Electroplating of Palladium for Electrical Contacts

By Ch. J. Raub

Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd, West Germany

When palladium is plated from an appropriate electrolyte the deposit possesses similar physical properties to those of hard gold, making it a very suitable electrical contact material. The relative cost of the two metals helps to account for the growing interest in the electrodeposition of palladium and the properties of the deposits, which are discussed here.

In one of the first appraisals of palladium electroplating it was remarked "that from a position of relative obscurity, palladium plating has advanced within a comparatively short time to a place of considerable importance among platinum metal finishes, particularly in the field of electrical contacts" (1). One of the reasons given for this was that some of the gold electrolytes used at that time—1965—to process printed circuit boards attacked the adhesives, lifting the copper foil in the boards. Another reason, favouring the use of palladium in contrast to gold, is the price per volume. Since the density of palladium is roughly one-half, and the price at present one-third to one-quarter that of gold, an equal thickness of palladium costs only one-sixth to one-eighth that of gold. This advantage is reduced if, for example, the higher forming and operating costs of palladium electrolytes and the refining of scrap are considered, but there is still quite an incentive to use palladium instead of gold. This is also probably the main reason why the interest in the electroplating of palladium and in the properties of the deposits has increased as the price of gold has risen. Today nearly all

suppliers of plated connectors and major users have accepted palladium as a reliable connector contact material, and it has been in practical and increasing use for many years (2).

General Properties of Palladium Deposits

In general, one has to keep in mind that palladium is a member of the transition metal group of the periodic system and that gold belongs to the non-transition metals. This is the cause of several basic differences in the behaviour of the two elements, for example, palladium is catalytically very active both in solution and as a metal, while under these circumstances gold is not. Therefore a palladium electrolyte tends to be much more sensitive to impurities or alterations in its composition than a gold bath, and the surface of palladium is well known for exhibiting the so-called "brown powder effect" which originates from the condensation or polymerisation of organic vapours, emanating from plastics in the surroundings. This brown powder increases the contact resistance to intolerably high levels (3,4,5,6) but the effect can be greatly reduced or avoided if care is taken to use only appropriate plastics in the circuitry, or if the contact pressures are high enough, or if a gold flash (≤ 0.1 μm) is applied on top of the palladium (7). A series of tests with plastics showed that polystyrene and PTFE caused the smallest increase in contact resistance of palladium, but that glass fibre reinforced plastic, polyethylene and especially hard paper (Pertinax) critically increased the contact resistance (3).

The electrical resistivity of electroplated palladium is between 10.7 and 15 $\mu\Omega$ cm, this being higher than that of bulk palladium and

Change of Hydrogen Concentration of the Palladium Deposits in Dependence on the SO_3^{2-} : Pd^{2+} Ratio in the Electrolyte

Sulphite concentration		Hydrogen concentration			
		1 A/dm²		2 A/dm²	
Molar concentration	SO_3^{2-} : Pd^{2+}	H : Pd	$NmlH_2/$ g Pd	H : Pd	$NmlH_2/$ g Pd
0.01	0.1	0.007	0.75	0.0017	0.177
0.02	0.2	0.0004	0.041	0.0004	0.044
0.05	0.5	0.0003	0.037	0.0002	0.021
0.1	1	0.0002	0.025	0.0003	0.035
0.2	2	0.0006	0.063	0.0015	0.155

four times as high as that of hard gold (gold-cobalt, gold-nickel, gold-iron alloys) layers, which is 2 to 3 $\mu\Omega$ cm, but similar to the value of 18 carat gold-copper-cadmium deposits (8). However for contact applications, the resistivity of the deposits in most cases is not as important as the contact resistance and its change with time under different environmental conditions.

The contact resistance of as-deposited palladium, measured against gold, is in the range of that of hard gold and varies—depending on the measuring method—between 1 and 7 mΩ (1,3,8 to 12). In extensive tests carried out in atmospheres containing various amounts of sulphur dioxide, hydrogen sulphide, nitrogen dioxide and hydrogen it was demonstrated that under these conditions electrodeposited palladium shows only a slight increase in contact resistance of up to about 30 mΩ, at the most (1,3,8,9,10,12,13). Under the same conditions 18 carat gold-copper-cadmium layers exhibit much worse behaviour, their resistance becoming about twice as high as that of palladium (4,10).

The contact resistance of a 2.5 μm thick palladium layer on copper did not change after a heat treatment of 200 hours at 125°C or one of 15 minutes at 200°C (3,9). However, that of a comparable gold layer had doubled under the same conditions (9), a behaviour confirmed for 2 hours at 165°C and 250 hours at 100°C (12).

