Electrodeposition of Platinum Metals from Molten Cyanides

A TECHNIQUE APPLICABLE TO ELECTROFORMING

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Platinum, palladium and iridium coatings have been electrodeposited on a variety of substrates from molten cyanides and the techniques, which are described in this paper, have also been used to electroform platinum and iridium crucibles. While the platinum and palladium electrolytes were prepared and used in vessels open to the atmosphere the molten iridium cyanide baths were kept under argon.

Atkinson (1), Withers and Ritt (2, 3), and Rhoda (4) described the electrodeposition of platinum group metals from molten cyanides under atmospheres of nitrogen or argon. However, the available information about the apparatus used in these experiments raises the possibility that the atmospheres over the molten electrolytes were not completely free of air. Later, work done by the Bureau of Mines in sealed systems showed that satisfactory deposits of iridium and rhodium do require an inert atmosphere (5, 6). On the other hand, good, thick deposits of platinum and palladium were made only in the presence of air (7, 8). Methods developed by the Bureau of Mines for electrodeposition of platinum, palladium, and iridium are described in this paper. A picture showing the tips of crucible tongs coated with platinum and electroformed crucibles of platinum and iridium appeared in an earlier issue of this Journal (9) and the Metals Research Department of Degussa, Frankfurt, Germany, has also shown objects plated with platinum in a molten cyanide bath (10).

Experimental Method

Platinum, palladium, and iridium were electrodeposited from molten sodium cyanide or from 50–50 weight per cent mixtures of sodium cyanide and potassium cyanide to which the metal ions had been added. The electrodeposition of platinum and palladium and the preparation of the corresponding electrolytes were done in vessels open to the atmosphere. Iridium electrolyte was prepared and used under argon.

Reagent grade sodium cyanide and potassium cyanide were used in preparing electrolytes. After drying the salts in a vacuum oven at 120°C for 2 hours, the metal ions were added by D.C. electrolysis using an anode of the particular platinum group metal and a cathode of the same metal or of molybdenum. Coatings were generally made with electrolytes that contained 1 to 3 per cent of the metal. Initially, the electrolyte temperature was 600°C for sodium cyanide and 550°C for sodium cyanide–potassium cyanide. When the electrolyte was prepared and used in contact with air, some of the cyanide was oxidised to cyanate and carbonate. The melting points of these baths decreased as the compositions changed and, consequently, they were operated at decreasing temperatures, generally 25 to 50°C above the melting point. Since the iridium cyanide bath was always kept in an inert atmosphere when molten, its operating

Fig. 1 An Inconel rod, 0.32 cm diameter, and a 0.64 cm diameter Inconel-sheathed Chromel-Alumel thermocouple with platinum coatings of 9.5 mils and 6 mils, respectively

temperature remained constant.

Mullite crucibles with volumes of 250 to 400 ml were used to contain the electrolyte and the electrodes. They were, in turn, positioned in an Inconel pot, which was heated in a resistance furnace. Cathodes were often in the form of sheet, 0.25 inch wide and 1 or 2 inches long, but coatings were also put on short rods, the tips of laboratory tongs or forceps, and thermocouple sheaths. Crucibles were electroformed. The cell usually had two anodes of the metal being plated, each 0.25 inch wide. These were immersed to a depth of 1 inch and positioned one on each side of the cathode. When the cathode had a shape other than that of a simple rod or sheet, it was surrounded by three or more sheet anodes. Cathode current densities varied from 5 to 30 mA/cm² and anode current densities varied from one-quarter to twice the cathode current density. Cell voltages were about 0.8 volt during the initial periods of platinum or palladium electrolyte formation and 0.1 to 0.2 volt when electrodepositing coatings of these metals at current densities of 10 to 20 mA/cm². Cathodes were generally rotated at 120 rpm during electrodeposition and the direction of rotation was reversed every 30 minutes. However, cathodes with special shapes were sometimes kept stationary.

Prior to electrodeposition, metal cathodes were prepared by wet pumicing, washing in distilled water, rinsing in ethyl alcohol, and drying in a flow of warm air. When successive deposits were made on the same cathode, the coating was smoothed between deposition periods by removing loose material, filing off dendrites, and polishing with 240-grit emery paper. The total quantity of electricity used for electrodeposition was measured with a copper coulometer and the number of coulombs thus determined was used in calculating both the cathode and the anode current efficiencies.

Platinum

Bright, smooth, and adherent deposits of platinum were made on molybdenum, tungsten, Inconel, columbium, stainless steel, and copper and on graphite precoated with palladium. Cathode current efficiencies were

as high as 76 per cent on the basis of bivalent platinum ions; apparent anode current efficiences were 98 to 150 per cent. Many deposits were approximately 63.5 μm (2.5 mils) thick and were made at the rate of 12.6 to 20.2 μm (0.5 to 0.8 mil) per hour. Much thicker coatings were sometimes made by putting successive deposits on the same cathode, with removal of loose material, smoothing, and pumicing the surfaces between deposits. Attempts to form platinum coatings in inert atmospheres resulted in thin deposits at very low current efficiencies.

