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Title: Evaluation of Chemical Coating Processes for AXAF

1.0 Background:

The need existed at MSFC for the development and fabrication of radioisotope calibration sources of cadmium 109 and iron 55 isotopes. This was in urgent response to the AXAF program. Several issues persisted in creating manufacturing difficulties for the supplier. In order to meet the MSFC requirements very stringent control needed to be maintained for the coating quality, specific activity and thickness. Due to the difficulties in providing the precisely controlled devices for testing, the delivery of the sources was seriously delayed. It became imperative that these fabrication issues be resolved to avoid further delays in this AXAF observatory key component.

Objectives:

1)   Research and provide expert advice on coating materials and procedures.
2)   Research and recommend solutions to problems that have been experienced with the coating process.
3)   Provide recommendations on the selection and preparation of substrates.
4)   Provide consultation on the actual coating process including the results of the qualification and acceptance test programs.
5)   Perform independent tests at UAH or MSFC as necessary.

2.0 Fabrication and Testing of the Devices:

During the course of developing the radiation sources several issues were addressed. Foremost in difficulty was the fact that the sources could only emit the prescribed x-ray energies and no other secondary radiation such as alpha or beta radiation by decay. This required that either of two approaches be taken.

1)   Plate onto most any suitable substrate with radioactive isotopes of ^{109}Cd and ^{55}Fe using best process approach.

2) Plate onto a discrete ultra-pure substrate with very selective processes using a lower isotope of ^{108}Cd and ^{54}Fe to be irradiated.

The first approach was to have Isotope Products of Burbank, California electrodeposit radioactive cadmium and iron directly onto the substrates. The other approach to be developed was to deposit an isotope of each metal which could subsequently be irradiated by neutron bombardment to the required isotopes of ^{109}Cd and ^{55}Fe. This required deposition of the isotopes ^{108}Cd and ^{54}Fe which are not radioactive but extremely expensive, about 2 million dollars per troy ounce if one were to measure this way. Needless to say the amount needed and the amount purchased of each was to be far less than this number.

The experimental work was performed with naturally occuring isotopes of ^{112}Cd and ^{56}Fe. Therefore a total of three isotopes of each material had to be dealt with. With the irradiation approach the very stringent requirement of no additional radiation required a very careful selection of substrate materials and interim processes. The irradiation would cause emmissions from most materials. The selection by NASA was to use ultra-pure aluminum, aluminum oxide and a thin copper layer for adhesion which would become irradiated but would decay rapidly to a harmless value. This substrate was then plated with the ^{108}Cd and ^{54}Fe isotopes followed by a final protective coating of aluminum oxide as a moisture barrier.

2.1 The sources produced by electrodeposition of the isotopic materials were according to proprietary methods. In all due respect for the proprietary issue of the company (Isotope Products Laboratory, Burbank, CA) the exact procedures in place are not revealed.

The primary issues include deposition parameters and measurement and control methods to assure an integral coating which will not release even the slightest measurable amount of material which could be dropped into the system during launch due to vibration. This was measured as the residual radiation after washing a source with alcohol and filtering the eluent. The residual radiation must be below 5 nanocuries measured at the strongest x-ray lines. The choice of substrate materials and process parameters were defined in detail to assure that the sources meet all requirements both for emission performance and integrity. The integrity must be assured for the life of the satellite.

2.2 Solutions to the problems with the coatings included testing to determine the electrochemical behavior of the deposition processes. Plating processes were formulated and tested using the anion - cation pair which constitutes the radio isotopic material available to produce the sources. The conductivity, solubility, limiting current density, supporting electrolyte requirements and self corrosion rates of the deposit in the electrolyte and the corrosion rate of the substrate were determined. An additional problem was the fact that only a very small amount of the isotopic material was available and an even more arduous smaller quanity could be handled in any one plating procedure. This is to insure the specific activity is high while the total emission is conservative. This task established the logical ratio of isotope to cold material and the minimum concentration of total metal which will still produce sound deposits as required.

2.3   In order for the cadmium starting layer to adhere to the substrate metallurgically it is imperative to have the proper conditions. The first condition is that the substrate be compatible with the cadmium plating process such that spontaneous high corrosion or rapid oxidation and passivation do not occur. The second condition is that the substrate be clean metallurgically. This mandates that the plating solution must remove any traces of surface contaminants including oxides or that some other solution plus rinsing is used. The total volume of the cell must be exceptionally small for this process. Also it is very difficult to implement a series of cleaning and rinsing procedures due to the very small size of the cell.