This is explained by the lower diffusion coefficients of metals such as copper and zinc through to palladium, compared with gold.

The different diffusion rate also plays a role, in the solderability of palladium layers (1,14). In general, dissolution of palladium is considerably slower than that of gold in 60 tin-40 lead solder, but the intermetallic compounds formed at the dissolving interface may result in fracture. It is therefore suggested that the amount of palladium dissolved in the solder be kept below 1 per cent by weight (14). The growth of intermetallic compound layers at room temperature is fairly rapid. After six months its thickness has increased to 3 μm (14), while after 25 days at 100°C it is between 3 (15) and 60 μm (14). The compound seems to be a lead-tin phase, with the rejected lead accumulating at the solder interface (14).

The other method of connecting leads to connector pins is by wire wrapping. From practical experience it is known that palladium layers behave in a similar way to hard gold, especially if they are heat treated. The microhardness of the deposits is generally in the range of 140 to 300 HV, this depending on the deposition parameters (8,9,16,17). It increases in the first hours after deposition and stays constant at longer times, or even drops slightly. This is due to the out-diffusion of hydrogen and to the corresponding volume changes (16,17,18).
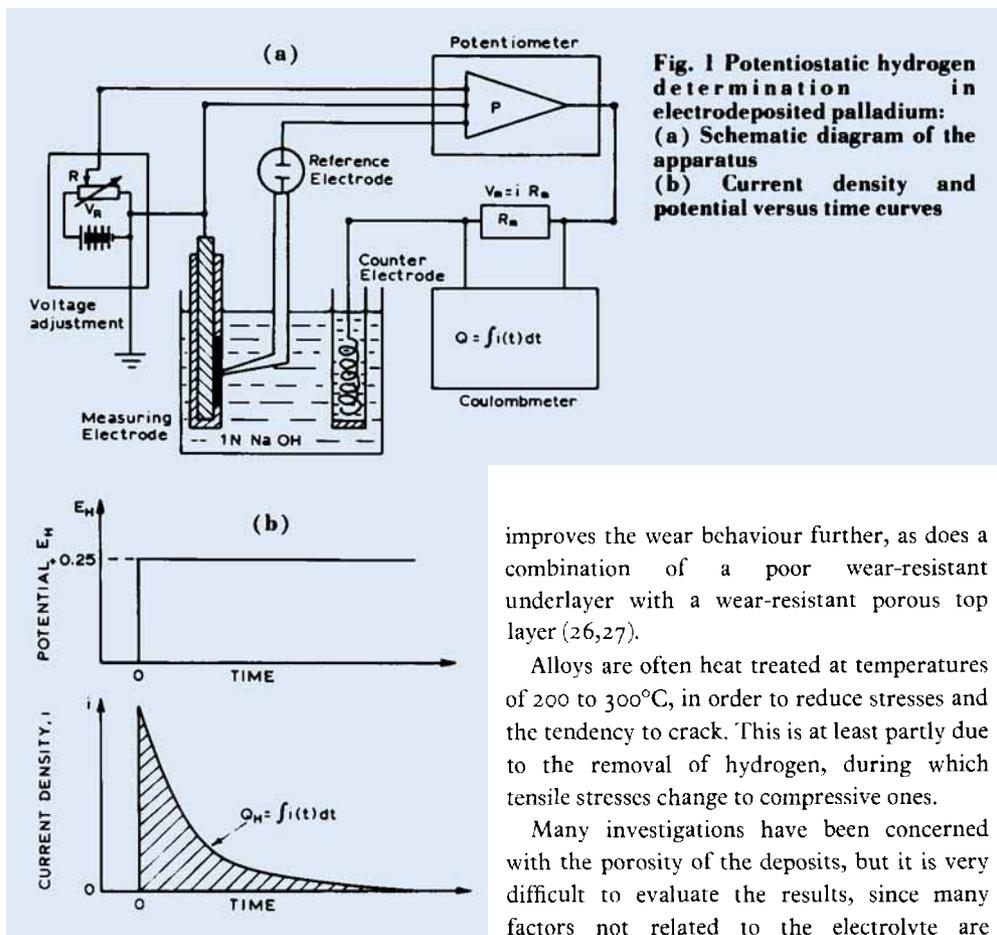
Fig. 1 Potentiostatic hydrogen determination in electrodeposited palladium:
(a) Schematic diagram of the apparatus
(b) Current density and potential versus time curves

The internal stress in the deposits is strongly dependent on factors such as the type of electrolyte and the deposition parameters (8,16 to 20). Tensile stresses observed are in the range of 50 to 200 N/mm², but they increase during storage of the deposits up to, for example, 400 N/mm² (20).

