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The Electrodeposition of Osmium

Osmium is a rare metal with some unique properties. It has the highest work function of any metal and this has led to its use as thin coatings in thermionic devices. It has also been suggested that, because of its high melting point (3050°C), osmium could find application as a coating material for reed switches particularly at higher loads where arcing temperatures are greater. Such uses require the development of methods for producing thin coatings of the metal and a recent paper by J. N. Crosby, of International Nickel (*Trans. Inst. Metal Finishing*, 1976, **54**, (11), 75) describes a novel method for the electrodeposition of osmium.

The new electrolyte is prepared by reacting sulphamic acid with osmium nitrosyl complexes, in particular $K_2[Os(NO)(OH)(NO_2)_4]$. Bright osmium deposits are obtained in both acid and alkaline conditions. However, below pH 7 the current efficiencies are low (~2 per cent) and base metals such as copper have first to be given a protective gold coating. For maximum current efficiency (8 to 12 per cent) the preferred operating range is pH 12 to 14 when a deposition rate of 2 to 3 $\mu\text{m/hr}$ can be achieved. Plating performance is critically dependent on temperature and 70°C is the optimum. A plot of plating rate against current density shows the former to pass through a sharp maximum at 2 to 3 A/dm^2 . An advantage of this system is that it is not markedly dependent on osmium concentration so that it can be run for long periods without replenishment (e.g. from its normal level of 4 g/l Os down to 0.5 g/l Os).

However, this advantage is offset by the electrolyte's unfortunate characteristic of producing blackened deposits after a period of satisfactory operation.

Investigation of the blackening phenomenon showed that an anodic reaction plays a particularly important part in the bath's operation. If an electrolyte producing blackened deposits is operated in the cathode compartment of a divided cell the deposits soon improve and the normal mode of operation can then be resumed. However, continued use in the divided cell leads to a dramatic reduction in efficiency. Furthermore osmium cannot be deposited from a fresh electrolyte in such a cell. Thus a certain amount of anodic oxidation is necessary for the operation of the electrolyte but too much is deleterious. This is consistent with the fact that the current efficiencies of freshly prepared solutions tend to be very low initially and to rise during use.

The osmium deposits obtained under the preferred conditions are bright and adherent but are highly stressed and at thicknesses greater than 1 μm are microcracked. Deposits become dull and heavily cracked at thicknesses of ~6 μm .

An account is given of infra-red studies carried out to elucidate the nature of the electrolytes.

The need to operate this electrolyte with the intermittent use of a divided cell suggests that it is likely to find somewhat limited application, while the highly stressed nature of the deposits tends to reduce the useful thicknesses obtainable.

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