2.4   Material properties of selected substrate candidates were compared and an evaluation including plating and testing of the deposits was performed. Corrosion data for the substrate in the cadmium plating solution was be evaluated and the required plating parameters for coating candidate substrates considered. It is desirable to have a marginal attack on the substrate material such as on silver or gold to ensure adequate adhesion of the plated cadmium. A material such as nickel can be used for the substrate but it will be more difficult to achieve adhesion due to the spontaneous passivation in the cyanide cadmium plating solution. Testing and evaluation processes determined all the better parameters including cleaning and encapsulation processes. The attenuation of the candidate encapsulation layers was determined by NASA and the application processes were determined and evaluated during this effort. The requirements of any coating were determined by NASA during the qualification and acceptance test program. UAH continued to provide consultation on the coating processes for this effort.

2.5   UAH provided testing independent of IPL in Burbank as required. This was done on site at MSFC as required. Testing included the stringent requirement that the sources produced must withstand ultrasonic cleaning. Travel to the isotope contractor's facility (IPL) to review and consult on these processes was required throughout the task.

3.0 Preparation of X-Ray Sources by Isotope Product Laboratories (IPL) Method 1

This method was selected as the final approach to the fabrication of the radiation targets.

3.1 Description:

Cadmium 109 isotope is to be coated to a deposited activity of 3.0mCi ± 10%.
This deposit is to be overcoated with gold by sputtering 1000 Angstroms thick over a 10mm circle. This is an addition to drawing 97M23663.

Iron 55 isotope is to be coated over the cadmium to a deposited activity of 2.17mCi ± 10%.

The substrate surface selected is gold-10% wt. copper to Dwg. 97M23663. This substrate was selected in order to assure the maximum adhesion of the cadmium deposit with a minimum of preparation.

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3.2 Considerations - Cadmium 109 -

The cadmium 109 will produce x-ray energy at several lines. These range from 88Kev to 3Kev. The lower energy lines will not penetrate to the required intensity through a deposit of cadmium (112/109) with a low specific activity as readily as the higher energy lines. Therefore in order to maintain an appropriate source ratio of high to low energy, the deposit must be thin. This in turn mandates that the specific activity be high.

Problems were encountered in deposition of high specific activity ^{109}Cd.

The ^{109}Cd plating material is more hazardous than the ^{55}iron due to the higher energy. In order to have a suitable Cd concentration at an appropriate specific activity the ratio of Cadmium ^{109} to Cadmium ^{112} must be at an activity of about 20 mCi/mgm of cadmium metal ion in solution. This in turn dictates that no more than 5 ml of solution be prepared in one vial for personnel handling with reasonable lead shield protection. Furthermore when using the Teflon cell designed by IPL no more than 1 mgm of 20mCi/mg is desired in order to achieve a total thickness Cd ^{109}+Cd ^{112} between 1000 angstroms and 3000 angstroms.

The plating solution is therefore about 1 ml volume and 0.01 Molar in Cd. This represents an extremely dilute solution of very small volume. In order to plate a sound adherent deposit it is necessary to plate at about 10% of the conventional Cadmium plating current.

This in turn creates new problems:

1) The corrosion rate of gold into the cyanide cadmium plating solution is significant at 14.9 ugm/min/cm^2.

2) Redeposition of the gold will likely occur but not necessarily as a sound Cd-Au alloy since the standard electrode potentials are not within 25 mv.

3) Corrosion of the cadmium in the same solution is also significant. This was determined by linear polarization corrosion measurements by MSFC.

It will be necessary to exceed the potential of gold corrosion to deposit cadmium and a further increase in current density is required to obtain a coherent deposit of cadmium.

It has been derived from measured data that the specific activity of the deposit is equal or at least nearly equal to the specific activity of the dissolved ionic cadmium.

3.3 Considerations - Iron 55

The iron 55 also produces lines at different intensities. These range from 6.49 to 0.556 Kev. The lower energy lines again are limited by the same restraints as the Cd 109.

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This mandates an iron layer of about 1000 angstroms thick at the specific isotope ratio of the proprietary solution. Again about 1 ml of solution is used. The deposit appears to be quite crystalline which is to be expected for the given plating conditions.

Ideally the iron will overplate the cadmium/gold area slightly to reduce edge effects.

3.4 Considerations - General

Based on the above criteria certain practices have been implemented:

1)   The cell will be prepared for plating and installed in the shaker used for agitation prior to adding solution.

