New PdNi Plating Bath:

Chemically Benign and Environmentally Friendly

I. Boguslavsky, J. A. Abys, H. Straschil, H. Tsuruta, J. Maisano, V. Eckert

Bell Laboratories, Lucent Technologies

Murray Hill, NJ

Most conventional Pd and PdNi plating chemistries contain ingredients that make them very corrosive towards base metals and stainless steel components. Typically they also operate at high pH which causes strong chemical odor and require frequent pH adjustment. This can make Pd plating process costly and environmentally hostile.

A new PdNi plating chemistry was designed with the objective to reduce the bath corrosiveness towards stainless steel and copper alloys, decrease chemical odor and pH adjustment. Characterization of the bath is presented in the paper. The effect of the bath components and plating conditions on PdNi alloy composition and material properties is described. The bath plates PdNi deposits with excellent appearance, ductility, and corrosion resistance.

Introduction

Over more than a decade, Pd and its alloys have emerged as a competitive substitute for hard gold, and in some instances, soft gold. The main driving force for the utilization of Pd finish in the late 1970s was the large increase and instabilities in the price of gold. Since the late 1980s, there has been a fundamental change in the perception of Pd and its alloys, not only as a low cost alternative for gold, but as an alternative that provides technological advantages /1-4/. For example, palladium finishes have higher hardness than gold and, thus, better wear resistance. They exhibit lower porosity which allows to reduce the thickness of precious metal layer and improve corrosion resistance and thermal diffusion properties of the deposit along with cost reduction. These reasons have caused extensive utilization of Pd-based finishes. Palladium and palladium alloys with nickel and silver have been primarily used in connector industry. More recently, they found their application in the decorative industry, as etch resist for PWB's, as a finish for lead frames for plastic packaged IC's and frame-lid assemblies for ceramic IC packages, etc.

Wide application of Pd and Pd alloys increases the demand for plating processes to satisfy certain technological requirements: stable and robust chemistry, low susceptibility to plating conditions, low environmental and occupational hazard. Two major classes of Pd and Pd alloy plating solutions currently exist: ammonia-based /5-9/ and organic amine-based /10-14/. The ammonia based chemistry usually contains palladium as $[Pd(NH_3)_4]^{2+}$ complex where counter-ion is Cl^- /9,10/ or NO_2^- / 13/

The second major class of plating solutions uses proprietary organic amines instead of ammonia to complex Pd. They are mostly used for plating pure Pd deposits. They operate in pH range from 9 to 12 and temperatures 40-65°C. This class of plating solutions has a much more narrow application comparing to ammonia-based chemistries.

There were two goals to this study:

- to reduce the corrosiveness of PdNi plating bath towards the equipment and plated substrates
- to reduce the environmental and occupational hazard connected with ammonia evaporation from the bath during plating.

Background

Corrosiveness of the bath

Two aspects of the plating solution corrosiveness were considered:

- attack on the equipment
- degradation of plated substrates

Attack on the equipment (line enclosure, exhaust system, etc.), usually made of stainless steel may be associated with the presence of volatile compounds in the bath which are chemically aggressive towards iron-containing alloys. Gas formation on the anode and cathode during the bath operation enhances the evolution of these compounds in the atmosphere and exposure of the equipment to the harmful vapors. In the presence of moisture, those chemicals form electrolytic film on the metal surface, thus, causing severe electrochemical corrosion which is much stronger than chemical corrosion due to environmental impact.

The degradation of the plated substrates in the bath solution is also important technological issue. Sometimes during emergency line stop, bare substrate is exposed to the plating solution. Etching of the substrate in the bath not only affects the appearance of the final product, but also causes contamination of the bath. All this leads to a loss of deposit quality with bath aging and shortens the useful life of the bath.

Therefore, a search for a more suitable bath chemistry was conducted and resulted in a new formulation.

Ammonia vapors.

Ammonia-based chemistries are most commonly used in PdNi plating. They usually exhibit a number of disadvantages, the most troublesome being the lack of pH stability which results in undesirable fluctuations in alloy composition. Another concern is the environmental impact connected with ammonia evaporation during plating. This is particularly true in most high speed operations where the pH, temperature and solution agitation tend to

be high, thus, favoring the release of ammonia vapors from the bath.
To minimize ammonia evaporation and the need to replenishing it, the recommendation should be made to operate the bath at low pH.
The advantages related to this solutions are:

- *high pH stability, more robust processes*
- less replenishing additions of ammonia
- low ammonia odor, low environmental and occupational hazards,
- high stability of the alloy composition.

