

ELECTRODEPOSITION OF IRIDIUM

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Platinum group metal deposits are widely used in the hightech areas for a number of applications. Electrodeposited iridium is used for many functional applications. An alloy of platinum and iridium is used as anode for electrochemical oxidative reactions. An attempt is being made at CECRI to develop platinum iridium alloy. A number of iridium electrolytes have been studied and the results are presented in the paper.

Keywords: Electrodeposition, Iridium

INTRODUCTION

Interest in the development of coatings both for corrosion protection and electrical contacts has focussed attention on the electrodeposition of platinum metals. The properties of iridium suggest that it should have many applications as a coating. Some of the applications of iridium plating are: 1. inert electrodes 2. sliding contacts 3. Reflectors and mirrors 4. vacuum tube elements 5. Laboratory equipment and 6. decorative [1].

One of the binary platinum metal alloys of particular interest was platinum-iridium [2] particularly, in view of its advantages over pure platinum as an electrode material. Solid Pt-Ir alloys were known to be more resistant than platinum to corrosion under oxidising acid conditions, and were at one time used as anodes for the industrial production of chlorine from brine. Pt-Ir alloys has a lower over voltage for certain electrode processes, including oxygen evolution in an alkaline electrolyte. With a view to develop the above alloy, the work on iridium deposition was initiated at CECRI.

Published information on iridium deposition is limited to a few brief notes about iridium deposition for use in surface studies. None of the electrolytes was suitable for producing other than very thin deposits [3]. This was due to the very low cathode current efficiencies obtained and in many instances the lack of stability of these solutions. The fused salt bath [4] has undesirable operating conditions, and the sulphamate bath works only with a particular make and involves the use of a auxilliary anode operating with alternating current to improve the stability of the electrolyte

[1]. The only bath which appears to work is the bromide electrolyte and this makes use of the costly ammonium chloroiridate and deposition needs a gold undercoat to obtain a reasonable current efficiency [5]. This paper describes the details on the preliminary studies on the electrodeposition of iridium using different electrolytes.

EXPERIMENTAL

Preparation of the electrolytes

Ammonium bromoiridate: This electrolyte was prepared by dissolving the proprietary bromoiridate salt in water and adjusting the solution pH to 1.9.

Iridium sulphamate: Iridium chloride was heated with sulphamic acid at 333 K [1].

TABLE I: Bath compositions and their operating conditions

Electrolyte	pH	c.d. A/dm ²	Ir.conc g/l	Temp K
A	1.0-1.9	0.2	1.0-2.7	348
B	1.0-2.5	0.15	1.0-8.3	328-353
C	1.5-1.8	0.15-0.3	2.1-4.3	348
D	1.8-7.0	0.15-1.0	1.0-5.0	303-353
E	1.8-2.4	0.15-1.0	1.0-3.0	303-343
F	1.8-2.4	0.15-0.3	2.0-5.0	303-348

A - Ammonium bromo-iridate; B - Iridium sulphamate
C - Iridium bromide from ammonium chloroiridate
D - Iridium nitrite; E - Iridium sulphate

TABLE II: Pretreatments for different substrates

Substrate	Treatment
Copper	Electroclean --> wash --> acid dip --> plate
Nickel	Etching in H_2SO_4 --> wash --> plate
Platinum	Clean in aqua regia --> wash --> plate
Titanium	Etch in CECRI solution --> wash --> plate

Iridium bromide: Prepared by reducing the ammonium chloroiridate [5] at 353 K with constant stirring for 2.5 hours. The iridium sesquioxide $Ir_2O_3 \cdot xH_2O$, precipitated by the controlled addition of sodium hydroxide to the above solution was refluxed with bromine and hydrobromic acid for 4 hours [6].

Iridium nitrite: Iridium oxide prepared as above was heated with sodium nitrite at 333 K [5].

Iridium sulphate: The iridium oxide prepared as above was treated with sulphuric acid [5].

Iridium salts supplied by M/s Arora Matthey Calcutta were used for the study. Six different electrolytes were taken for the study. The electrolytes used and the operating conditions are as given in Table I.

Platinum or platinised titanium anode having twice the area of the cathode was used. Cathodes of copper, nickel plated copper, platinum plated copper, gold plated copper or titanium were used for the study. They were of 5 x 1 cm size, suitably masked to expose an effective area of 2 x 1 cm. Suitable pretreatments were given to the substrates as given in Table II. Experiments were conducted in a thermostated glass vessel containing 30 ml of the plating electrolyte. Fresh solutions were taken every time to assess the effect of the parametric variables. Cathode current efficiency was determined from the mass of metal deposited for a known quantity of energy passed.

TABLE III: Effect of plating time on the efficiency ammonium bromoiridate bath. Ir conc. 2.7 g/l. pH 1.90

Duration mts	Efficiency		Thickness	
	Cu	Ti	Cu	Ti
30	33.70		0.265	
60	24.70	21.34	0.389	0.336
90	22.40		0.528	
120	19.77	7.86	0.622	0.283
180	13.48		0.600	
210	5.00		0.600	

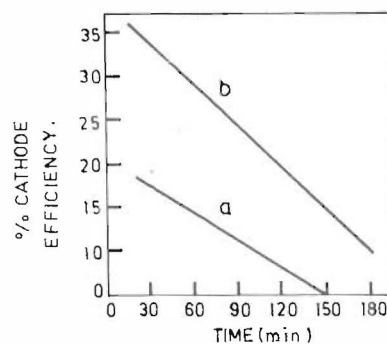


Fig. 1: Variation of current efficiency with time
Bath 1, Ir concn g/l
(a) 1.35 (b) 2.7

RESULTS

Out of the six different solutions tried, the nitrite and sulphate baths did not give any deposit. The bromoiridite bath prepared using the commercially available salt yielded high efficiency of the order of 20% in the beginning of the electrolysis but, gradually showed reduction in efficiency after 30 minutes of electrolysis. The maximum thickness that could be obtained with this bath on copper substrate never exceeded $0.6 \mu m$ at the rate of $0.3 \mu m/hr$ and on titanium only $0.3 \mu m$. (Table III, Fig. 1).

