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ELECTRONICS II

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The Plating of Gold and Nickel for Electronic Applications

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THE PLATING OF GOLD AND NICKEL FOR ELECTRONIC APPLICATIONS

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ABSTRACT

In the electronics industry, gold is usually plated on copper tabs, leads, lands, or contacts to improve solderability and wear resistance. Also, it is often necessary to plate an intermediate nickel layer to retard copper diffusion through the exterior gold layer to extend the life of the tab or land bonding. In our experiments, we plated high-purity gold onto copper lands to evaluate gold-to-gold bond strengths. We examined the reduction of gold land-to-land bonding by contaminating the gold solutions with copper. We also aged plated hard- and soft-nickel intermediate layers under the high-purity gold to find out whether the nickel reduced copper diffusion to the gold surface. Auger analyses revealed that nickel does reduce copper diffusion to the gold surface; they also revealed that nickel itself diffused to the surface resulting in lower thermocompression-bonded strengths.

INTRODUCTION

Modern methods of protecting the solderability and wear resistance of copper tabs and contacts of electronic components usually rely on a plated coating. Because gold has excellent resistance to oxidation, it is usually the preferred coating for surfaces that need to be joined or that need to retain their contact resistance. A common practice in the electronic industry is to use a nickel underlayer so that the gold will retain its original, oxide-free color over long periods of time. The intent of the nickel barrier is to retard the diffusion of copper (or other base materials) to the outer gold surface. At the same time, it is believed that the nickel diffusion barrier might minimize intermediate phases or Kirkendall voids, thereby increasing long-term reliability.

To meet our specific requirements, we needed to plate a gold deposit onto copper lands for thermocompression bonding of a flex circuit to matching gold lands of an electronic component. Thermocompression bonding is a modern, high-speed method for attaching multilead cables or frames to metallurgy deposited on substrates [1]. Panousis and Hall [2] recommended a layer of nickel 0.25 to 1.3 µm thick under a layer of gold 2.5 µm thick for optimum bond strength and reliability. However, Johnson [3] demonstrated higher bond strengths without a nickel layer. Our purpose in this study was to define appropriate parameters (thickness, composition, and hardness) of a nickel barrier for reliable performance without sacrificing bonding strength.

PROCEDURE

Electroplating and Analysis

Nickel deposition was accomplished using a nickel-sulfamate electroplating solution for soft-nickel deposits and an electroless nickel-1% boron solution

for hard-nickel underlayers. Gold deposits were obtained from a cyanide solution to meet Mil. Spec. Type III, grade A specifications [4]. To achieve acceptable adhesion values between the bulk gold layer and the substrate material, a similar, high-purity, cyanide-gold-strike solution was used (see Table 1 for solution conditions). When a low-ripple dc power supply was used as a source of current, a nonuniform gold-deposition layer was obtained. This problem was overcome by replacing the dc power supply with a pulsed power source.

The bulk gold-plating solution was purposely contaminated with copper to determine copper impurity effects on bonding. Levels of copper impurity in the deposits were detected using auger-spectroscopy techniques. Percentages of deposit contaminates were estimated using standard energy-dispersive x-ray and emission-spectroscopy analyses. Metal impurity levels in the gold-plating solutions were monitored using atomic-absorption techniques.

Our application required that we use thermocompression to bond multiple cable lands, nominally 0.1 mm wide by 0.035 mm thick (prior to plating) on 0.25-mm centers, to vacuum-evaporated gold pads on ceramic substrates.

Aging, Bonding, and Mechanical Testing

Bonding tests were conducted with cables in an "as plated" condition, as well as with cables that were plated and then aged for 18 hours at 200°C. Cleaning prior to bonding included plasma ashing. All assemblies were bonded for 3-4 seconds with an interface temperature of about 400°C. The bonding pressure was varied slightly to accommodate small deviations from the nominal 0.1-mm cable-land width. The quality of the bonded joints was largely determined by "pull strength" tests--the force required to separate all the cable lands from a substrate when they are pulled at an angle of 45°. A minimum of three pull tests were conducted for each plated condition. The percentage of lateral deformation was also determined for most of the bonded lands.

RESULTS

Electroplating

In our application, the cable lands were of a trapezoidal geometric shape. When we attempted to plate these cable lands with gold using a standard dc power supply, a nonuniform gold deposition resulted, as seen in Figure 1a. Due to this unique geometry and tiny area of the cable to be plated (0.2 cm^2), we replaced the dc power supply with a pulsed power source, and a uniform deposit resulted, as shown in Figure 1b. We plated three cables at a time to increase the overall area to be plated, and thus were able to maintain a recommended current density of 0.4-0.5 A/dm^2 (4-5 A/sq. ft.) using a 10% pulsed current, duty cycle. Emission-spectroscopy and atomic-absorption analyses of the plated-gold deposit revealed that we were achieving a plated, four-nines-purity gold (per Mil. Spec. Type III, grade A specifications).

Before using either of the nickel-plating solutions to deposit a nickel undercoat, we plated thick (>25 μm) test samples of each type of nickel to measure the hardness of each deposit. The nickel deposit from the nickel-sulfamate solution had a hardness of 400 $Knoop_{50}$ (soft); the electroless nickel deposit from the nickel-boron solution had an average hardness of 550 $Knoop_{50}$ (hard).

Bonding

Mechanical test results on several samples undercoated with nickel from each nickel solution allowed us to determine thickness limits of soft and hard nickels (i.e., no land deformation during the bonding operation). Once these limits were established, we repeated some of the bonding tests on cables that were aged prior to bonding. We determined that an acceptable process window for our thermocompression-bonding application was 3-4 seconds dwell time, 500-600°C temperature, and 90-180 N pressure. Our results follow.

1. Soft Nickel

   Most of our bonding experiments were performed using the soft nickel as the gold undercoat because of our prior knowledge that good land deformation was a key to good bond adhesion. Figure 2 shows the average lateral deformation and pull strengths for increasing soft-nickel-underlayer thicknesses up to 30 μm. The results for the same conditions without nickel plating are plotted along the ordinate. The average strength (23.2 N) and range (10.0-34.2 N) were obtained from 40 tests. Deformation decreased slowly with increasing nickel thicknesses up to about 5 μm, then decreased rapidly to zero as the nickel thicknesses approached 25 μm. The average pull strengths were relatively unaffected by soft-nickel thicknesses up to about 5 μm, but then (as with deformation) the strengths fell off rapidly. It is desirable for all the lands to break outside the joint sites because this reveals that the thermocompression bonds can withstand a higher force than the cable lands. A great deal of scatter in the pull-strength data was shown with nickel thicknesses near 5 μm. This likely resulted from two competing mechanisms:

   a. Increasing land cross-sectional areas

   b. Decreasing land lateral deformation.

   Because the cross-sectional area of the land increased as the nickel thickness increased, high pull strengths resulted if land breaks occurred. On the other hand, deformation decreased with increasing nickel thickness, favoring bond breaks at low strengths. These results imply, therefore, that soft-nickel barriers up to 2.5 μm thick did not appreciably affect bonding strength.

2. Hard Nickel

Hard-nickel underlayers, thicker than about 0.25 µm, reduced bonding strength, as shown in Figure 3. Also, for hard-nickel layers thicker than about 2.5 µm, cracks were observed in the deformed portions of the lands after bonding. Cracks were unacceptable because they might lead to decreased long-term reliability.

3. Impure Gold

The group of cables intentionally plated with contaminated gold (no nickel underlayer) had lower pull strengths (17.8 N) than those plated with pure gold (23.2 N). Most of the failures were at the bonded interfaces (bond breaks). Auger analysis revealed that these lands were contaminated with about 14 atomic percent copper.

4. Aging Effects

Table 2 shows the results of cables aged at 200°C for 18 hours to simulate long-term storage conditions prior to bonding. Note that while nickel was effective in reducing the amount of copper that diffused to the surface, nickel itself also diffused to the surface. All of the aged cables had low bond strengths compared to similarly plated unaged ones, except those with the thickest (5.0 µm) nickel, which were low even without aging. Again, the predominant failure mechanism was bond breaks. Metallographic examination of cross sections through the aged cables did not show any evidence of porosity or intermediate phase formation at gold-copper, gold-nickel, or nickel-copper interfaces. This result is consistent with the findings of low-temperature studies conducted by Pinnel and Bennett [5].

DISCUSSION

The small exposed surface area of the copper cable lands were not conducive to plating single units at a time. At the current density ranges used it was predicted that we would require 1 mA current per exposed copper area on each cable. Plating of several cables and a test coupon permitted us to plate at average current values around 5 mA. A manufacturing environment would require a higher current value, say at least 0.1 A, to be more manageable. Therefore, sheets of 100 of the small cables per plating cycle would be more acceptable for plating economy. The pulsed power source is a necessary tool in controlling the plating uniformity on this small land area. Thermocompression bonding of mating surfaces relies on good overall surface-to-surface contact to effectuate good bonding strengths.

Our results show that soft (sulfamate) nickel layers up to 2.5 µm thick, or hard (impure) nickel layers up to 0.25 µm did not significantly affect thermocompression bonding by limiting deformation. However, during aging, nickel itself diffused to the bonding surfaces. This result is predictable from Fick's second law of diffusion [6], which, with some assumptions, can be simplified to:

$$x = 2\sqrt{Dt}$$

where x = Distance in cm
D = Diffusion coefficient in cm^2/sec
t = Time in seconds.

For 18 hours at 200°C:

$$D_{Ni \text{ in } Au} = 5 \times 10^{-13} \text{ cm}^2/\text{sec}, \quad x = 3.6 \text{ μm}$$

$$D_{Cu \text{ in } Au} = 8 \times 10^{-14} \text{ cm}^2/\text{sec}, \quad x = 1.4 \text{ μm}$$

The above values for D are for grain-boundary diffusion [7]. These calculations show that both diffusion distances are on the order of the gold-plating thickness and that nickel should diffuse somewhat faster than copper through gold. Actually, nickel or copper accumulated to about 20 atomic percent on the outer gold surfaces, as shown in Table 2. Once on the surface, both presumably oxidized and inhibited bonding. In addition, nickel oxide is reportedly more difficult to bond through than copper oxide [7].

Provided the nickel barrier is thin (less than 0.25 μm), its purity and hardness are of little concern. Thicker barriers require pure, soft nickel, or perhaps a different set of thermocompression-bonding parameters. Rigorous inspection of the quality of thin nickel layers on actual parts is often not possible. Thicknesses greater than about 0.25 μm can be measured by optical microscopy on cross sections, but thicker test specimens are required for accurate microhardness testing. Chemical analyses of nickel deposits are best performed prior to gold plating.