PdNi Plating Process

Plating parameters.

New PdNi plating chemistry was designed to provide high stability of the alloy composition under various plating conditions (temperature, pH, agitation, current density) and low corrosiveness of the bath towards equipment, plated substrates, anodes and organic components of the bath. Alloy composition is one of the most important characteristics of the deposit. It strongly affects such material properties as corrosion resistance, hardness, ductility, etc. The alloy composition is a function of the ratio of Pd and Ni concentrations in the bath, current density and other plating parameters. While other plating conditions are easy to control, current density variation across the surface of the plated article is inevitable attribute of any plating process. The larger the size of the part and the more complex shape, the higher the gradient in current density across the surface. That makes the low susceptibility of Ni content to the current density variation a desirable characteristic of the bath. Figure 1 shows the change in %Ni in the alloy over current density range from 50 to 800 ASF for typical and our proprietary formulations. It shows excellent stability in alloy composition over broad current density range for the new chemistry.

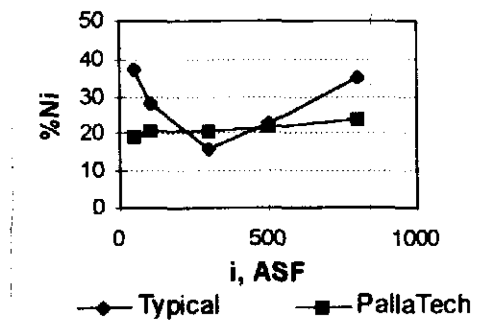


Figure 1. Alloy composition versus current density (total metal 45 g/l; T=40℃; pH=7.3; 200 cm/sec)

The ability to understand how plating conditions affect the %Ni in the alloy and how to manipulate those conditions to produce the desirable alloy composition is critical as well. The influence of temperature and pH on the Ni content can be seen in the Figure 2.

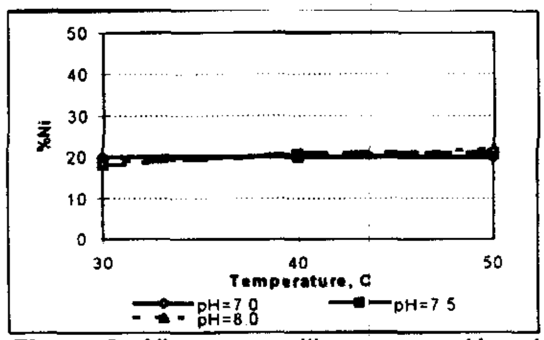


Figure 2. Alloy composition versus pH and temperature (total metal 45 g/l; T=40℃; pH=7.3; 200 cm/sec)

In the operating range of pH from 7.0 to 8.0 and the temperature between 30 and 50°C, percent Ni in the alloy remains about 20%. These data indicate that alloy composition is relatively insensitive to the variations in the plating conditions. Based on this conclusion, we suggest wide operating window for the new bath which is summarized in the Table 1.

Operating parameters	*Typical*	*Range*
Total metal, g/l	45	40-55
Temperature, °C	40	35-55
pH	7.2	7.0-8.0
Current density, ASF	300	50-800
Agitation, cm/sec	200	100-300

Effect of additives.

Organic additives are a powerful tool to manipulate the material properties of the deposit. We studied the effect of brightener (M2B) and surfactant (M2S) on the hardness, ductility and impurity level in the deposit in their concentration range of 2-20 ml/l and 1-10 ml/l respectively. The Knoop hardness was measured by Tukon microhardness tester Model 300 using diamond indenter at 50 g load. Ductility was measured by the ASTM-B-489-85 bend test described elsewhere /15/. The results are presented in the Figures 3 and 4.

