [24]. The presence of an oversized EN plating tank can be compensated for by increasing throughput or lowering plating rate by reducing bath temperature.

Conclusion

This presentation has focussed on the methods used to reduce the direct material cost associated with EN plating. The methods used to reduce direct material consumption include: 1) optimizing plating thickness using a predictor calculation with an x-ray fluorescent thickness gauge; 2) minimizing extraneous bath plate-out by controlling factors of excessive heating, improper activation, extraneous activation and undesirable drag-in; and 3) maintaining a homogeneous bath by the use of minimally sized chemical additions, operating an EN bath without chemical imbalances, using a properly sized plating tank and setting the correct frequency of replenishment additions. In an effort to facilitate a cost reduction program, models have been presented to calculate optimum plating time for proper thickness and to calculate chemical costs. The chemical cost model can be used to calculate baseline chemical costs and can be used to calculate the changes in bath cost associated with manufacturing improvements.

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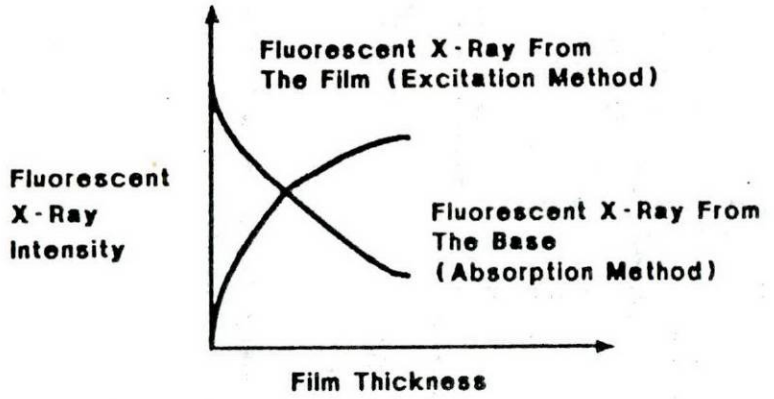
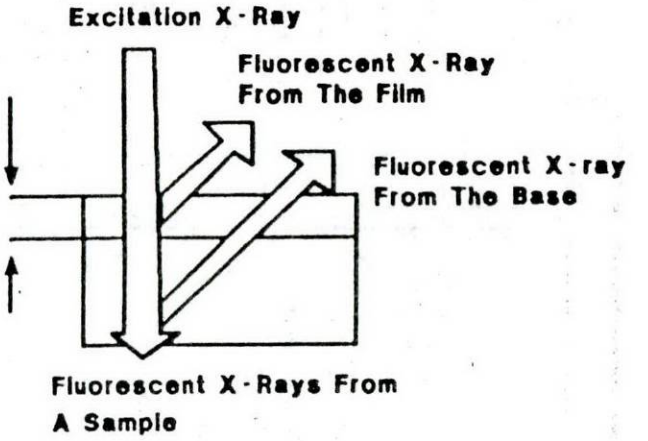
PRINCIPLE OF MEASUREMENT





$I = (I_\infty - I_0)(1 - e^{-\mu x}) + I_0$

μ: Absorption Coefficient

I: Fluorescent X-Ray Intensity

I_0: Background Intensity

x: Thickness Of The Film

I_∞: Saturation Intensity

Figure 1. Graphic Depiction of the Principle of Thickness Measurement for X-ray Fluorescence Using Fluorescent X-rays from the Surface and the Base.

