

Platinum and Palladium Electrodeposits on Refractory Metals

AQUEOUS ELECTROLYTES TO YIELD THICK COATINGS

The platinum metals are well known for their resistance to oxidation and chemical corrosion over a wide range of temperatures, these properties being exhibited to a higher degree than for any other metal. However, economic considerations prohibit the total construction in these metals of large parts for arduous duty at high temperatures and it has been the practice to utilise the mechanical properties of the refractory metals and to protect the surfaces against oxidation by cladding with platinum or its alloys. It is difficult to construct complex parts in this manner, and thus there is a need for electro-deposition systems capable of yielding substantial thicknesses.

Platinum group metal plating baths have been in use for many years in the jewellery industry and more recently in the production of contact surfaces in electronic and communication equipment. Here, however, the coatings are thin (for jewellery less than 50

micro-inches and for contacts from 50 to 300 micro-inches) and the solutions in use generally give cracked deposits at thicknesses in excess of 500 micro-inches.

A recent study at the U.S. Bureau of Mines by S. D. Cramer, C. B. Kenahan, R. L. Andrews and D. Schlain (R.I. 7016, September 1967) has examined the use of the previously available proprietary electrolytes for deposition on refractory metals such as niobium, molybdenum, tantalum, titanium, tungsten, vanadium and zirconium at thicknesses in excess of 2000 micro-inches. In almost every case they were found to be inadequate in the sense of producing either non-adherent or heavily cracked plates. Three platinum and two palladium formulations were, however, found to be more successful, and these solutions are set out in the table. Deposits of 0.010 to 0.020 inch were produced, but the platinum electrolyte No. 2 was chemically unstable and was not finally recommended.

Platinum Group Metal Electrolytes					
Electrolyte designation	Constituents	Concentration	Temperature °C	Cathode current density A/ft ²	Anode
Platinum electrolyte No. 1	{ Pt (as Pt(NH ₃) ₂ (NO ₂) ₂) H ₂ NSO ₂ OH	6-40 g/l 20-100 g/l	65-100	5-100	Platinum
Platinum electrolyte No. 2	{ Pt (as Pt(NH ₃) ₂ (NO ₂) ₂) H ₂ SO ₄ (66° Bé) H ₃ PO ₄ (85 per cent)	6-40 g/l 10-100 ml/l 10-100 ml/l	75-100	5-30	„
Platinum electrolyte No. 3	{ Pt (as H ₂ Pt(OH) ₆) KOH	8 g/l 1.25 g KOH/g Pt	70-80	7.5	
Palladium electrolyte No. 1	{ Pd (as PdCl ₂) NH ₄ Cl HCl (conc.)	25-175 g/l 0-50 g/l 50-700 ml/l	25-85	5-50	Palladium
Palladium electrolyte No. 2	{ Pd (as Pd(NH ₃) ₂ (NO ₂) ₂) H ₂ NSO ₂ OH	15-40 g/l 60-135 g/l	85-100	20-30	

The authors point out that the pre-treatment of the refractory metal is of the utmost importance, total failures occurring when an inadequate procedure was employed. Indeed a considerable part of the report is concerned with this aspect of the problem, and a table of procedures found to be satisfactory is included. Thick, adherent deposits of platinum and palladium could be formed on some metals after a cathodic pre-treatment in an alkali cyanide fused salt mixture containing platinum ions.

Stress measurements of the deposits were taken in a number of instances, and electron probe studies on the effect of high temperature anneals on interdiffusion are reported; little diffusion of the deposit into the substrate took place but diffusion of substrate into deposit was extensive.

This investigation adds a great deal to our knowledge of heavy platinum metal deposition and is to be commended to those working in this field.

J. H.

Effectiveness of Platinum Fuel Cell Catalysts

POSSIBLE ROUTES TO IMPROVEMENTS IN ECONOMICS

Throughout the massive literature on fuel cell research and development run two consistently recurring but conflicting strains; one, the acceptance of platinum as the most effective electrocatalyst, and the other the need to increase its effectiveness—and thus to reduce the amount of metal required—on economic grounds. This problem has been discussed at almost innumerable conferences, and will doubtless remain a lively issue for a long time.

A useful restatement of the position, together with some attempts towards a solution, are contained in three papers recently emanating from the General Electric Research and Development Center, Schenectady. In one of these E. J. Cairns and E. J. McInerney (*J. Electrochem. Soc.*, 1967, **114**, (10), 980) set out the possible routes towards improving the economics of an otherwise feasible fuel cell system operating by the direct anodic oxidation of saturated hydrocarbons as:

- (1) Make more effective use of the platinum by preparing higher area blacks.
- (2) Prepare very high-area platinum on a support which can act as a current collector and perhaps also as an enhancement to the platinum activity.
- (3) Alloy the platinum with other metals in such a way that more activity per unit weight of platinum is obtained.
- (4) Replace the platinum with a less costly, but effective, electrocatalyst.

These authors discount the fourth method, primarily on grounds of resistance to corrosion, and go on to report their work along

approaches (1) and (2). Both the use of higher activity forms of unsupported platinum, particularly one reduced from Adams' catalyst, and the use of carbon-supported platinum were found to be more effective in reducing the amount of platinum required for a given amount of power. In the case of a propane-oxygen fuel cell, a carbon-supported platinum electrocatalyst was able to reduce the amount of platinum required by a factor of around 10 and the view is taken that further improvements are likely.

In the two other papers from General Electric, L. W. Niedrach, D. W. McKee, J. Paynter and I. F. Danzig (*Electrochem. Tech.*, 1967, **5**, 318 and 419), adopting approach (3), are concerned more with fuel cells operating on reformer hydrogen in which resistance to catalyst poisoning by the carbon monoxide impurity in the gas is of major importance. Ruthenium-platinum catalysts prepared by a modified Adams' procedure were found to be markedly more resistant to poisoning than platinum, particularly in the temperature range 65 to 85°C, optimum performance being obtained with catalysts containing about 30 weight per cent ruthenium. The second paper reports similar work on iridium-platinum and rhodium-platinum catalysts, these also showing an exceptional tolerance for carbon monoxide in hydrogen. Such binary mixed oxides were first prepared, and found to have exceptional catalytic properties, by G. C. Bond and D. E. Webster (*Platinum Metals Rev.*, 1965, **9**, 12; 1966, **10**, 10) in the Johnson Matthey Research Laboratories.

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