Surface Finishing of the Precious Metals

ELECTRODEPOSITION OF THE PRECIOUS METALS: OSMIUM, IRIDIUM, RHODIUM, RHENIUM, RUTHENIUM
BY TERRY JONES, Finishing Publications Limited, Stevenage, U.K., 2003, 165 pages,
ISBN 0-904477-22-4, £30, U.S.$ 60; post & packaging free in the U.K., £10 Rest of the World

This compilation of review papers written by Terry Jones describes the electrodeposition and electroless deposition of the metals: rhodium (Rh), ruthenium (Ru), iridium (Ir), osmium (Os) and rhenium, from liquid media (primarily aqueous and molten salt). The book is divided into six chapters, with Chapter 1 being an "Introduction to Plating of the Rarer Precious Metals". Each metal has a chapter which begins with a brief account of its plating history. Only the four platinum group metals are highlighted in this review.

The longest chapter, Chapter 2, deals with Rh plating which only began commercially in the late 1920s, possibly due to the high cost and the many processes available. Rh coatings became more popular for industrial and decorative use in the 1930s and 1940s, for instance, silver-plated searchlight mirrors were Rh plated. Rh electrodeposits are hard, tarnish-free, wear and corrosion resistant and Rh has a very high melting point. All the metals share these properties to varying degrees.

Rhodium is very resistant to acidic attack, being insoluble in *aqua regia*, in hot concentrated HCl and in HNO_3. It only dissolves in hot concentrated H_2SO_4 and in fused $KHSO_4$. On heating, it decomposes readily to finely divided metallic Rh sponge, "Rh black", which is a starting material for many Rh compounds.

Modern Rh plating solutions are based on sulfate and phosphate electrolyte. Rh sulfate concentrate is prepared from Rh black. Rh phosphate concentrate is produced from Rh hydroxide. Plating bath performance depends on the preparation sequence. The quality of Rh electrodeposits can be greatly improved by including certain additives in the electrolytes; for example, sulfonic acids improve brightness; selenium works as an anti-stress agent; and crack-free deposits have been obtained by adding a mixture of H_2SO_4, sulfamic acid, thallium nitrate and various sulfonic acids. Data on the properties of the coatings are given.

Chapter 3 deals with Ru electrolytes, which are generally derived from $RuCl_3$. Ru electrolytes are acidic and are operated at high temperature so will corrode most substrates before electrodeposition begins. Thus, substrates should be pretreated, for example, by a gold flash prior to Ru plating.

Chapter 4 relates to electrolytes for Ir plating. Ir has a number of industrial applications, most notably being as a hardening constituent in Pt. Pt-Ir alloys (for jewellery use) are harder and stiffer than pure Pt. Ir is used in Pt-10%Ir thermocouple junctions, and as anode coatings. Processes for the aqueous electrodeposition of Pt-Ir, fused salt electrolyte plating of Ir and Pt-Ir deposits and non-aqueous Ir coating of graphite are described. Metal treatments prior to Ir plating are given.

Osmium is not thought of as an electroplating material. However, Chapter 6, describes Os electrodeposits as very hard and very wear resistant. With the highest work function known and a high melting point, Os was used in thermionic valves. It has high resistance to chemical attack by strong acids, but dissolves in *aqua regia*, molten alkalis and oxidising fluxes. Electroplating processes with Os sulfamate electrolyte, Os hexachloro-osmate and Os nitrosyl complex/sulfamate are reviewed.

The author has spent many years in the metal finishing industry. In his book he provides practical information on many processes and lists the optimum conditions to obtain successful deposits for various plating processes. He gives extensive details of the properties of the deposits. The book is well supported by tables, figures, and by literature and patent references. Supplementary literature has been added at the end of each chapter for up-to-date reading.

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