Developments in Electroplating of Palladium and its Alloys

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With the escalating price of gold the demand for palladium and its alloys in electronic applications has seen resurgence as the cost savings achieved by utilizing palladium and its alloys are now very significant. This paper gives a status report on the current situation and applications, highlighting the features and benefits of the deposits, whilst also technically updating on the innovative generation of environmentally aware non-ammonia, non-chloride processes that are the future of palladium and palladium alloy plating. Physical properties of the deposits including porosity and deposit structure are investigated. Application of standard specifications for testing palladium and its alloys are explained and highlighted.

Keywords: *Electronic applications, palladium, palladium alloys*

Introduction

Palladium and its alloys have been used on electronic connectors for more than 25 years. Palladium, and more frequently palladium-nickel (Pd = 80%; Ni = 20%) have usually offered a cost saving in comparison to the traditional connector finish of acid gold - but has it always been cheaper?

The answer to this question is, generally, yes. However, for a period in 2000 and 2001, palladium prices soared (mainly as a result of Russia restricting exports of palladium) and the price of palladium exceeded $1,100 per Troy oz, making the cost of deposition of palladium and its alloys more costly than gold for the first, and only, time in its history (Fig. 1). Coincidentally the gold price had tumbled from a steady price around $350 to 400 per Troy oz to a record low below $260 per Troy oz (Fig. 2).[1]

Naturally at this time, people looked closely at their costs and then made a rapid switch back from palladium-nickel to traditional gold plating.

This price differential continued, however, for only a few months and soon palladium prices tumbled. The gold price since September 2001 (possibly influenced by 9/11) has continued to rise, exceeding $1,000 /Troy oz in early 2008. This has restored the more usual situation where palladium-nickel plating is significantly cheaper than gold. Currently palladium-nickel offers savings of around 80% when compared, thickness for thickness, to acid gold plating.

Connector manufacturers are now rapidly switching back to palladium-nickel and are pleased to find that a vastly improved process is available with the emergence of ammonia-free palladium-nickel.**

This process is the world´s first commercially available truly ammonia-free palladium-nickel plating process. It removes the unpleasant odors that were always a troublesome and harmful part of the previous ammonia-based palladium-nickel plating systems.[2] Being ammonia-free, of course it removes the hazards and odors related to using ammonia, but in addition offers the benefit of reduced plant corrosion and reduced corrosion of copper-based connector parts.

This non-aggressive electrolyte increases bath life and reduces costs further as plant reliability and service life are increased, maintenance costs are reduced and connector rejects are minimized, with failures due to ammonia corrosion eliminated.

With an operating pH of around 4.0 the bath is synergistic with both the acid gold plating and nickel plating processes utilized in a plated connector.

The whole sequence of nickel, palladium-nickel and gold plating (gold flash) are performed in a pH range of 4.0 to 5.0. This commonality of pH range also makes the sequence less prone to adhesion failures that were a common and inherent difficulty in utilization of the ammonia-based systems.

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*** MetPal III Pd-Ni: Ammonia-free Palladium-Nickel Plating Processes: Metalor Technologies International SA, Neuchâtel, Switzerland.*

Figure 1—*Palladium price, $ per Troy oz - September 1991 to March 2008.*

Figure 2—*Gold price, $ per Troy oz - September 1991 to March 2008.*

Deposit comparison

Since the 1980s, the connector industry has studied functional properties of gold and palladium alternatives and has made a definitive choice with a typical high specification connector now often utilizing palladium-nickel and gold flash:[3]

0.75 μm (30 μ-in.) palladium-nickel + 0.05-0.10 μm (2.0-4.0 μ-in.) gold flash.

This duplex layer is used as a direct substitute for the traditional finish that had previously simply utilized acid hard gold plating at a nominal thickness of 0.75 μm (30 μ-in.).

Similarly for lower thicknesses, the substitution of gold by palladium-nickel is usually done on a μm-for-μm basis, with a gold flash of around 0.05-0.10 μm (2.0-4.0 μ-in.) always applied.

