The Electrodeposition of Platinum and Platinum Alloys

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Work on the electrolytic deposition of platinum and some platinum alloys is reviewed, and the results of our recent work on the deposition and the proper- ties of the layers produced from some promising electrolytes are briefly dis- cussed. In general, studies of plating solutions are restricted by the economic availability of the relevant platinum salts. On the other hand the hydrolysis of the platinum salts in solution, and the incorporation of decomposition pro- ducts are also critical factors, especial- ly for their influence on internal stress. Recent work has shown that it is possi- ble to deposit platinum-cobalt alloys which have excellent magnetic and mechanical properties, and these alloy deposits look very promising for data storage applications and for small per- manent magnet layers.

Research on the electrodeposition of platinum has been rather neglected recently, and as a result there has been little discussion of it in the literature. The last review paper on the subject, by F. H. Reid, appeared in 1970 (1), while a more general review of the electro- deposition of the platinum group metals, by one of the present authors, appeared in the Gmelin Handbook (2).

In the main, the published literature contains only general statements about the bath com- position; often information is lacking on the preparation of the bath, its operation, and the properties of the deposits obtained. However, a survey of hardness, ductility and the internal stresses in platinum layers deposited from various electrolytes is given in (3).

No literature has appeared on the production of platinum alloy films, especially the electro- deposition of alloys of platinum with the iron- group metals. The present paper reviews pre- vious work, tries to find guidelines for future research and in addition discusses recent results obtained at the authors' Institute on the electro- deposition of platinum and platinum-cobalt alloys, and their properties.

Electrolytes for the Deposition of Platinum

The first experiments on the electrolytic deposition of the platinum group metals were made over 150 years ago by Elkington, who obtained a patent in 1837 (4), and later by Böttger (5). The electrolytes contained simple metal salts and were rather unstable, while the deposits could not be used for any application. A review in 1910 stated simply that "electro- lytic platinum is hard" despite the fact that it listed no fewer than nine different processes (6). In general, present day electrolytes contain the platinum as stable but quite different, com- plexes. An advantage of these complexes is that they show a smaller degree of hydrolysis in the bath, as compared to simple salts, and therefore the electrolytes are much more stable.

These electrolytes may be divided into two groups: [a] baths containing platinum in the divalent state and [b] those with it in the tetravalent state. Within both groups a further differentiation can be made based on the typical salts used, which may not always be identical with the metal supplying compounds. In Tables I and II a survey of electrolytes pro- ducing worthwhile deposits is given. Tests to

produce deposits from aqueous cyanide solutions proved to be unsuccessful (7). A Mond Nickel Company patent describes the deposition of platinum from a complex amine compound which should generate good layers (8). Apparently deposition is possible if the cyanoamine platinum complexes contain at least one, if possible co-ordinated, CN^- group bound to the metal (8). The electrolyte, however, did not find wide use.

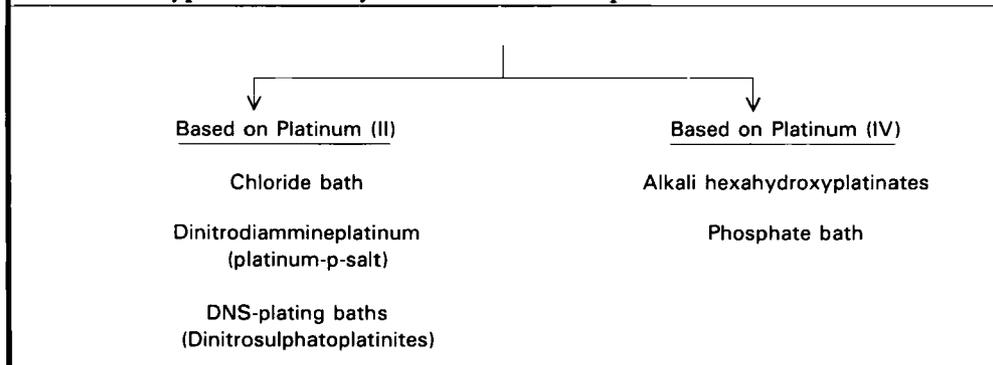## Electrolytes with Divalent Platinum Compounds

Electrolytes Based on Chlorides

Today this type of bath has no great significance, however it was one of the first to achieve technical importance. The basic salts are $PtCl_4.5H_2O$, $H_2PtCl_6.6H_2O$ and $(NH_4)_2PtCl_6$, and in general the bath operates in the acidic range. The fundamentals of these solutions were developed between 1840 and 1900. According to Böttger (5), 500 grams of citric acid should be dissolved in 2 litres of water and carefully neutralised with sodium hydroxide. During continuous stirring, 75 grams of dry ammonium hexachloroplatinate is then added to the boiling solution which is finally diluted with water to 5 litres. Current efficiency is nearly 70 per cent and the operating temperature is about 90°C.

