A Helping Hand

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Dear Advice & Counsel,

I read with great interest the complete report, IBM Corporate Manufacturing Specification CMH 6-0420-013: Porosity Testing of Electroplated Gold, published in the Advice & Counsel section of *Plating and Surface Finishing* (November 2006). As part of AESF Research Projects that I have worked on, I have developed a method for evaluating the porosity of thin (up to 2 μm thickness) metal coatings following almost the same principles that Gel Porosity Testing is based upon, namely by applying anodic polarization in appropriate electrolytes. I am convinced, however, that the Linear Polarization Resistance (LPR) technique can be used as a more precise means for quantitative comparative evaluation of porosity. I came to this opinion after researching the LPR-method and concluding that it offers a quick, effective and reliable way of determining the best plating conditions (electrochemical parameters and the bath's contents) for deposition of high quality metal coatings.

Since *P&SF's* readers are interested in porosity determinations, I am sending you as an attachment a description of the porosity test that I use. I hope that it will be beneficial to other platers and metal surface finishers who can refine it or develop it further.

Sincerely,
Dr. Mois Aroyo
Associate Professor at Technical University of Sofia, Bulgaria,
AESF Member

Response:

Thank you, Dr. Aroyo. With your permission, I hereby reproduce your procedure for porosity determination:

Porosity Measurements by Applying the LPR Method

This porosity test is based on the method of linear polarization resistance (LPR) applied, for example, in CORRATER electronic devices for corrosion monitoring manufactured some years ago by *Rohrback Instruments* (USA). The well-known Stern and Geary relation[1] is used to define the instantaneous corrosion rate of the metal in contact with the corrosive agent:

$$i_{corr} = \frac{b_c \cdot b_a}{2,3(b_c + b_a)} \quad \text{or} \quad i_{corr} = \frac{b}{R_p} \qquad (1)$$

where R_p is the polarization resistance of the metal-electrolyte system and b_a and b_c are Tafel slopes of the anodic and cathodic polarization curves, respectively.

Our electrochemical equipment for porosity testing has been described earlier.[2] It was designed for comparative evaluation of the porosity of thin metal coatings (up to 2 μm thick) deposited on different metals. Two flat metal-coated specimens are pressed to rubber **O**-rings, closing two identical axial openings located at the bases of the cylindrical electrochemical cell (Fig. 1). The electronic device measures the polarization conductance $1/R_p$, which represents the ratio between the resulting current ΔI (mA) and the voltage ΔE which is within ±10 mV of the applied sign-changing pulses. The current ΔI is automatically measured after eliminating the transition current occurring at the beginning of each pulse. The integral $Q = \int(1/R_p)dt$ is calculated for a definite test period of 5 or 10 min and displayed by the $1/R$-time integrator.

The porosity of the metal coating was proportional to the integral value Q, provided that the corrosion rate of the metal-deposit is negligibly low in comparison to the dissolution rate of metal-substrate through the pores. Therefore, when the goal is to provide the largest possible difference between the dissolution rates of the two metals, the most important problem with such porosity measurements was the accurate choice of a test electrolyte.

Example 1

The electrolyte used in the porosity measurements of nickel deposits on mild steel contains:

NaCl	- 18 g/L
Na-gluconate	- 8 g/L
NH_4F / HF	- 2 g/L
H_3PO_4 , 85%	- 2 mL/L

When uncoated steel electrodes were in contact with the electrolyte for 5 min, the $1/R$-time integrator displays a value assumed to correspond to 100% porosity. For a two-pure nickel-electrode assembly in contact with the same test electrolyte, the Q values obtained were assumed to correspond to 0% porosity. The deposition time for all nickel coatings was the time required to obtain the same approximate thickness of 1.5 μm. The roughness of the steel substrate was the same in all cases and was equivalent to that obtained by treatment with #600 grit paper. The average porosity values were obtained from the large number of measurements.

