Determination of Composition For Electroplated Pd-Ni Alloy Coatings

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Rapid, accurate and precise determination of electrodeposited Pd-Ni alloy composition is essential for controlling and maintaining performance characteristics of the coating system. A procedure that utilizes SEM/EDS to rapidly determine composition has been developed. Commercial use and precision of ±0.2 mass percent Pd has been demonstrated. This paper defines the instrumentation and techniques for accurate determination of Pd-Ni composition, offering numerous advantages over XRF and atomic adsorption.

Engineered electrodeposited coating systems based on Pd-Ni alloy coatings, a nickel underplate, and a thin gold overplate were commercialized in the early 1980s as replacements for electrodeposited hard gold in electronic connector applications.[1] These systems had properties that were equivalent, and in some cases superior, to those of electrodeposited hard gold.[1-5] Assurance of their desired performance, particularly with respect to coating ductility, thermal stability of contact resistance, and resistance to intermetallic compound formation at soldered joints, requires control of the Pd-Ni alloy composition. Other properties of the engineered system, such as environmental corrosion resistance and wear resistance, are strongly influenced by the thickness of the Pd-Ni alloy coating.

The ability to measure Pd-Ni alloy thickness quickly and accurately with bench top X-ray fluorescence (XRF) instruments requires careful control of alloy composition when a nickel underplate is present. If the Pd-Ni alloy composition is held constant, accurate XRF measurements of alloy thickness can be easily obtained by monitoring the intensity of the characteristic Pd K_{α} radiation. If the alloy composition varies, however, an independent determination of both the alloy composition and the nickel underplate thickness would be required to determine the alloy thickness. Because of this complication, the time required for a thickness measurement would be extremely long and its accuracy would be greatly diminished.

The objective of this investigation was to develop a rapid, precise method for measuring Pd-Ni alloy composition, under production conditions, to assure the quality of the product and to facilitate the XRF measurement of alloy thickness. The technique developed uses a scanning electron microscope (SEM), equipped with an X-ray energy dispersive spectrometer (EDS), and it is based upon standards certified by electron probe microanalysis (EPMA).

Comparison of Analysis Techniques

Background

A large number of conventional and non-conventional analysis techniques was considered as potential candidates for measurement of electrodeposited Pd-Ni alloy composition on commercial products with a nickel underplate and a gold overplate. The thin gold overplate component of these systems does not present a problem with Pd-Ni alloy thickness or composition measurement because the gold can be easily removed by conventional commercial stripping solutions without affecting the Pd-Ni layer. The presence of the Ni underplate does, however, influence and, in some cases, severely limit the utility of techniques for measurement of electrodeposited alloy compositions on commercial products, under production conditions.

XRF Technique

If Pd-Ni alloy coatings are plated directly onto pure Cu or Cu-alloy substrates that do not contain Ni, conventional bench-top XRF instruments can be used for accurate and precise measurement of Pd-Ni alloy composition. When they are deposited onto a Ni underplate or a Ni-containing substrate, excitation of strong Ni radiation from beneath the Pd-Ni alloy creates difficulties that diminish the accuracy and precision of the measurement and significantly increase the time required to obtain a result. These difficulties can be overcome if the Pd-Ni coating is deposited to a thickness equal to or greater than about 40 μm, because no radiation will be emitted from the Ni beneath the alloy coating. This is not a practical solution from a process or product quality control viewpoint, however, because the parts currently marketed contain only 0.4 to 3.0 μm of Pd-Ni alloy. Plating Pd-Ni alloy coatings 1 to 3 μm thick onto special pure Cu test coupons is a viable option. A technique for Pd-Ni alloy analysis on actual Ni-underplated products would have obvious advantages.

Atomic Adsorption Technique

Atomic adsorption is also a precise and accurate technique for determination of the composition of Pd-Ni alloys plated directly onto Cu. The time required to calibrate equipment is about two min. After calibration, the time for repetitive analyses, including the time required to dissolve the coating sample and prepare it for analysis, is about 15 to 20 min.