Deposits produced using this bath are fine grained but irregular. The addition of citric acid increases the electrolyte stability by complexing the platinum ion. Electrolytes with citrates, phosphates and ammonium compounds react in a weakly acidic, or sometimes even alkaline state, but their make-up is not always as simple as it may at first seem to be. Interest in chloride-based electrolytes recurred in 1931 with investigations by Grube and Reinhardt (9). Later Atkinson further developed these baths by studying their deposition mechanism (10). He suggested as optimum operating parameters: platinum as $H_2(PtCl_6)$ 10–50 g/l, hydrochloric acid 180–300 g/l, 45–90°C, current density 2.5–3.5 A/dm^2, current efficiency 15–20 per cent, and a soluble platinum anode. Under carefully controlled conditions, this solution apparently produces crack-free, ductile crystalline layers of up to 20µm in thickness. As with most transition metals in aqueous solutions, the pH must be kept within a narrow range in order to avoid hydrolysis, which in this bath starts between pH 2.0 to 2.2 (10). It has to be stated that even today these baths generally tend to be fairly unstable. Deposition begins at a high polarisation, causing high hydrogen co-deposition and a current efficiency which is mostly below 50 per cent. The lifetime of the solutions is not very long and in addition, they are rather corrosive, which requires most base metals to be given a proper protective intermediate layer of, for example, gold, silver or

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Table I

Types of Electrolyte for the Electrodeposition of Platinum

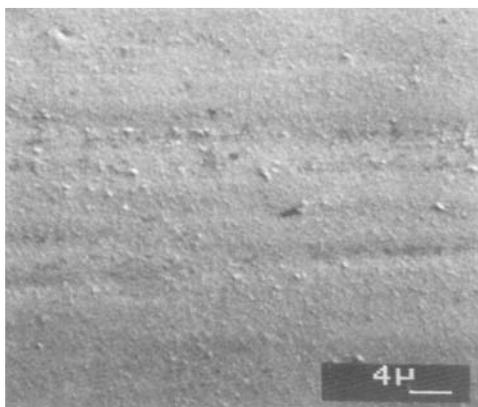| Based on Platinum (II)	Based on Platinum (IV)
Chloride bath	Alkali hexahydroxyplatinates
Dinitrodiammineplatinum (platinum-p-salt)	Phosphate bath
DNS-plating baths (Dinitrosulphatoplatinites)	

Fig. 1 Using an acidic phosphoric-sulphuric acid bath, at 40°C, pH 1.5 and a current density of 1 A/dm² a bright surface, free from cracks, may be produced

palladium. During operation Cl⁻ ion concentration increases in most cases, generating discoloured deposits. At higher hydrochloric acid concentrations and operating temperatures, and at too low current densities, the platinum anodes dissolve, so no additions of platinum salts will be necessary. At lower hydrochloric acid concentrations an insoluble yellow deposit of $(NH_4)_2PtCl_6$ may form at the anode, acting as an insulating layer. Finally it should be explained why chloride electrolytes may be considered as of a "divalent" type. If the electrolysis begins with a $(PtCl_6)^{2-}$ solution the Pt^{4+} ion is cathodically reduced to Pt^{2+} and we have to consider the equilibrium:

$$2(PtCl_4)^{2-} \rightleftharpoons (PtCl_6)^{2-} + Pt + 2Cl^-$$

At the high concentrations of hydrochloric acid used, equilibrium is strongly shifted to the left side of the above equation.

Dinitrodiammine-Based Solutions

In order to maintain the concentration of divalent platinum in solution and to avoid oxidation of Pt(II) to Pt(IV), it is necessary to stabilise the Pt(II) ion by complexing it with suitable amino compounds. The basis of this kind of solution is cis-dinitrodiammine-platinum $Pt(NH_3)_2(NO_2)_2$, which is frequently called Pt-p-salt (11). Its use for electroplating applications was discovered by Keitel and Zschiegner in 1931 and resulted in a strong

resurgence in platinum electroplating (12, 13) The most simple type consists of Pt-p-sa: 8–16.5 g/l, ammonium nitrate 100 g/l, sodiun nitrite 10 g/l, ammonia (28 per cent) 50 g/l. 90–95°C, current density 0.3–2.0 A/dm², current efficiency 10 per cent, and an insoluble pure platinum anode. However the electrolyte reacts irregularly, due to changes in the nitrite concentration, which with increasing concentration influences the dissociation of the platinum complex. The initial current efficiency can be regained by boiling the bath with added NH_4NO_3. On reacting with $NaNO_2$ it forms NH_4NO_2 which, as a free compound, dissociates into nitrogen and water.