Why?

Of course reduced cost was a big factor, but additionally performance benefits influenced the decision.

- Improved ductility
- Reduced porosity
- Better solderability
- More stable contact performance
- Non-cyanide process

All of the above are true for palladium-nickel deposits. The only negative aspect was the use of ammonia in all of the available palladium-nickel electrolytes.[4]

Industry choices in recent years

In the 1990s, palladium-nickel was extensively used, but in 2001, many people reverted to gold because the palladium price had escalated dramatically. Now metal prices have drastically reversed, so why is the return to palladium-nickel since 2001 not so swift?

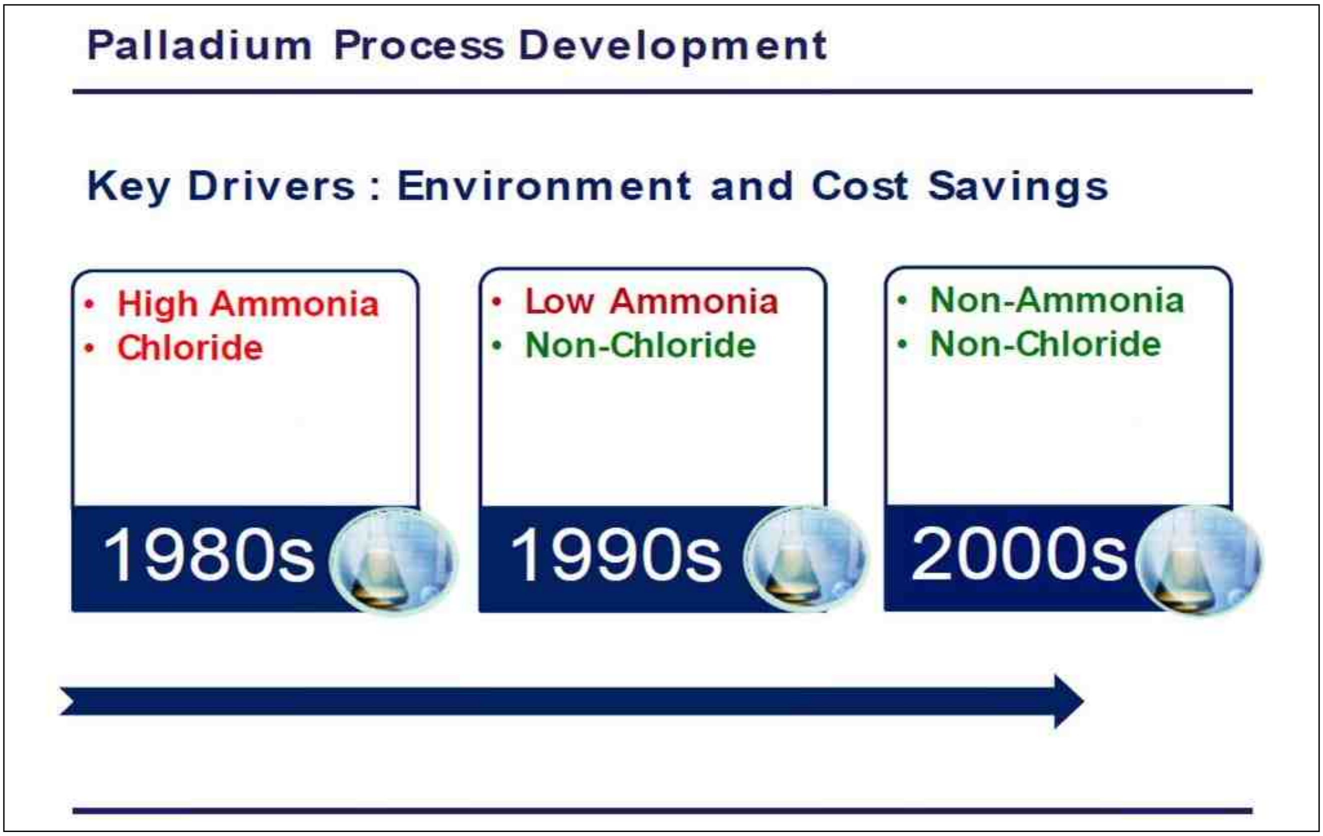
One possibility is maybe a suspicion of palladium price stability, but this is surely a very small part of the reason. History has shown palladium-nickel to be cheaper than gold in its entire history for all except a very few months in 2000 and 2001. All indications are that this situation will remain for the foreseeable future, and currently 80% of any precious metal costs can be saved immediately by reverting to palladium-nickel.