It might be less costly to substitute nickel for gold preplating on a high-speed line, but reduced bond strengths can be expected from impure gold. Most of our reliability testing was performed on assemblies without nickel underlayers, and no premature failures were encountered. Based largely on the above aging results and considerations, we concluded that nickel was unnecessary and not a suitable diffusion barrier for our application.

SUMMARY

We ascertained that nickel limited the copper diffusion to the gold surface, and that, in fact, the nickel itself diffused to the surface and thus decreased the bond strengths. Our calculations using a modified Fick's law equation predicted the nickel diffusion. We were successful, in our preliminary testing and in some long-term reliability testing of the cables, in showing that, for our application, nickel was not required as a diffusion barrier.

ACKNOWLEDGMENTS

We wish to thank R. A. DiCenzo for plating many of the cables; S. A. Hawthorne, C. J. Malone, and H. D. McCabe for performing the chemical analyses; and M. M. Yang, R. P. Zammit, J. J. Gniewek, and N. T. Panousis for providing valuable consultation.

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7. P. M. Hall and J. M. Morabito, "Diffusion Problems in Microelectric Packaging," Thin Solid Films, Vol. 53, 1978, pp. 175-182.

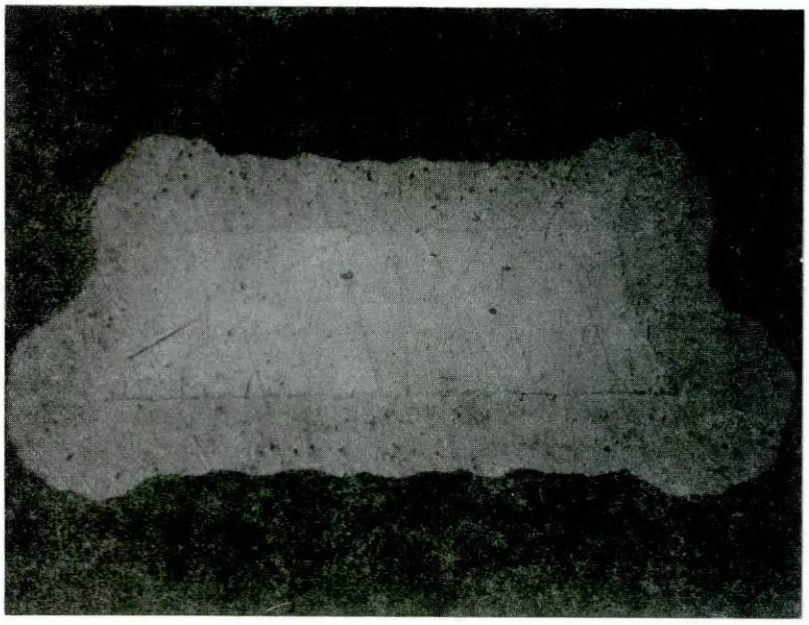
Gold-Plating Solutions*	Strike	Main
pH	3.8	6.0
Temperature	45°C	60°C
Current Density	0.33 A/dm² (3 A/sq. ft.)	0.33 A/dm²
Type	Carboxylic Acid	Carboxylic Acid
Gold Concentration	0.5 Troy oz./gal.	1 Troy oz./gal.
Other	Thallium	Thallium

* To meet Military Specification MIL-G-45204B, Amendment-2

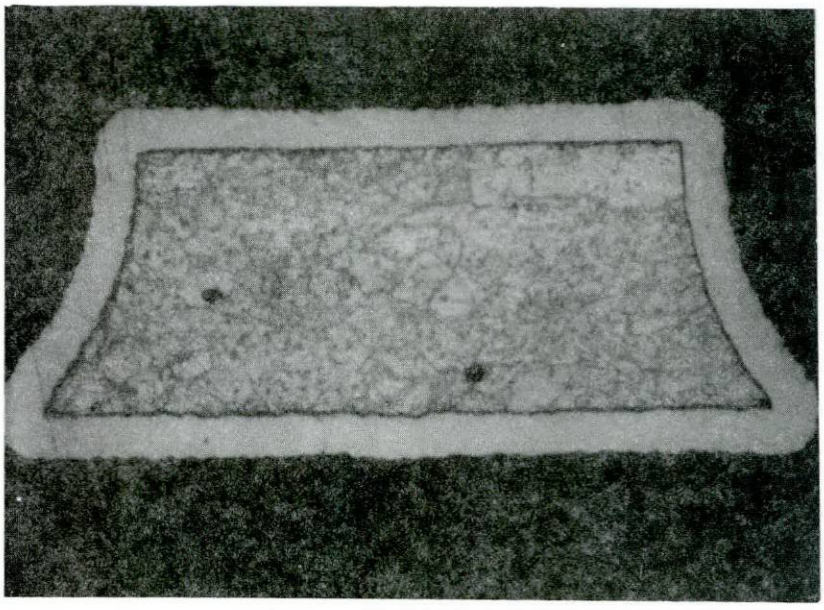
Table 1. Gold-Plating Conditions

Soft-Nickel Thickness µm (under 2.5-3.5 µm gold)	Auger Analyses At % Cu	At % Ni	Average 45° Pull Strength, N
0	21.0	0	7.2
0.5	10.0	20.0	10.4
5.0	0.2	20.0	7.0

Table 2. Surface Composition and Pull Strength of Cables Aged for 18 Hours at 200°C