During deposition nearly all nonmetallic constituents of the Pt-p-salt are removed from the bath in gaseous form, so the electrolyte has a longer lifetime than halide systems. The bath can be replenished by frequent additions of Pt-p-salt. However its levelling power is fairly poor. Deposits are of a similar quality to those obtained from phosphate baths. The advantage of these electrolytes is that they are relatively easy to prepare. However, the quality of the electrodeposited layer depends largely on the concentration of the metal salt in solution and its purity; the higher the platinum concentration, the better the deposits.

A further improvement was reached by periodically reversing the 5–6 A/dm² current, 5 seconds cathodic being followed by 2 seconds anodic current (14). In this way a platinum deposition rate of 5μm per hour was obtained. It is assumed that this depolarisation of the cathode also reduces the porosity of the platinum layer, producing such a low porosity that a 5μm plate (Pt) over nickel withstood boiling hydrochloric acid (20 per cent) for five hours with no weight loss (15). A different electrolyte of the Pt-p-salt type contains fluoroboric acid (16); its composition being: Pt-p-salt 20 g/l, fluoroboric acid 50–100 g/l, sodium fluoroborate 80–120 g/l, 70–90°C, current density 2–5 A/dm², current efficiency 14–18 per cent, insoluble platinum anode. Layers up to 7.5μm in thickness can be deposited. According to Hänsel defect free

copper overplate

← platinum layer →
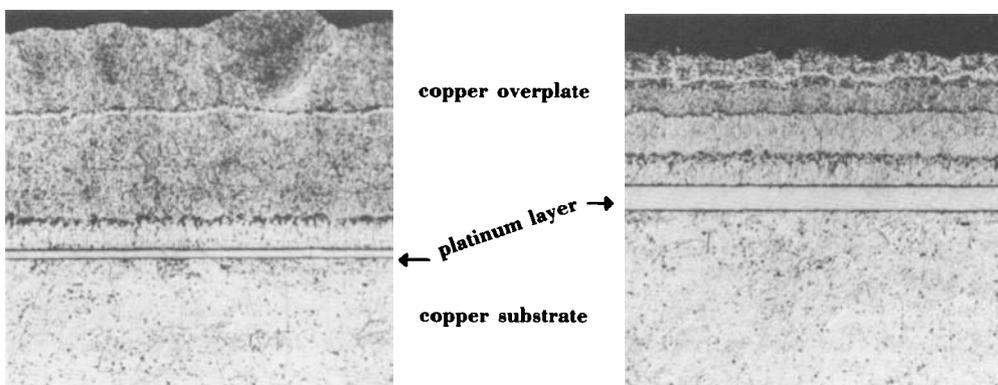
copper substrate

Fig. 2 Replacing ammonium salts with sodium acetate and sodium carbonate results in improved current efficiency, and enables smooth, bright layers free from cracks and pores to be deposited; left 2.5μm platinum layer, right 10μm platinum

layers can be achieved only if the platinum is present in the solution in the divalent state (12). A different Pt-p-salt solution contains 20–100 g/l sulphamic acid (17) or phosphoric acid, or a mixture of phosphoric and sulphuric acids (18, 19). For all these electrolytes insoluble platinum anodes are used; good electrolyte stirring and movement of the cathode are important. The layers produced from this electrolyte are crack free, shiny, bright and up to 2μm in thickness. Figure 1 shows the surface of a 1μm thick layer deposited from a phosphoric and sulphuric acid bath. The highest current efficiency is obtainable from an electrolyte in

which ammonium salts are replaced by sodium acetate and sodium carbonate, which also improves stability (1). Deposits from this bath are smooth, bright and free of pores and cracks at thicknesses up to 10μm, as shown in Figure 2. The use of the sodium instead of the ammonium salts improves current efficiency and avoids the formation of a salt layer on the anode. The cathodic current efficiency of 35 to 40 per cent may be further improved by movement of the cathode or the electrolyte, as is shown in Figure 3.

