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PALLAMET™ 600 Low Ammonia, High Speed Palladium-Nickel Electroplating Bath for Connector Applications: One Year Industrial Practice

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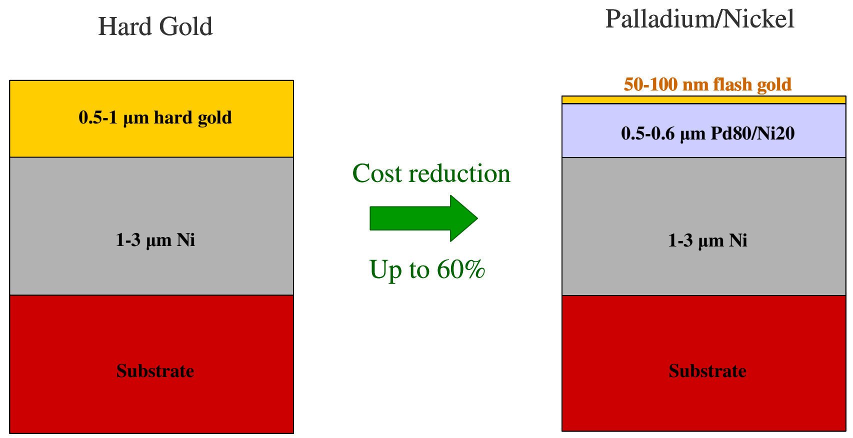

Abstract

In view of the high cost of gold used in contact finishing, electroplated palladium-nickel has become an attractive alternative contact material. PALLAMETTM 600 Palladium Nickel, a low ammonia high speed electroplating bath, introduced into the market in 2007, shows considerable advantages over both conventional ammonia-based processes and new ammonia-free processes. The resulting Pd-Ni deposit (80/20% w/w) is ductile and has a contact resistance similar to hard gold. With a thin gold flash top layer, the palladium-nickel deposit also exhibits excellent corrosion resistance and wear resistance. After minor modifications during the industrial trials, the process has found substantial acceptance in the connector plating industry and by end users.

Introduction

Electroplated hard gold (Au-Co, Au-Ni alloys) has been utilized for decades as a contact material in the electronic industry, especially for high reliability applications, where good corrosion/wear resistance and low contact resistance are required. Electroplated PdNi alloy (80/20% w/w) has received great attention in the connector industry over the last few years, as a hard gold replacement, owing to the lower cost and comparable deposit characteristics. In recent years, the price of gold has ranged from around $800 – 1000 US per troy oz, while palladium has ranged from as high as $550 to as low as $170 US per troy oz . Upon taking all factors into account, such as cost of gold, palladium and nickel, density difference of deposits and the minimum layer thickness required, the cost savings by using PdNi with a thin gold flash instead of using a hard gold layer is estimated to be around 60% (based on late 2007 gold and palladium prices of $850 and $350 US per troy oz respectively). With recent increases in the price of gold and reductions in the price of palladium, the potential for cost savings has increased even further.

The typical layer structures of hard gold and PdNi as contact materials are shown in Figure 1.

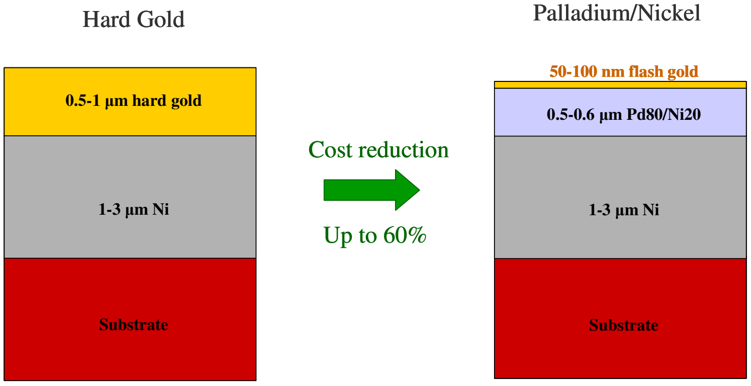

Fig.1. Layer structures for connector applications and the cost reduction compared to hard gold contacts (Data 2007).

