The Impact of Substrate Roughness on Porosity: A Comparison of Electroplated Palladium, Palladium-Nickel & Cobalt Hard Gold

By E.J. Kudrak, J.A. Abys and F. Humiec

The porosity of electroplated deposits is known to be related to certain substrate conditions, such as inclusions, purity, and particularly, roughness. As few commercial substrates are finely polished, a means of understanding the impact of surface finish was desired. A comparison of porosity was made between electrodeposited palladium, palladium-nickel (80/20) and cobalt hard gold over varying degrees of substrate roughness and deposit thicknesses. OFHC copper disks were abraded to various degrees of roughness from 0.05 to 1.0 µm (center line average). These samples were then plated with individual layers of the metal of interest under controlled, high-speed conditions using a Rotating Disk Electrode. Thicknesses ranged from 0.25 to 2.0 µm. The plating conditions were determined previously in order to produce minimal levels of intrinsic porosity from each of these specific chemistries. Porosity was determined by subjecting the plated disks to sulfurous acid vapor according to ASTM B799-88 (Standard Test Method for Porosity in Gold and Palladium Coatings by Sulfurous Acid Vapor) and subsequently to vapors of ammonium sulfide. The pore corrosion was tallied and reported as a percentage of salt-covered area for the various conditions.

When considering functional properties of electroplated deposits, porosity is of particular significance, not as an intrinsic property, but rather for damage that may occur at some later date.[1] Pore corrosion and the subsequent degradation of a finished item's surface can range from simple tarnish or discoloration on cosmetic items to more serious deterioration. Increased contact resistance or loss of solderability of electronic components can lead to significant deterioration in overall system performance, and occasional failure during critical operations. Protection against this problem is one reason, among many others, that precious metals have enjoyed widespread use as surface finishes. Their ability to protect underlying base metal substrates or underplates against the effects of corrosion generally goes unchallenged.

Porosity of electroplated finishes, precious metals in particular, has typically been investigated as a function of deposit thickness or plating solution operating parameters, most commonly as single variable experiments. Many times, when investigating the properties of electrodeposits, experiments are carried out under one set of conditions and extrapolated to include others. For example, high-speed plating conditions (high solution metal concentration, elevated current density, and vigorous agitation) can produce deposits that appear similar to ones obtained under low-speed conditions. But further investigation may point out that other, more subtle, properties—hardness, wear resistance and porosity—may be substantially different.

To obtain a more thorough understanding of these properties, it is necessary to perform the study at conditions as close as possible to those to be experienced in the field. One past effort was an attempt to reconcile the effect of several interrelated variables (current density, agitation and deposit thickness) acting simultaneously in a statistical fashion.[2] These trials, run under high-speed plating conditions (50-200 A/ft^2), illustrated the average effect of one variable over all conditions of the other variables. It was found, for example, that deposits from a cobalt hard gold solution produced large changes in porosity with respect to changes in current density, while palladium-nickel deposits exhibited little or no change under all conditions of the variables examined.

Table 1
Summary of Roughness Parameters

Roughness Category	Grade of Metallographic Paper	Representative CLA Roughness µm
Coarse	240	1.25
Medium	400	0.44
Fine	600	0.12
Polished	0.05 µm alumina	0.03

Table 2
Summary of Other Parameters

	Cobalt Hard Gold	Palladium	Palladium-Nickel
Metal, g/L	Au 24, Co 1.0	25	Pd 22, Ni 8
pH	4.2	7.8	7.5
Temp, °C	50	50	50
CD, A/ft^2	100	100	100
Agitation, rpm	1000	1000	1000
Time	(As required to obtain thickness)		

Table 3
Summary of Average Porosity Values
% Area Covered

	Gold				Palladium				Palladium-Nickel			
	Finish Category				Finish Category				Finish Category			
Thickness, µm	P	F	M	C	P	F	M	C	P	F	M	C
0.25	85	92	92	95	85	70	85	90	95	85	70	80
0.5	68	82	92	88	65	40	80	70	28	60	40	80
1	15	88	92	92	20	15	40	50	<5	20	55	45
2	<5	28	48	72	10	20	45	45	<5	<5	15	30