Since the metal concentration in the electrolyte is fairly low, the diffusion controlled transport of the dischargeable ionic species through the Nernst diffusion layer soon becomes the dominating step in the discharge. Furthermore, this increases both the diffusion overvoltage and the hydrogen deposition, which gets even stronger at higher current densities. This mechanism explains the increase in current efficiency with higher relative movements of cathode and electrolyte. Additional agitation, and a reduction of the thickness of the Nernst diffusion layer, is also provided by hydrogen evolution at the cathode.

Another method of improving the current efficiency of this bath is to increase the operating temperature. The influence of electrolyte temperature on the cathodic current efficiency is shown in Figure 4, a sudden increase in current efficiency near 60°C reaches almost 60 per cent close to 90°C. Below 50°C
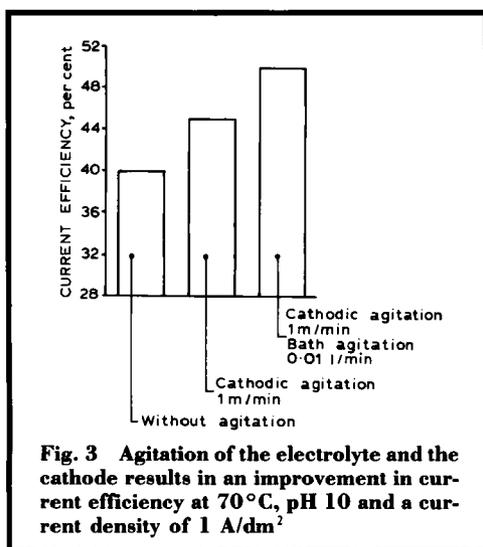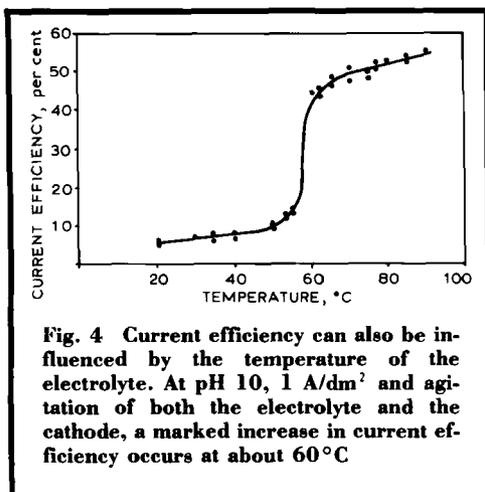

Fig. 3 Agitation of the electrolyte and the cathode results in an improvement in current efficiency at 70°C, pH 10 and a current density of 1 A/dm^2

Fig. 4 Current efficiency can also be influenced by the temperature of the electrolyte. At pH 10, 1 A/dm² and agitation of both the electrolyte and the cathode, a marked increase in current efficiency occurs at about 60°C

the value is only about 10 per cent. If this electrolyte is newly made up, the pH adjusts itself to about 10. The dependence of cathodic current efficiency on pH is approximately linear, see Figure 5. This is further proof that the importance of hydrogen co-deposition increases with pH value. At the same time less metal is deposited—the current efficiency for metal deposition decreases with pH. A pronounced influence of metal deposition on current efficiency is shown by the platinum metal concentration, Figure 6. A decrease of metal concentration causes a reduction in current efficiency. On replenishing the electrolyte with new Pt-p-salt, intermediate products may be
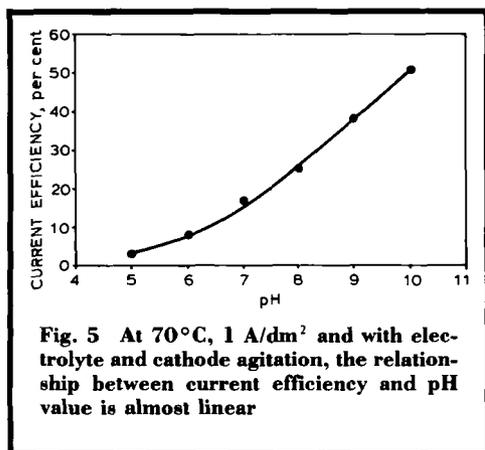
formed and the nitrite concentration increases, reducing the concentration of the dischargeable platinum ionic complex.

