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Electrodeposition of Platinum-Group Metals

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ELECTRODEPOSITION OF PLATINUM-GROUP METALS

by

David Schlain,[1] F. X. McCawley,[2] and G. R. Smith[3]

ABSTRACT

The Bureau of Mines investigated methods for electrodepositing platinum-group metals from molten cyanide baths. The preparation of thick, protective coatings on molybdenum, Inconel, graphite, stainless steel, copper, and other structural metals were studied, as well as the electroforming of platinum and iridium crucibles. Iridium, rhodium, and ruthenium can be electrodeposited under an inert atmosphere, while platinum and palladium require the presence of air. Electrolytes may be prepared by direct-current electrolysis in NaCN or mixtures of NaCN and KCN using anodes of the particular platinum-group metal. When the concentration of metal increases to about 0.3 or 0.4 percent, the deposits become bright, adherent, and coherent. Current densities may be 10 to 25 ma/cm^2, and plating rates are often 0.5 mil/hr. Platinum and palladium baths deteriorate because of the oxidation of cyanide to cyanate and carbonate, and the precipitation of metal. Changes in the platinum cyanide bath are relatively slow. The protection against oxidation afforded by the platinum-group metal coatings is evaluated by testing encapsulated specimens in a thermogravimetric balance. Surface pretreatment and the use of undercoats are discussed.

INTRODUCTION

Modern technology often requires the use of structural materials that combine high strength with resistance to oxidation and corrosion at high temperatures. Molybdenum, tungsten, columbium, and alloys of these metals retain their strength at high temperatures but are readily oxidized and are generally reactive at elevated temperatures. On the other hand, the platinum-group metals and some of their alloys have superior resistance to oxidation and corrosion at high temperatures and are often ductile, but these metals have low strength-to-weight ratios and are scarce and expensive. Therefore,

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refractory metals with suitable protective coatings of a platinum-group metal would have valuable combinations of properties and, if such coatings were available, they would find many applications. In certain circumstances, some of the more common structural metals, such as stainless steel, Inconel,[4] nickel, and titanium may also require a coating of a platinum-group metal. Platinum-group-metal coatings on an appropriate, less costly metal could sometimes be substituted for solid structures of platinum. Finally, advances in electroplating technology could result in electroforming certain complex shapes of the platinum-group metals that are difficult to fabricate by normal methods. This is especially true of iridium. To achieve these objectives, deposits of the platinum-group metals would have to be thicker than 1 mil. The techniques now in commercial use for forming decorative coatings of these metals, usually of the order of 0.1 mil in thickness, involve electrodeposition from aqueous baths.

Experimental deposits of platinum-group metals made from molten cyanide baths have been described by Atkinson (4),[5] Withers, and Ritt (12-13), and Rhoda (9). However, some of the reported results are inconsistent. In his patent, Atkinson claims to strip coatings of the platinum-group metals and redeposit them in molten cyanides under an atmosphere of nitrogen, but he does not describe his apparatus nor does he discuss his results in detail. Withers and Ritt were successful in electroplating iridium from a bath containing 70 parts of sodium cyanide and 30 parts of potassium cyanide by weight at a temperature of 500° C under a flow of argon. Rhoda later reported that he was able to make good deposits of iridium and platinum from molten sodium cyanide at 600° C under a flow of argon, but he was not able to deposit palladium or rhodium and he obtained less than satisfactory deposits of ruthenium. Careful review of descriptions of the apparatus used by Withers and Ritt and by Rhoda leads to the belief that in both instances the atmospheres over the molten electrolyte were not completely free of air. This hypothesis is supported by the results obtained in this Bureau of Mines investigation.

In the initial stage of these studies, aqueous baths were developed by Cramer, Kenahan, Andrews, and Schlain (5) and Cramer and Schlain (6) for electrodepositing thick coatings of platinum, palladium, rhodium, and iridium. One difficulty, the tendency for poor adherence on some substrates because of thin surface layers of oxides, was overcome by pretreatment in research by Andrews, Cramer, Kenahan, and Schlain (1), and Pennington and Cramer (7). Another problem emerged when thick coatings of platinum were electrodeposited in aqueous baths--highly stressed and cracked deposits--and it was not solved so readily. Heat-treating was sometimes effective in eliminating stress. It should be noted that high internal stresses and cracking did not appear as major problems when palladium was electrodeposited in aqueous baths.

Later, research on the electrodeposition of platinum-group metals from molten cyanide baths was undertaken to avoid the difficulties associated with

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[4] Reference to trade names is made for information only and does not imply endorsement by the Bureau of Mines.

[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

the use of aqueous baths. The presence or absence of air was shown to be the key factor in electrodeposition from molten cyanides. Data of Andrews, Kenahan, and Schlain (3), and Smith, Kenahan, Andrews, and Schlain (11) have shown that an inert atmosphere is essential for the formation of thick, coherent, adherent deposits of iridium and rhodium. On the other hand, platinum and palladium were electrodeposited in the presence of air by Andrews, Smith, Kenahan, and Schlain (2). This report includes the results of research on the electrodeposition of platinum, palladium, and ruthenium as well as some additional work with iridium. A picture showing objects coated with or electroformed of platinum or iridium in molten cyanide baths was published earlier by Schlain, McCawley, and Smith (10). A publication of the Metals Research Department of Degussa, Frankfurt, Germany, also shows objects plated with platinum in cyanide baths (8).

EXPERIMENTAL TECHNIQUES

Platinum-group metals were electrodeposited from molten sodium cyanide or mixtures of sodium cyanide and potassium cyanide to which the appropriate metal ions had been added. Some platinum-group metals were electrodeposited in the presence of air, while others required an inert atmosphere. On the other hand, electrolyte temperature, cathode and anode current densities, electrode configuration, cathode rotation, and platinum-metal concentration in the electrolyte are less critical conditions, and these may vary over wide ranges.

Electrodeposition of Coatings

Reagent-grade sodium cyanide and potassium cyanide were used in preparing the electrolytes. As analyzed by a commercial firm, the sodium cyanide contained the following impurities, in percent: Cl, 0.1; PO_4, 0.006; SO_4, 0.01; S, 0.004; CNS, 0.02; Fe, 0.003; and Pb, 0.0005. Impurities in the potassium cyanide follow, in percent: Cl, 0.35; PO_4, 0.004; SO_4, 0.03; S, 0.002; CNS, 0.02; Fe, 0.01; Pb, 0.0001; and Na, 0.28. Prior to preparation of electrolytes, the salts were dried in a vacuum oven at 120° C for 2 hours. The platinum-group metal was generally added to the molten cyanide by direct-current electrolysis at 600° C. Platinum was sometimes added to the molten electrolyte as $PtCl_2$.

Mullite crucibles with volumes of 250 to 400 ml were used to contain the electrolyte. Typically, the cell had two anodes, 0.25 inch wide and immersed to a depth of 1 inch, made of the particular platinum-group metal being plated and positioned one on each side of the cathode. The cathodes had many shapes and were made of several materials. In most experiments, they were sheets or rods 0.25 inch in width or diameter and 1 or 2 inches long. However, the cathode was sometimes a mandrel shaped like a crucible, the tips of laboratory tongs or forceps, a bent rod, or a flat piece of metal with a special shape. When the cathode had a shape other than that of a simple rod or sheet, it was often surrounded by three or more anodes instead of the usual two. The most common cathode material was molybdenum or graphite, but deposits were also made on nickel, Inconel, copper, tungsten, columbium, stainless steel, and several other types of steel. In most experiments, the cathode was rotated

at 120 rpm during electrodeposition, and the direction of rotation was reversed every 30 minutes. The electrolytic cell was contained in an Inconel pot, which was heated in a resistance furnace. The atmosphere over the cell was either argon or air, depending on the particular metal being electrodeposited. When the process required an inert atmosphere, the pot was tightly sealed to insure the total exclusion of air. A drawing of this apparatus was included in an earlier publication by Smith, Kenahan, Andrews, and Schlain (11). Before each experiment, the pot was evacuated and refilled with argon several times. The flow of argon was maintained at 350 ml/min during heating, electrolysis, and cooling. An interchange chamber made it possible to make a deposit in an argon atmosphere at an elevated temperature and to cool and remove the cathode with its deposit, without allowing the hot cell or the hot deposit to come in contact with air or moisture. In experiments in which the molten electrolyte was to be exposed to air during electrodeposition, the electrolyte cell was heated in an open pot furnace. The temperature of the electrolyte was kept constant by a Chromel-Alumel thermocouple and an electronic controller-recorder. A constant direct-current power supply was used for electrodeposition.

Prior to immersion in the electrolyte, the cathode was prepared by wet-pumicing, washing in distilled water, rinsing in ethyl alcohol, and drying in a flow of warm air. After the deposit was removed from the cell, it was washed in boiling distilled water, rinsed in alcohol, and dried in a steam of warm air. When successive deposits were made on the same cathode, the coating was smoothed between deposition periods. This usually consisted of removing loose material, filing off dendrites, and polishing with 240-grit emery paper. Then the surface was pumiced, washed, rinsed, and dried as previously described. In starting and stopping a run, the circuit was normally made and broken by lowering or raising the cathode into or out of the electrolyte. The exception to this rule was when, in electroforming experiments, the cathode was a relatively large mass of metal in the form of a mandrel. Electrolyte coming in contact with this quantity of cold metal quickly solidified on the surface and then redissolved in an uneven manner, causing local areas of high current density and hence a rough deposit. To avoid this problem, the mandrel was placed in the bath and allowed to heat up for about 5 minutes before the current was applied.

