

PALLADIUM ELECTROPLATING

JOSEPH A. ABYS

Palladium (Pd) metal was discovered and named by the English medical doctor W. H. Wollaston in 1803 while he was conducting experiments on the isolation and purification of platinum. Dr. Wollaston, a renowned scientist and astronomer, initially named his discovery “ceresium” after the newly discovered asteroid Ceres; however, he quickly changed his mind and named the metal in honor of the then newly discovered asteroid Pallas.

“Pallas” has its roots in Greek mythology and relates to the “gift by Zeus” of the statue of Pallas Athena that stood at the gates of Troy to “safeguard” the city. Mythology tells us that during the Trojan Wars, Odysseus and Diomedes stole the statue and carried it to the Greek camp, after which Troy was conquered. Pallas is most likely derived from the Greek *pallo*, meaning “to brandish a spear.”

In Roman legend, Pallas Athena was obtained by Aeneas during the sacking of Troy and taken to Italy where it was installed in the Temple of Vesta in Rome. The Romans venerated the statue and believed it would ensure the existence of the Empire. Thus, the word palladium became synonymous with “safeguard” and more specifically the “safeguard of liberty” [1, 2]. An excellent review [3] of the discovery and history of palladium was written by Ian E. Cottington of Johnson Matthey.

12.1 GEOLOGICAL OCCURRENCE [4–6]

Unlike other metals, the platinum group metals (PGMs) exist in the earth’s crust mostly as metallic alloys, especially of nickel and iron, and only a few mineral compounds are known. Their natural abundance in the earth’s crust is very low with palladium being the most abundant [5] (see

Table 12.1). Interestingly enough, PGMs exist in relatively high concentrations in meteorites rich in iron and nickel as opposed to the “stony” or rock-type meteors. This has led geochemists to the supposition that on earth a similar metallurgy took place, and PGMs concentrated during the earth’s formation mainly in the iron–nickel core. This accounts for their relatively low abundance in the lithosphere. An interesting phenomenon is the presence of unusually high concentrations of iridium in layers of rock dating to the time of the disappearance of the dinosaurs. This fact supports the scientific postulate that the extinction of the dinosaurs was caused by the impact of a large meteor on the Yucatan peninsula in Mexico.

12.2 SUPPLY, DEMAND, AND USES OF PALLADIUM

The economically significant sources of PGMs are Russia, South Africa, and North America. PGMs from these countries are primary deposits usually associated with platinum, copper, and nickel mining. Table 12.2 provides the estimated concentration of PGMs for each geographic region [7]. The Russian sources of Pd are the most abundant, and indeed Russia is the largest supplier of Pd today. However, the Stillwater mine in southern Montana (United States) contains the richest Pd deposits in the world and output has grown rapidly since the late 1990s. Figure 12.1 is a history of the Pd supply [7] from 1995 to 2008 which reached a peak of $\sim 8.6 \times 10^6$ troy ounces (TrOz)* in 2004. Palladium shipments averaged $\sim 8 \times 10^6$ TrOz over the last five years with Russia and South Africa supplying the majority of the yearly demand.

* One troy ounce equals 31.1 g

TABLE 12.1 Concentration of Platinum Group Metals in Earth's Crust

Metal	Concentration in Crust (ppm)
Palladium	0.01
Platinum	0.005
Rhodium	0.001
Iridium	0.001
Ruthenium	0.001
Osmium	0.001

Figure 12.2 exhibits the demand by geographic region from 1995 to 2008 and clearly demonstrates the globalization of manufacturing and its shift from the industrialized world (North America, Japan, and Europe) to China and other parts of Asia. It is interesting to note the convergence of demand in 2008 as Asia rapidly industrialized. Demand hit a low of $\sim 4.9 \times 10^6$ TrOz in 2002 following the burst of the “dot-com” bubble and the ensuing economic recession. Since then, demand has increased $\sim 45\%$ reaching $\sim 7.2 \times 10^6$ TrOz in 2005. China's demand grew rapidly, surpassing Japan in 2008 with a consumption of 1.445×10^6 TrOz. The increases in North America and Europe were spurred by auto catalysts, and it is noteworthy that recycling programs increased supply from $\sim 100,000$ TrOz in 1995, or $\sim 2\%$ of total demand, to $\sim 1.2 \times 10^6$ TrOz in 2008, or $\sim 15\%$ of total demand. Supply–demand charts shown in Figure 12.3 indicate that cumulatively from 1995 to 2008 more than 6×10^6 TrOz is in surplus not including the supply from recycling of auto catalysts.

Consumption of Pd by individual applications [7] is seen in Figure 12.4. Electronics was the largest consumer, accounting for $\sim 42\%$ of total demand in 1995; however, by 2008 the automotive sector accounted for 54% of demand and electronics at $\sim 17\%$. If recycling of auto catalysts is included, the automotive sector accounts for $\sim 61\%$ of demand with electronics as the second largest consumer at $\sim 15\%$.

Palladium is extensively used in electronic devices from basic consumer products to complex military hardware. Although each component contains relatively small quantities of metal, they are produced in the billions accounting for the substantial demand of $\sim 1.3 \times 10^6$ TrOz in 2008. “Pastes” in multilayered ceramic capacitors represent the largest demand with smaller amounts used in sputtering and plating operations.

The dental industry accounted for 21% of Pd consumption in 1995 but only 8% by 2008. This drop in demand is attributed to “speculative” increase in the price of Pd from 1999 to 2001 (Fig. 12.6). Dental, jewelry (nonplated), and in

TABLE 12.2 Concentration of Platinum Group Metals: Geographic Distribution (wt %)

Metal	Percentage by Weight		
	Canada	Russia	South Africa
Platinum	43.4	30	64.02
Palladium	42.9	60	25.61
Iridium	2.2	2	0.64
Rhodium	3.0	2	3.20
Ruthenium	8.5	6	6.40
Approximate ratio Pt : Pd	1:1	1:2	2.5 : 1

recent years investments accounted for the remaining 29% of consumption. It is interesting to note the increase in jewelry applications is driven by the rapid economic rise of China and a significant increase in investment stocks in North America.

12.3 BRIEF HISTORY OF ELECTROPLATED PALLADIUM

The earliest known example of plated Pd is in the Percy collection at the Science Museum of London. It is a thin sheet of copper coated with Pd prepared by T. H. Henry circa 1855 [35]. Henry's initial formulation used a nitrate electrolyte from Smee [35], and in a later formulation an ammoniacal solution of “ammonia-muriate.” Interestingly enough, today the most utilized processes for Pd and Pd alloy electrodeposition are based on ammoniacal electrolytes. An excellent historical review including numerous recipes for plating Pd was written by Atkinson and Raper in 1933 [35].

Electroplating accounts for $\sim 4\text{--}8\%$ of worldwide Pd consumption. Figure 12.5 is a chronological overview of major applications and demonstrates that in the mid-1970s plating Pd became technologically significant. Palladium is utilized in interconnection products especially for telecommunication, computer, and automotive connectors; semiconductor packaging and recently in the printed circuit industry; integrated circuit (IC) packaging substrates; land grid arrays; IC wafer probe cards; and a variety of nanotechnology applications. Furthermore, since the emergence of legislation in Europe banning nickel due to nickel dermatitis, Pd found wide acceptance in the decorative industry.

The use of thick electroplated gold (Au) films for electronic applications was common until the mid-1970s. The relatively low cost of gold and the availability and reliability of existing gold electrodeposition technologies precluded the use of any alternate material. However, the deregulation of gold in the early 1970s coupled with the political and economic events of that era brought about an astronomical

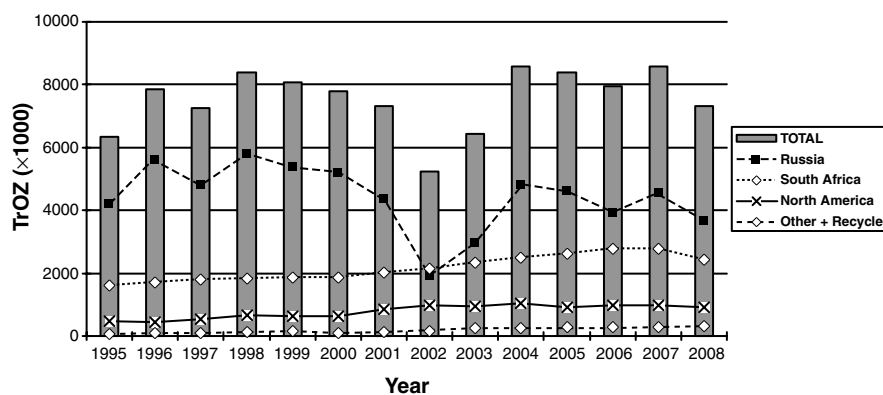


FIGURE 12.1 World Pd supply by geographic region, 1995–2008, in troy ounces.

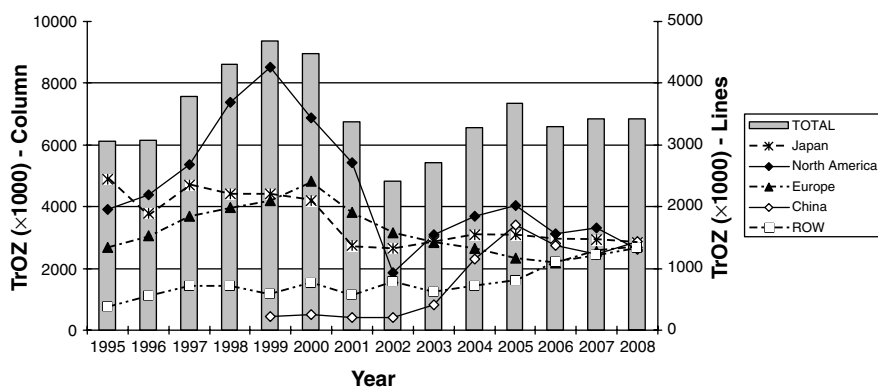


FIGURE 12.2 World Pd demand by geographic region, 1995–2008, in troy ounces.

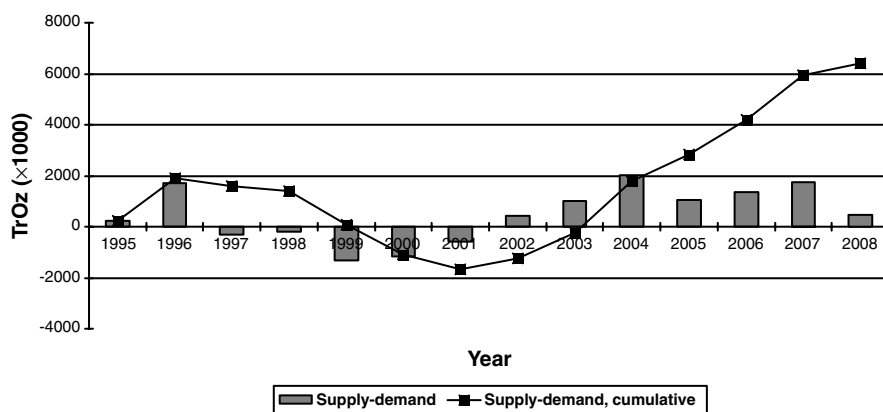


FIGURE 12.3 World Pd supply–demand, 1995–2008, in troy ounces.

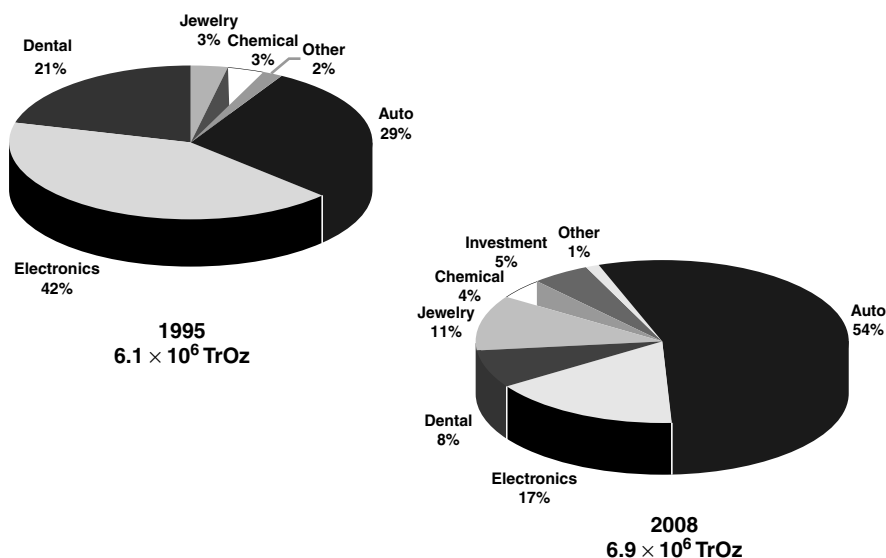


FIGURE 12.4 World Pd demand by industry, 1995 and 2008, in troy ounces.

increase in its price in the late 1970s and early 1980s (Fig. 12.6). From 1981 to 2002, gold traded in the range of \$320–\$440 TrOz^{-1} ; since 2002, gold has again seen a meteoric rise in its price to greater than \$900 TrOz^{-1} . Thus, the major impetus for substituting gold has been and remains economic. The rise in the price of gold spurred significant research in the reduction of gold usage [19, 20] and in the search for a suitable, more economic alternative [8–34].

Palladium is viewed as a suitable alternative. Figure 12.6 compares the relative price of Pd to Au and demonstrates Pd's historical lower price with the exception of a four-year period from 1999 to 2002. Disruptions of supplies from Russia, lower output from South Africa, the increased usage of Pd for automotive catalysts, and speculative activities in Pd stocks conspired to increase its price [7]. However, increased production and active recycling programs resulted

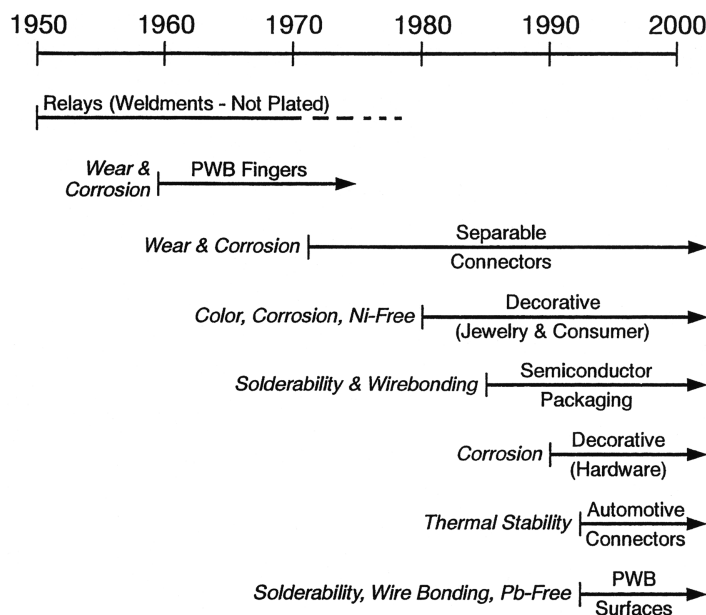


FIGURE 12.5 History of Pd electroplating by application from about 1960 to 2000.

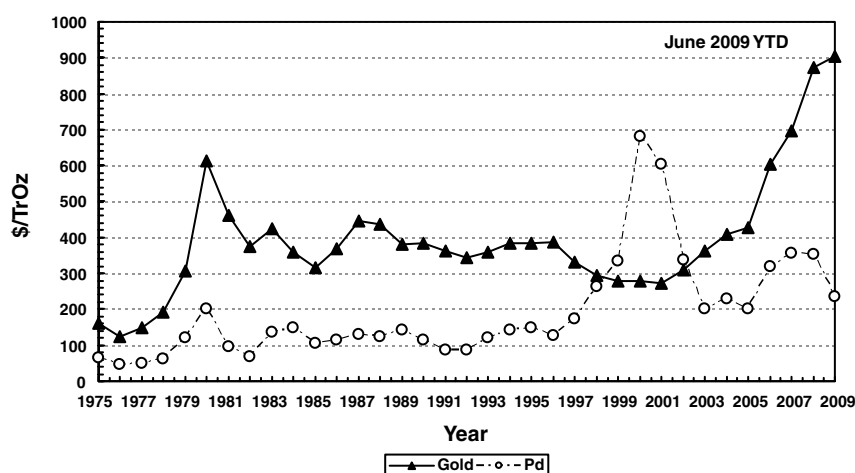


FIGURE 12.6 Gold and Pd bullion prices in dollars per troy ounce, 1975–2009.

in an “excess” supply (Fig. 12.3) and correspondingly lower prices.

The price of Pd coupled with its lower density (Table 12.3) implies considerable cost savings in replacing gold or other metals such as platinum. Today not only the economic but also the technological advantages of substituting Pd or Pd-alloys for gold are generally recognized [8–27]. The material properties (e.g., hardness, ductility, thermal stability) of Pd

are in many instances superior to hard gold. For example, higher hardness is beneficial for wear resistance, which can be further enhanced by a thin coating of electroplated gold as a solid lubricant [16]. The lower porosity of electroplated Pd alloys (e.g., PdNi) enhances the corrosion resistance of plated articles [29].

Electroplated Pd, first plated by Henry circa 1855 [35], found numerous technological uses only during the last two

TABLE 12.3 Physical Properties of Palladium, Platinum, and Gold

Properties	Palladium	Platinum	Gold
Atomic structure	Kr-4d ¹⁰ 5s ⁰	Xe-4f ¹⁴ 5d ⁹ 6s ¹	Xe-4f ¹⁴ 5d ¹⁰ 6s ¹
Atomic number	46	78	79
Atomic weight	106.4	195.09	196.967
Crystal structure	fcc	fcc	fcc
Atomic radius, Å	1.37	1.39	1.46
Covalent radius, Å	1.28	1.30	1.34
Ionic radius, Å	0.896 (+ 2)	0.96 (+ 2)	1.37 (+ 1)
Density, gFcm ⁻³	12.16	21.4	19.3
Hardness (DPN)			
Annealed	37	37	
Electrodeposited (KHN ₅₀)	250–400	400–500	140–200 ^a
Ultimate tensile strength (annealed), lb in. ⁻²	25,000	18,000	
Young's modulus, lb in. ⁻² × 10 ⁶	16	25	
Coefficient of linear thermal expansion, 20°C, μ in.°C	11.8	8.9	14.2
Thermal conductivity (0–100°C), J cm ⁻¹ , cm ⁻² °C s ⁻¹	0.76	0.73	
Electrical resistivity, μ Ω-cm	10.8 (20°C)	9.83 (0°C)	2.19 (0°C)
Reflectivity (average over visible spectrum), %	62	67	
Electronegativity	2.2	2.2	2.4
First ionization potential, k cal, g-mol ⁻¹	192	207	213
Common oxidation states	+ 2, + 4	+ 2, + 4	+ 1, + 3
Melting point, °C	1552	1769	1063
Boiling point, °C	3980	4530	2970

^a Ni/Co-hardened gold; DPN is the hardness in older SI system.

decades. Demand was low due to the relative difficulty of plating Pd with satisfactory material properties. Several critical reviews on this subject were published in the 1960s and 1970s [35–40]. Since then, Pd electrodeposition technology evolved slowly [35–40], and in the 1980s processes suitable for large-scale manufacturing became available [8, 14–20]. This was especially true for high-speed ($>50 \text{ mA cm}^{-2}$) plating operations [8].

12.4 PHYSICAL AND CHEMICAL PROPERTIES OF PALLADIUM

12.4.1 Physical Properties of Palladium, Platinum, and Gold [41–43]

Table 12.3 describes the significant physical properties of Pd and compares them to platinum, the most widely recognized PGM, and gold, the “target metal” that Pd has been substituting. The properties cited are descriptive only insofar as possible to obtain the purest available specimens since they are greatly affected by the presence of impurities. Furthermore, since PGMs have a marked tendency to absorb gases such as hydrogen, it is understandable that obtaining accurate quantitative data on their properties is problematic. Nonetheless, Table 12.3 provides needed information utilized in practical applications. For additional information on the properties of other PGMs see [41–49].

Properties such as melting point, boiling point, hardness, or mechanical strength can be understood by examining the electronic structure of these elements and other PGMs: iridium, osmium, rhodium, and ruthenium. This analysis reveals a progressive decrease in coherence or bond strength among atoms in each of the periodic groups (Ru, Rh, and Pd vs. Os, Ir, and Pt where Au is associated with the latter group). For example, the melting points of Os, Ir, Pt, and Au are 3050, 2443, 1768, and 1063°C, respectively, and correlate with progressive decrease in the number of electrons available for bonding in the solid state that occupy hybridized orbitals from s, p, and d states. The amount of “d character” hybridization is presumed to decrease as electrons become paired in atomic d orbitals and thereby prevent them from contributing

to metallic bonds. This tendency continues to the corresponding members of groups I and IIB [44]. Thus, it is the electronic structure that dictates the physical and chemical properties of Pd and other PGMs.

Palladium is silvery white, malleable, and ductile with a face-centered cubic (fcc) crystal structure. It Pd, has the electronic structure $(\text{Kr})4d^{10}5s^0$, element number 46 with atomic weight of 106.4 g mol^{-1} , a density of 12.16 g cm^{-3} , and a melting point of 1555°C. Table 12.3 compares the material properties of Pd with two other precious metals, gold and platinum [41–43]. Palladium is known to form alloys with other metals of groups VIII and IB that display distinct advantages over the pure metals [45]. In general, the alloying elements tend to increase resistivity, hardness, and tensile strength of Pd. Copper, nickel, gold, iridium, rhodium, and ruthenium have been used to manufacture Pd alloys for many practical applications. For example, an alloy of silver (60/40 weight percent Pd/Ag) is commonly used in electric relay contacts.

12.4.2 Chemical Properties of Palladium

General Reactivity PGMs are relatively inert with respect to chemical attack by oxygen or many acids, and this is one of the properties that make them of practical value. The formation and decomposition of the oxides of PGMs are summarized in Table 12.4 [43]. Osmium forms a considerably volatile oxide at room temperature, and to a lesser extent Pd forms an oxide when heated in air to $\sim 350^\circ\text{C}$; however, the other PGMs require temperatures exceeding 700°C to form oxides. This provides some understanding of their chemical inertness. However, it must be emphasized that the chemical reactivity of the PGMs is greatly affected by the state of the subdivision of the metal or the particle size (i.e., surface area). Thus, Pd “sponge” is more readily attacked than the compact metal and is readily used in the synthesis of Pd compounds. Also, if alloyed with other metals, namely lead or silver, it is more reactive. Palladium finely dispersed on supporting media such as silica gel is still more reactive and displays remarkable catalytic properties.

TABLE 12.4 Reaction of Platinum Group Metals with Oxygen

Metal	Extent of Oxide Formation (25°C)	Oxide Formed	Formation Temperature ($^\circ\text{C}$)	Decomposition Temperature ($^\circ\text{C}$)
Platinum	Negligible	Platinum (IV) oxide, PtO_2	<1000	
Palladium	Superficial	Palladium (II) oxide, PdO	>350	>870
Rhodium	Superficial	Rhodium (III) oxide, Rh_2O_3	~ 700	1100
Iridium	Superficial	Iridium (IV) oxide, IrO_2	~ 700	1140
Osmium	Considerable	Osmium (VIII) oxide, OsO_4	200	
Ruthenium	Superficial	Ruthenium (IV) oxide, RuO_2	700	

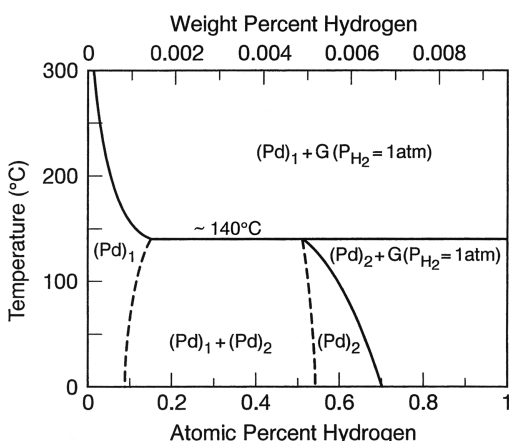


FIGURE 12.7 Binary alloy phase diagram of palladium–hydrogen system.

The “inertness” of PGMs stems from their strong atomic bonds in the solid state. The increase in reactivity exhibited by samples with high surface area, compared to the bulk, is attributed to an increase in the number of atoms with higher energy associated with surface sites, or “dangling bonds.” This becomes especially significant in electroplated Pd where the grain size can be on the order of 50–250 Å, and thus the reactivity at the grain boundaries can be significantly higher than the bulk metal by the argument presented above.