The current density-potential curves of these electrolytes show very characteristic behaviour in the alkaline pH range, insofar as the current density increases up to a maximum limiting value of 1.5 A/dm² at about 500 mV, and then within a further 50 mV it drops to a low value of 0.2 A/dm² before increasing again with potential due to hydrogen production. How far this kind of "cathodic passivation" is connected with the hydrogen co-discharge, and the adsorption of hydrogen, is not as yet clear. Another explanation might be a sudden change in pH value in the cathodic layer caused by hydrogen evolution. The critical current density can be increased by an increase in the concentration of the Pt-p-salt, as well as by the sodium acetate addition but not by changes in the sodium carbonate concentration. Temperature has a very decisive influence on the critical current density, while potentials remain nearly constant. "Passivation" is no longer observed at pH values below 7, since hydrogen evolution starts before platinum discharge begins. Figure 7 shows typical current density-potential curves for the electrolyte and for various pH values, at a temperature of 70°C.

Electrolytes Based on Dinitrosulphatoplatinous Acid

These electrolytes are free of ammonia or amines, and are based on the complex $H_2Pt(NO_2)_2SO_4$. With them it is possible to coat directly with platinum a wide range of materials including copper, brass, silver, nickel, lead and titanium. However, metals such as iron, zinc or cadmium have to be preplated with a dense layer of nickel or silver (20).

The salts for making up the solutions are potassium salts of nitro-, chloro- and sulphatoplatinous acid, such as: $K_2Pt(NO_2)_3Cl$, $K_2Pt(NO_2)_2Cl_2$ and $K_2Pt(NO_2)_2SO_4$, respectively. If bright deposits are required the work has to be carried out at low current densities and the pH of the electrolyte must be kept below 2 by the addition of sulphuric acid.

Fig. 5 At 70°C, 1 A/dm² and with electrolyte and cathode agitation, the relationship between current efficiency and pH value is almost linear

Typical baths have the composition: dinitro-sulphatoplatinous acid (DNS) 10 g/l, sulphuric acid up to pH 2, temperature 30 to 70°C, current density 2.5 A/dm^2, current efficiency 10–15 per cent, insoluble pure platinum anode. The advantages of the DNS electrolyte are claimed to be as follows: the deposits produced are smooth and bright, and do not have to be polished; layers up to 25μm thickness can be produced, however cracks form at greater thicknesses; electrolytes are stable, producing constant results and do not degrade on standing; it is possible to coat a wide range of base metals without using an intermediate layer.

Electrolytes with Tetravalent Platinum Complexes

Alkaline Solutions

In general alkaline electrolytes contain the sodium or potassium salts of hexahydroxy-platinic acid $Na_2Pt(OH)_6$ or $K_2Pt(OH)_6$, respectively (21). A typical bath is: sodium hexahydroxyplatinate 20 g/l, sodium hydroxide 10 g/l, 75°C, pH 13, current density 0.8 A/dm^2, current efficiency 100 per cent, insoluble nickel or stainless steel anode. Deposits are dense and bright, if the electrolyte is freshly made up. In older solutions they become matte and spongy. An advantage of these kinds of electrolytes is their easy regeneration. If the pH of the electrolyte is decreased by the addition of acetic acid, hexahydroxyplatinic acid salts are
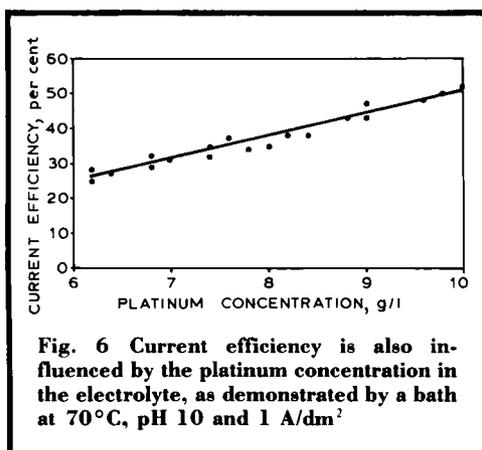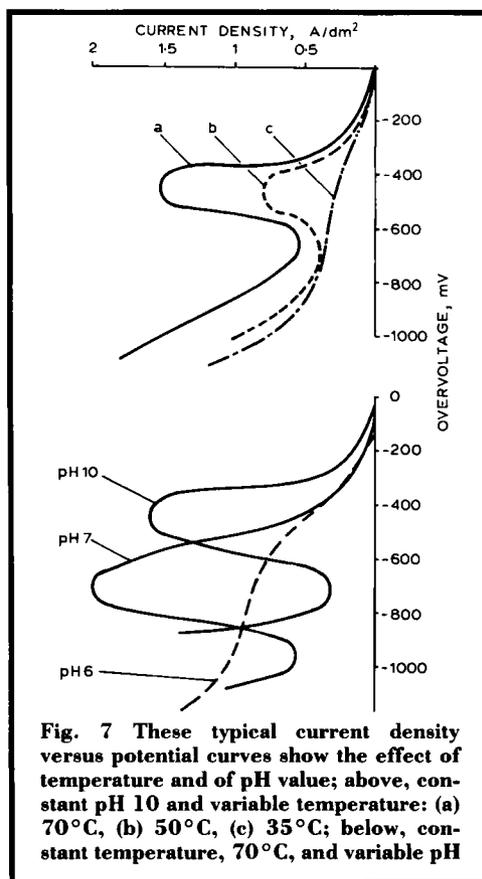
Fig. 7 These typical current density versus potential curves show the effect of temperature and of pH value; above, constant pH 10 and variable temperature: (a) 70°C, (b) 50°C, (c) 35°C; below, constant temperature, 70°C, and variable pH