P = polished, F = fine, M = medium, C = coarse

Substrate roughness is another variable that has been shown to exert a considerable effect on the porosity of precious metal coatings.[3-5] To examine the relative benefits of several types of deposits, a comparative evaluation was performed, using cobalt hard gold,[6] pure palladium and palladium-nickel electroplating solutions.[7] The experiments were performed under high-speed plating conditions, using a modified Rotating Disk Electrode.[8] This study involved plating samples of varying roughness (0.05-1.0 µm, CLA) and deposit thickness (0.25-2.0 µm) and assessing the resulting porosity.

Sample & Substrate Preparation

The samples consisted of 0.4 cm dia. OFHC copper disks, manufactured from the same lot of stock material. They were prepared according to four categories of roughness, using random abrasion on metallographic polishing papers. Representative samples were measured on a surface profilometer and center-line averages calculated. The roughness categories, grade of papers and representative surface profile measurements are summarized in Table 1. Representative surface profilometer tracings of roughness on rotating disk specimens, showing surface height (µm) vs. length of track (mm) are also shown and can be seen in Fig. 1.

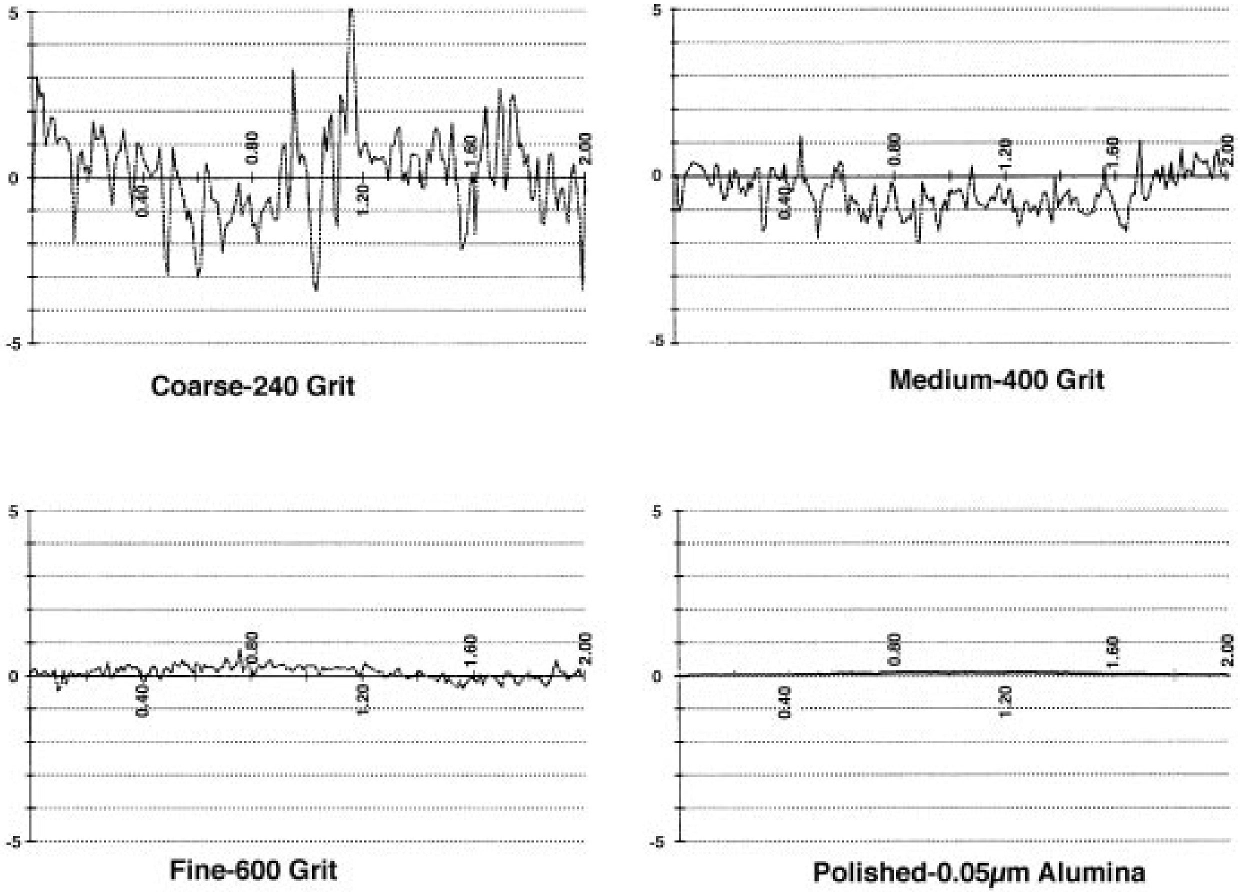
To illustrate the roughness levels achieved, scanning electron (SEM) micrographs, taken at 1000X, of the various abrasion categories are shown in Fig. 2. It is clear from these photos that substantial differences exist in surface morphologies between the categories. What is not clear is the effect that each may have on the porosity of subsequently applied deposits.