The sulphamate bath yielded an average efficiency of 18% which increased with metal ion concentration in the electrolyte. However, the solubility of hydrated iridium oxide in aqueous media was only $5.0 g/l$. With increase in bath temperature improvement in current efficiency was observed. However, maintenance of the bath with respect to pH and metal ion concentration was very difficult. Also, conversion

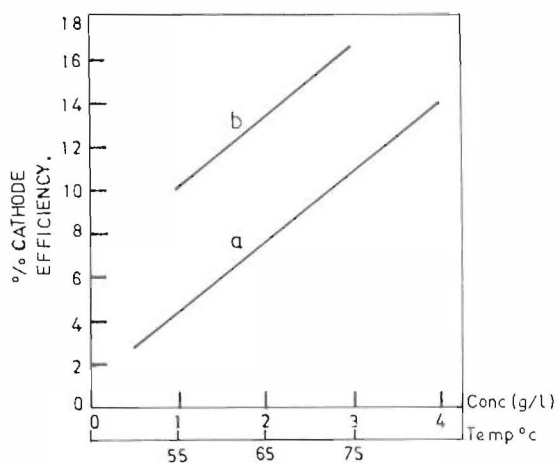


Fig. 2: Effect of temperature and concentration on plating efficiency
Bath 2, a = Concn, b = Temp

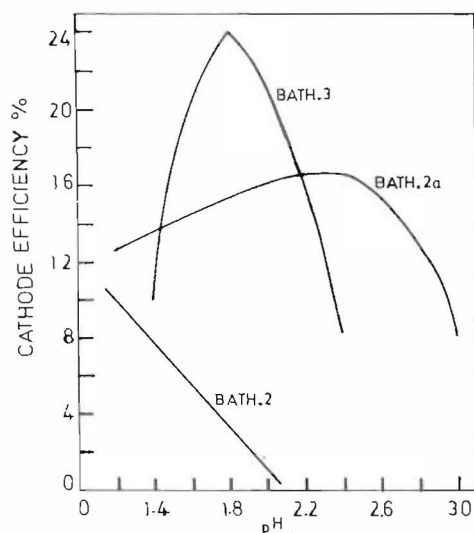


Fig. 3: Effect of pH on cathode efficiency in various baths

of sulphamate to sulphate, as in the case of nickel electrolyte, above 333 K was suspected (Fig. 2).

Fig. 3 shows the behaviour of iridium plating baths at different pH levels. At a concentration of 2 g/l, the sulphamate bath showed a reduction in current efficiency from 10% to 2% when the pH was increased from 1.2 to 2.0. But, at a concentration of 4.3 g/l, the efficiency was maximum at a pH of 2.4 above which gradual precipitation of the bath was observed. The iridium bromide bath showed a maximum of 24% efficiency at pH 1.8 which got reduced to around 8.0 at pH 2.4.

Fig. 4 shows the effect of cathode current density on the current efficiency of iridium deposition in the iridium bromide electrolyte. A sharp increase in the current efficiency was observed at 0.15 A/dm². It was also observed that while plating iridium on platinum or platinum plated copper substrate, an increased efficiency of above 40.0% could be obtained. As given in Table IV, the substrate metal has a tremendous influence in altering the efficiency of deposition, the maximum being obtained with platinum and gold substrates. This agrees with the reported literature [5]. Unlike the ammonium bromoiridate bath, the iridium bromide bath yields consistent efficiency with time. On titanium the efficiency was 42% and 44% at 60 and 120 minutes respectively and deposits more than 3.0 μm have been successfully produced for industrial electrolysis.

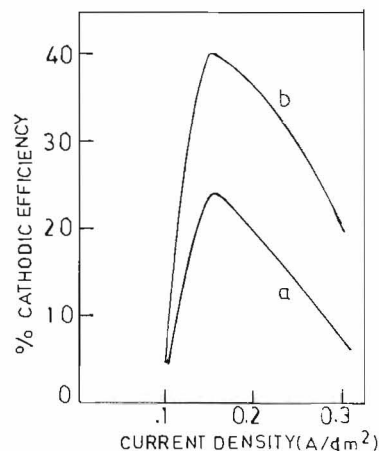


Fig. 4: Effect of current density on cathode efficiency Bath 3 (a) On copper and (b) On platinum

TABLE IV: Effect of substrate material on the current efficiency of iridium deposition

Substrate	Ir concn g/l	c.d. A/dm ²	pH	Efficiency %
Copper	2.15	0.15	1.5	12.0
Copper	4.30	0.15	1.5	25.8
Pt-Cu	2.15	0.30	1.9	20.0
Pt-Cu	4.30	0.15	1.5	40.0
Gold-Cu	4.30	0.15	1.5	39.0
Titanium	4.30	0.15	1.8	44.0

CONCLUSION

Of all the electrolytes tested, the iridium bromide electrolyte prepared from commercially available iridium chloride was found to be good. It is not only cheaper than that prepared using ammonium chloroiridate, mentioned in the literature, but also yields better life and performance and is capable of yielding deposits directly on copper, nickel substrates without the need for any undercoat. Further studies with this electrolyte is however needed to increase the current efficiency.

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