Improvements in Platinum Plating

A NEW GENERATION OF ELECTROPLATING BATHS

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Platinum and platinum alloy films electrodeposited from conventional aqueous electrolytes find application for a wide range of uses. During deposition a variety of problems have to be overcome, necessitating optimisation of process conditions; in addition currently available platinum plating processes are not considered to be particularly efficient. The invention of a new series of aqueous platinum or platinum-alloy electroplating baths which permits thick and adherent deposits to be produced, and which are more efficient than other commercial plating solutions, is now reported. Some results of investigations made on test pieces and limited pre-commercial proving samples, are also given.

Although the electrodeposition of platinum has been practised for over 150 years, it is still a subject that attracts great interest, as demonstrated here by a recent review paper (1). This is because deposits of platinum metals and alloys are used, for a variety of reasons, in many different applications; but often there are difficulties associated with the process, or the properties of the deposit obtained may limit, in some way, the length of time or conditions under which the plated component can be employed. While the end user may only be concerned with the performance and cost of the plated piece, the ability of the electroplater to satisfy the needs of the customer depends ultimately upon the available materials and the conditions required to deposit them successfully, so in fact the problems are common to all parties.

The results of a continuing development programme demonstrate that many of the difficulties associated with existing platinum electroplating systems, including low efficiencies and fluctuating operating conditions, can be eliminated, or substantially reduced, by a new generation of electroplating baths which are now approaching full commercialisation. Established processes are based on materials such as diamminedinitroplatinum(II), alkali metal hexahydroxyplatinates(IV), hydrogen hexachloroplatinate(IV) or hydrogen dinitrosulphatoplatinate(II). The new development consists of a range of complexed platinum salts, some of which are believed to be novel, which are used in alkaline aqueous solution (2).

A platinum plating preparation may thus be based upon ammine or amine platinum(II) complexes combined with neutral, acidic or alkaline organic or inorganic anions. The most significant operating variables for several tetrammineplatinum(II) compounds have been studied, and some typical results from a promising system are given. Plating trials showed that pH control was necessary to keep the bath running at maximum efficiency, adjustment being made by the addition of sodium hydroxide solution or a relevant acid. In general, the optimum range of pH values is from 10.0 to 10.6. No permanent harm occurs outside this range, however, the cathode efficiency being restored when the pH value is brought back within the recommended limits. The influence of pH on current efficiency is shown in Figure 1.

Early trials indicated that the bath operated most efficiently at temperatures >90°C and this was confirmed by later experiments, the results of which are shown in Figure 2. The need to minimise evaporation losses imposes an upper temperature limit; generally the plating temperature should be in the range of 91 to 95°C.

The appropriate concentration of platinum varies according to the task being undertaken, the lowest feasible concentration of platinum being about 2 g/l, and the upper platinum concentration about 30 g/l. Platinum concentrations in the baths are maintained by the addition of calculated amounts of a platinum replenisher. Remarkably, tests have shown that the bath will still plate platinum even when its concentration has been reduced to less than 10 parts per million, a feature that can be made use of for the recovery of platinum from spent solutions. One of the disadvantages of the long-established process based upon platinum-P-salt, diamminedinitroplatinum(II), is that it may cease to deposit platinum, due to the formation of non-active plating species. A measure of the long-term performance of a platinum bath can be gained from turnover trials; one turnover being taken to mean that the weight of platinum originally present in the bath has been removed by deposition and the bath replenished by the addition of concentrated platinum solution. Operating under experimental conditions, a bath based upon a new tetrammineplatinum(II) system maintained high efficiency even after 10 turnovers, showing that it is superior to platinum-P-salt baths.

