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Electrochemical Studies of Platinum-Group Metals in Molten Alkali Metal Cyanides

By D. R. Flinn and C. L. Manger

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By D. R. Flinn and C. L. Manger

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CONTENTS

Page

Abstract 1
Introduction 2
Experimental techniques 2
Experimental results and discussion 4
  Electrochemical studies and plating bath preparation 4
    Platinum 4
    Rhodium 5
    Iridium 7
    Palladium 9
  Coatings 12
    Substrates 12
    Plating parameters 12
    Cementation reactions 12
    Coating of large vessel 12
    Coating within small holes 12
Scanning electron microscopy 14
Summary 15
References 16

ILLUSTRATIONS

1. Controlled atmosphere chambers for platinum metals electrodeposition studies 3
2. First cycle of cyclic voltammetric curves for a platinum electrode in molten sodium cyanide-potassium cyanide 5
3. First cycle of cyclic voltammetric curves for a rhodium electrode in molten sodium cyanide-potassium cyanide 6
4. Cyclic voltammetric curve for an iridium electrode in molten sodium cyanide-potassium cyanide; slow sweep rate polarization curve for the diffusion current of iridium reduction in the presence of dissolved iridium 7
5. Iridium dissolution and deposition current efficiencies as a function of anode current density 8
6. Slow sweep rate polarization curve showing the diffusion current for palladium reduction in the presence of dissolved palladium; cyclic voltammetric curve for palladium electrode in molten sodium cyanide-potassium cyanide 10
7. One-liter pressure vessel, top and lid after electrodeposition of platinum coating 13
8. Scanning electron photomicrograph of platinum coating electrodeposited at diffusion limited current, one-half diffusion limited current, and one-quarter diffusion limited current 14
9. Scanning electron photomicrograph of platinum electrodeposited by direct-current plating and current reversal 15

TABLE

1. Reduction of Pd^{2+} to Pd^{0} in a molten NaCN-KCN bath produced by additions of disodium cyanamide 11

ELECTROCHEMICAL STUDIES OF PLATINUM-GROUP METALS IN MOLTEN ALKALI METAL CYANIDES

by D. R. Flinn[1] and C. L. Manger[2]

ABSTRACT

The Bureau of Mines has studied the electrochemical parameters important to the preparation of coatings of the platinum-group metals. Using molten mixtures of sodium and potassium cyanides in an inert atmosphere, techniques have been developed that permit the preparation of baths for platinum, rhodium, and iridium electrodeposition. Cyclic voltammetric and slow sweep rate linear polarization techniques have been utilized to determine optimum potential and current values for preparation of plating baths and for the electrodeposition of coatings. Techniques are described for the deposition of platinum and rhodium coatings at near 100 percent anode and cathode current efficiencies, and for iridium at approximately 80-percent efficiency. Palladium deposition from these molten cyanide baths remains unsatisfactory. The chemistry of the palladium-containing cyanide bath is discussed. Examples of scanning electron microscope photomicrographs of typical platinum coatings are presented. Techniques are described for the preparation of platinum coatings on large objects.

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INTRODUCTION

The platinum-group metals are unique in their high-temperature oxidation and corrosion resistance. Because of these properties, these metals are desired for use in many environments. Their use as bulk materials of construction is not feasible in most cases owing to their great cost. In addition, the low strength of these metals limits their areas of use where the freestanding bulk material might otherwise be usable. Many of these limitations could be avoided through the use of high-strength, high-temperature materials of construction coated with a platinum-group metal. For example, refractory metals such as molybdenum, which have high strength at high temperatures, may be readily oxidized or corroded in severe chemical and physical environments. A thick platinum-group metal coating on the substrate would result in a structural material offering high strength as well as oxidation and corrosion resistance at high temperatures. Not only could this offer increased component life, it might also allow an increase in process operating temperatures and possible improvement of process efficiencies. For example, in the glass fiber manufacturing industry there are several potential applications. Cobalt superalloy crucibles, currently used in the production of glass fibers, contain very many small holes, and these holes become enlarged during use owing to oxidation, resulting in the end of the crucible's usefulness. A platinum coating on such a crucible could greatly increase the component's lifetime, while still retaining the required structural properties.