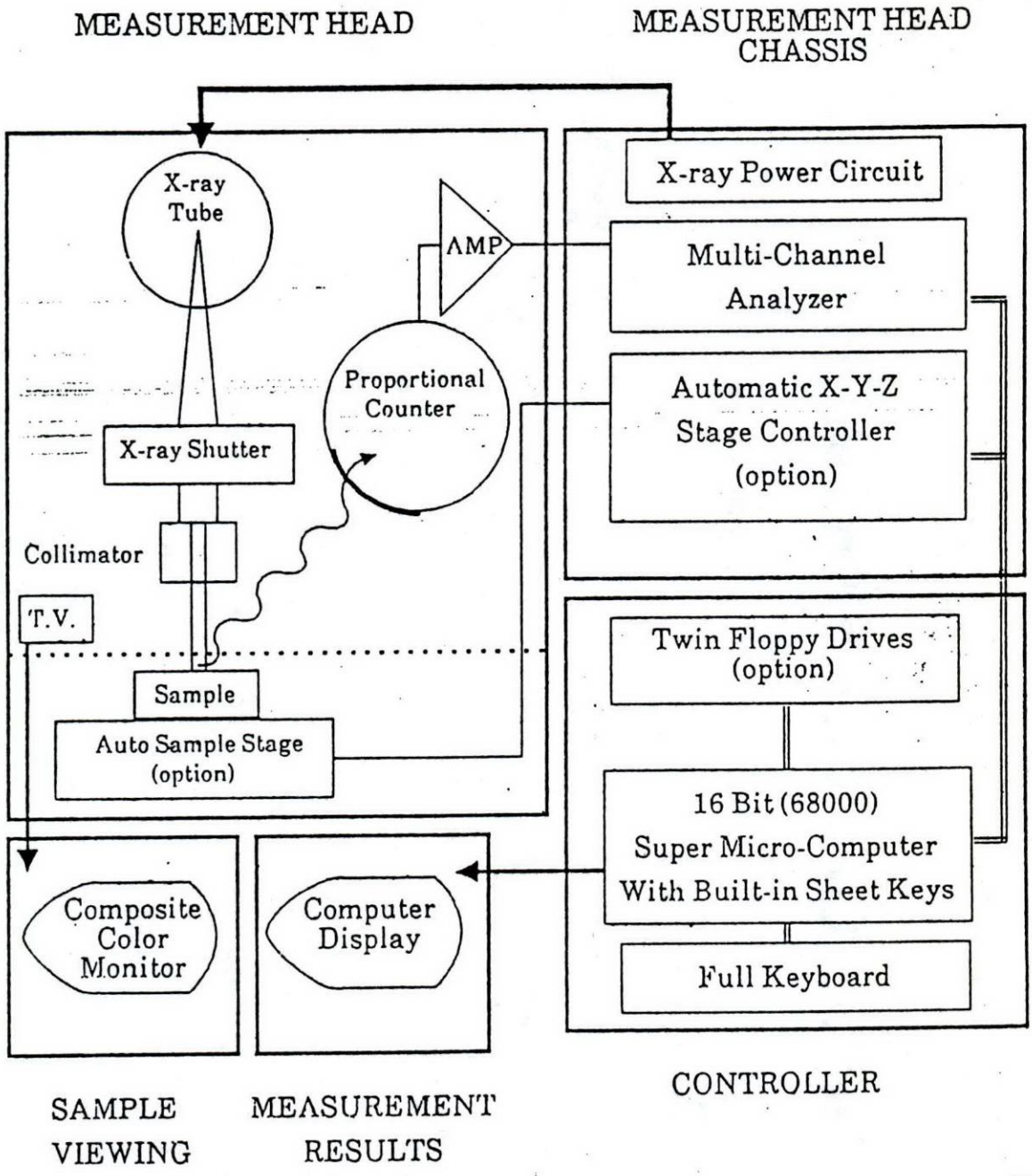


Figure 2. Functional Components Contained within a Typical X-ray Fluorescent Thickness Gauge.