Palladium, of all the PGMs, has the highest capacity to absorb hydrogen [47]—as much as 900 times its own volume. The uptake of hydrogen corresponds roughly to the composition Pd_2H , but modern studies appear to have largely ruled out the formation of such discrete substance (Fig. 12.7). Instead it is inferred that below 300°C there are two phases, each consisting of a solid solution, whereas above this critical temperature there is only a single solution phase. In each phase, hydrogen atoms are held interstitially in such a way as to involve actual chemical bonding, as deduced from changes in electric conductance and magnetic susceptibility. To a smaller degree, platinum and rhodium exhibit similar absorption characteristics.

The ability of Pd to absorb hydrogen poses a significant problem for electrodeposition from aqueous solution. This issue—the hydrogen embrittlement problem—will be discussed in some detail in Section 12.5.2.

Table 12.5 summarizes the reaction of acids on PGMs [43] where resistance to attack is shown in increasing order. Palladium is more reactive and dissolves in nitric acid, giving $\text{Pd}^{\text{IV}}(\text{NO}_3)_2(\text{OH})_2$; in bulk form attack is slow but is accelerated by oxygen and oxides of nitrogen. As a sponge, Pd dissolves in HCl in the presence of chlorine or oxygen. The action of aqua regia on Pd yields chloropalladic acid, H_2PdCl_6 ; however, on evaporation of this solution the polymeric dichloride, $(\text{PdCl}_2)_x$, is formed. Thus PdCl_2 is a significant starting material for the synthesis of most electrolytes used for the electrodeposition of Pd.

TABLE 12.5 Attack of Platinum Group Metals by Mineral Acids

Metal	Form	Nature of Attack
Palladium	Compact	Attacked by hot concentrated nitric acid and boiling sulfuric acid; Dissolved by aqua regia
	Sponge	Dissolved by all the above acids
Platinum	Compact or sponge	Not attacked by single mineral acids; dissolved by aqua regia
Rhodium	Compact	Attacked by boiling sulfuric acid or hydrobromic acid
		Not dissolved by aqua regia
Iridium	Compact	Practically Insoluble in mineral acids or aqua regia
	Sponge	Dissolved in Carius tube by hot hydrochloric acid plus an oxidizing agent (nitric acid or sodium chlorate) [4]
Ruthenium	Any	Virtually Insoluble in hot mineral acids or aqua regia
Osmium	Any	Virtually Insoluble in hot mineral acids or aqua regia

Oxidation States and Coordination Chemistry The principal oxidation state of Pd is +2, although less common there exists a rich chemistry for Pd^{4+} . There is also some important chemistry in the monovalent state, where metal–metal bonds are involved, and in the zerovalent state for certain tertiary phosphine, CO, or other π -acid organometallic compounds [48–50].

The coordination chemistry of Pt and Pd has attracted considerable attention because of the large numbers of compounds of great intrinsic value. For example, use of these metals as catalysts and more recently as anticancer agents has spurred significant technological interest. Furthermore, the square-planar geometry of the bivalent oxidation state made possible the study of cis and trans isomerism which is of great academic interest [51, 52]. Coordination chemistry of Pd(II) is of importance since electrodeposition from aqueous solution is basically the chemistry of the bivalent state. Therefore, the rest of this discussion will be restricted to the Pd(II) oxidation state.

Palladium +2 is the most common oxidation state and possesses a d^8 electronic structure [49]. Most Pd(II) complexes have a coordination number of 4 and form stable 16-electron complexes. The tendency of transition metals to form complexes in which the metal has an “effective number” corresponding to the next higher inert gas has long been recognized [53]. Therefore, the group VIII elements form well-characterized stable compounds with either 16 or 18 valence electrons [54, 55]. Furthermore, the structure of tetracoordinated Pd is square planar rather than tetrahedral, since ligand field stabilization energy is relatively more

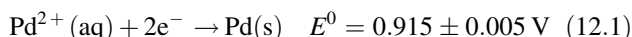
important than valence shell electron pair repulsion, which would dictate a tetrahedral structure. A detailed discourse on the chemistry and structure of Pd compounds can be found in [43, 48] and references within.

12.5 ELECTROCHEMISTRY OF PALLADIUM

12.5.1 General Electrochemistry: Thermodynamics

One of the most complete thermodynamic considerations of the electrochemistry of Pd can be found in Chapter 12 of the handbook *Standard Potentials in Aqueous Solutions* [56]. Under standard conditions, in solutions of zero ionic strength, the standard potentials for the electroreduction of Pd^{2+} were reported by various investigators to occur between 0.915 and 0.979 V.

The half-cell potential of the Pd^{2+}/Pd couple in HClO_4 solutions at zero ionic strength was reported by Izatt et al. [57] as follows:



However, Templeton [58, 59] reported a value of $E^0 = 0.987$ V from an HClO_4 solution at ionic strength $I = 4 \text{ mol L}^{-1}$ which, when adjusted to zero ionic strength [59], yields $E^0 = 0.945$ V. Other measurements by various investigators [60] have yielded $E^0 = 0.978 \text{ V} \pm 0.0005 \text{ V}$ while polarographic [61] measurements confirmed the value of Izatt et al.

Pourboix [62] used thermodynamic data to calculate the formal potential of the formation of palladium from palladium hydroxide:

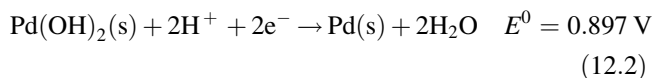
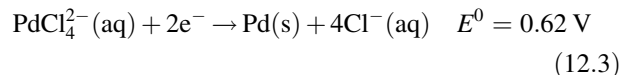
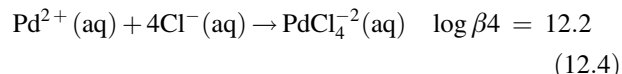


Table 12.6 provides available thermodynamic data for various aqueous complexes of $\text{Pd}(\text{II})$ along with either the

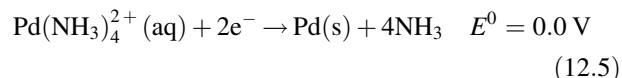
measured or calculated E^0 . For example, the electroreduction of Pd from PdCl_4^{2-} in $\text{HCl}(\text{aq})$ media was reported by several authors [58, 63] to be



and $E^0 = 0.60$ V for 1 M KCl. These values were confirmed [64] for 1 M HCl, $E^0 = 0.59$ V, and by the study of the equilibrium constants for the stepwise dissociation [65]

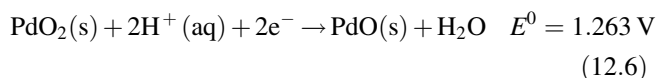


For the amine complex, which is very important for the electrodeposition of Pd, the following potential has been calculated:



on the basis of the stability constants ($\log \beta_4 = 30.5$) measured for the equilibrium in ammonia solutions at $I = 1 \text{ mol L}^{-1}$.

For $\text{Pd}(\text{IV})$, one of the potentials for the half reaction is



This was calculated by Pourboix [62] from thermodynamic data. Furthermore, for Pd^{4+} in the important ethylenediamine systems the following potentials were obtained from electromotive force (emf) determinations [66] at 25°C and 10^{-5} – $10^{-6} \text{ mol L}^{-1}$ nitrate solutions:

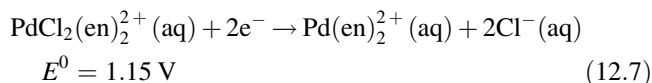
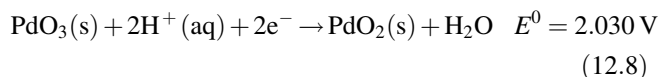


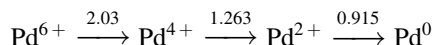
TABLE 12.6 Thermodynamic and Electrochemical Data on Palladium (II)

Formula (Aqueous)	ΔH° (kJ mol $^{-1}$)	ΔG° (kJ mol $^{-1}$)	S° (J mol $^{-1}$ K $^{-1}$)	$\log \beta_x$	E^0 (V)
Pd^{2+}	149.0	176.5	−184	<3	0.915
$\text{Pd}(\text{SO}_4)^{2-}$				3.16	0.82
PdCl_4^{2-} (1M HCl)	−550.2	−417.1	16.7	12.2	0.62
PdBr_4^{-2}	−384.9	−318.0	247	15	0.49
PdI_4^{-2}		−159.0	—	25	0.18
$\text{Pd}(\text{NO}_2)_4^{+2}$		−68	—	—	0.34
$\text{Pd}(\text{OH})_2$					0.07
$\text{Pd}(\text{en})_2^{+2}$				26.9	−0.79
$\text{Pd}(\text{NH}_3)_4^{+2}$		−75	—	30.5	0.0
$\text{Pd}(\text{CNS})_4^{-2}$		410.5			
$\text{Pd}(\text{CN})_4^{-2}$		628	—	51.6	−1.52

For Pd(VI), from data on the anodic formation of PdO₃ in alkaline solutions, Pourboix [62] found the following:



Thus, the overall potential diagram for the electroreduction of Pd is as follows:



However, normal electrodeposition conditions deviate significantly from the standard, or equilibrium, condition. The reduction potential at any given temperature and concentration for a simple ion reaction can be expressed by the following equation:

$$E = E^0 + \left(\frac{RT}{nF} \right) \ln a + C \quad (12.9)$$

It can be seen that in addition to the standard or formal potential, the reduction potential for Pd or any other species (e.g., H₃O⁺) can be affected by temperature and concentration of the species at the electrode surface and any other factors that contribute to the C term, such as complexing ligands for metals, and organic additives that may affect the overvoltages for the metal deposition.

Finally, the deposition of Pd from aqueous solutions is usually accompanied by the codeposition of hydrogen and the formation of palladium hydrides, PdH_x. As will be seen in Section 12.5.2, the successful electrodeposition of Pd and its alloys is highly dependent on the avoidance of codeposited hydrogen. In this regard, we will attempt to understand this phenomenon and how to control it by treating the electrode surface as the scene of more than one electrochemical reaction; see Section 12.5.3.

12.5.2 Hydrogen Embrittlement Problem

So-called hydrogen embrittlement is a generic term used to describe a variety of fracture phenomena having a common relationship to the presence of hydrogen in a metal or alloy as a solute element [67]. The ramifications of hydrogen-embrittled metals and alloys can be very serious and in some cases, such as aircraft parts or nuclear reactor components, even life threatening.

It appears that most materials can become embrittled if hydrogen is introduced under “pressure” by means such as electrodeposition and this state remains unchanged until hydrogen escapes [69]. The failure can be abrupt and forceful as to become almost explosive [70]. It has been said that “one of the most spectacular and memorable sounds associated with zinc plating is standing in a quiet storage room next to drums of freshly zinc plated steel springs and listening to the metallic shriek as the springs slowly destroy themselves in

order to release occluded hydrogen” [68–71]. Likewise, the author personally plated palladium with such large amounts of occluded hydrogen that immediately after electrodeposition the plated coupons violently twisted into a cylindrical shape and released enough heat from the exothermic release of hydrogen to turn the coupons “red hot” and burn his fingers.

The phase diagram of Pd and hydrogen is seen in Figure 12.7. This system has been well studied [47], and in the 1980s renewed interest was triggered by the speculative phenomena of “cold fusion” [72–74]. Classical fundamental work on this system was carried out by Lacher [75] and Gillespie and co-workers [76, 77] from 1935 to 1939. They determined that palladium hydride exists as a fcc α phase up to an atomic concentration of [H]/[Pd] = 0.03, which is thermodynamically stable. Simons and Flanagan [78] found that the lattice of α -PdH_x increases slightly from pure Pd, which is 3.889–3.893 Å due to hydrogen absorption. However, the pure β phase prevails at a minimum atomic ratio of [H]/[Pd] = 0.57. This phase, also fcc, has a larger lattice constant of 4.04 Å. Furthermore, the β phase is dependent on the temperature of the system and on the hydrogen pressure and is thermodynamically unstable under ambient conditions. For example, Frumkin and Aladjalowa [79] state that an atomic ratio of [H]/[Pd] = 0.68 is obtained from 1 atm of hydrogen pressure; furthermore, Hoan and Arrowsmith [80] state that this ratio equals 0.61 between 20 and 30°C. In the concentration range of ratios from 0.03 to 0.57 [H]/[Pd], the two phases are at heterogeneous equilibrium.

The hydrogen embrittlement problem stems from the thermodynamic instability of β -PdH_x. Immediately after deposition, β -PdH_x spontaneously decomposes evolving H₂ gas and is transformed to the thermodynamically stable α -PdH_x. This transformation is accompanied by corresponding lattice contractions and changes in the mechanical properties of the Pd films (Fig. 12.8). During the contraction, the deposits become highly stressed, and as the tensile components of this stress exceed the yield point, the stress is relieved by cracking. The effects of such a phenomenon are seen in Figure 12.9.

The electrodeposition and material properties of Pd are thus greatly affected by the chemistry and deposition parameters (e.g., temperature and pH) since they determine the amount of codeposited hydrogen. The electrochemistry and mechanisms of hydrogen inclusion during Pd electrodeposition are discussed elsewhere [72–74, 81–87]. This phenomenon and the electrochemical parameters that affect it must be understood if one is to successfully electroplate Pd with the desired material properties.

12.5.3 Electrochemistry of Simultaneous Reactions: Electrokinetics

The hydrogen embrittlement of electrodeposited Pd is a matter of great concern when one attempts to deposit Pd

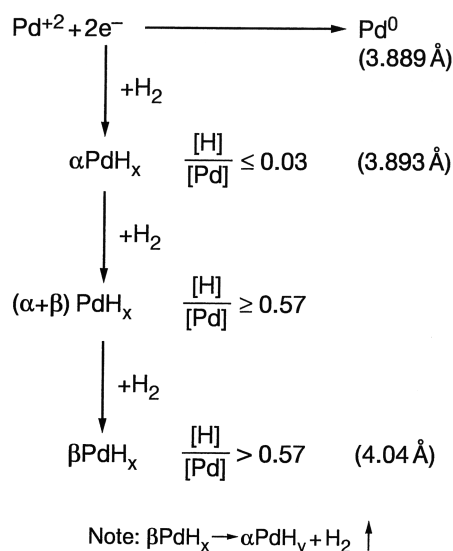


FIGURE 12.8 Schematic of palladium–hydrogen embrittlement phenomenon.

films of technological use. Obviously these films must possess mechanical integrity and thus be crack free and of low stress. Therefore, it is important to eliminate or inhibit the codeposition of hydrogen with Pd. Alternatively, the electrodeposition of Pd alloys such as PdNi, PdCo, and PdAg where the alloying metals are in the range of 10–50% are of significant technological interest. Thus, there exists the situation where in the latter case a high degree of codeposition for alloy formation is desired and in the former case codeposition is undesirable. Identical electrochemical considerations can be utilized to understand both phenomena in which the interface is the scene of more than one electrochemical reaction.

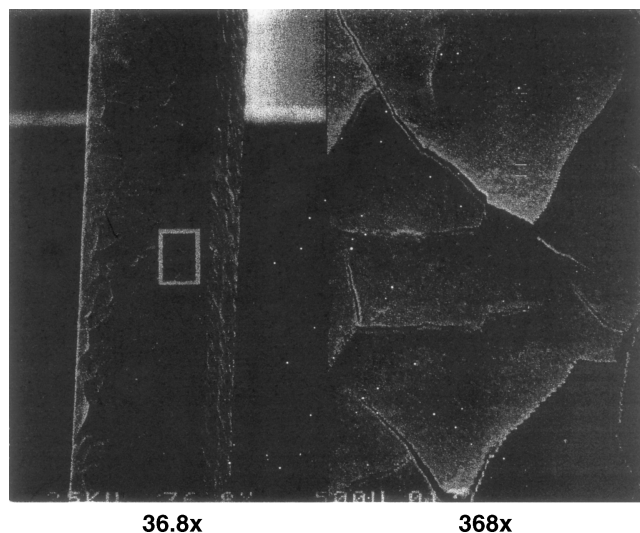


FIGURE 12.9 Scanning electron micrograph of hydrogen-embattled Pd film.

The treatment of simultaneous reactions at an electrode interface [88, 89] is based on an important fact: Although the current densities of $i_1, i_2, \dots, i_n$ may be different for each reaction, they are produced by the same absolute Galvani potential difference $\Delta\phi$ at the interface. In the case of two simultaneous reactions, the following equation will determine the relative current densities for each electroreduction:

$$\begin{aligned}
 \frac{i_1}{i_2} &= \left[\frac{i_{0,1}}{i_{0,2}} \exp\left(\frac{F}{RT}\right) \left[(\alpha_1 \Delta\phi_{e,1} - \alpha_2 \Delta\phi_{e,2}) \right] \right] \\
 &\quad \times \exp\left(\frac{F}{RT}\right) (\alpha_1 - \alpha_2) \Delta\phi
 \end{aligned} \quad (12.10)$$

Thus, the value of the current density ratio and the degree of “codeposition” depend not only upon the exchange current densities ($i_{0,i}$), the transfer coefficients (α_i), and the equilibrium potentials ($\Delta\phi_{e,1}, \Delta\phi_{e,2}$), but also, in an exponential way, upon the potential difference across the interface ($\Delta\phi$). Thus, even if the deposition of a second species (i_2) is inhibited by lower exchange current density (i.e., $i_{0,2} < i_{0,1}$) and more negative equilibrium potentials (i.e., $\Delta\phi_{e,2} < \Delta\phi_{e,1}$), it can have a higher deposition–current density if its transfer coefficient α_2 is greater than that of the other, α_1 .

Another situation in which a species with a more negative equilibrium potential can be deposited to a greater extent occurs when the deposition of the second species is limited by mass transport. Under such conditions

$$i_1 = i_L = \frac{DnFC_1^0}{\delta} \quad (12.11)$$

where D = diffusion coefficient

n = number of electrons

F = Faraday’s constant

δ = diffusion layer thickness

C_1^0 = concentration in the bulk

If i_2 is not transport limited, then i_2 can, most likely, be greater than i_1 .

Electrokinetics of Hydrogen Evolution The arguments in Section 12.5.3 are equally valid for a situation where metal deposition occurs with any other cathodic reduction such as the formation of hydrogen [88, 89]. From a technological point of view, in most cases, one seeks to electrodeposit a metal at high current efficiencies (i.e., limit hydrogen formation). The reasons are obvious since hydrogen embrittlement, as discussed in Section 12.5.2, can be problematic. Furthermore, a high current efficiency implies that the desired reaction occurs at a faster rate and less time is utilized to deposit the desired amount of metal at a given total current density. Technologically speaking, this is

of great importance since it “speeds up” the process and increases manufacturing throughput.

In order to achieve this objective, it becomes important to understand the current density ratio i_H/i_M or the percentage of current efficiency $[i_M/(i_M + i_H)] \times 100$ which is attributed to metal deposition. The intent is to utilize the current only for metal deposition, that is, metal deposition current efficiency equals 100%.

The basic factors determining current efficiency are revealed by considering i_1 as the hydrogen evolution current and i_2 as the metal deposition current in Eqs. (12.10) and (12.11). Thus, the same principles apply, that is, the current going toward hydrogen evolution depends upon the ratio of the exchange current densities, the equilibrium potentials, and the relative transfer coefficients of hydrogen evolution and metal deposition reactions. In general, the deposition of metal is favored by a more positive equilibrium potential with respect to hydrogen, a higher exchange current density, and a lower value of the transfer coefficient. Even if these parameters are unfavorable for the deposition of a metal, it may be possible to obtain high current efficiencies by ensuring that i_H is transport limited. Utilizing Eq. (12.11) for i_L it becomes clear that limiting $C_{H^+}^0$ can be accomplished by manipulating the pH of the reaction. However, if one exceeds i_L for metal deposition (there is always a limit), hydrogen evolution will occur. In aqueous solutions, hydrogen evolution will always occur if the total deposition current is made sufficiently high and exceeds the limiting current of the metal in question; the hydrogen may come not only from H_3O^+ but, if limited at high pH, from water itself.

The effects of hydrogen codeposition on the crystallography of metal deposition are rather complicated and beyond the scope of this chapter. However, several ramifications of hydrogen evolution must be noted. As discussed in Section 12.5.2, hydrogen may codeposit with a metal and change its structural and mechanical properties. It may also adsorb more efficiently on certain crystal planes “blocking” them from further deposition so that the metal grows preferentially on others. If hydrogen gas evolution is significant, a “curtain” of gas may inhibit the transport of certain species to the electrode surface and thus impair any intended reaction. Finally removal of H_3O^+ from the diffusion layer may significantly increase the pH, which may alter the intended chemical and electrochemical reactions at the interface. If the solution at the interface becomes sufficiently alkaline, it may cause the solubility product of a hydroxide of the metal ion present to be exceeded, which may cause inclusion of such a species in the deposit. This can be problematic in terms of deposit properties or mechanical properties such as stress and ductility. Alternatively, it could cause the formation of relatively thick (10^2 – 10^3 Å) films on plated parts, thus “passivating” the cathode surface.

In summary, hydrogen codeposition usually leads to many undesirable effects in metal deposition. Therefore, selective

control over the rate of hydrogen evolution is vital—hence the need to understand the reaction. Electrode kinetics, as discussed above, is important in determining i_H/i_M and the factors that affect it; however, the “hydrogen overvoltage” is also an important phenomenon that determines the parameters under which a metal can be deposited.

Hydrogen Overvoltage An operating electrolytic cell that has net current flowing through it is not at equilibrium [88]. The potential will differ from equilibrium as follows:

$$\eta = E_i - E_q \quad (12.12)$$

Where E_i is the potential when current is flowing and E_q is the potential at equilibrium. The overpotential or overvoltage, η , is impacted by several factors. For example, concentration polarization at the electrode surface caused by depletion of reactants is described by the Nernst equation:

$$\eta_{\text{conc}} = \frac{RT}{nF} \ln \left(\frac{a_e}{a_o} \right) \quad (12.13)$$

This is referred to as concentration overpotential, where a_e is the activity of the depositing ion at the electrode surface and a_o that of the bulk solution. In the case of hydrogen evolution, concentration overpotential occurs when surface hydrogen concentration changes (i.e., is depleted) with surface pH changes. Alternatively, overpotential may be required to overcome various kinetic barriers to a reaction; this is referred to as activation overpotential [88]. This is the minimum energy or potential barrier that must be overcome for the reaction to proceed, and for the hydrogen evolution reaction occurring on specific metals, it is referred to as the “hydrogen overvoltage.”

If it were not for hydrogen overvoltage, many metals could not be deposited from aqueous solutions. For example, at pH 4, which is a common pH for nickel plating, E^0 for hydrogen evolution is about -0.236 V; in alkaline solutions with pH 10, it is -0.59 V. These potentials are significantly more positive than the reduction potentials of many metals plated from these solutions. Activation overvoltage is extremely high in the evolution of hydrogen, and it enables metal deposition or inhibits hydrogen evolution.

The hydrogen overvoltage is dependent on the nature (i.e., electronic structure) and structure (morphology) of the electrode surface. For example, at cathodes of tin, zinc, or lead, it can be more than 1 V negative than its equilibrium potential, and this is why these metals can be deposited from very acidic solutions, $\text{pH} < 1$, where the concentrations of H_3O^+ is very high. Alternatively, it is extremely low for metals such as Pt or Pd. On platinum black it is negligible, which is why it is used in “setting up” the hydrogen electrode. Therefore, it is a challenge to plate Pd from aqueous solution without the interference of hydrogen, and one cannot rely on the

hydrogen overvoltage to avoid codeposition. Thus, most chemical formulations used to deposit Pd are neutral to alkaline in order to reduce or inhibit the evolution of hydrogen.

An additional factor that can suppress hydrogen formation is the use of additives or “poisons” that adsorb on an electrode surface but are essentially electrochemically inactive. Such impurities adsorbed on the cathode surface may increase hydrogen overvoltage. Furthermore, such impurities often include addition agents that poison selected sites and are useful for leveling or brightening the deposit. A detailed discussion of the mechanisms of hydrogen formation is beyond the scope of this chapter and can be found in [88].

Minimization of Hydrogen Codeposition So far this section has demonstrated, in a theoretical sense, what is required to either minimize or maximize the current ratio, i_1/i_2 , of two simultaneous reactions occurring at an electrode interface. It now becomes important to understand what factors, chemical, physical, and/or electrochemical, can be utilized to achieve the end objective, which in the case of Pd plating is to minimize i_1 and maximize i_2 . It is stated by the arguments Section 12.5.3 that the following parameters must be considered:

1. Exchange current densities, i_0
2. Transfer coefficients, α
3. Equilibrium potentials, ΔE_e
4. Potential difference, ΔE , across interface
5. $i_{L,1}$ versus. $i_{L,2}$, limiting current
6. Hydrogen overvoltage modifiers
 - Metallic (e.g., Ni for PdNi alloy)
 - Organic (surfactants, brighteners, etc.)