2)   A resistor will be placed temporarily across input to cell and current will be set to apply small forward bias:

        o   50 ohms is used for Cd at 5mA, (0.159V).
        o   75 ohms is used for Fe at 20mA, (1.5V).

        This appears to eliminate or at least minimize corrosion of the substrate into the plating solution.

3)   A 1000 Angstrom layer of gold is coated over the CD.

4)   A 400 Angstrom layer of gold or; 2200 Angstrom layer of nickel is coated over the iron.

        The coatings 3 and 4 are to minimize any chance for isotopic material to fall onto the final product detector.

5)   Reduction potential plus overpotential at the anode is about 1.4 volts (calculated) so the -0.159V is only enough to slow the corrosion of gold, especially with the CN solution added. The impedance of the solution is about 2K ohms and the cell voltage is about 2.86V at the start and decays to about 3.28V after deposition of 0.2 mg Cd.

6)   Cleaning by ultrasonic agitation has been implemented at each interface.

        Alcohol rinse is 50% each EtOH + MeOH.
        Water rinse is high purity.
        Weigh sample prior to and after Cd and Fe plating.

3.5 Cadmium 109 Plating Process:

3.5.1   Clean Au-Cu (90-10) source substrate -

Rinse with pure acetone
Rinse with pure H2O
Ultrasonic clean in pure H2O

NOTE: Do not touch with fingers or with gloves.

3.5.2   Plate cadmium 109 -

1 mg/ml Cd total metal
20 mCi Cd 109 per mg total Cd specific activity
0.01 M KCN, 100ppm Thiourea
100 ppm Surfactant
0.2 M potassium citrate

Premix plating solution - 5cc

Place clean substrate in cell and assemble

Attach BNC cable to power supply

Attach alligator clips to cell, red = pos, black = neg.

Attach BNC 50 ohm resistor to BNC Tee.

Set power supply to 3.18mA (5mA/cm2) and switch on.
Check to be certain overvoltage light is off.

Add 1.1 ml of plating solution

Switch agitation on--approximately 1.0 inch stroke X 180 strokes/min.

After 15 seconds - remove resistor and attach voltmeter.

After 45 additional seconds reduce current to 1.32 mA (2mA/cm2).

Plate 2750 to 3100 Angstroms Cd, 18-19 minutes total. (Measure activity of first piece and adjust plating time to plate 2.0 mCi). Observe voltage and record periodically. The final voltage should reach about 3.27 volts.

3.6 Cleaning Procedure -

Pour all of plating solution into separate vial.
Rinse thoroughly with pure H2O.
Let cell dry before opening.
Open cell and remove source.
Rinse with pure H2O.
Rinse with alcohol.
Ultrasonically clean 30 seconds in 50ml H2O.
Rinse with alcohol-pure water-dry.
Measure activity--2.0mCi±10%
Weigh sample and record.

3.7 Plate gold -

Sputter 1000 Angstroms Au over 10mm circle centered on 9mm Cd circle.
Weigh sample and record.
Repeat 2.3.5-2.3.8 inclusive
Measure leakage -
Rinse with 20 ml alcohol mix
Collect alcohol in syringe and filter assembly with 0.2-0.5 micron membrane.
Filter alcohol and cut open filter.
Measure activity of filter--should be less than 5nCi above background.

3.8 Iron 55 Plating Process:

Iron 55 Test -

In order to test the iron adhesion and integrity two test pieces will be prepared for comparison.

Au/Fe/Au/Cd/Au-Cu substrate (1)

(a)   Plate 1000 angstroms Au in 10 millimeter circle over Cd/Au-Cu substrate, weigh and measure activity per 2.4 through 2.5.4.

(b)   Plate 2.17 mCi Fe 55 in 9mm circle over Au/Cd/Au-Cu, clean, weigh and measure activity.

(c)   Plate Au 400-500 angstroms over 10 mm circle.

Ni/Fe/Au/Cd/Au-Cu substrate (1)

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(a)　Plate 1000 angstroms Au over entire source face after plating Cd and cleaning per 2.0 through 2.5.4 and weigh.

(b)　Plate 2.17 mCi Fe 55 in 9mm circle over Au/Cd/Au-Cu, clean, weigh and measure activity. (See next sectiuon for details)

(c)　Plate electrolytic nickel 2200 angstroms over entire source face, clean and weigh.

Compare results of leak test and record.

(a)　Perform leak check on each part per 2.5 through 2.5.4.

(b)　Select process with the least leakage.