Another possible and maybe more likely reason is the fact that palladium-nickel use is associated with ammonia use, and at operating temperatures in the range of 45 to 60°C, where ammonia evolves as irritating fumes. Ammonia fumes make life uncomfortable for operators working long hours on reel-to-reel production lines.

A reliable, ammonia-free industrial alternative was not available, however. Metalor Technologies has conducted extensive research in order to improve this situation with particular focus on electrodeposition for the connector industry. An innovative and novel ammonia-free process has been developed, based on a radically different chemistry. The result is a truly ammonia-free process.

Historically (Fig. 3), alkaline ammonia baths have predominated the market, with typical formulations comprised as below:

- Ammonium chloride, sulfate or nitrite
- Palladium present as an ammonia-based complex
- Alkaline pH of 7.0 to 9.0
- Stress reducing additives
- Brighteners
- Surfactants
- Stabilizers



Palladium Process Development

Key Drivers : Environment and Cost Savings

- High Ammonia
- Chloride

1980s

- Low Ammonia
- Non-Chloride

1990s

- Non-Ammonia
- Non-Chloride

2000s

Figure 3—*History of palladium-nickel process development.*

These baths have been optimized[4] but inherently have the following production concerns:

- Irritant ammonia vapors
- Necessity of frequent and costly ammonia additions
- Adhesion failures between nickel and palladium-nickel
- Corrosive attack, by ammonia, of copper alloys used in connectors
- Corrosion of plant and equipment, by both ammonia and chloride
- Corrosion of stainless steel
- Risk of metallic contamination by corrosive attack of basis materials
- Insoluble salts formation issues at anodes, in brush applications
- Nickel hydroxide formation *in-situ* by drag-in of Ni^{+2} ions into the ammonia-based Pd-Ni bath.

Palladium-nickel: ammonia-free

The ammonia-free process is suitable for both low and high speed applications and some key features and benefits are shown in Table 1. Typical deposit properties from the ammonia-free palladium-nickel process are given in Table 2, and the process operating parameters are given in Table 3.

Specifications

It is often mistakenly assumed that specifications designed for detecting porosity in gold electrodeposits can simply be applied to the equivalent thickness of palladium-nickel deposits, but a simple understanding of the very different chemistries should show that this cannot be the case.

Before going further, it is critically important to note that the nitric acid vapor porosity test should not be applied to palladium-nickel deposits[5] as both palladium and its alloys are chemically attacked by oxidizing acids.[6]

It cannot be overstated that the function of the test is to expose porosity and NOT to attack perfectly good plated layers. For this reason, specific tests are outlined for palladium-nickel deposits and are defined in the relevant ASTM specification, B 867-95.[5] The tests defined within this specification are designed to detect porosity in palladium-nickel deposits and, as stressed above, the nitric acid vapor test is not utilized.

Despite this knowledge there are still many specifications that demand the use of nitric acid vapor on palladium-nickel plated connectors. This of course results in many difficult situations for connector manufacturers who often see failures despite excellent plating practices being employed.

It is the authors' opinion that this is an area that clearly needs addressing and highlighting to enable more meaningful test procedures to be universally accepted for palladium-nickel deposits to the benefit of all.