The exchange current densities, the transfer coefficients, and the equilibrium potentials are, for the most part, determined by the nature of species 1 and 2, in this case palladium and hydrogen, and the nature of the electrode material, which in this case will be palladium. These are constants at a given temperature and cannot be manipulated. In this situation only the relative concentration of species 1 and 2 at the electrode surface and the temperature can be altered significantly. However, what can be modified by changing the chemical system and the plating conditions (e.g., solution agitation) are the relative reduction potentials of each species, the concentration of each at the electrode surface, and potentially the overvoltage of hydrogen and/or metal deposition at a “modified” palladium surface through the use of metallic or organic additives.

As stated in Section 12.5.1, the reduction potential of an element at any given temperature and concentration is described by the sum of its standard potential and a term expressing its activity (a) as shown below:

$$E_1 = E_1^0 + \frac{nF}{RT} \ln(a_1) + C_1 \quad (12.14)$$

$$E_2 = E_2^0 + \frac{nF}{RT} \ln(a_2) + C_2 \quad (12.15)$$

The difference in potential between the two elements involved can be expressed as

$$\Delta E = E_1 - E_2 \quad (12.16)$$

For successful alloy deposition, ΔE must be minimized. The condition can be met when the two values E_1^0 and E_2^0 are similar or by adjusting the concentration of one species in solution, so altering its activity, or by arranging a suitable difference in the C term, which can be achieved by introducing complexants. The latter is the most common manipulation, especially when the difference between the standard potentials is large.

Alternatively, to avoid or inhibit hydrogen codeposition one must maximize ΔE . That is, the reduction potential for Pd must be as positive as possible while the hydrogen reduction potential must be as negative as possible. In this regard, we will utilize cyclic voltammetry to examine the reduction characteristics (peak potentials, E_p) of various chemical systems and demonstrate how to achieve the above objective.

For a totally irreversible system, the expression for the peak potential E_p is [90]

$$E_p = E^{o'} - \frac{RT}{\alpha n F} \left[0.78 + \ln \left(\frac{D_0^{1/2}}{k^0} \right) + \ln \left(\frac{\alpha n F v}{RT} \right)^{1/2} \right] \quad (12.17)$$

where $E^{o'}$ is the formal potential [see Eq. (12.27)], α is the transfer coefficient, n is the number of electrons, F is Faraday's constant, D_0 is the diffusion coefficient, k^0 is the standard heterogeneous rate constant, and v is the linear potential scan rate. The objective is to obtain maximum separation of $E_p(\text{Pd})$ and $E_p(\text{H}_2)$ as shown below:

$$\Delta E_p = E_p(\text{Pd}) - E_p(\text{H}_2) \quad (12.18)$$

Examination of the expression for E_p [Eq. (12.17)] indicates that the formal potential of each species and to some extent temperature, transfer coefficients, diffusion coefficients, and standard rate constants for each reaction will dictate the reduction potential of each species in question. The reduction potential E is described through the Nernst equations below:

$$E(\text{Pd}) = E_{\text{Pd}}^0 + \frac{0.0591}{2} \log [\text{Pd}^{2+}]_0 \quad (12.19)$$

$$E(\text{H}_2) = E_{\text{H}_2}^0 + 0.0591 \log [\text{H}^+]_0 \quad (12.20)$$

where E^0 are formal potentials and $[\text{Pd}^{2+}]_0$, $[\text{H}^+]_0$ are the concentrations at the electrode surface.

Formal potentials, of course, are dependent on the standard potential [Eq. (12.27)] and the relative concentration of each species at the electrode surface, which in turn is dependent on the equilibrium constants for specific Pd chemistries (Table 12.6) and the pH for the hydronium ion concentration. In Section 12.6, we will examine how to manipulate these factors to maximize ΔE_p . However, prior to this discussion, we must examine the equilibrium constants of various Pd complexes and other factors that are important in these considerations.

Theoretical and Practical Considerations for Palladium Plating The standard potential E^0 of $\text{Pd}^{2+}/\text{Pd}^0$ as described in Section 12.5.1 ranges from +0.915 to +0.979 V. This highly positive value, as would be expected for a noble metal, implies facile reduction of Pd (II) to Pd(0) metal from an aqueous solution of its simple salts, namely noncomplexed ion. For example, for the $[\text{Pd}(\text{SO}_4)_4]^{2-}$ system in Table 12.6, $\log \beta_4 = 3.16$ indicates that this aquo species is of low stability. As a matter of fact, tetra-aquo Pd(II), present in acidic media, can be reduced by less noble metals (e.g., Cu) as a result of charge exchange or “displacement” plating. In this case, even though the H_3O^+ concentration is high, it can be plated with 100% efficiency and thus avoid hydrogen codeposition. However, Pd films produced as a product of electrodeposition coupled with displacement plating are powdery and nonadherent [37]. Furthermore, electrodeposition from solutions of $\text{pH} < 1$ is problematic in a practical sense.

On the other hand, reduction from aqueous solution of highly stable complexes such as $[\text{Pd}(\text{CN})_4]^{2-}$ is impractical. The stability constant β_4 of tetracyanopalladate is

$$\beta_4 = \frac{[\text{Pd}(\text{CN})_4^{2-}]}{[\text{Pd}^{2+}][\text{CN}^-]^4} = 10^{51.6} \quad (12.21)$$

which indicates this complex is much too stable with a reduction potential more negative than the onset of hydrogen evolution, and thus hydrogen is preferentially discharged. It has been reported [35] that only traces of Pd can be deposited from this complex even if the electrolyte is strongly alkaline and a metal with a high hydrogen overvoltage is employed as the cathode. In 1919 Smee made use of this fact to separate Au from Pd by electrolysis of a solution containing the complex cyanides of both metals [34]; he found that Pd was not deposited from such a solution until the cyanide species had been decomposed. The relationship between β_x and E^0 can be seen in Table 12.6.

Complexes with nitrogen-containing ligands, such as ammonia, are well suited for Pd deposition; they are stable enough to prevent immersion plating and yet amenable to

cathodic reduction. For example, Pd tetra-ammine complex has the following stability constant:

$$\beta_4 = \frac{[\text{Pd}(\text{NH}_3)_4^{2+}]}{[\text{Pd}^{2+}][\text{NH}_3]^4} = 10^{30.5} \quad (12.22)$$

which is more than 20 orders of magnitude lower than the cyano complex. Likewise, monoamines such as $\text{CH}_3\text{-NH}_2$, and multidentate ligands such as diamines (e.g., 1,3-diaminopropane) can be used to electrodeposit Pd. Thus Pd complexes within an intermediate range of stability are very useful in practical electroplating processes.

Hydrogen embrittlement is the most prominent but not the only challenge that needs to be considered when developing a Pd plating process. In summary, the factors that must be considered are as follows:

Hydrogen embrittlement: all factors that affect hydrogen evolution and incorporation

Stability of the chemical system

- Pd complex electrolyte (also solubility)
- Ligands for Pd complex (chemical and electrochemical stability)
- Replenishment system (ligand buildup)
- Counterion effects (e.g., salt buildup)
- Conducting electrolyte effects
- Additives and their decomposition products: brighteners, levelers, stress-reducing agents

Buffer system

- Ability to maintain pH at cathode and anode
- Stability at cathode and anode

Chemical attack on non-noble metal substrates

- Cu and Cu alloys (e.g., parts being plated)
- Steel (e.g., parts for the plating machine)
- Platinized anodes

Environmental considerations

- Toxicity of chemicals
- Waste disposal
- Vapor discharge (e.g., NH_3)

Cost of process

- Cost of chemicals
- Speed of deposition
- Efficiency of deposition
- Analysis and maintenance procedures
- Precious metal recovery

In the following section, we will discuss electrodeposition chemistries for alkaline, neutral, and acid electrolytes. We will begin with the examination of a highly alkaline ($\text{pH} \sim 12$), additive “free” chemistry which utilizes 1,3-diaminopropane as the ligand of choice. This analysis will demonstrate how to manipulate the chemical and physical properties of the

process in order to avoid hydrogen embrittlement and deposit “smooth,” “crack-free” Pd films.

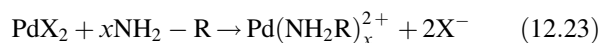
12.6 ELECTRODEPOSITION OF PALLADIUM

Palladium has been plated from a wide variety of electrolytes which are far too numerous to include in this chapter. This work will summarize what the author believes to be the most important processes, and in an attempt to organize this information, the processes will be broadly classified as alkaline (pH 9–13), neutral (pH 5–9), and acidic (pH < 1–5).

12.6.1 Alkaline Electrolytes (pH 9–13)

In the presence of ammonia or amines, Pd ions exhibit a very strong tendency to form stable complexes. As shown in Table 12.6, $\log \beta_4$ and $\log \beta_2$ for ammonia and ethylenediamine are 30.5 and 26.9, respectively. While certainly not as stable as the cyano complex, they are nonetheless more stable than the aquo or halide complexes and are not susceptible to displacement plating.

The amine complexes are readily formed in palladium chloride solutions by the general equation:



where X = halides (Cl^- , Br^- , I^-); NO_3^- ; SO_4^{2-}
 R = H; CH_3 ; $\text{C}_y\text{H}_{2y}-\text{CH}_3$; $\text{C}_y\text{H}_{2y}-\text{NH}_2$
 $x = 2, 4$ (depending on whether it is a diamine or a monoamine)
 $y = 1, 2, \dots$

Table 12.7 is a summary of various alkaline processes that have been found in the literature.

In this pH range (>9), only the diamine processes can be considered of practical use. While ammonia systems certainly can plate Pd with respectable properties, additives and wetting agents are essential if one requires smooth, bright to semibright deposits. In the absence of additives, the deposits are nodular, of dull appearance, and susceptible to “fingerprinting” or easily stained [37, 40]. Furthermore, at pH > 8, the presence of high concentrations of ammonia, especially at elevated temperatures, becomes problematic due to its excessive outgassing from solution, which in many cases is being subjected to aggressive solution movement or agitation. This makes it difficult to control pH, requires extensive replenishment with ammonium hydroxide, and poses an obvious environmental challenge. Thus, the only real contenders in this pH range are the “ammonia-free” systems. The remainder of this section will be restricted to the diamine processes (C, Table 12.7), which are an excellent example to demonstrate the hydrogen embrittlement issues discussed above [8, 99].

1,3-Diaminopropane Electrolyte [8, 99] The ligand of choice in the formulation of bath C is 1,3-diaminopropane (pn), whose formula is $\text{NH}_2\text{C}_3\text{H}_6\text{NH}_2$. It is a bidentate nitrogen-containing ligand that forms a classical 16-electron, square planar coordination complex, $[\text{Pd}(\text{pn})_2]^{2+}$.

The choice of 1,3-diaminopropane was based on the analysis of numerous possibilities. Other ligands considered were additional aliphatic diamines (e.g., 1,4-diaminobutane), aliphatic triamines (e.g., diethylenetriamine), substituted diamine and triamine species (e.g., 2-hydroxypropanediamine), numerous substituted and unsubstituted monoamines (e.g., triethanolamine), and pyridines and numerous substituted and unsubstituted aromatic amines (e.g., diphenylamine). 1,3-Diaminopropane was chosen based on an exhaustive diagnostic analysis which took into account the requirements of performance, cost, and environmental considerations.

Counterion Effects Equation (12.23) describes the synthesis of an amine Pd complex where the counterion can be Cl^- , Br^- , NO_3^- , and SO_4^{2-} . Cyclic voltammograms of these systems are shown in Figure 12.10. The Pd^{2+} reduction peak potential [−0.91 V vs. the saturated calomel electrode (SCE)] is essentially unaffected by the change in anion, and it is concluded that the counterion has little or no effect on the electrochemical reduction of Pd. This phenomenon was also studied in an ammonia system by LePenven et al. [100] for Br^- , Cl^- and NO_2^- electrolytes.

However, there are other factors which must be considered in choosing the counter ion. For example NO_3^- is not electrochemically stable. This is also true for the nitrite systems where ammonium nitrate is subsequently formed by electrolysis but is itself unstable [101]. The SO_4^{2-} ion is electrochemically stable, but due to the difficulty of preparing PdSO_4 , the cost becomes prohibitive, although within the last decade a number of sulfate systems have been formulated which can provide advantages over the chloride systems at a reasonable cost differential [126, 160, 162, 163]. The Br^- ion is easily oxidized at an insoluble anode, and one would like to avoid the formation of Br_2 .

The most reasonable choice from a technical and cost perspective is chloride. It is “relatively” electrochemically stable at a Pt anode, very soluble, and easily transported across anion-permeable membranes [36].* Furthermore, the starting chemical, PdCl_2 , is readily available and the least expensive of the Pd salts. The remainder of this discussion will deal solely with the $\text{Pd}(\text{pn})_2\text{Cl}_2$ system.

Temperature and pH Effects Figure 12.11 shows a cyclic voltammogram of the $\text{Pd}(\text{pn})_2\text{Cl}_2$ system at a gold rotating-disk electrode (RDE, 0.49 cm^2 ; $w = 0$) at 25°C . At pH 11.5,

*This property becomes important when removal of excess anion is necessary.

TABLE 12.7 Palladium Electroplating Alkaline Electrolytes (pH 9–13)

Parameter	Bath Type						
	A ^{71,37,35,98}	B ⁹²	C ^{8,99}	D ^{81,40,96}	E ^{93,94}	F ⁹⁷	G ⁹⁸
Source of Pd	PdCl ₂	PdCl ₂	PdCl ₂	Pd(NH ₃) ₂ (NO ₂) ₂	Pd(NH ₃) ₂ Br ₂	Pd(NH ₃) ₂ (NO ₂) ₂	Pd(OOOC(H ₄ NH ₂) ₂
Pd metal (g/L)	10–20	28	1–40	4–25	25–35	4–18	1–50
Ligand*	NH ₃	en ⁺	pn ⁺	NH ₃	NH ₃	NH ₃	OOCCH ₂ NH ₂ ²
Amino acetic acid (g/L)					45	20	1–150
Ammonium bromide (g/L)							
Ammonium chloride (g/L)	60–90						
Ammonium hydroxide (g/L)			25–75	Adjust pH	Adjust pH		
Ammonium sulfate (g/L)							
Ammonium sulfamate (g/L)				90–100		5–300	
Ammonium nitrate (g/L)						Adjust to pH	Adjust to pH
Tetrapotassium pyrophosphate (g/L)							
Potassium chloride (g/L)							
Potassium hydroxide (g/L)			50–100				
Potassium phosphate (g/L)			Adjust to pH				
Potassium hydroxide (g/L)							5
EDTA (g/L)							
Sodium sulfate (g/L)		140		9–12			
Sodium nitrate (g/L)							
Hydrochloric acid (g/L)			Adjust pH				
Additives	See appropriate data in the literature	None	See appropriate data in the literature	See appropriate data in the literature	See appropriate data in the literature	See appropriate data in the literature	See appropriate data in the literature
pH	9–10	11–12	10–13	9–10	9–9.5	8.5–11	7–12
Temperature (°C)	25–50	25	40–70	25–55	25–55	35–45	60
Current density mA/cm ²	0.1–2.5	20	1–500	1–300	2.5–100	2–50	1–100

*Ligand is used in approximately stoichiometric (e.g. PdNH₃ 4:1) or slight excess of stoichiometry ~0.2–0.3 molar. + en = 1,2 ethylenediamine pn = 1,3 diaminopropane

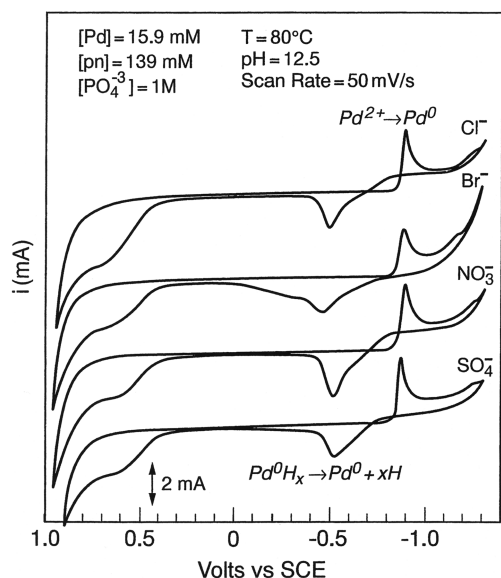


FIGURE 12.10 Cyclic voltammograms: palladium-diaminopropane with chloride, bromide, nitrate, and sulfate counterions.

the Pd reduction peak potential (-1.04 V vs. SCE) and the H^+ reduction peak potential (-1.10 V vs. SCE) are separated by only $\sim 60 \text{ mV}$. Formation of PdH_x is evident by both the reduction peak (labeled PdH_x) and the hydrogen oxidation peak at -0.32 V observed on the reverse waves.

As the pH is varied from 11.5 to 12.5, the hydrogen reduction peak is shifted to more negative potentials. This shift ($\sim 0.059 \text{ V/pH}$) decreases the overlap with Pd reduction peak and reduces the formation of PdH_x , as evident by the relative decrease in the height of the PdH_x peak and the corresponding decrease in the hydrogen oxidation peak. Thus ΔE_p [see Eq. (12.18)] is increased and an overall reduction in hydrogen incorporation is accomplished by controlling the $C_{\text{H}^+}^0$, as was discussed in Section 12.5.3.

A further increase in the value of ΔE_p is achieved by thermal destabilization of the Pd chelate complex which

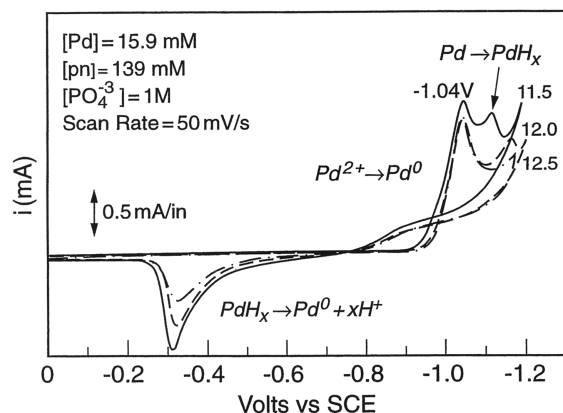


FIGURE 12.11 Cyclic voltammograms: palladium-diaminopropane system; variation of pH 11.5–12.5.

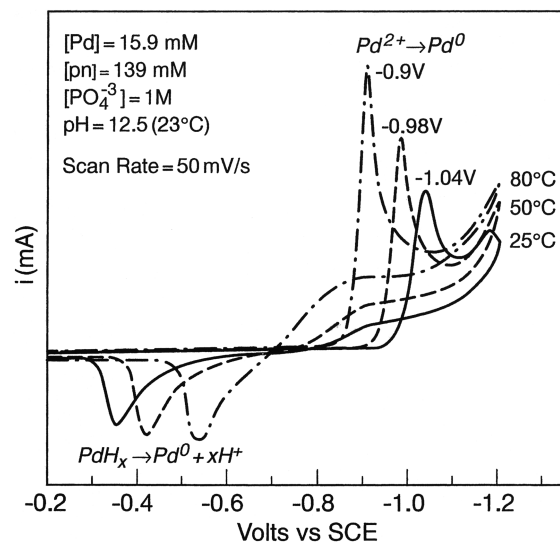


FIGURE 12.12 Cyclic voltammograms: palladium-diaminopropane system; variation of temperature, 25–80°C.

shifts Pd reduction to more positive potentials and away from the hydrogen reduction, as illustrated in Figure 12.12. Temperature variation from 25 to 80°C shifts the peak potential E_p from -1.04 to -0.91 V , or approximately 130 mV . A corresponding increase in i_p is realized due to an increase in the diffusivity of ions.

The shift in E_p with temperature is mostly due to the thermodynamic destabilization of the Pd chelate complex, which changes $E^{\circ'}$, and to a lesser extent changes in RT and k^0 , which affect $E^{\circ'}$ and E_p , as predicted by Eq. (12.17).

The pH dependence at elevated temperature is dramatically demonstrated in Figure 12.13. Voltammograms taken at

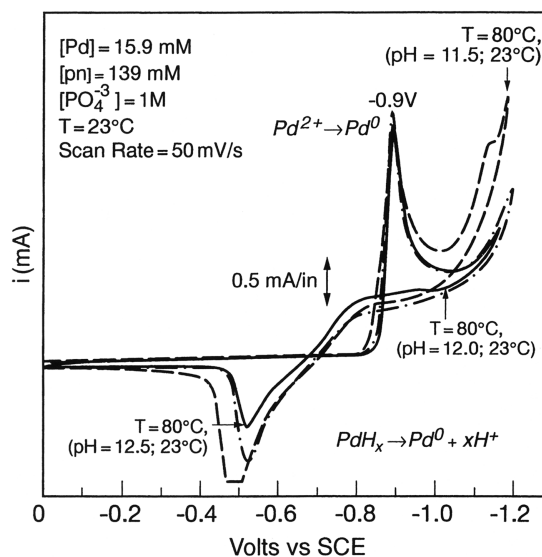


FIGURE 12.13 Cyclic voltammograms: palladium-diaminopropane system; variation of pH 11.5–12.5 at 80°C .

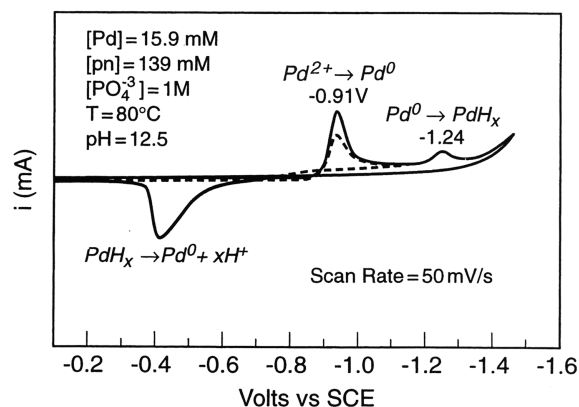
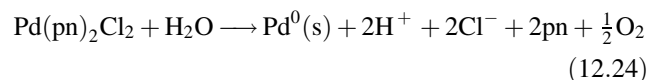


FIGURE 12.14 Cyclic voltammograms: palladium–diaminopropane system.

80°C and various pH show a decrease in the formation of PdH_x and the corresponding hydrogen oxidation peak with decreasing $[\text{H}^+]$. Therefore, through the use of $\text{Pd}(\text{pn})_2^{2+}$ as the complex electrolyte, the exclusion of additives which cause strong kinetic inhibition of the Pd reduction, and the manipulation of temperature and pH, one can separate the Pd^{2+} reduction peak from the hydrogen reduction peak and obtain a ΔE_p of approximately 330 mV. Figure 12.14 demonstrates that one can reach the limiting current and avoid hydrogen incorporation as evident by the absence of a hydrogen oxidation peak.

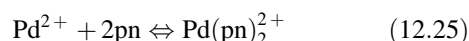
Ligand Concentration Effects and Replenishment Schemes The overall reaction for Pd electrodeposition using a nonconsumable anode is



This indicates that for every Pd^{2+} reduced 2pn molecules and 2Cl^- ions remain in solution, and 2H^+ are generated lowering the pH of the solution.

Figure 12.15 shows voltammograms of $[\text{Pd}(\text{pn})_2]^{2+}$ as the pn concentration is varied from stoichiometry to 100X excess. The Pd^{2+} reduction peak shifts to more negative potentials and thus closer to the hydrogen regime. This phenomenon can be predicted through use of the Nernst relationship [see Eq. (12.19)] and stability constants.

Also, the formation of the Pd diamine complex is represented by the following equilibrium:



for which the formation constant is

$$K_f = \frac{[\text{Pd}(\text{pn})_2^{2+}]}{[\text{Pd}^{2+}][\text{pn}]^2} \quad (12.26)$$

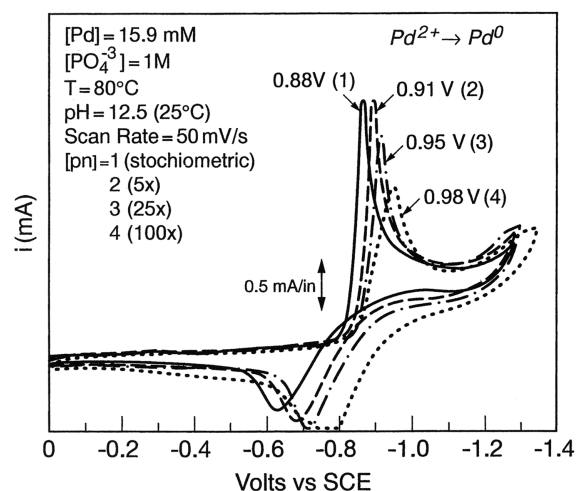


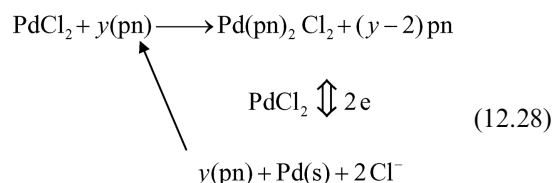
FIGURE 12.15 Cyclic voltammograms: palladium–diaminopropane system; ligand concentration effects.