The most common PdNi plating processes available on the market utilize ammonia-based electrolytes. The differences among the ammoniacal processes from various plating chemical suppliers are the selection of counter ions (chloride or sulphate) and brightener systems. The sulphate-based electrolytes have become increasingly popular, compared to the chloride-based electrolytes, because of the chloride attack on the expensive selective plating equipment. Few commercial products of ammonia-free plating processes are presently also available. The major advantage of ammonia-free processes is the elimination of ammonia odour under high speed plating conditions. However, this advantage usually comes at the cost of the deposit characteristics and the solution stability.

A newly developed low ammonia plating bath, PALLAMETTM 600 Palladium Nickel, provides the major advantages of an ammoniacal process and at the same time the ammonia odour under high speed plating conditions is dramatically reduced owing to the low ammonia content in the plating electrolyte. In this paper, the major characteristics of the PALLAMETTM 600 Palladium Nickel plating bath as well as the advantages of the process over both conventional ammoniacal and ammonia-free processes are described. The solution maintenance and the deposit characterization methods used by the plating and electronic industries are also discussed.

Ammonia-based PdNi plating processes

Ammonia is a unique complexing agent for plating PdNi alloys. In spite of the significant difference in the reduction potentials of Pd2+ and Ni2+ (more than 1V apart), a desired alloy composition can easily be achieved by adjusting the metal concentrations in the ammonia-based electrolytes at the proper solution pH (7-9). Under these conditions, the plating potentials or the plating current densities applied bear little influence on the alloy composition. The tensile stress in the deposit obtained by using an ammoniacal plating solution is relatively low and therefore the ductility of the deposit is normally extremely good (> 10%). The palladium concentration in the solution is usually maintained by adding the readily available and water soluble tetrammine palladium salts. Another benefit of using ammonia in the plating electrolyte, especially for high speed plating is, that there is no accumulation of ammonia or its anodic oxidation products in the plating solutions during operation, even though ammonia is continuously introduced into the solution with the metal replenishment. Therefore the performance of the process is expected to remain constant throughout the bath life.

Nevertheless, the high ammonia vapour loss during the high speed plating has been recognized as a major drawback of the conventional ammoniacal processes. This rapid ammonia vapour loss may lead to an unstable bath performance and to the formation of insoluble compounds if the rate of the ammonia replenishment is insufficient. The ammonia loss by evaporation, as well as the need for frequent replenishment using ammonia gas or ammonium hydroxide, has also raised environmental concerns for such plating processes. In order to maintain a constant bath performance and to avoid the formation of insoluble compounds, the free ammonia level in a conventional ammoniacal process is maintained at around 80-150 g/l, and in most cases above 100 g/l. Additionally, due to the high ammonia vapour loss, the on-line applicable temperature is limited in order to reduce the unpleasant ammonia odour, and consequently the maximum plating speed is also limited.

Ammonia-free PdNi plating processes

Ammonia-free PdNi electroplating processes have been only recently introduced to the market. Most of the ammonia-free systems employ amines or polyamines as ammonia replacements. The more exotic and higher cost ammonia-free palladium salts are partially responsible for the limited popularity of ammonia-free processes in industry, despite the advantage of complete elimination of on-line ammonia odour. The ammonia-free palladium salts, which may be used in the plating systems, are usually not water soluble and must often be supplied in a solution which contains a high concentration of complexing agents. Unlike ammonia, the lower vapour pressure of the amines or polyamines may lead to the accumulation of the complexer in the plating solution. The carbon chains of those amines cannot be completely decomposed to CO2 at the anode, even under high speed plating conditions, where the anode potential is very high. The detrimental effects of the accumulated or the partially decomposed complexing agents during operation are a major concern of the ammonia-free systems. The pronounced dependency of current density on the PdNi alloy composition due to the nature of amine complexing agents is another drawback of such systems. Additionally, it has been observed by the authors that the PdNi deposits obtained by using non-ammonia processes often suffer from higher tensile stress, which leads to a reduction in ductility.

PALLAMETTM 600 Palladium Nickel– A low ammonia PdNi plating bath

PALLAMETTM 600 Palladium Nickel is a proprietary chloride-free high speed PdNi plating bath, introduced by Rohm and Haas Electronic Materials (now Dow Electronic Materials) in 2007. The operating parameters of this bath are given in Table I.