Use of platinum coatings may also serve as a conservation measure. In many cases a platinum-group metal coating on some suitable material could be substituted for a bulk platinum metal shape, not only conserving a critical material, but also possibly reducing the cost of the component. For some high-temperature glass production, bulk shapes of a platinum-rhodium alloy are currently used. These could possibly be substituted for by a shape of molybdenum that has been coated with a platinum-rhodium alloy. Many other conceivable applications might be realized if it were possible to prepare reproducibly adherent, pore-free coatings of the platinum metals and their alloys.

At the present time, more than 90 percent of the platinum-group metals used in the United States must be provided by imported materials. As part of its goal to minimize the requirements for such important minerals through conservation and substitutes, the Bureau of Mines studied methods to prepare electrodeposited coatings of the platinum-group metals.

To improve the quality and reliability of the platinum-group metal plating baths, the chemistry and electrochemistry of the electroplating baths has been examined.

The electrodeposition of coatings of the platinum-group metals from aqueous baths is well established (*5*).[3] However, many problems are associated with the preparation of thick, protective deposits of several of the platinum-group metals from these aqueous baths (*5, 11*), including high internal stresses within the deposit, low current efficiencies, high sensitivity to impurities, and the requirement that the precious metal content that is removed from the bath during use be replaced by expensive platinum-group metal compounds rather than by soluble anodes. While the process is not yet perfected, it appears that many of the problems that can occur using aqueous plating baths can be overcome by the use of molten alkali metal cyanide baths (*7-8, 11*).

Comprehensive listings of references for the electrodeposition of the platinum-group metals from molten salts have been compiled (*8, 11*). It has been shown that platinum, rhodium, iridium, palladium, and ruthenium can all be electrodeposited in thick coatings from molten alkali cyanide electrolytes. Earlier work (*11*) had shown that the coatings were adherent to many substrates, including Mo, Ni, W, Ta, Cu, and graphite, as well as alloys of Fe-Cr and Fe-Cr-Ni. In addition, some electrochemical studies have been reported. Van Der Kouwe and Von Gruenewaldt (*12*) have studied the electrochemical reduction of platinum in the molten cyanide eutectic, while Harding (*7*) has reported some electrochemical studies of the electrodeposition of platinum and iridium

Researchers, however, have come to various conclusions regarding the effect and necessity of maintaining an air- or an oxygen-free atmosphere in the preparation of the plating baths and during electrodeposition of the platinum-group metals. Investigators had found (*11*) that requirements for the type of atmosphere was dependent on the particular metal being deposited. It was determined that iridium and rhodium required an inert atmosphere, while platinum and palladium required the presence of oxygen.

This previous work (*11*) also identified several problems regarding bath stability and plating parameters. Exposure of the alkali cyanide plating baths to air resulted in the oxidative decomposition of the cyanides. This decomposition was found to be greatly accelerated when a small amount (0.06 percent) of palladium was dissolved in the bath. Eventually, this decomposition results in the precipitation of platinum or palladium from the bath as fine particles. In addition, current efficiencies for electrodepositing coatings were found to be unreproducible, with cathode current efficiencies generally low.

This report describes recent studies of the electrochemical dissolution and deposition of the platinum-group metals in controlled atmospheres with the objective of determining methods of preparing stable plating baths of known composition for use in the preparation of electrodeposited coatings. The specific effect of the presence or absence of oxygen on the preparation of plating baths and on the electrodeposition of the platinum-group metals was studied to determine if all platinum-group metals could be electrodeposited from the same atmosphere. A common atmosphere is a necessity for the electrodeposition of some of the more useful platinum-group metal alloys such as platinum-rhodium, platinum-iridium, and platinum-palladium.

