Palladium-Nickel Alloys Electrodeposited from Chloride-Free Electrolytes

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The following article highlights the introduction of a new chloride-free, weakly ammoniacal, palladium-nickel process providing enhanced corrosion resistance via chloride replacement with sulfate.

Keywords: *Palladium-nickel, gold substitute, alloy electrodeposition, chloride-free electrolyte*

Introduction

The interest in palladium-nickel alloys as a gold substitute for the electronics industry can be traced back to the 1960s, although at that time, the price of gold was a mere 35 US$ per ounce. Since then, the gold price has increased twentyfold (Fig. 1).[1]

The requirement and the necessity of reducing costs have increased with this enormous price increase. However, the departure from gold is not easy. Its physical and chemical characteristics are exceptional with respect to corrosion and tarnish resistance as well as its thermal and electrical properties. Only copper and silver possess higher electrical conductivity, but without the corrosion and tarnish resistance of gold.

This important characteristic of gold ensures long term stability of its electrical properties. In addition to the risks of its high and volatile price, gold has intrinsic technical disadvantages such as comparatively low friction resistance and hardness. In order to increase these properties, a small amount of cobalt or nickel (ca. 0.1 to 1%) may be added to the gold electrolytes. Further disadvantages of gold electrolytes are the presence of cyanide (from the gold source)[2,3] and the fact that most electrodeposits suffer from porosity, resulting in failure to provide corrosion stability.

Palladium and palladium alloy deposit properties

Palladium and palladium alloys have significant advantages when compared to gold. They possess low porosity at very low, nano-range thicknesses, resulting in excellent corrosion protection in addition to high hardness values.[4,5,6]

The downside for pure palladium electrolytes, however, is their sensitivity to impurities such as copper or cyanide, in addition to the co-deposition of hydrogen, which may result in significant deposit stress.[2,7] This observed microcrack formation of pure palladium electrodeposits due to hydrogen absorption, resulting in internal stress by grid contraction, does not occur for palladium-nickel electrodeposits containing approximately 15 wt% nickel. Moreover, palladium-nickel electrolytes form homogeneous mixed crystals, reducing tension within the electrodeposited crystal structure.

Deposit hardness increases with the increasing nickel concentration, yet high ductility is achieved compared to pure palladium coatings. In addition to this increase in hardness, the trend of the electrodeposit properties with increasing nickel content can be summarized as follows:[2]

- Decrease in corrosion resistance
- Increase in abrasion resistance
- Increase in frictional forces
- Increase in oxidation susceptibility
- Decrease in porosity
- Decrease in crack formation
- Decrease in hydrogen brittleness
- Decrease in solderability

The above trends are directly dependent on the electrolyte and plating conditions used.

The following article highlights the introduction of a new chloride-free, weakly ammoniacal, palladium-nickel process which provides enhanced corrosion resistance through chloride replacement with sulfate.[8]

The important technical properties of the electrodeposits, such as solderability, ductility and hardness are not affected by this formulation change. Contact resistance of the Pd/Ni and the subsequent flash gold-plated surface must correspond to the relevant standard, ASTM B867.[9]

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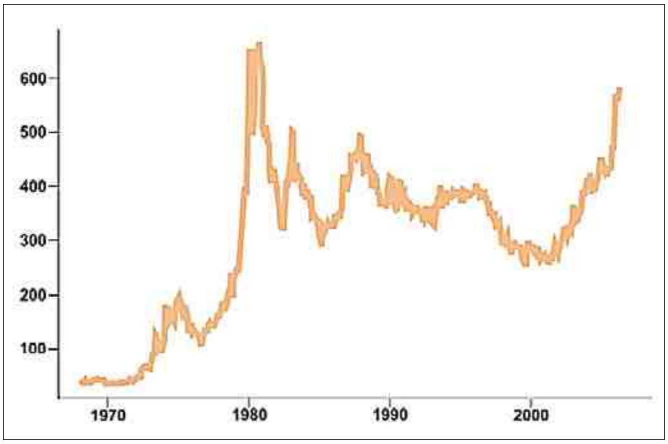


Figure 1—The price of gold since 1968 in US$ per ounce.[1]

Process performance with respect to the applied current density is determined by the Pd:Ni alloy ratio. In an extensive design of experiments (DOE) study, the alloy composition relationship with palladium content, temperature, pH and solution "make-up" concentration was evaluated.

