Technical Article

Evaluation of Electrolytic Nickel-Phosphorus Finish For Applications in Electronics

by C. Fan,* C. Xu, E.J. Kudrak & J.A. Abys

An amorphous nickel-phosphorus surface finish was electrodeposited and characterized for its structure and material properties. Corrosion protection/porosity, contact resistance and wear behavior were evaluated on a gold-flashed amorphous nickel-phosphorus finish plated on copper and copper alloy and compared with a standard nickel-hardened-gold finish. In addition, a post-plating surface treatment was used to enhance the performance of the gold-flashed nickel-phosphorus finish. The combination showed promising results.

In the electronics segment of the surface finishing industry, precious metals, such as hard-gold, gold-flashed palladium and their alloys, are commonly electrodeposited as contact finishes on electronic connectors, usually made of copper alloys. Sufficient corrosion protection, high surface contact conductivity, low frictional coefficient and high wear resistance are the primary requirements for these surface coatings. To meet these requirements, the precious metal coating is usually plated over a nickel underlayer coating on the copper alloy. The nickel underlayer functions as a barrier to the diffusion and migration of substrate metal towards the surface and improves wear resistance of the composite finish. To make a process cost effective and competitive, the precious metal coating(s) should be as thin as possible without sacrificing the desired functional properties.

For connector applications, the precious metal is usually plated to a thickness of 1.0 μm (39.4 μ-in.). As the thickness is decreased below 1.0 μm, the porosity of the composite coating increases dramatically, exposing the nickel and the copper substrate.[1,2] The exposed basis metals are susceptible to corrosion which can increase the surface contact resistance. Compared with nickel corrosion products, copper corrosion products are much more detrimental because of their higher migration/spreading rate on the gold surface. Additionally, thin precious metal layers are susceptible to wear and can compromise the integrity of the contact system. Therefore, in order to utilize thinner precious metal coatings and maintain the required functional properties, the following conditions must be satisfied:

- a highly corrosion-resistant and pore-free underlayer coating

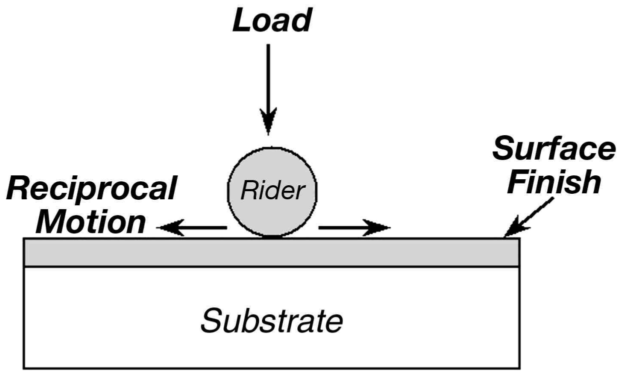

Fig. 1—Schematic drawing of the sliding wear test set-up.

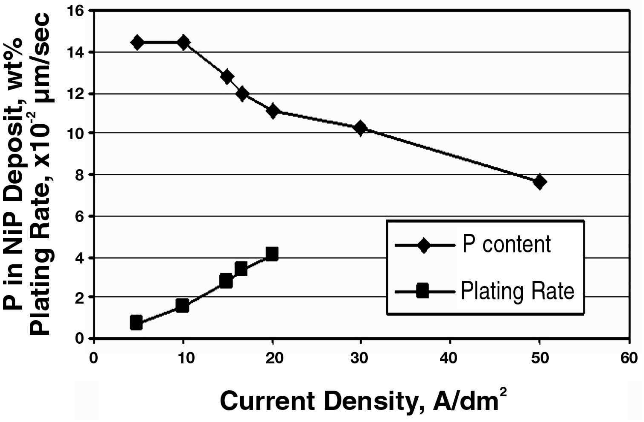

Fig. 2—Phosphorus content in the nickel-phosphorus deposit and plating rate vs. plating current density; pH, 1.64; additive concentration, 100 g/L (13.3 oz/gal); bath temperature, 58°C (136°F); agitation, 26 cm/sec (10.2 in./sec).