Figure 1 shows a 0.32 cm diameter Inconel rod and a 0.64 cm diameter Inconel sheathed Chromel-Alumel thermocouple with platinum coatings. The 241 μm (9.5 mils) coating was put on the rod in four plating periods with a total time of 16.83 hours (rate, 14 μm/h). A freshly prepared platinum–sodium cyanide electrolyte was used. The 152 μm (6 mils) coating was put on the thermocouple in two plating periods with a total time of 9 hours (rate, 17 μm/h). The platinum–sodium cyanide electrolyte in this case had been in use for 115 hours before this coating was made; it was maintained by occasional additions of fresh sodium cyanide. Neither of these objects was rotated during the electro-deposition. The cathode current densities were 10 to 14 mA/cm^2 and the current efficiencies were 74 to 71 per cent, respectively. The coatings thus formed were bright, smooth and adherent.

Molybdenum rods, 0.64 cm in diameter and 2.22 cm long, were encapsulated first with 63.5 μm (2.5 mils) of iridium as a diffusion barrier and then with 101 μm (4 mils) of platinum. Iridium was electrodeposited from an electrolyte that had been in use 45 hours, and platinum from one with 100 hours of use.

Platinum Coatings on Graphite

The graphite surfaces were cleaned with ultrasonic agitation, first in a solution containing sodium hydroxide, sodium phosphate, sodium carbonate, and a wetting agent and then in boiling water. Before platinum coat-

ings were put on, the surfaces were precoated with 1 or 2 mils of palladium from an aqueous bath (palladium chloride, 50 g/l; hydrochloric acid, 400 ml/l; ammonium chloride, 20 g/l). Protective coatings of platinum, 4.5 to 7 mils thick, were then applied as previously described. The precoat prevents the rapid absorption of molten salt when the sample is first placed in the bath. If this is allowed to happen, considerable quantities of salt will be trapped under the platinum coating. Later, when the specimen is heated, the salt will melt and rupture the coating, exposing the graphite to oxidation. Figure 2 shows a graphite rod encapsulated with a precoat of palladium and 114 μm (4.5 mils) of platinum. Such encapsulated specimens were evaluated in a thermogravimetric apparatus. It was found that they lost an average of 3 mg per hour at 1400°C and that the coatings were still adherent and effective after several hours at this temperature. Similar graphite specimens without coatings lost 120 mg per hour at a temperature of 600°C.
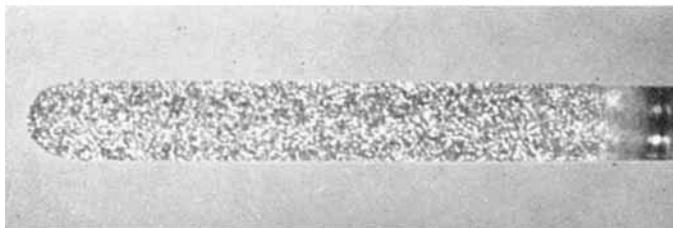
Palladium

Bright, smooth, adherent deposits of palladium were made on molybdenum or graphite. Figure 3 shows a 4.5 mil deposit of palladium on a molybdenum rod. Temperatures varied from 575 to 445°C for the sodium cyanide-potassium cyanide baths. Cathode current efficiencies ranged from 35 to 70 per cent on the basis of the discharge of bivalent palladium ions. Apparent anode current efficiencies were 120 to 140 per cent when the cathode and anode areas were equal, and 300 to 400 per cent when the anode area was about 4 times the cathode area. The presence of air was found to be essential for the formation of good deposits, but again there was oxidation of cyanide, and in palladium baths this oxidation was rapid. After the first few hours of electrolysis, there was a steady accumulation of white, flocculent material in the bath, chiefly sodium carbonate. Later, there was also some finely divided palladium metal. As these changes occurred,

Fig. 2 A graphite rod, 0.64 cm diameter, encapsulated with a precoat of palladium and 4.5 mils of platinum
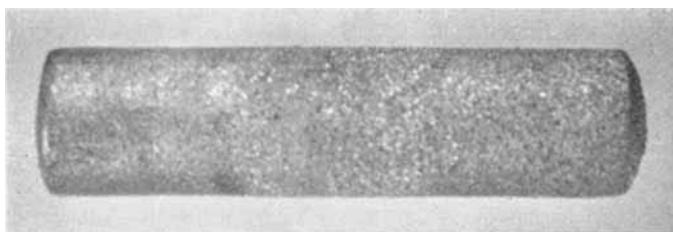
Fig. 3 A 4.5 mil deposit of palladium on a 0.64 cm diameter molybdenum rod. Bright, smooth, adherent deposits of palladium have been made on molybdenum and graphite

the palladium deposits became less adherent. Eventually, in 10 to 20 hours, the bath became inoperable.