Industrial experience 2002 - 2008

In August 2002, the first ammonia-free production bath was installed in Taiwan in a reel-to-reel line plating connectors in a brush plating cell.[7] The original bath has now been in operation for almost seven years without the need for bath replacement. Over this period of time, the bath chemistry, alloy composition and solution density have all remained stable.

In brush plating, it is often the case that agitation and flow rates are very low. This is particularly true when smaller and more complex connector designs are plated. A palladium concentration, typically, 12 to 14 g/L is sufficient to achieve a current density of 20 A/dm².

Ammonia-free palladium-nickel operates at its best when solution agitation is high, typically in moving mask, wheel/jet plating and dip selective/partial immersion reel-to-reel lines. Line speeds of 10 m/min and current densities of around 15 to 25 A/ dm² are applied.

The process prefers high temperatures for operation and 65°C (149°F) is the usual choice. Ammonia-free palladium-nickel will perform best with maximum deposition speed at 70°C (158°F), but most people are satisfied operating at 65°C (149°F), which is more than fast enough to meet production needs.

Many successful installations have subsequently been made for connector plating worldwide including China, Taiwan, Germany, Ireland, India, Singapore, Finland, USA and the United Kingdom.

The bath has performed well and in a wide variety of plant designs. The number of successful installations is continuously growing as more and more connector manufacturing companies move back to palladium-nickel and utilize this innovative ammonia-free technology.

Ammonia-free palladium strike

An ammonia-free palladium strike, while not essential for the process operation, does offer many advantages for trouble-free production. A strike layer:

- Ensures good adhesion to a nickel underplate
- Reduces contamination of main process bath
- Greatly improves porosity
- Improves bath life
- Avoids use of a cyanide-based gold strike (with attendant contamination issues).

Using an ammonia-free palladium strike naturally yields improved quality connectors with reduced porosity and as a consequence it enables lower thickness deposits to be utilized leading to further cost savings.

Table 1

Features and benefits of ammonia-free palladium-nickel

Feature	Benefit
Ammonia-free	Improves working environment
Ammonia-free	Reduces attack of copper and its alloys
Ammonia-free	Eliminates the cost of ammonia replenishment
Chloride-free	Reduces costly plant corrosion
Ammonia and chloride-free	Reduces metallic contamination
Ammonia and chloride-free	Increases bath life
Odor-free / no smell	Improves working environment
Operation at pH 4.0	Improves process compatibility
Production proven process	Easy to operate

Table 2
Deposit properties of ammonia-free palladium-nickel

Properties	Units	Values
Palladium	%	80 ± 5
Appearance	-	Fully bright
Ductility	180° bend test (on an 8-mm rod)	Very good
Hardness	VHN$_{100}$ KHN$_{100}$	420–520 (Range 390–560) 462–572 (Range 429–616)
Contact resistance	mΩ	< 10
Wear test	British Telecom test	Pass
Deposit density	g/cm^3	11.1
Porosity	On Nickel, copper or brass (Paper electrographic test)	Good
Nitric acid	HNO$_3$ drop test 30 sec in 50% nitric acid	Pass; No chemical attack
Sulfurous acid	ASTM B799-95	Pass
Hydrogen sulfide	ASTM B765-93	Pass

Table 3
Operating parameters of ammonia-free palladium-nickel

	Unit	Medium-speed		High-speed	
		Range	Optimum	Range	Optimum
Palladium	g/L	10 - 15	12	18 - 23	20
Nickel	g/L	8 - 12	11	9 - 13	11
Replenisher brightener	mL/L	4 - 8	6	4 - 8	6
Complexing agent	mL/L	67 - 81	74	67 - 81	74
Current density	A/dm^2	10 - 30	20	25 - 56	42
Deposition speed 20 A/dm^2 42 A/dm^2	mg/A-min	14 - 18	16.0	23 - 27	24.8
Deposition speed Time for 1 μm 20 A/dm^2 40 A/dm^2	sec		26		7
pH	-	3.5 - 4.5	4.0	3.5 - 4.5	4.0
Temperature	°C	55 - 75	60	60 - 75	65
Solution density	°Be g/ml	10.8 - 33.5 1.08 - 1.30	17.8 1.14	10.8 - 33.5 1.08 - 1.30	17.8 1.14
Anodes		Platinum or platinized titanium			
Agitation	-	Vigorous to very vigorous	Very strong (maximum)	Vigorous to very vigorous	Very strong (maximum)