From the high-speed 'Jet-lab' experiments undertaken, bonding and "bend test" ductility properties, together with maximum achievable current density and tolerance to impurities, *e.g.* copper and cyanide, complimented the experimental design.

A new alternative for palladium-nickel electrodeposition

A new chloride-free palladium-nickel electrolyte** has been tested for high speed plating applications. The electrolyte is sulfate-based at a neutral pH and has significantly reduced ammonia content, resolving corrosion and odor issues that are experienced with chloride systems.

With plating rates of 8.0 µm/min and current densities to 40 A/dm^2, cathodic efficiencies of 85 to 95% are achievable. Deposits possess high hardness, good bonding and high ductility (>4%) properties.

Neutral pH electrolyte	pH 7.0 to 7.5
Alloy ratio	Pd/Ni; 80/20
Density	11.22 g/cm^3
Knoop hardness	500 to 575 HK$_{25}$
Operating temperature	65°C
Current efficiency	85 to 95%
Current density range	20 to 40 A/dm^2
Deposition rates	~ 8.0 µm/min (at 40 A/dm^2)
Contact resistance (Pd/Ni)	~ 1.0 mΩ
Contact resistance (Pd/Ni+Au flash)	~ 0.8 mΩ

Design of experiments (DOE)

In order to examine the influence of individual electrolyte parameters on the limiting current density and alloy composition, test results were processed using special DOE-software[10] which identified and assessed the main parameters. Concentration of the solution matrix (make-up), palladium concentration, temperature and pH were all varied. The variation ranges used and results are shown in Table 1.

Effect of electrolyte parameters on Hull cell characteristics

Figure 2 shows an example of homogeneous Pd/Ni deposit from the Hull cell investigation. To simulate normal electrolyte conditions, paddle agitation was used and a high current loading of 5.0 A for one minute was used. This produced a band of high current density (HCD) burn with a maximum width of 1.0 cm.

Within the scope of the DOE analysis, electrolyte parameter influences were quantified and the trends (with respect to HCD burning) were determined from Hull cell tests as graphically illustrated in Fig. 3. High current density burn could be reduced by increasing either temperature or palladium concentration. Increasing the solution "make-up" concentration increased the HCD burn area. Variation of the pH showed little effect.

** *Pallacor HSN-S, Atotech Deutschland GmbH, Berlin, Germany.*

Table 1
DOE: Effect of electrolyte parameters on deposit properties

Make-up Concentration, mL/L	Palladium Concentration, mL/L	pH	Temperature, °C	Palladium, %	HCD Burning Range, cm
560	160	6.75	65	82.09	3.00
480	200	7.50	65	79.65	2.10
400	240	6.75	65	82.61	1.60
400	160	8.25	65	70.80	1.70
560	240	8.25	65	86.44	1.80
560	240	8.25	55	88.96	3.50
560	160	8.25	75	75.17	2.10
400	240	6.75	75	79.74	1.20
400	160	8.25	55	77.65	2.80
560	160	6.75	55	84.30	3.70

Figure 2—Typical bright and homogeneous deposit of electrodeposited Pd-Ni alloy as shown by Hull cell.

Effect of electrolyte parameters on alloy composition

Using the experimental design parameters shown in Table 1, the effects on alloy composition were measured. The results are shown in Fig. 4.

The DOE analysis results highlight extreme alloy stability within the designated pH range. As expected, the wt% of palladium increased with increasing solution "make-up" and palladium concentrations. By contrast, raising the temperature decreased the palladium content.

Testing was undertaken using a high-speed Jet-lab cell to derive relationships between alloy composition and current density. The flow rate was fixed at 600 L/min. Two test electrolytes were used at different palladium and nickel concentrations:

1. 12 g/L Pd; 8 g/L Ni
2. 15 g/L Pd; 10 g/L Ni

It was observed that even at the low palladium content, alloy composition remained stable over a very wide current density range (Fig. 5).