Iridium

The electrodeposition of iridium in adherent, compact form from molten sodium cyanide baths at 600°C under an argon atmosphere was described by Andrews and others (5). Only thin deposits, often cracked and non-adherent, were formed when these processes were conducted in the presence of air. In experiments performed after the paper by Andrews and others was prepared, deposits of iridium were made on nickel, Inconel, copper, molybdenum, AM 353 steel, and 403 steel. The cathode current densities were usually 20 to 30 mA/cm² and the anode current density was 15 mA/cm². The deposits were up to 63.5 μm (2.5 mils) thick. Cathode current efficiencies were usually 25 to 40 per cent, assuming the discharge of trivalent

Fig. 4 Crucibles produced by electroforming in molten cyanide electrolytes. Crucible (A) is iridium while (B) and (C) are platinum. In all cases the platinum group metal was built up on the mandrel in a series of deposits, each of which was followed by careful grinding and polishing
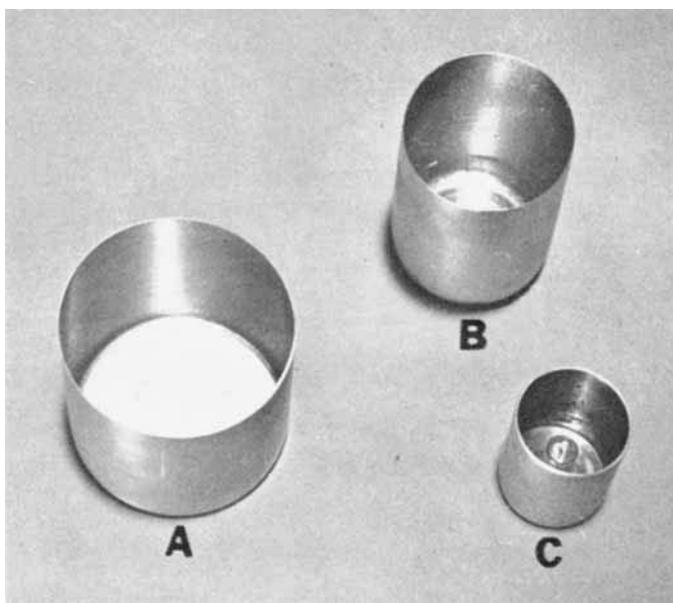
iridium ions; deposition rates were about 10 μm (0.4 mil) per hour. However, in one group of experiments 2.5 μm (0.1 mil) deposits were made on nickel discs with cathode current efficiencies up to 66 per cent. Apparent anode current efficiencies were sometimes less than 100 per cent, but more often they were 120 to 150 per cent. The best deposits of iridium were made when the cathode was rotated at 120 rpm. Deposits made on stationary cathodes were often cracked and non-adherent; deposits on cathodes rotating at 30 rpm were better, but even these had some loose material.

Electroforming

Platinum and iridium crucibles were electroformed from molten cyanide baths by the electrodeposition methods previously described, using mandrels of copper for platinum and of molybdenum for iridium. The general procedure was to electroplate the platinum group metal on the mandrel to the desired thickness in a series of successive deposits, with careful grinding and polishing of the surface between deposition periods. The initial deposit of platinum or iridium was always made over the entire surface of the mandrel, including the top. Later deposits were made on enough of the mandrel surface

to give a crucible of the desired depth. When the deposit reached the desired thickness the top of the piece was cut away and the mandrel was dissolved away with nitric acid.

Crucibles electroformed in this way are shown in Figure 4. Crucible (A), made of ridium, is 0.75 inch deep and has a 1 inch inside diameter with a 5 mil wall thickness. The crucible (B) is of platinum; it is 1 inch deep, the inside diameter is $\frac{3}{4}$ inch, and the wall thickness is 5 mils. Crucible (C) is also made of platinum and has a thermocouple well for differential thermal analysis work. This crucible is $\frac{5}{8}$ inch deep with a $\frac{1}{2}$ inch inside diameter and a wall thickness of 15 mils.

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Catalysts for Removing Oxygen from Stack Gases

A number of processes have been developed for the removal of air pollutants such as nitric oxide and sulphur dioxide from stack gases and one of these catalytically reduces the pollutants with carbon monoxide. Stack gases generally contain 1 to 3 per cent oxygen and there are a number of reasons why it is necessary to remove this prior to the gas entering the main catalytic reactor.

Ajay Sood, C. W. Quinlan and J. R. Kittrell of the University of Massachusetts have reported a comparison of the activities of several catalysts for the reduction of oxygen with carbon monoxide, both in the presence and in the absence of sulphur dioxide (*Ind. Eng. Chem., Prod. Res. Dev.*, 1976, **15**, (3),

176–179). Although initial testing of the catalysts was done using dry cylinder gas, three catalysts were also evaluated using wet flue gas.

The results demonstrated that in the presence of sulphur dioxide, of which 2500 ppm are typically present in stack gases, supported platinum and palladium catalysts were superior to the others tested. It is concluded that both alumina supported platinum and palladium have potential for the removal of oxygen from stack gases. The relative activity of these two was difficult to compare because of the experimental conditions; the platinum being supported on monolithic alumina while the palladium was on pellets.