The total quantity of electricity used for electrodeposition was measured with a copper coulometer. The number of coulombs thus determined was used in calculating cathode and anode current efficiencies. Any metallic deposit that fell off during the washing operation or could be removed by scraping was classified as "nonadherent deposit." Cathode current efficiencies were calculated using the weight of the "adherent deposit."

Mullite crucibles sometimes cracked when the cold melt was reheated. In the later experiments of the program, this was avoided in the case of the platinum cyanide baths by pouring the molten bath from the mullite crucible into a silica crucible with a smaller diameter. When beginning the next experiment, the cold melt was transferred to the mullite crucible and remelted.

A technique of encapsulation was developed primarily for use with those specimens that were to be tested in the thermogravimetric balance. The substrate specimens were rods, 0.62 cm (0.25 inch) in diameter and 2.54 or 3.175 cm (1 or 1.25 inches) long. The ends of the rods were rounded. During the first step in the encapsulation, the specimen was immersed to a depth of 1.90 or 2.54 cm (0.75 or 1 inch) and, as the coating proceeded, periodically raised in 0.635-cm (0.25-inch) steps to an immersion level of 0.635 cm (0.25 inch). Then the ends were reversed and the process was repeated. The final result was a completely covered specimen with a broad overlap band that tended to prevent breaks in the coating.

Evaluating Coatings

A continuously recording thermogravimetric apparatus was used to evaluate the protection against oxidation that is given to substrates such as molybdenum or graphite by coatings of the platinum-group metals. Encapsulated specimens were positioned on a balance in a stream of air as the temperature was raised from room temperature to 1,400° C at some constant rate. The temperature was increased at 238° C per hour in some experiments and at a somewhat higher rate in others. The temperature at which the coating was said to fail was that at which rapid oxidation occurred, as indicated by a rapid loss in weight.

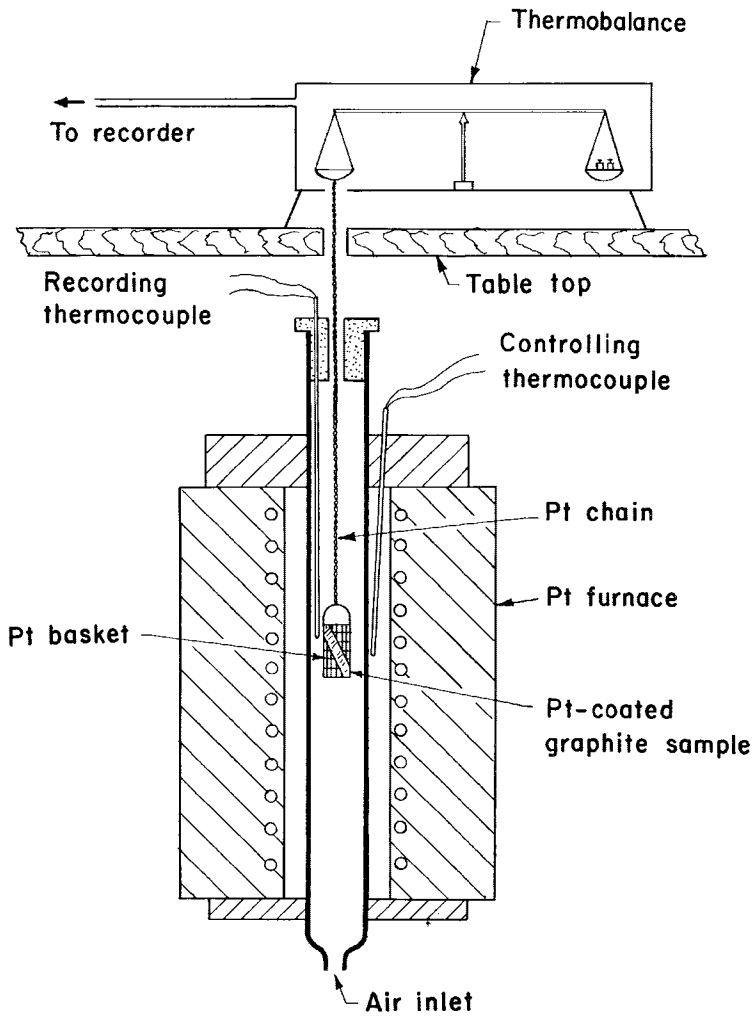

FIGURE 1. - Thermogravimetric apparatus used to evaluate protection against oxidation given by coatings.

The thermogravimetric apparatus included a vertically positioned tube furnace with a mullite combustion tube and a chemical balance (fig. 1). The test specimen was in a platinum basket located in the center of the tube and suspended from one of the balance pans. The tube was 4.45 cm (1.75 inches) in diameter and had a volume of 600 ml. Dry air that had been preheated in a 17.8-cm (7-inch) bed of crushed firebrick was passed into the tapered bottom end

of the combustion tube at the rate of 300 ml/min. The sample temperature was recorded by means of a platinum versus platinum-10 percent rhodium thermocouple located near the lower end of the specimen. The temperature of the furnace tube was controlled by means of a second thermocouple placed just outside the platinum basket. A recorder connected to the balance gave a continuous record of weight changes for the specimen.

IRIDIUM, RHODIUM, AND RUTHENIUM

The electrodeposition of iridium and rhodium in adherent, compact form from molten sodium cyanide baths at 600° C under an argon atmosphere was described in earlier papers. Andrews, Kenahan, and Schlain (3) made smooth, adherent deposits of iridium up to 127 μm (5 mils) thick on molybdenum from a bath contain 2 percent or more of iridium at a current density of 50 ma/cm^2. A 382-μm (15-mil) coating was made in several stages; surface nodules were removed between deposits. Smith, Kenahan, Andrews, and Schlain (11) obtained adherent, compact deposits of rhodium up to 198 μm (7.8 mils) thick on molybdenum or tungsten from a bath containing 0.8 to 0.9 percent rhodium at a current density of 10 ma/cm^2. The inert atmosphere is essential for the formation of satisfactory coatings of iridium and rhodium. Only thin deposits, often cracked and nonadherent, were formed when these processes were conducted in the presence of air. Smith, Kenahan, Andrews, and Schlain (11) also reported that the rhodium bath deteriorated rapidly in an air atmosphere, as indicated by the precipitation of finely divided rhodium metal and the loss of the yellow color.

In experiments performed after those of Andrews, Kenahan, and Schlain, smooth, coherent, adherent deposits of iridium were made on nickel, Inconel, copper, molybdenum, AM 353 steel, and 403 steel from molten sodium cyanide baths at 600° C in argon atmospheres. The electrolytes contained 1 to 3 percent iridium and were prepared by direct-current electrolysis with iridium electrodes. The cathode current densities were usually 20 to 30 ma/cm^2, the anode current density was 15 ma/cm^2, and the deposits were up to 63.5 μm (2.5 mils) thick. Cathode current efficiencies were usually 25 to 40 percent, assuming the discharge of trivalent 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 disks with cathode current efficiencies of up to 66 percent. The best deposits of iridium were made when the cathode was rotated at 120 rpm. Deposits made on stationary cathodes were often cracked and nonadherent; deposits on cathodes rotating at 30 rpm were better, but even these had some loose material. Apparent anode current efficiencies were sometimes less than 100 percent but more often they were 120 to 150 percent.

Smooth, adherent deposits of ruthenium were put on molybdenum from an electrolyte containing 60.3 mole-percent (53 weight-percent) NaCN and 39.7 mole-percent (47 weight-percent) KCN in an argon atmosphere at 550° C and at a current density of 10 ma/cm^2. The cathode was rotated at 120 rpm. Apparent cathode current efficiences were as high as 137 percent on the basis of trivalent ruthenium, presumably because at least some of the ruthenium ions in the bath were in a lower valence state. A 152-μm (6-mil) deposit of ruthenium