EXPERIMENTAL TECHNIQUES

In order to closely control the atmosphere during the experiments, a controlled atmosphere chamber was designed. The enclosure consisted of two glove boxes, interconnected as shown in figure 1. The left-hand chamber contained the furnace, and the right-hand chamber was used for salt preparation. A high-capacity gas circulation and purification system removed oxygen and water from the helium gas, which was continually recirculated through the chamber. Oxygen levels in the system were maintained at a few parts-per-million level.

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

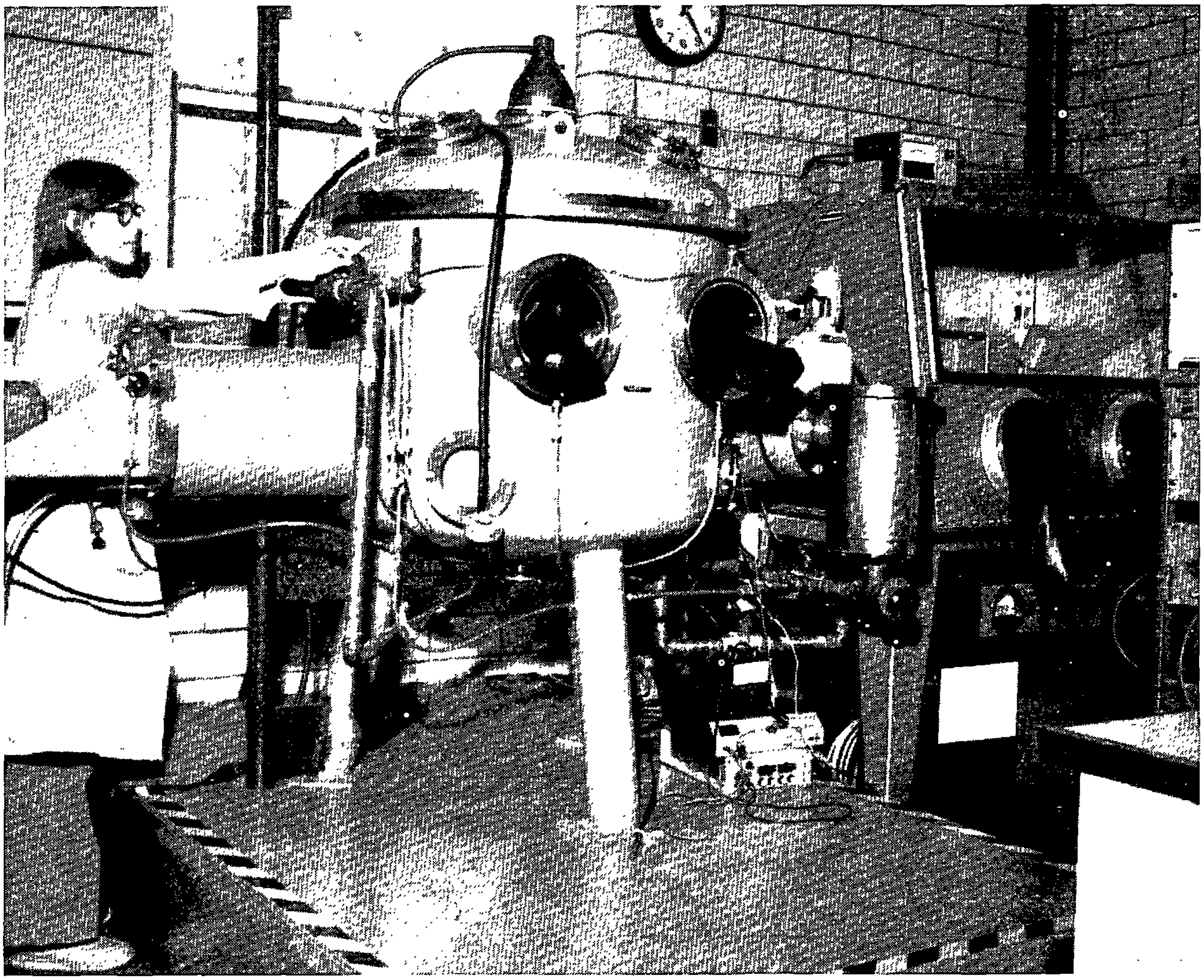

FIGURE 1.—Controlled atmosphere chambers for platinum metals electrodeposition studies. Gas purification system is located under the chamber on the right.