Plating Equipment, Solutions & Matrix

As previously mentioned, a modified Rotating Disk Electrode (RDE) assembly was used to plate all samples in preparation for porosity testing. This arrangement was required to provide the uniformly high agitation rates necessary to achieve current densities essential for high-speed plating simulation. The modification allows the disks to be removed easily from the rotating shaft to facilitate characterization and analysis of the plated surface and for ease of storage. A disassembled RDE is shown in Fig. 3.

The electroplating solutions were contained in jacketed beakers connected to a circulating constant temperature water bath that maintained consistent temperature control (Fig. 4). Other controls included a constant current rectifier capable of maintaining 50 mA and a digital timer controller to regulate the duration of plating. This served to minimize thickness variation between runs.

Three types of electroplated deposits were to be evaluated—cobalt hard gold, pure palladium, and an 80/20 palladium-nickel alloy. The plating conditions were obtained after first evaluating the Main Effects Estimates of agitation and current density on porosity and were chosen to produce moderate levels of porosity for the solutions involved.[2] All samples were plated at 100 A/ft^2 and a solution agitation rate of 1000 rpm. The solutions were filtered through 0.5-µm media prior to use. Other operating parameters were based on



Coarse-240 Grit

Medium-400 Grit

Fine-600 Grit

Polished-0.05µm Alumina

Fig. 1—Profilometer tracings of surface roughness on Rotating Disk specimens; surface height (µm) vs. length of track (mm).

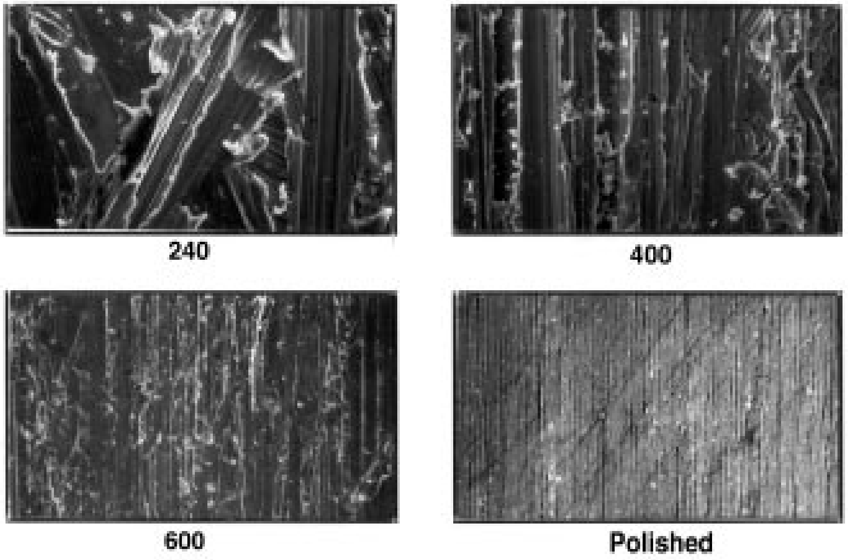


Fig. 2—Scanning electron micrographs showing various levels of the abraded substrate surface. 1000X.

standard manufacturers' guidelines and are summarized in Table 2.