precipitated and can then be filtered off and used for the preparation of a new bath. However, a disadvantage is low stability, since during operation, or on standing, a yellow deposit forms by decomposition of the hydroxy salt according to the equation:

$$3\ Na_2Pt(OH)_6 \longrightarrow Na_2O.3PtO_2.6H_2O + 4\ NaOH + H_2O$$
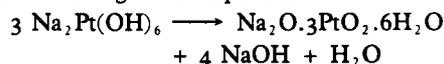
The reaction is catalysed by impurities in the make-up salts. Another problem is the take up of carbon dioxide from the air, so the carbonate concentration increases and has to be reduced regularly by precipitation with $Ba(OH)_2$. In this connection potassium salts show a better performance than sodium salts. It is claimed that an improvement in stability is obtained by adding sodium oxalate, sodium sulphate or sodium acetate (22, 23). Other researchers state, however, that these additions are detri-

Fig. 6 Current efficiency is also influenced by the platinum concentration in the electrolyte, as demonstrated by a bath at 70°C, pH 10 and 1 A/dm^2

Table II
Baths for Platinum Electrodeposition

Type of bath	Formula	Chloride			Dinitrodiammineplatinum					DNS	Alkali hexahydroxyplatinates				Phosphate
Reference		(10)	(1)	(13)	(16)	(17)	(18)	(19)	(1)	(20)	(21)	(24)	(26)	(26)	(4)
		Concentrations, g/l													
Chloroplatinic acid	$H_2[PtCl_6]$	10–50													
Ammoniumhexachloro-platinate	$(NH_4)_2PtCl_6$		15												
Platinum-p-salt	$Pt(NH_3)_2(NO_2)_2$			8–16.5	20	6–20	8	6–20	16.5						
Dinitrosulphato-platinous acid	$H_2Pt(NO_2)_2SO_4$									10					
Sodium hexahydroxy-platinate	$Na_2[Pt(OH)_6].2H_2O$										20	18.5			
Hexahydroxyplatinic acid	$H_2[Pt(OH)_6]$												20		
Potassium hexahydroxy-platinate	$K_2[Pt(OH)_6]$													20	
Platinum chloride	$PtCl_4.5H_2O$														7.5
Ammonia (28%)	NH_3			50											
Hydrochloric acid	HCl	180–300	100												
Sodium citrate	$Na_3C_6H_5O_7.2H_2O$	100													
Ammonium chloride	NH_4Cl		4–5												
Ammonium nitrate	NH_4NO_3			100											
Sodium nitrite	$NaNO_2$			10											
Fluoroboric acid	HBF_4				50–100										
Sodium fluoroborate	$NaBF_4$				80–120										
Sulphamic acid	NH_2SO_3H					20–100									
Phosphoric acid	H_3PO_4						80	10–100							
Sulphuric acid	H_2SO_4							10–100		pH 2					
Sodium acetate	$NaCH_3COO$								70						
Sodium carbonate	Na_2CO_3								100						
Sodium hydroxide	$NaOH$										10	5.1			
Sodium oxalate	$Na_2C_2O_4$											5.1			
Sodium sulphate	Na_2SO_4											30.8	15		
Potassium hydroxide	KOH														
Diammonium hydrogen phosphate	$(NH_4)_2HPO_4$														20
Disodium hydrogen phosphate	Na_2HPO_4														100
Potassium sulphate	K_2SO_4													40	
Temperature, °C		45–90	80–90	90–95	70–90	65–100	75–100	75–100	80–90	30–70	75	65–80	75	70–90	70–90
Current density, A/dm^2		2.5–3.5	0.5–1.0	0.3–2.0	2–5	0.2–2	0.5–3.0	0.5–3	0.5	2.5	0.8	0.8	0.75	0.3–1	0.3–1
Current efficiency, per cent		15–20	70	10	14–18	15	15		35–40	10–15	100	80	100	10–50	10–50

mental to the stability of the electrolyte since they were inclined to increase the tendency for precipitation of insoluble platinum compounds (12).