3.9 Plate Iron 55 -

The specific activity of Fe 55 is to be sufficient for 2.17 mCi in approximately 1000 angstroms.

Gram mass Fe in 1000 A deg x 9mm 0;

gm Fe= 7.86 * thickness * (0.452)(1.0x10-5) gm

$gm\ Fe = 5.00x10^{-5} = 50u\ gm$

Specific Activity = 2.17 mCi/0.05mgm

Specific Activity $\geq$ 43.4 mCi/mgm Fe in solution

The efficiency of the proprietary iron plating solution is very low.

The plating is performed at　20 mA/0.636cm or 31.4 mA　cm^2, which is very high for a dilute solution.

The high current was determined to cause corrosion of the Cd coating. With Au over the Cd the corrosion is however minimized and it may be desirable to reduce this value.

The high C.D. will however produce good coverage over the Au plated Cd if porosity exists. No burning is noticed for the Fe deposit up to this value.

Solution consists of a proprietary Ferric ammonium chloride in sodium carbonate and ammonia solution. One ml at S.A. of about 50mCi/mg is used.

3.9.1   Plate iron -

Clean:
Rinse with pure acetone
Rinse with pure H2O
Ultrasonic clean in pure H2O

NOTE: Do not touch with fingers or with gloves.

Plate per 3.5 except --

75 ohm resistor
Set power supply 20 mA
Plate 11 minutes
Plate 900-1100 Angstroms Fe
Clean per 3.9.1

3.9.2   Measure activity to be 2.17 mCi Fe 55 $\pm$ 10%

Weigh sample and record

Plate gold 500 Angstroms by RF sputtering or nickel 2000 Angstroms by electrodeposition
as final cover: (To be Determined by NASA)

3.10   Final Leak Test per 2.5.1-2.5.4

4.0 Non-Radioactive Isotope Plating on Pure Alumunum (Method 2)

Although not selected in the final analysis a significant effort has been put forth to produce the
end products through the use of electrodeposition of Cd^{108} and Fe^{54} which in turn were sent to
Oak Ridge National Laboratories for irradiation. The substrates were aluminum believed to be of
the highest puity obtainable. The processes used for the plating were as described for the plating
of the gold substrates with the sulfamate cadmium and the non-alloyed alkaline iron process
selected.

4.1 The aluminum was electropolished in a phosphoric - hydrochloric acid mix. The substrate
was then coated with an aluminum oxide adhesion layer followed by copper. These coatings
were about 500 - 1000 Å thick applied by RF sputtering at MSFC. The substrates were masked
with photomask and plated in a small cell using the very minimum of the extremely expensive
isotope metal salts. The cadmium was purchased as the oxide and dissolved into sulfamic acid.
The iron was purchased as the metal isotope and dissolved in a minimum amount of sulfuric
acid. A minimum amount of each solution was then prepared and used in the miniature plating
cell for each of four sizes. All sources were ultrasonically cleaned after plating the cadmium and

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iron. No gold was used to increase the output and eliminate the chance for irradiation to unwanted isotopes. The deposits were very sound with about half of the samples leaving very small particles from the edges, later detrmined to be due to break down of the photomask. However all samples were cleaned ultrasonically and polished with 0.3 micron alumina prior to a final overcoat of alumina by RF sputtering. All work was non-radioactive and was completed at MSFC in the 4612 Corrosion Laboratory.

The electroplated sourcees were sent ORNL for a one month irradiation in the swimming pool reactor using neutron bombardment from a beryllium source. Upon cooling the irradiated copper to safe levels the deadline time for the installation was nearing. Tests by MSFC using MICOM counters revealed that of all things unexpected the sources were contaminated with scandium, either from the base material or some unknown cause during fabrication or irradiation. This caused unacceptable emissions other than the x-ray lines predicted. Therefore it was neccessary to very heuristically proceed with the sources from IPL.

4.2 The renewed effort at IPL required that the substrates of gold alloy be wire cut to achieve a small tab for locating the sources in the respective mounts. This caused a new problem in that the edges were rough and required hand polishing and subsquent vigorous ultrasonic cleaning. Figure 1 shows the type of defects left by the wire cutting prior to hand polishing.

After polishing the samples were sent to IPL for the plating. Both UAH and MSFC sent personnel to IPL to monitor the coatings. Althogh the procedures to be defined in Appendix I were given to IPL their decision was to use only a portion of the tested methods. The reasoning was that they had experience with the radioactive isotopes using IPL proprietary procedures and UAH/MSFC had only worked with each of two non-radioactive isotpes. Although no known reason was evident for electrodeposition to be different the apprehension, time constraint and extraordinarilly high material costs drove this decision. As a result the adhesion and residual material which was shown to be close to zero for the aluminum parts was significantly poorer for the final parts.