Combining Eqs. (12.19) and (12.26) yields the following at $T = 25^\circ\text{C}$:

$$E^{o'} = E^o - \frac{0.0591}{2} \log \beta_2 - \frac{0.0591}{2} \log [\text{pn}]^2 + \frac{0.0591}{2} \log [\text{Pd}(\text{pn})_2^{2+}] \quad (12.27)$$

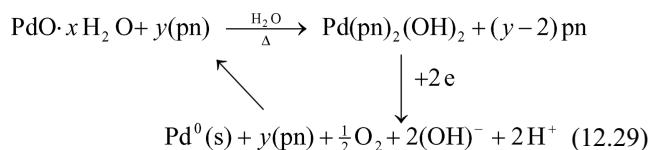
This equation predicts a negative shift in $E^{o'}$ as the pn concentration increases. This, of course, shifts E_p in a similar direction [see Eq. (10.17)] as is experimentally observed in Figure 12.15.

In order to avoid this situation, PdCl_2 is used as the starting and replenishment chemical. The overall reactions are shown below:



For this chemical system, it is optimum to maintain the [pn] in excess of stoichiometry (y varies from 3 to 5 excess) which is useful in the dissolution of PdCl_2 ; however, the pn concentration remains relatively constant and the problem of the Pd^{2+} reduction shifting closer to the hydrogen is eliminated. As can be seen, the Cl^- buildup and pH control remain potential problem areas.

The pH is controlled through use of a buffer system and periodic additions of KOH. While large amounts of Cl^- (KCl) do not seem to adversely affect the process, eventually salts may precipitate, necessitating filtration of the system. In this regard, a soluble form of $\text{PdO} \cdot x\text{H}_2\text{O}$ as the starting material and replenishment salt solves both problems and is preferred [102–104]. Equation (12.29) describes the system if a soluble form of $\text{PdO} \cdot x\text{H}_2\text{O}$ could be utilized:



Buffer System and Supporting Electrolyte The buffer of choice is $\text{K}_2\text{HPO}_4/\text{K}_3\text{PO}_4$ since the pH range desired is from 10.5 to 12.5. It is fortuitous that the phosphate system is also desirable from a stability perspective. It is electrochemically and thermally stable and does not significantly affect the morphology of the deposit. In this case the buffer salts also act as the supporting electrolyte.

Limiting Currents i_L The concentration and mobility of metal ions and the degree of solution agitation dictate the limiting current. Figure 12.16 shows current–voltage profiles of the Pd reduction process and demonstrates how i_L varies with rotation speed (ω) at a RDE. The Levich equation

$$i_L = nFAC_T D^{2/3} \omega^{1/2} \nu^{-1/6} \quad (12.30)$$

where i_L is the limiting current, n is the number of electrons, F is Faraday's constant, A is the area of the electrode, C_T is the total bulk concentration of Pd^{2+} , D is the diffusion coefficient, ω is the rotation speed, and ν is the kinematic viscosity implies that a process is mass transfer controlled when a linear relationship exists between i_L and $\omega^{1/2}$, where ω is the only changing variable. Figure 12.16b shows that this reduction process is mass-transfer controlled. Furthermore, the relatively “flat” current plateau implies that all metal ions reaching the surface are reduced, that no other reaction is taking place, and that the surface of the deposit is macroscopically smooth.

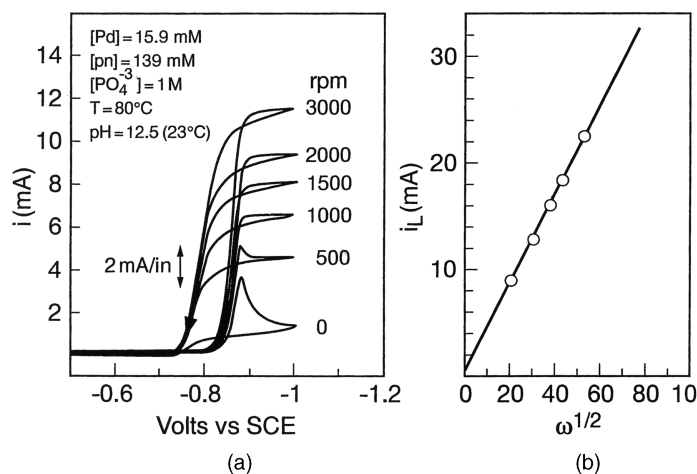


FIGURE 12.16 (a) Cyclic voltammograms, palladium–diaminopropane system, i_L versus rotation speed ω ; (b) plot of i_L versus $\omega^{1/2}$.

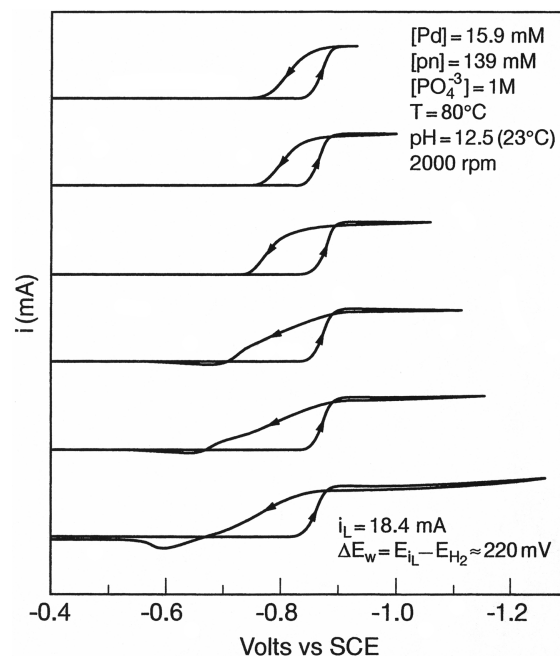


FIGURE 12.17 Cyclic voltammograms: palladium–diaminopropane system; determination of ΔE_w .

Quantitative Hydrogen Analysis Figure 12.17 demonstrates qualitatively how the pn process behaves regarding hydrogen incorporation. The limiting current is reached with little or no incorporation of H_2 , as is evident by the smooth plateaus and the absence of a hydrogen oxidation peak until the termination potential of the cathodic scan reaches approximately -1.1 V . An operating window (ΔE_w), which is described as the difference in potential between $E_{i_L}(\text{Pd})$ and $E_{\text{onset}}(\text{H}_2)$, is given as

$$\Delta E_{i_L}(\text{Pd}^{2+}) \text{ and } E_{\text{onset}}(\text{H}_2) \quad (12.31)$$

where ΔE_w of approximately 220 mV (compare to $\Delta E_p \sim 330 \text{ mV}$) is realized. Thus to a first approximation, ΔE_p and ΔE_w yield information regarding the probability of a system to avoid hydrogen incorporation. Maximization of ΔE_p and ΔE_w is desired.

However, a quantitative, albeit more time-consuming, analysis is obtained via the coulometric anodic stripping of hydrogen described elsewhere [8, 86, 102]. Figure 12.18 is a plot of $\%\text{H}_2$ versus i/i_L at pH 12.5 (25°C)*. The increase in temperature (25–70°C) substantially reduces the amount of hydrogen incorporated in the Pd films. It must be kept in mind that the $[\text{Pd}]$ is 15.9 mM and that operating at higher Pd concentrations and greater solution agitation allows much

* The parameter i/i_L is more informative than merely $i(\text{mA})$ for it takes into account the operating parameters of ω , $[\text{Pd}]$, and T . It is believed that morphology and material properties vary with this parameter and not simply $i(\text{mA})$.

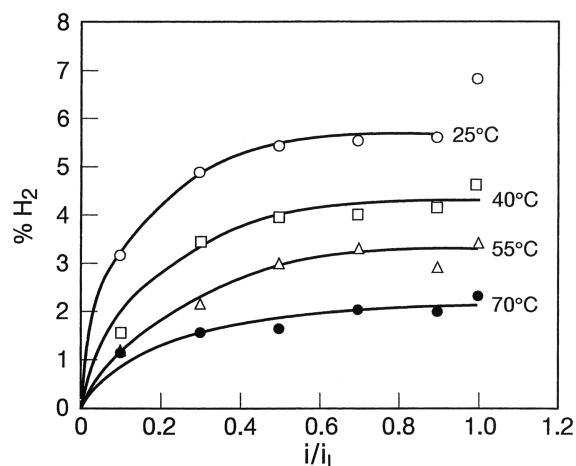


FIGURE 12.18 Percentage of hydrogen versus i/i_L at various temperatures.

higher limiting currents, making high rates of deposition possible with reduced hydrogen content (see arguments in Section 12.5.3). Note also that the Pd films deposited under these conditions were bright to semibright, adherent, and crack free up to thicknesses exceeding $2.5\ \mu\text{m}$. Figures 12.19 and 12.20 are scanning electron micrographs of Pd deposited at high speeds. As can be seen, the deposits are smooth, uniform, and crack free at current densities of $500\ \text{mA cm}^{-2}$.

Material Properties [8, 102] Deposits plated from the diaminopropane system have been found to exhibit excellent properties for technological applications. The deposits are smooth and the brightness can be controlled by the bath temperature, pH, and operating current density. In general, the brightness, hardness, and internal stress are increased by operating at lower temperatures (25°C) and lower pH (10.5) and higher current densities (i.e., $i/i_L > 0.6$).

The deposit hardness ranges from 250 to 350 KHN₅₀ (Knoop hardness), where the values increase as i/i_L increases. Ductility, measured by the method of Nakahara et al. [105], is in the range of 3–7% elongation for films of $1.25\ \mu\text{m}$

thickness. In general, the films are harder and more ductile than hard gold.

Transmission electron microscopy indicates that the grain growth is not epitaxial and that grain size varies with the operation current ratio, i/i_L . Preliminary results show that for $i/i_L = 0.1$ the grain size ranges from 150 to 800 Å, while for $i/i_L = 0.9$ the grain size ranges from 30 to 50 Å. Thus, as the operating i/i_L increases, one obtains smaller grain, smoother deposits. Comparably hard gold grain size ranges from 150 to 350 Å.

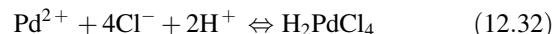
Mass spectrographic evolved gas analysis performed on Pd films electroplated at various i/i_L indicates that the amount of occluded impurities is independent of the operating current ratio. A total weight loss ranging from about 0.8 to 1.7% occurred when the films were treated at $260\text{--}270^\circ\text{C}$; all other gases evolved above 1000°C . Overall the Pd films are substantially cleaner than electrodeposited gold films [113].

Environmental and standard wear tests [27] and fretting wear tests [16] have demonstrated that this process produces deposits which can be utilized for connector and other applications.

12.6.2 Acid Electrolytes ($\text{pH} < 1\text{--}5$)

Table 12.8 provides the formulas for a number of acid electrolyte processes.

Acid Chlorides ($\text{pH} < 1$) The simplest bath to prepare is an acid chloride system (A, Table 12.8) according to the following equation:



In these systems [37] of high acid and chloride content, the equilibrium constant is

$$\beta_4 = \frac{[\text{H}_2\text{PdCl}_4]}{[\text{Pd}^{2+}][\text{Cl}^-]^4[\text{H}^+]} = 10^{12.2} \quad (12.33)$$

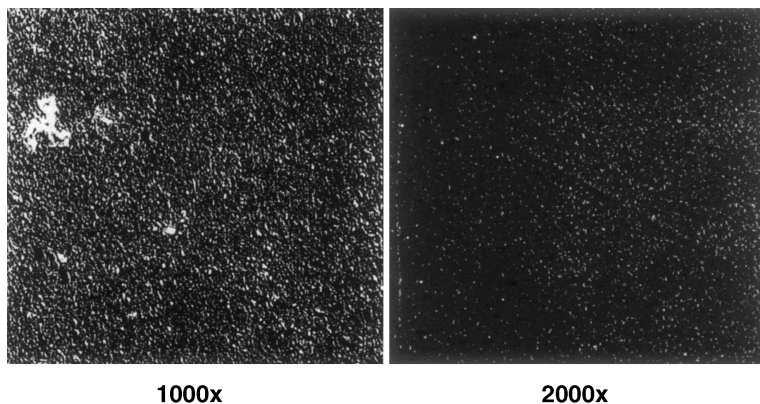


FIGURE 12.19 Scanning electron micrograph: palladium plated at $500\ \text{mA cm}^{-2}$ and $2.5\ \mu\text{m}$ in thickness.

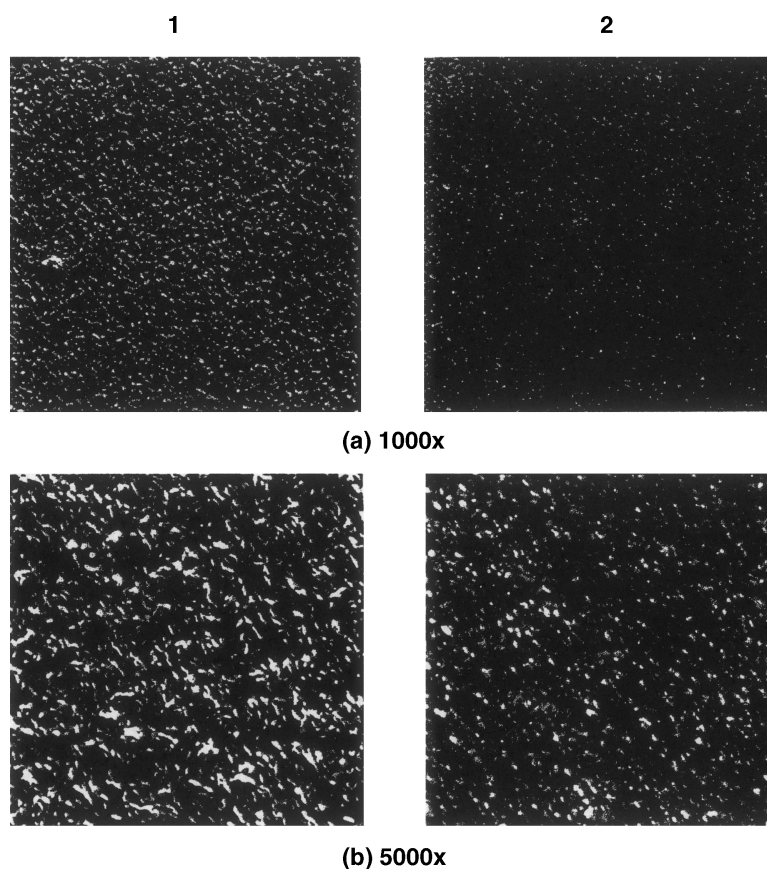


FIGURE 12.20 Scanning electron micrograph: palladium plated at i/i_L value of 0.1, 0.3, and 2.5 μm in thickness.

TABLE 12.8 Palladium Electroplating Acid Electrolytes pH (<1 to 5)

Parameter	Bath Type				
	H ^{35,37,39,109}	I ³⁵	J ^{39,110}	K ³⁵	L ¹¹¹
Source of Pd	PdCl ₂	H ₂ PdCl ₄	Pd(NO ₃) ₂	Na ₂ Pd(NO ₂) ₄	PdCl ₂
Pd metal (g/L)	5–50	5	2–15	5–10	0.1–3.0
Pd sulfite (g/L)			0.2–2		
Ligand	H ₂ O	Cl [−]	H ₂ O	NO ²	Organic diamines
Ammonium chloride (g/L)	20–50				
Sodium nitrite (g/L)		14			
Sodium chloride (g/L)		40		10–40	10–60
Sodium sulfite (g/L)					
Phosphoric acid (g/L)	As needed				
Boric acid (g/L)	As needed	10–30			
Oxalic acid (g/L)	As needed				
Hydrochloric acid (g/L)		As needed			
Sulfuric acid (g/L)			98		
Additives				See appropriate data in the literature	See appropriate data in the literature
pH	0–0.5	4.5–6	0	4.9–8	2–6
Temperature (°C)	25–60	50	20–35	40–50	25–45
Current density mA/cm ²	10	4–10	5–80	~1	5–50

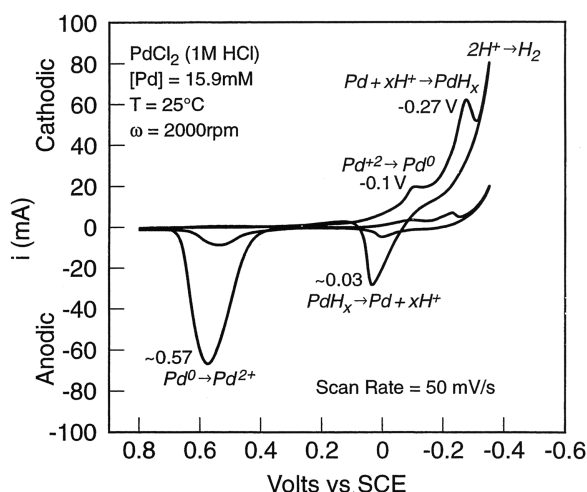


FIGURE 12.21 Cyclic voltammograms: PdCl_2 , in HCl, 0 and 2000 rpm.

This relatively weak Pd complex implies that immersion plating on a non-noble metal would occur quite readily.

A cyclic voltammogram of PdCl_2 in 1 M HCl electrolyte is seen in Figure 12.21 [114]. The $E_p(\text{Pd}^{2+})$ is about 0.1 V relative to SCE, and the PdH_x peak potential is at about 0.27 V before bulk hydrogen evolution. On the return scan, the hydrogen is anodically stripped [8, 102] from Pd hydride [E_p (oxidation) +0.03 V]. Finally, Pd is dissolved at about 0.57 V.

Palladium deposition from acid electrolytes is typically 97–100% efficient. Compact, dense crack-free films have been reported even at thicknesses of 10 μm (Table 12.8). The deposits generally have a satin finish extending to full bright and gray. Depending on deposition conditions, they have a microhardness of 250–350 HV (HV = Vickers hardness) [37].

According to Hedrich and Raub [37], in the current density of 1–100 mA cm^2 at temperatures of 10–50°C, Pd is deposited at +0.1 to +0.5 V relative to the normal hydrogen electrode (NHE). The temperature dependence of the cathodic overpotential can be easily observed in Figure 12.22.

Palladium deposited from an electrolyte with lower chloride content exhibits a lower cathodic overvoltage for reduction (see Fig. 12.23). This occurs because the Pd free-ion concentration remains higher since the lower chloride and hydrogen concentrations reduce the stability of the Pd(II) chloro complex; see Eqs. (12.32) and (12.33) and arguments in Section 12.5.3.

For this system, low hydrogen codeposition has been reported at potentials of +0.5 to +0.1 V. Hydrogen discharge complies with Nernst's law at an equilibrium potential; see Eq. (12.20). Thus, even in strong chloride solutions with 10 N hydrogen ion concentration, the H_2 evolution starts only at an equilibrium of +0.059 V.

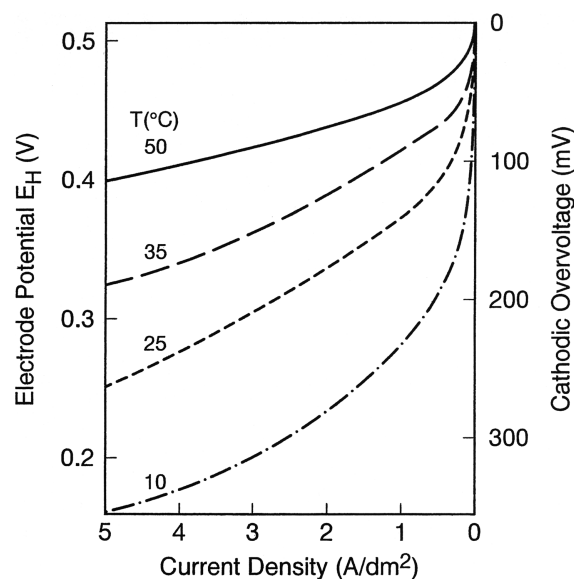


FIGURE 12.22 Current voltage curves: 0.1 M PdCl_2 , in 5 M HCl, $di/dt = 0.2 \text{ A dm}^{-2} \cdot \text{s}$ at various temperatures.

At current densities between 1 and 5 A dm^{-2} it is below 3 N ml H_2/gPd , which makes the $[\text{H}]/[\text{Pd}] < 0.03$. This implies that deposited films are in the range of the α phase.

X-ray analysis of Pd films deposited from 0.1 M PdCl_2 solution at 5 N HCl concentration at current densities of 1–3 A/dm^2 shows a slight expansion of the α -Pd lattice to 3.895 Å compared to 3.890 Å for pure Pd. These films are finely crystalline and irregularly oriented with no preferential

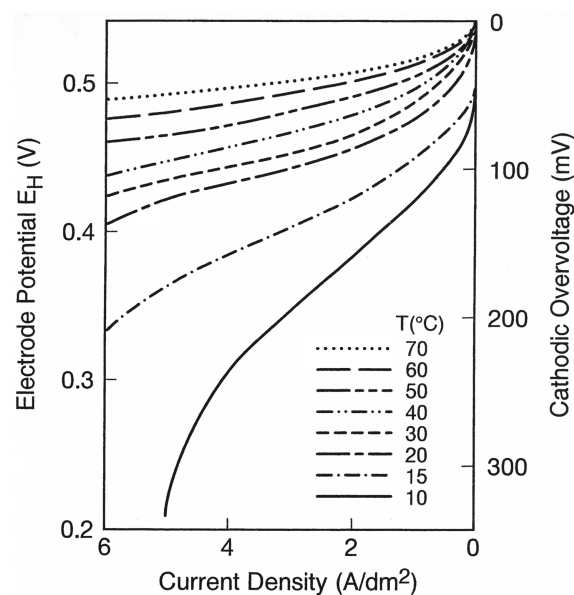


FIGURE 12.23 Current-voltage curves: 0.1 M PdCl_2 in 0.5 M HCl, pH 5.0, for $di/dt = 0.2 \text{ A dm}^{-2} \cdot \text{s}$.

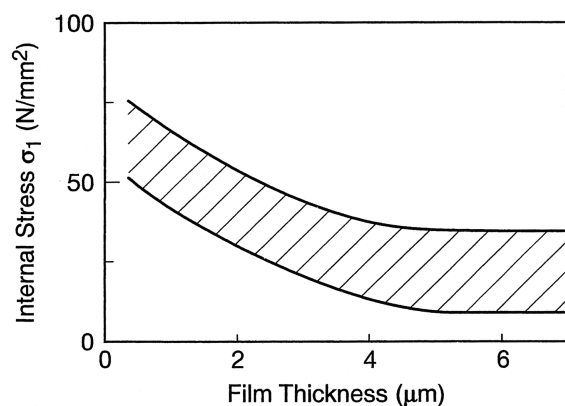


FIGURE 12.24 Internal stress versus film thickness, 0.1 M PdCl₂ in 5 M HCl at 1 and 3 A dm⁻².

orientation. They exhibit very low internal stress which decreases with increasing film thickness (Fig. 12.24).

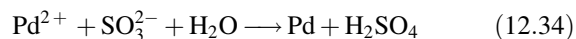
Hedrich and Raub [37] stated that acid Pd chloride electrolytes are well suited for depositing thick Pd films of low internal stress at about 100% current efficiency. The disadvantages of these systems is their attack on non-noble base metals used for substrates which cannot be directly plated and their attack of metals used in plating equipment. An excellent analysis of this system, including the measurement of exchange current densities and the determination of an activation energy for charge transfer reaction of Pd²⁺/Pd, is found in [37].

Acid Sulfates (pH < 1) Sulfuric acid electrolytes that used a Pd nitrate salt (bath J, Table 12.8) were investigated by Hedrich and Raub [39] and Simon and Zilske [110], who reported that the drawbacks of the Cl⁻ baths are eliminated. A solution of Pd nitrate in sulfuric acid produces black, spongy, loosely adhering Pd films. Alternatively, smooth, lustrous Pd precipitates can be obtained only after adding 5–20% Pd sulfite. The formation of a Pd sulfite complex ([Pd(SO₃)₂]²⁻) decreases the Pd free-ion concentration and shifts its reduction potential to a more negative point. The increased cathodic overvoltage for metal deposition has a positive effect on the film properties.

Smooth, lustrous, low-stress films that contain relatively little hydrogen with a hardness of 350 HV are obtained [39]. Sulfite is reduced to sulfide during deposition of the Pd and adsorbed on the cathode. Palladium sulfide inhibits Pd deposition and is incorporated during crystallization. The sulfur content increases with electrolyte sulfite content and cathodic current density. The properties of these films are largely determined by the sulfur content and in general are fine grain sized, relatively hard, and have a pronounced <100> orientation.