MECHANICAL FILTRATION SPECTRUMS

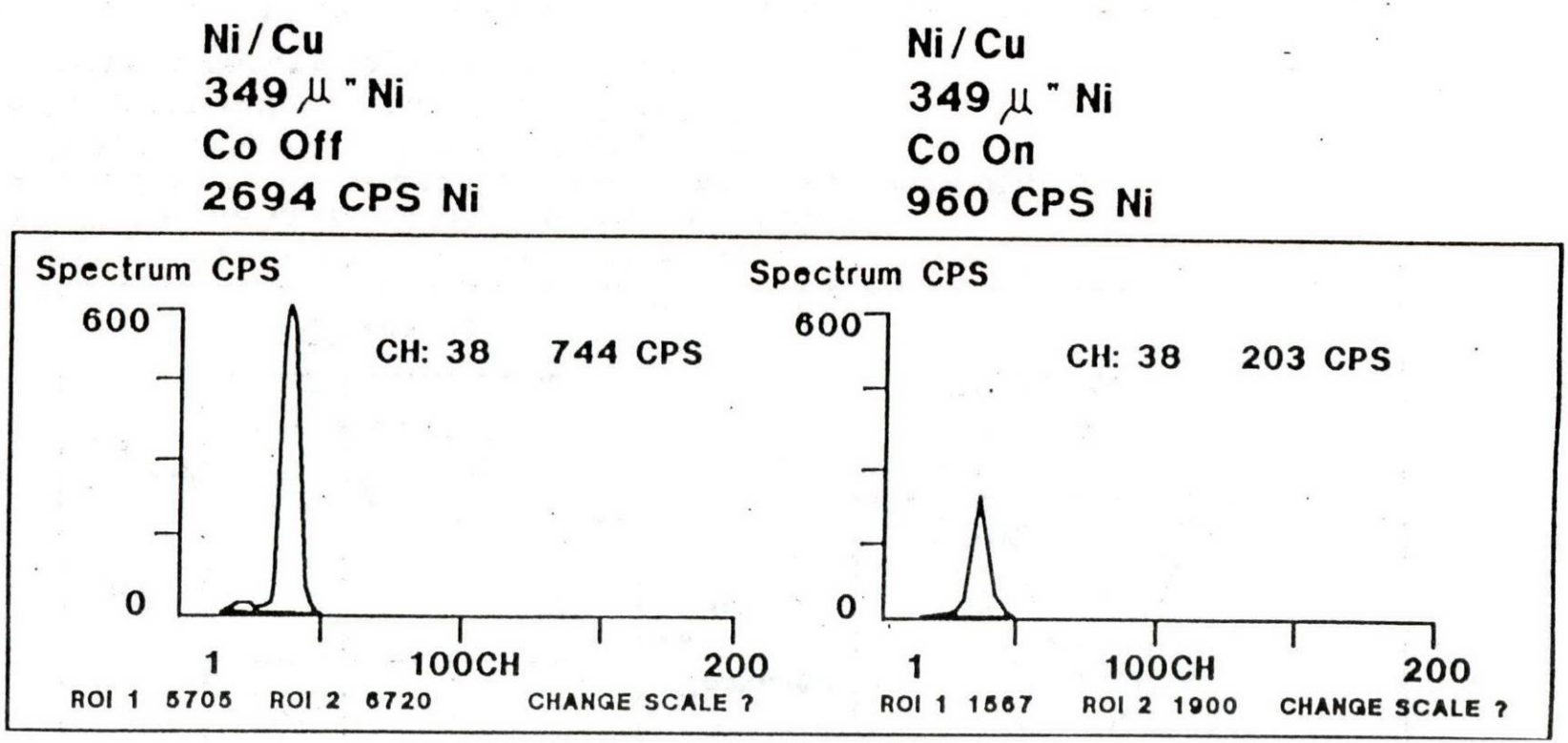
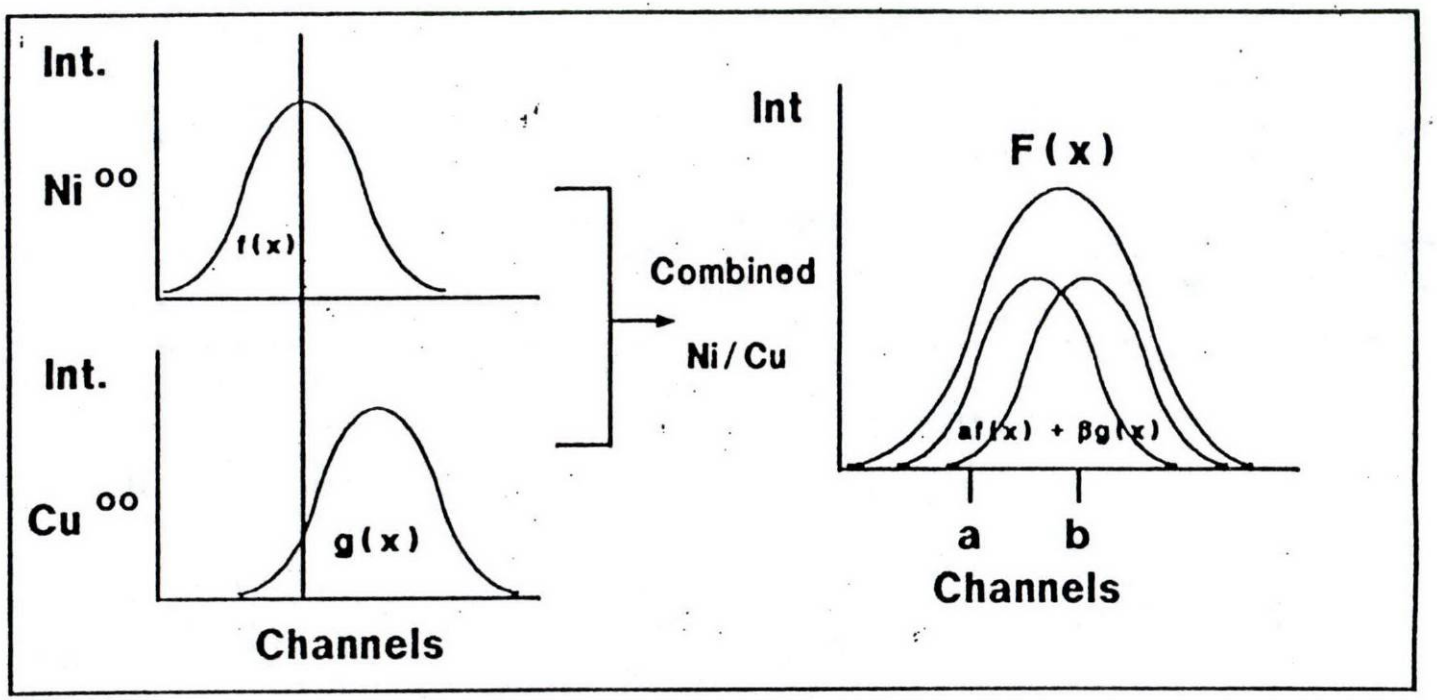