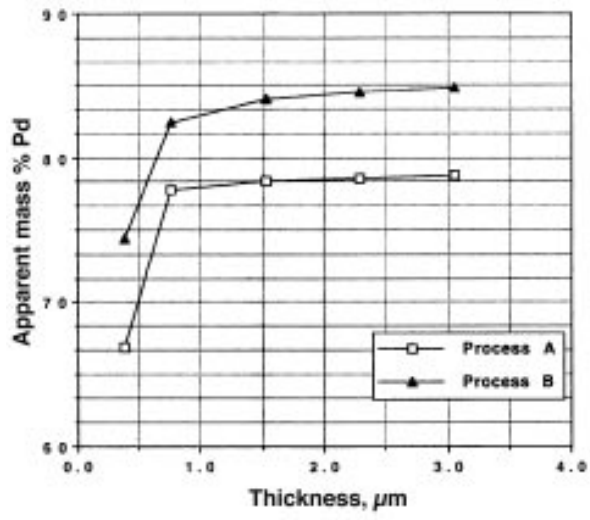

Fig. 1—Effect of Pd-Ni thickness on SEM/EDS analysis of alloy composition in the presence of a nickel underplate.

Use of the conventional atomic adsorption technique to analyze Pd-Ni alloys deposited on Ni-plated production parts would require a separate determination of the amount of Ni in the underplate, because conventional solvents for Pd-Ni will also dissolve Ni. The necessity for separate determination of the amount of Ni under the alloy significantly decreases precision and accuracy and greatly increases analysis time. Although this difficulty might be avoided by development of special strippers or stripping techniques to preferentially remove Pd-Ni alloy from a Ni-plated surface, there would always be a potential source of resulting from dissolution of a small amount of Ni from the underplate. Because the alloys of commercial interest are Pd-rich (i.e., 70 to 95 mass percent Pd), inclusion of a small amount of Ni from the underplate creates a much larger error in the analysis of the alloy.

SEM/EDS Technique

Attention was focused on development of a Pd-Ni alloy composition measurement technique for conventional scanning electron microscopes that are equipped with X-ray energy dispersion spectrometers for two reasons. The first was that principles of physics for characteristic X-ray excitation by electron beam bombardment of metals predict that such an instrument should be able to give quick analyses of the composition of Pd-Ni alloys on top of a Ni underplate, if the alloy coating thickness is greater than, or equal to, about 1.0 μm.[6] This would permit alloy composition measurements on top of Ni for the upper two-thirds of the thickness range of interest for Pd-Ni alloys in electronic connector applications. The time required to charge a SEM with a number of plated parts for analysis will vary with the instrument, but it should be on the order of 3 to 10 min. The time required for repetitive SEM/EDS analyses of the parts is only two min.

The second reason for investigating a SEM/EDS technique was that these instruments are readily available to producers of high-quality electronic connectors for the telecommunications and computer industries. Many of these producers have a SEM equipped with an EDS because of its value in quality control and in trouble-shooting occasional problems. If an in-house instrument is not available, there is a large number of characterization services available.

Table 1
Effect of Coating Thickness on SEM/EDS Analysis of Pd-Ni Alloy Composition

Process	Thickness μin.	Thickness μm	Apparent Alloy Composition Mass % Pd	Δ Error (Mass % Pd)
A	15	0.38	66.9	-11.9
	30	0.76	77.8	-1.0
	60	1.5	78.4	-0.4
	90	2.3	78.6	-0.2
	120	3.0	78.8	0.0
B	15	0.38	74.4	-10.4
	30	0.76	82.5	-2.3
	60	1.5	84.0	-0.8
	90	2.3	84.5	-0.3
	120	3.0	84.8	0.0

Characteristics of the SEM/EDS Technique

Theoretically Predicted Thickness Constraints

An equation developed by Castaing for the depth of X-ray production (D_x) from the surface of a metal bombarded by a high-energy beam of electrons, as a function of physical parameters is:[7]

$$\rho D_x = 0.033\ A/z\ (E_0^{1.7} - E_c^{1.7})$$

where A is atomic weight, z is atomic number, ρ is mass density (g/cm^3), E_0 is energy of the incident electron beam (20 keV) and E_c is the critical excitation potential for the characteristic x-ray radiation of the metal.