5.0 Definition of Plating Processes

Faradaic Equivalency -

Faraday's Law is absolute and must account for all material reduced at a cathode. The cathode efficiency is defined as the net metal plus reaction products, predominantly hydrogen, deposited for the equivalent current and time of application.

Faraday's Law;

$$\frac{\text{Mass (milligrams)} = \text{M.W.} * \text{Time (sec)} * \text{I (mA)}}{\text{n(valence electrons)} * 96500 \text{ (Faraday's Constant)}}$$

$$Cd\ gm = \frac{112 * 2x10^{-3}*20*60*0.646}{2\ *96500} = 8.997x10^{-4}\ gm$$

$9.0x10^{-4}$ gm = 900 ugm = 45 ugm/min

Actual rate = 9 ugm min

Efficiency = 20%

Actual current at limiting value = 0.4 mA/cm2

Original estimate was 0.5 mA/cm2 but produced low cadmium deposit. Note that this was with citrate at 0.1N. The citrate was later raised to 0.2N to minimize burning (dendritic deposits due to diffusion limitation through double layer. The use of thiourea and surfactant had been employed.

At 0.2 N citrate, the limiting current density would be expected to decrease slightly but the deposit would hopefully be more repeatable and smoother with excess current carried by the citrate. Some reduction of both citrate and thiourea may occur at the substrate. Also oxidation could occur at the platinum anode, more so for the thiourea than citrate. The very low concentration of thiourea should prevent excess carbon or sulfur from being produced at the cathode. The total current passed is about 0.4 mA-Hr/milliliter which would result in the 45 mgm/min rate for cadmium at 100% efficiency. The effective metal removed by corrosion is 0.04 mgm/Hr which must be offset. The net result is that hydrogen evolution is about 70% accountable for the reduction current.

The cell voltage started at 2.86V @ 2 mA/cm2 and rose to 3.27V in 18 minutes. About 1.4 volts is reduction and 1.4 is overpotential at the electrodes and resistance of a very complicated nature depending on agitation, hydrogen production, reactions with the supporting electrolyte and temperature.

Although the use of true reference electrodes was not employed, this change of cell voltage should be a good measure of the amount of cadmium removed from solution in a short time at constant temperature. The change of 20% loss in metal corresponds approximately to the 29% change in the approximately 1/2 of the cell voltage predominantly due to reduction of cadmium and a combination of changes including the conversion of the surface from gold to cadmium resulting in increased cell impedance. This is measured as the voltage increase at constant current.

The same logic follows for the iron deposition with the substitution of the molecular weight for iron and a valence of three due to the fact that the iron is assumed to be complexed to ferric iron with ammonia although sufficient detail on the proprietary process for depositing

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the iron was not available. It can be expected that the limiting current density for deposition is about 0.5 mA although this has not been confirmed by polarization tests as in the case of the cadmium, and that the efficiency is perhaps even lower than 5%.

The rate tests performed indicated a plating thickness of 1000 angstroms, producing 2.2 mCi, required about 10 to 11 minutes when plated at 20 mA. Actually the amount of iron increased when the current was reduced from 71.6 mA to 20 mA. This may have been due to excess hydrogen formation at the extremely high current density, which along with oxygen produced at the platinum anode, may have simply blocked transport of the metal ions to the cathode surface, increasing the cell voltage beyond the limit of the compliance of the source. The plating rate even at 20 mA is considerably below the rate which would be achieved at 100% efficiency. With the introduction of the gold layer between the iron and the cadmium layer it should not be required to use such high current density to avoid the corrosion of the cadmium.

One additional consideration is the area of the platinum anode. If the area is small compared to the cathode then the evolution of oxygen at the anode may cause a significant rise in the cell voltage resulting in a similar limiting effect if the compliance is too low to overcome the increased impedance.

With sufficient knowledge of each process it would be possible to control the cell voltage to the minimum value for complete coverage and avoidance of corrosion and plate the metals coulometrically to achieve accurate thickness or mass values. For such a small and dilute plating process however this is extremely difficult.

The use of quartz crystal oscillator nanobalance technology would appear to be a better and more viable technology. It should be readily possible to use a circular quartz crystal of the required dimensions, masked and coated with gold or platinum to the 9 millimeter central dimension for the Cd and Fe, as the substrate and monitor in real-time the deposition rate and thickness to one part in one thousand or better.