The results obtained from experimental porosity measurements confirmed our theoretical considerations that there was a correlation between the leveling performance and some coating properties; namely that the maximum leveling power value corresponds to minimum porosity, and the minimum leveling power value corresponds to maximum porosity.[3] The comparison between the porosity of DC deposits and that of pulse-deposited

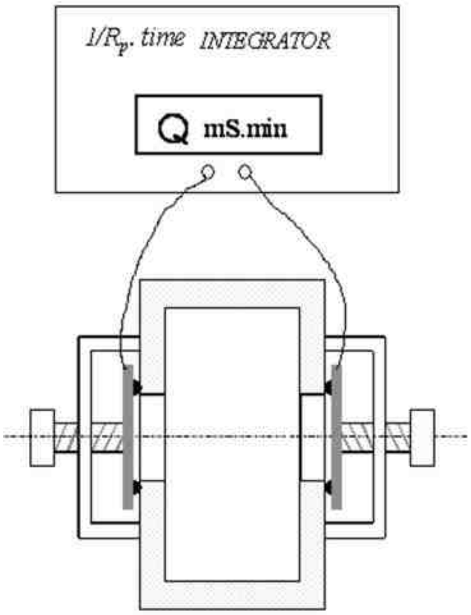

Figure 1—Schematic diagram of porosity measurement equipment.

coatings demonstrated the advantages of deposition at pulse plating conditions that ensure maximum leveling power.

At the same time, by comparing the different pulse plating regimes for metal coating deposition, we came to the conclusion that the (DC+AC) pulse-reverse plating technique had definite advantages. Bright nickel coatings deposited from a Watts electrolyte by unipolar pulses had higher porosity (11%) than those deposited by the application of (DC+AC) bi-polar pulses (6% porosity). *P&SF*

References

1. F.P. Ijsseling, *British Corrosion Journal,* **21** (2), 95 (1986).
2. M. Aroyo & N. Tzonev, *Plating & Surface Finishing*, **90** (2), 50, (2003).
3. M. Aroyo, D. Stoychev & N. Tzonev, *Plating & Surface Finishing*, **85** (9), 92 (1998)

Test Your Plating I.Q. #430

By Dr. James H. Lindsay

Commonly plated alloys

Based on materials from the AESF Foundation Educational Courses, authored by Frank Altmayer, MSF, AESF Fellow

1. Name the individual metals that can be found in the following alloys: brass, bronze and solder.

2. Ammonia is sometimes added to brass plating solutions to improve the _____________ of the deposit.

3. Bronze plating solutions employ two complexes for copper and tin respectively. The copper is complexed by _____________, while the tin is complexed by ___________________.

4. The most popular substitute for decorative chromium is an alloy of _______________ and _______________. Why?

5. For two or more metals to be deposited as alloys, generally, a plating solution where the _______________ for deposition of each of the alloying metals are within ____ volts is required.

Answers on page 49.

Fact or Fiction?

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Perhaps the simplest answer to chemophobia is this. It is based on a misperception. Everything is made of up chemicals. A report by the National Research Council noted that about 5,000,000 different chemical substances are known to exist. Of those 5 million, less than 30 have been definitely linked to cancer in humans, 1,500 have been found to be carcinogenic in tests on animals and about 7,000 have been tested for carcinogenicity. Again, if you missed those numbers, less than 30 out of five million known chemical substances have been definitely linked to cancer in humans.[5] *P&SF*

References

1. Eric Schlosser, *Fast Food Nation*, Perennial Press, New York, NY, 2002; p. 195.
2. *The Food Defect Action Levels*, Food and Drug Administration, Washington, DC, May 1998. (See http://vm.cfsan.fda.gov/~dms/dalbook.html).
3. Todd Seavey, “A Chemical (Over) Reaction,” Tech Central Station, January 20, 2003 (See http://techcentralstation.com/, search “Todd Seavey”).
4. Maria Cone, “Traces of Prescription Drugs Found in Southland Aquifers,” *Los Angeles Times*, January 30, 2006.
5. John Adams, *Risk*, University College Press, London, UK, 1995; p. 45.