Nuts & Bolts: What This Paper Means to You

In the electrical contact field, precious metal plating is used to get the lowest contact resistance, lowest friction and highest wear resistance. Nickel is plated over the copper contact material under the precious metal to prevent the copper from diffusing into and ruining the top plate. Like everything else, that contact finish has gotten thinner to save money. Indeed, it has gotten so thin that there is danger of porosity in it, exposing what is underneath. This work considers a low cost alternative, a gold-flashed amorphous nickel-phosphorus coating. It shows promising results.

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Table 1
Operating Conditions for Nickel Phosphorus Plating

Plating current density	5.0 to 50.0 A/dm^2 (46.4 to 464.5 A/ft^2)
Bath temperature	55 to 60°C (131 to 140°F)
pH	0.68 to 1.64
Agitation	Moderate

- a much less porous precious metal finish and
- a technique to increase the surface wear resistance.

It is well known that amorphous nickel-phosphorus electrodeposits are less porous than standard nickel electrodeposits.[3] They can be used in a multilayer finish with a precious metal layer for porosity reduction and corrosion protection.[4] The crystallographic structure of the nickel-phosphorus deposits is controlled by plating parameters and bath composition. An amorphous structure can be obtained by selecting appropriate plating chemistry and operating conditions. In addition, to increase corrosion protection, a novel, proprietary chemical process can be applied to the plated surfaces. The objective of this study was to evaluate gold-flashed (0.1μm (3.94 μ-in.) gold layer plated) nickel-phosphorus deposits with a novel chemical process that enhances the corrosion protection and functional properties of the composite finish. The results were compared with those obtained with the standard electronics contact finish, *i.e.*, 1.0 μm (39.4 μ-in.) of hard gold plated over a 2.5 μm (98.4 μ-in.) nickel underlayer.

Experimental procedure

The nickel, nickel-phosphorus and hard-gold deposits were plated from proprietary chemistries. The operating conditions for nickel-phosphorus plating are listed in Table 1. The hard-gold deposit was a gold-nickel alloy with a nickel content ≤ 0.3 wt%. The substrate used for corrosion/porosity testing was Olin 725 copper alloy (88.2 Cu/9.5 Ni/2.3 Sn). Copper coupons were used as substrates for x-ray diffraction (XRD) and wear tests. The composition (weight percentage) of the nickel-phosphorus deposits was determined by a scanning electron microscope equipped with an energy dispersive spectrum analyzer.* The SEM/ EDS system was calibrated for the quantitative analysis.

The nickel-phosphorus deposits were plated 2.5 μm thick except for the specimens for hardness measurement. The structure of the nickel-phosphorus deposits was examined by XRD. The hardness of the deposit was measured on a cross-section by means of indentation with a load of 50 g.** For the hardness measurement, the deposit thickness was 25 to 50 μm (0.001 to 0.002 in.). The ductility/elongation of the deposit was assessed by a bending test (ASTM B489) and the internal stress of the deposit was determined by plating on bifurcated copper alloy sheet and calculated after the plating.***

A sulfurous acid vapor (SO_2) corrosion/porosity test was used in this study.[1] During the test, each sample with a surface area of about 4.5 cm^2 (0.7 in^2.) was exposed to a sulfur dioxide atmosphere for 1.5 or 24 hr then to a hydrogen sulfide environment for 15 min. The 1.5-hr exposure to sulfur dioxide is a standard practice, and the 24-hr exposure is an intensified test. The surface of each tested sample was observed under an optical microscope and the pores/corrosion product spots were counted at a magnification of 10X. A porosity index system,[1] taking into account not only the numbers of the pores but also their sizes, was used to evaluate the porosity. The porosity index was determined using the following equation:

$$\text{Porosity Index (cm}^{-2}) = (0.2n_1 + 1n_2 + 3n_3 + 5n_4)/(\text{surface area in cm}^2)$$

where n_1, n_2, n_3 and n_4 are the numbers of the counted pores with a sizes (diameters) of 50 to 124, 125 to 249, 250 to 374 and ≥ 375 μm, respectively. Each result was an average of two or three tests. The corrosion products were examined by Auger electron spectroscopy† (AES) to identify their nature.