(a) dc Source



(b) Pulsed Source

Figure 1. Comparison of dc vs. Pulsed Power Source--Land Cross Sections

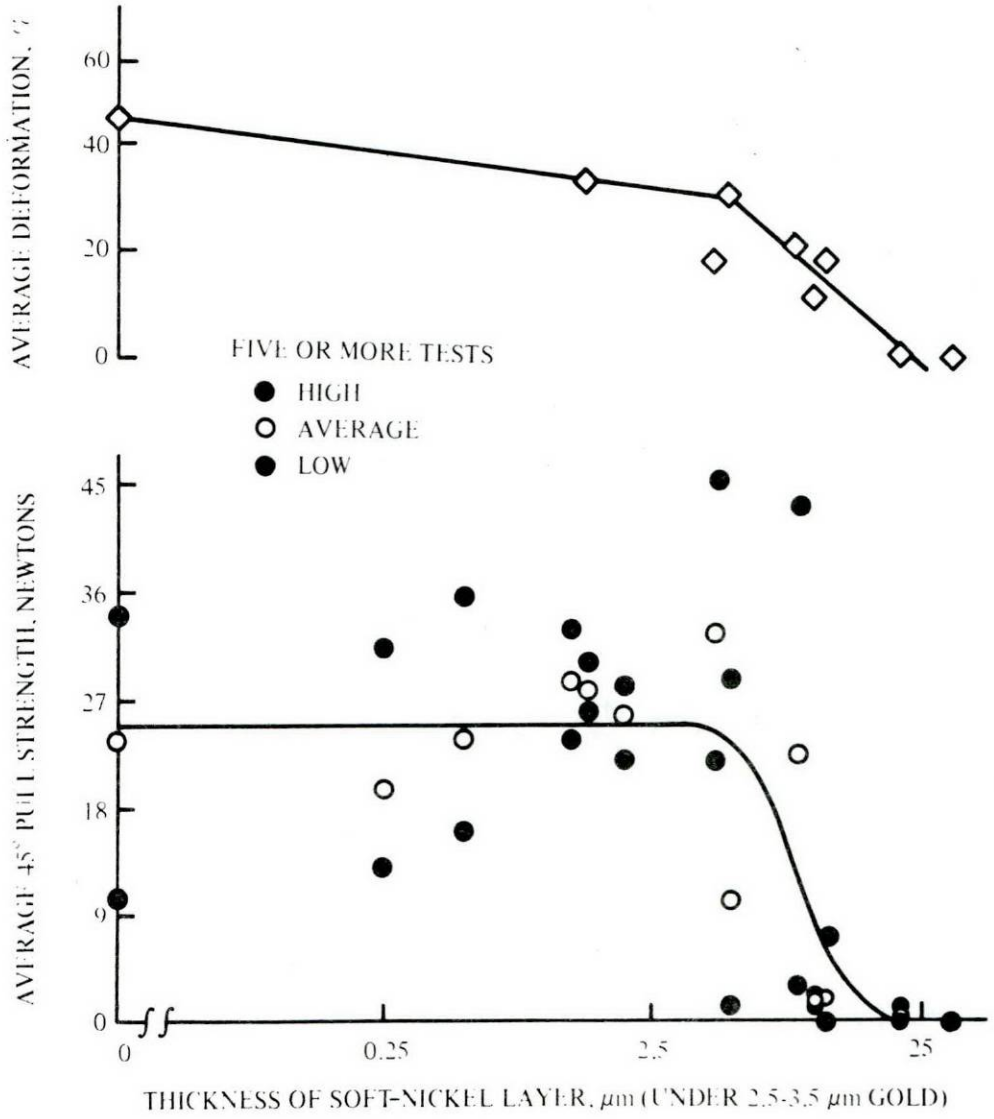


Figure 2. Deformations and Strengths for Increasing Soft-Nickel Thicknesses

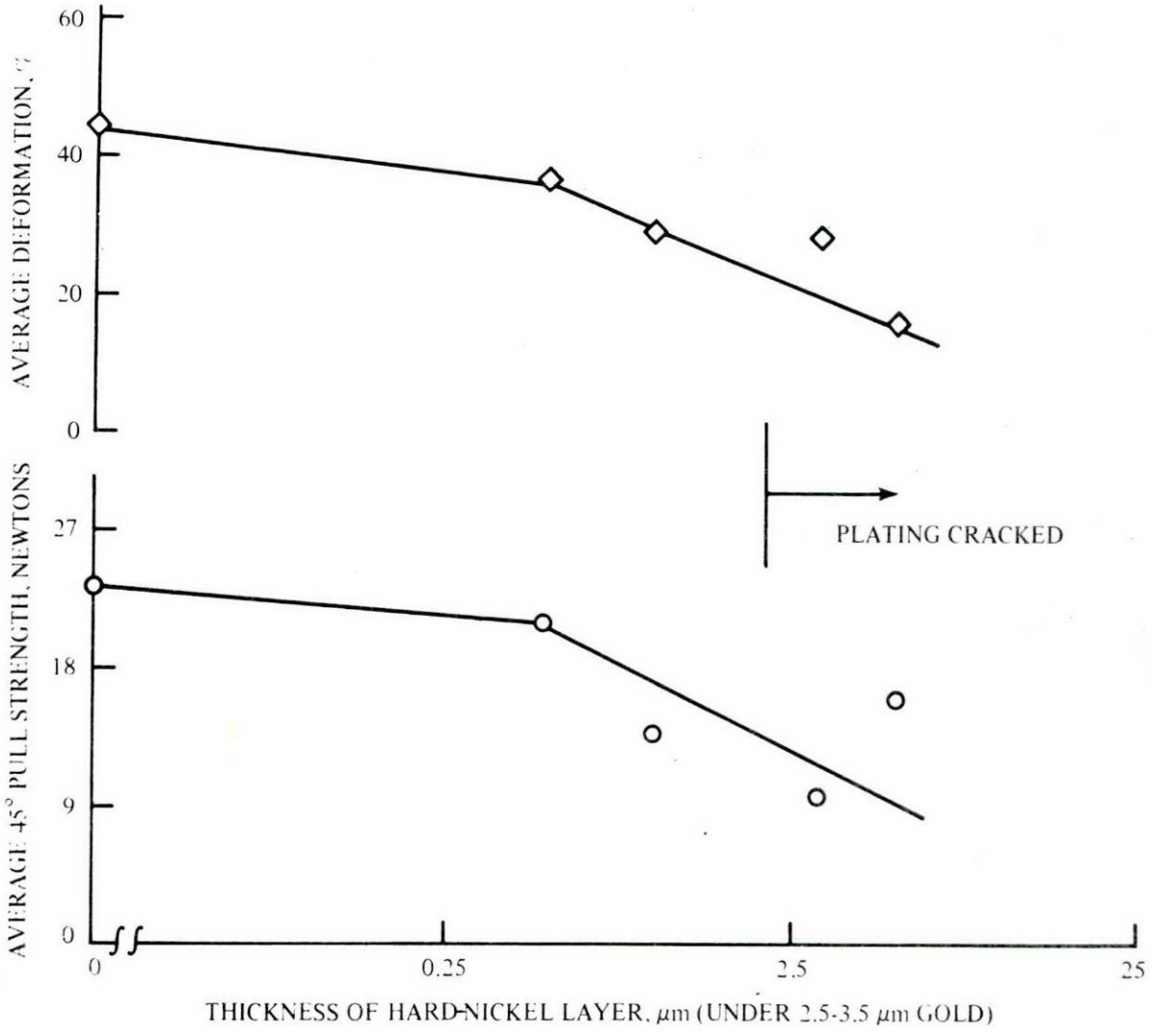


Figure 3. Deformations and Strengths for Increasing Hard-Nickel Thicknesses

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Design Considerations for Reel-to-Reel Selective Plating

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DESIGN CONSIDERATIONS FOR REEL-TO-REEL SELECTIVE PLATING

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Electronics II
Session M

Precision Plating: A Fundamental Approach

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PRECISION PLATING: A FUNDAMENTAL APPROACH

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Introduction

The requirement for greater interconnection density at the PWB has been brought on by increased chip function and subsequent pin density. The density increase has forced PWB multilayer designs with increased numbers of layers, increasing the final board thickness. The board thicknesses have increased, yet to accommodate additional planar layer density, pad and hole diameters have decreased. The result is the need for production of high aspect ratio plated through-hole connections. The challenge is to uniformly deposit conductive metal in the through-hole providing continuity for interconnection with adequate strength to withstand repeated thermal cycles. In high technology multilayer construction 5:1 aspect ratios are becoming more common. PWB designs incorporating aspect ratios of 15:1 and up to 20:1 are being prototyped.

Several process options exist to copper plate these high aspect boards. The plated options include full electroless deposits and initial electroless, final electrolytic deposition. Of the two processes, electrolytic plating over thin electroless provides metallic physical properties which will withstand repeated thermal cycling. This paper will discuss three factors which have been studied to improve on the final electrolytic deposit uniformity and quality. The factors are:

1. Plating bath agitation.
2. Chemical bath composition and control.
3. The primary and secondary current effects due to plating cell design.

Agitation

Plating speed and uniformity is a function of the rate at which fresh electrolyte reaches the plated part or cathode.

This plating rate is governed by the thickness of the diffusion layer. The diffusion layer is the region near the electrode surface where the concentration of electrolyte varies from that in the bulk of the system. Uniform mechanical agitation at the cathode or anode uniformly reduces the diffusion layer thickness by reducing the concentration gradients that occur in solution. The reduced diffusion layer thickness at the electrode surface allows increased plating speeds. The mathematical relationship describing the limiting current at the electrode surface is:

$$i_{lim} = \frac{nFADC_b}{\delta} \quad (1)$$

Where; i_{lim} = Limiting current at the electrode

F = Faraday constant

A = Area of the surface

D = Species diffusion coeficient

C_b = Concentration of electoactive species in bulk of solution

δ = Diffusion layer thickness

n = Number of electrons

Two important relationships are noted:

$$i_{lim} \propto \frac{1}{\delta} \text{ and } i_{lim} \propto C_b \quad \text{and} \quad i_{lim} \propto \frac{1}{\delta} \quad (2)$$

$$i_{lim} \propto C_b \quad (3)$$

From relationship (2), decreasing layer thickness while maintaining other variables constant, results in a proportional increase in the limiting current. Similarly, from (3), increasing the concentration of electroactive species at the work surface with effective agitation allows plating to take place at a higher current density. Moreover, an agitation system which minimizes concentration gradients over the entire plating surface produces a much higher degree of plating uniformity. One method of examining the effect of solution agitation on the diffusion layer is shown by the relationship between applied voltage and current given by Ohms Law.

$$V = I \cdot R_{total} \quad (4)$$

Where; V = Voltage applied to cell (anode to cathode)

I = Current flowing through the cell

R_{total} = Total of resistance elements in the cell

R_{total} is the sum of several resistance terms:

$$R_{total} = R_{diff} + R_{junc} + R_{bulk}$$

R_{diff} = Resistance due to diffusion layer

R_{junc} = Resistance due to junctions

R_{bulk} = Resistance due to plating solution

At a constant voltage, temperature and bulk solution composition, R(junc) and R(bulk) are constants. R(diff) is proportional to thickness of the diffusion layer. Therefore, decreasing the diffusion layer decreases the total resistance of the cell resulting in a higher current at the constant voltage. Figure 1 shows the current-voltage relationship in a plating cell that employs a solution impingement agitation. Increasing the manifold pressure in this system results in an increase in the velocity and volume of solution impinging at the surface of the cathode. This causes a proportional decrease in the diffusion layer and a subsequent drop in the voltage required to support a given current.

The agitation system is an important consideration as it must set up a uniform "flow field" at the work surface. In several high speed cell designs, the flow field is created and maintained during the plating cycle by a manifold which has jet impingement of solution to the work surface (see Figure 2). As the jet streams overlap at the work surface, interference zones are established. The interference zones result in thicker, non-uniform diffusion layer conditions which result in non-uniform or, in a worst case, current limited plating. The use of overlappng jet streams and a return or "pull" capability to eliminate the overlap or interference zones (see Figure 3) will allow uniform flow distribution over the work surface. The "pull" effect allows each jet impingement to act as a single jet in solution with return of flow with a reduction in the interference zones.

The diffusion layer affects the deposition rate and uniformity not only the PWB surface, but to an even greater degree, the plated-through-hole. As the hole size decreases, a proportional decrease in the efficiency of solution agitation in the through-hole occurs. As the diameter of the hole becomes smaller, greater solution turnover is required to replenish the amount of copper and additives needed to uniformly plate the walls of the hole. The dramatic increase in the number of hole volumes of plating solution needed to plate one mil of copper in the

hole can be seen by comparing the hole volume calculations of copper solution required for a 0.74:1 aspect ratio to those for 5.2:1. See Figure 4. The 0.74:1 hole requires the solution in the hole to be exchanged 15 times while the 5.2:1 hole requires the solution to be changed 100 times for an equivalent deposit thickness. The exchange rate for the solution in a hole is also a function of current density. Increasing the current density decreases the time the platng system has to exchange the solution volume in the PTH as demonstrated in Figure 5. The graph assumes all of the copper can be removed from the plating solution without detrimental effect to the plate. However, a 10 percent change in the plating bath chemistry will cause a degredation in the quality of the copper deposit. This means that the solution must be exchanged not 100 times, but 1000 times in the 5.2:1 hole at 90 ASF. When plating a 5.2:1 hole at 90 ASF, the agitation system has less than 1 second to exchange the solution in order to maintain the quality of copper deposited in the hole.

Presently, agitation in the plated-through-hole is commonly provided by air sparging. Air bubbled from the tank bottom moves upward, displacing solution as it rises, causing visual turbulence. But solution agitation in the plated-through-hole is a minimum as it is perpendicular to the major agitation force. Jet impingement of solution is designed to force solution through the holes. As described before, the effect of addressing the solution surface uniformity is one aspect to the reduction of the diffusion layer, with the second aspect being the net charge of pressure at the work surface as a function of time. The desired uuniformity effect can be achieved with a knife edge agitation of the cathode (work piece) across the set of impinging jets. The pressure fluctuation effects are important at the surface as well as being important in the flow through the plated-through-hole. Additionally, the manifold configuration on one side of the cathode is offset from that on the opposite side. The jet impingement on one side are lined up oppositely with return flow on the opposite side. See Figure 6. As a third dimension, in this case the plated-through-hole, passes in front of a jet, solution is directed toward the hole. The "pull" opposite the jet creates a lower pressure area on the "pull" side of the board creating less solution resistance than is more a static jet impingement from both sides. The plating solution, thus, takes the path of least resistance through the holes to be plated. As aspect ratios incease, agitation will become critical. Strategic solution agitation is one key element to precision electrodeposits.

Plating Bath Composition and Control

Plating bath chemistry and real time analysis and control of the chemistry provide the second key element to precision

electrodeposits. The formulation of "high throw" acid copper plating baths can be attributed to a basic electrochemical understanding of the plating phenomena. High current density regions on the PWB surface are areas that have the greatest net charge difference in solution due to the concentrated surface potential. The relative ratio of copper being deposited versus solution conductance dictates the amount of ion migration that occurs in the cell and the region to where the counter ion will migrate. The total conductivity of the solution is given by the equation:

$$A = F \left(\sum_{i=o}^{i=n} \mu_i + \sum_{e=o}^{e=m} \mu_{e^-} \right) \qquad (6)$$

Where; A = Total conductivity

F = Faraday constant

μ = Ion mobility

The equation expresses a contribution from both the negatively and positively charged species. The negative ions species in an acid copper bath is the sulfate while the positive ion species are a combination of hydrogen and copper ions. Consequently, migration of copper ions can be reduced by increasing the concentration of sulfuric acid, thus, allowing charge neutrality. The reduction in copper ions causes a decrease in the migration current inhomogeneties, resulting in improvements in uniformity. The result is better "throw", allowing improvements in plating through-holes.