The test pieces were plated in a relatively conventional process consisting of one of the following compositions:

Bath (I)

1)	30 gm/L	Potassium Chloride
2)	30 gm/L	Boric Acid
3)	30 gm/L	Ferrous Chloride Hydrate
4)	0.5 gm/L	EDTA (Acid) or Citric acid
5)	2.5 - 3.0	pH adjusted down with sulfamic acid
6)	110	Deg. F.

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Bath (II)

1)   (2 -5) gm/L   Ferrous Sulfate
2)   50 - 200 ml/L   NPA Surfactant
3)   25 - 50 gm/L   Sodium Citrate to pH = 7.0 to 7.5
4)   0 - 20 gm/L   Boric Acid
5)   10 - 40 mA/cm^2 Pulsed plating with 10% duty cycle on - 90% off
7)   Substrate   22 carat gold, Stainless steel or copper/A$_2$lO$_3$/Al

Bath (II) was selected for the plating of the samples with the expensive isotopes.

Cleaning   Polish with 1000 then 2000 grit SiC, followed by 1 micron alumina.
            Rinse and clean ultrasonically in Bowden AW-100 Citrate based cleaner.
            Rinse in Deionized water.
            Assemble in holder and immerse with no current into iron solution.

The samples were held in an EG&G corrosion cell with Kalrez rectangular cross section seal. Stirring was performed with a magnetic stir bar on hot plate.

The test was to determine the effect of the seal edges on the quality of the plating. It is desired to have very uniform edges with good adhesion overall. When the iron is plated onto the sample at high current density, hydrogen is evolved and the bubbles cling to the sample edges. By lowering the current density the problem is minimized but is not eliminated. Upon adding surfactant to the process to lower the surface tension and lowering the current density to lower the amount of hydrogen formed it is possible in this process to very nearly eliminate the effects of the bubbles.

Several tests were performed at the zero surfactant level and even at the lowest current density of 10 mA/cm^2 the iron would appear scalloped around the edge of the seal. This persisted even when the stir bar was at maximum velocity.
When the gold alloy was plated in this fashion the scalloped edges were non adherent and some particles were removed by the cellophane tape tests. This high rate of agitation would not be achieved in the small Isotope Products cell with the shaker table only. By adding small amounts of sodium laurel sulfate, which is a common nickel plating surfactant, it was possible to achieve a much better coverage in the crevice between the seal and the substrate.

The first samples were plated with no surfactant at about 35 mA/cm^2. This approximates the process at IPL. The iron solution used by IPL had no surfactant and also the current density was about this value for the latter plating tests.

The second samples had a small amount (10 ppm) of NaLSO4. The plating was at 10 mA/cm^2. This sample was improved but still shows some effects of hydrogen trapping at the edges.

The third sample had a higher level of surfactant (25 ppm) and the current density was again 10 mA/cm^2. This sample was much improved over the other two pieces. No particulates were noted in the tape test. Tests were also performed with the NPA surfactant which appeared to be more consistant in the results obtained. This additive in larger quantity increased the iron deposition rate and efficiency dramatically and as such was selecterd.

The addition of the sodium laurel sulfate (SLS) surfactant in larger quantity to the plating solution may make the iron deposit more brittle. The iron plating also seemed to degrade the photomask. The cause of this was not determined but appeared to be the result of the low efficiency causing hydrogen evolution.

An appropriate fabrication sequence includes cleaning, assembling, current limited plating and final rinsing. A number of experiments were performed with the following solution formulation and determined that it is possible to plate the cadmium from a non-cyanide solution which does not measurably attack either the gold or itself in the nominal processing time. This formulation appears to plate smooth cadmium from 2.6 mg/ml down to essentially zero cadmium extinction without additives such as surfactant or thiourea. For concentrations above 2 mg/ml the current density may be up to 3.0 mA/square cm. Below this the current density must be lowered but appears to produce sound deposits as low as one mA/square cm. The cadmium solution tested was:

Sulfamic acid	3.6	mg.ml
Boric acid	30.0	mg/ml
Potassium sulfate	60.0	mg/ml
Cadmium oxide	2.28	mg/ml

Cadmium oxide ..... 2.28 mg/ml (2.0 mg/ml as Cd)

Dissolve CdO and then adjust pH to 1.5 with sulfamic acid

Also a series of tests with the iron plating was completed. This metal deposition occurs so near to hydrogen that it is very difficult to achieve high efficiency at low current density. Rather the deposition efficiency actually increases up to about 20 mA/cm^2. For solutions under about 5 mg/ml, the use of a pulsed current was advantageous. A pulsed signal of 100 to 200 mA/cm^2 for a duty cycle of 10% on - 90% off with a cycle time of 10 milliseconds was used. This produced an average current density of the same proportions as was used for direct current plating. With these conditions it was possible able to achieve about 60 - 70% efficiency with as low as one mg/ml Fe in solution. Other experiments included addition of nickel to the iron plating process and markedly improved the quality of the deposit.