Table I. PALLAMETTM 600 Palladium Nickel Bath Operating Ranges (to obtain Pd80/Ni20)

Parameters	Range
Palladium	15 – 35 g/l
Nickel	6 – 15 g/l
Palladium to Nickel Ratio (weight)	2.5 : 1
Temperature	50 – 70 °C
pH	7.0 – 7.5, using NaOH solution
Current Density	5 – 60 A/dm^2
Deposition rate	up to 15 µm/min
Free ammonia	< 10 g/l

The major improvement to the PALLAMETTM 600 Palladium Nickel bath compared to other conventional ammonia-based PdNi plating baths is the significantly reduced ammonia content in the electrolyte. The free ammonia in the plating bath, obtained by analyses of bath samples from various production lines, is less than 10 g/l, which is approximately 10 times lower than that in a conventional ammoniacal electrolyte. At the operating pH (7.0-7.5), the ammonia in the solution exists mainly in the form of palladium and nickel complexes. This limited ammonia content in the electrolyte retains the characteristics of conventional ammonia-based palladium-nickel plating products (eg PALLAMETTM 500 Palladium Nickel), such as stable PdNi alloy composition (80/20) over a wide current density range (Figure 2), and a highly ductile PdNi deposit. The alloy composition is usually determined by XRF analysis of the PdNi deposit directly over a copper based substrate.

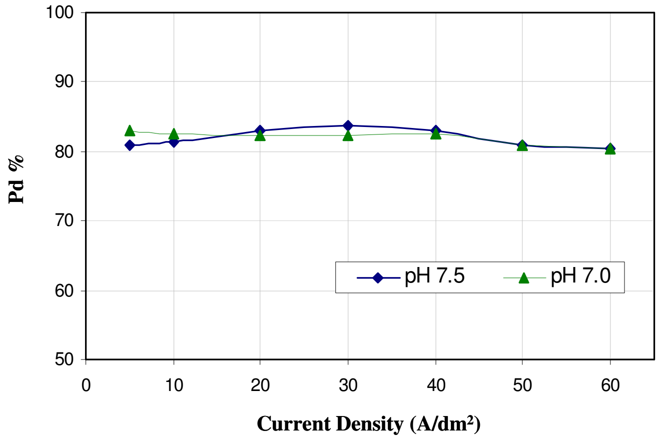

Fig.2. Pd % (w/w) in the deposit from the PALLAMETTM 600 Palladium Nickel bath and the influences of the current density and pH

The stability of the electrolyte under high speed production conditions was a major concern for many customers before commencing the trials with PALLAMETTM 600 Palladium Nickel. The stability of the plating solution is maintained by an auxiliary complexing agent, in addition to the minimum ammonia in the solution. Since this compound is a weaker complexing agent for Pd2+ and Ni2+ compared to ammonia, the addition of this second complexing agent hardly affects the function of ammonia during deposition. It is proven that this second complexing agent slowly and completely decomposes to CO2 and other harmless gas phase compounds on the insoluble anode under high speed plating conditions, thereby producing no detrimental effect to the performance of the electrolyte with bath age. The production trials at different customers show that the PALLMETTM 600 Palladium Nickel electrolyte is chemically stable, even though the free ammonia concentration in the bath is extremely low.

The on-line ammonia odour is hardly noticeable when operating the PALLAMETTM 600 Palladium Nickel bath under the recommended conditions. No ammonia replenishment or pH adjustment using ammonia is required for this process. The addition of ammonia to the electrolyte stems solely from the replenishment of the metals, mostly from the palladium salt. Two water soluble palladium salts can be used for palladium replenishment, namely tetrammine palladium sulphate, which has been used for many years in practice in the PALLAMETTM 500 Palladium Nickel bath, and a newly introduced sulphate-free tetrammine palladium (PALLAMET Special Pd Salt). Using the PALLAMET Special Pd Salt is beneficial, as it does not introduce sulphate continuously into the plating solution which would cause rapid specific density increase of the solution followed by crystallization, so-called “salt-out”. Using the PALLAMET Special Pd Salt will extend the bath life significantly.