Table 2
Material Properties of the Amorphous Nickel-phosphorus Electrodeposit

Hardness, KHN_{50}	520—580
Ductility, Elongation %	3—4
Internal Stress	62 MPa (9,000 psi)

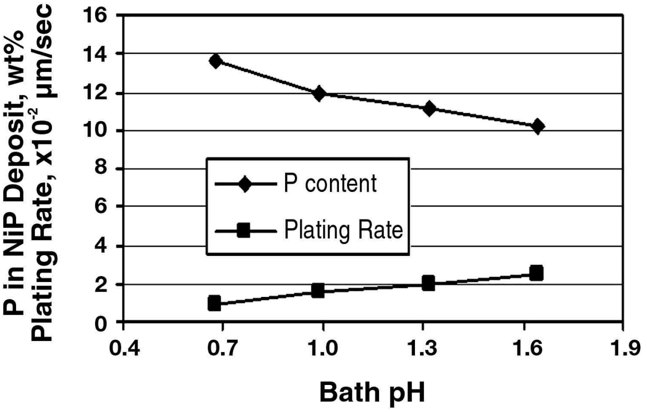

Fig. 3—Phosphorus content in the nickel-phosphorus deposit and plating rate vs. bath pH; plating current density, 10 A/dm^2 (93 A/ft^2); additive concentration, 40 g/L (5.3 oz/gal); bath temperature, 58°C (136°F); agitation, 26 cm/sec (10.2 in./sec).

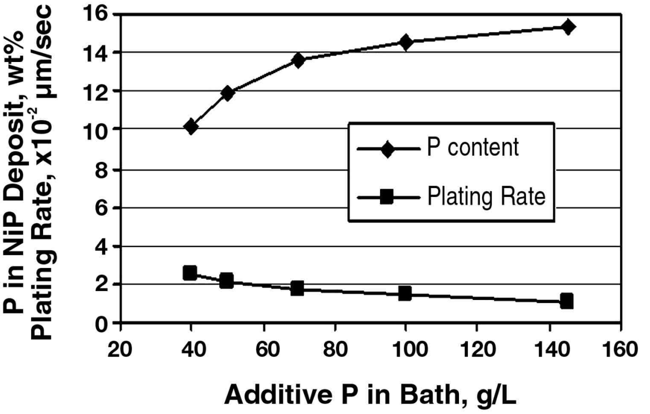

Fig. 4—Phosphorus content in the nickel-phosphorus deposit and plating rate vs. additive concentration, plating current density: 10 A/dm^2 (93 A/ft^2); pH, 1.64; bath temperature, 58°C (136°F); agitation, 26 cm/sec (10.2 in./sec).

Surface contact resistance and frictional force were recorded during a sliding wear test†† and subsequently, the friction coefficient was calculated. A schematic drawing for the wear test is given in Fig.1. In the wear test, a copper ball with a diameter of 4 mm

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* *SEM, Hitachi Model 2500, Hitachi Ltd., Japan; EDS, Kevex Inc, Valencia, CA.*

** *Wilson/Tukon Model 300 Micro-Hardness Tester, Instron Corp., Canton, MA.*

*** *Deposit Stress Analyzer, Model 683EC, Specialty Testing & Development Co., Jacobus, PA.*

† *Physical Electronics Model 595, Physical Electronics USA, Eden Prairie, MN.*

†† *CETR Tribology Tester, Center for Tribology, Inc. (CETR), Campbell, CA.*

Table 3
Surface Contact Resistance & Its Variation During The Wear Test (1000 cycles) on Gold-flashed 2.5 μm Amorphous Nickel-phosphorus Finish

Surface Treatment	Contact Resistance (mΩ)	Contact Resistance Variation (mΩ)
As-plated	18—20	2
With surface treatment	17—22	5
With enhanced surface treatment	15—18	3

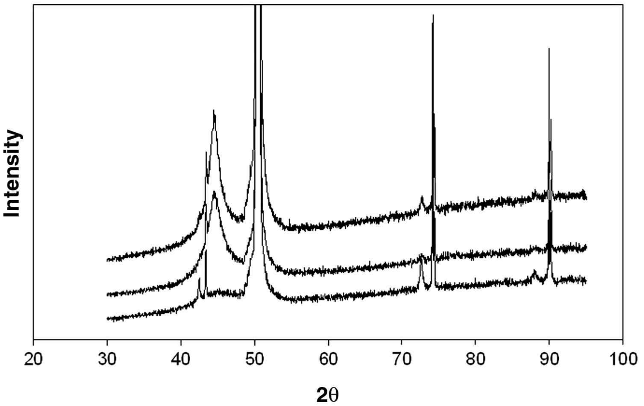

Fig. 5—XRD spectra of the nickel-phosphorus deposits plated on copper at different current densities.