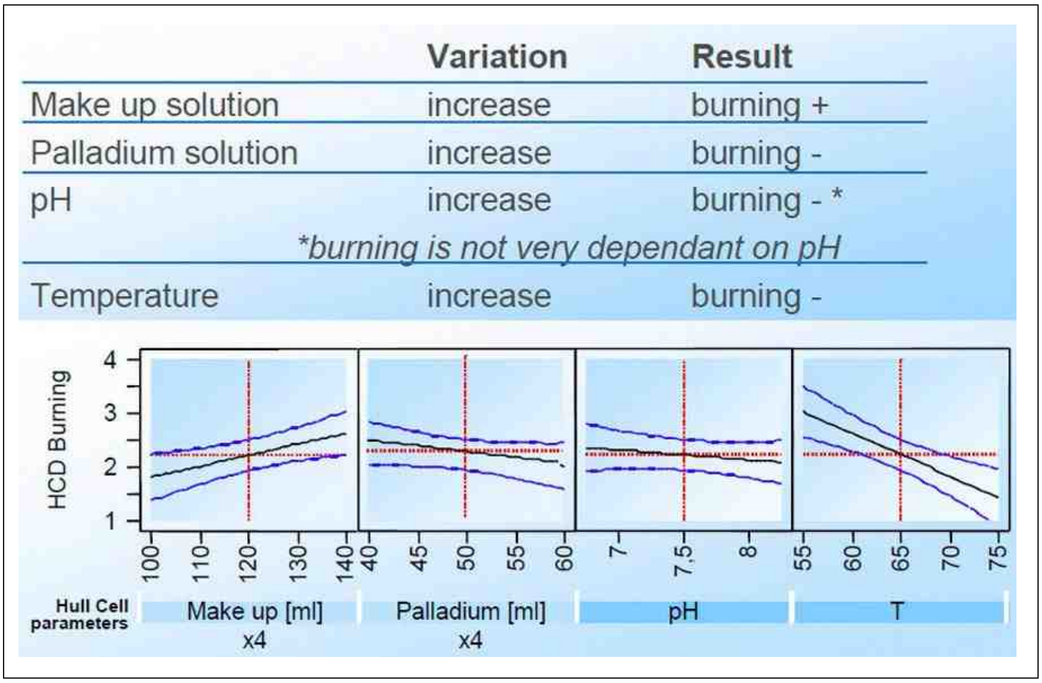
By operating at the higher palladium concentration, reduced HCD burning of the Jet-lab test samples was observed, to a limit of 70 A/dm^2. The appearance of the individual test specimens are shown in Figs. 6 and 7.

At the lower value of 12 g/L palladium, good appearance was obtained up to 50 A/dm^2, increasing to 70 A/dm^2 at 15 g/L Pd.

Solderability investigations

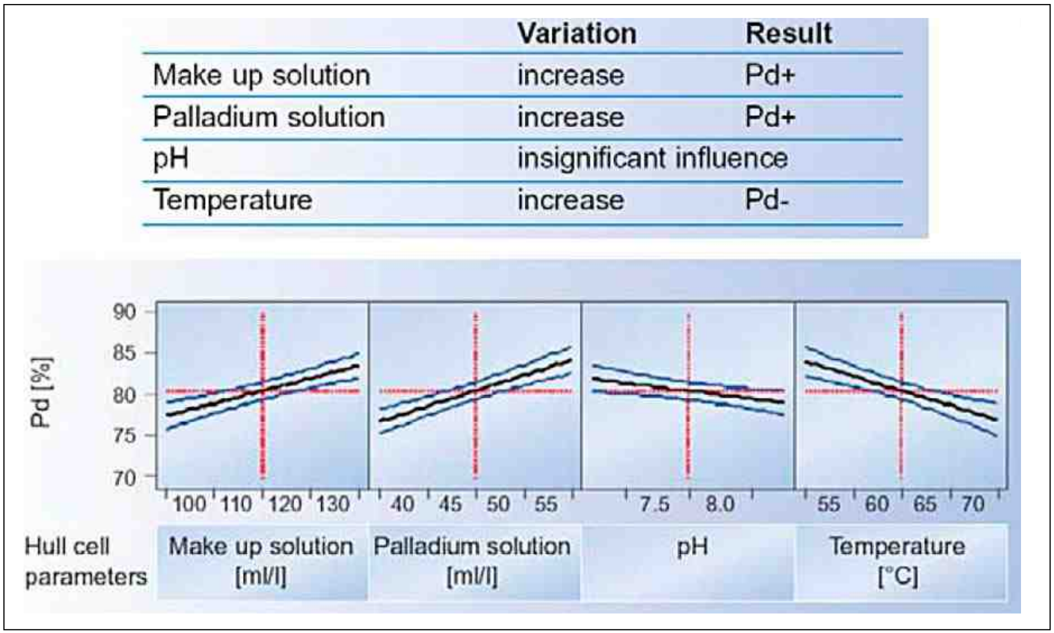
Using a solderability wetting device, results were obtained for the wetting speed, the wetting force and the soldering behavior (Fig 8). The lead-free solder, a Sn-Ag-Cu alloy, was used. The soldering parameters were as follows:

Solder	Sn-Ag-Cu
Temperature	245°C
Density	7.2 mg/mm^3
Immersion time	5 sec
Sensitivity	10
Immersion depth	4 mm
Immersion speed	21 mm/sec



	Variation	Result
Make up solution	increase	burning +
Palladium solution	increase	burning -
pH	increase	burning - *
	**burning is not very dependant on pH*	
Temperature	increase	burning -

Figure 3—DOE: Effect of electrolyte parameters on Hull cell deposit character.



	Variation	Result
Make up solution	increase	Pd+
Palladium solution	increase	Pd+
pH	insignificant influence	
Temperature	increase	Pd-

Figure 4—DOE: Effect of electrolyte parameters on alloy composition.

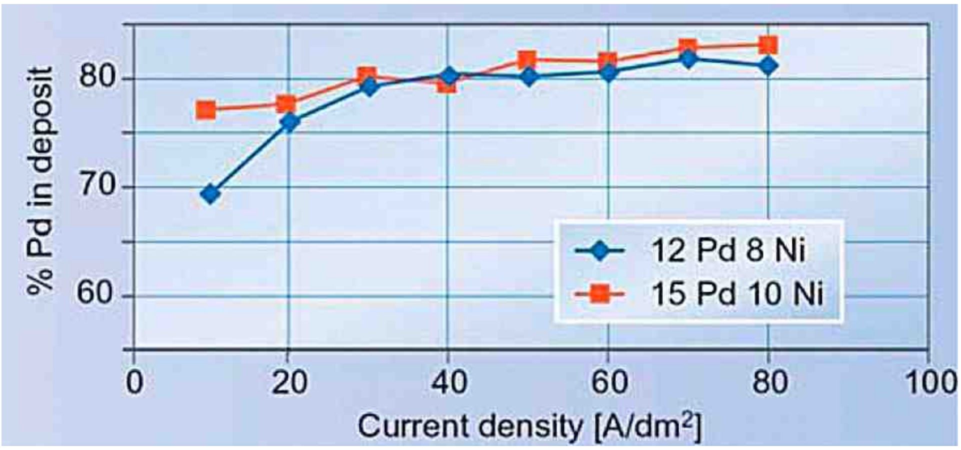


Figure 5—Very stable Pd/Ni ratio (80:20) over a wide current density range.

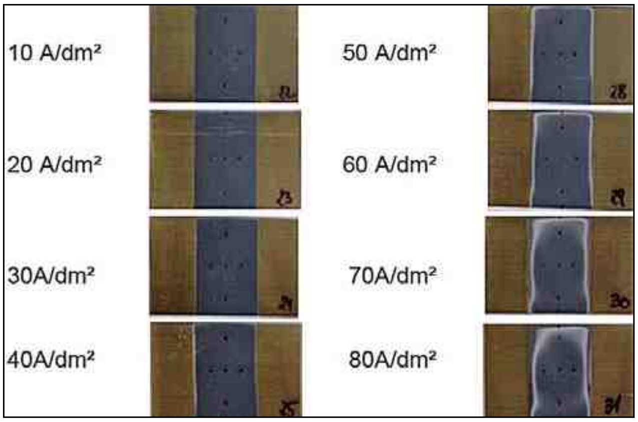


Figure 6—Jet-lab test specimens - bath metal concentration: Pd 12 g/L, Ni 8 g/L. Good quality to 50 A/dm².

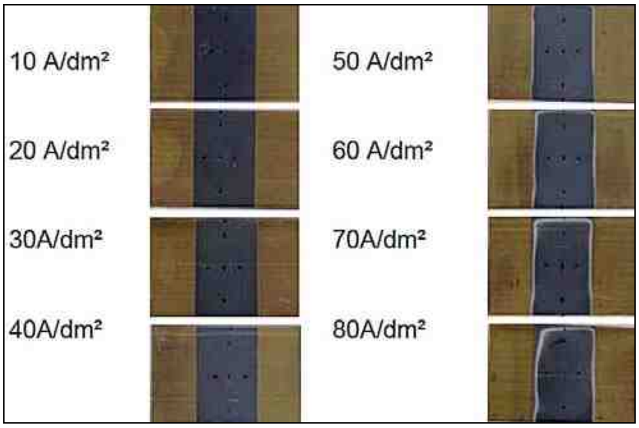


Figure 7—Jet-lab test specimens - bath metal concentration: Pd 15 g/L, Ni 10 g/L. Good quality to 70 A/dm².