Organic chemical additives have a significant effect on the plating quality and electrodeposition rate. Many commercial additives cause deposit enhancements when added to the bath in concentrations of a tenth of a percent. The addition of these additives modifies the structure of the electrodeposit. The properly modified structure will exhibit physical properties of high elongation and moderate-to-high ultimate tensile strength. The additives cause the plating process to be mediated over a range of plating current densities which exist on the panel surface due to non-uniform area considerations. Each additive constituent has a purpose, with the total impact beng grain structure modification and uniformity improvement or improved ultimate deposit performance. As the individual additive components are "consumed" in the plating process, changes take place in the quality of the electrodeposit. To maintain consistent electrodeposit product quality, proper analysis and control of the additive components is critical.

The traditional method of controlling low concentrations of additives in the bath has been the Hull Cell. Most recently, CVS (Cyclic Voltametric Stripping) has been

employed to yield more information on control. However, as line widths shrink and aspect ratios increase, tight real time control on the bath chemistry becomes paramount. Procedures have been developed to allow incoming quality of commercial additives to be examined. Additional procedures allow the separation, identification and qualification of each organic constituent in the plating bath, insuring total mass balance in the plating cell. Quality control of the brightener, before use, is an important safeguard against lot to lot variations as demonstrated by the chromatograms. See Figure 7. These two analyses are of two different lots of the same commercial organic additive. The analyses are statistically different and yield different actual plating results.

Control of the concentration of each organic component in the bath is important because of the many variables that affect their use and non-use rates. During a laboratory examination, the concentraton of one of the organic components in a commercial additive, under controlled conditions, was monitored for several days. During this period additions were made according to the amp hour consumption. The plating bath was worked for approximately 8 hours per day and allowed to set for the remaining 16 hours. It was found that, during the working hours, the concentration of one of the additive components stayed at a mean value of approximately ± 5 percent (with proper amp hour additions); however, overnight the concentration dropped 35-40 percent and by the third day the plating bath was producing unacceptable deposit properties. Because the actual concentration of this constituent had been determined, it was a simple matter to bring the bath back into line. Establishing process and bath control charts to monitor the constituent levels of the additive can minimize downtime, maximize product quality and reduce final costs.

Figure 8 shows the degredation of the molecular moity and concentration of a second additive component of freshly made up plating bath. Initially, the distribution of molecules is narrow. Figure 9 shows the profile of the same additive component from a production bath. As can be seen, there is a substantial decrease in the additive base and an increase in the smaller breakdown products as highlighted. It has been demonstrated that these breakdown products affect both the physical properties of the copper plate and the efficiency of the electrodeposition process. Each of these analytical procedures, when used together, can provide an early warning indicator predicting the need for bath adjustment or carbon treatment. Remember, a chemical change of as little as 10 percent in the through-hole or at the surface will change the electrodeposit physical characteristics.

Conclusion

The deposition of uniform copper on the PWB surface and in the plated-though-hole is a function of plating solution agitation at the work surface and of the bath concentration including organic additives. Control of the additives cannot be overlooked. As high technology PWBs are designed with increasing aspect ratios and fine line features, knowledge of basic electrodeposition phenomena and methods to improve the process are critical. Proper agitation of plating solution in the through-hole and on the surface, in conjunction with a synergistic plating solution additive, can solve uniformity problems providing the performance required to make precision electrodeposition of high technology PWBs in production baths a reality.

Acknowledgment

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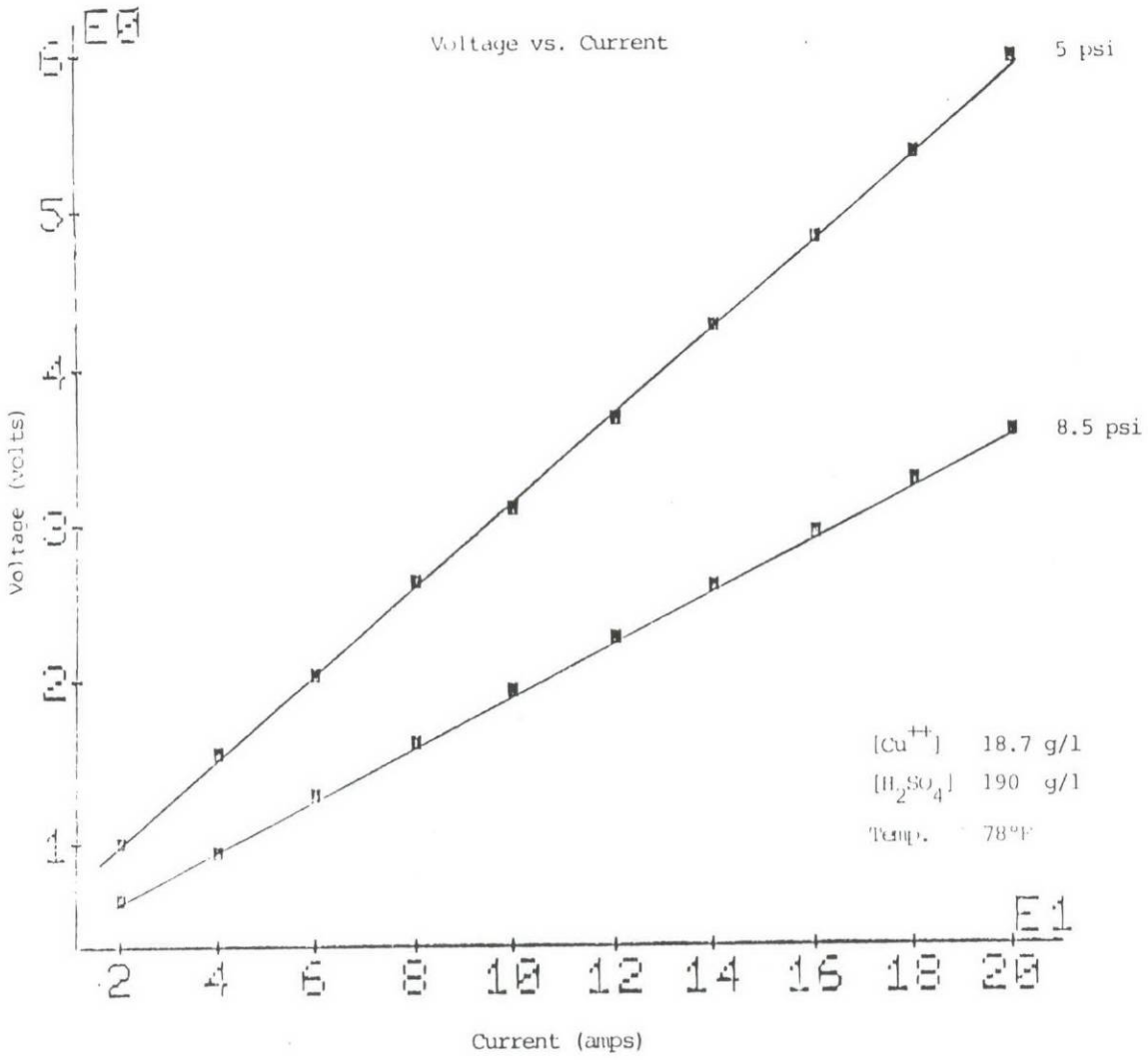

Voltage vs. Current
5 psi
8.5 psi
[Cu++] 18.7 g/l
[H2SO4] 190 g/l
Temp. 78°F
Voltage (volts)
Current (amps)
2
4
6
8
10
12
14
16
18
20

FIGURE 1.

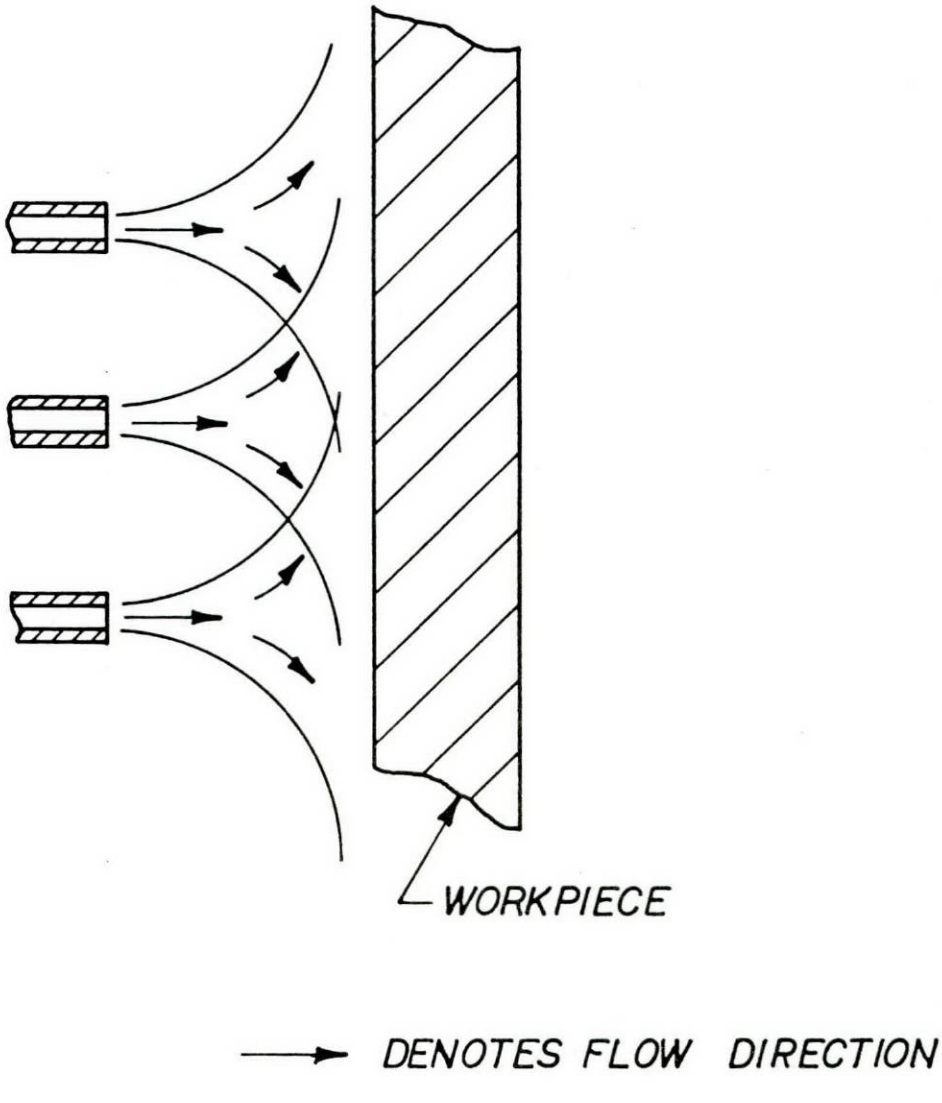


FIGURE 2.