According to Davies and Powell, a typical bath composition is: sodium hexahydroxyplatinate 18.5 g/l, sodium hydroxide 5.1 g/l, sodium oxalate 5.1 g/l, sodium sulphate 30.8 g/l, 65–80°C, current density 0.8 A/dm², current efficiency 80 per cent, insoluble pure platinum anodes (24). With this electrolyte dense, sparkling platinum deposits can be produced which are comparable to rhodium electrodeposits (25). However if the platinum concentration drops below 3 g/l the current efficiency drops to only a few per cent. At higher platinum concentrations (12 g/l) current densities of up to 2.5 A/dm² may be achieved. Current efficiency versus temperature data display a maximum of about 80 per cent at 65 to 70°C, which is not further improved, even at higher temperatures. Large temperature variations of the bath during deposition may generate scaling of the layers (25). Gold, silver, copper and their alloys may be used as base materials. However the electrolyte seems to be tolerant of impurities, especially against cyanides, which mask the platinum ions, so reducing current efficiency. Platinum must always be present in the tetravalent state of the hydroxy complex. The bath tolerates up to 300 g/l potassium carbonate but only 60 to 80 g/l sodium carbonate, before cathodic current efficiency drops (26). For deposition onto metals which react in strong alkaline solutions potassium hydroxide may be replaced by 40 g/l of potassium sulphate (26).

Phosphate Based Electrolytes

As early as 1855 Roseleur and Lanaux suggested the use of phosphate based electrolytes for the deposition of platinum (27). The baths contain platinum as a chloro compound, such as Pt(IV) chloride, hexachloroplatinic acid or its alkali salts. To improve conductivity alkali phosphates and ammonium phosphates are used; the presence of the latter is supposed to enhance deposition. Pfanhauser suggests as the electrolyte: platinum(IV) chloride 7.5 g/l,

diammonium hydrogen phosphate $(NH_4)_2HPO_4$ 20 g/l, disodium hydrogen phosphate Na_2HPO_4 100 g/l, ammonium chloride 20–25 g/l, 70–90°C, current density 0.3–1.0 A/dm², current efficiency 10 to 50 per cent, insoluble platinum anode (4). Layers up to a thickness of 0.5μm can be deposited. By increasing the platinum concentration up to 5–10 g/l it is, however, possible to obtain deposits which, after dissolution of the substrate metal, remain as solid foils, tubes or other hollow structures. Using a similar electrolyte comparable results were reported by Grube and Beischer (7). A great disadvantage of this electrolyte is that it is difficult to prepare. Before a freshly prepared solution can be used, it has to be left until a deposit which forms is completely dissolved. If the solution is made up without ammonium phosphate, the deposits are rather porous and sometimes spongy. Apparently the ammonium phosphate improves the dissolution of an $(NH_4)^+$-containing platinum complex in the solution. Under certain conditions, this electrolyte also forms a layer of insoluble yellow salt which serves as an insulating "barrier" on the anode surface; this is most likely ammoniumhexachloroplatinate.

Platinum Alloy Deposits

A general review of work on the electrodeposition of platinum alloys up to 1963 has been given by Brenner (28). The earliest alloy deposition seems to have taken place in 1894 from alkaline cyanide solutions. A patent describes the deposition of platinum with cobalt, nickel, copper, zinc, cadmium and tin (29). A later literature survey of the subject covering the period from 1965 to 1970 was given by Krohn and Bohn (30). However their remarks are very general and no information on electrolyte compositions is given. Bogenschütz and George mention the compositions of certain electrolytes for the deposition of platinum with ruthenium, palladium, iridium and rhenium, as well as a solution for producing platinum-cobalt alloys. Regrettably information on deposition conditions and properties is not given (31).
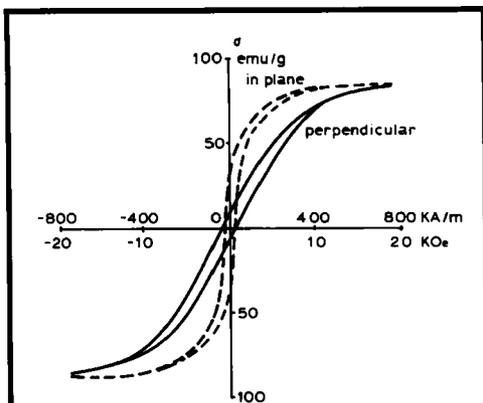
Angus studied platinum-palladium and

