

Cyclic Voltammetry of Cyanide Melts Containing Platinum Group Metals

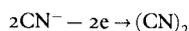
PROGRESS IN UNDERSTANDING PLATING ANOMALIES

The use of molten alkali metal cyanides as solvents during the electrodeposition of the platinum group metals has been reported in this journal on a number of occasions (1,2,3,4). Additionally, the platinum group metals may be recovered from cyanide melts by solvent extraction into liquid metals such as tin or bismuth, but this work is possibly less well known (5,6).

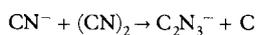
In aqueous solution reactions, cyanides are reducing agents and also form stable complexes with the platinum group metals. This situation also occurs with the fused salts, but is modified by side reactions which reach greater prominence in the melt than in aqueous solution.

This was revealed in a paper presented at a meeting of the American Electrochemical Society by E. Th. van der Kouwe and D. J. Muller, who are part of the team working with K. F. Fouché at the Atomic Energy Board, South Africa. It was reported that high temperature solvent extraction chemistry of the platinum group metals had resulted in an extensive study of oxidation/reduction reactions of the metal ions and of the cyanide melt itself, and their latest paper described cyclic voltammetry of cyanide melts containing most of the Group VIII metals, as well as copper, silver and gold.

The basic melt used was the sodium cyanide-potassium cyanide eutectic. In the melt, the cyanide ion can be oxidised, either electrochemically at the anode, or chemically by reaction with high oxidation state metal ions which results in the formation of cyanogen



Cyanogen reacts with more cyanide ions to produce the dicyanamide ion $\text{N}(\text{CN})_2^-$ which is an oxidant in its own right



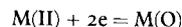
The cyanamide ion, CN_2^- , on the other hand is

a reducing agent, and has been added to melts containing dicyanamide to obtain control of the redox potential of the melt.

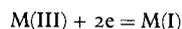
Metal-containing melts were made either by adding the appropriate metal cyanides or by anodic dissolution of the metal. Cyclic voltammetry was carried out over the range 0 to 1.9V with respect to a sodium reference electrode, these limits being imposed by the generation of sodium or potassium on the one hand and by the oxidation of cyanide ions on the other.

Of all the metals tested titanium was found to be the most resistant to attack with the potential at the anodic limit; dissolution of the other metals was apparently increased by the dicyanamide which formed under these conditions. Some of the metals were dissolved at potentials less than 1.9V, notably palladium, rhodium and gold.

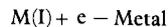
Most platinum group metals showed more than one oxidation state when dissolved in the melt; rhodium and iridium occurred as M(I) and M(III) and platinum and palladium as M(II), M(I) and M(O); the M(O) state being produced by a two electron transfer reaction with soluble reactants and products:



Reduction of rhodium and iridium is a two stage process:



which is reversible, followed by:



However, for iridium a stripping peak showing this reaction in reverse was not found, the only dissolution reaction for iridium being a direct oxidation to Ir(III) at the anodic limit.

Gold and silver peaks were also obtained by cyclic voltammetry but the cyanide medium is

too reducing and both metals are precipitated. Nickel and cobalt showed differences in behaviour from the noble metals in that the potential of the reversible redox reaction and the metal deposition potential are very close together. Cobalt also shows an unusual peak shape.

This work is of special interest to those actively engaged in fused salt plating with platinum metals and goes a long way towards explaining some of the apparent anomalies that exist in the published literature of this electroplating art.

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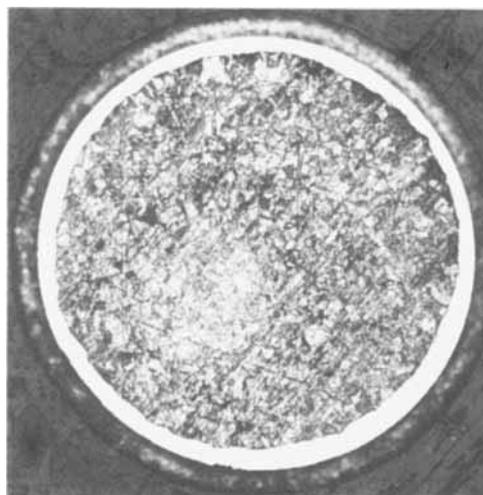
References

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Platinum Plated Palladium Leadout Wires

Platinum resistance temperature detectors can be used with suitable electrical instruments to measure or control temperatures between -70 and 600°C , over which range the relationship between electrical resistance and temperature is approximately linear. Initially the platinum was used in the form of a wire coil but now thick film resistance detectors have been developed and are finding increasing industrial application, while in addition they have great potential for domestic use. These detectors comprise a resistance track of high purity platinum film bonded to an inert ceramic substrate and protected from the environment by a glaze. To achieve the required resistance only a thin particulate film is needed, and as both the production and the checking stages are largely automated the devices are relatively low cost items (W. D. J. Evans, *Platinum Metals Rev.*, 1981, **25**, (1), 2-11).

The ends of the thermometer resistance element, whether wire wound or thick film, have to be attached to the instrumentation in a reliable manner. A robust connection that will give long life free from corrosion at temperatures up to 600°C is required, while thermal e.m.f.s must be avoided where the leadout wires are joined to the device. In the past, platinum wire has invariably been used to make the initial connection but now a suitable cost effective alternative is available. Using a fused salt technique Johnson Matthey Metals Limited has produced a palladium-cored wire coated with platinum. Typically, 20 microns of platinum is employed, this thickness of plating being both uniform and non porous, and the wire may be resistance welded to the usual base metal extension wires without difficulty. This



The thickness and uniformity of the platinum coating may be checked by microscopical examination of cross-sections of the wire. The outer edge of the platinum is preserved by plating the wire with copper prior to sectioning, but this is partially removed when the polished specimen is chemically etched to differentiate between the platinum plating and the palladium core. The section here is reproduced at a magnification of approximately $\times 125$

material is now being used by Matthey Printed Products Limited on their Thermafilm[®] detectors, and it has proved to be an effective alternative to pure platinum.

It is anticipated that fused salt platinum plated palladium will find additional applications where similar conditions are encountered, and similar properties required.

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