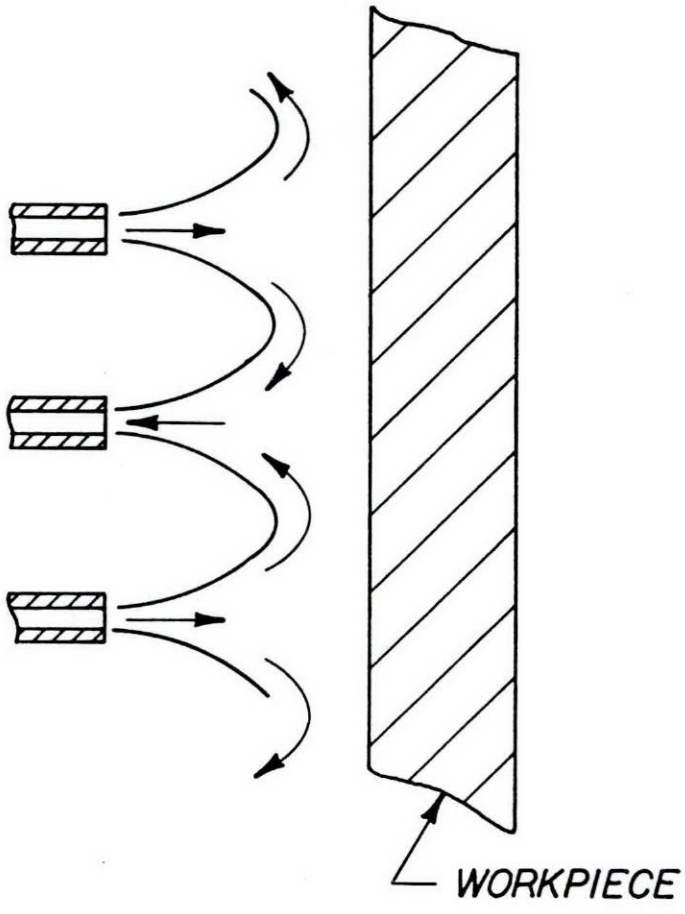
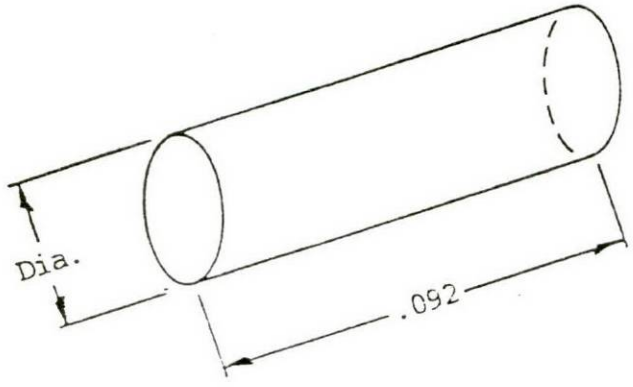


FIGURE 3.

Aspect Ratio	Diam. (in.)	V_{hole}[1] ($cm^3 \times 10^3$)	Wt. 1 mil deposit (ug)	Wt. Cu^2 in. Sol. per V_{hole} (ug)	Wt. deposit / Wt. Cu in V_{hole}
.74:1	.125	18.7	5300	350.	15.1
1.1 :1	.083	8.25	3510	154.	22.8
1.5 :1	.062	4.60	2610	86.1	30.3
2.2 :1	.042	2.11	1750	39.5	44.3
3.0 :1	.031	1.15	1280	21.5	59.5
3.7 :1	.025	0.748	1030	14.0	73.6
4.4 :1	.021	0.528	855	9.88	86.5
5.2 :1	.018	0.388	727	7.26	100.



1. Board thickness = .092 in.
2. Concentration Copper = 18.7 g/l

FIGURE 4.

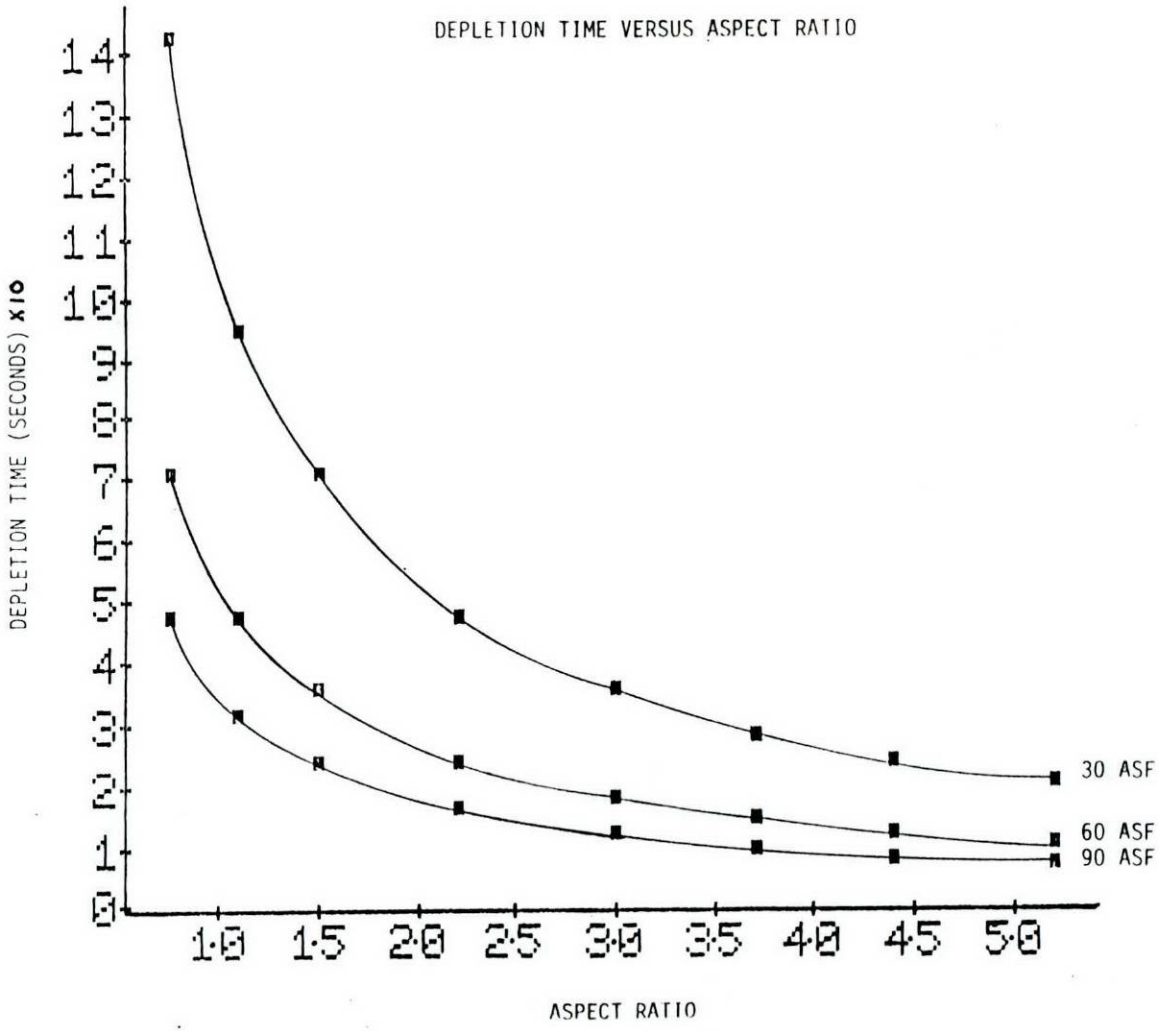

DEPLETION TIME VERSUS ASPECT RATIO
DEPLETION TIME (SECONDS) X10
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
ASPECT RATIO
30 ASF
60 ASF
90 ASF

FIGURE 5.

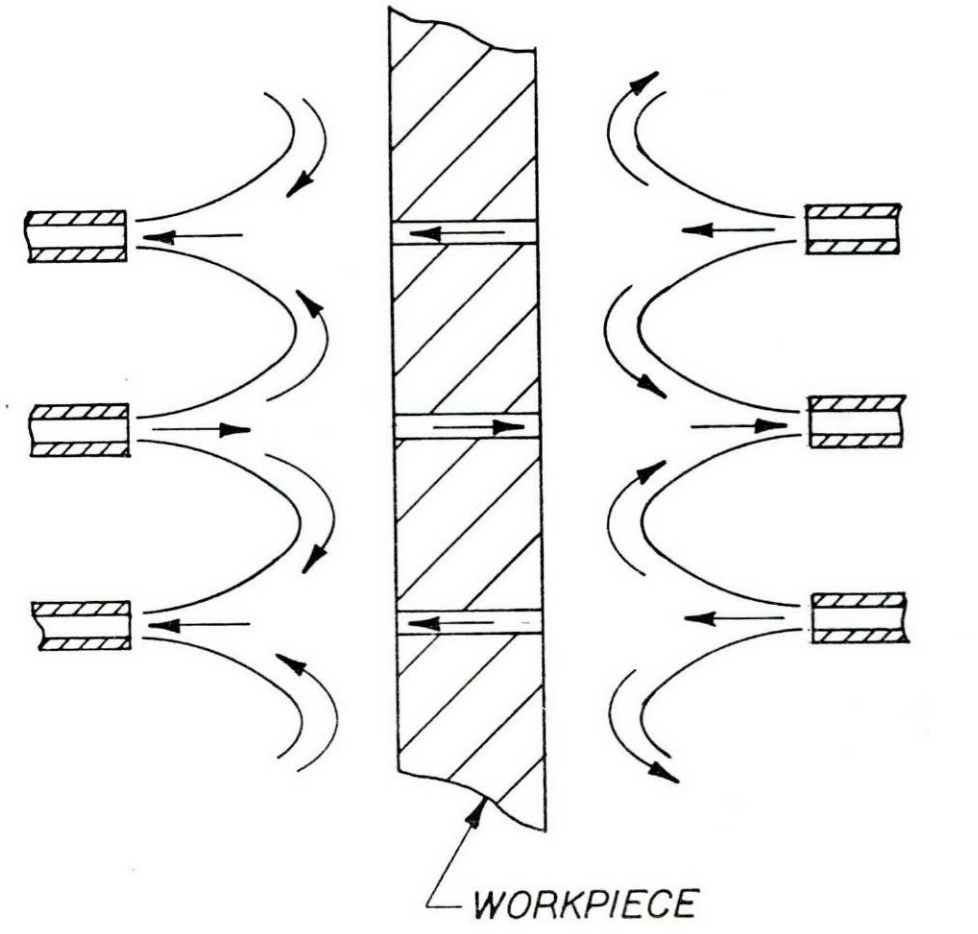
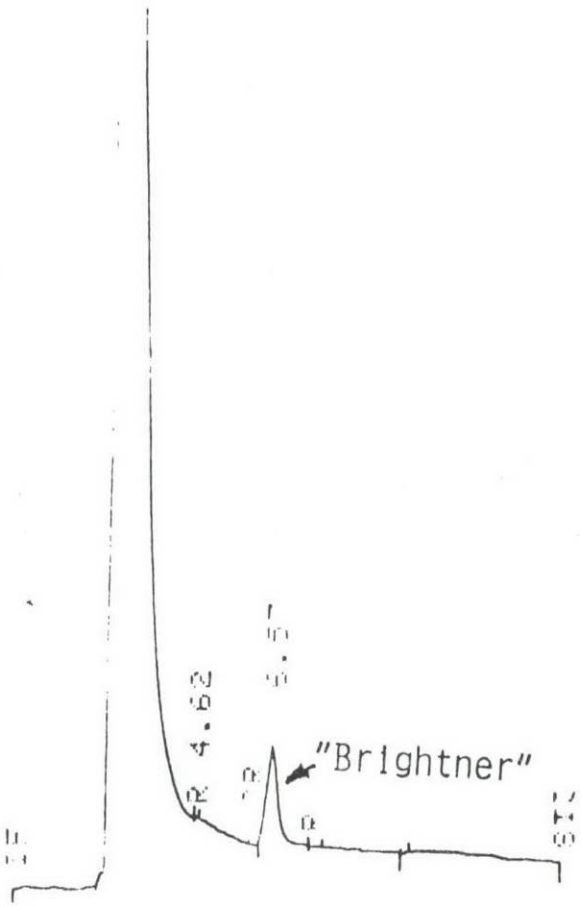


FIGURE 6.