Figure 3. Mechanical Filtration Spectrum of an X-ray Fluorescent Thickness Gauge with and without a Cobalt Filter.

DIGITAL FILTRATION METHOD



- F(x) = αf(x) + βg(x) total coating signal
- a and b are channel limits for signal processing
- α and β are the Ni and Cu intensity ratio coefficients derived from a complex least square fitting routine
- Using the ratios α and β, A calibration curve is derived for each component

Figure 4. Digital Filtration Used in X-ray Fluorescent Thickness Measurements to Deconvolute Two Overlapping Spectra into Two Component Curves.

J-7

Electroless Deposition II
Session J

Hope for the Best But be Prepared for the Worst

David Kunces, CEF
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ABSTRACT

HOPE FOR THE BEST
BUT BE PREPARED FOR THE WORST

By David Kunces CEF
MacDermid Incorporated

Waste treatment regulations are becoming more stringent. Each day the public becomes more concerned over our natural resources and they do have a right to protect them.

Methods to meet today's electroless nickel waste treatment standards, i.e. removal of metal, as well as methods for tomorrow's worst, i.e. all the constituents, will be discussed.

To meet today's regulations for waste treating electroless nickel and to prepare for tomorrow is a constant concern to all users. Regulations affecting the plater varies in different locations. The nickel and any other trace metals associated in the solution is the only common restriction with today's baths. Today's chal-challenge to the electroless nickel plater is to develop an acceptable method of disposal of the metal in an electroless nickel bath. This method encompasses the "cradle to grave responsibility". Specifically, (1) locating a licensed hauler for the solutions and/or sludge, (2) locating a disposal site for above, and (3) making sure that the waste is disposed of in an acceptable manner as the plater will in most cases retain liability.

Tomorrow's regulations most likely will be more stringent due to an increase in public concern over our natural resources. The ability to be able to waste treat all of the constituents in an electroless nickel bath may be necessary, i.e. (1) nickel and heavy metal stabilizer, (2) reducers, (3) complexor/chelator, (4) buffers (i.e. ammonia), and (5) phosphite by products.

To do this, new technologies will either have to be developed or present technologies refined to meet these needs.

Nickel and other heavy metals normally in an EN bath are treated in one of the following ways:

1. Reduction - in which powerful reducing agents such as sodium borohydride, hydrazine, sodium hydrosulfite, DMAB, or even sodium hypophosphite reduce Ni^{+2}-Ni^{0}. The reduced metals can be made to deposit on metal parts or scrap metal (controlled plateout) or can be made to form a precipitate.

2. Precipitation - of Ni^{+2} with hydroxides, sulfides, carbonates, carbamates and starch xanthate products to produce an insoluble nickel compound that is removed from solution after settling; a (sludge) precipitate is also produced.

3. Separation - of nickel ions. Ion exchange is one example. Nickel ions are absorbed onto cationic resin and replated by H^{+} or Na^{+} ions. Another example is electrodialysis. An electric current induces partial separation of components in an ionic solution. Reverse osmosis is a third possibility, which utilizes a semi-permeable membrane to separate, under pressure, nickel ions (as well as other ions) from the solution.

Of all the above methods, reduction is the most popular. To avoid any precipitation, the control plateout method will meet today's as well as tomorrow's regulations. Control plateout will eliminate the need to haul away solid waste thereby lessening the liability.

Controlled plateout is a reduction method which simply continues to plate out the nickel alloy (Ni^{+2} reduced to Ni^{0}) until very low levels are obtained. No precipitate or sludge is produced, thereby eliminating the need to haul away solid waste. Control plateout can be performed in one's production EN tank. You operate the spent EN bath at normal plating temperatures with metal (steel or aluminum) scraps in the bath. Addition of reducing agents and stabilizers control the rate and amounts of deposition. The nickel concentration in an EN solution can easily be brought down below 10 ppm using control plateout.