Cost comparison (metal prices as of July 10, 2009)

As shown in Fig. 4, it can clearly be seen that at today's prices the cost of palladium-nickel deposits in comparison to acid gold is significantly lower and offers savings of around 85% in precious metal costs. This is a very significant cost saving and the higher the metal prices rise the bigger the actual dollar value saved.

For palladium to become more expensive than gold the palladium price would need to be double that of gold.[8] For example, if the price of gold is $1,000 per Troy oz., then the price of palladium would need to exceed $2,000 per Troy oz. before a Pd-Ni deposit would be more expensive than acid gold. As we know, at its peak in 2001, the price of palladium only reached $1,100 per Troy oz, and this was its highest value in the history of mankind!

Structure and porosity

It has been demonstrated many times[8-11] that palladium-nickel deposits are less porous than acid gold deposits (Fig. 5). This has largely been attributed to the deposit structure of acid gold usually being columnar, as seen in Fig. 6, while palladium-nickel is typically laminar, as in Fig. 7.[12]

Ammonia-free structures

More recent evaluations by focused ion beam (FIB) and scanning electron microscopy (SEM) have shown the ammonia-free palladium-nickel to give the added benefit of a very fine-grained amorphous deposit (Fig. 8).

Metal cost per m² plated (USD) @ 0.75 micron thickness	
Pure Gold	424.9
Acid Hard Gold	380.9
Pure Palladium	66.3
Palladium Nickel	50.58

Palladium Price	235	USD /Troy Oz
Gold Price	913	USD /Troy Oz
Nickel	100	USD / 100g Ni Replenisher

Metal Prices : 10th July 2009

Figure 4—*Cost comparison: pure gold vs. acid gold vs. palladium vs. palladium-nickel.*