HPLC Analysis of Production Bath for EL 112 ACB

FIGURE 7.

[redacted] = Breakdown Products Caused by Plating

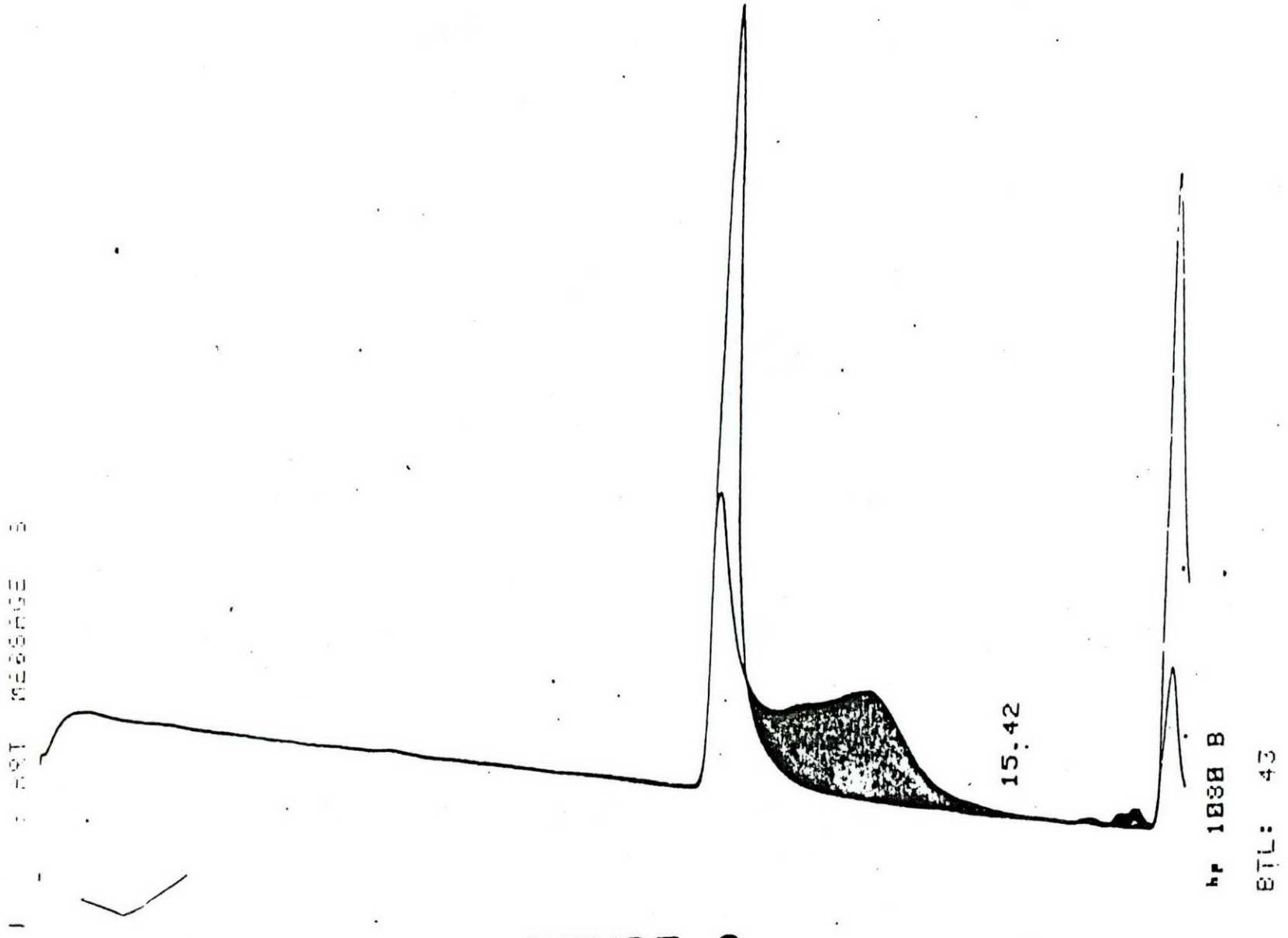


FIGURE 8.

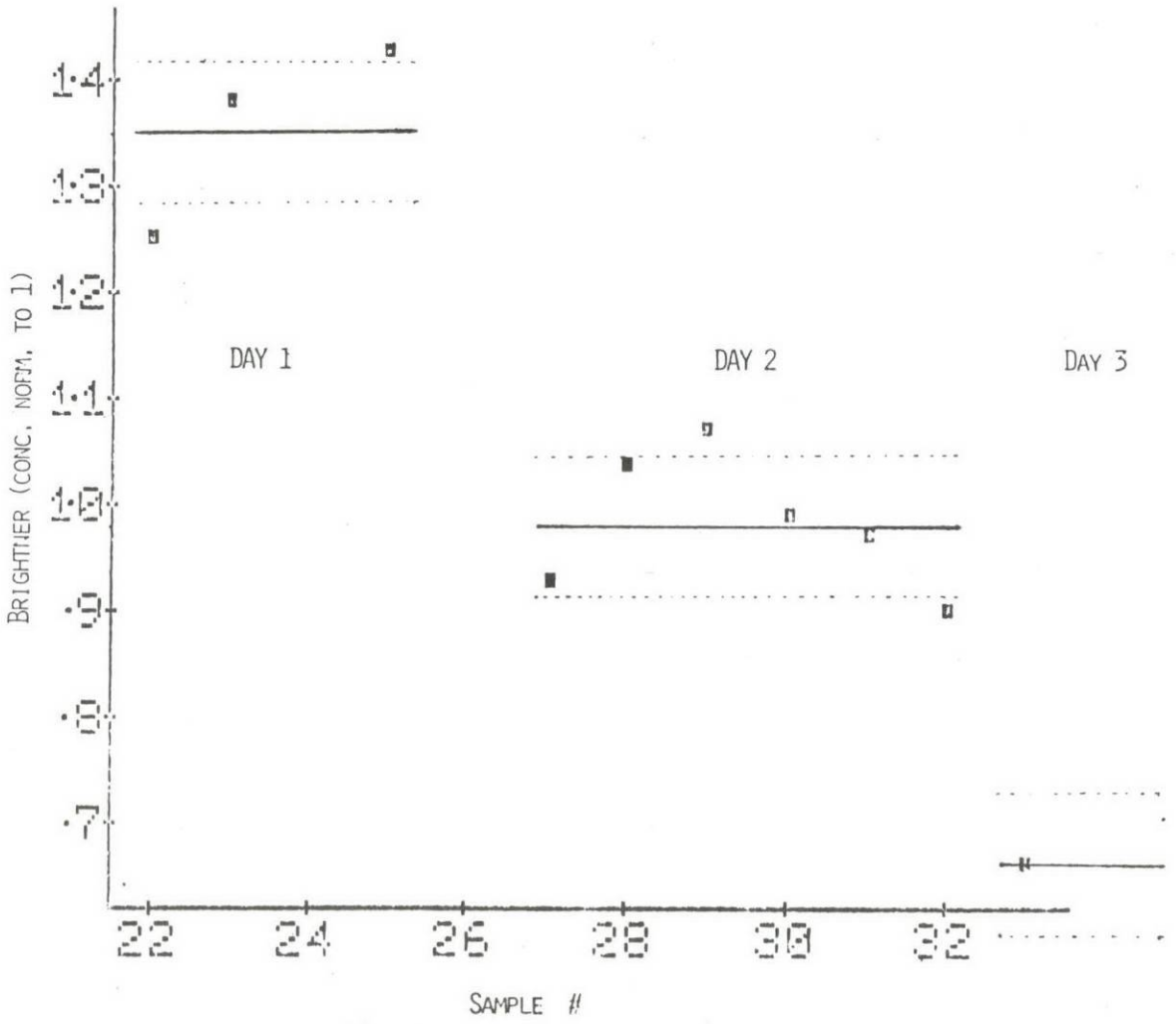

BRIGHTNER (CONC. NORM. TO 1)
1.4
1.0
1.2
1.1
1.0
.9
.8
.7
DAY 1
DAY 2
DAY 3
22
24
26
28
30
32
SAMPLE #

FIGURE 9.

M-4

Electronics II
Session M

A Comparison of Cobalt and Nickel as Additives for Acid Hard Gold Plating Processes

Alan Blair, George Karustis, Michael Wild and Peter Wilkinson
Engelhard Corporation
East Newark, NJ

A COMPARISON OF COBALT AND NICKEL AS ADDITIVES FOR ACID HARD GOLD PLATING PROCESSES

By

Alan Blair, George Karustis, Michael Wild
Peter Wilkinson - Engelhard Corporation

INTRODUCTION

Acid hard gold deposits have established themselves as a standard finish in connector and dry contact applications. Transition metals, such as cobalt, nickel, iron or indium, have been used to modify deposit structure to achieve the desired properties. The most commonly employed additive is cobalt but significant quantities of nickel-hardened gold is in use. Iron and indium based formulations are very small in number by comparison with the other two metals.

The chemistry of cobalt and the effects of electrolysis on this chemistry have been the subject of previous papers.[1,2] Processes utilizing nickel additives appear to be more chemically stable, although generally a greater concentration of this metal is required in solution to achieve similar deposit purity and appearance compared with cobalt processes. To the authors' knowledge there has never been a quantitative comparison of deposit properties from these two systems.