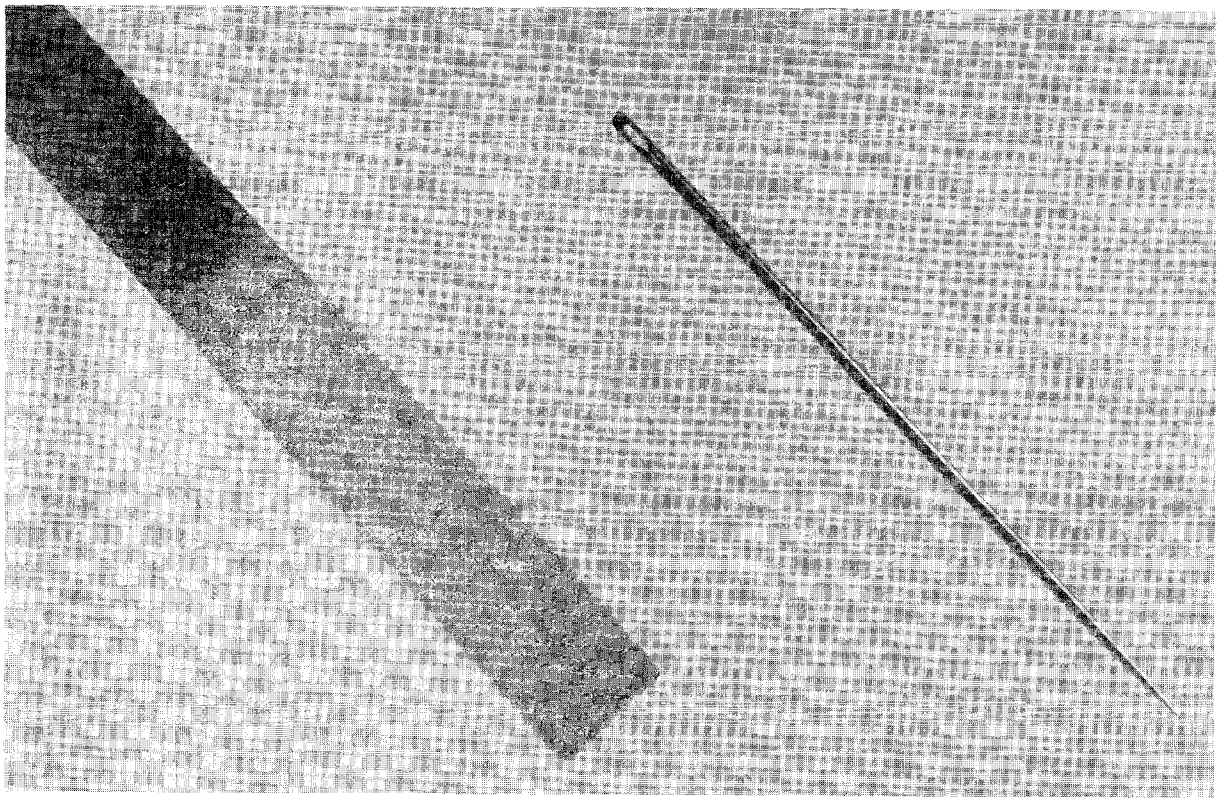

FIGURE 2. - A 0.64-cm-wide molybdenum sheet coated with ruthenium 152 μm (6 mils) thick.

was formed during several deposition periods with smoothing between deposits (fig. 2). The electrolyte was prepared by direct-current electrolysis. During the initial period of the preparation, an insoluble black film formed on the anode surfaces and had to be removed mechanically. According to X-ray diffraction analyses, this film had a structure similar to RuS_2. It probably was formed as a result of small amounts of sulfur compounds present in the cyanides used in preparing the electrolyte. Eventually, the formation of the film stopped.

PLATINUM

Electrodeposition of Platinum Coatings

Platinum was electrodeposited under an air atmosphere from molten salt baths of sodium cyanide or 50-50 weight-percent mixtures of sodium cyanide and potassium cyanide. The electrolyte temperature varied over wide ranges, being 465° to 575° C for sodium cyanide, and 475° to 525° C for sodium cyanide-potassium cyanide mixtures. Deposits were made on molybdenum, tungsten, Inconel, columbium, stainless steel, and copper, and on graphite precoated with palladium. Cathodes were often in the form of sheet 0.635 cm (0.25 inch) wide and 2.54 or 5.08 cm (1 or 2 inches) long, but objects with other shapes were also coated. Crucibles were electroformed. The anodes were made of

platinum. There were usually two of them, in the form of strips 0.25 inch wide and immersed to a depth of 1 inch. The anode configuration was modified when the cathodes had special shapes. Cathode current densities were 5 to 25 ma/cm^2, and anode current densities varied from one-half to twice the cathode current density. Cell voltages were about 0.8 volts during the periods of electrolyte formation and 0.1 to 0.3 volts during the formation of coatings. The cathodes were generally rotated at 30 to 120 rpm, but those with special shapes were sometimes kept stationary during electrodeposition. The surfaces of the platinum deposits tended to have small amounts of loose material, especially on the sharply pointed areas, such as the extreme tips of forceps. This loose material could be minimized by using a large enough anode area properly positioned, by using low current densities, and by limiting the thickness of the individual deposits.

Platinum deposits were bright, smooth, and adherent. Cathode current efficiencies varied from 30 to 76 percent on the basis of bivalent platinum ions; apparent anode current efficiencies were often 98 to 150 percent. 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, and removing loose material, smoothing, and pumicing the surfaces between deposits.

Typical electrolytes contained 1 to 3 percent platinum. Starting with 400 grams of the pure cyanide, they were prepared by direct-current electrolysis in the presence of air with platinum anodes and a cathode of platinum or molybdenum. During the preparation, there was at first no deposit on the cathode. Then, as the amount of dissolved platinum in the bath increased, deposits began to form. The first deposit consisted chiefly of loose, unconsolidated material and was made at low current efficiency. As electrolysis continued, the deposits improved. Finally, after about 5 hours of electrolysis at 150 ma, when the bath contained 0.8 to 1.0 percent platinum, the deposits became smooth, bright, and adherent. Initially, the bath temperature was 600° C for NaCN and 525° to 575° C for NaCN-KCN but, as electrolysis proceeded, first in bath preparation and then in use, operating temperatures could be lowered because the melting points decreased as a result of the partial oxidation of the cyanide. For example, the melting point of a NaCN electrolyte decreased from 564° to 435° C during 75 hours of electrolysis; the melting point of NaCN-KCN decreased from 494° to 424° C in 70 hours. An effort was made to maintain bath temperatures at 25° to 50° C above the melting point to minimize the rate of oxidation and thus prolong the life of the bath.

Baths used in this investigation were operated for as long as 120 hours. Aging baths required periodic additions of fresh portions of NaCN or NaCN-KCN. As a result of the oxidation of cyanide mentioned previously, bath composition changed with use and exposure to air. On particular bath made with 400 grams of NaCN and electrolyzed in eight experiments for a total of 28.8 hours at an average current of 168 ma (17,500 coulombs) had the following composition by analysis, in percent (before additions of fresh NaCN): Pt, 1.8; CN, 16.6; CNO, 26.9; and CO_3, 17.6. The calculated platinum content, based on the difference between the weights of platinum dissolved and deposited during the

life of the bath, was 2.8 percent. This difference between the calculated and analyzed platinum contents of the bath is accounted for by a small amount of platinum that is not in solution at the operating temperature and sinks to the bottom of the vessel. The melting point of the bath at this point was 430° C. As these baths were used, more and more materials remained solid at the operating temperature and accumulated. In old electrolytes, the solid sometimes interfered with the formation of coatings or caused rough coatings. Stirring the electrolyte, deep immersion of the cathode, or low operating temperatures tended to increase these detrimental effects.

Figure 3 shows stainless steel laboratory tongs with 132 μm (5.2 mils) of platinum on a 3.8-cm (1.25-inch) length of the tips and 66 μm (2.6 mils) on 7 cm (2.75 inches) above the tips. The coating was put on in two electrodeposition periods of 2.5 and 3 hours for the tips and the area above the tips, respectively. Prior to the first platinum deposit, the surface to be plated was etched for 5 hours in a solution of 50 percent HNO_3 and 5 percent HF. The tongs were not rotated during electrodeposition. Cathode current efficiency for the whole coating was 75 percent.