Once mounted in the assembly, the copper surface was subjected to routine cleaning and plated according to a predetermined matrix. The cleaning cycle consisted of a commercial alkaline electrocleaner for 10 sec at 30 A/ft^2 and 20-percent HCl dip for 10 sec. Conditions in the various plating baths (metal content, pH, temp, etc.) were not necessarily identical, as the nature of the individual chemistries, as well as the manufacturer's recommendations, entailed several differences. Overall, however, as many variables as possible were held constant.

Disk electrodes were plated for each roughness category, as described above, at four different thicknesses: 0.25, 0.5, 1.0 and 2.0 µm in all solution types. Runs were performed in triplicate, yielding a total of 144 disk samples.

No nickel underplate was used in these tests, as it was previously found to produce pore counts very similar to bare copper substrate after exposure to the particular type of porosity test used.[9] The aggressive nature of the test corrodes nickel underplate at a rate similar to that for copper. Accordingly, it measures the porosity of the precious metal with little interference from underplates.

Thickness measurements were accomplished with standard X-ray fluorescence techniques. Plating times were adjusted to maintain thickness tolerances within ±5 percent of the target value. For the palladium-nickel samples, composition and thickness measurements were obtained simultaneously.

Of the three disks plated in each series, one was characterized by SEM for classification of the surface morphology. All deposits examined were considered acceptable from the standpoint of being smooth, that is, non-nodular, and continuous, especially considering the conditions of the roughened substrate.

Porosity Corrosion & Measurement

Porosity was evaluated on all disks by exposure to sulfurous acid[10] and ammonium sulfide vapors, separately. The details of the porosity test are elaborated elsewhere.[11] Porosity evaluations were made at 10X through a stereo microscope. A circular fiber optic illuminator was used to produce an even and diffuse illumination over the surface of the samples.

Porosity is typically measured as a function of the number of pore decorations, or corrosion spots, per cm^2. During these experiments, however, the rougher, and to a greater degree, the thinner specimens, exhibited gross corrosion over large portions of the disk surface. The results, therefore, are reported in terms of a percentage of the surface covered with corrosion salts and discussed subsequently. This was accomplished by superimposing a 5 x 5 grid over the surface to be measured and counting individual squares containing corrosion. When discrete, low-level pore decorations were evident, the area covered is referred to as < 5 percent; accordingly, no readings would be recorded below this minimum level. This was found in several of the polished samples, particularly those with greater thickness.

Results

Average results for each deposit type are summarized in Table 3 and presented graphically in Fig. 5. The results illustrate that 0.25 µm of any finish is not sufficient to protect even the polished samples from corrosive attack in this environment. At 0.5 µm, the palladium-nickel provides noticeably increased protection for the polished, fine and medium surface finishes. This trend continues as roughness increases and for thicknesses up to 2 µm. It should be noted that thickness of 2 µm is not adequate for sufficient protection of the roughest surfaces. Hard gold also exhibited gross amounts of corrosion salts for all samples except polished, below thicknesses of 2 µm. The polished hard gold samples begin to display lower porosity, but not until thicknesses of one µm or greater. Pure palladium appears to be approximately equal to palladium-nickel with the latter exhibiting slightly better substrate protection (lower porosity) at increased roughness and decreased thickness.

Fig. 3—Disassembled view of Rotating Disk Electrode and removable Rotating Disks.