The wear and friction behaviour has also been studied extensively (1,3,8,9,13,16,17,23). F. H. Reid reports on field tests and production experience up to 1965 (1) and G. Schachmann (24) and G. D. Fatzer (25) on the experience of I.B.M. with palladium plated connectors. All investigations showed that palladium deposited in the form of single or duplex layers compares favourably with hard gold in its wear resistance. A thin gold layer on top of the palladium improves the wear behaviour further, as does a combination of a poor wear-resistant underlayer with a wear-resistant porous top layer (26,27).

Alloys are often heat treated at temperatures of 200 to 300°C, in order to reduce stresses and the tendency to crack. This is at least partly due to the removal of hydrogen, during which tensile stresses change to compressive ones.

Many investigations have been concerned with the porosity of the deposits, but it is very difficult to evaluate the results, since many factors not related to the electrolyte are involved. However, it seems to be established that, if a proper base material and pretreatment procedures are used, a level of porosity can be obtained at a given thickness which is equal to that of cobalt, nickel or iron hardened gold.

Hydrogen in Electrodeposited Palladium

The importance of dissolved hydrogen has been recognised since the earliest deposition experiments, but a method for its quantitative determination was only developed in recent years (18). This method was adopted and developed further for investigations on d.c. and pulse plated palladium (18).

Palladium dissolves appreciable amounts of hydrogen as a face centred cubic α-palladium solid solution at hydrogen to palladium ratios up to 0.03, at atmospheric pressure and room

temperature. At higher hydrogen concentrations the face centred cubic β-PdH phase with hydrogen : palladium $\geqslant$ 0.57 is observed. Its lattice constant is higher by about 3.8 per cent than that for the α-Pd-H solid solution. These data refer to equilibrium conditions. In highly distorted electrodeposited layers solubility is much higher.

The hydrogen concentration of electrodeposits is important insofar as there is a connection between stress in the deposits and the hydrogen dissolved in the as-deposited material. Furthermore, if during storage hydrogen diffuses from deposits with higher hydrogen : palladium ratios, the decomposition of the β-phase and the accompanying change in volume may cause stresses and cracks in the layers, sometimes even days after deposition took place (18 to 22).

In general, the determination procedure for hydrogen by vacuum extraction is so slow that it catches only part of the hydrogen which is very rapidly diffusing out from the deposit ($D_{0,H_2} \sim 1.10^{-6}$ cm^2/s in β-PdH). Therefore an electrochemical method was developed which is very fast, and permits the first hydrogen measurements to be made within a few seconds of deposition (18). It uses the electrochemical oxidation of the hydrogen diffusing from the palladium layers to determine its amount via the charge Q used: $Q = \int i(t)dt$, where i = anodic current and t = time. Figure 1 shows the circuitry used. The anodisation of hydrogen is done in 1N sodium hydroxide at a constant potential of +0.25V, which is high enough to oxidise hydrogen, but low enough to avoid other electrochemical reactions. The anodic current is dependent upon the diffusion rate of the hydrogen to the metal/electrolyte interface and the charge can be measured by integration with respect to time; thus via Faraday's law the hydrogen quantity is calculated. Certainly there are limitations to this method, such as the loss of hydrogen in the short time between deposition and measurement, but it has proved to be a simple and reliable method for establishing the influence of deposition parameters, at least relatively, for the various electrolytes. Com-
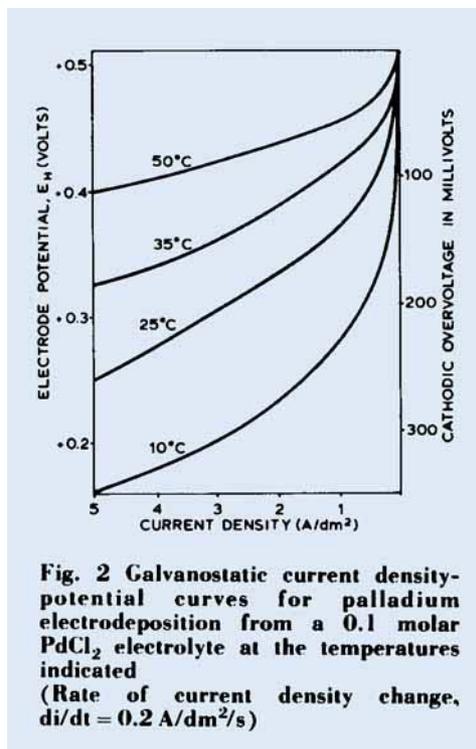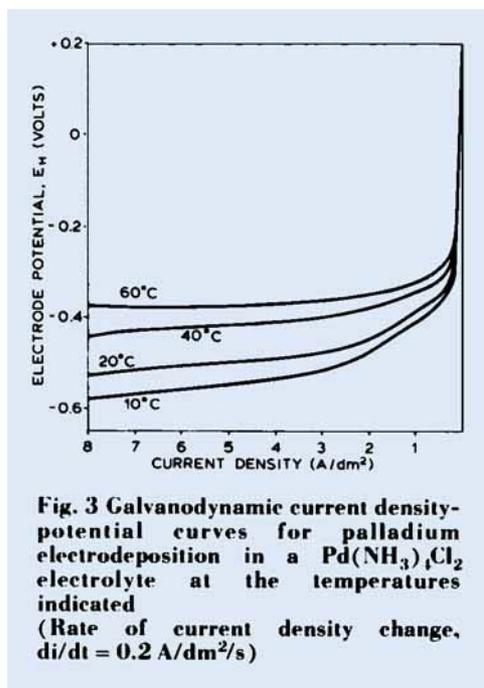