The disadvantages of this process are the necessity of a noble metal strike (e.g., gold) to prevent attack of non-noble metal surfaces and the necessity for continuous filtration to

reduce the tendency for the reduction of Pd ions to metal according to the following equation [39]:



Acid Strikes (pH 3–4) An acidic Pd “strike” process was developed by Straschil et al. [111, 112] (bath L, Table 12.8). This process uses organic diamines to stabilize a complex in the pH range of 3–4. Unlike the highly acidic baths with pH ≤ 1, this chemistry does not undergo “displacement” plating or attack on non-noble metal substrates. However, it promotes the removal of surface oxides, especially on nickel, which makes it ideal as a strike process. This process also reduces the porosity of subsequent noble metal layers by increasing the nucleation and “coverage” of substrate surfaces. It exhibits good chemical and electrochemical stability along with stable pH due to the high buffer capacity. The limitations of this process are the inability to plate greater than 0.2 μm without the formation of cracks due to hydrogen embrittlement [112]. However, for a strike process only thin layers are required.

Dullaghan et al. [176] reported a very low pH Pd strike with unique capabilities that combines the “activating” power of a very low pH (<1) with the advantage of room temperature operation. Bright Pd is deposited on various substrates with surprisingly high cathode efficiencies. The system leads to improved adhesion on easily passivated surfaces (e.g., nickel) and reduces the porosity of subsequent Pd and Pd alloy or other precious metal deposits.

The chemistry is robust and can withstand relatively high levels of foreign metal contamination, for example, copper and nickel. The components are claimed to be compatible with chloride- and sulfate-based Pd plating electrolytes. One other important advantage over prior art is the ability to plate relatively thick deposits with a high degree of leveling, as seen in Figure 12.25.

12.6.3 Neutral Electrolytes (pH 5–9)

Numerous chemical systems have been investigated in this pH range, including oxalates and sulfamates. While in many cases these systems possessed the proper current–voltage profiles to deposit Pd and avoid hydrogen codeposition and the initial deposits from a “nonaged” electrolyte could provide films of excellent hardness, ductility, and surface appearance, these systems did not stand up during extensive aging or bath use.

Hydrogen embrittlement is not the only challenge when developing a plating process for commercial use. The chemical and electrochemical stability of the ligand system poses concern. Furthermore, simple replenishing systems were difficult to devise due to slow attack of these ligands on salts such as PdCl₂. Furthermore, the decomposition and buildup of ligands in solution lead to an aggravation of the hydrogen

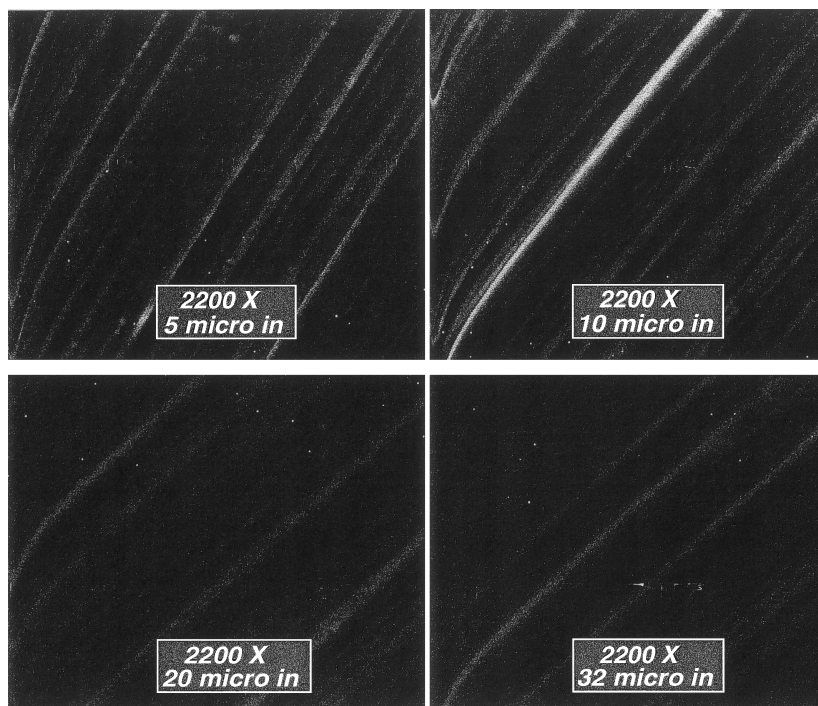


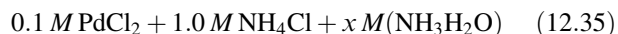
FIGURE 12.25 Scanning electron micrographs: palladium acid strike at 5, 10, 20, and 32 μm .

problem and microcracking. However, Pd electrolytes based on ammonia ligand have proved to be viable and are used almost exclusively in the pH range of 5–9.

Hedrich and Raub [37, 39, 40] studied “nonadditive” ammonia systems extensively and found them “well suited to deposit palladium films for technological applications” (baths N and O, Table 12.9). The reduction takes place at essentially less noble potentials than in acid systems (see Fig. 12.26). For example, the Pd potential E_H in 0.1 M PdCl_2 solution is +0.55 V, whereas the Pd tetramine complex of the same concentration is +0.22 V. In Pd diamino dinitro electrolyte, P-Salt, reduction takes place in approximately the same potential range as the ammonia system.

Tetramine Electrolytes: “Nonadditive” Systems Amine complexes form in Pd chloride solutions in the presence of ammonia at pH values above 4.5 and are completely transformed into the square planar complex at pH 7.5. Upon acidification with hydrochloric acid, the complex is transformed step by step into Pd diamino complex, which is stable in the acid range. Starting from pH 6, yellow $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is precipitated in cold 0.1 M solution; the precipitation process is complete at pH 4.

The following composition was chosen as the standard electrolyte for electrodeposition experiments:



The pH value was set between 8 and 10 with NH_4OH .

Palladium is deposited from the tetramine complex at current densities from 1 to 5 A dm^{-2} at an overpotential of 300 and 600 mV (Fig. 12.27). The current–voltage characteristics exhibit a strong temperature dependence since the stability of the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ decreases with increasing temperature. The current efficiency is below 100% so that the cathode always represents a double electrode. Current efficiency measurements in agitated electrolytes indicate that hydrogen evolution is strongly dependent on the current density and electrolyte temperature (Fig. 12.28). The current yield increases with increasing cathodic current density and at high higher electrolyte temperatures [37]. The Pd tetramine complex stability increases with increasing pH values, so the cathodic overpotential required for Pd deposition increases distinctly (Fig. 12.29).

The hardness of these Pd deposits varies according to the deposition conditions (usually measured at $\sim 25\text{-}\mu\text{m}$ -thick films). Palladium deposited at electrolyte temperatures between 15 and 25°C and at current densities from 1 to 2 A dm^{-2} have hardness values between 270 and 320 HV directly after deposition, which is significantly reduced to between 150 and 180 HV when deposited at 60°C.

The deposits exhibit tensile stresses (Fig. 12.30) that decrease with increasing electrolyte deposition temperature and increasing film thickness. Hydrogen codeposited is associated with this phenomenon, which results in considerable stress in the lattice as revealed by X-ray analysis.

Quantitative hydrogen analysis via anodic stripping indicates the hydrogen content is strongly affected by current

TABLE 12.9 Palladium Electroplating Neutral Electrolytes (pH 5–9)

Parameter	Bath Type						
	M ^{35,37,35,40,98}	N ^{36,40}	O ^{36,40}	P ^{40,81,96}	Q ^{93,94,106}	R ^{97,107}	S ^{98,108}
Pd source	Pd(NH ₃) ₄ (NO ₃) ₂	Pd(NH ₃) ₂ (NO ₂) ₂	Pd(NH ₃) ₂ Cl ₂	Pd(NH ₃) ₄ Cl ₂	Pd(NH ₃) ₂ Cl ₂	Pd(NH ₃) ₂ Cl ₂	Pd(NH ₃) ₄ Cl ₂
Pd metal (g/L)	10	4	20	10–20	20–30	10	5–25
Ligand	NH ₃	NH ₃	NH ₃	NH ₃	NH ₃	NH ₃	NH ₃
EDTA (g/L)						20	
Ammonium nitrate (g/L)	90–100						
Ammonium chloride (g/L)		10		60–90	30–60		90
Ammonium sulfate (g/L)		20					
Ammonium carbonate (g/L)		10					
Sodium nitrate (g/L)		10–11					
Ammonium sulfamate (g/L)					30–40		
Ammonium hydroxide (g/L)		Adjust pH	Adjust pH	Adjust pH			Adjust pH
Ammonium phosphate (g/L)							90
Sodium sulfite (g/L)					1–1000 ppm	28	
Potassium phosphate (g/L)						80	Adjust to pH
Hydrochloric acid (g/L)							Adjust to pH
Additives			Proprietary (see data in the literature)	Proprietary (see data in the literature)	Proprietary (see data in the literature)	Proprietary (see data in the literature)	Proprietary (see data in the literature)
pH	9.1	7.5–10	7.5–9	8.0–9.5	~9	8.5–9	7–8
Temperature (°C)	60–80	40–55	20–40	25–50	25–40	35	30–50
Current density mA/cm ²	5–20	1–40	5–15	1–25	15–25	50	1–>250

*Diaphragm process.

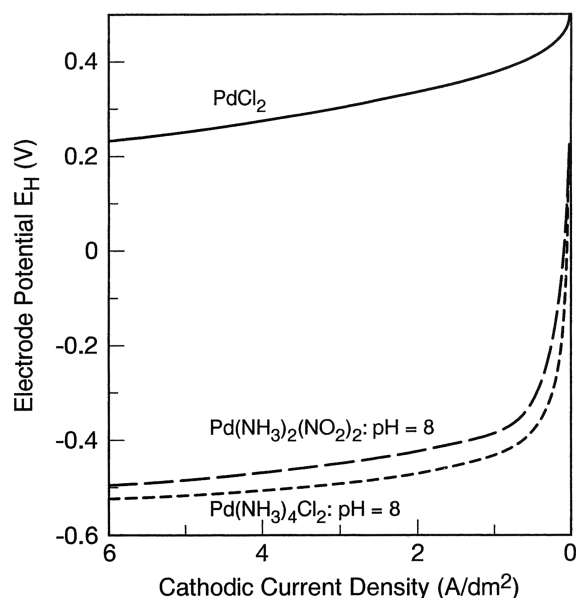


FIGURE 12.26 Current-voltage curves: acid Pd versus ammoniacal Pd chemistries, $di/dt = 0.2 \text{ A dm}^{-2} \cdot \text{s}$.

density and deposition temperature (Fig. 12.31). At low deposition temperatures, $<40^\circ\text{C}$, the hydrogen content increases rapidly with current densities, whereas at temperatures greater than 40°C , the increase in hydrogen content is much lower.

Hedrich and Raub [37] found that Pd films with a hydrogen content below $10 \text{ N ML H}_2/\text{g Pd}$ or atomic H/Pd ratios below 0.1 have a metallic brilliance and are suited for decorative and technological applications. For higher H/Pd ratios, the Pd deposits become dull and dark, and at H/Pd

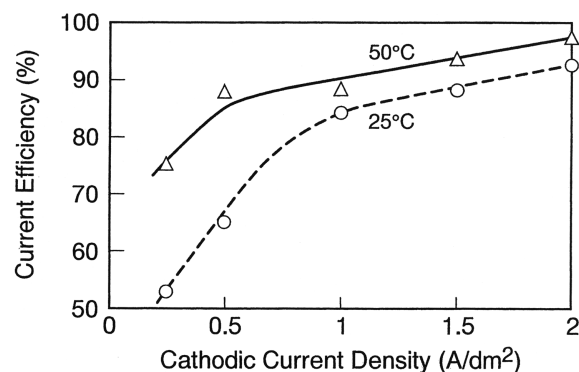


FIGURE 12.28 Current efficiency versus current density: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ at 25 and 50°C .

ratios ≥ 0.8 they are black and powdery, that is, the so-called burned deposits.

Palladium deposits from tetramine electrolytes without additives are dull and gray in appearance. Viewed under a scanning electron microscope, the deposit surface is “budded” and nodular [40]. These deposits are very sensitive to “finger prints” and other contaminants since “oils” readily adhere to microrough surfaces.

In terms of processing technology, electrolytes high in ammonia content are difficult to operate and control at $\text{pH} > 7.5$ and temperature $>35^\circ\text{C}$. Ammonia vaporization losses are significant and require the pH be monitored and controlled. In the presence of halides, significant attack on metals such as copper, brass, and stainless steel (in plating equipment) occurs. Furthermore, the resulting metallic impurities degrade the appearance and the mechanical properties and decrease the partial current density and the covering power of Pd deposition.

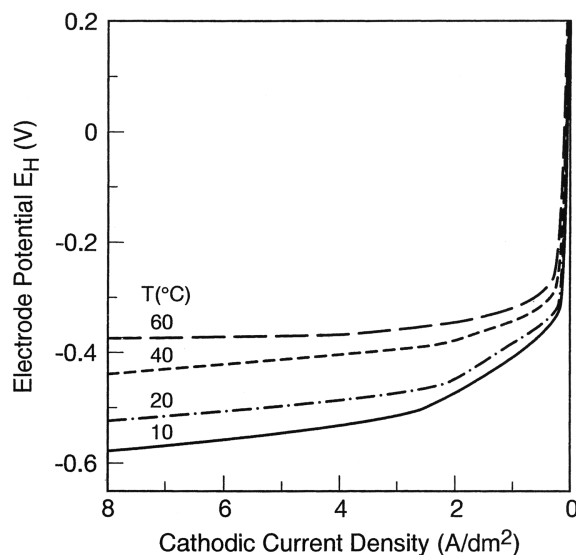


FIGURE 12.27 Current-voltage curves: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ at various temperatures, $di/dt = 0.2 \text{ A dm}^{-2} \cdot \text{s}$.

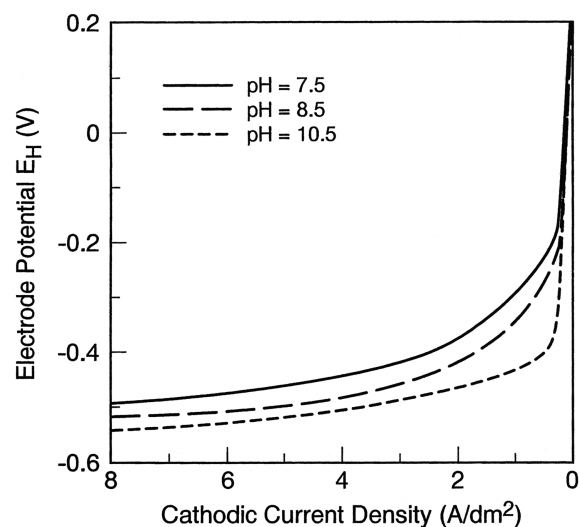


FIGURE 12.29 Current-voltage curves: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ at various pH, $di/dt = 0.2 \text{ A dm}^{-2} \cdot \text{s}$.

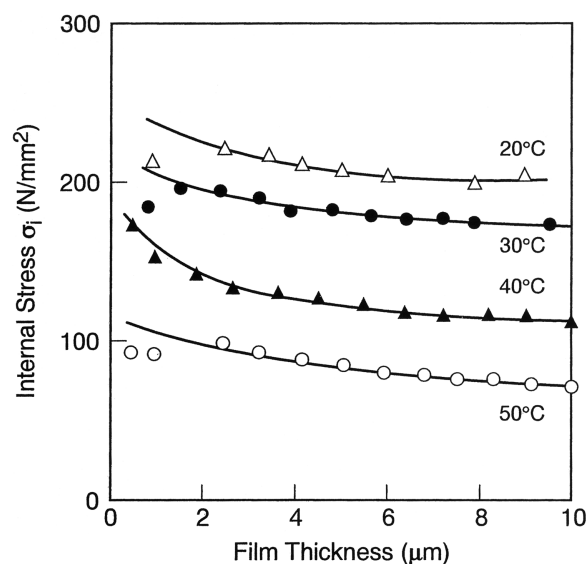


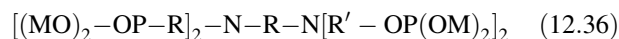
FIGURE 12.30 Internal stress versus film thickness: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$; pH 9; at 2 A dm^{-2} .

Hedrich and Raub [115] also studied the effects of “additives” in these systems to improve the surface appearance and reduce the “roughness” of the deposits. They studied the effects of citrates, benzoates and salicylate, nicotinic acid, and nicotinamide. In general, these additives displace the reduction potential to more negative values closer to the hydrogen regime and increase the hydrogen content of the films.

Aliphatic citrates produce an irregular crystallization, whereas benzoates and salicylates produce a $\langle 110 \rangle$ preferred orientation; however, they also increase the hydrogen content and tensile stress in the plated films resulting in microcracked deposits. The electrodeposition of smooth, full-bright, adherent, crack-free films from tetramine systems requires the use of additives. In the next section, we will discuss some of these systems.

Tetramine Chloride Electrolytes with Additives There exists numerous patents on the use of additives in palladium–ammonia electrolytes whose function is to deposit dense, full-bright Pd films of low porosity without microcracks at thicknesses in excess of $25 \mu\text{m}$.

For example, Deuber [107] patented a process (bath R, Table 12.9) using an alkylene diamine phosphonate derivative of the following formula:



where R is an alkylene group of two to six carbon atoms, each R' is an alkylene group of one to four carbon atoms, and each M is a nondeleterious cationic moiety which does not interfere with the plating process, such as hydrogen, alkali metals, and ammonium moiety. This phosphonic compound is be-

lieved to act as a buffering compound, a conducting salt, and a complexing agent for contaminant metal ions which are not desired to plate out. The concentration of the phosphonic compound should be from 5 up to 100 g L^{-1} . Dequest 2041 is ethylene diamine tetramethylphosphonic acid which contains approximately 10% water and is one of the preferred phosphonates.

The pH of the electroplating solution should be maintained at a value of from 4.5 to 12 in order to avoid stability problems. Values from 4.5 to 7.0 are preferred for strike plating. For ordinary electroplating, a pH value from 7 to 10 is preferred. The bath parameters are as follows:

Component	Concentration (g L^{-1})
Ethylene diamine	45
tetramethylphosphonic acid	
$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	1–10 (metal)
Sulfamic acid	40
Ammonium chloride	50–150
Ammonium monohydrogen phosphate	25–75
Ammonium hydroxide	pH 6.5–10

The bath may be employed to plate Pd or its alloys. Deuber makes use of class I and class II organic brighteners with this palladium–amine system.

The Pd is supplied as any electrodepositable form (e.g., $[\text{Pd}(\text{NH}_3)_4]^{2+}$). The stability is by employing ligands such as urea or an amine complex with the following counterions: chloride, bromide, nitrite, and sulfite. The Pd concentration is in the range of $0.1\text{--}50 \text{ g L}^{-1}$.

Class I brighteners are generally unsaturated sulfonic compounds with the general formula



where A is an aryl or alkylene group, substituted or unsubstituted; B is OH, OR, OM, NH_2 , NH, H, R; M being an alkali metal, or else ammonium, and R being an alkyl group of not more than six carbon atoms.

Class II brighteners are generally unsaturated or carbonyl organic compounds. Examples are compounds containing $>\text{C}=\text{O}$; $>\text{C}=\text{C}<$; $\text{C}\equiv\text{N}$; $>\text{C}=\text{N}$; $\text{C}\equiv\text{C}$; $\text{N}=\text{N}$. Concentration of the individual brighteners may range from 0.001 to 25 g L^{-1} . Some compounds may fall within the description of both class I and class II. Such compounds may be employed alone, but particularly improved results are obtained when a second different compound of either class is also employed.

The temperature of the Pd bath should be maintained between room temperature and approximately 50°C . Current densities from 0.1 to 50 mA cm^{-2} are suitable. For rack plating, a current density from 5 to 15 mA cm^{-2} may be employed. For barrel plating, the preferred range is from 0.5 to 3 mA cm^{-2} .

An example of such a bath is as follows:

Component	Concentration (g L^{-1})
Ethylenediaminetetraacetic acid EDTA	20
$(\text{NH}_4)_2\text{HPO}_4$	80
Na_2SO_3	28
Pd as $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	10
Class I brightener	0.005–2
Class II brightener	0.005–2

The pH is maintained between 8.5 and 9 and plating performed at a temperature of 40°C and current density of 5 mA cm^{-2} .

When neither brightener was present, only hazy deposits were obtained. The class I brightener employed was methylenebisnaphthalene sodium sulfonate, and the class II was benzaldehyde-*o*-sodium sulfonate. The class I brightener was added first and was ineffective at concentrations up to 2 g L^{-1} . The class II brightener resulted in a semibright deposit at 0.02 g L^{-1} and bright deposits from 0.37 to 2.0 g L^{-1} . Similar results were obtained when 2-butene-1,4-diol was employed as the class II brightener. Please note that unlike the work of Hedrich and Raub [115] with extensive electrochemical and material properties data, no such information was found in regard to these systems. Furthermore, in neither Hedrich and Raub's [115] nor Deuber's [107] work is there any information on the aging of such systems.

Absys et al. [12, 108] developed a process to electroplate full-bright pure Pd to thicknesses of $>25 \mu\text{m}$ with low porosity and high hardness. This chemistry employs a tetrammonium chloride complex in a buffered electrolyte system containing a combination of two additives. Low- and high-speed formulations are shown below:

Chemical Constituent	Low Speed	High Speed
Pd (as metal)	$2\text{--}10 \text{ g L}^{-1}$	$15\text{--}40 \text{ g L}^{-1}$
NH_4Cl	$50\text{--}100 \text{ g L}^{-1}$	$50\text{--}200 \text{ g L}^{-1}$
K_2HPO_4	$80\text{--}100 \text{ g L}^{-1}$	$80\text{--}100 \text{ g L}^{-1}$
Surfactant	$2\text{--}25 \text{ mL L}^{-1}$	$2\text{--}50 \text{ mL L}^{-1}$
Brightener	$0.1\text{--}20 \text{ mL L}^{-1}$	$0.2\text{--}20 \text{ mL L}^{-1}$
Specific gravity	1.05–1.15	1.10–1.25

The surfactant improves wettability and acts as a carrier for the brightener which imparts luster and leveling to the deposit. Potassium phosphate and ammonium chloride are used as buffering agents and supporting electrolytes for conductivity. This chemistry was developed to operate under generally mild conditions of low temperature ($\sim 35^\circ\text{C}$) and a neutral to slightly alkaline pH. Operating parameters for low- and high-speed plating baths are shown below:

Operating Parameter	Low Speed	
	Typical	Range
Temperature	35°C	$30\text{--}40^\circ\text{C}$
pH	7.5	7.0–8.0
Current density	5 mA cm^{-2}	$2\text{--}10 \text{ mA cm}^{-2}$
Agitation	5 cm s^{-1}	$5\text{--}50 \text{ cm s}^{-1}$
Cathode efficiency	87%	75–98%
Plating rate	$0.12 \mu\text{m min}^{-1}$	$0.04\text{--}0.25 \mu\text{m min}^{-1}$
Anode/cathode area	2 : 1	1 : 1–5 : 1

Operating Parameter	High Speed	
	Typical	Range
Temperature	35°C	$30\text{--}40^\circ\text{C}$
pH	7.5	7.0–8.0
Current density	100 mA cm^{-2}	40 to $\geq 500 \text{ mA cm}^{-2}$
Agitation	100 cm s^{-1}	50 to $\geq 200 \text{ cm s}^{-1}$
Cathode efficiency	87%	75–98%
Plating rate	$2.2 \mu\text{m min}^{-1}$	$0.75\text{--}12.4 \mu\text{m min}^{-1}$
Anode/cathode area	2 : 1	1 : 1–5 : 1

The current density can be varied from <5 to $>500 \text{ mA cm}^{-2}$ with the appropriate selection of metal content, additive balance, and agitation conditions. It can be used for barrel, rack, and reel-to-reel applications [12, 108].

An important aspect of any electrodeposition technology is to determine the physical characteristics of plated films. Below is a discussion of the material properties deposited from the above-described formulation.

1. *Grain Size* Transmission electron microscopy studies show that the grain size depends on the presence or absence of additives (Fig. 12.32). The additive-free deposits exhibit grain size ranging from 500 to $5000 \text{ \AA}$, in contrast to the additive system where the size decreases to 50 and $200 \text{ \AA}$. This change in crystallinity contributes to the brightness and hardness of the deposit.
2. *Surface Appearance* Deposit brightness varies with plating conditions and is often a measure of the surface microroughness. Reflectivity measurements were made using a bifurcated fiber system with a green light-emitting diode (LED) source ($\lambda_{\text{max}} \sim 560 \text{ nm}$, $\lambda_{\text{range}} \sim 535\text{--}625 \text{ nm}$). Both specular and diffuse reflectivities were measured, in contrast to the reflectivity of a highly polished bulk Pd metal standard set at 100% reflectance. Figure 12.33 shows the relative reflectivity of Pd films as a function of bath aging, which is constant at about 98%, indicating that this specular surface does not degrade with bath aging.