(0.16 in.) was used as the rider and plated with the same surface finish as the tested sample. A copper substrate was used for plating the wear test samples to match the substrate material of the rider. A vertical load of 100 g (0.22 lb.) was used in the test with 1000 wear cycles. The amplitude of the sliding was 14 mm (0.55 in.) and the frequency of the reciprocal sliding motion was 0.5 Hz.

As a chemical post-treatment, a proprietary chemical solution was used. For the wear test, an enhanced surface treatment was also used to improve the wear behavior.

Results & Discussion

Nickel-phosphorus Deposition

The phosphorus content in the electrodeposited nickel-phosphorus and the plating rate was strongly dependent on plating conditions, particularly, on current density, pH and concentration of the additive that supplies phosphorus for deposition (Figs. 2 thru 4). A high phosphorus content was obtained with a low plating current (Fig. 2). The phosphorus content also increased with reduced pH (Fig. 3) and increased additive in the bath (Fig. 4). The plating rate increased with increasing current density, increasing pH and decreasing additive concentration.

As reported in literature, the structure of the nickel-phosphorus deposits was related to the phosphorus content in the deposits.[5] A crystalline structure was obtained with a low phosphorus content. However, at a relatively high phosphorus content, the structure was amorphous. It was reported that at phosphorus content ≥ 7 wt%, the deposit was amorphous.[6] However, the phosphorus content at the crystalline/amorphous structure transition has not been well defined and probably extends over a broad concentration range.[7] As can be seen in Figs. 2 thru 4, the phosphorus content and thus the crystalline/amorphous nature of the electrodeposits and the plating rate are highly dependent on bath composition and plating conditions, including additive concentration, current density and pH. A relatively high phosphorus content in deposit was accompanied with a relatively low plating rate in this study. Therefore, if an amorphous structure is desired, the operation would necessarily be restricted to a relatively low plating rate to obtain the requisite high phosphorus contents in the deposit.

Structure & Material Properties Of Nickel-phosphorus Deposits

The XRD spectra of the nickel-phosphorus deposits plated at different current densities on copper are given in Fig. 5. With the plating current density of 20 or 30 A/dm^2 (186 or 279 A/ft^2), the phosphorus content in the deposits was about 11 or 10 wt%, respectively. An outstanding XRD intensity signal of nickel could be identified on the spectra in addition to the intensity signals of copper generated from the substrate material. The deposits had a crystalline structure. As the current density was decreased to 10 A/dm^2 (93 A/ft^2), the phosphorus increased to about 14 wt%, the intensity signal of nickel in the XRD spectrum disappeared and the spectrum corresponding to the deposit was characteristic of amorphous materials.

The hardness, ductility and internal stress of the amorphous nickel-phosphorus deposit are listed in Table 2. The hardness of the amorphous nickel-phosphorus deposits was considered to be about 20% higher than that of a conventional nickel electrodeposit used for connector finishes and may improve wear resistance in applications. The elongation of the nickel-phosphorus was relatively low and it was not a ductile deposit. The deposit had a moderate internal tensile stress.

Corrosion/Porosity Tests

The porosity index of the gold-flashed 2.5 μm (98.4 μ-in.) amorphous nickel-phosphorous deposit and a finish of 1.0 μm (39.4 μ-in.) hard-gold over 2.5 μm (98.4 μ-in.) nickel are shown in Fig. 6. These were as-plated surface finishes without the chemical post-treatment. The gold-flashed nickel-phosphorus finish provided a significantly lower porosity index than the nickel/hard-gold finish. Underneath the very thin gold flash that is supposed to be porous,[1,2] the nickel-phosphorus deposits should have a very low porosity and be corrosion-resistant to the environments in the test.