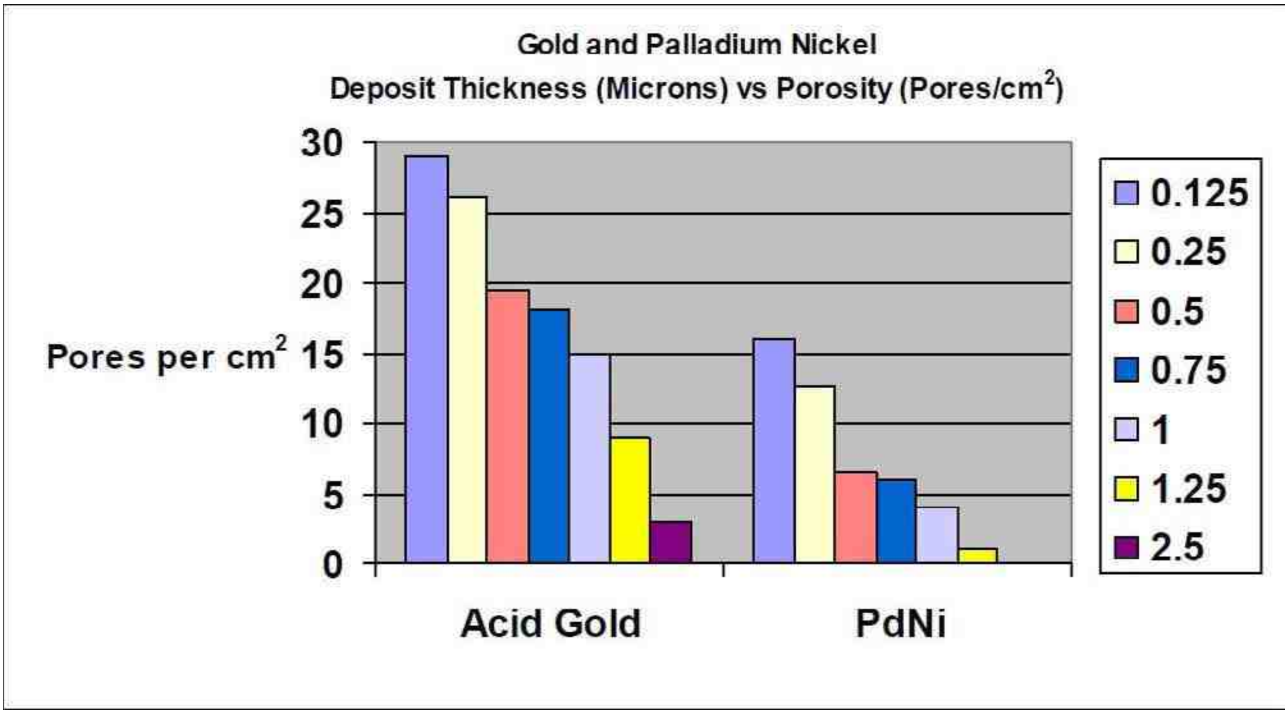


Figure 5—*Comparison of porosity in acid gold vs. palladium-nickel showing superior performance of palladium-nickel at all thicknesses.*