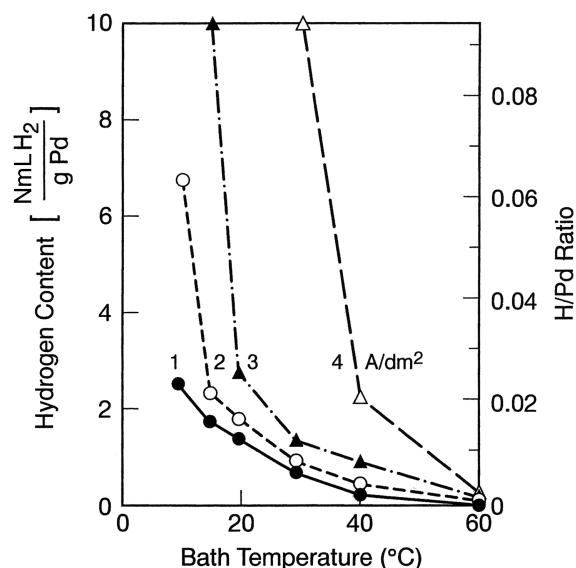


FIGURE 12.31 Hydrogen content versus bath temperature at various current densities: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, 1 min after termination of electrolysis.

3. *Leveling Effect* Figure 12.34 exhibits the leveling capability of this process under high-speed plating conditions. Scanning electron micrography (SEM) of a 5- μm -thick deposit clearly shows the rolling marks of the copper substrate at 0 μm of Pd which disappears as the thickness of Pd increases to 25 μm .
4. *Density* The density of the plated deposit was measured via pycnometry and is approximately 11.75 g cm^{-3} , that is, 98% of the theoretical value. Values for low- and high-speed deposited films are shown below:

Bath Type	Density of Deposits	
	Plated Density (g cm^{-3})	Theoretical Density (g cm^{-3})
High speed ($\sim 250 \text{ mA cm}^{-2}$)	11.79	12.02
Low speed ($\sim 5 \text{ mA cm}^{-2}$)	11.71	12.02

5. *Density Purity and Thermal Stability* Thermogravimetric and differential scanning calorimetry were performed on Pd films electroplated at current density of 100 mA cm^{-2} . The films were plated at 0, 1.0, and 3.5 metal turnovers. The films were heated from 30–950°C at the rate of 20°C/min under an atmosphere of nitrogen. As can be seen from the data below, essentially no weight loss was observed:

Pd Samples (Metal Turnover (MTO))	Thermogrammetric Analysis	
	(TGA)(%W)	Weight Loss (%)
0	99.79	0.21
1.0	99.68	0.32
3.5	99.89	0.11

The purity of the deposits are high ($>99\%$), and the contaminant inclusion is low ($<1\%$) and remains low throughout the lifetime of the bath. Differential scanning calorimetry was carried out from 25 to 450°C at a scan rate of $10^\circ\text{C min}^{-1}$. No thermal reaction was detected in Pd deposits, which implies good bulk thermal stability up to 450°C .

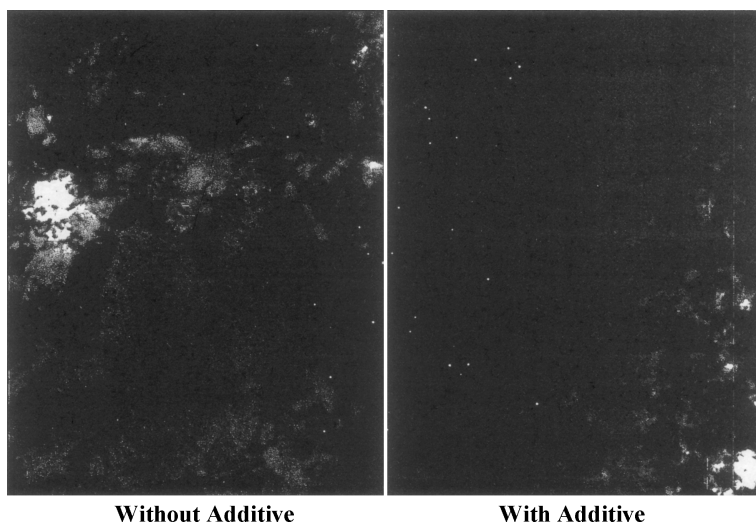


FIGURE 12.32 Transmission electron micrographs at 100,000 $\times$: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ electrolyte effect of additive.

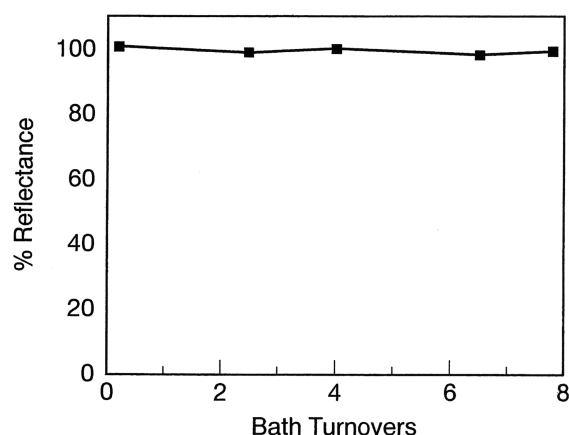


FIGURE 12.33 Percentage of reflectance versus bath turnovers: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ electrolyte.

6. **Solderability** Solderability was determined by the IPC method TM-650-2.414.1, which entails immersion in molten solder. Palladium deposits were exposed to 90% humidity at 90°C for 8 and 36 h to simulate “shelf life.” The results below of Pd solderability test solder coverage (IPC-TM-650) indicate that both 0.75- and 0.15- μm -thick deposits provide excellent solderability:

Sample Preparation	% Coverage		
	As Is	8 h	36 h
Cu Substrate			
0.75 μm Ni	0	0	0
0.75 μm Ni/0.075 μm Pd	99	99	98
0.75 μm Ni/0.15 μm Pd	99	99	99
1.5 μm Ni/0.15 μm Pd	99	99	97

7. **Ductility** Ductility was measured by the American Society for Testing and Materials (ASTM) B-489-85 method, which entails plating Pd on a thin Cu substrate and bending through a series of angles over mandrils of various diameters. Inspection for cracks

is conducted at $10\times$ magnification. The angle of bend was 180° , and the diameter of the mandrils varied from 3.3 to 0.5 mm. A more rigorous inspection was carried out at $1000\times$ magnification.

Five-micrometer-thick deposits from a low-speed bath were bent over 0.5 mm diameter while the high-speed samples were bent over 1.25 mm diameter (Fig. 12.35). In both instances, the deposit elongation was greater than 9% and is comparable to soft gold and far superior to cobalt-hardened gold.

8. **Hardness** The Knoop hardness was measured by a Tukon hardness tester using a diamond indenter at 50 g load. Figure 12.36 shows the effect of brightener concentration on hardness, which is in the range of 100–150 KHN_{50} for the additive-free bath. The hardness increases to 400–500 KHN_{50} at 1 mL L^{-1} of brightener and remains unchanged at higher additive concentrations.

Overall, this process is reported to produce adherent, mechanically stable, specular Pd films at rates ranging from <5 to $>500\text{ mA cm}^{-2}$. The deposits are smooth and crack free.

12.7 PALLADIUM ALLOYS

Palladium is known to form alloys with other metals of group VIII and IB that display distinct advantages over the pure metals [45]. The alloys tend to exhibit higher hardness, tensile strength, and ductility. They can be plated with a smaller grain size and are brighter than Pd even in the absence of additives. Furthermore, and of great importance, is the ability of the alloying element, in some cases, to increase the hydrogen overpotential and thus decrease the amount of codeposited hydrogen.

The arguments for the technological use of Pd could thus be more valid for Pd alloys. Accordingly alloys such as PdNi (80/20 wt %) have been extensively studied [8–33]. This alloy

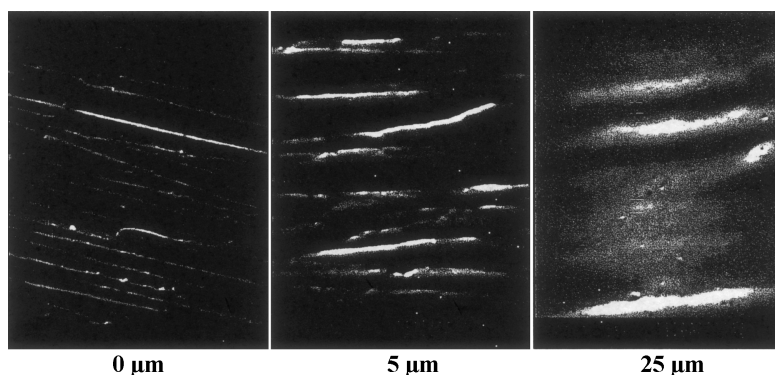


FIGURE 12.34 Scanning electron micrographs at $1000\times$: levelling effect at 0, 5, and 25 μm film thickness; $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ electrolyte.

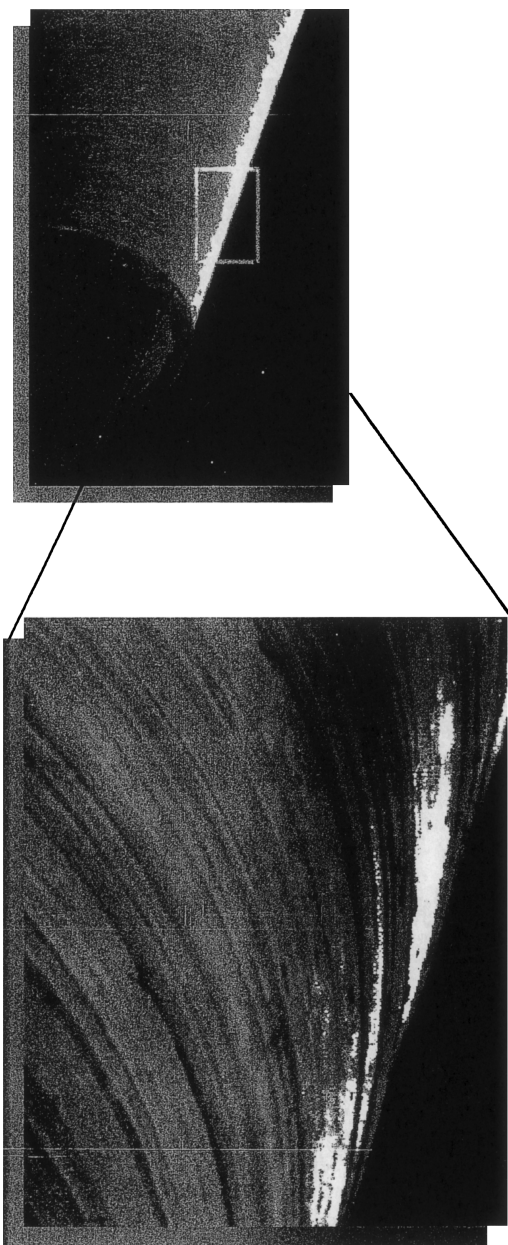


FIGURE 12.35 Scanning electron micrographs of bent 5- μm deposit: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ electrolyte.

is much less susceptible to hydrogen embrittlement, exhibits a brighter appearance, forms harder and more ductile deposit, and has lower porosity and better wear characteristics than either pure Pd or Au. Overall, the general material properties of Pd–Ni suggest that it is an excellent contact material, and indeed it is in significant commercial use for connector applications worldwide. Likewise metallurgically prepared PdAg (60/40 wt %) exhibits excellent material properties but has not been successfully plated in commercial applications [116–118]. The reasons of course lie in the fundamental differences among the chemistry of Pd, Ni, and Ag.

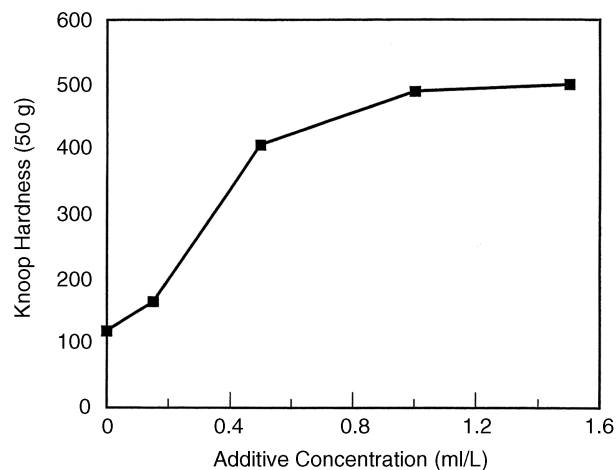


FIGURE 12.36 Hardness versus additive concentration: $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ electrolyte.

The development of electrodeposition processes for plating Pd alloys requires considerations of phase diagrams, coordination chemistry in the aqueous phase, understanding of redox potentials, thermodynamics, and kinetics. For the electrodeposition of an alloy, as discussed in Section 12.5.3, the ΔE [Eq. (12.16)] must be minimized in order to successfully control the alloy composition. In general, the respective metals should have similar reduction potentials, preferably less than 200 mV apart. As previously discussed, this is highly dependent on the specific metal(s) and the chemical system employed.

Table 12.10 exhibits standard reduction potentials for various metals in aqueous media and demonstrates that the relative standard potential for Pd and the desired alloying metals are significantly different. This requires manipulation of the complexing ligand and of the additive systems in order to codeposit a stable alloy composition. In this section, we describe the chemical systems that have been reported for Pd alloys and pay specific attention to Pd–Ni because of its technological importance while briefly describing other alloy systems.

12.7.1 PdNi (80/20 wt %)

While acidic Pd–Ni electroplating baths have been proposed [119], most processes appear to be ammoniacal solutions in the pH range from 7 to 9. Recommended metal sources for Pd are complexes with ammonia or organic amines; for Ni, the chloride, sulfate, hydroxide, and sulfamate complexes. A Pd–Ni plating bath reported by Morrissey [91] contains 6 g L^{-1} $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$, 3 g L^{-1} nickel sulfamate, 90 g L^{-1} ammonium sulfamate, and ammonium hydroxide to pH 8–9. This bath operates at 20–40 °C at current densities between 5 and 10 mA cm^{-2} , and it is suitable for plating an alloy of about 25% Ni. Other chemistries use

TABLE 12.10 PdNi Alloy Plating

Parameter	Bath Type			
	120T	121–123U	124V	125W
Pd Source	$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$	$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$	Pd sulfamate
Pd metal (g Li^{-1})	25	20	20	10.6
Ni source	$\text{Ni}(\text{NH}_3)_4\text{SO}_4$	$\text{Ni}(\text{NH}_3)_6\text{SO}_4$	$\text{Ni}(\text{NH}_3)_4\text{SO}_4$	Ni sulfamate
$(\text{NH}_4)_2\text{SO}_4$ (g Li^{-1})	50	10	9	5.9
NH_4Cl (g Li^{-1})	—	50	10	—
NH_4OH (mL Li^{-1})	100	To pH	To pH	—
Ligand (other) additives	—	—	—	—
3-Pyridine sulfonic acid (g Li^{-1})	5	See appropriate data in the literature	See appropriate data in the literature	en 80 g Li^{-1}
pH	7.74	8.5	8	4.5 – 6.0
Temperature ($^{\circ}\text{C}$)	60	30	25	20–60
Current density (mA/cm^2)	3–250	10	10	10–30

plating temperatures up to 60°C in the pH range 7–9, metal concentrations of up to 25 g L^{-1} Pd and 30 g L^{-1} Ni, and up to four different proprietary additives.

Such processes exhibit a number of disadvantages in their operation, most notably lack of pH stability, which results in undesirable fluctuations in alloy composition and material properties. Another concern is the environmental and occupational hazards associated with ammonia vapors during plating. This is particularly true in high-speed operations where the pH, temperature, and solution agitation tend to be high, thus favoring the release of ammonia. Additionally the loss of deposit brightness with bath aging can shorten its useful life. Last, but not least, highly stressed and cracked deposits are frequently encountered, especially in high-speed operations.

Chemistries and Material Properties of PdNi Figure 12.37 is the phase diagram of PdNi demonstrating that it forms a solid solution across all compositions. This implies the possibility to plate PdNi of any composition; however, the 80/20 PdNi alloy is preferred, although in some cases a 90/10 alloy is utilized commercially.

Table 12.10 exhibits four PdNi bath compositions, and in general, they utilize a Pd diamine or tetramine chloride salt and a nickel hexamine sulfate salt. The supporting electrolytes are either ammonium sulfate or ammonium chloride, and ammonium hydroxide is used to adjust pH in the range of 6–8.5. The temperature is in the range of $25\text{--}60^{\circ}\text{C}$ and the maximum current density [120] reported is 250 mA cm^{-2} . Organic surfactants, brighteners, levelers, and stress reducers are commonly added to the bath composition, but in most situations they are proprietary and are either patented or kept as a trade secret.

The only nonammonia system extensively studied was reported by Walz and Raub [125]; it is based on ethylene diamine. It was reported that bright Pd–Ni deposits up to 40%

nickel could be obtained over a wide current density range, Figure 12.38. This system does not suffer from evaporation of ammonia and subsequently has a stable pH. There is less attack on substrate metals such as copper and brass and thus less chance of contaminating the plating solution. However, in general, this system suffers from high tensile stress.

Abys et al. reported a highly stable process that was widely commercialized in the 1990s [13]. Boguslavsky et al. [126] further developed this process to overcome many deficiencies as noted above. The deposits from this chemistry exhibit excellent alloy stability ($+2\text{ wt } \%$) over a wide current density range ($\sim 50\text{--}800\text{ mA cm}^{-2}$) (Fig. 12.39) and are full bright in appearance, of high hardness ($\sim 550\text{ KHN}_{50}$), and of good ductility. This process is reported to be less corrosive than previous processes and environmentally benign. The chemistry, material properties, and contact reliability of this technology are detailed by Abys et al. [159–161, 163].

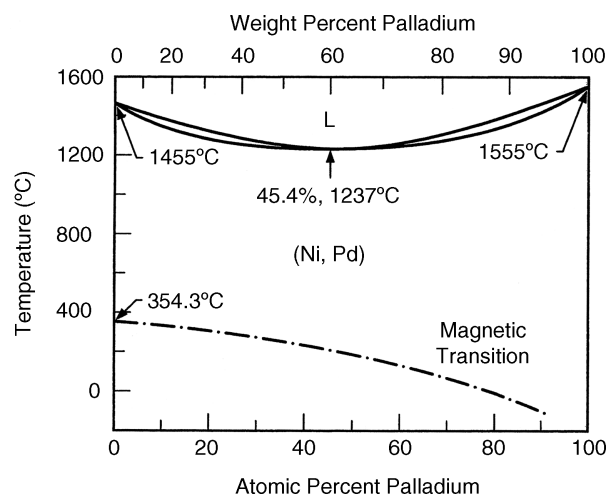


FIGURE 12.37 Binary alloy phase diagram of Pd–Ni system.

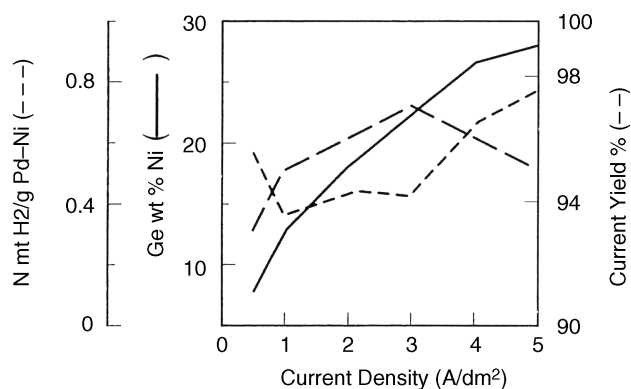


FIGURE 12.38 Hydrogen content versus current density at various wt % Ni content: Pd(en)₂Cl₂ + Ni sulfamate system at 50°C, pH 4.5.

12.7.2 Palladium–Cobalt

Palladium–cobalt, like Pd–Ni, forms a solid solution over the entire composition range and exhibits similar materials properties. Unlike Ni, Co has a +2 and +3 aqueous chemistry, and the standard potentials for Co reduction are significantly more negative than Pd (see Table 12.11). However, the stability of Co complexes with various ammonia electrolytes at relatively neutral pH indicates that its reduction potential could be nobler than Pd in the same electrolyte. This becomes problematic when attempting to plate a consistent alloy composition over a wide range of operating parameters.

Kume [127] reports on the electrochemical behavior and effect of plating parameters on the alloy composition of PdCo from an ammoniacal electrolyte. The basic bath composition is as follows:

Parameter	Concentration
Pd(NH ₃) ₂ Cl ₂	0.1 M
CoSO ₄ ·7H ₂ O	0.03 M
(NH ₄) ₂ SO ₄	0.4 M
NH ₄ OH	pH 7–10

Kume states that the standard potentials for Pd and Co are, respectively +0.987 V and –0.250 V, the difference being

TABLE 12.11 Standard Potentials in Aqueous Media

Half Reaction	Acid	Neutral/Basic
Pd ²⁺ + 2e [–] → Pd(s)	0.915	0
Ag ⁺ + 2e [–] → Ag(s)	0.799	0.342
Cu ²⁺ + 1e [–] → Cu(s)	0.340	–0.100
Bi ³⁺ + 3e [–] → Bi(s)	0.317	0.072
Sn ²⁺ + 2e [–] → Sn(s)	–0.137	–0.631
Ni ²⁺ + 2e [–] → Ni(s)	–0.257	–0.49
Co ²⁺ + 2e [–] → Co(s)	–0.277	–0.733
Fe ²⁺ + 2e [–] → Fe(s)	+0.44	–0.8

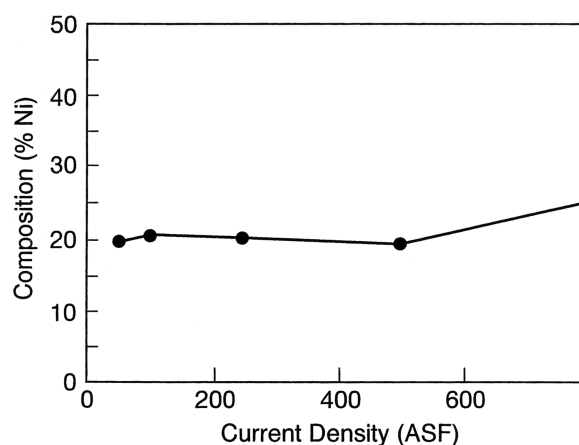


FIGURE 12.39 Percentage by weight of nickel versus current density: Pd–Ni system from ammoniacal electrolyte.

1.23 V. However, in ammoniacal plating baths, the potential difference is much smaller, for example, 0.27 V at current densities of 10 mA cm^{–2}. Figure 12.40 shows polarization curves for the deposition of Pd, Co, and Pd–Co alloys. Figure 12.41 is a graph of alloy composition as a function of current density and shows that Co varies between 20 and 30% by weight when plated between 5 and 20 mA cm^{–2} and clearly demonstrates that a higher Co content is deposited at lower current densities. This seems in conflict with Kume's assertion that the Co deposition is either at the same or more negative potential than Pd. When one considers that Pd concentrations are three times greater than Co, once again the conclusion must be that the electrochemistry needs to be reexamined. Cavallotti et al. plated Pd–Co from electrolytes based on Co amino-citrates and Pd amino-nitrite complexes [147]. However, none of these technologies appeared to have been commercially developed.

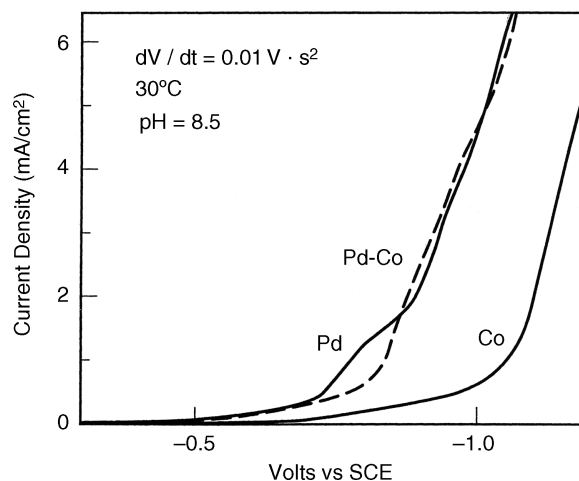


FIGURE 12.40 Current–potential curves: palladium, cobalt, and palladium–cobalt from ammoniacal electrolyte.

TABLE 12.12 80/20 PdCo Alloy Plating Chemistry

Component	Typical
Pd as metal (g Li ⁻¹)	40
Co as metal (g Li ⁻¹)	8
Conducting Salt (g Li ⁻¹)	40
Additives (mL Li ⁻¹)	20
Ligand (mL Li ⁻¹)	150

Chemistry and Material Properties of PdCo The development of a controllable and stable plating chemistry capable of depositing an 80/20 alloy of Pd–Co was reported in 1996 [180]. Additional publications detailing the chemistry and more importantly its deposit properties and new applications have appeared in the literature [157–163, 181, 184]. An attempt will be made here to summarize and identify the key features of PdCo as compared to hard gold.