Figure 7 illustrates the results of the intensified porosity test on the same two finishes, with or without the post-treatment. Without the treatment, the porosity of the gold-flashed nickel-phosphorus was considerably higher than the hard-gold finish. However, the porosity was dramatically reduced after the post-treatment and was comparable to the porosity of the hard-gold over nickel without the treatment. During the intensified long-term corrosion/porosity test and without the surface treatment, the nickel-phosphorus deposit exposed to the corrosive environments through the pores in the gold flash was corroded. The pores in the nickel-phosphorus could be generated during the test and subsequently left the substrate copper exposed and corroded. With the surface treatment, however, the pores in the gold-flash layer were reduced and the corrosion of the nickel-phosphorus underlayer was inhibited.

The surfaces of the tested finishes in Fig. 7 (intensified corrosion/porosity test) are shown in Fig. 8. The black spots seen are corrosion products related to the pores in the finishes. Without the surface treatment, the gold-flashed nickel-phosphorus finish was considerably more porous than the nickel/hard gold. However, a comparable porosity was produced by the treatment. To confirm that the porosity was related to corrosion, AES was performed on the black spots and the pore-free surface. The results are provided in Fig. 9 and demonstrate that the black spots contained copper, sulfur, chlorine, carbon, nitrogen and oxygen. The corrosion

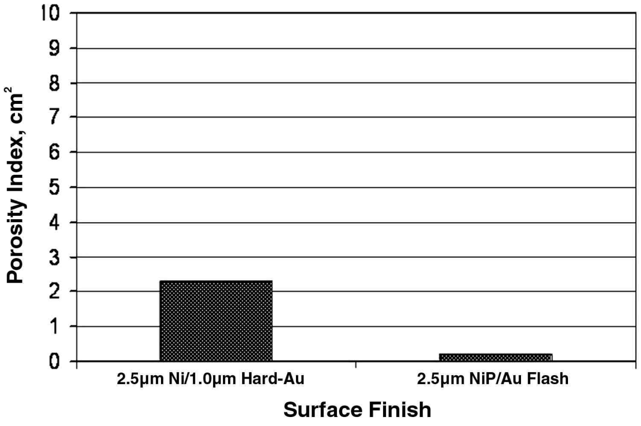

Fig. 6—Porosity index of different surface finishes without applying the surface treatment. The standard porosity test is: 1.5 hr exposure to SO_2 and 15 min exposure to H_2S.

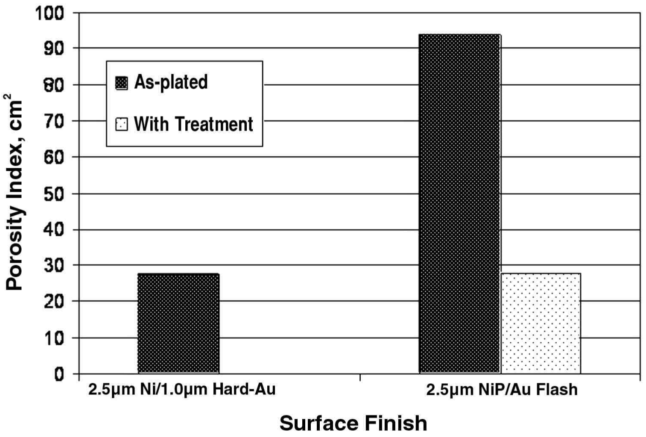

Fig. 7—Porosity index of different surface finishes with or without applying the surface treatment. The intensified porosity test is: 24 hr exposure to SO_2 and 15 min exposure to H_2S.

products were thus the result of the pores extending to the copper alloy substrate material. The chlorine may come from the plating process. It is interesting to notice that no nickel was involved at the surface of the corrosion products. The migration of copper onto the surface was overwhelming compared with nickel. On the pore-free areas, gold, sulfur and carbon were present. Neither copper nor nickel was detected. The corrosion protection was provided by the gold flash and nickel-phosphorus deposit.

Wear Behavior

Figure 10 illustrates the wear test results, the frictional coefficient of the gold-flashed amorphous nickel-phosphorus finish as a function of wear cycle. The friction coefficient was about 0.5 on the as-plated finish and around 0.2 on the finish with the surface treatment. With the enhanced surface treatment, the frictional force was slightly reduced, with the friction coefficient between 0.1 and 0.2. It is well known that the contact finish of a hard-gold finish over nickel has a friction coefficient of 0.5 to 0.8 without using lubrication and below 0.2 with a lubricant. The friction coefficient of the gold-flashed nickel-phosphorus finish without treatment was at the low end of that range. After the treatments, the friction coefficient of the gold-flashed nickel-phosphorus was comparable to that of the hard-gold over nickel with lubrication. It seems that the surface treatment can improve not only corrosion protection but also wear behavior.