Although much data is available for plating of Ni-Fe it remains to test the alloy and quality of a process suitable for plating these parts. The use of a specific surfactant and the elimination of a strongly conductive supporting electrolyte improved the quality of the deposit. The use of a commercial surfactant NPA, from Allied Kellite (now McDermid) at 100 to 1000 ppm and the addition of only boric acid at 20 mg/ml produced excellent quality iron deposits from iron sulfate produced by dissolving iron metal stoichiometrically in

sulfuric acid and adjusting the final pH to within 2.2 to 2.3. The efficiency was sensitive to agitation with higher efficiency at lower agitation. Some of the parameters appear to be conflicting with reason but were verified several times.

When the NPA was used in excess of about 200 ppm some included carbon was evident from a darkening of the deposit if it was subsequently dissolved in mild sulfuric acid.

Significant work was also performed with the use of a masking material to provide sharp edges, particularly with regards to the iron. The use of ultraviolet developed materials from Shipley and others behaved similarly, with the best results obtained from Shipley 4620 cured at elevated temperature. This material could easily be removed with acetone if cured at less than 120° C. When the material was cured at higher temperatures it was tougher and also more resistant to the acetone. A more severe stripper (NMP) is available but is more difficult to handle than acetone. Alternate printed wiring board masking materials which are readily stripped are available but require special equipment for the application. The following general process steps work.

1)   Clean gold with electronic grade acetone;
2)   Rinse with high purity water;
3)   Dry with nitrogen or pure air;
4)   Apply photo mask in clean fixture.

Note that acetone will leach material from the gloves or hands and spread a film over the parts which will adversely affect the plating. Therefore the parts must be held by inert tweezers or some fixture, preferably by the edges, during the solvent cleaning.

5)   Plating solutions formulated per the following formulations were found to produce excellent deposits. The metal concentration should be in excess of 1 mg/ml if at all possible. The use of the surfactant and the thiourea in the cadmium was found to be unnecessary.

The power supply sent to IPL is a very precise laboratory instrument and will provide the control needed to assure uniformity in thickness from part to part at the very low current range required for the cadmium, the use of pulsed plating as described is strongly recommended for the iron.

By Faraday's Law ie, weight of metal / Amp * seconds = (MW * 1) / n * 96500 gms/A*s. The following estimates for the control of thickness of both isotopic and non-radio isotopic deposits of cadmium, iron and also non-isotopic nickel are obtained at about 70% efficiency. The efficiency of the cadmium was about 70% and for the iron varied from about 40% at the lowest concentration of 1.0 mg/ml to about 75% at 10 mg.ml with slow agitation.

Thickness Angstroms Area Plated	Isotope At. No.		Plating Time Min.	Current mA
12000 cm^2	108 Cd +2	18.0	2.0	0.635
12000	112 Cd +2	15.0	2.0	0.635
6000	54 Fe +2	1.70	16.5	0.635
6000	55.85 Fe +2	1.54	16.5	0.635
3540	58.7 Ni +2	3.50	6.3	2.0

Note that the electrolytic nickel as a final coating is optional over the vacuum coated nickel. If the electrolytic coating is used then the additional area must be plated which will require a second fixture. Also iron oxidizes very quickly and so the nickel would need to be plated over the iron soon after the plating of the iron or else the part would need to be stored in a dry box.

6)   Coat cadmium using NASA sulfamate solution in a cell as before except not masked by the chimney fixture down to the part spot size since the photo mask will take care of this issue. The sulfamate solution may remain in contact with the gold with no applied current and still produce very good adherence without excessive corrosion to the gold.