Fig. 2 Galvanostatic current-potential curves for palladium electrodeposition from a 0.1 molar PdCl$_2$ electrolyte at the temperatures indicated
(Rate of current density change, di/dt = 0.2 A/dm^2/s)

parative tests with the vacuum hot extraction analysis gave lower values, since some hydrogen had diffused out before it could be measured.

Palladium Electrodeposition Processes

Only a few comparative laboratory investigations have been published which give details of the electrolyte compositions, deposition parameters and properties of deposits (3,9,18 to 23). F. H. Reid (1) tested seven electrolytes: (a) Tetrammino-palladous nitrate, (b) Sodium-pallado-nitrite, (c) Diammino-dinitrito-palladium (P-salt), (d) Dicyano-diammino-palladium, (e) Acid-palladous-chloride, (f) Palladosammine-chloride and (g) Palladium-sulphamate (developed by the Automatic Telephone and Electric Company). Of these electrolytes he found only (c) and (g) to be commercially interesting. Later, electrolyte prototypes (a), (e), (f) and a newly developed acid type bath (17,22) were tested at the Forschungsinstitut für Edelmetalle und

Fig. 3 Galvanodynamic current density-potential curves for palladium electrodeposition in a $Pd(NH_3)_4Cl_2$ electrolyte at the temperatures indicated
(Rate of current density change, $di/dt = 0.2$ A/dm²/s)

electrodeposited as a compact crackfree layer, even at higher thicknesses, with a microhardness of about 250 to 350 HV. At current densities between 0.1 and 10 A/dm² deposition at 10 to 50°C occurs at potentials of +0.5 to +0.1 V/NHE, see Figure 2. The activation energy of the reaction Pd^{2+}/Pd was found to be $\Delta H = 17.1 \pm 1$ kcal/mol (18). The hydrogen content of the deposits is less than hydrogen : palladium = 0.03. X-ray analysis of such deposits shows only a slight expansion of the f.c.c. a-palladium lattice. The layers are fine, crystalline and non-oriented, with low internal stresses of about 60 N/mm², which are reduced to 20 N/mm² at 7 μm thickness. This makes the electrolyte suitable for producing thick layers.

Recently the electroplating of palladium-silver alloys from a LiCl containing $PdCl_2/HCl$ type electrolyte was reported (29).

Unfortunately the emission of hydrochloric acid vapour and the tendency of these electrolytes to self-decompose makes them unsuitable for industrial production, at this stage of development.

These problems are avoided to a certain extent by a proprietary acid electrolyte based on $Pd(NO_3)_2/H_2SO_4$ (17,22,30), and containing sodium sulphite. Depending on the sulphite concentration and current density, the current efficiency for palladium deposition varies from 108 per cent (0.01 mol/l Na_2SO_3, 1 A/dm²) nominal (electroless deposition) to 63 per cent (0.2 mol/l, 2 A/dm²). The sulphite concentration of the electrodeposits increases from 0.15 per cent (0.01 mol/l Na_2SO_3, 1 A/dm²) to 10 per cent (0.2 mol/l Na_2SO_3, 1 A/dm²) and the H : Pd ratio

Metallchemie (18,20,21,22) and the Technisch-Chemisches Laboratorium of the ETH Zürich (19). The sulphamate electrolyte has recently been re-evaluated (28).