If necessary, any of the remaining amounts of nickel metal not plated out can be reduced further with any of the polishing agents commonly used in waste treatment. The solution is now free of any metals and can be directly dumped down the drain. With regard to any further regulating, local and state ordinances should be contacted.

The solution still contains ammonia (if used), phosphorous and chelators/complexors which usually are organic acids.

Ammonia which is used to adjust pH and as a buffer in some electroless nickel baths can be expelled. If ammonia is left in the bath, it may become a hinderance for complete removal of nickel as shown in Table 1 or a hinderance down the waste stream.

TABLE 1

Bath	w/o NH_4^+	w/10% NH_4^+ added
Med P % Semi Bright 1	5.3 ppm Ni	16 ppm Ni
Med P % Bright 2	<1	18.6
High P % w/NH_4^{++} Buffer 3	6.2	179

NOTE: All above baths had 6 metal turnovers. Precipitation method was used.

Baths using the control plateout method were were reduced to <1 ppm of nickel metal even with a 10% NH_4^+ added.

Ammonia can be removed from the solution by the following method:

1. Add caustic soda to raise pH above 12.5
2. Agitate solution with air
3. Heat bath to 185°F or higher to hasten the reaction

A spent bath after control plateout with 10% by volume 28% NH_4OH added took 2 hours to expell the ammonia by the above method.

Phosphorous

Typically, electroless nickel baths are high in phosphorous, all of it coming from the reducing agent hypophosphite (NaH_2PO_2) and the breakdown products, sodium phosphite (Na_2HPO_3). Where phosphorous is restricted, the following can be performed to oxidize the PO_2 ion to PO_4 so as to form the insoluble phosphate, calcium phosphate.

1. Raise pH to 10.5 with lime
2. Add peroxide
3. Filter solution

In Table 2, a spent electroless nickel bath with 8 turnovers was treated.

TABLE 2

	Spent EN Bath	After Treatment
Nickel* (Ni^{++})	5 g/l	.2 g/l
Hypophosphite (NaH_2PO_3)	4 g/l	0.0 g/l
Phosphate (PO_4)	.32 g/l	0.023 g/l
Phosphite (PO_2)	12.2 g/l	0.0 g/l
Total P as PO_4	12.5 g/l	0.023 g/l

*Precipitation method used.

In the above table, the PO_2 ion was oxidized by the H_2O_2 to PO_4 where the excess lime reacted to reduce the phosphorous. In order to reduce the phosphorous to the lowest levels, the PO_2 ion must be oxidized to PO_4 since calcium phosphite is slightly soluble. A possibility to make the hauling of this sludge non-hazardous is that the insoluble phosphate may have commercial use in the fertilizing industry, thus further eliminating the location of a disposal site.

Chelators (organic acids) which could affect phosphorous removal can all to a greater or lesser extent react with $KMNO_4$. The end product formed is dependent on the reaction conditions which include:

1. $KMNO_4$ concentration
2. Concentration of organic acids
3. Temperature
4. pH of reaction
5. Presence of ion, such as Ca or F, which may increase the reaction rate.

To simply illustrate the several reaction paths using citric acid per the following example:

$$H_2C\text{-}COOH \xrightarrow[\text{alkaline}]{+\ 4KMNO_4\ +\ 2OH} 6CO_2 + 5H_2O + 4MNO_2$$

$$HO\text{-}C\text{-}COOH \xrightarrow{+\ 3KMNO_4\ +\ 14H^+} 6CO_2 + 7H_2O + 3MN^{++}$$

$$H_2\text{-}C\text{-}COOH \xrightarrow[\text{slightly acidic } 80°C]{+\ KMNO_4} COOH + \overset{CH_3}{\overset{|}{C}} = O + CO_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad COOH \quad CH_3$$

For waste treatment of citric, lactic and hydroxy acetic acid, the $KMNO_4$ will oxidize their hydroxy groups. For the other organic acids, maleic, succinic and EDTA, the $KMNO_4$ cleaves the double bond. The reaction products MN^{++} or MNO_2 may have commercial value for the steel industry in its manufacturing process, thus eliminating the location of a disposal site and associated problems.

CONCLUSION

The oxidation/reduction and destruction of the constituents of an electroless nickel bath is possible. Such a method would include:

1. Control plateout of the nickel method
2. Removal of NH_3
3. Destruction of chelators/complexors
4. Precipitation of phosphorous compounds as calcium phosphate.

The regulations dictating what the plater can introduce into the environment are becoming more stringent. There may come a day when all the constituents of any electroless nickel bath is regulated. The time is now to be prepared with a method. Whether or not the individual uses one or more of these methods will depend on the regulations specific to the area and the economics involved.

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