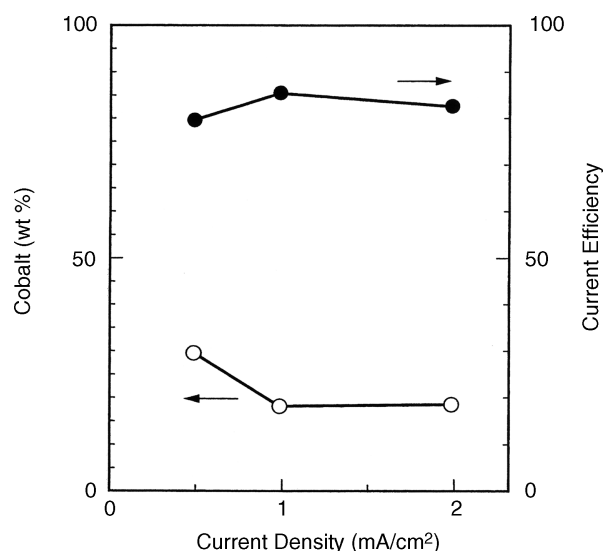
With respect to bath chemistry, Table 12.12 provides a snapshot of the key chemical components and their respective concentrations. A key innovation was the choice of the appropriate ligands and buffer systems which controlled the relative reduction potentials of Pd and Co and minimized ΔE , as discussed in Section 12.5.3 [159, 163]. The PdCo alloy composition is also highly dependent on metal concentration, pH, current density, temperature, and solution agitation. This system allows excellent control of PdCo alloy composition and provides deposits that are bright, hard, and of very low porosity. For a detailed discussion on how the alloy composition varies as a function of any of the aforementioned variables, the reader is referred to [159, 160, 163].

Following is a summary of important material properties for both gold-flashed palladium cobalt (GFPdCo) and hard gold in Table 12.13 [160]:

1. **Density** The density of plated hard gold is 17.3 g cm^{-3} compared to 80/20 PdCo, which is $\sim 10.8 \text{ g cm}^{-3}$. Thus, for an equivalent surface area and thickness an

TABLE 12.13 Comparative Material Properties

Material Properties	Hard Au	GFPdCo
Density (g cm^{-3})	17.3	10.8
Thermal stability ($^{\circ}\text{C}$)	150	395
Hardness (KHN ₂₅)	140–200	590–640
Ductility (%E at 2.5 μm)	<3	3–9
Porosity index		
Connector pins (1.5 μm /2.5 μm Ni)	0.70	0.02
Wear properties (load 100 g)		
Cycles to failure ($\times 1000$)	20	>80
Coefficient of friction at 10,000 cycles	0.60	0.43

**FIGURE 12.41** Percentage by weight of cobalt versus current density: Pd–Co system from ammoniacal electrolyte.

immediate material “mass” reduction of $\sim 40\%$ can be realized. Figure 12.42 compares the cost savings in dollars per troy ounce of gold substituted with either GFPdNi or GFPdCo based on relative density and price differences (Fig. 12.6). For example, in 2009 the average price per troy ounce for Au was approximately \$905, in contrast to the price of Pd, which averaged \$235 per troy ounce. Figure 12.41 demonstrates that a greater than 85% dollar savings could be achieved in 2009 by replacing gold with an equivalent thickness of GFPdNi or GFPdCo. The following hardness and porosity summaries support further cost savings through a reduction in deposit thickness due to the superior material properties of Pd alloys compared to hard gold.

2. **Hardness** A Knoop hardness value in the range of 590–640 for PdCo can be obtained using the plating chemistry described by Abys et al. [160] compared to “hard” gold, which is ~ 150 Knoop. The higher hardness of Pd alloys should increase wear resistance, inhibit wear through to the base metals (i.e., exposed nickel or copper alloys), and thus result in lower contact resistance change. To test this hypothesis, a sliding wear test (the conditions and experimental details are given elsewhere [160]) was conducted. The results, summarized in Figure 12.43, clearly demonstrate that gold-flashed PdCo exhibits higher wear resistance when compared to hard gold (or even gold-flashed PdNi). These results make an argument for utilizing the lower thickness of Pd alloys to obtain equivalent performance to gold (see Fig. 12.42).

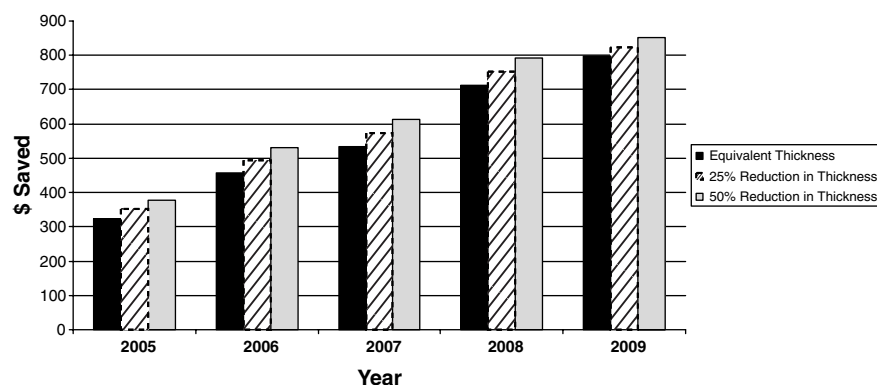


FIGURE 12.42 Cost savings per ounce—80/20 Pd alloy versus hard gold from 2005 to 2009 for an equivalent thickness and 25 and 50% reduction in Pd alloy thickness.

3. *Porosity* One of the most common failure mechanisms, which for electronic connectors are typically a change in contact resistance greater than 10 mΩ, is pore corrosion [164]. The creep of corrosion salts through pores—especially copper salts on precious metals—results in high contact resistance. Thus, a porosity test (ASTM B799-88) is typically utilized for many qualification programs. This entails exposure to SO₂ followed by ammonium sulfide for fixed periods of time. A porosity index scale, described elsewhere by Kudrak [112, 160, 165], can be used for comparative purposes. GF PdCo possesses the lowest intrinsic porosity and is unequivocally superior to hard gold in its overall ability to inhibit corrosion and provide excellent wear; see Figures 12.43 and 12.44.

In summary, PdCo is a fine-grain, single-phase alloy with high hardness, low porosity, and high thermal stability that

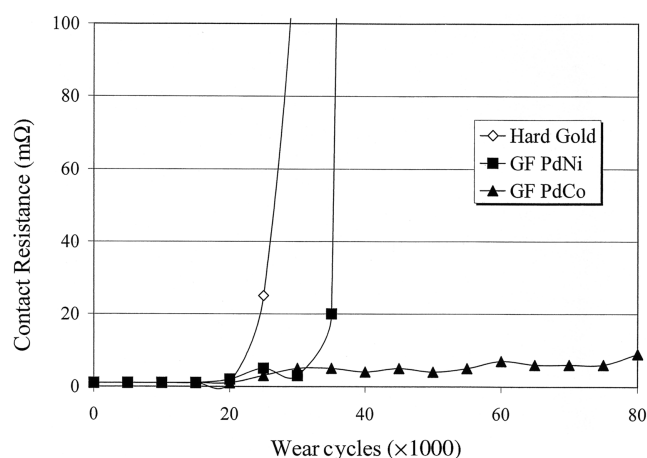


FIGURE 12.43 Sliding wear—contact resistance (100 g load).

outperforms hard gold and in many instances pure Pd and PdNi for high-wear applications such as connectors and printed wiring boards (PWBs) in circuit testing (ICT) pin probes [160].

12.7.3 Palladium–Iron

The Pd–Fe alloys prepared metallurgically are known to be hard magnetic materials [1]. These alloys can also be used as CO sensors in catalytic combustion chambers [129].

The galvanic deposition of Pd–Fe alloys is reported by Juzkis et al. [130] from an ammoniacal electrolyte containing a complexing agent for Fe(III). The electrolyte composition and operating temperature are as follows:

Parameter	Concentration/Operating Conditions
PdCl ₂	0.05–0.2 M (as Pd)
Fe ₂ (SO ₄) ₃	0.1–0.3 M (as Fe)
Sulfosalicylic acid	0.2–0.6 M
NH ₄ OH	0.3 M
Temperature	25–50°C
Current density	5–300 mA cm ⁻²

Palladium–iron alloys deposited from the above electrolytes produce a light gray satin finish. Figure 12.45 shows the dependency of Pd content on the current density as the Fe content is kept constant. Thus a 0.1 M Pd–0.15 M Fe bath composition results in a Pd content of approximately 80 ± 5%. Utilizing direct-current plating at 50°C, the current efficiency is about 75%, and a significant amount of hydrogen is codeposited. The H/Pd + Fe ratio is about 0.15 and results in brittle deposits which are cracked. However, with pulsed electrolysis, the deposits contain less hydrogen and they are brighter in appearance and can be plated to 10 μm crack free.

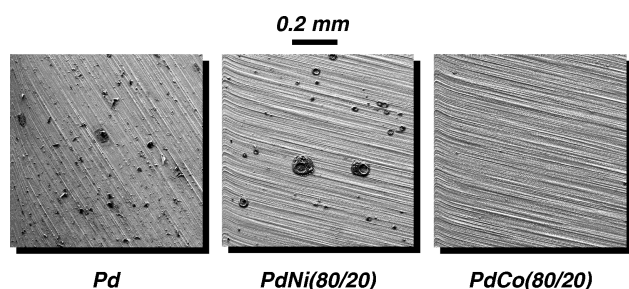


FIGURE 12.44 Scanning electron micrographs: porosity tested Pd, PdNi, and PdCo deposited films; Cu substrate without Ni under layer.

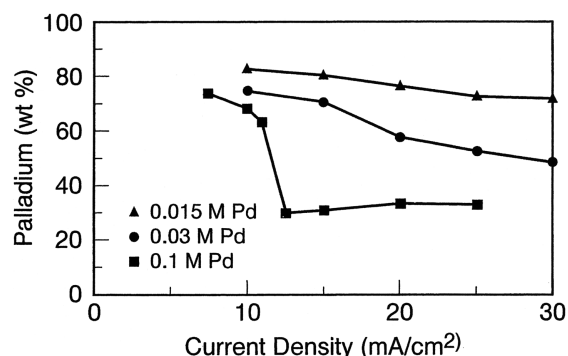


FIGURE 12.45 Percentage by weight of Pd versus current density at various [Pd]: Pd-Fe system from ammoniacal electrolyte.

Two noteworthy publications on the deposition of PdFe alloys were written by Baugartner and Gabe [177].

12.7.4 Palladium–Gold

A slightly alkaline gold plating solution, free of cyanide and phosphates, containing a sodium gold sulfite complex and a palladosamine chloride complex is used to plate a palla-

dium–gold alloy [131]. A typical electroplating formulation is as follows:

Parameter	Concentration/Operating Conditions
$\text{Pd}(\text{NH}_3)_2 \text{Cl}_2$	1.8 g L^{-1}
$\text{NaAu}(\text{SO}_3)_2$	10 g L^{-1}
$(\text{NH}_4)_2\text{SO}_3$	15 g L^{-1}
CuSO_4	0.095 g L^{-1}
$\text{Na}_2\text{As}_2\text{O}_3$	0.03 g L^{-1}
pH	8.2
Temperature	58°C

At 5 mA cm^{-2} a plating rate of $100 \text{ mg A min}^{-1}$ can be achieved which yields a fully bright, gold “flesh-toned” deposit.

12.7.5 Palladium–Indium

Interest in Pd–In goes back to the late 1970s and early 1980s [132–137]. According to these studies, Pd–In alloy crystallizes at 1285°C in a simple cubic structure of the CsCl type with a lattice parameter of $3.22 \text{ \AA}$. This alloy belongs to compounds of the colored β -brass group and, depending on the In content, has a yellow, golden, or rose-lilac color. An article by Reshetnikova and Pedan [138] describes Pd in various properties, including coefficients of friction, resistivity, and contact resistance. A summary of their results is shown in Table 12.14. Another study by Dzhandubaeva et al. [139] provides the following recipes:

Parameter	Concentration/Operating Conditions
Palladium	20 g L^{-1}
Indium	20 g L^{-1}
Trilon β	60 g L^{-1}
pH	25 g L^{-1}
NH_4Cl	~ 8.5
Temperature	20°C

Film thicknesses of $10 \mu\text{m}$ could be deposited utilizing direct and pulsed electrolysis.

TABLE 12.14 Palladium–Indium Materials Properties

Coating Type	Indium Content (mass %)	Resistivity ($\mu\Omega\text{-cm}$) At 20°C	Microhardness (kg/mm^{-2})	Constant Resistance (Ω) 10 mA		Mass Loss Wear Resistance Rest (mg)	Coefficient of Friction Versus Steel	Internal Stress (log/cm^2)	Spreading Area POS-61 Lead–Tin Solder (mm^2)
				Current Under Load (g)					
				50 g	100 g				
Solid solution	3–6	59	290	0.0035	0.0023	20.9	0.18 – 0.19	3200	56–79
Intermetallic	45–55	88	450	0.0240	0.0740	2.7	0.12–0.13	8700	5–6
Palladium	0	20	260	0.0020	0.0015	28.3	0.2	3600	44–77

Additional formulations and material properties data can be found in publications by Su et al. [185].

12.7.6 Palladium–Silver

The properties of Pd–Ag alloys are known to be suitable for contact materials [140–144]. In particular, savings in material costs and comparable corrosion behavior to either Au or Pd have led a number of researchers to investigate the electrochemistry of Pd–Ag.

The PdAg forms homogeneous solid solutions over the entire composition range. The mechanical and electrical properties therefore will not be susceptible to precipitation of a second phase, as in a multiphase alloy, and will not exhibit erratic, abrupt, or irreproducible changes. Small changes in alloy composition have only a minor effect on such properties since, in a homogenous phase, properties, in general, vary gradually with composition. Cohen et al. [142–145] chose to utilize a concentrated lithium chloride bath which contains simple ions and no additives, as shown below:

Parameter	Concentration/Operating Conditions
PdCl ₂	3 g L ⁻¹
AgCl	12 g L ⁻¹
LiCl	500 g L ⁻¹
HCl	20 mL L ⁻¹
Current density	0.5–20 mA cm ⁻²

From this electrolyte it was possible to plate dense, uniform, single-phase alloys with Ag content of 40–70% at about 100% current efficiency. The Ag–Pd alloy properties appear to be favorable for contact applications processing a micro-hardness of about 200 KHN₂₅, very low compressive internal stress, 1 kg mm⁻², and similar wear, friction, and corrosion properties to hard gold. However, this electrolyte composition is extremely corrosive and undergoes displacement plating with non-noble metal substrates.

Nobel et al. [145, 146] claimed to have developed a proprietary process for electroplating PdAg over a wide range of current densities. Deposits from this proprietary alloy are said to be “pore free” and comparable to hard gold in terms of excellent wear and fretting resistance, contact resistance, and corrosion resistance.

Kume and Tadeo [148] report plating a Pd–Ag alloy from ammoniacal alkaline solutions. Silver deposition takes place under mass transport controlled conditions. Their conclusion is that Pd–Ag is a useful substitute for hard gold in contact applications. However, they not discuss the possibility of the formation of silver fulminates (from ammonia-type systems), which could potentially be explosive. The author of this chapter is not aware of plated PdAg being used in any

commercial application, and plating Pd–Ag with the desired composition remains a challenge today.

12.7.7 Other Palladium Alloys

Numerous Pd binary and ternary alloys have been reported in the literature or in patents; however, it is beyond the scope of this chapter to discuss them all. Two publications by Baumgartner and Gabe on PdFe contains a review of other “significant” Pd alloys (i.e., PdNi, PdAg, PdCo, PdFe), many useful formulations, and a long list of references [177]. Another notable alloy of Pd is a PdRe alloy [149] plated from ammoniacal solutions with Trilon as an additive. The Re content is about ~24% and current efficiency 63–90%. The PdSn alloys plated from pyrophosphate baths contain diethylenetriamine pentaacetic acid [150]. Palladium–antimony alloy deposition was reported in a patent [153] where a Pd salt was dissolved in Trilon β at 60–70°C and pH 4. The plating of PdZn alloy and its comparison to Pd and PdNi are reported in [178, 179] and that of PdCu alloys in [182], the latter providing formulations, fundamental electrochemistry, and material properties. Alloys of PdTi and PdTe were reported by Nowsky et al. [183]. Palladium–arsenic alloy processes were patented by Abys and Straschil [151] in 1991 and Wang [152] in 1994. This alloy, usually 20 wt % arsenic, is extremely ductile and can be electroformed into various shapes, such as bellows, which can be “flexed” without cracking.

All novel Pd alloy developments focused on improving the materials properties of Pd for technological applications such as contact material or enabling new applications.

12.8 RECENT TECHNICAL ADVANCES AND EMERGING APPLICATIONS

12.8.1 Use of Palladium for PWB Applications

A detailed discussion of the uses of Pd, with particular reference to PWB-type applications is beyond the scope of this chapter. The PWB industry has been under severe stress to meet the demands of miniaturization and environmental legislation (i.e., Restriction on Hazardous Substance (ROHS)) that bans the use of lead and other typically used materials in electronic applications [166]. Certain original equipment manufacturers (OEMs) have self-imposed environmental programs which are even more aggressive than current legislation in their efforts to embrace the “green” movement. Lead is currently one of the principal components of soldering systems and ROHS legislation banned its use for many electronic applications.

This legislation had a dramatic effect in many sectors of the electronic markets, most notably “final finishes” for PWB applications. Furthermore, surface-mount technology dictated that the following must be taken into consideration in

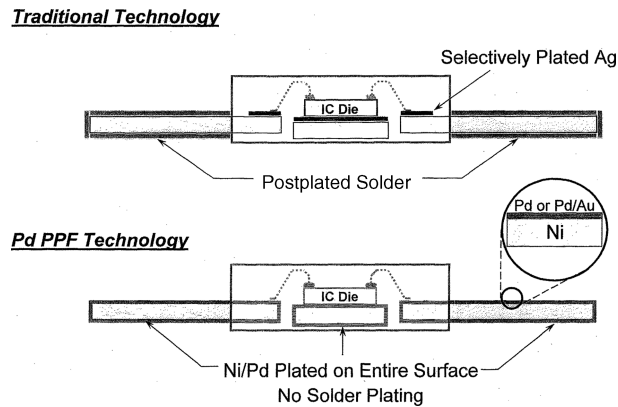


FIGURE 12.46 Schematic cross sections of leadframes plated with silver/solder or nickel/palladium after die attachment, wirebonding, and encapsulation and before trimming and forming.

order to meet the key current and future requirements of this industry:

- Enhanced uniform thickness distribution
- Solderability that meets lead-free requirements
- Wirebondability
- Use of lead-free materials
- Environmental acceptability
- Favorable economics

The idea of using Pd in PWB assembly was proposed as early as 1984 by Wilkinson and O'Hara [167] but was dismissed as the technology for plating pure Pd at the time was not as advanced as it is today; that is, deposits suffered from microcracking and low ductility. However, developments in Pd plating technology and its current use in large-scale leadframe applications (see Section 12.8.4) imply that it should be considered once again for PWB finishes. Thin Pd and Au-flashed Pd deposits, that is, $<0.5\ \mu\text{m}$ in thickness, could be used as an etch-resist, final finish for solderability and a contact surface for PWBs.

Literature exists to support this claim [168–174]. The benefits are (1) elimination of lead, (2) improved processing times (reduction in cycle times), (3) higher yields, and (4) ionically cleaner substrate. The benefits of using Pd as a final finish are (5) good solderability, (6) good wire and die bondability, (7) excellent diffusion/migration barrier properties, (8) thermally stable surfaces, (9) component coplanarity, (10) compatibility with active devices, and (11) compatibility with lead-free solders [170].

12.8.2 Palladium Preplated Leadframes

Palladium preplated leadframes (PPFs) were advanced in the mid-1980s [171–174]. This technology utilizes high-speed Ni and Pd plating over the entire leadframe surface, as opposed to selective Ag plating for die attachment and

wirebonding, and solder plating for external leads. Schematically the two very different technologies are illustrated in Figure 12.46. There are four distinct areas where Pd PPF technology offers significant advantages [168, 175]:

1. *Plating Process Improvements* Whereby the need for costly selective plating is removed, yields and throughput are increased, and all wet processes are completed prior to package assembly.
2. *Quality Improvements* Enhanced coplanarity and the elimination of solder bridging with no possibility for silver migration.
3. *Environmental Improvements* Cyanide and lead are eliminated from the plating process.
4. *Overall Packaging Cost Reduction* Simplification of the plating process, the elimination of postassembly processing, reductions in waste treatment, and extension of the lead frame shelf life.

This technology has gained significant market share over the standard silver spot technology over the last decade.

12.8.3 Codeposited Palladium with Nanoparticles

The emergence of nanotechnology with its promises of enhanced functionality provided the impetus for Abys and Kudrak [186] to codeposit nano-Teflon particles in Pd in an attempt to further reduce its coefficient of friction and improve its wear resistance. Figure 12.47 is a scanning electron micrograph of a cross section of electroplated Pd with 200–80-nm Teflon spheres occluded in electroplated palladium [186].

12.9 CURRENT ECONOMIC CONCERNS

Early in 1998, the bullion prices of Au and Pd converged and consequently diverged, as depicted in Figure 12.6. Simple

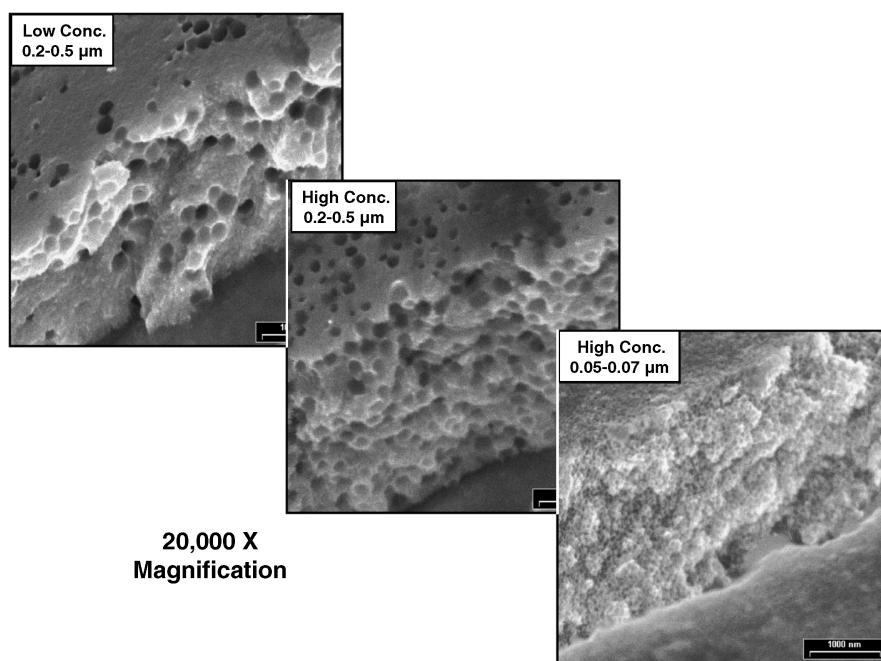


FIGURE 12.47 Scanning electron micrographs: cross section of Pd codeposited with Teflon particles of 50–500 nm; cross section coupon bent 180°.

economic principles of supply and demand rationalize this inversion of metal prices with significant increases for Pd. With respect to demand, there had been a strong trend toward increased use of Pd in automotive catalysts; for example, in 1996 auto catalyst demand was approximately 2.4×10^6 TrOz and in 1998 this figure almost doubled, to 4.5×10^6 TrOz [154]. Notwithstanding the increased demand from the automotive industry, there was increased demand from the electronics sector [154], as traditionally Au-plated components switched to Pd and its alloys. Relatively speaking, Au prices remained steady, trading in a low narrow range of \$270–\$300 per troy ounce from 1998 to 2001.

Supply nuances and speculation played a key role in the increase of Pd bullion prices from 1999 to 2001. As stated earlier (Section 12.2), almost two-thirds of the world's supply of Pd originated in Russia. In the 1990s lack of investments in mining infrastructure coupled with political and labor instability resulted in interruptions of Pd shipments. South African supplies were also reduced due to lower Pt production, which lowered Pd output. Furthermore, speculative activity from hedge funds played a role in artificially increasing the bullion price of Pd [156]. There has however never been a problem in delivering Pd-containing products to the consumer.

The outlook for a sharp downward correction in the price of Pd was predicted and occurred starting in 2001. There are abundant deposits of Pd in the world. Current *U.S. Geological Survey* reports [155] indicate that there is a total of 100×10^6 kg PGMs in reserves (metal in the ground at current mine

sites) and in the reserve base (metal in the ground but having no current mining operation).

In contrast to the falling price of Pd, the price of Au has increase dramatically since 2002 and in 2009 averaged >\$900 per troy ounce (Fig. 12.6). Once again, the significant difference in price, density, and material properties dictate that Pd should be utilized to replace Au for many applications. Figure 12.42 provides the cost reduction per troy ounce of Au metal in replacing Au with Pd at equivalent thickness and also at 25–50% thickness reduction. As can be seen, significant cost reductions with equivalent performance can be obtained.