Fig. 8 The hysteresis loops of platinum-70 atomic per cent cobalt demonstrate the attractive magnetic properties of this material
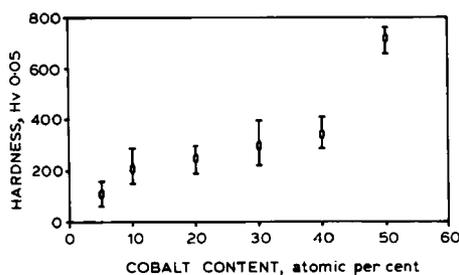

Fig. 9 The hardness of electrodeposited platinum-cobalt depends largely upon the cobalt content. Here the base metal concentration in the electrolyte was 10 g/l, pH 5, and current density 2 A/dm^2

used a chloride electrolyte with ammonium hexachloroplatinate and the respective iridate, and disodium hydrogen phosphates as a buffer (pH 8.5) for the platinum-iridium alloy deposition. The best platinum-rhenium alloys were produced from a fluoroboric acid solution; however sulphamic acid caused high internal stresses in the layers.

An acidic platinum-iridium alloy bath (pH 1–2) is described by Tyrell (34). The bath is based on hexabromoplatinic acid and hexabromoiridic acid with 1.5 g/l iridium and 3.5 g/l platinum. The iridium concentration in the solution and the temperature strongly influence the iridium content of the deposit. At 4 and 30 per cent iridium the layers tend to crack. However, layers with 10 per cent iridium can be produced up to a thickness of 10 μm.

The deposition of platinum-cobalt alloys and the properties of the deposits have been studied recently in the authors' Institute (35). The basic electrolyte composition was sodium acetate, sodium carbonate, platinum-p-salt, cobalt sulphate and triethanolamine. It was shown that it is possible to deposit platinum-cobalt alloys containing low to high cobalt concentrations (more than 50 atomic per cent), which combine high hardness and wear resistance with excellent magnetic properties. For example, the deposits show high coercive forces of up to 400 kA/m at a relatively small
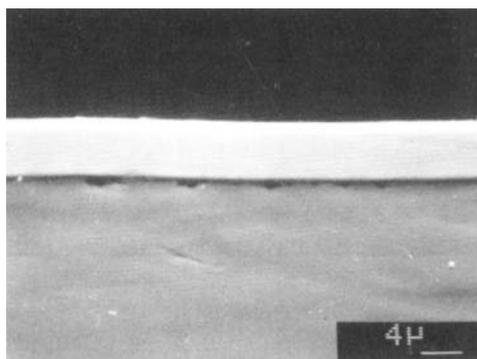
platinum-ruthenium alloys, for depositing layers containing 20 to 80 per cent platinum (32). In these baths, current density is the dominant influence on alloy composition. Electrolytes for both alloys are quite different. In the platinum-palladium solution, with increasing current density, less palladium is codeposited, while in the platinum-ruthenium alloy solution the ruthenium content of the layers increases from 10 to 50 per cent as the current density is raised from 0.5 to 2.0 A/dm^2.

Studies by Hänsel showed that electrodeposited alloys of platinum-7 per cent iridium and platinum-5 per cent rhenium have a much higher hardness than pure platinum layers, the increase being more than 200 per cent (33). He

Fig. 10 Platinum-cobalt alloys, containing 10–12 weight per cent cobalt, can be deposited as bright shiny layers which are crackfree at thicknesses up to about 6 μm, and which show excellent adhesion to the substrate

anisotropy, making them very interesting materials for applications such as data storage devices or permanent magnets, see Figure 8.

The hardness of the layers depends strongly on their cobalt concentration, increasing cobalt resulting in an increase in hardness. In particular, an alloy with about 50 atomic per cent cobalt shows a major increase in hardness, as illustrated in Figure 9.

As yet it is not clear how much the effect is due to the deposition of platinum-cobalt in the ordered state. For comparison, metallurgically produced platinum-50 atomic per cent cobalt alloys exhibited hardness values around 200 HV, while electroplated deposits of this composition have a hardness of 700 HV.

The composition of layers electrodeposited from these electrolytes is strongly influenced by electrolyte temperature and pH value. If the electrolyte is operated in the neutral or alkaline range, no more than 10 to 12 weight per cent cobalt can be co-deposited with platinum. Depending on the pH value, the current efficiencies are between 15 and 30 per cent. All deposits are shiny bright, show excellent adhesion and are crack-free up to thicknesses of 6μm (Figure 10).

Acknowledgements

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