The appropriate characteristic X-ray radiation for Pd in a SEM/EDS instrument is L_{α} (3.17 keV), and for Ni it is K_{α} (7.47 keV). The appropriate electron beam accelerating potential is 20 kV. With these parameters, the equation predicts that the D_x for X-ray production from pure Pd and for an 80 mass percent Pd/20 mass percent Ni alloy is 1.0 μm. This prediction means that a large error should occur in the SEM/EDS analysis of Pd-Ni alloys that are plated over Ni as the alloy thickness decreases below 1.0 μm. The apparent mass percent of Pd in the alloy should decrease as the alloy thickness decreases below 1.0 μm as a result of excitation of K_{α} radiation from the Ni underplate.

Experimentally Measured Thickness Constraints

The effect of Pd-Ni alloy thickness on SEM/EDS analysis of alloy composition was investigated with sets of nickel-plated brass coupons plated with Pd-Ni coatings ranging in thickness from 0.38 to 3.0 μm. Analytical results for two sets of coupons plated by two different proprietary processes of significantly different chemistries are reported in Table 1 and plotted in Fig. 1. Process A produced an alloy of 84.8 mass percent Pd/15.2 mass percent Ni, and Process B produced an alloy of 78.8 mass percent Pd/21.2 mass percent Ni. The plots in Fig. 1 indicate that there is an abrupt decrease in the apparent mass percent Pd as the thickness decreases below 1.0 μm, as predicted by Castaing's equation.

Plots of the difference or "Δ Error" between the apparent and the actual Pd content vs. alloy thickness appear in Fig. 2. At a thickness of 1.0 μm, the Δ Error for Process A is only -0.8

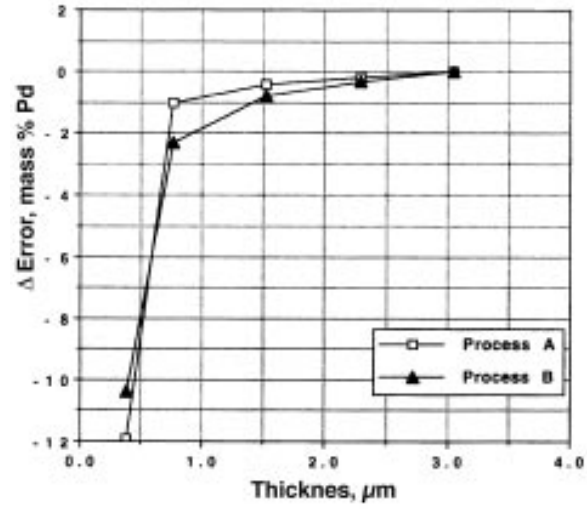

Fig. 2—Delta error in a SEM/EDS analysis because of insufficient Pd-Ni alloy thickness.

mass percent, and for Process B is -1.8 mass percent Pd. These Δ Errors represent extremes of those observed for similar experiment runs with other processes and for other alloy compositions in the range of 75 to 90 mass percent Pd.