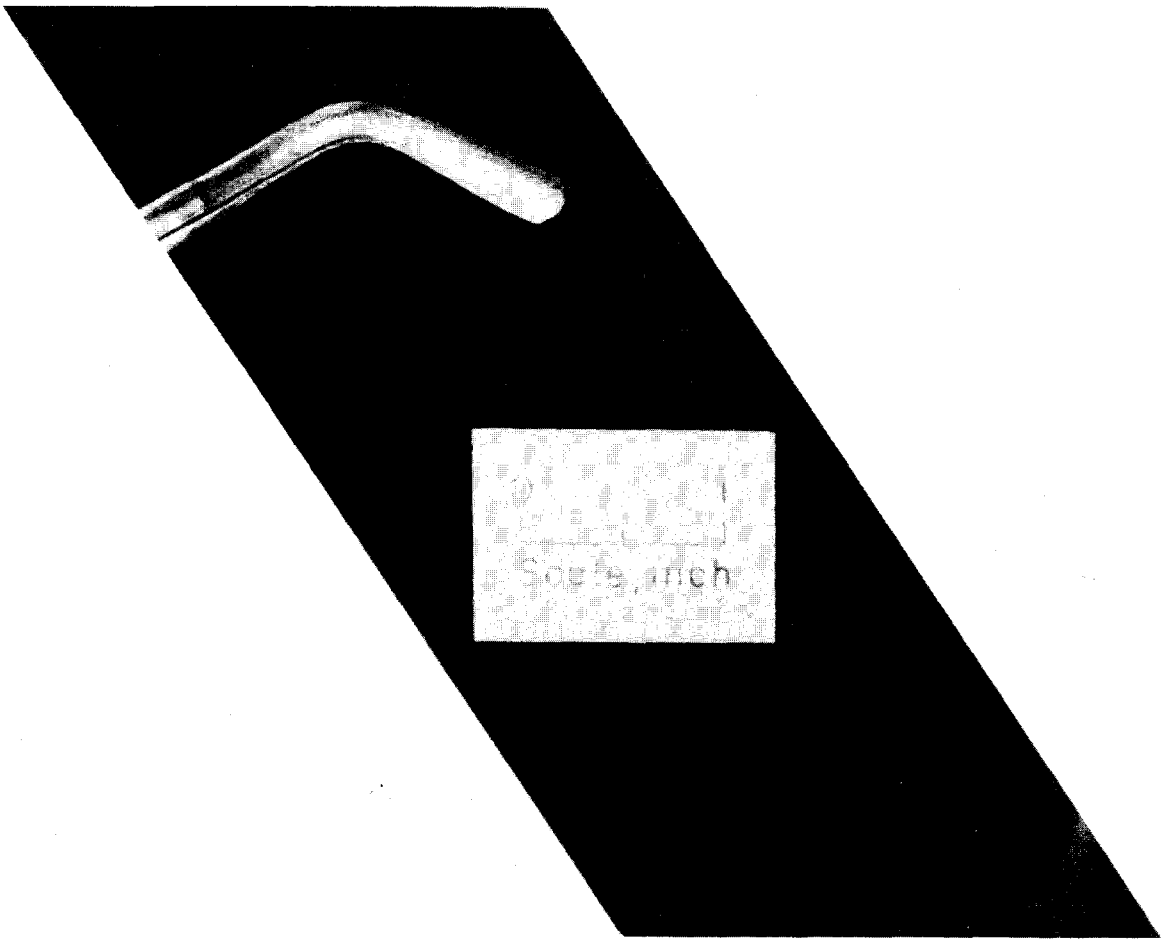

FIGURE 3. - Stainless steel laboratory tongs with a 132-μm (5.2-mil) coating of platinum.

Figure 4 shows a 0.317-cm- (0.125-inch-) diameter Inconel rod and a 0.635-cm- (0.25-inch-) diameter Inconel sheathed Chromel-Alumel thermocouple with platinum coatings. The 241-μm (9.5-mil) coating was put on the rod in four plating periods with a total time of 16.83 hours (rate, 14 μm/hr). A freshly prepared Pt-NaCN electrolyte was used. The 152-μm (6-mil) coating was put on the thermocouple in two plating periods with a total time of 9 hours (rate, 17 μm/hr). The electrolyte used for these deposits was also Pt-NaCN; however, it had been used for 115 hours of electrodeposition before the coating was made, and fresh portions of NaCN had been added from time to time. Neither of these objects was rotated during the electrodeposition. The cathode current densities were 10 to 14 ma/cm^2 and the current efficiencies were 74 and 71 percent, respectively. Both coatings were bright, smooth, and adherent.

An Inconel rod 12.7 cm (5 inches) long and 0.635 cm (0.25 inch) in diameter was encapsulated with a bright, smooth, adherent coating of platinum in a Pt-NaCN-KCN electrolyte at a temperature of about 500° C. The bath had been in use 57 hours before this coating was made. The coating was 45.6 μm (1.8 mils) thick at one end, 88.7 μm (3.5 mils) thick at the other end, and 135 μm (5.3 mils) thick in the overlap area. The cathode current efficiency was about 70 percent.

Figure 5 shows molybdenum rods, 0.635 cm (0.25 inch) in diameter and 2.22 cm (0.875 inch) long, encapsulated first with 63.5 μm (2.5 mils) of

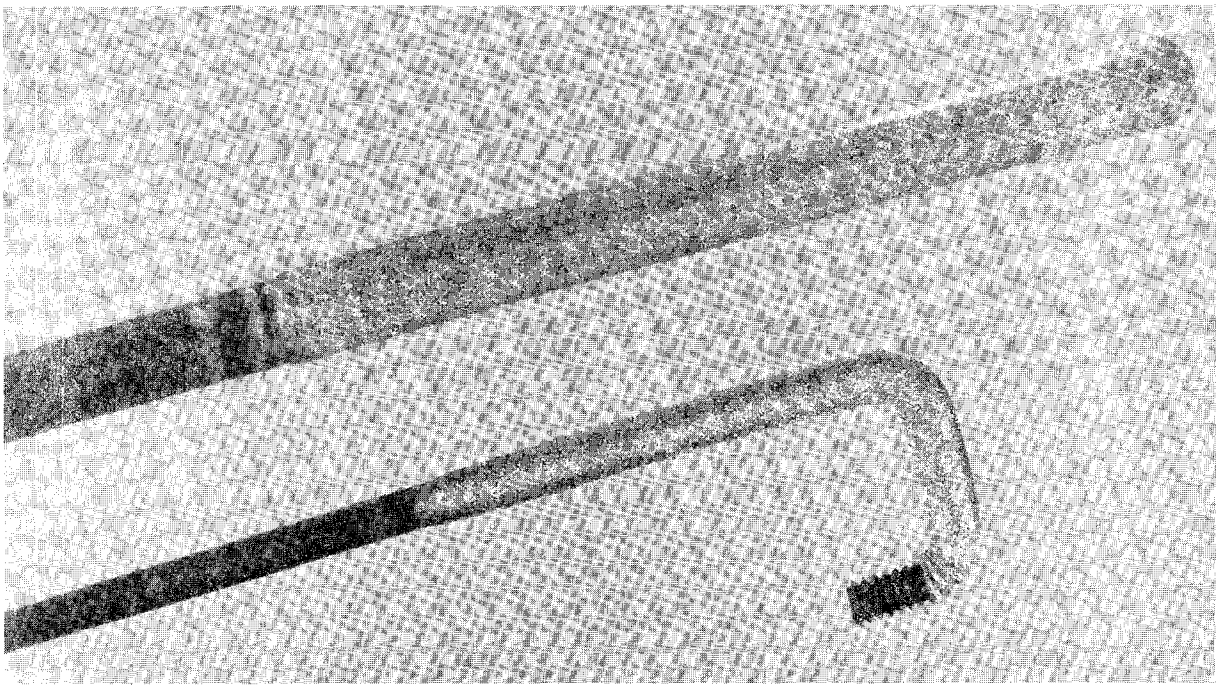

FIGURE 4. - A 0.32-cm-(0.125-inch-) diameter Inconel rod and a 0.64-cm- (0.25-inch-) diameter Inconel-sheathed Chromel-Alumel thermocouple with platinum coatings of 9.5 mils and 6 mils, respectively.

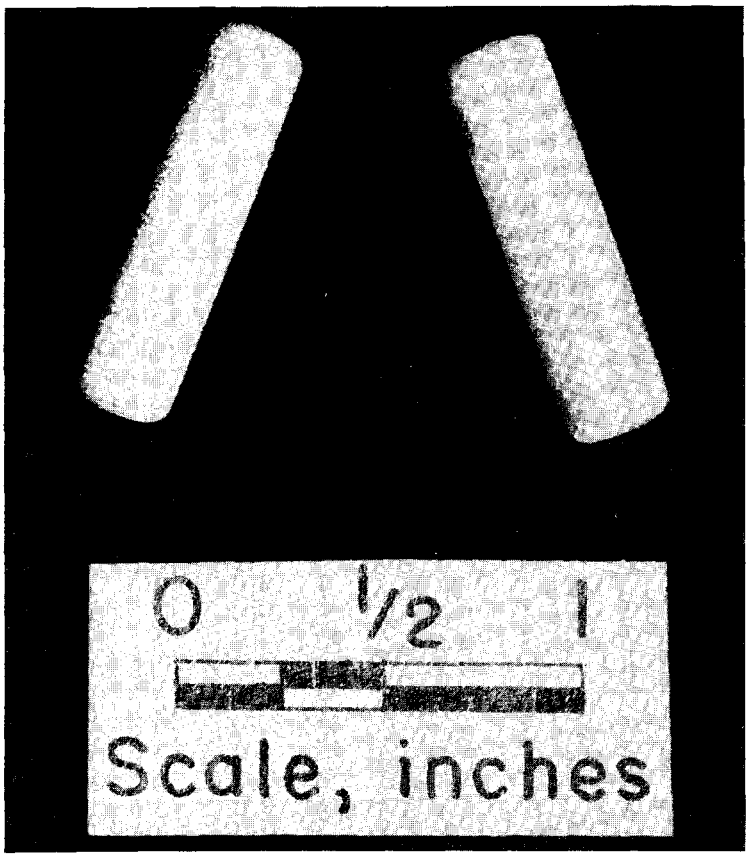

FIGURE 5. - Molybdenum rods 0.64 cm in diameter, coated first with 63.5 μm (2.5 mils) of iridium as a diffusion barrier, then with 101.5 μm (4 mils) of platinum.

iridium as a diffusion barrier and then with 101.5 μm (4 mils) of platinum. In these experiments, a smoother coating was obtained by adding an additional step to the surface treatment between individual deposits. This consisted of ball-milling in wet, 1,200-grit grinding powder after rubbing with 240-grit emery paper. Both metals were deposited from NaCN electrolytes under the usual conditions and with the normal results. Iridium was electrodeposited from an electrolyte that had been in use 45 hours, and platinum, from one that had been used for 100 hours.