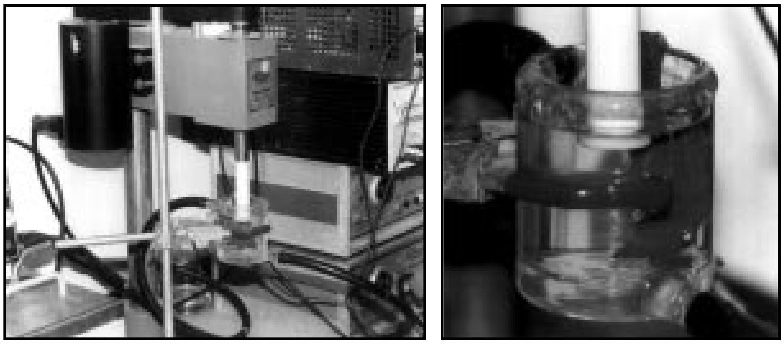


Fig. 4—Apparatus used to simulate high-speed plating conditions; includes Rotating Disk Electrode, rotator, constant temperature water bath, and timed rectifier.

Discussion

When plated on polished substrates, consequently minimizing the effect of surface imperfections, electroplated materials exposed to corrosive environments usually produce well-defined pore decorations easily amenable to quantification. One of the effects of the increased roughness used in these trials was to mask individual decorations. For many of the polished samples (with the exception of 0.25 µm thickness), pore sites could be readily isolated and counted. As roughness increased, however, the corrosion effects began to agglomerate as large masses of salt on the sample surface, resulting in loss of definition of individual pore sites. This necessitated a variation in the method used for tallying and comparing porosity effects. Consequently, porosity was evaluated in terms of a percentage of the area covered with salts, in the manner previously described. Some of this effect may also be related to the aggressiveness of the porosity test itself. Less corrosion might be found in more benign environments typically found in other types of tests (*e.g.*, electrographic or long-term/low-concentration gaseous testing). Although plating parameters were not specifically evaluated in these trials, the trend of decreased porosity for palladium and palladium-nickel, over the given thickness and roughness ranges, were found to be similar to past data.

Earlier investigations[12-14] have shown that palladium-nickel and, to a large extent, pure palladium, possess a lower intrinsic porosity than standard hard gold deposits over a wide range of operating parameters. This is especially true for deposits greater than one µm in thickness.

A factor that also needs to be considered, when plating on roughened substrates, is the difference between true and apparent area. As the roughness of a surface is increased, so is its true surface area, while the apparent area remains constant. Literature values for abraded metal surfaces show an increase in true area of as much as 4.2 times for 320 grit paper on copper.[15,16] This would imply a reduction in thickness of nearly equal magnitude as sample roughness is increased. Thicknesses believed to be on the order of 2 µm may actually be closer to 0.5 µm in some areas. With the additional complication of increased local thickness on asperities in the deposit producing further unevenness, low-lying valleys may have substantially less plating thickness. This would go undetected by XRF or weight gain measurements, as they rely on mass per unit area on a much larger scale.

Also, the porosity may be affected by other factors in or on the surface; for example, inclusions or impurities in the substrate, asperities acting as local plating current thieves, or an increase in the number of substrate surface defects acting as precursors to pore formation.[17]

Summary

Porosity has been compared for cobalt hard gold, pure palladium and an 80/20 palladium-nickel alloy over surface roughness ranging from 0.05 to 1.25 µm (CLA) and deposit thicknesses from 0.25 to 2.0 µm. Samples were plated to simulate high speed conditions (100 A/ft^2, 1000 rpm) and subjected to an aggressive sulfurous acid vapor porosity test.

The results show palladium and palladium-nickel to be approximately equal in reducing pore corrosion at deposit thicknesses greater than 0.5 µm, with decreasing effectiveness as roughness increases. The cobalt hard gold shows