Error Analysis and Recommendations

Minimum Pd-Ni thickness levels were established for acceptable alloy composition measurements with Ni underplates based on data and plots similar to those in Fig. 2 for a number of different processes and alloy compositions. Conservative recommendations of minimum Pd-Ni alloy thickness levels for the SEM/EDS analysis technique developed in this investigation are:

- For applications that can tolerate a Δ Error in composition of -2 mass percent Pd, SEM/EDS composition measurements can be made on Pd-Ni alloy coatings equal to, or greater than, 1.0 μm thick.
- For applications that require accuracy within 1 mass percent Pd, a minimum thickness of 1.5 μm is recommended.
- For production of composition standards, the Δ Error should be comparable to the precision or reproducibility of the SEM/EDS technique, which is on the order of ±0.2 mass percent Pd. The recommended minimum thickness to achieve this goal is 2.3 μm.

Certification of Alloy Composition Standards

Standards for the SEM/EDS technique were regions approximately 0.4 cm in diameter in the center of carefully plated coupons whose composition had been certified by electron probe microanalysis (EPMA), using a computer program developed by the National Institute of Standards and Technology (NIST). The electron probe microanalyzer is equipped with extremely sensitive X-ray wavelength dispersive spectrometers (WDS) for determination of characteristic X-ray intensities, and a sophisticated computer program developed by NIST to correct the intensities for background, absorption, secondary fluorescence, and atomic number effects.[6,8]

The EPMA technique is based on pure elemental standards and the selection of the appropriate electron accelerating potential for each element being analyzed. The electron beam was perpendicular to the as-plated surface and the beam was rastered to sample an area 200 X 200 μm. Analytical conditions and typical data for the certification of a standard appear in Table 2. If there is an unexpected impurity in the alloy or if there are pores in the coating system as a result of poor substrate preparation, the sum of the unnormalized data for mass percent Pd, plus mass percent Ni, will be less than 99 percent. This is a criterion for rejection of the sample as being unsuitable for a standard.

The procedure for standard certification is to perform an EPMA of three different areas selected at random in the designated 0.4 cm diameter region and to record the unnormalized data, as shown in Table 2. If the sums of the mass percent Pd, plus mass percent Ni for all three readings is greater than 99 percent, the sample is accepted as a standard and the normalized composition for each area is calculated. The certified standard composition is the average of the normalized mass percent Pd for the three analyses, as shown for Standard SQ-18 in Table 2. The standard deviation of 0.1 mass percent for this standard is typical of that for EPMA analysis of Pd-Ni electrodeposits, and it is indicative of the excellent precision of the technique.

The issue of possible variation of Pd-Ni alloy composition across the thickness of alloy coatings was addressed during the evaluation of six different proprietary Pd-Ni alloy electroplating processes. All yielded alloy coatings with composition profiles that were uniform to ±0.3 mass percent Pd, or better, across thicknesses ranging from 3 to 20 μm. The EPMA analysis of the metallographically prepared cross section of a Pd-Ni alloy standard, shown in Fig. 3, is indicative of the excellent uniformity that can be obtained from a stable commercial process. The EPMA analyses at the three locations indicated on the SEM in Fig. 3 are summarized below:

Location a	Next to Ni underplating	78.87 mass percent Pd
Location b	Mid thickness	78.82 mass percent Pd
Location c	Next to Cu overplating applied for edge protection	78.68 mass percent Pd

The standard deviation for these measurements is ±0.1 mass percent. These and other data indicate that non uniform thickness composition profiles are not a concern in the characterization and quality control of Pd-Ni alloy electrodeposits for the processes evaluated to date.

Composition standards for some electrodeposited alloys, such as those for certain Sn-Pb alloys, exhibit changes in apparent composition during prolonged storage at ambient conditions as a result of unusual diffusion or a solid state reaction phenomenon.[9] Data collected for Pd-Ni alloy samples over the past 12 years have failed to reveal any indication of a significant change in measured composition with time. The results in Table 3 illustrate this. They are also indicative of the excellent reproducibility and precision of the EPMA and the SEM/EDS techniques for determination of electrodeposited Pd-Ni alloy composition.