Effect of Air Atmosphere on Platinum Cyanide Baths

Several unsuccessful attempts were made to prepare and use molten platinum cyanide baths in inert atmospheres. Starting with either sodium cyanide or sodium and potassium cyanide mixtures, the deposits obtained were always thin and the cathode current efficiencies were only 1 or 2 percent. This led to a study of the effect of air on the cyanide electrolytes.

Two series of electrolyses were done, one in open air and the other under an atmosphere of argon, starting in each case with a 50-50 weight-percent mixture of sodium cyanide and potassium cyanide. Molybdenum cathodes and platinum anodes were used at 15 ma/cm^2. The cathodes were rotated at 120 rpm, and the electrolyte temperature was 520° C.

Smooth, bright adherent platinum deposits were obtained in electrolyses done in an atmosphere of air after the "preparatory" period, during which the metal contents of the bath increased to about 0.3 percent. Even as the deposits were made, the concentration of platinum in the electrolyte continued to increase (table 1). Also, some cyanide was oxidized to cyanate and carbonate, and these changes in bath composition resulted in a lower melting point. The solidified electrolyte was yellow in color. Cell voltage was 1 volt at the beginning of the preparatory period and 0.2 volt after 10 hours of electrolysis.

TABLE 1. - Effect of air on composition of molten Pt-NaCN-KCN baths during electrolysis, weight-percent

Hours of electrolysis	Pt		CN^-		CNO^-		$CO^{3=}$	
	Air	Argon	Air	Argon	Air	Argon	Air	Argon
0	-	-	37.2	37.8	0.8	0.4	0.8	0.6
2	0.17	0.02	36.6	35.1	1.5	1.0	.8	.7
4	.38	.09	35.6	37.3	2.8	.3	1.1	.6
6	.51	.09	32.8	37.7	4.1	.4	1.8	.6
10	.76	.1	32.5	37.3	6.2	.5	2.3	.7

On the other hand, deposits were never satisfactory in the melt operated under argon. After 10 hours of electrolysis, the cathode current efficiency was still only about 2 percent. Although the anodes corroded, the dissolved platinum content of this bath was never more than 0.1 percent; in the absence of air, almost all of the platinum removed from the anodes precipitated and settled to the bottom of the melt. Little if any cyanide was oxidized and the bath composition remained substantially the same, as did the melting point (496° C). The color of the electrolyte changed from white to faint yellow. Under argon, the cell voltage remained high at 1 volt after 10 hours.

Platinum Coatings on Graphite

Platinum electroplated directly on graphite surfaces from molten cyanide baths was not effective in preventing oxidation of the graphite at high temperatures. When the porous graphite is first immersed in molten cyanide baths, it quickly absorbs large amounts of the low-viscosity salt before the coating forms. Later, when the coated structure is heated, the absorbed salt melts and ruptures the platinum coating, exposing the graphite to oxidation. The porous graphite was prevented from absorbing molten electrolyte by precoating its surfaces with palladium from an aqueous bath. Some experiments were also done with a precoat of nickel from a sulfamate bath, and it is believed that this could be substituted for the palladium. Adherent coatings of platinum, which protected the graphite against oxidation at high temperatures, were then applied to the precoat. The optimum thickness for the palladium coating is 25.4 or 50.8 μm (1 or 2 mils). Thicker coatings from the aqueous baths are more likely to develop cracks. The platinum coatings were 114 to 178 μm (4.5 to 7 mils) thick. Careful preparation of the surfaces between deposits is essential, and frequent inspection of the deposits for cracks and other defects is important. Common trouble spots are small, deep pores in the graphite surfaces and the overlapped areas in the palladium precoat.

Several types of graphite, which varied in porosity, grain size, and surface characteristics, were used in this investigation. These included spectrographic-grade (anisotropic) as well as three commercial brands. The samples were in the form of rods, 2.54 cm (1 inch) long and 0.635 cm (0.25 inch) in diameter. Testing at high temperature in the thermobalance required that the specimens be encapsulated with each of the metals used.

The preparation of the graphite specimen prior to the formation of the precoat included the following steps. (1) The edges on the ends of the rod

were rounded with fine (3/0) emery paper. (2) The surface was cleaned by a 30-minute immersion in an alkaline solution with ultrasonic agitation. This solution contained 7.5 g/l NaOH, 30 g/l $Na_3PO_4 \cdot 12H_2O$, 15 g/l Na_2CO_3, and 2.2 g/l wetting agent (Fisher SO-A-292, density 1.15 g/ml). (3) The specimen was washed in boiling distilled water with ultrasonic agitation. (4) The specimen was dried in an oven at 120° C for 10 to 15 minutes and then weighed. (5) The specimen was kept immersed in the palladium bath until the electrodeposition was started.

The palladium preplate was a two-part process. First, the specimen was encapsulated with a 5.1- to 7.6-μm (0.2- to 0.3-mil) strike from a bath containing $PdCl_2$, 100 g/l (Pd, 60 g/l); HCl, 400 ml/l; and NH_4Cl, 20 g/l. The bath temperature was 75° C, the cathode was rotated at 180 rpm, the cathode current density was 159 ma/cm^2, and the palladium anode current density was 34 ma/cm^2. The specimen was immersed to a depth of 1.9 cm (0.75 inch) for 1 minute of deposition, the ends were reversed, and the electrodeposition was repeated. The sample was then cleaned using steps 2 and 3 of the graphite-specimen preparation described previously. The second part of the preplating was the formation of an additional 25.4- or 50.8-μm (1- or 2-mil) deposit of palladium from a bath containing $PdCl_2$, 50 g/l; HCl, 400 ml/l; and NH_4Cl, 20 g/l. This deposit was made at a temperature of 75° C, a cathode current density of 15 ma/cm^2, a current density on the palladium anode of 12 ma/cm^2, and a cathode rotation rate of 120 rpm. The normal encapsulation technique was used. The encapsulated sample was washed in boiling water, wet-pumiced in a ball mill with porcelain balls, ultrasonically washed in hot water, and dried for 2 hours in a vacuum oven at 200° C. If salt appeared on the surface of the sample after the drying step, the sample was discarded or an additional palladium deposit was added. At this point, the coating was also examined microscopically for defects.

The platinum coating was deposited on the palladium-precoated graphite specimens from molten platinum cyanide baths using the techniques already described. The platinum coating also consisted of two steps. First the specimen was quickly encapsulated with 17.8 to 22.8 μm (0.7 to 0.9 mil) of platinum to prevent rapid corrosion of the palladium precoat in the molten salt bath. This was done by making a 1-hour deposit at 13 ma/cm^2 on 1.9 cm (0.75 inch) of each end of the specimen. During electrodeposition, the sample was rotated at 120 rpm. After the first platinum coating, the specimen was washed, pumiced, and dried in the usual manner. The final, heavy coating of platinum was formed with the encapsulation technique described in the "Experimental Techniques" section. At each of the immersed positions of the specimen--1.9 cm (0.75 inch), 1.27 cm (0.50 inch), and 0.635 cm (0.25 inch)--an 80- to 120-minute deposit was made at 15 ma/cm. Each specimen was encapsulated twice. The heavy platinum coating was made without specimen rotation. Figure 6 shows a graphite rod with a precoat of palladium and 114 μm (4.5 mils) of platinum. It was tested at 1,400° C.

The oxidation protection provided by palladium-platinum coatings for graphite was evaluated by exposing encapsulated specimens in the thermogravimetric apparatus. The temperature was increased from room temperature to 1,400° C at the rate of 238° to 383° C per hour with an airflow of