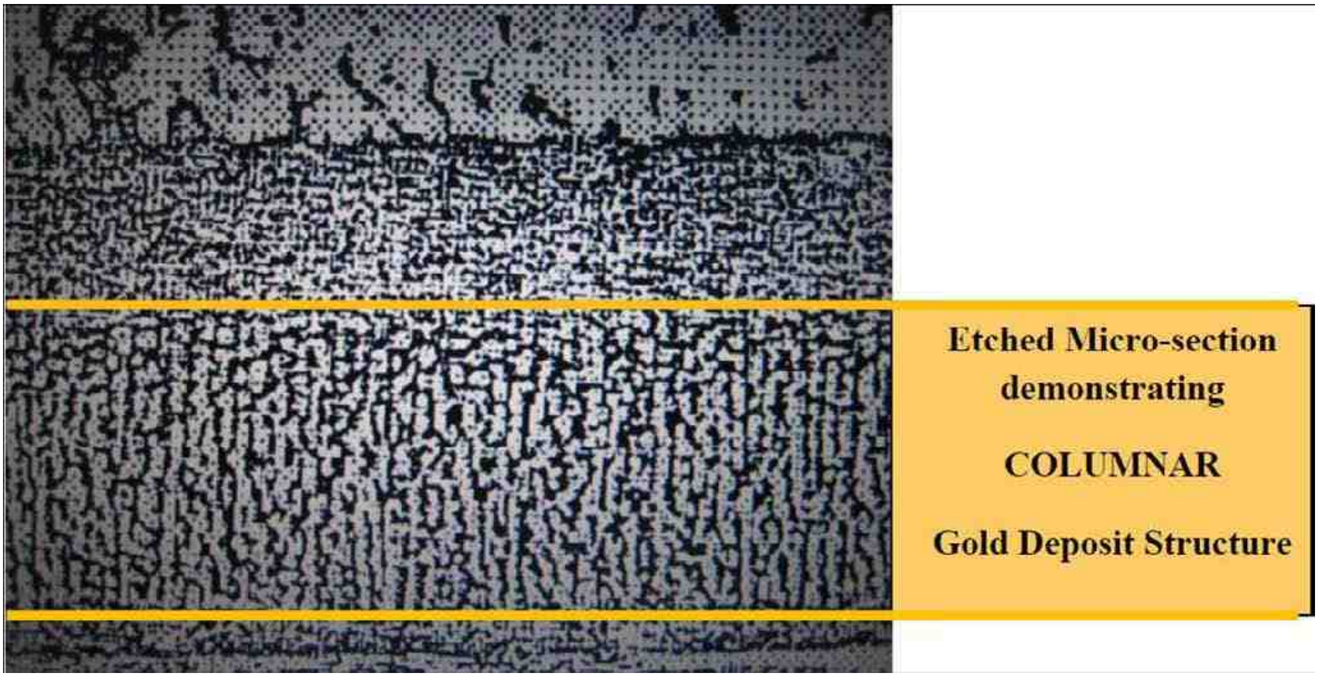


Figure 6—*Etched micro-section showing columnar structure of a typical acid gold deposit.*

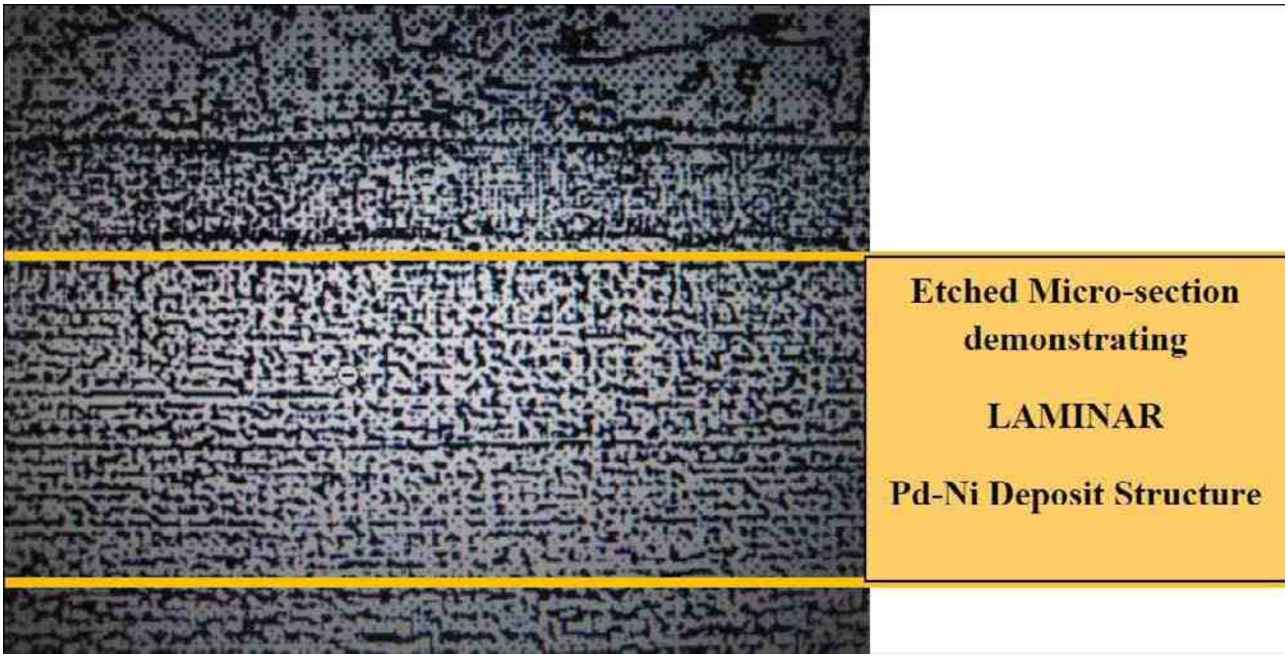


Figure 7—*Etched micro-section showing columnar structure of a typical palladium-nickel deposit*