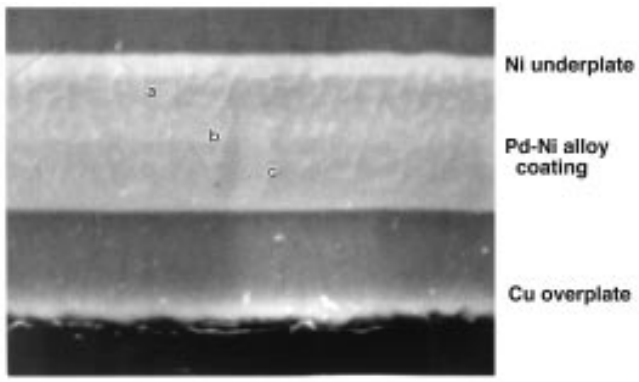

Fig. 3—SEM photo of Pd-Ni deposit cross section showing locations of EPMA analyses. 10,000X.

SEM/EDS Analysis Technique

Normal Procedure

The normal procedure developed for SEM/EDS analysis of the composition of Pd-Ni alloy electrodeposits has worked well on nine of the ten different instruments used for this purpose in the U.S. and Europe during the past 12 years. The group of nine instruments with a successful performance record includes models from four different equipment manufacturers.

Table 2
EPMA Data for Certification of a
Pd-Ni Alloy Composition Standard

Standard Code: SQ-18
Pd-Ni Alloy Thickness: 3.0 μm
Certified Alloy Composition: 83.0 mass % Pd, 17.0 mass % Ni

Location	Unnormalized Data Mass %			Normalized Data Mass %		
	Pd	Ni	Pd + Ni	Pd	Ni	Pd + Ni
Area 1	83.66	16.94	100.59	83.15	16.85	100.00
Area 2	82.30	16.96	99.26	82.94	17.06	100.00
Area 3	82.69	16.90	99.59	83.04	16.96	100.00
Average	82.88	16.93	99.81	83.04	16.96	100.00
	Standard Deviation:			0.105	0.105	

Operating Parameters
Instrument: Cameca Model BMX

Standards	Radiation	Crystal	Count Time (sec)	Voltage kV
Pure Pd	L_α	PET*	20	10
Pure Ni	K_α	LiF	20	20

* A crystal of Pentaerythritol

Table 3
Typical Data Illustrating Stability of Measured
Pd-Ni Alloy Composition as a Function of Time

Sample Code	Analysis Technique	Measurement Date	Alloy Composition Mass % Pd	Δ Change Mass % Pd
SQ-18	SEM/EDS	7/31/91	83.1	
	SEM/EDS	12/12/91	83.1	0.0
	EPMA	7/30/92	83.0	-0.1
	EPMA	10/13/94	82.9	-0.2
8/24/18	SEM/EDS	7/21/82	83.7	
	SEM/EDS	6/14/84	83.5	-0.2
	SEM/EDS	4/8/86	83.7	0.0
	SEM/EDS	3/16/88	83.7	0.0
	SEM/EDS	5/14/90	83.8	0.1

The procedure is based on the use of EPMA certified standards to correct for instrumental errors, such as those caused by changes in filament alignment, stage alignment, and detector performance. It corrects for differences between instruments resulting from model or manufacturer design, and for errors resulting from differences in EDS software programs. The normal SEM/EDS procedure for analysis of Pd-Ni alloys containing 70 to 95 mass percent Pd is as follows:

1. Obtain two EPMA certified composition standards that bracket the desired range of Pd-Ni alloy compositions.

2. Make three Energy Dispersive Spectrometer (EDS) analyses of mass percent Pd in the certified region of each standard under the following conditions:

   Area analyzed: 200 x 200 μm (1000X magnification)
   Accelerating voltage: 20 kV
   Working distance: optimum for the microscope
   Tilt angle: 0°
   Count time: 100 sec
   Beryllium window: in

The sample should be moved slightly between readings, and obvious coating defects such as pores or mechanical damage should be avoided if they are present.