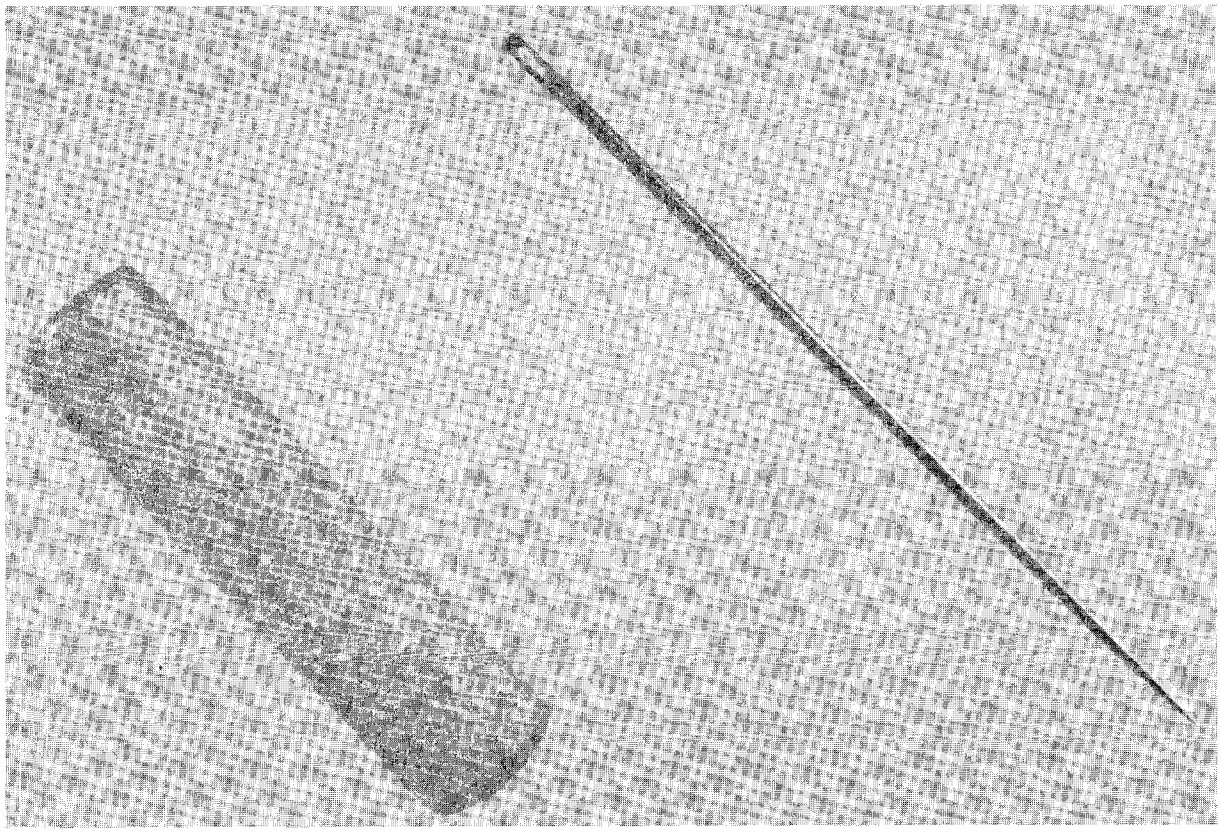

FIGURE 6. - A 0.64-cm-diameter graphite rod encapsulated with a precoat of palladium and 114 μm (4.5 mils) of platinum. It was evaluated at 1,400° C.

300 ml/min. The uncoated graphite specimens were 2.54 cm (1 inch) long and 0.635 cm (0.25 inch) in diameter, the total surface area was approximately 6.2 cm^2, and they weighed approximately 1.4 grams. The coatings added 2.2 to 2.3 grams to the weights of these specimens. Among the results obtained were the following. (1) A specimen of Poco graphite with 30.5 to 33 μm (1.2 to 1.3 mils) of palladium and 158 to 162 μm (6.2 to 6.4 mils) of platinum lost 4 mg in weight as the temperature was increased to 1,400° C at the rate of 280° hr. (2) A similar specimen of Poco graphite with 30.5 to 45.7 μm (1.2 to 1.8 mils) of palladium and 150 μm (5.9 mils) of platinum leaked some salt as it was dried at 200° C. An additional 12.7 μm (0.5 mil) of platinum was added before the specimen was tested. As the temperature was increased to 300° C at 238°/hr, the specimen lost 88 mg, which was assumed to be water. The specimen then lost an additional 10 mg as the temperature was increased to 1,400° C. (3) An unprotected specimen of Poco began to lose weight at 540° C and lost 53 mg in 22 minutes as the temperature was raised to 660° C. (4) A specimen of United Spectrographic with 56 to 58.5 μm (2.2 to 2.3 mils) of palladium and 127 to 134 μm (5.0 to 5.2 mils) of platinum lost 0.6 mg as the temperature was raised to 1,400° C at the rate of 383° C/hr. (5) A similar specimen of United Spectrographic graphite with 30.4 to 33 μm (1.2 to 1.3 mils) of palladium and 152 to 190 μm (6.0 to 7.5 mils) of platinum repeatedly

leaked salt during the drying periods. As the temperature of this specimen was increased at 263° C/hr, it began to lose weight at 750° C; it lost 123 grams as the temperature reached 1,400° C. The defect in the coating was identified as a small hole at the flat end of the specimen. (6) An unprotected specimen of United Spectrographic graphite began to lose weight at 520° C and lost 31 mg in 42 minutes as the temperature was raised to 690° C.

In general, it was found that properly encapsulated specimens of graphite lost an average of 3 mg/hr at 1,400° C. The coatings were still adherent and effective after several hours at this temperature. Similar graphite specimens without coatings lost 120 mg/hr at 600° C.

PALLADIUM

Bright, smooth, adherent deposits of palladium were made on molybdenum from molten baths of sodium cyanide or 50-50 weight-percent mixtures of sodium cyanide and potassium cyanide. The molten baths were in contact with air during both bath preparation and deposit formation. However, the oxidation rate of cyanide in this bath was such as to cause fairly rapid deterioration. After the first few hours of electrolysis, there was a steady accumulation of white flocculate in the bath, chiefly Na_2CO_3. Later, there was also some finely divided palladium metal. At the same time, the palladium deposits became less adherent. Eventually, in 10 to 20 hours, the bath became inoperable.

Electrodeposition of Palladium Coatings

Starting with the pure molten cyanide, electrolytes were prepared by direct-current electrolysis with palladium anodes and a cathode of palladium or molybdenum. Satisfactory deposits required that the electrolyte contain about 0.3 grams of palladium per liter. Cathode current densities were 10 to 20 ma/cm^2; anode current densities were sometimes approximately the same and at other times were as low as one-fourth of the cathode current density. In some experiments the cathode was stationary, while in others cathode rotation was as high as 120 rpm. Cathode current efficiencies varied from 35 to 70 percent on the basis of the discharge of bivalent palladium ions. Apparent anode current efficiencies were 120 to 140 percent when the cathode and anode areas were about equal, and 300 to 400 percent when the ratio of cathode to anode areas was 1 to 4. Rapid dissolution of the palladium anodes resulted in correspondingly large increases in the palladium concentration of the bath. The bath melting point decreased as the cyanide was oxidized and operating temperatures could be decreased correspondingly. Hence, bath temperatures ranged from 575° to 445° C for the sodium cyanide baths and from 500° to 400° C for the sodium cyanide-potassium cyanide baths.

In a typical experiment, a bright, smooth, adherent deposit of palladium was made on a 0.635-cm- (0.25-inch-) diameter molybdenum rod from a sodium cyanide-potassium cyanide electrolyte at 450° C. The electrolyte contained 1.7 to 2.2 percent palladium. The cathode current density was 20 ma/cm^2 and the anode current density was 5 ma/cm^2. The cathode was rotated at 120 rpm. The cell voltage was 0.18 volts. The cathode current efficiency was 35 percent

for the 4-hour deposit. The calculated thickness of the deposit was 2 mils, and the measured thickness was 2.5 to 3.5 mils. The apparent anode current efficiency was 300 percent. The bath was 14 hours old at the end of the deposition period and contained considerable solid, white material. Figure 7 shows a 4.5-mil deposit of palladium on a molybdenum rod.

Effect of Air Atmosphere on Palladium Cyanide Baths

Attempts to prepare and use molten palladium cyanide baths in inert atmospheres were unsuccessful. The results were similar to those obtained with the platinum cyanide melts--thin deposits and low cathode current efficiencies. Again, a study was made of the effect of air. The first part of this experiment and the results obtained were the same as those described under platinum. Smooth, bright, adherent palladium deposits were obtained in the air atmosphere, after the initial period of bath preparation. Some cyanide was oxidized to cyanate and carbonate, and these reactions were more rapid than the corresponding reactions in the platinum cyanide bath (table 2). The melting point of the bath decreased. Cell voltage was 1.3 volts at the beginning of the preparatory period and 0.2 volts after 7 hours of electrolyses. Again, good deposits were not made in the melt operated under argon and, after 7 hours of electrolysis, cathode current efficiencies were still