Conclusions

- Palladium-nickel is clearly more economical than gold and offers significant cost savings in precious metal usage.
- Palladium-nickel is currently only 20% of the cost of gold and as the prices of both metals increase, the real dollar value of this percentage saving becomes bigger proportionally. An 80% saving on a big number cannot be ignored.
- Innovative ammonia-free palladium-nickel processes resolve all the issues related to ammonia usage that hindered universal acceptance of the earlier ammonia-based processes.
- Almost six years of production experience have proven the ammonia-free process to be robust, reliable and easy to use.
- Structures of ammonia-free deposits exhibit, in FIB and SEM studies, a very fine-grained uniform amorphous deposit demonstrating a true alloy formation.
- Research and development will continue to innovate and enhance the benefits of electroplating processes. Ammonia removal is a small step forward as we focus more and more onto environmental issues. The next challenge will become the removal of cyanide from our working environment.

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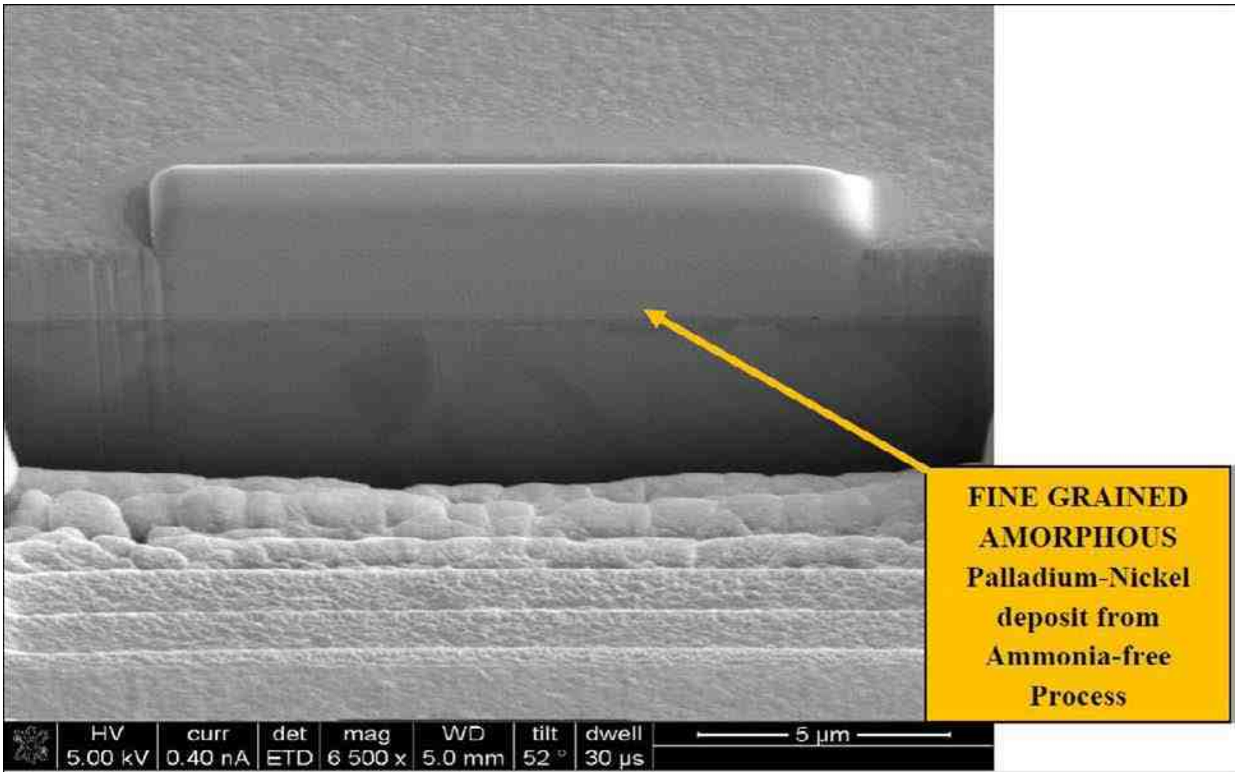

Figure 8—*Ammonia-free palladium-nickel deposit exhibiting fine grained amorphous structure.*

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