The Acid $PdCl_2/HCl$ and $Pd(NO_3)_2/H_2SO_4$ Electrolytes

In the $PdCl_2/HCl$ electrolyte deposition occurs from an equilibrium $Pd^{2+} + 4Cl^- + 2H^+ \rightleftharpoons H_2PdCl_4$. The palladium is rather loosely bound, so it deposits easily without external current on to less noble metals in a blackish powdery form. At a current efficiency of between 97 and 100 per cent palladium is

Fig. 4 Hardness change of palladium layers, deposited from a $Pd(NH_3)_4Cl_2$ electrolyte at pH = 9.0, during storage at room temperature

varies from 0.007 (0.01 mol/l Na_2SO_3, 1 A/dm^2) to 0.0006 (0.2 mol/l Na_2SO_3, 1 A/dm^2) see the Table. The deposits have a microhardness of 350 HV, which can be increased to 430 by annealing for 1 hour at 100°C. After 1 hour at 400°C it dropped to 200 HV (11,22). Deposits show a fibrous texture, the <100> orientation being the preferred crystal axis. Internal tensile stresses are very low at nearly 50 N/mm^2 but even at 10 μm thickness they never exceed 100 N/mm^2. Due to their low hydrogen concentration, deposits do not change their stress values during storage. The deposits made at low sulphite levels are bright, but on less noble base metals they need a gold or palladium prestrike.

A common feature of all acid electrolytes of low pH values seems to be their current efficiency of about 100 per cent, and the low hydrogen concentration and low tensile stresses of deposits produced from them. A problem with this type of electrolyte is its tendency to show electroless deposition on base metals, but this can be overcome by using gold or palladium prestrikes.

The Alkaline $Pd(NH_3)_4Cl_2$ Electrolyte

The alkaline $Pd(NH_3)_4Cl_2$ complex seems to be completely stable above pH 7.5, but below pH 6 the $Pd(NH_3)_2Cl_2$ form is the stable one (18). Palladium deposits at 1 to 5 A/dm^2 and −300 to −600 mV at a current efficiency of less than 100 per cent. The potential-current density curves show a strong temperature dependence explained by a decreasing stability of the complex, as can be seen from Figure 3. Current efficiency increases from about 60 per cent at 0.2 A/dm^2 to 90 per cent at 2 A/dm^2 and from 82 per cent at 25°C to about 85 per cent at 50°C. Deposits are highly stressed (100 to 200 N/mm^2) and tend to form cracks at high thicknesses. Stresses and hardness values decrease with deposition temperature and thickness. Layers deposited at temperatures below 30°C show age hardening, during which crack formation is often observed, see Figure 4. The hydrogen concentration of the deposits increases with current densities, but decreases
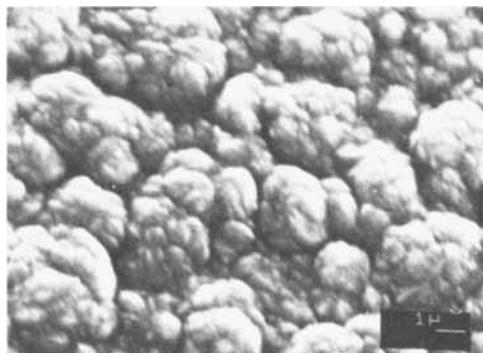

Fig. 5 The surface of a 10 μm thick layer deposited from a $Pd(NH_3)_4Cl_2$ solution of pH = 8.5 at current density = 1A/dm^2 and 25°C exhibits a cauliflower-like structure; (Scanning electron microscope photograph)
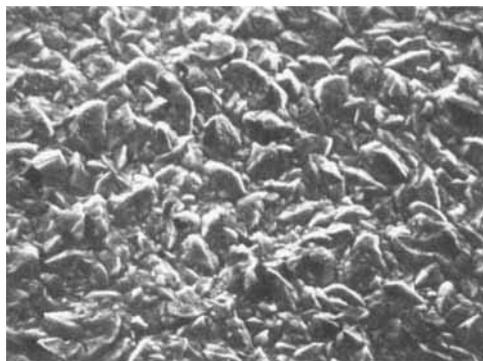

Fig. 6 Surface structure of a deposit from a $Pd(NH_3)_4Cl_2$ solution pH = 9, 1A/dm^2, 25°C, thickness 10 μm (SEM photograph)