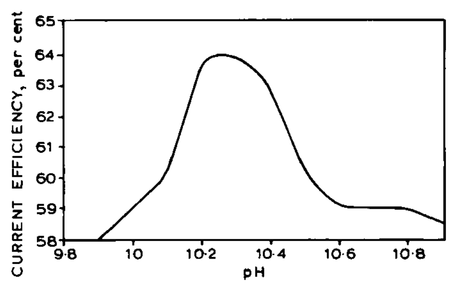

Fig. 1 Control of pH value above 9.8 has been shown to be an important factor in maximising bath efficiency. For a bath containing 5 g/l of platinum, at 91 °C, the optimum pH range is between 10.0 and 10.6

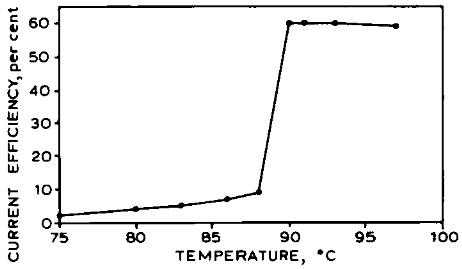

Fig. 2 Tests conducted in a bath with pH = 10.5 and a platinum concentration of 5 g/l show the advantage of operating at temperatures above 90 °C. However, the need to minimise losses by evaporation suggests that 95 °C is a sensible upper temperature limit

The bright, white, lustrous deposits that can be obtained with some anionic components are suitable for jewellery applications without the addition of brighteners, which are generally unnecessary in these new systems.

Laboratory work has demonstrated that the new system is very versatile and can be used to electrodeposit platinum and platinum alloys. Thus, for example, the addition of compatible tetramminepalladium(II) or hexamminenickel(II) species to the bath enables the corresponding alloys to be deposited. Suitable substrates include brass, copper, gold, nickel, niobium, superalloys and titanium. Other metals, and also conductive resins and composites, are regarded as candidate materials for plating in this system for a variety of applications including electroforming. As with other electroplating systems, the pretreatment of the substrate is of crucial importance, and the most advantageous combination of chemical and mechanical preparations must be established and utilised. In-house and customer assessments of platinum and platinum alloy deposits on these substrates, in various physical forms, including sheet, gauze, wire, chain and preformed and fabricated items, have been undertaken or are currently being carried out. Examples of work completed are listed in Tables I and II.

For industrial applications, the properties expected of platinum electrodeposits may include high temperature resistance to corrosion and oxidation, good adhesion to the substrate and good electrical conductivity. These in turn depend upon other factors, such as the uniformity of thickness of the deposit and the effectiveness

Table I

Industrial Items Electroplated with Platinum

Object	Substrate	Thickness, micrometres	Surface area, square decimetres
Aviation components	Niobium superalloy	20	0.38
Aviation components	Stainless steel 347	55	25.00
Bursting discs	Titanium	5	1.50
Electrodes	Stainless steel 316L	10	0.55
Electrodes	Titanium	29	4.80
Electrodes	Titanium mesh	5	2.20
Electrodes	Tungsten wire	10	
Turbine blades	Superalloy	7	0.12
Wire	Copper	15	
Wire	Molybdenum	10	

Table II

Jewellery and Decorative Items Electroplated with Platinum

Object	Substrate	Thickness, micrometres	Method
Paper weights	Nickel plated gunmetal	0.1	Vat
Ear-rings	Nickel	0.4	Vat
Electroformed orchid	Gold	0.5	Vat
Chain	Gold, 9 carat	0.5	Vat
Watch case	Brass	1.0	Vat
Washers	Titanium	1.0	Barrel
Semicircular components	Silver plated aluminium	1.5	Vat

of the pretreatment. Additional desirable properties for decorative applications include abrasion resistance, absence of "finger printing", brightness, purity of colour and reflectivity. While some of these properties can be assessed by tests such as the Sebastian pull test for adhesion, or microscopic examination of prepared sections, others can only be judged by the results of field trials. Although plated platinum deposits thicker than 5 micrometres are generally highly stressed and, therefore, very brittle, a simple bend test is sufficient to demonstrate that the new system is capable of producing low stress deposits, and thicknesses of up to 50 micrometres have been successfully deposited.