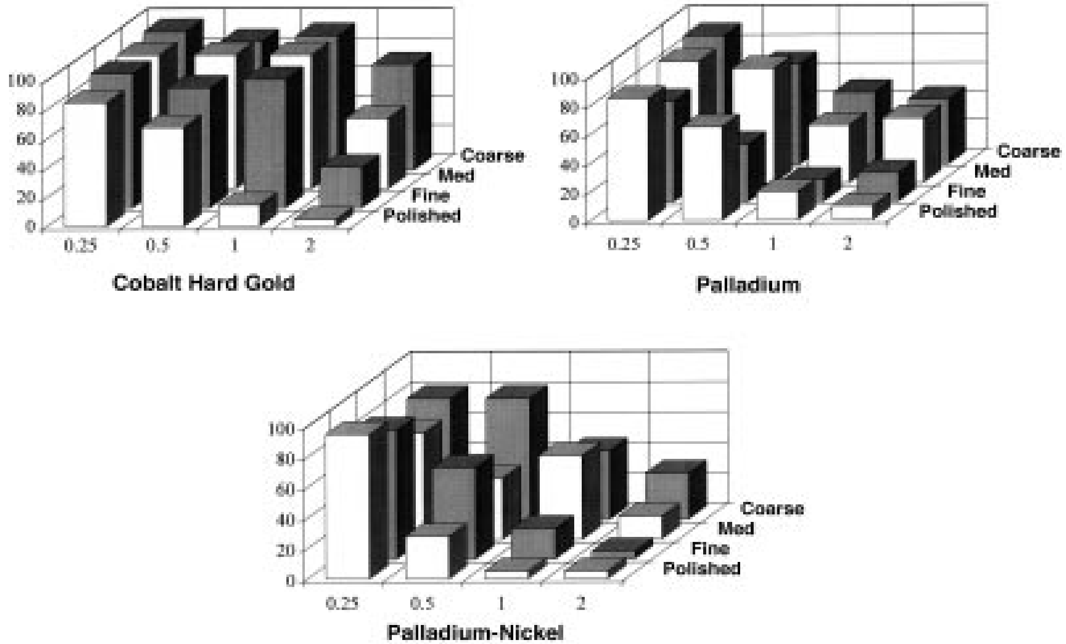


Fig. 5—Relative porosity results of hard gold, palladium and palladium-nickel, as plated on RDE apparatus at 100 A/ft^2 and 1000 rpm.

exaggerated amounts of corrosion salts at all thicknesses below 2 µm for all surface finishes. The highly polished samples of hard gold begin to display lower porosity, but not until thicknesses greater than one µm are obtained.

Several effects may account for the increase in porosity found in these samples as roughness increases, most notably:

- A reduction in true plate thickness, resulting from increase in true area,
- An increase in the number of substrate surface defects

Porosity results can, of course, be altered by varying certain operating parameters and it is this sensitivity to change, or rather the lack of it, that characterizes a robust process. Hard gold plating solutions, for example, are known to exhibit sensitivity to certain operating parameters, specifically current density, not found in properly formulated solutions of palladium-nickel. Judicious choice of substrate materials and plating chemistries, together with proper operating conditions can result in superior products that can withstand certain corrosive environments for very long periods of time, providing assurance of excellent reliability in the field.

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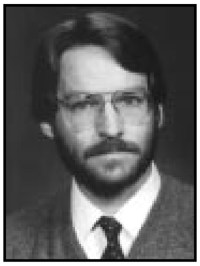
About the Authors



Edward J. Kudrak, CEF, is technical service manager for the Electroplating Chemicals & Services Group at Lucent Technologies, 600 Mountain Ave., Murray Hill, NJ 07974. He holds a BS in chemical engineering from the New Jersey Institute of Technology. His experience covers more than 16 years of development and implementation of electroplating solutions and processes for manufacturing environments, specifically for the electronics industry. In addition to many scientific publications, he holds two U.S. patents.

Dr. Joseph A. Abys is the business manager of the Electroplating Chemicals & Services Group, Lucent Technologies, Murray Hill, NJ. He received a PhD in inorganic chemistry from Brown University. He has been working in the field of electrodeposition for 16 years, with concentration on plating of palladium and its alloys. Recently, the groups efforts have expanded in the areas of gold-tin alloys, oxide anodes, electroforming and fundamental work on the hydrodynamically controlled Hull Cell. In addition to many scientific publications, Dr. Abys holds more than 25 patents in the U.S. and abroad.

Frank Humiec is a member of the Electroplating Development Group at Lucent Technologies. His work includes plating, process improvements, analytical and technical services. He holds a BS in chemistry from Niagara University and an MS in chemistry from Fairleigh Dickinson University. He is co-author of several papers in the areas of inorganic and pharmaceutical chemistry.