The object of this study was to compare the properties of cobalt and nickel hardened gold deposits in the cases where the metals were added as simple ions and when they are present as proprietary complexed species. Of interest were solderability, stress, the chemical composition of the deposit and whether relationships existed among these factors.

While stress of hardened gold deposits has been measured, these results do not appear to be systematically collected for the systems in question and for a sufficient variety of conditions. We have chosen to measure stress by the method of Vrobel & Dvozak[3] who have devised a technique which relates stress to the forces of elongation or contraction of a plated strip of steel. The procedure is carried out, reproducibly on a stress meter that is readily available and comparatively inexpensive. Moreover, the results are obtained as a standard unit, kP/mm^2, that needs no interpretation or correlation to another set of numbers.

Solderability was determined with a Multicore Universal Solderability Tester. This instrument measures the buoyant or wetting forces on an item immersed in molten solder, displays them graphically and calculates several numbers from this data that then may be used as a measure of solderability. This instrument has the advantage of quantifying a property that previously had been subjectively interpreted.

Deposit compositions were determined by standard analytical methods.

The Electrolytes

The simple electrolytes contained 100 g/l citric acid adjusted to the operating pH with potassium hydroxide. Gold, at 12 g/l, was added as potassium gold cyanide and the cobalt and nickel were added as sulphates. The complexed systems used were proprietary electrolytes with a citrate based conducting salt and the cobalt or nickel added as similar complexes. In the simple electrolytes, the cobalt or nickel concentrations were 25% above the minimum amount needed to obtain a bright deposit at 30 A/ft^2.

TABLE 1

Solution Designation	Additive Metal Concentration	pKa of Metal Complex[4]
A	1000 ppm Co	10
B	200 ppm Co	2.47
C	1000 ppm Ni	11
D	800 ppm Ni	2.40

These types of electrolyte are fairly typical of those used for connector or PWB contact applications since the deposits have good wear resistance and sliding contact properties.

Deposit Analysis

Pure copper coupons were plated in each of the solutions at pH values from 3.8 to 5.0 and at current densities between 5 and 40 A/ft^2. The deposits were analysed for cobalt or nickel and potassium by Atomic Absorption Spectrophotometry and for carbon by the Strolien method.

The atomic ratios of potassium and carbon to cobalt or nickel were calculated and the results are shown in Tables 2 - 5.

The percentages of cobalt or nickel follows definite relationships to variations in pH or current density whereas the carbon and potassium show less dramatic trends. This tends to suggest that the co deposition of these elements is taking place by more than one mechanism and various theories have been put forward to explain this.[5,6]

TABLE 2

DEPOSIT COMPOSITION OF GOLD OBTAINED FROM SOLUTION A

pH	Current Density	Current Efficiency %	%Co	%C	%K
3.8	30	33	0.49	0.32	0.23
4.2	30	59	0.28	0.37	0.44
4.6	30	53	0.18	0.36	0.44
5.0	30	55	0.15	0.32	0.38
4.2	5	62	0.25	0.26	0.22
4.2	10	59	0.28	0.40	0.26
4.2	20	51	0.30	0.44	0.32
4.2	30	56	0.23	0.34	0.44
4.2	40	37	0.35	0.29	0.39

			ATOMIC RATIOS		
pH	Current Density	Current Efficiency %	Co	C	K
3.8	30	33	1	3.2	0.7
4.2	30	59	1	6.5	2.4
4.6	30	53	1	10.0	3.75
5.0	30	55	1	10.6	3.9
4.2	5	62	1	5.0	1.3
4.2	10	59	1	7.0	1.4
4.2	20	51	1	7.3	1.6
4.2	30	56	1	7.7	2.9
4.2	40	57	1	4.8	2.0

TABLE 3

DEPOSIT ANALYSES OF COBALT HARDENED GOLD

SOLUTION B

pH	Current Density	Current Efficiency %	%Co	%C	%K
3.8	30	22	.23	.34	.27
4.2	30	33	.25	.28	.29
4.6	30	36	.18	.20	.24
5.0	30	49	.05	.12	.20
4.2	5	41	.19	.23	.20
4.2	10	43	.27	.24	.26
4.2	20	42	.21	.24	.29
4.2	30	48	.17	.24	.24
4.2	40	41	.15	.24	.25

ATOMIC RATIOS

pH	Current Density	Current Efficiency %	Co	C	K
3.8	30	22	1	4.75	1.2
4.2	30	33	1	5.5	1.75
4.6	30	36	1	5.5	2.0
5.0	30	49	1	11.8	6.0
4.2	5	41	1	6.0	1.6
4.2	10	43	1	4.3	1.5
4.2	20	42	1	5.6	2.0
4.2	30	48	1	6.9	2.0
4.2	40	41	1	7.8	2.5

TABLE 4

DEPOSIT COMPOSITIONS OF NICKEL HARDENED GOLD

SOLUTION C

pH	Current Density	Current Efficiency %	%Ni	%C	%K
3.8	30	32	.38	.43	.58
4.2	30	43	.21	.34	.31
4.6	30	59	.17	.25	.32
5.0	30	56	.13	.22	.27
4.2	5	32	.55	.21	.12
4.2	10	44	.41	.33	.30
4.2	20	34	.27	.38	.30
4.2	30	30	.20	.34	.32
4.2	40	24	.20	.33	.27

ATOMIC RATIOS

pH	Current Density	Current Efficiency %	Ni	C	K
3.8	30	32	1	5.5	2.3
4.2	30	43	1	7.9	2.2
4.6	30	59	1	7.1	2.8
5.0	30	56	1	8.2	2.1
4.2	5	32	1	2.0	3.0
4.2	10	44	1	4.0	1.0
4.2	20	34	1	7.0	1.66
4.2	30	30	1	8.3	2.4
4.2	40	24	1	8.0	2.0

TABLE 5

DEPOSIT COMPOSITIONS OF NICKEL HARDENED GOLD

SOLUTION D

pH	Current Density	Current Efficiency %	%Ni	%C	%K
3.8	30	44	0.09	0.26	0.29
4.2	30	53	0.08	0.21	0.27
4.6	30	54	0.07	0.22	0.28
5.0	30	55	0.09	0.25	0.26
4.2	5	57	0.21	0.22	0.20
4.2	10	65	0.15	0.29	0.24
4.2	20	65	0.06	0.23	0.28
4.2	30	53	0.06	0.21	0.27
4.2	40	57	0.08	0.25	0.26

			ATOMIC RATIOS		
pH	Current Density	Current Efficiency %	Ni	C	K
3.8	30	44	1	14	5
4.2	30	53	1	13	5
4.6	30	54	1	15	6
5.0	30	55	1	14	4
4.2	5	57	1	5	1
4.2	10	65	1	9	2
4.2	20	65	1	19	7
4.2	30	53	1	17	7
4.2	40	57	1	15	5

The presence of the K Co $(Au(CN)_2)_3$ complex is indicated by the K:Co:C atomic ratio of 1:1:6 which is predominant in the results obtained.

At low pH values the ratio of cobalt/nickel atoms increases significantly indicating perhaps the codeposition of elemental cobalt or nickel being deposited as a solid solution or intermetallic in the gold.

At high pH, the ratio of cobalt/nickel atoms decreases while the potassium and carbon levels increase proportionally. This could be explained by the codeposition or entrapment of a potassium cyanide polymer since this would be much more stable in a solution at the higher pH, particularly as the cathode film generally exhibits a pH value well above that of the bulk electrolyte.

The results from the simple nickel solution (D) do not show these trends and this may be due to analytical errors at the low level of nickel obtained or it may be due to different mechanisms taking place at this level of nickel.

The most significant results are shown by electrolyte A where the cobalt content increases with current density. In all the other electrolyes the converse is true. Further work will have to be carried out to investigate this effect.

It is unfortunate that the nitrogen content of the deposit could not be determined at this time, which may have helped to explain some of the phenomena.

STRESS

Deposit stress was measured with an IS meter by the method of Vrobel and Dvozak as previously stated. In this procedure a steel strip 10 mm by 130 mm was plated at 10 or 40 asf while taking 20 readings at half or minute intervals. In all cases the strip decreased in length indicating the stress was tensile. While the IS meter is not difficult to use, the initial stress forces, due to the very thin deposit, are not enough to overcome the frictional forces in the instrument. The value quoted for the internal stress (Table 6) has been determined once the plateau had been reached (Figure 1).

At the low current density both cobalt solutions produced deposits with similar stress, about 9 - 11 kP/mm^2. At high current density the stress of deposits from the simple solution is substantially higher than that from the complexed cobalt, 21 to 24 kP/mm^2 vs. 15 kP/mm^2. While we do not attribute any significance to the slight slope of the lines at low current density, being virtually horizontal, the decreasing slope of the high current density simple solution is too great to ignore. Obviously, deposits do not become less stressed as thickness increases. This decrease is generally attributed to microcracking, which temporarily relieves some stress.

Nickel hardened golds show increased stress with higher current density and the simple bath shows lower stress than the complexed one. Deposit stress in the simple nickel electrolyte is lower than that from the equivalent cobalt system but the reverse is true for the complexed electrolytes. There is no correlation between the metallic, carbon or potassium contents and the internal stress of the deposits, and the only significant fact that emerges is that the complexed systems are more consistant over a range of current densities.