To ensure perfect adhesion of PdNi over nickel under all circumstances of production, an activation step prior to PdNi plating is recommended. Among several available activation solutions which have been tested during the industrial trials, a novel acidic nickel strike (PALLAMET Acidic Strike) exhibits the best results, promoting consistently reliable adhesion under production conditions. The low cost PALLAMET Acidic Strike, compared to palladium or gold strikes, is designed for use prior to the PdNi plating processes, and no foreign chemicals will be introduced into the PdNi plating solutions, even without an intermediate rinsing step. Frequently changing the PALLAMET Acidic Strike solution will extend the bath life of the costly PdNi plating solution by preventing drag-in of contaminations from other plating solutions. The adhesion of the PdNi deposit over nickel was tested on-line by bending plated connector pins 180° with a smallest possible radius and checking the bent areas under a microscope. The criterion for good adhesion is no lift-off of the PdNi layer from the Ni-undercoat.

The standard process sequence of plating PdNi alloy using PALLAMETTM 600 bath is given in Table II. The production trials show that the PALLAMETTM 600 Palladium Nickel bath can be used for various reel-to-reel applications with differing cell designs of selective plating, such as control depth, brush plating, jet plating and spot plating.

Table II. Standard process sequence using PALLAMETTM 600 Palladium Nickel

Step	Process
1.	Soak clean or electroclean
2.	Activation
3.	Bright or semi-bright nickel plating
4.	Pallamet Acidic Strike
5.	Pallamet 600 Palladium Nickel
6.	Flash gold (< 0.1 µm)

Characteristics of the PdNi deposit

It has been concluded by various connector manufacturers that the optimum PdNi alloy composition for gold replacement is Pd/Ni 80%/20% w/w. As mentioned above, this optimum alloy composition is achievable over the current density range of 5 – 60 A/dm2 using PALLAMETTM 600 Palladium Nickel. Depending on the applications, the PdNi alloy composition can also be adjusted by changing the metal concentrations in the bath. The properties of deposits from this bath are given in Table III.

Table III. Properties of deposits from the PALLAMETTM 600 Palladium Nickel Bath

Appearance	white and bright	
Pd%	80% ± 5, adjustable	
Density	11 g/cm^3	
Hardness	320-450 HV	
Ductility	> 8%	ASTM B 489-85 (2003)
Contact resistance	< 5 mΩ at 5cN	DIN EN 60512
Porosity	Pass (with flashgold)	ASTM B-735-06

The deposits are bright and highly ductile. The brightness of the PdNi deposit produced by the bath without addition of any brightening agent is satisfactory for connector applications. For special cases where a highly bright deposit is desired, PALLAMETTM 600 Brightener can be applied. No negative influence of the addition of the PALLAMETTM 600 Brightener on the deposit ductility or the adhesion over nickel has been observed in the lab or reported from production. Another function of the PALLAMETTM 600 Brightener is to increase the tolerance of the electrolyte against contamination, especially cyanide contamination from gold strike solutions.

A most commonly applied porosity test is the nitric acid vapour test (ASTM B-735-06), which was originally designed for gold contact material. It should be noted that, unlike gold, the PdNi layer alone will react with nitric acid vapour forming a brown film because of the nature of palladium and nickel. However, a thin gold flash layer (50-100 nm) on top of PdNi is sufficient to resist the attack of nitric acid vapour. It has been observed that the gold flash plating parameters are even more critical than the PdNi bath itself for obtaining good porosity test results.

Summary

PALLAMETTM 600 Palladium Nickel presents the advantages of both conventional ammoniacal and ammonia-free palladium-nickel plating products. The on-line ammonia odour in a production environment is dramatically reduced owing to the extremely low free ammonia in the electrolyte. In addition, the PALLAMET TM 600 Palladium Nickel bath does not require any additions of ammonia for pH adjustment during use. The beneficial characteristics of the plating process and the PdNi deposit of the conventional ammonia-based products are retained with PALLAMETTM 600 Palladium Nickel. The production trials show that the PallametTM 600 bath is suitable for various reel-to-reel selective plating techniques and the plating bath is chemically stable, in spite of the low ammonia content. The quality of the PdNi deposits produced by the PALLAMETTM 600 Palladium Nickel bath is well accepted by end users as a viable hard gold replacement at substantially lower cost.

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