7)   Coat iron with proprietary solution. It appears that the valence (n) is + 3 but not knowing the exact formulation process this is uncertain. If the valence should be +3 under the appropriate conditions, then the plating time will be about 3/2 that listed for the same efficiency. The weight per unit time can be verified if a sufficiently accurate scale is available Note that if the iron solution is alkaline then the photomask must be fully cured and removed with stripper other than acetone. An alternative is to adopt the pH 2.2 acid sulfate solution tested at NASA. This solution was demonstrated to have very low corrosion effects on the cadmium deposit. Also since the lower iron x-ray line is lost due to a window, then the use of nickel in the iron plating solution as the "carrier" should seriously be considered. This alloy plating in conjunction with the pulsed plating should minimize the problems with hydrogen codeposition or "burning" even at very low metal concentration. The use of nickel in the iron plating process also produces an alloy which is more resistant to corrosion than pure iron.

8)   The iron or iron - nickel alloy can be plated over the cadmium with good adherence in this process with very little attack on the cadmium. The masking is next removed. The overall process must be discussed.
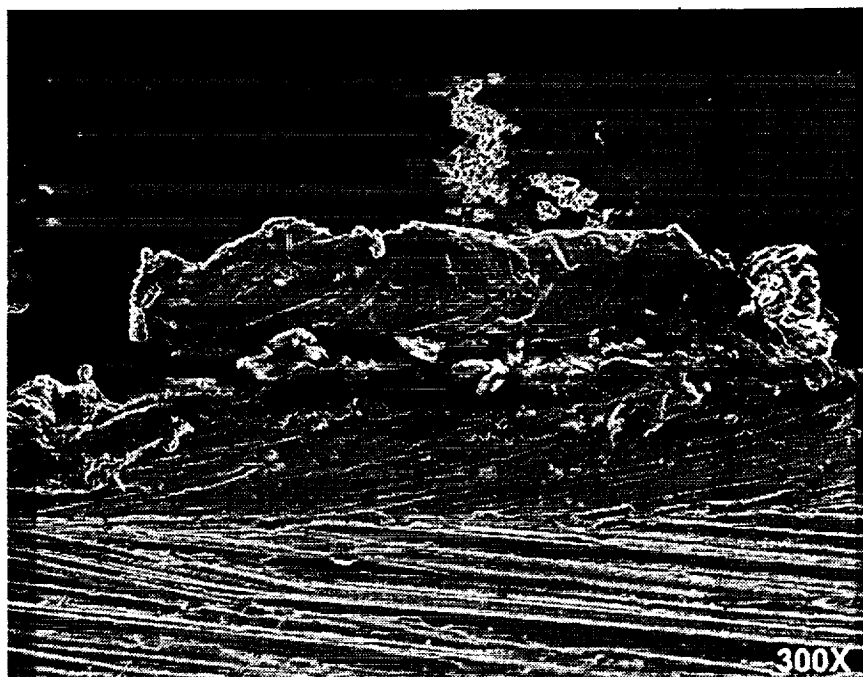
9)   Coat final sample with nickel or gold. It may be possible at this point to use a circular frame for the parts and simply plate the nickel from a common beaker.

6.0   Recommendations:

It appears that the addition of the surfactant in an iron solution which is stable and plates at high Faradaic current efficiency (low hydrogen) is mandatory in this type operation. Also the current density for the plating should be low to avoid the formation of hydrogen. The hydrogen will permeate the iron and cause adhesion and embrittlement problems. This is no different than the cadmium plating issues. The cadmium posed the additional difficulty of passivating some substrates of nickel or corroding substrates of gold, silver or copper. The iron solution corrosion on the cadmium should not pose a problem since the cadmium will plate preferential to the iron. The same procedures can be used to avoid the initial corrosion occurring with the gold. That is to start the plating by filling the cell with a small bias applied to start the plating immediately. An option to the formulation of a more suitable iron plating process is to simply add the isotopic iron to a standard nickel solution with a small amount of EDTA and the pH reduced. This would still behave similar to the present process except that the iron 55 would preferentially plate out in a higher percentage than its concentration in the solution. This would actually be an improvement since the overall solution concentration could be increased. The nickel would also reduce the corrosion of the coating.

If vacuum coatings are applied it may be possible to use something like silicon monoxide, silicon or dioxide or aluminum oxide to form a protective coating. These coatings are very hard and if the thickness can be increased without absorption at the low energy it should help.

Discussions with Maxtek Inc. of Torrance, CA were very encouraging. This company manufactures a quartz crystal oscillator probe which could be readily modified to produce this part. Although time did not permit this option for this task, it may be possible to adopt this for other programs requiring isotopic sources. The use of a standard unit modified only by manufacturing a small cell to be attached to the unit would still be of significant benefit to the production testing of the meniscal plating processes.

X49-1 edge view

Figure 1

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