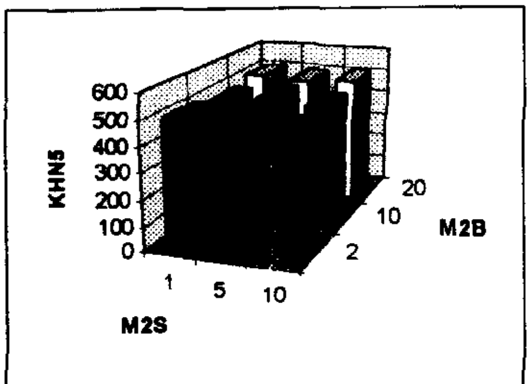


***Figure 3.** Effect of additives on the hardness of PdNi deposit (total metal 45 g/l; T=40°C; pH=7.3; 200 cm/sec)*

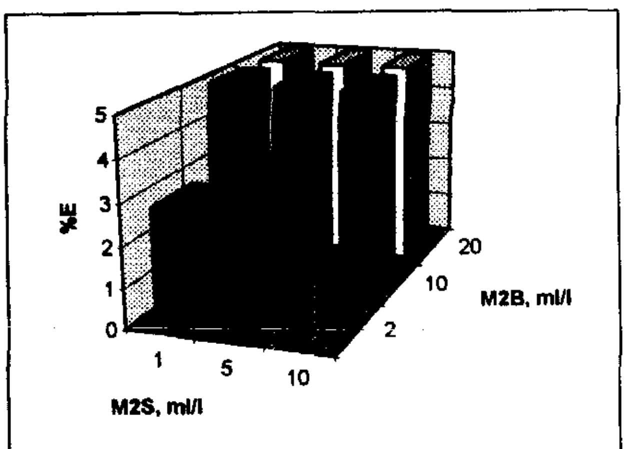


***Figure 4.** Effect of additives on the ductility of PdNi deposit (total metal 45 g/l; T=40°C; pH=7.3; 200 cm/sec)*

The average hardness is in the range of KHN50=490±10 in the tested concentration range without significant influence of either one of the additives. However, both additives affect the ductility. The surfactant slightly reduces ductility which may be overcome by significant positive effect of the brightener when it is present in the concentration higher that 5 ml/l.

To characterize the effect of the additives on the deposit purity, the carbon content was determined by gas fusion analysis. The results are shown in parts per million (ppm) on a weight/weight basis (Figure 5). The data randomly fluctuate below 100 ppm in the tested concentration range which is typical for PdNi plating processes.

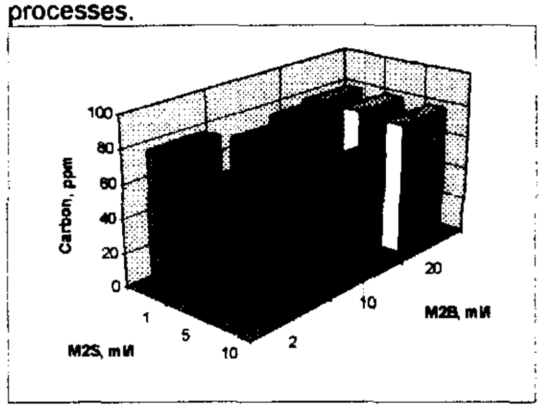
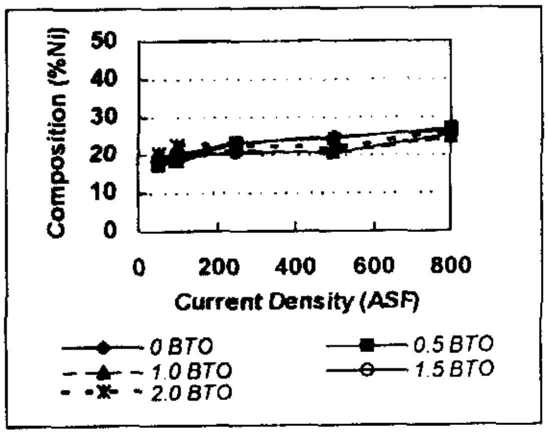


***Figure 5.** Effect of additives on the carbon content in the PdNi deposit (total metal 45 g/l; T=40°C; pH=7.3; 200 cm/sec)*

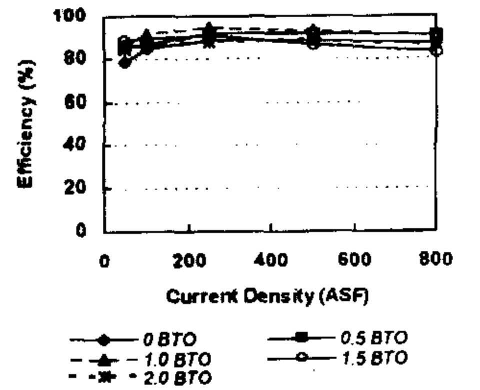
Bath aging study

Accelerated bath aging was done to test the degradation in the bath performance, to verify the effectiveness of maintenance procedures and to monitor the material properties of the deposit. Figure 6 represents the variation in the Ni content (a) and current efficiency (b) versus current density at different stages of the aging process.