with deposition temperature. It depends on the relative movement of the electrolyte with respect to the sample. The hydrogen : palladium ratio of deposits from a still electrolyte increases from about 0.1 at 1 A/dm^2 to 1 at 2 A/dm^2. Deposits with hydrogen : palladium below 0.1 are bright and exhibit metallic lustre, but for hydrogen : palladium $\geqslant$ 0.8 they are powdery black. The layers show a cauliflower-like surface structure shown in Figure 5, and are rather sensitive to finger prints. This structure is strongly influenced by additions of carbonic acids or their derivatives, see Figures 6 and 7. When benzoic and nicotinic acid and their derivatives are added deposition potentials are shifted to more negative values, Figure 8 (20).
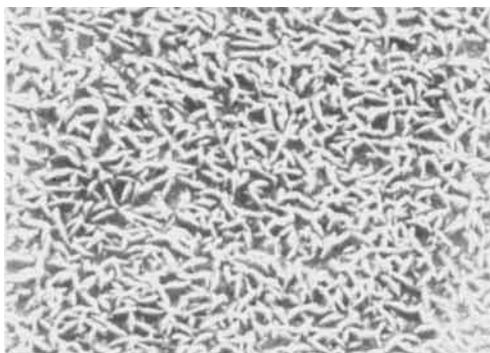
Fig. 7 Surface structure of a deposit from a $Pd(NH_3)_4Cl_2$ solution + 0.5 molar sodium citrate addition, immediately after deposition, conditions analogous to Figure 6 (SEM)
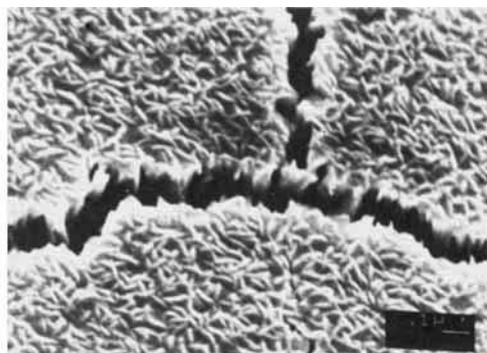

Fig. 9 Surface structure of the deposit in Figure 7 after storage for 1 hour in the high vacuum conditions, (10^{-8} bar), of the scanning electron microscope

Citrates have a similar effect. If the citrate concentration is 0.5 mol/l, the hydrogen concentration increases from hydrogen : palladium 0.02 to 0.08 at 2 A/dm². In general citrate reduces the tensile stresses, but the deposits are still highly stressed (150 N/mm²) and tend to crack as illustrated in Figure 9 (20). Sodium salicylates increase the hydrogen concentration

from hydrogen : palladium<0.01 to 0.18 (0.5 molar sodium salicylate at 2 A/dm²). Benzoates and salicylates, as well as heterocyclic N-containing compounds result in a sharp fibrous (110) orientation. At concentrations above 5 mmol/l phenacetine reduces the tensile stress of the deposits to values below those of deposits from addition-free electrolytes (20).
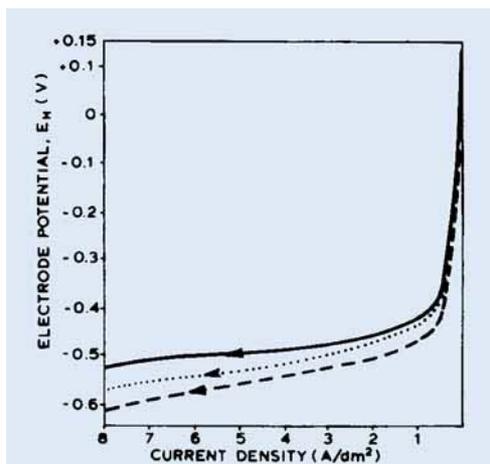
The influence of deposition parameters on the porosity of deposits from a palladosammine solution and the influence of saccharin were investigated by Fatzer (25). Apparently saccharin reduces hardness, but increases the porosity of the layers. The best deposits were obtained at room temperature and 60 g/l $Pd(NH_3)_4Cl_2$ at a current density of 2.4 A/dm². Such deposits are glossy or bright and at thicknesses greater than 1.25 μm are pore free. A soluble anode process with a Na_2PdCl_2 solution produced highly stressed, porous deposits (25).

The Alkaline $Pd(NH_3)_2(NO_2)_2$ Electrolyte (P-salt Type)

Electrolytes of this type are among the most widely used solutions for palladium electrodeposition. They work at a pH value of between 7.5 and 10, and palladium is electrodeposited at −300 to −700 mV as dense, bright layers. At higher temperatures the deposition potential becomes more positive, and at higher pH values more negative. The current efficiency for palladium deposition increases

Fig. 8 Current density-potential data for deposits from $Pd(NH_3)_4Cl_2$, pH = 10, with sodium benzoate and sodium salicylate (di/dt = 0.1 A/dm²/s)

——— addition free

·········· 0.1 mol addition

− − − − 0.5 mol addition

from about 40 per cent at 20°C to nearly 60 per cent at 60°C; correspondingly the hydrogen : palladium concentration drops from about 0.04 (20°C, 1 A/dm²) to 0.005 (70°C, 1 A/dm²). Tensile stresses of 250 to 300 N/mm² drop sharply with increasing deposition temperature and thickness, and there seems to be a relationship between hydrogen concentration and stress, see Figure 10 (21). The change in the hydrogen : palladium ratio at various storage temperatures with storage time is shown in Figure 11. It is observed that at pH values between seven and eight, insoluble palladium salts are incorporated in the deposit (21).