The molten salt bath used was an equimolar mixture of reagent-grade sodium cyanide and potassium cyanide which was used at 550° C. As observed by others (*7, 9*) carbon particles formed upon initial heating of the salts. These particles have been found to interfere with current efficiencies and coating quality. Consequently, the salts were premelted in air at 600° C for 2 to 4 hours, causing some of the carbon to be oxidized and permitting fine particles to settle to the bottom, after which the clear melt was decanted. Alumina crucibles were used to contain the molten salts during the experiments. At the end of each experiment the salts were poured onto a silica tray, allowed to freeze, and then were broken up and stored in the helium-filled chamber for future use.

Cyclic voltammetry (CV) was utilized to determine the range of potentials and current densities required for the dissolution of the metal and the electrodeposition of coatings. In cyclic voltammetry, the potential of a test (working) electrode, measured with respect to a stable reference electrode, is varied at a fixed rate over a set voltage range, and then returned to the initial value. The pattern of the current measured during the oxidation and reduction processes is indicative of the electrochemical reactions occurring at the test electrode.

In addition to the CV studies, slow sweep rate polarization curves (direct-current polarograms) were also recorded for salt baths that contained dissolved platinum-group metals. These studies involved monitoring the current at a test (working) electrode as the potential of the electrode was slowly made more negative, usually at a scan speed of 20 mv/sec or slower. The shape and magnitude of the current observed, which normally included reduction of the dissolved platinum-group metal ions in the bath, yielded information regarding the reactions occurring at the electrode. In some cases, the magnitude of the wave could be related to the concentration of dissolved metal in the bath.

For most of the cyclic voltammetric and slow sweep rate polarization studies, the test electrode was the platinum-group metal being studied, usually a thin strip or wire sealed in Pyrex[4] glass to provide a known geometric surface area. The counter electrode was a 0.6- to 1.3-cm wide strip of the same metal. The reference electrode used in all the studies was an Ag, AgCl electrode which may be written as

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[4] Reference to specific trade names does not imply endorsement by the Bureau of Mines.

$$\text{bulk melt}\ \Big|\ \begin{matrix}\text{Pyres or}\\ \text{Vycor tube}\end{matrix}\ \Big|\ \text{NaCl}(x = 0.05), \text{AgCl}(x = 0.95)\ \Big|\ \text{Ag.} \qquad (1)$$

This reference electrode responds only to changes in the sodium ion concentration (4) and, since that remains constant, the electrode yields a very stable, although poorly defined (6), potential permitting the potential at the working electrode to be measured with good reproducibility. In addition, cyclic voltammograms and sweep polarization responses were recorded utilizing a vitreous carbon test electrode. The vitreous carbon electrode, when sealed in a Pyrex tube with only a cut and polished section exposed to the molten bath, offered a very reproducible surface area and avoided problems encountered quite often with the soluble test electrodes. Use of this electrode also permitted the potential range to be expanded in the positive direction to determine if the dissolution current for the platinum-group metal test electrode was masking other electrochemical reactions occurring at these more positive potentials.

A high-current potentiostat and associated waveform generator were used to generate the triangular waveforms for the cyclic voltammetric traces as well as the linear-voltage ramps for the sweep-polarization studies. An X-Y recorder was used to record traces for scan speeds of 200 mv/sec or less, while traces at faster scan speeds were recorded on an oscilloscope. The potentiostat voltage limit of ± 20 volts between anode and cathode was often reached in plating bath preparation due to the high resistivity of the ion-conducting membrane used. In these cases a direct-current source was used, and an ammeter and digital voltmeter were used to monitor the potentials of the cell electrodes and the cell current. An integrating coulometer was used to record the amount of charge passed in all experiments.