It can be seen that there is little change in the bath performance with bath aging and the solution maintains excellent characteristics. Plating rate versus current density data are shown in the Figure 7 and indicate that plating rate also remains steady and fairly insensitive to the bath aging process.



a



b

Figure 6. *Ni content and current efficiency versus current density during bath aging*

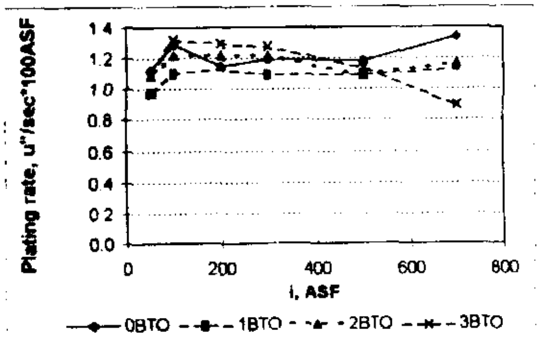


Figure 7. ***Plating rate versus current density during bath aging***

Interesting observation was made when we monitored the pH change during bath aging (Figure 8). Unlike most conventional baths, for the new chemistry, the pH tends to increase slightly during bath operation. The pH adjustment required additions of acid rather than base which indicates that evaporation of ammonia is very low.

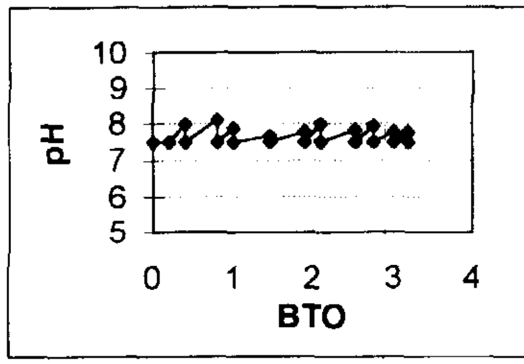


Figure 8. *The pH variation during bath aging*

Corrosiveness of the bath

Corrosiveness of the PdNi plating solution was tested towards the materials *usually used for equipment manufacturing* and as a substrate for common parts in the electronic industry: pure copper and its alloy A194, iron-nickel alloy A42 (common materials for lead-frames), and two types of *stainless steel - SS302 and* SS304. The results were compared for both typical and the new proprietary PdNi plating chemistries and the bath available from other suppliers. The samples of all materials were exposed to the PdNi plating solutions at the temperature 40°C for 147 hours. The percent weight loss was determined after dissolving corrosion products in 20% HCl. The results are presented in the Figure 9.

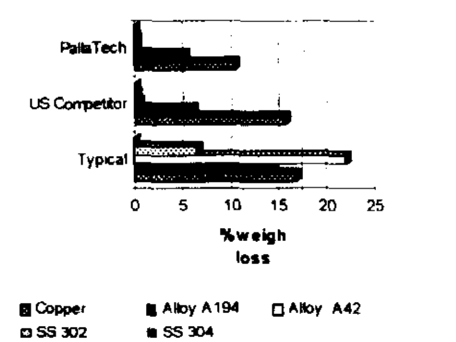


Figure 9. ***Corrosion of different materials (as %weight loss) in PdNi plating solutions***

Our proprietary chemistry exhibits significant corrosion reduction for all materials, but most notably for A42 and

SS302. This implies that less expensive type of stainless steel may be utilized in the line equipment and less attack on the A42 substrate will occur in the lead-frame manufacturing.

Conclusion

The PdNi electroplating process described in the paper provides two important technological advantages:
- it exhibits good pH stability, low evaporation of ammonia during the bath operation and excellent consistency in the alloy composition over wide range of current densities and operating parameters
- PdNi deposit plated from the bath possesses high hardness, good ductility and low level of impurities.

Utilization of this process in different applications will provide technological and environmental advantages.

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