The behaviour of a P-salt type electrolyte and the deposits obtained by both pulse and d.c. plating were reported by Locarnini and Ibl (19). In general, the results of Hedrich and Raub (21) are confirmed. Under certain conditions pulse plating produces harder deposits than d.c. plating. For thicknesses of less than 2.5 μm, crack and pore free deposits are more readily achieved in pulsed than in d.c. plating (19).

Excellent wear resistance and very low transverse porosity was obtained with doublex coatings consisting, for example, of a 1 μm base layer from a $Pd(NH_3)_2Cl_2$ type solution, with low wear resistance of its own, and a top layer (2 μm) from an ammonia free electrolyte believed to contain $Pd(NO_2)_4^{2-}$ as the predominant species. This combination proved better than a single layer from a $Pd(NH_3)_4NO_2$ electrolyte, which worked at a deposition speed of 12 μm/hour and a current efficiency of 75 per cent at 50°C and 1 A/dm² (26).

An interesting variation of a palladium electrolyte with ammonia as a complexing agent is the use of higher alipathic polyamides, such as tetraethylenepentamin, as complex formers (31). Another solution based on P-salt was developed by the Automatic Telephone and Electric Company of Liverpool (32). These electrolytes contain 10 g/l P-salt, 100 g/l ammoniumsulphamate and operate at pH 7.5 to 8.3, 32°C and 0.6 to 1 A/dm², with a cathode efficiency of 70 per cent. Deposits are milky in appearance at least up to 20 μm, but at this thickness cracks appear. Apparently the current
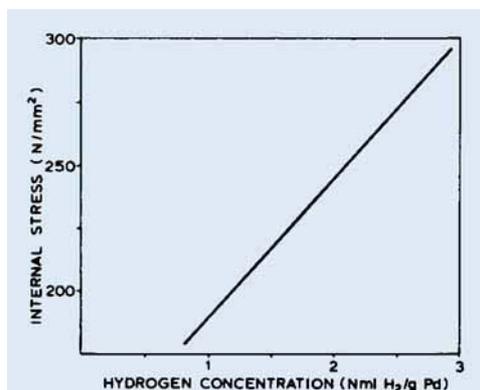

Fig. 10 The internal stress in palladium layers deposited from a $Pd(NH_3)_2(NO_2)_2$ solution, pH = 9 at current density 1A/dm², appears to depend on hydrogen concentration
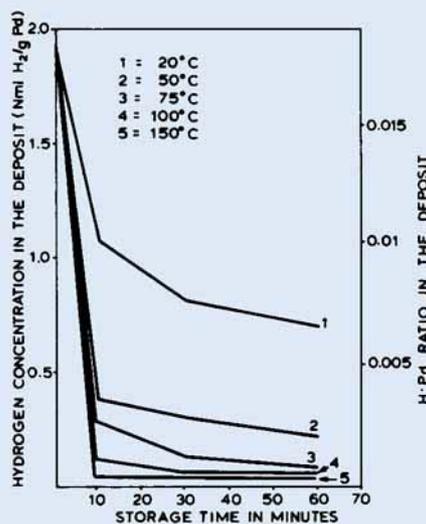

Fig. 11 The hydrogen concentration of deposits from $Pd(NH_3)_2(NO_2)_2$ electrolyte, pH = 9 at current density 1 A/dm², decreases during storage

density of 2 A/dm² is a limit, above which edge blackening of the deposits occurs.

Atkinson patented a process for deposition of palladium and a number of other metals from ammoniacal solutions in a diaphragm-cell (33,34). Further literature on deposition of palladium alloys was reviewed by Brenner (34).

The deposition of a palladium-nickel alloy with 27 per cent nickel from a bath containing

0.05 to 0.1 mol/l $Pd(NH_3)_4Cl_2$ is discussed by McCaskie, Nobel and Whitlaw (12). Palladium-nickel deposits up to 50 per cent nickel, with or without a final gold flash, were studied by Pike-Biegunski and Bazzone (35). After ageing one month at 125°C in air, the contact resistance of 50 palladium-50 nickel increased to 12 ± 8 $\mu\Omega$. The films with a microhardness of 240 to 450 Knoop show good wear characteristics, comparable to hard gold. These palladium-nickel alloys seem to be quite interesting as underplates for electrical contacts (35) or for decorative applications.