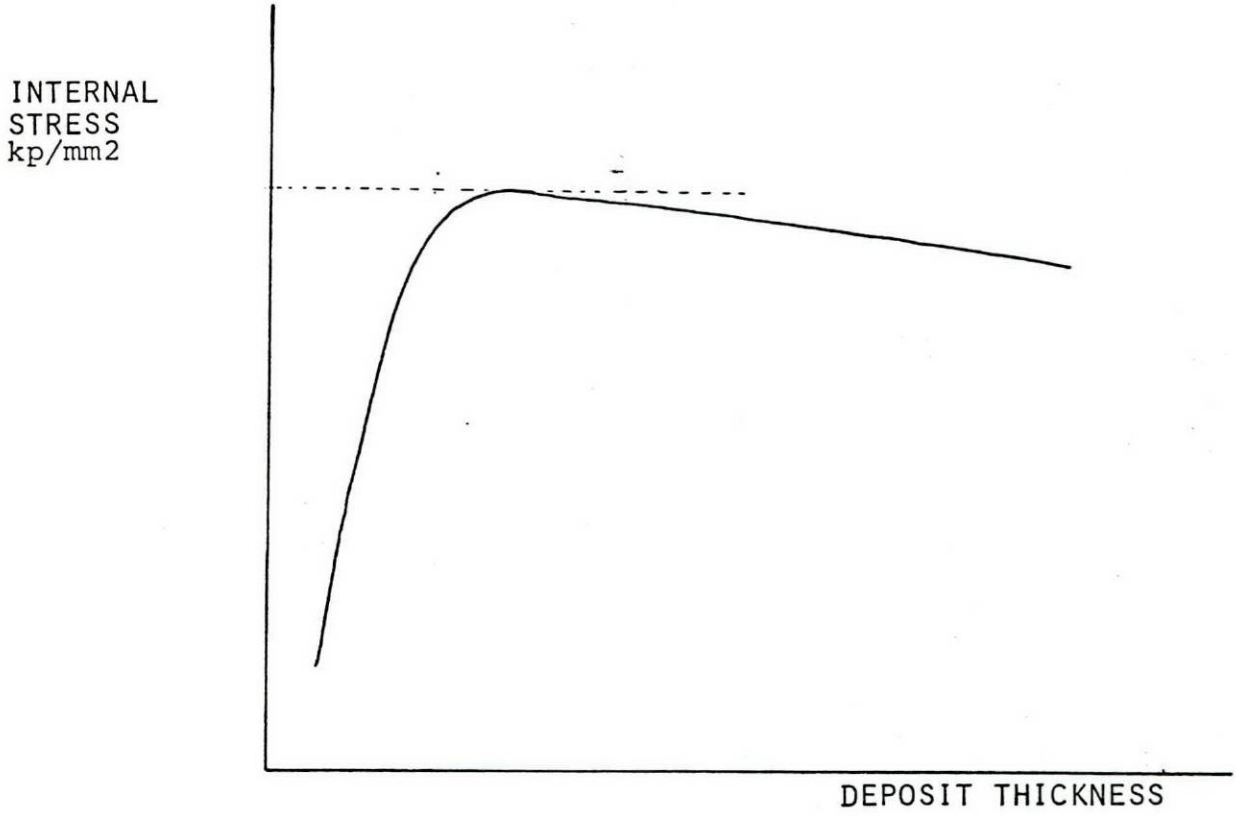
TABLE 6

SUMMARY OF INTERNAL STRESS MEASUREMENTS

Solution Type	Current Density A/ft^2	Average Internal Stress kp/mm^2
A	10	11
A	40	15
B	10	9
B	40	22
C	10	14
C	40	20
D	10	7
D	40	18

FIGURE 1

TYPICAL STRESS GRAPH



SOLDERABILITY

The solderability of the deposits was examined using the Multicore Universal Solderability Tester. This measures the surface forces acting on the specimen as it is immersed and becomes wetted by the molten solder.[7,8,9] While there is some discussion as to the interpretation of the data produced by the instrument, it is consistant and gives a good comparison between specimens.

A solderable sample displays an exponential rise in the wetting forces, similar in shape to the charging pattern of a capacitor. A theoretical curve can be calculated from the data which is characterized by two values, the time constant and the final wetting force. In addition a third figure, the time to zero, or neutral buoyancy, may be used (Wetting Time).

A typical solderability plot is shown in Figure 2 where wetting forces are shown in milli-newtons on the vertical axis and time is drawn on the horizontal axis. P, the time to zero buoyancy is usually close to S, the time constant, and therefore, while it has little theoretical significance, it has a greater practical meaning. Many samples showing poor solderability never reach zero buoyancy in this type of determination. The maximum wetting force, F, may not be attained in practice and is generally only reached after 9 seconds exposure to solder. Most of the data can be visualized as variations of Figure 2 with the tabular values for Table 7. The microprocessor uses the time constant and the maximum wetting force to calculate the theoretical curve representing the data. The actual fit of the data to this curve is the coefficient of correlation.

FIGURE 2

GOOD SOLDERABILITY

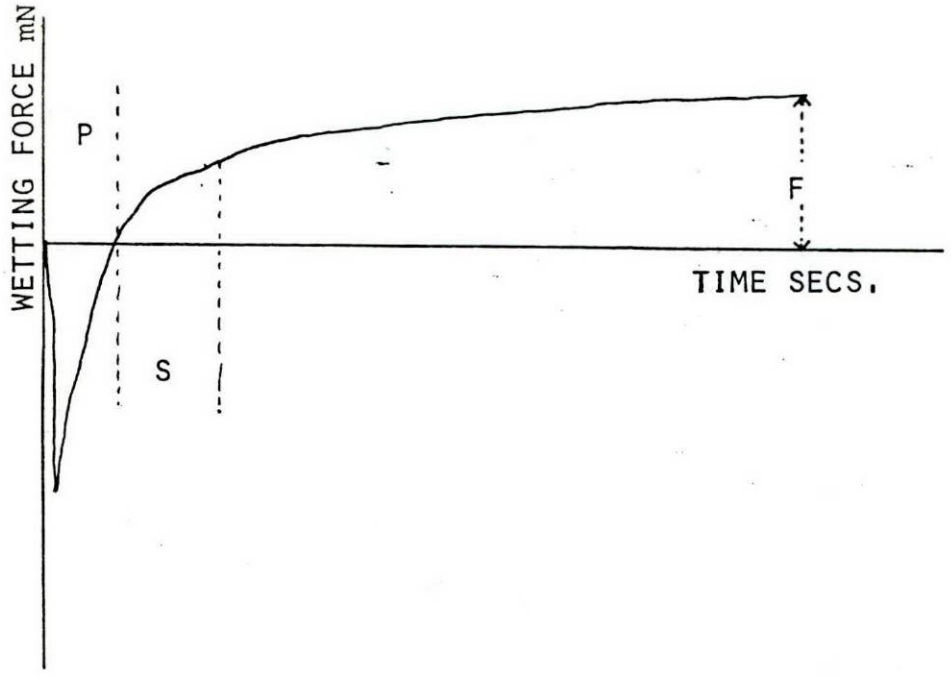


FIGURE 3

MARGINAL SOLDERABILITY

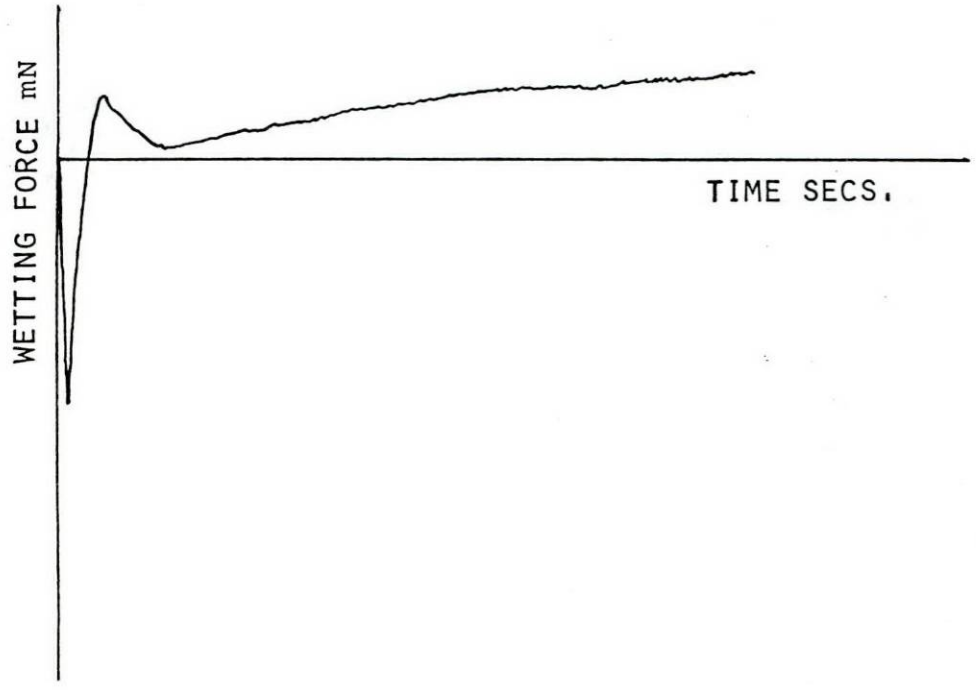


TABLE 7

SOLDERABILITY

ELECTROLYTE C

Current Density ASF	Deposit Thickness microinches	Substrate	F	S	P	% Dewetting from time of maxium force
10	10	Cu	10	.75	.5	
10	40	Cu	11	.80	.6	
10	10	Ni	9	.55	.3	
10	40	Ni	12	.68	.4	
40	10	Cu	12	.45	.35	0
40	40	Cu	14	.3	.4	3
40	10	Ni	14	.66	.5	0
40	40	Ni	12	1.5	1.0	4

ELECTROLYTE D

Current Density ASF	Deposit Thickness microinches	Substrate	F	S	P	% Dewetting from time of maxium force
10	10	Cu	15	.53	.4	0
10	40	Cu	12	.67	.5	0
10	10	Ni	13	.49	.4	0
10	40	Ni	10	.56	.6	3
40	10	Cu	14	.63	.5	0
40	40	Cu	13	.79	.6	2
40	10	Ni	15	.70	.5	0
40	40	Ni	11	.83	.7	2

F - Maximum Force in milli-newtons
S - Time constant in seconds
P - Time to buoyancy in seconds

Samples were plated in each of the electrolytes to thickness of 10 and 40 microinches over pure copper and nickel plated copper substrates.

The substrate did not appear to have a significant effect on the solderability but in all cases the thicker deposits showed inferior results as was expected. There was little difference between the samples plated from equivalent cobalt and nickel baths and the only sample showing marginal solderability (Figure 3) was from Electrolyte A plated to 40 microinches at 40 ASF over copper.

No definite correlation was seen between the cobalt or nickel content of the deposit and solderability and it appears that the deposit structure and organic content have more effect than the hardening metal. The samples showing the best solderability were those plated at lower current density giving a finer grained deposit and lower carbon and potassium contents but higher metal content. The exception to this is Electrolyte A which has a higher cobalt content at 40 ASF but exhibits inferior solderability.

Contact Resistance and Thermal Aging

At this time there is insufficient formal data for presentation and this may be the basis for a future paper. However, general observations indicate that there is little difference in contact resistance between similarly produced cobalt or nickel hardened gold deposits.

The effects of thermal ageing on contact resistance appears to relate more to carbon content of the deposit rather than transition metal content.

Magnetic susceptibility of deposits may influence the choice of cobalt over nickel additives for specific applications. This property has not been included in the current project.

Conclusions

Deposit analysis indicates the possible existence of several codeposition mechanisms related to electrolyte pH and current density. Some differences were observed between cobalt and nickel systems.

Internal stress is generally comparable and shows little correlation with deposit composition. Evidence of stress relieving was seen, possible due to microcracking.

Solderability of the deposits has been quantified and the results indicate generally little difference between cobalt and nickel hardened gold deposits. This result is surprising since nickel hardened gold deposits are believed to be generally more readily solderable than cobalt equivalents. In only one case did this belief hold true. The results indicate that if deposit impurities, other than the alloying metal, are controlled than solderability might be enhanced.

Areas for further work might include; nitrogen analysis of deposits, contact resistance as deposited and after ageing and magnetic susceptibility.

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