Table 3 lists the surface contact resistance recorded and its variation during the wear tests. No significant difference in contact resistance was seen among all three surfaces tested. The variation in the contact resistance during the wear test was a few mΩ on all the surfaces. The surface treatments did not increase the contact resistance.

As we know, the reliability of a surface finish is related to the corrosion behavior, porosity and thermal stability of the finish. In addition, the diffusion of the basis metal(s) through the precious metal layer towards the surface can be accelerated at an elevated temperature. The corrosion of the basis metal(s) on the surface may increase the contact resistance and deteriorate the wear behavior. The contact resistance of the gold-flashed nickel-phosphorus finishes after 500 hr aging at 125°C (257°F) was reported to be below 30 mΩ.[8] The effect of the surface treatments on the thermally aged finish will be studied in future work.

Summary

1) The amorphous nickel-phosphorus electrodeposit with a gold-flash and a proprietary surface post-treatment provide promising improvements in corrosion protection and wear performance.

2) The gold-flashed nickel-phosphorus with the surface treatment may replace the hard-gold over nickel as a contact finish for applications in the electronics industry. A significant cost-saving can be achieved.

References

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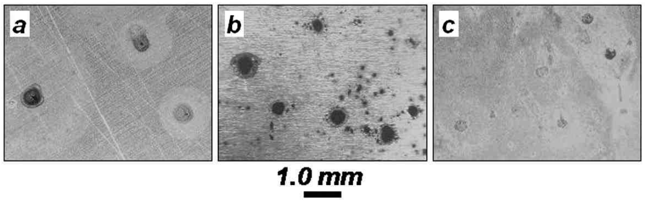

Fig. 8—Surface microscopy of the finishes after the intensified porosity test, 24 hr exposure to SO_2 and 15 min exposure to H_2S. The finishes were a) 1.0 µm hard-gold on 2.5 µm nickel, no surface treatment, b) gold-flashed 2.5 µm nickel-phosphorus, no surface treatment and c) gold-flashed 2.5 µm nickel-phosphorus, with the surface treatment.

About the Authors

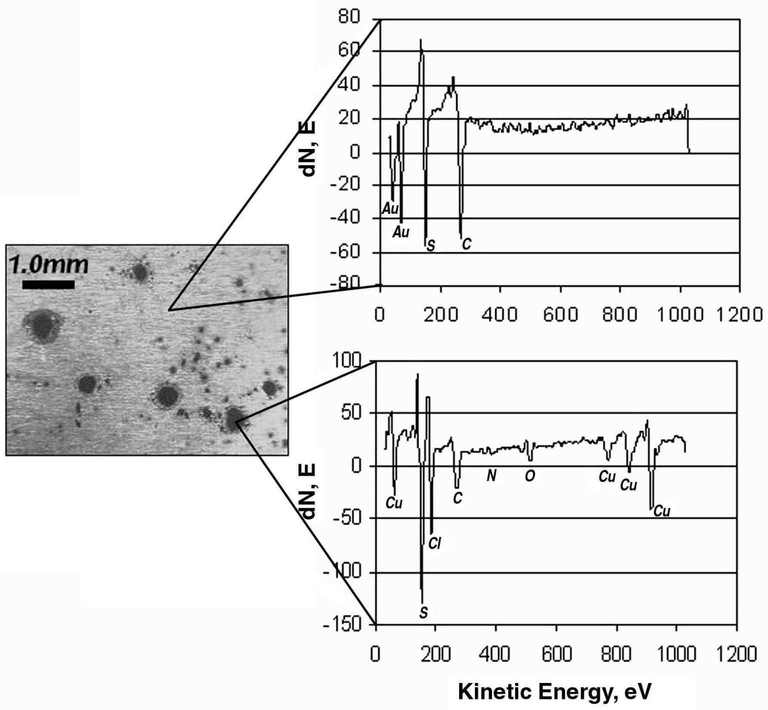

Fig. 9—AES of a pore and a pore-free area, respectively, on the surface of gold-flashed 2.5 µm nickel-phosphorus after the intensified porosity test, no surface treatment.