Summary

The electrodeposition of palladium and the properties of deposits obtained are discussed.

There are two groups of electrolyte prototypes, one operating at pH values below 7 and the other one at values mostly above 10. The deposits are similar to hard gold in the properties required for electrical contacts. The hydrogen concentration seems to be a critical factor, since it has an influence on both internal stress and porosity. Today, palladium electrodeposits with or without a gold top layer are finding a widening application range as a contact finish for connector contacts.

References

1 F. H. Reid, Plating, 1965, **52**, 531

2 M. Antler, *Platinum Metals Rev.*, 1982, **26**, (3), 106

3 H. Grossmann, M. Huck and G. Schaudt, *Galvanotechnik*, 1980, **71**, (5), 484

4 H. Hermance and T. F. Egan, *Bell Syst. Tec. J.*, 1958, **37**, 739

5 H. J. Keefer and R. H. Gumley, *Bell Syst. Tec. J.*, 1958, **37**, 777

6 L. H. Germer and J. L. Smith, *Bell Syst. Tec. J.*, 1957, **36**, 769

7 H. Grossmann, M. Huck and G. Schaudt, *Metall (Berlin)*, 1982, **36**, (7), 746

8 W. H. Safranek, "The Properties of Electrodeposited Metals and Alloys", American Elsevier Publ., New York, London, Amsterdam, 1974, p. 345

9 H. C. Angus, *Trans. Inst. Met. Finish.*, 1962, **39**, 20

10 U. Mayer, *Metalloberflaeche*, 1978, **32**, (1), 3

11 F. Simon, in Proc. 8th Symp. on Plating in the Electronics Industry, Am. Electroplat. Soc., Winter Park, Fla., 1980

12 J. E. McCaskie, B. Nobel and K. Whitlaw, in Proc. AES Symp. on Economic Use of and Substitution for Precious Metals in the Electronics Industry, Am. Electroplat. Soc., Winter Park, Fla., 1980

13 K. L. Schiff and R. Schnabl, *Metalloberflaeche*, 1978, **32**, 423, 495

14 W. G. Bader, *op. cit.*, ref. 12

15 P. J. Kay and C. A. McCay, *Trans. Inst. Met. Finish.*, 1976, **54**, (1), 68

16 E. A. Sauter, in Moderne Gesichtspunkte der Galvanotechnik, Teil I, TA Esslingen, Lehrgang 5315/78.002, Esslingen, 1981

17 F. Simon, *op. cit.*, ref. 16

18 H. D. Hedrich and Ch. J. Raub, *Metalloberflaeche*, 1977, **31**, (11), 512

19 J. M. Locarnini and N. Ibl, in Proc. AES 2nd International Pulse Plating Symp., Am. Electroplat. Soc., Winter Park, Fla., 1981

20 H. D. Hedrich and Ch. J. Raub, *Metalloberflaeche*, 1979, **33**, (8), 308

21 H. D. Hedrich and Ch. J. Raub, *Surf. Technol.*, 1979, **8**, (4), 347

22 H. D. Hedrich and Ch. J. Raub, *Galvanotechnik*, 1979, **70**, (10), 934

23 A. W. Grobin and V. Veronesi, *Prakt. Metallogr.*, 1981, **18**, 181

24 G. Schachmann, presented at 23rd Annual IPC Conference, Orlando, Fla., April, 1980

25 G. D. Fatzer, *Plating*, 1963, **50**, 1000

26 J. N. Crosby, *op. cit.*, ref. 12

27 A. Keil and K. Klein, *Metall*, 1978, **32**, (4), 352

28 F. Friedrich and Ch. J. Raub, results to be published in *Metalloberflaeche*

29 U. Cohen, K. R. Walton and R. Sard, Electrochem. Soc., Fall Meeting, Extended Abstracts of Electrodeposition Div., Abstr. No. 309, p. 759, Denver, Col., Oct. 11–16, 1981

30 DEGUSSA, *German Patent*, 2,105,626

31 INOVEN-STROEBE. *German Patent*, 2,360,834

32 J. J. Miles, *Autom. Teleph. Electr. J.*, 1962, **18**, 63 cit. in (1)

33 R. H. Atkinson, *U.S. Patent*, 1,981,715; 1934

34 A. Brenner, "Electrodeposition of Alloys", Vol II, Academic Press, New York, London, 1963, p. 542

35 M. J. Pike-Biegunski and R. Bazzone, *op. cit.*, ref. 12