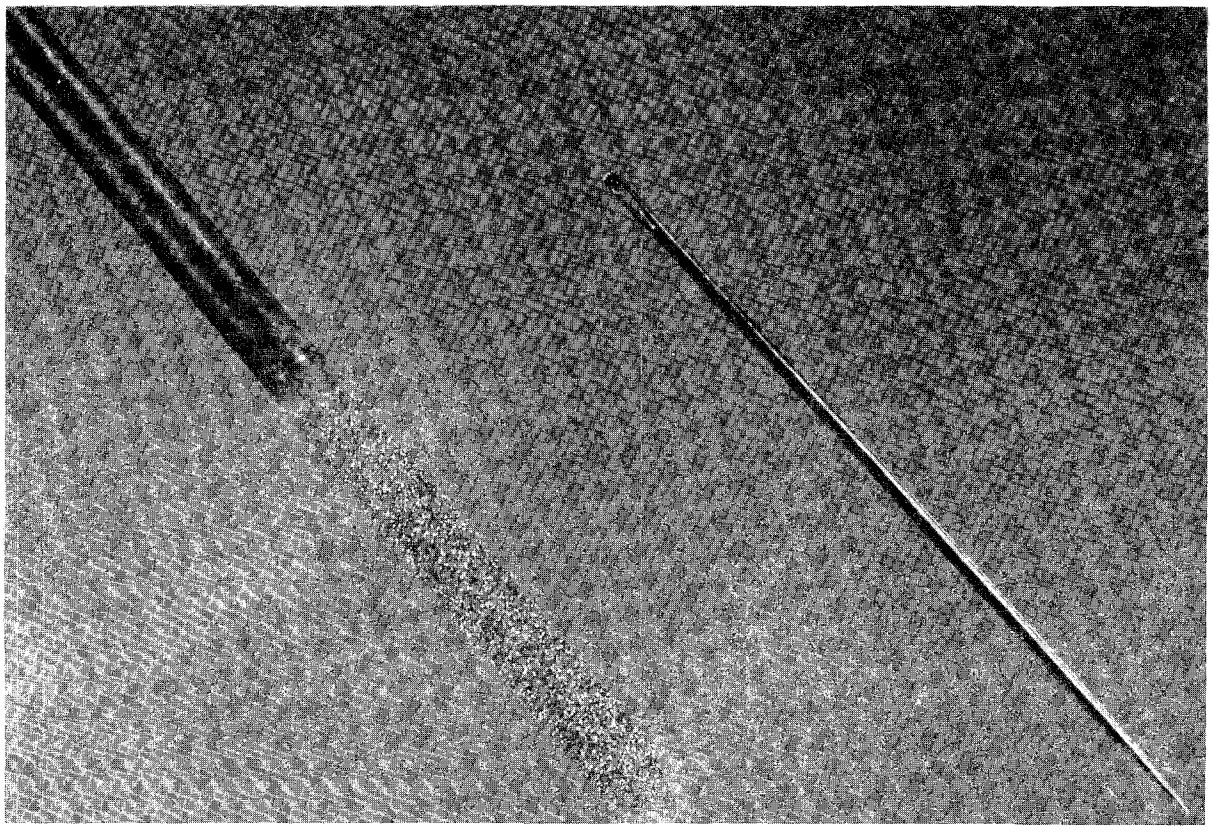

FIGURE 7. - A 114-μm (4.5-mil) deposit of palladium on a 0.64-cm-diameter molybdenum rod.

less than 2 percent. The anodes corroded but nearly all of the palladium precipitated. Little, if any, cyanide was oxidized, and the melting point of the bath remained the same (496° C). The cell voltage was still 1.2 volts after 7 hours.

TABLE 2. - Effect of air on composition of molten Pd-NaCN-KCN baths during electrolysis, weight-percent

Hours of	Pd		CN^-		CNO^-		$CO^{3=}$	
electrolysis	Air	Argon	Air	Argon	Air	Argon	Air	Argon
0	-	-	38.5	38.6	0.8	0.6	0.9	0.8
2	0.17	0.04	35.4	38.3	4.3	.9	1.1	.9
4	.37	.04	30.8	38.1	10.1	.9	1.7	.9
6	.48	.06	25.8	38.3	15.4	.9	2.7	.8
7	.55	.05	23.0	38.0	19.4	.8	3.6	.9
BATH IN AIR TRANSFERRED TO ARGON ATMOSPHERE[1]								
8	-	0.2	-	22.3	-	20.8	-	3.8
9	-	.09	-	22.3	-	20.9	-	3.9
10	-	.06	-	22.1	-	20.9	-	4.1

[1] Both originally in argon was discontinued.

In the case of palladium, the experiment was extended. At the end of 7 hours, electrolysis in the bath operated under argon was discontinued; the bath which had been operated in air was transferred to the argon atmosphere, and electrolysis was resumed. Under argon, the deposits in the bath that had been producing good deposits under air quickly decreased in quality and quantity. The concentration of palladium in the bath decreased, the oxidation of cyanide stopped (table 2), and the melting point of the bath remained constant.

Another experiment investigated the changes that occur in the molten palladium cyanide bath as it is used in the presence of air. A 50-50 weight-percent mixture of sodium cyanide and potassium cyanide (melting point: 496° C) was melted under argon at 575° C. Five deposits were made from this bath at 520° C in air with a palladium anode and a molybdenum-rod cathode. The cathode current density was 15 ma/cm^2. When it was not in use, the bath was kept under argon if it was hot, and in a dessicator if it was at room temperature. The total electrodeposition time during this series of experiments was 14 hours; the total time of exposure to air was 17.75 hours.

After about 8 hours of electrolysis, the palladium deposits on the cathode were bright and smooth. White, fluffy Na_2CO_3 appeared in the electrolyte early in the series of experiments and became more and more voluminous until the end. Palladium in finely divided form was observed in the electrolyte before the end of the experiments. The freezing point of the bath dropped from 496° C to about 412° C. The apparent anode current efficiency was 239 percent in the first experiment and 97 percent during the fifth deposit. There was obviously excessive corrosion of the anode at the solution line. The electrolyte was analyzed at the end of each deposit and the results are shown in figure 8. The cyanate and carbonate contents of the electrolyte increased and the cyanide content decreased with total electrolysis time. The palladium concentration increased for a time up to about 0.3 percent, and then

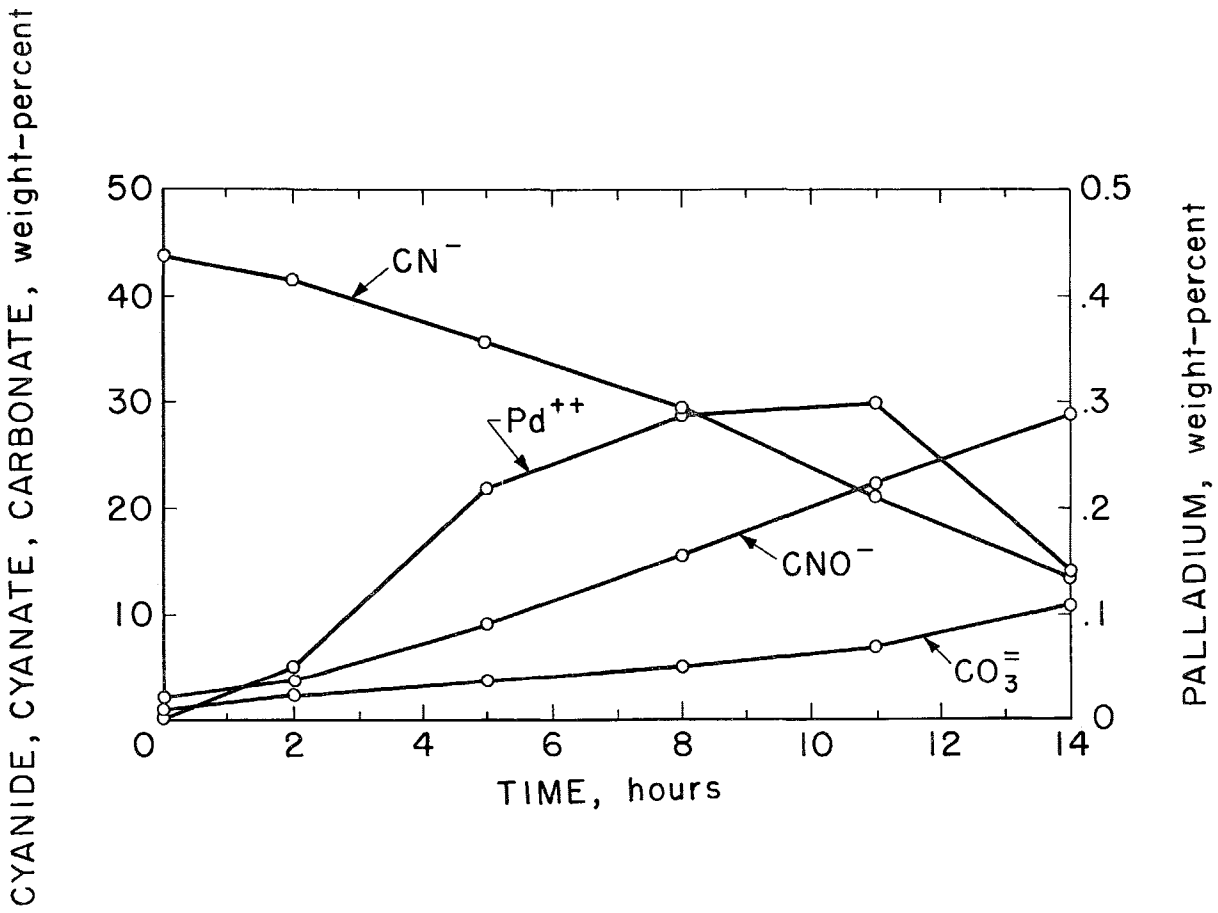

FIGURE 8. - Composition changes in Pd NaCN-KCN bath with use, in air at 520° C.

decreased, partly because of the precipitation of palladium but also as a result of lower anodic dissolution rates and the electrodeposition of palladium on the cathode.