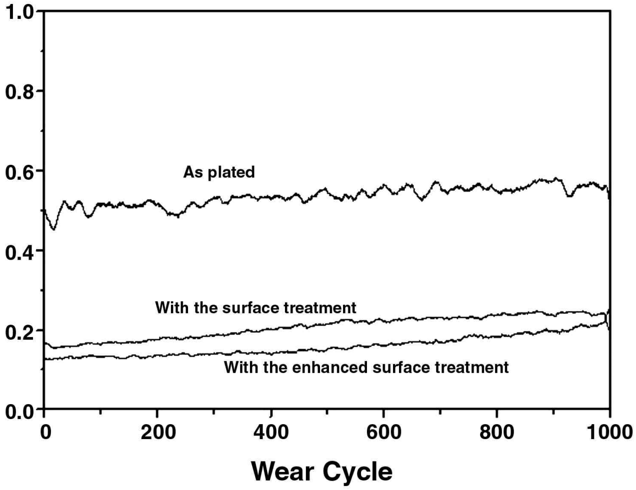

Fig. 10—Friction coefficient vs. wear cycle on the gold-flashed 2.5 µm nickel-phosphorus finish with and without surface treatment.

Chonglun Fan is a senior scientist with Enthone, Inc. of Cookson Electronics, Jersey City, NJ. His primary responsibilities are to characterize the material properties and functionality of different surface finishes and to develop new surface finishes. Before joined Enthone, he worked with Electroplating Chemical & Services at Lucent Technologies/Bell Labs as a Member of Technical Stuff. He holds a B. Eng. from Beijing University of Science and Technology (China) and a PhD in electrochemical engineering from Katholieke Universiteit Leuven (Belgium). He worked on electrocatalysis and electroplating as a Post-Doctoral Fellow at Ecole Polytechnique de Montréal (Canada). He has over 50 scientific and technical publications and holds 9 U.S. patents.

Chen Xu received his BS degree in chemistry from Tongji University in Shanghai, China, and his PhD in physical chemistry from Ruhr-University Bochum, Germany. Prior to joining Enthone as senior scientist, Xu was a project leader (Member of Technical Staff) with Electroplating Chemical & Services at Lucent Technologies, where his primary responsibilities included materials development and characterization, understanding the relationship among deposition conditiona, structure and properties of electroplated films and failure mode analysis. Xu has extensive experience in the fields of surface science, thin film technology and material science.

Edward Kudrak is manager of the Enthone Materials Analysis group, SAMPL (Surface Analysis & Materials Properties Laboratory), a part of Cookson Electronics. He holds a BS degree in chemical engineering from the New Jersey Institute of Technology. His professional experience covers twenty-five years of development and implementation of electroplating processes, particularly in the electronics industry, at Lucent Technologies (Bell Laboratories), OMI/Sel-Rex and Automata, Inc. His papers have garnered several awards, particularly those from AESF. Additionally, Kudrak is a co-author on various patents and multiple publications involving diverse aspects of electrodeposition.

Joseph A. Abys has recently joined Cookson Electronics Enthone as vice president and chief technical officer. He received his doctorate in physical inorganic chemistry from Brown University in 1979. He joined AT&T Bell Laboratories in 1979 as a Member of Technical Staff, where he conducted research in the fields of chemical vapor deposition and electrodeposition. He was the president of Electroplating Chemicals & Services (EC&S), a venture business of Lucent Technologies Inc. Abys has received numerous honors and awards throughout his educational and professional career. He has received seven AESF Silver Medal Awards and the 1996 Gold Medal for Best Published Papers in Plating & Surface Finishing. In 1995, Abys was awarded the D. Gardner Foulke Memorial Award from the American Electrochemical Society for his contributions to the field of electrodeposition. He was inducted into the New Jersey Inventors Hall of Fame in 1998. He has been granted 30 US patents and has 13 patents pending with numerous foreign patents. He has co-authored three book chapters, and more than 90 technical papers covering all aspects of electrodeposition and it's applications to electronics and functional coatings. He is member of AESF and IMF.