12.10 CONCLUSIONS

The electrodeposition of Pd was first reported by Henry around 1855; however, it took well over one hundred years for this technology to mature. Knowledge of the electrochemistry of Pd and the effects of hydrogen codeposition were essential in devising robust chemical systems that plate Pd under a variety of conditions in a manufacturing environment. Furthermore, extensive material and reliability data on the use of Pd as a technologically useful finish was instrumental in its adaption for electronic components and other applications.

Palladium and its alloys have thus emerged as competitive substitutes for Au in electronic applications, and for Rh and Ni in the decorative industry, and enable new technical application in their own right. The electrodeposition of Pd

alloys, including Ni, have overcome many technical challenges and alloys with controllable composition and material properties under a variety of plating conditions are now commonplace [159–163].

ACKNOWLEDGMENTS

The author wishes to thank E. J. Kudrak, the late Dr. H. Strachil, Dr. C. Fan, Dr. C. Xu, Dr. I. Kadija, Dr. Y. Okinaka, and the R&D staff of Lucent Technologies Electroplating Chemicals & Services, who contributed much of the development work cited in this chapter and for many helpful discussions and recommendations. The author also wishes to extend a special note of appreciation to Dr. CH Raub for much of the seminal work on the electrochemistry and electrodeposition of palladium. A special note of gratitude to M. Klein of Cookson-Enthone and M. Lake, formerly of Lucent Technologies, for the long hours spent in the preparation of this chapter.

REFERENCES

1. Encyclopedia Americana, International Edition, Grolier Education, Danbury, CT, 1829–present.
2. *Compton's Interactive Encyclopedia*, 1993; 94 Compton's News Media, Inc.
3. I. E. Cottingham, *Platinum Met. Rev.*, **35** (3), 141–151 (1991).
4. J. H. Crockett, "Platinum," in *Handbook of Geochemistry*, Vol. 2, H. H. Wedepohl, Ed., Springer-Verlag, New York, 1969, Sections B–G, K, M, O.
5. T. L. Wright and M. Fleischer, "Geochemistry of the Platinum Metals," in *Geological Survey Bulletin*, 1214-A, U.S. Government Printing Office, Washington, DC, 1965, p. 24.
6. B. Mason, *Principles of Geochemistry*, 2nd ed., Wiley, New York, 1951, p. 310.
7. *Platinum*, Johnson Matthey, 1996–2009.
8. J. A. Abys, "A Unique Palladium Electrochemistry—Characteristics and Film Properties," paper presented at Second American Electroplaters Society Symposium on Economic Use of and Substitution for Precious Metals in the Electronics Industry, Danvers, MA, Sept. 1980.
9. H. K. Straschil, I. Kadija, J. J. Maisano, and J. A. Abys, *PCIF Circuit World*, **17** (2), 9–15, (1991).
10. E. J. Kudrak, J. A. Abys, I. Kadija, and J. J. Maisano, "Wear Reliability of GFPd vs. Hard Gold on a High Speed Digital Connector System," in *Proc. 4th Annual Conf. American Electroplaters and Surface Finishers Society*, Vol. II, Boston, MA, July 1990, p. 739.
11. H. K. Straschil, I. Kadija, J. J. Maisano, and J. A. Abys, "Electroplating of Thick and Ductile Palladium Nickel Alloys," in *Proc. 4th Annual Conf. American Electroplaters and Surface Finishers Society*, Vol. II, Boston, MA, July 1990, p. 1003.
12. I. Kadija, J. A. Abys, V. Chinchankar, and H. K. Straschil, "Electroplating of Thick and Ductile Palladium: A New Electroplating Technology," in *Proc. 4th Annual Conf. American Electroplaters and Surface Finishers Society* Vol. II, Boston, MA, July 1990, p. 759.
13. J. A. Abys, H. K. Straschil, I. Kadija, E. J. Kudrak, and J. Blee, *Met. Finish.*, **89**, 43 (1991).
14. J. Stevenson and L. Mayer, paper presented at IICIT Annual Symp., Philadelphia, PA, 1989.
15. J. A. Abys, J. J. Maisano, C. Wolowodiuk, and H. K. Straschil, "Palladium Nickel Alloy Electroplating," *Proc. Connectors '89 Conf.*, Coventry, England, The Institute of Metal Finishing, March 1989, p. 19.
16. M. Antler, *Platinum Met. Rev.*, **31** (1), 13–19 (1987).
17. W. A. Fairweather, *Trans. Inst. Met. Finish.*, **64** (3), 1 (1986).
18. A. Graham and S. Updegraff, "Properties of Palladium-Nickel Alloy and Pure Palladium for Connector Applications," in *Proc. NEPCON Conf.*, Anaheim, CA, 1984.
19. American Electroplaters Society Symp. on Economic Use of and Substitution for Precious Metals in the Electronics Industry, Danvers, MA, 1982.
20. American Electroplaters Society Symp. on Substitution for Gold, Milwaukee, WI, 1980.
21. D. Gravitz, *Electronic Packaging Prod.* (Feb. 1982).
22. I. H. Brockman et al., in *Proc. Holm Conf.*, 1988, pp. 73–83.
23. H. Grossman et al., in *Proc. Holm Conf.*, 1984, pp. 551–560.
24. D. Ruhlicke et al., in *Proc. Holm Conf.*, 1984, pp. 83–88.
25. S. W. Updegraff, in *Proc. ICEC*, 1986, pp. 399–403.
26. A. H. Graham, in *Proc. Holm Conf.*, 1984, pp. 61–67.
27. G. J. Russ, *IEEE Trans. Component Hybrid Manuf. Tech.*, **CHMT 6** (4), 389–395 (Dec. 1983).
28. E. J. Kudrak, J. A. Abys, I. Kadija, and J. J. Maisano, in *Proc. Annual Conf. American Electroplaters and Surface Finishers Society*, Boston, MA, July 1990.
29. E. J. Kudrak et al., in *Proc. of the 78th Annual Conference of the American Electroplaters and Surface Finishing Society*, July 1991; H. K. Straschil et al., *Metal Finish.* (Jan. 1992); E. J. Kudrak et al., *Plating Surf. Finish.* (Feb. 1992).
30. T. Sato et al., in *Proc. 26th Annual Holm Conf. on Electrical Contacts*, 1980, pp. 41–47.
31. A. H. Graham, in *Proc. 30th Annual Holm Conf. on Electrical Contacts*, 1980, pp. 61–67.
32. T. Sato, *Plating Surf. Finish.*, **74**, 55–59 (1987).
33. M. Antler, *ASLE Trans.*, **26** (3), 376–380 (1983).
34. W. O. Freitag, in *Proc. of Holm Seminar on Electrical Contacts*, Chicago, 1975, pp. 17–23.
35. R. H. Atkinson and A. R. Raper, *J. Electrodep. Tech. Soc.*, **8** (10), 1 (1933).
36. F. H. Reid, *Plating*, **52**, 531 (1965).
37. H. D. Hedrich and C. J. Raub, *MetallOberfläche*, **311** (11), 512–520 (1977).
38. R. Weil, *Plating*, **60**, 1231 (1970); **61**, 50, 127 (1971).

39. H. D. Hedrich and C. J. Raub, *Gaivanotechnik*, **70** (10), 934–939 (1979).
40. H. D. Hedrich and C. J. Raub, *Surface Technol.*, **8**, 347–362 (1979).
41. F. H. Reid, *Metall. Rev.*, **8** (30), 167–211 (1963).
42. Periodic Table of the Elements, Sargent-Welsh Scientific Company, Skokie, IL.
43. *Platinum Group Metals*, Printing and Publishing Office, National Academy of Science, Washington, DC.
44. A. R. Powell, "The Platinum Metals in the Periodic System: A Comparative Study of the Transition Metals," *Platinum Met. Rev.*, **4**, 144–149 (1960).
45. E. M. Wise, *Palladium Recovery, Projection and Use*, Academic, New York, 1968, p. 187.
46. W. Hume-Rothery, "The Platinum Metals and Their Alloys: A Review of Their Electronic Structure and Constitution," *Platinum Met. Rev.*, **10**, 94–100 (1966).
47. F. A. Lewis, *The Palladium-Hydrogen System*, Academic, New York, 1967, p. 178.
48. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, 1980.
49. F. R. Hartley, *The Chemistry of Platinum and Palladium*, Wiley, New York, 1973, p. 544.
50. S. Otsuka, S. Y. Tatsuno, and K. Ataka, "Univalent Palladium Complexes," *J. Am. Chem. Soc.*, **93**, 6705–6706 (1971).
51. R. A. Reinhardt and W. W. Monk, *Inorg. Chem.*, **9**, 2026–2030 (1970).
52. F. Bosolo and R. G. Pearson, *Proc. Inorg. Chem.*, **4**, 381–453 (1962).
53. N. V. Sidgwick, *The Electronic Theory of Valency*, Oxford University Press, London, 1929, p. 163.
54. F. Basolo and R. O. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1967, p. 526.
55. G. E. Coates, M. L. H. Green, and K. Wade, *Organometallic Compounds*, Vol. 2, *The Transition Elements*, Methuen, London, 1968, p. 6.
56. A. F. Bard, R. Parsons, and J. Jordan, Eds., *Standard Potentials in Aqueous Solutions*, Marcel Dekker, New York, 1988.
57. R. M. Izatt, R. Eatough, and J. J. Christensen, *J. Chem. Soc. A*, 1301 (1967).
58. D. H. Templeton, G. W. Watt, and C. S. Garner, *J. Am. Chem. Soc.*, **65**, 1608 (1943).
59. R. N. Goldberg and L. H. Hepler, *Chem. Rev.*, **68**, 229 (1968).
60. R. M. Izatt et al., *J. Chem. Soc. A*, 2514 (1970).
61. E. Jackson and D. A. Pantony, *J. Appl. Electrochem.*, **1**, 283 (1971).
62. M. Pourboix, Ed., *Atlas Dequilibres Electrochimiques @ 25°C*, Gothier-Villars, Paris, 1963, p. 359.
63. A. B. Fasman, G. G. Kutyyukov, and D. V. Sokalski, *Zh. Neorg. Khim.*, **10**, 1338 (1965).
64. V. L. Kravstov and M. I. Zelenski, *Elektrokimiya*, **2**, 1138 (1966).
65. T. Ryhl, *Acta. Chem. Scand.*, **26**, 2961 (1972).
66. A. V. Babaeva and E. Y. Khananova, *Zh. Neorg. Khim.*, **10**, 2579 (1965).
67. H. K. Birnbaum, "Hydrogen Embrittlement," in *Encyclopedia of Material Science and Engineering*, M. B. Bever, Ed., Pergamon, New York, 1986.
68. J. W. Dini, *Electrodeposits, The Material Science of Coatings and Substrates*, Noyes Publication 367, Noyes, Park Ridge, NJ, 1993.
69. S. Nakahara and Y. Okinaka, "Microstructure and Ductility of Electroless Copper Deposits," *Acta Metall.*, **31**, 713 (1983).
70. L. J. Durney, "Hydrogen Embrittlement: Baking Prevents Breaking," *Prod. Finish.*, **49**, 90 (1995).
71. H. Geduld, *Zinc Plating*, ASM International, Columbus, OH, 1988, p. 203.
72. M. Fleischmann, S. Pons, and M. Hawkins, *J. Electroanal. Chem.*, **261**, 301 (1989).
73. S. E. Jones et al., *Nature*, **338**, 737 (1989).
74. J. M. Rosamilia, J. A. Abys, and B. Miller, *Electrochimica Acta*, **36** (7), 1203–1208 (1991).
75. J. R. Lacher, *Proc. Roy. Soc.*, **A161**, 525 (1937).
76. L. J. Gillespie and L. S. Galstoun, *J. Am. Chem. Soc.*, **58**, 2565 (1935).
77. L. J. Gillespie and W. R. Downs, *J. Am. Chem. Soc.*, **61**, 2496 (1939).
78. J. W. Simons and T. B. Flanagan, *J. Phys. Chem.*, **69**, 3581, 3773 (1965).
79. A. N. Frumkin and N. Aladjalowa, *Acta Physiochem. USSR*, **19**, I (1944).
80. T. P. Hoan and D. F. Arrowsmith, *Electroplat. Met. Finish.*, **10**, 5, 1 (1957).
81. M. Baidouf and D. M. Kolb, *Electrochim. Acta*, **38** (15), 2145–2153 (1994).
82. V. D. Jovic et al., *J. Serb. Chem. Soc.*, **57** (12), 951–962 (1993).
83. M. Enyo and P. C. Biswas, *J. Electroanal. Chem.*, **335** (1–2), 309–319 (1993).
84. L. J. Vracar and M. Stojanovic, *J. Serb. Chem. Soc.*, **61** (7), 567–575 (1996).
85. B. I. Podlovchenko, E. A. Kolyadko, and S. Lu, *J. Electroanal. Chem.*, **399** (1–2), 21–27 (1995).
86. I.-Y. Wei and J. Brewer, in *Proc. Annual Technical Conf. on American Electroplaters and Surface Finishers Society*, 1995, pp. 321–332.
87. A. V. Smolin, Y. M. Maksimov, and B. F. Podlovchenko, *Russ. J. Electrochem.*, **31** (6), 520–525 (1995).
88. J. O. M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum, New York, 1970, pp. 1223, 1227, 1053.
89. P. H. Rieger, *Electrochemistry*, 2nd ed., Chapman and Hall, London, 1984, pp. 183–194.
90. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
91. R. J. Morrissey, *Metal Finishing Guidebook-Directory* 97, p. 288.
92. USSR Patent 519,497 (June 30, 1976).

93. F. A. Lowenheim, *Electroplating*, McGraw-Hill, New York, 1978, p. 299.
94. J. M. Stevens, *Trans. Inst. Met. Fin.*, **46**, 26 (1968).
95. H. L. Grube, *MetallOberfläche*, **B5** (4), 61 (1953).
96. W. Keitel and H. Zschiegner, *Trans. Electrochem. Soc.*, **59**, 273 (1931).
97. T. F. Davis, U.S. Patent 4,092,225 (May 30, 1978).
98. H. J. Schuster and K. D. Heppner, U.S. Patent 4,144,141 (Mar. 3, 1979).
99. J. A. Abys, U.S. Patent 4,486,274 (Dec. 4, 1984).
100. R. LePenven, W. Levanson, and W. Pletcher, *J. Appl. Electrochem.*, **22** (51), 421–424 (1992).
101. L. A. Heathcote, *Platinum Met. Rev.*, **9** (3), 80–82 (1965).
102. J. A. Abys, *The Electrodeposition of Pure Palladium with a Palladium Hydroxide Replenishment System*, American Electroplaters Society Symposium, AESF Week, Orlando, FL, 1991.
103. J. A. Abys and Y. Okinaka, U.S. Patent 4,468,296 (Aug. 28, 1984).
104. J. A. Abys and Y. Okinaka, U.S. Patent 5,135,622 (Aug. 4, 1992).
105. S. Nakahara et al., *J. Testing Eval.*, **5**, 178 (1977).
106. J. J. Caricchio and E. R. York, U.S. Patent 4,076,599 (Feb. 28, 1978).
107. J. M. Deuber, U.S. Patent 4,098,656 (July 4, 1978).
108. J. A. Abys, V. Chinchankar, V. T. Eckert, I. Kadija, E. J. Kudrak, J. J. Maisano, and H. K. Straschil, U.S. Patent 4,911,799 (Mar. 27, 1990).
109. U.S. Patent 2,457,021 (1948).
110. F. Simon and W. Zilske, *Plating Surf. Finish.*, **69**, 86 (1982).
111. J. A. Abys and H. K. Straschil, U.S. Patent 5,178,745 (Jan. 12, 1993).
112. H. K. Straschil, J. A. Abys, E. J. Kudrak, J. J. Maisano, and S. Nakahara, "New Palladium Strike Improves Adhesion and Porosity," *Met. Finish.*, **90**, 42–47 (1992).
113. P. K. Gallagher, *Thermochimica Acta*, **41**, 323–327 (1980).
114. J. A. Abys, unpublished data.
115. H. P. Hedrich and Ch. J. Raub, *MetallOberfläche*, **33** (8), 308–315 (1979).
116. F. I. Nobel et al., *Plating Surf. Finish.*, **73** (6), 88–93 (1986).
117. U. Cohen and R. Sard, U.S. Patent 4,269,671 (May 26, 1981).
118. U. Cohen, F. Kohn, and R. Sard, *J. Electrochem. Soc.*, **130**, 1987 (1983).
119. D. Walz and Ch. J. Raub, *MetallOberfläche*, **40**, 162–166, 199–203 (1986).
120. T. Hirano and M. Tsukemato, U.S. Patent 5,342,504 (Aug. 30, 1994).
121. K. S. Berge, U.K. Patent Application 2,115,440A (Sept. 22, 1982).
122. K. S. Berge, U.S. Patent 4,416,740 (Nov. 22, 1983).
123. K. S. Berge, U.S. Patent 4,430,172 (Feb. 7, 1984).
124. P. Wilkinson, U.K. Patent Application 2,115,440A (Sept. 7, 1983).
125. D. Walz and Ch. J. Raub, *MetallOberfläche*, **40** (6), 239–241 (1986).
126. I. Boguslavsky, J. A. Abys, H. K. Straschil, M. Tsuruta, J. J. Maisano, and V. T. Eckert, in *Proc. Annual Conference American Electroplaters and Surface Finishers Society*, Detroit, MI, June 1997.
127. M. Kume, paper presented at 76th Technical Conf. of the Metal Finishing Society of Japan, Paper 3OC-7, 1987.
128. G. T. Rado and H. Suhl, *Magnetism*, Vol. 5, Academic, New York, 1973.
129. *Platinum Met. Rev.*, **37** (2), 120 (1993).
130. P. Juzkis, M. U. Kittel, and Ch. J. Raub, private communication, Research Institute for Precious Metals.
131. P. Stevens, U.S. Patent 4,048,023 (Sept. 13, 1977).
132. S. N. Vinogradov and P. Yu. Perehygin, *Zashch. Met.*, **16** (4), 507 (1980).
133. A. A. Tikhonov, P. M. Vyacheslavov, G. K. Burkat, and V. P. Bursin, *Modern Methods of Deposition of Electrolytic and Chemical Coatings* (in Russian), Izd. Mosk. Doma Nauchn.-Tekhn. Propagandy Im. F. E. Dzerzhinskogo, 1979, p. 79.
134. E. M. Savitskii et al., *Metallic Single Crystals* (in Russian), Izd. Nauka, Moscow, 1976, p. 127.
135. E. M. Savitskii et al., *Alloys of Noble Metals* (in Russian), Izd. Nauka, Moscow, 1977, p. 224.
136. L. M. Nomerovannaya et al., *Dokl. Akad. Nauk SSSR*, **246** (3), 585 (1979).
137. A. M. Meretskii et al., *Metally*, **5**, 193 (1976).
138. N. F. Reshetnikova and K. S. Pedan, *Zh. Prikladnoi Khimii*, **55** (9), 1966–1999 (1982).
139. F. M. Dzhandubaeva, P. M. Vyacheslavov, and G. K. Burkat, *Zashchita Metallov*, **18** (3), 427–430 (1982).
140. R. Long and K. F. Bradform, in *Proc. 8th International Conf. on Electrical Contact Phenomena*, Tokyo, Japan, 1970.
141. W. A. Crossland and E. Knight, in *Proc. Seminar on Electrical Contacts*, Chicago, 1973, p. 247.
142. U. Cohen and R. Sard, U.S. Patent 4,269,671 (May 26, 1981).
143. U. Cohen, F. Kohn, and R. Sard, *J. Electrochem. Soc.*, **130**, 1987 (1983).
144. U. Cohen, K. R. Walton, and R. Sard, *J. Electrochem. Soc.*, **131** (11), 2489 (1988).
145. F. I. Nobel, *IEEE Trans. Components, Hybrids Manuf. Technol.*, **9** (1), (1985).
146. F. I. Nobel et al., *Plating Surf. Finish.*, **73**, 88 (1986).
147. P. L. Cavallotti et al., *Proc. Electrochem. Soc.*, **6**, 261–276 (1994).
148. M. Kume and U. Tadeo, *Hyomen Gijutsu*, **46** (17), 663–666 (1995).
149. S. N. Vinogradov and S. V. Plokohov, *Gai'venotekh Obrab. Poverkh.*, **1** (1–2), 32–34 (1992).
150. M. Noro et al., *Kagaku to Kogyo*, **69** (3), 89–94 (1995).
151. J. A. Abys and H. K. Straschil, U.S. Patent 5,024,733 (June 18, 1991).

152. L. Wang, *Cailiao Baohu*, **27** (5), 24–25 (1994).
153. Soviet Union Patent 535,378 (Nov. 26, 1976).
154. *Platinum 1998*, Johnson Matthey.
155. *U.S. Geological Survey*, Mineral Commodity Summaries, Jan. 1999.
156. M. Lovatt, *Bridge News*, Feb. 16, 2000.
157. C. Fan et al., in *Proc. Annual Conference American Electroplaters and Surface Finishers Society*, Chicago, IL, June 2000.
158. E. J. Kudrak et al., *Proc. 32nd IICIT Connector and Interconnection Technology Symposium*, Anaheim, CA, Sept. 1999.
159. J. A. Abys et al., *Trans. Inst. Metal Finish.*, (July 1999).
160. J. A. Abys et al., *Connector Specifier*, Feb. 1999, p. 12.
161. J. Abys, paper presented at Fleck Materials Conf., Indian Wells, CA, Sept. 1998.
162. I. Boguslavsky et al., in *Proc. Annual Conference American Electroplaters and Surface Finishers Society*, Session L, Minneapolis, MN, June 1998.
163. J. A. Abys et al., *Plating Surf. Finish.*, **86**, 108 (Jan. 1999).
164. M. Clarke, in “*Properties of Electrodeposits*,” R. Sard, H. Leidheiser, and F. Ogburn, Eds., The Electrochemical Society, Princeton, NJ, 1975, p. 122.
165. Standard 17000, Sect. 1275, Western Electric Manufacturing, 1982, based on ASTM B-799.
166. G. C. Munie et al., *J. SMT*, Jan. 2000, p. 15.
167. P. Wilkinson and B. O’Hara, *IPC PC World Convention*, May 1984.
168. L. J. Mayer et al., in *Proc. IPC—Fall Session*, Sept. 1986.
169. I. Kadija et al., in *Proc. Annual Conference American Electroplaters and Surface Finishers Society*, June 1993.
170. I. Kadija et al., *Plating Surf. Finish.*, **82** (2), 56 (Feb. 1995).
171. T. Mc Guiggan and E. E. Benedetto, “Impact of Palladium Leadframes on PCA Manufacturing,” *Circuits Assembly*, Nov. 1997, pp. 32–36.
172. C. Fan et al., in *Proc. Symposium on Environmental Aspects of Electrochemical Technology: Applications in Electronics*, M. Datta, J. M. Fenton, and E. W. Brooman, Eds., PV 96-21, The Electrochemical Society, Pennington, NJ, 1997, p. 188.
173. European Patent Application 87305080.1 by Texas Instruments (1987).
174. European Patent Application 89302939.7 by Texas Instruments (1989).
175. D. C. Abbott et al., *IEEE Trans. Components Hybrids Manufacturing Technol.*, **14** (3), 567 (Sept. 1991).
176. C. A. Dullaghan et al., in *Proc. Annual Conference American Electroplaters and Surface Finishers Society*, Session 1, Chicago, IL, June 2000.
177. M. E. Baugartner and D. R. Gabe, *Trans. IMF*, **78** (1), 11; **78** (2), 79 (2000).
178. E. Von Gunther et al., *Galvanotechnik*, **1**, 206 (2007).
179. S. V. Kabanov et al., *Russian J. Appl. Chem.*, **74** (11), 1895 (2001).
180. I. Bouglavsky and J. A. Abys, in *Proc. 29th Annual Conference and Interconnection Symposium*, Oct. 1996.
181. M. Zhong, L. He, K. Xia and Z. Z. Chen, *J. Mater. Protection (Chinese)*, **39** (6), 26 (June 2006).
182. S. N. Vinogradov et al., *Russian Electrochem.*, **37** (7), 838–840 (2001).
183. H. H. Nowsky et al., *Russian J. of Electrochem.*, **42** (3), 264–271 (2006).
184. I. Gadschov and R. Mantcheva, *Galvanotechnik*, **97** (8), 1850–1854 (2006).
185. F. Y. Su, I. W. Sun, and C. C. Tai, Meeting Abstracts, presented at 207th Electrochemistry Society Meeting, Quebec, Canada, Mar. 2005.
186. J. A. Abys, in *Proceeding of the Symposium on Surface Engineering For Electronics, Singapore, Dec. 2006; Proceedings of EUROMAT*, Nuremberg, Germany, Sept. 2007.