Other experiments proved that, in air, both the corrosion of palladium and oxidation of cyanide take place rapidly in the 50-50 weight-percent mixture of sodium cyanide and potassium cyanide at 520° C, even without electrolysis. Also, the pure cyanides open to the atmosphere at 520° C are oxidized and the presence of only 0.06 percent dissolved palladium greatly increases the oxidation rate.

ELECTROFORMING

In electroforming crucibles, the general procedure was to electroplate the platinum-group metal on a mandrel of copper or molybdenum to the desired thickness, and then to dissolve the mandrel away with acid. Each crucible was electroformed in a series of successive deposits, which varied in length from 1 to 5 hours. The piece was removed between deposition periods and smoothed by grinding and polishing. Each time, before beginning the next deposit, the

surface was rubbed with 240 emery, polished on a wire wheel, washed in boiling water, and dried with ethyl alcohol. 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.

Platinum

Attempts to electroform a platinum crucible on a brass mandrel were unsuccessful because when the mandrel was immersed in the bath a loose, flakey deposit of platinum was quickly formed by displacement on zinc. This did not happen with mandrels of copper. A platinum crucible was formed on a copper mandrel 1.9 cm (0.75 inch) in diameter and 4.45 cm (1.75 inches) high (total area, 32.3 cm^2). An Inconel rod was screwed into a small knob on the top of the mandrel to support it. The crucible was formed in nine deposition periods with a total time of 27.83 hours. The initial 2-hour deposit was made over the entire area of the mandrel. Subsequent deposits were made on a 2.54-cm (1-inch) depth of the mandrel (area, 18.1 cm^2). The anode consisted of two strips of platinum, each bent and positioned around the cathode at a distance of 1.27 cm (0.5 inch) from it; total area, 8 cm^2. The electrolyte was Pt-NaCN and was operated at 520° C under an atmosphere of air. The cathode was rotated at 30 rpm. The cell voltage was maintained at 0.2 volts, and this resulted in a cathode current density of 10 to 13 ma/cm^2 and an anode current density of about 25 ma/cm^2. The average cathode current efficiency was about 45 percent (plating rate, 6.35 μm or 0.25 mil per hour). Loose material in the deposits varied from none to a maximum of 3 pct. When the last deposit was completed, the piece was removed and the mandrel was cut off 2.54 cm (1 inch) from the bottom. The top was polished with a wire brush and sanded with 240-grit emery paper. It was then drilled to 1.27 cm (0.5 inch) deep with a 19/64-inch drill to provide more exposed surface. The piece was placed in 20 percent HNO_3, and the solution was heated to boiling with stirring. The copper mandrel dissolved away in about 6 hours. The inside of the crucible was pumiced, washed with boiling water, and dried with ethyl alcohol. The final crucible (fig. 9) was 2.54 cm (1 inch) high, 1.9 cm (0.75 inch) wide, weighed 7 grams, and had an average wall thickness of 178 μm (7 mils).

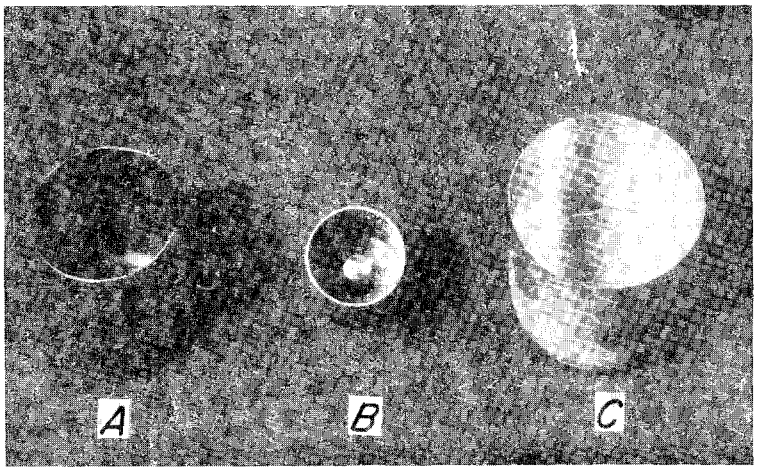

FIGURE 9. - Crucibles electroformed in molten cyanide electrolytes: *A*, Platinum; *B*, platinum; and *C*, iridium.

A second platinum crucible was electroformed. This crucible was designed for differential thermal analysis (DTA) and, therefore, the mandrel had a recess in the bottom. The mandrel had an area of 9.06 cm^2. In the cell it was

surrounded by four platinum sheets with a combined area of 26 cm^2. It was positioned with the recess facing up to avoid the entrapment of air bubbles. The cathode was not rotated. The crucible was formed in five successive deposits with a total plating time of 21.8 hours. The cell voltage was 0.10 to 0.12 volt and the cathode current density was 11 to 20 ma/cm^2. The temperature of the bath was 528° to 540° C. The average cathode current efficiency was 50 percent. After the last deposit, the mandrel was cut off 1.59 cm (0.625 inch) from the bottom, and the piece was placed in hot 20 percent HNO_3. The copper was dissolved away in 7 hours. The crucible was cleaned up in the usual way. The final crucible was 0.625 inch high and 0.50 inch in diameter. The sides and bottom of the crucible were 349 μm (13.7 mils) thick and the wall in the recess was 132 μm (5.2 mils) thick (fig. 9).

Iridium

The use of a copper mandrel for iridium resulted in cracked deposits, apparently because of large differences in the linear thermal coefficients of expansion for the two metals. Molybdenum proved to be a more satisfactory mandrel material for iridium, again perhaps because the coefficients for these metals are similar. An iridium crucible was electroformed on a molybdenum mandrel 2.54 cm (1 inch) high and 2.54 cm (1 inch) in diameter. The mandrel was suspended from an Inconel rod in the same manner as the first platinum crucible, and its total area was 30.4 cm^2. It was surrounded by an anode of four iridium strips with a total area of 49 cm^2, positioned 1.27 cm (0.5 inch) from the cathode. The bath was sodium cyanide with an estimated 2 percent iridium at the beginning of the electroforming. The bath temperature was 600° C, and it was operated in an argon atmosphere. The crucible was electroformed in three deposition periods with a total time of 900 minutes (15 hours). The cathode was rotated at 120 rpm. The cathode current density was 25 ma/cm^2, and the anode current density was 15 ma/cm^2. The cell voltage was 0.75 volts. The cathode current efficiency was 34 percent, and the anode current efficiency was 68 percent. After the third deposit, the mandrel was cut off 1.90 cm (0.75 inch) from the bottom, and the cut surface was smoothed with emery paper. The piece was placed in hot 50 percent HNO_3 to dissolve away the molybdenum. This required about 20 hours. During this time, the piece was occasionally removed from the nitric acid so that the white molybdenum-complex compound that formed on the surface could be dissolved in hot concentrated H_2SO_4. After the molybdenum was removed from the iridium, the crucible was cleaned in the usual way. The final crucible had walls 127 μm (5 mils) thick (fig. 9).

CONCLUSIONS

Platinum, palladium, iridium, rhodium, and ruthenium can be electrodeposited in thick adherent, coherent coatings from molten sodium cyanide or sodium cyanide-potassium cyanide baths. Platinum and palladium molten cyanide baths were prepared and used in the presence of air. On the other hand, iridium, rhodium, and ruthenium baths must be prepared and used in inert atmospheres.

Platinum and palladium cyanide baths change in composition as they are used under an atmosphere of air. The cyanide ion is oxidized to cyanate and then to carbonate. Eventually, a white solid appears in the bath; this is chiefly carbonate with smaller amounts of cyanate and cyanide. When the oxidation of cyanide has proceeded to a certain point, some of the platinum or palladium precipitates in the form of fine particles. As these baths age, the melting points decrease and the operating temperatures can be lowered correspondingly.

The deterioration of the platinum cyanide baths during electrolysis in contact with air is relatively slow. In this investigation, such baths were still usable after more than 115 hours of electrodeposition. Bath life was extended by adding portions of fresh cyanide and lowering the operating temperature when possible. The use of various mixtures of air and argon with the platinum cyanide baths should be investigated as a means of obtaining more stable baths.

The palladium baths deteriorate rapidly during electrolysis under air. Palladium accumulates in the bath faster because the dissolution rate of palladium anodes is faster than that of platinum anodes. The oxidation of cyanide is faster in palladium baths than it is in platinum baths.

Cyanide in a mixture of sodium and potassium cyanides exposed to air at 520° C is oxidized even without electrolysis, and the rates of oxidation are increased by the presence of even a small concentration of dissolved palladium. Furthermore, palladium corrodes in the molten cyanides without an impressed current.

Since the iridium, rhodium, and ruthenium cyanide baths are prepared and used in inert atmospheres, there is little or no oxidation of cyanide, and the bath melting points and operating temperatures remain relatively constant. However, there may be some precipitation of metal and some loose deposits, causing a slow accumulation of sludge. Hot filtration techniques can be used to remove this solid material from the molten salt baths.

When platinum-group metals are deposited directly on graphite surfaces, some of the electrolyte is often absorbed before the deposit is well formed. When the deposit is cooled and later reheated, the salt is forced out of the pores and ruptures the deposit. This phenomenon can be avoided by applying a precoat of palladium from an aqueous bath.

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