The sample illustrated in Figure 3 has a platinum coating 2 micrometres thick on a polished copper substrate, and has been bent

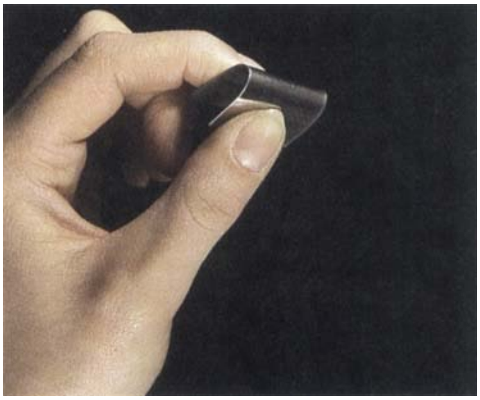

Fig. 3 A simple bend test clearly demonstrates the low stress, ductile nature of the platinum electrodeposit, and shows good adhesion of the coating to the substrate. The latter has been confirmed by Sebastian Adhesion Testing when a sample of platinum plating on a copper substrate survived a pull of 16,536 kN/m^2 normal to the surface

through an angle of 180°C and then straightened four times successively. The platinum remains firmly adhered to the substrate.

While all plating systems have to be handled and used with due regard to the health and safety of operators and the environment, the new platinum and platinum alloy system has clear advantages over most conventional commercial systems, being non-toxic and non-explosive in either the wet or the dry state. In addition, as it is only mildly alkaline, it is less hazardous than the strongly alkaline or acidic materials of some existing baths.

Following the granting of provisional patent coverage worldwide, the new platinum and platinum alloy plating process was launched by Johnson Matthey in the Pacific Basin region during the latter part of 1988, and has been well received. It is confidently expected that continuing development work will further extend the range of industrial applications that can be achieved with the new system.

References

1 M. E. Baumgärtner and Ch. J. Raub, *Platinum Metals Rev.*, 1988, **32**, (4), 188

2 P. E. Skinner, Proc. Conf. Inst. Met. Finish., Annual Technical Conference, Brighton, April 1989, p. 187

Ignition and Engine Performance Conference

Twenty-two motor companies and seven spark plug manufacturers were represented at the 26th Champion Ignition and Engine Performance Conference, held in Munich, West Germany on 25th and 26th April, 1989. The various areas of technology addressed included spark plug and ignition system developments, engine design and the effects of fuel, fuel lubricants and fuel additives on engine performance.

Discussions on the current and future requirements for electrode materials in spark plugs, and new operational design concepts were confined mainly to Champion, Robert Bosch and Nippondenso. Each of these spark plug manufacturers use platinum or noble metal alloys for electrode tips, or as fine wires for complete electrodes. The reasons for their use include the need to provide high performance and reliable ignition, and to ensure that the ignition system is capable of surviving for the lifetime of the engine. The engine manufacturers gave a clear indication that, because of a desire to completely seal the engine compartment, future designs would necessitate the use of totally reliable plug systems. Indeed, the plug systems on some existing engines are not readily accessible, and must therefore provide guaranteed performance and lifetime.

Informative discussions took place on engine cold start, the advantages and disadvantages of projected nose plugs and operating heat range. AC-type, dual plug and coil-on-plug ignition systems were also considered, and some thoughts on "knock" detectors were given.

This well organised conference enabled the 130 delegates to increase their awareness of the opportunities for innovation in materials technology which will accompany new concepts in engine design. I.R.M.

Combustion Research in Japan

Prepared by the Global Competitiveness Council and published by the Society of Automotive Engineers, the latest volume in a most useful series devoted to increasing the awareness worldwide of Japanese research on spark ignition engines contains extended abstracts of some two hundred papers. The wide range of topics covered includes some applications where the platinum metals are currently in use, namely: emission control catalysts, sensors and spark plug materials. It also embraces subjects such as alternative fuels, improved engine design and the reduction of unregulated secondary pollutants, which may affect future demand for the platinum metals.

The investigations summarised have been carried out by researchers affiliated with Japanese corporations, research institutes and universities, and this volume will enable English speaking readers to gain a valuable introduction to Japanese technical literature on the subject. Furthermore seventeen key sources of information are listed, as are the organisations which originated most of the work.

Combustion Research in Japan, Volume 5, Spark Ignition Engine Research, ISBN 0–89883–676–X, may be obtained from: SAE Customer Service, 400 Commonwealth Drive, Warrendale, PA 15096–0001, U.S.A., price $102.00, or from the SAE European Office, 68a Wilbury Way, Hitchin, Herts SG4 0TP, England, price £79.00.