Figure 8—Wetting balance equipment used to measure solderability of lead-free solders (wrt ZCT).

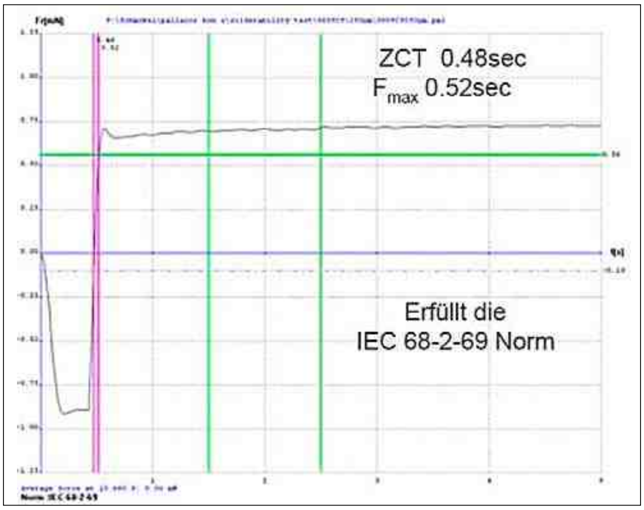


Figure 9—Solderability profile from wetting balance measurements.

The test samples were inspected after one week of dry storage at room temperature. The palladium-nickel plated deposits (without gold flash) were tested for wetting and solderability. A weak activating flux*** was used throughout.

The wetting balance profile shown in Fig. 9 is the mean of ten individual measurements. The measured zero point crossing, "ZCT" (Zero Crossing Time) is shown as 0.48 sec. All solderability results meet the specifications of standard DIN IEC 68-2-69.[11,12]

Bonding and ductility investigations

To assess the bonding properties of palladium-nickel deposits, test samples were prepared using a copper substrate containing a 3-μm nickel layer, rinsed, then plated with 0.4 μm of the chloride-free palladium-nickel. A palladium strike was not used (Fig. 10).

Figure 10—Test sample sequence prior to bond testing.

The plated surface was then mechanically scored as a cut grid and bonding assessed by a "pull-test" using an adhesive strip. No peeling of the coating itself could be observed (Fig. 11). Hence, the palladium-nickel deposits can be applied directly to nickel without the need of a palladium strike.

To test ductility, brass connectors (Cu 63/Zn 37) were plated and then bent 180° (0.3 mm) using the previous process sequence. Microscopic evidence highlighted crack formation within the nickel, with excellent bonding and flexibility of the subsequent palladium-nickel coating.

Bonding tests were repeated after contamination with copper and cyanide. For this study, 1.35-μm nickel and 0.25-μm Pd-Ni was used. Contamination levels were set very high at 100 mg/L with no observed deterioration of the plating characteristics.

Figure 11—No peeling of either Ni or Pd-Ni coating from the copper substrate; no Pd strike necessary.

Figure 12—Cracks in the nickel layer, with excellent bonding of the Pd-Ni after the bend test.

**** Litton Kester 950E3.5, Litton (Kester Solder), Litton Industries, Inc., Des Plaines, IL.*

Summary

The process described here is a slightly ammoniacal, chloride-free electrolyte for high-speed palladium-nickel deposition. Using a design of experiments study, the electrolyte "make-up" and palladium concentrations were varied together with pH and temperature. The influences on alloy composition and high current density burning in Hull cell testing were examined.

The process showed exceptionally high alloy stability with respect to pH and current density variation. It was also shown that low palladium concentration could be tolerated.

By increasing both the palladium and nickel content to 15 and 10 g/L, respectively, the maximum achievable current density can be extended to 70 A/dm^2. Palladium-nickel deposits provide excellent solderability properties with a zero crossing time of less than 5.0 sec, thus meeting the requirements of DIN IEC 68-2-69. Good bonding of the palladium-nickel coatings was also observed from both bond and bend tests. The process shows excellent tolerance to high (100 mg/L) contamination levels of both copper and cyanide.

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