3. Average the three EDS composition analyses on each standard and calculate a correction factor (CF) for each composition standard from the equation below:

$$CF = \frac{\text{(Certified mass \% Pd for Standard)}}{\text{(Average measured mass \% Pd on Day X)}}$$

4. Calculate the average correction factor $(CF)_{avg}$ for the two standards.

5. Make three EDS mass percent Pd composition analyses on the unknown coating samples, according to the procedure outlined in Step 2.

6. Multiply the average EDS mass percent Pd for an unknown sample times $(CF)_{avg}$ for day X to obtain the correct alloy composition.

The $(CF)_{avg}$ is stable, according to our experience, for at least 4 hr, and does not require a repeat determination in that interval. The standard deviation for $(CF)_{avg}$ is usually equal to, or less than, 0.005. If the standard deviation for $(CF)_{avg}$ is greater than 0.010, an alternate procedure should be adopted.

Alternate Procedure

A more complex alternate procedure developed for the only SEM/EDS instrument, for which the normal procedure was unsatisfactory, is outlined below:

1. Obtain three EPMA certified composition standards, two of which bracket the desired composition range and one that is in the vicinity of the mid-range value.

2. Make three EDS analyses of mass percent Pd on each standard under conditions specified for the normal procedure.

3. Average the three analyses for each composition standard.

4. Plot a calibration curve on arithmetic graph paper of the averaged measurement on a standard on day X vs. the certified composition for the standard and determine the line of best fit.

Table 4
Round-Robin SEM/EDS Analyses
Of Pd-Ni Alloy Composition

Analysis Location	Pd-Ni Alloy Composition (Mass % Pd) Sample CS-9	Sample CS-13	Sample CS-24
Research Lab.	85.4	85.3	78.8
Product Qual. Lab.	85.3	85.2	78.8
Plant #1 (USA)	85.4	85.3	79.0
Plant #2 (Europe)	85.4	85.1	78.5
Mean	85.4	85.2	78.8
Standard Deviation	0.1	0.1	0.2

5. Make EDS composition measurements on the unknown samples.

6. Determine the corrected composition for the unknown samples from the calibration curve.

Coating Thickness Effects

The coating thickness constraints for SEM/EDS analysis of Pd-Ni electrodeposits on top of Ni underplates were discussed in detail earlier. The composition of Pd-Ni alloys on Ni underplates can be analyzed to a precision of ±0.2 mass percent Pd by the SEM/EDS procedures outlined above, if the alloy thickness is equal to, or greater than, 2.3 μm. For 1.0-μm-thick Pd-Ni coatings plated over Ni, the Pd content measured by the SEM/EDS technique will be about 0.3 to 1.0 mass percent less than the actual composition. For 0.75-μm-thick Pd-Ni coatings plated over Ni, the Pd content measured by the SEM/EDS technique will be about 1.0 to 2.0 mass percent less than the actual composition.

Round-Robin Analyses

A round-robin evaluation of the normal SEM/EDS procedure for analysis of Pd-Ni alloy electrodeposits was conducted among a research laboratory, two electronic connector plating plants, and a connector product qualification laboratory. The same three samples, plated with alloy coatings of unknown composition, were sent to each location with a detailed procedure and a blank data sheet. The results of their analyses are summarized in Table 4. The standard deviation for the mean of the four independent analyses ranged from 0.1 mass percent Pd for samples CS-9 and CS-13 to 0.2 mass percent Pd for sample CS-24. These data and those from other evaluations have established that the precision of the SEM/EDS technique is equal to or better than ±0.2 mass percent Pd.

Summary

A viable SEM/EDS technique has been developed for quick and accurate determination of electrodeposited Pd-Ni alloy composition on electronic connector products. The technique has been used to control commercial production during the past 12 years, with a demonstrated precision of ±0.2 mass percent Pd in round-robin testing.

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