EXPERIMENTAL RESULTS AND DISCUSSION

ELECTROCHEMICAL STUDIES AND PLATING BATH PREPARATION

Platinum

In order to determine the cause of the previously reported requirement (11) for the presence of oxygen in the electrodeposition of platinum, cyclic voltammetric studies were conducted for a platinum test electrode in molten alkali cyanide salt baths in both air and helium atmospheres. For both atmospheres, it was found that the electrochemical dissolution of platinum occurs at the same potential at 20 ma/cm^2 current density. The low rate at which the current increased with applied potential indicates that the dissolution process is inhibited at small positive applied potentials. At higher positive applied potentials, the current increased very rapidly. The reduction of platinum ions, dissolved in the bath from the test electrode during the positive potential scan, occurred at the same potential for both atmospheres and was independent of potential scan rate. The cyclic voltammetric trace in a helium atmosphere for a platinum test electrode in a molten cyanide electrolyte containing some platinum is shown in figure 2. The potential of the test electrode was scanned at 100 mv/sec from the open-circuit potential, A, in the positive potential direction to an arbitrary potential, B, then negatively to another arbitrary potential, D, then back to the open-circuit potential. At point B, the dissolution of the platinum test electrode is occurring, while the current peak at C represents the reduction of platinum ions that were dissolved in the bath during the positive going part of the scan plus a small contribution from the platinum present initially in the bath. At point D, a small amount of reduction of the sodium and/or potassium ions of the electrolyte is observable. Even though the potential at point E is equal to the open-circuit potential, A, a positive current is observed at E during the transient potential sweep. At the steady-state, open-circuit potential, A, the platinum is thought to be in a passive state; the platinum appears to become activated during the cyclic voltametric sweep.

The results of these cyclic voltammetric studies indicated that it should be possible to prepare a platinum-containing electrolyte by electrolytic dissolution of the platinum in an oxygen-free environment, and to use this electrolyte for the electrodeposition of platinum coatings (1) by careful control of the potentials at which the two processes occur, and (2) by preventing the cathodic reaction product formed during electrolyte preparation (probably sodium metal) from reacting with the platinum ions dissolved in the bath. To test this plating bath preparation method, an experimental electroplating cell was designed. A graphite cathode was placed in a melt-filled glass (Pyrex or Exax) test tube, which was dipped into the bulk melt. The bulk melt also contained a platinum anode and a Ag, AgCl reference electrode. A known constant current was passed between the platinum anode and graphite cathode. An anode current density of 30 ma/cm^2 or less was used to prepare the electrolyte. Although it appears that the cathode current density during the electrolyte preparation is not important, it was normally approximately the same as that for the anode. Charge transport through the glass was primarily by mobile sodium ions (4). After the desired amount of platinum, as determined by the amount of charge passed, was added to the bath, the melt-containing tube was removed from the bath. A liquid metallic reaction product, probably sodium metal, was clearly visible inside the tube. This product would have reacted with dissolved platinum ions to produce metallic platinum in the melt if the glass membrane had not been present. A clarification of the results of earlier Bureau work (11), in which the presence of oxygen was required for successful platinum electrodeposition, is thus provided by this study. In air, the metallic cathodic reaction product would react with oxygen to form sodium oxide, and not react with the dissolved platinum ions in the bath. Another advantage of using the glass separator during the preparation of the platinum-containing electrolyte is that no platinum comes in contact with the cathode during this procedure.

Thus, through the use of an ion-conducting glass to separate the anode and cathode compartments and by controlling the potential of the platinum anode during dissolution, platinum plating baths of known composition can be prepared. The cell used for this both preparation may be written schematically as

$$\begin{matrix}\text{Pt}\\ \text{(anode)}\end{matrix}\ \Big|\ \text{Pt}^{2+} \text{ in NaCN-KCN}\ \Big|\ \begin{matrix}\text{ion-conducting}\\ \text{glass}\end{matrix}\ \Big|\ \text{NaCN-KCN}\ \Big|\ \begin{matrix}\text{graphite.}\\ \text{(cathode)}\end{matrix} \qquad (2)$$

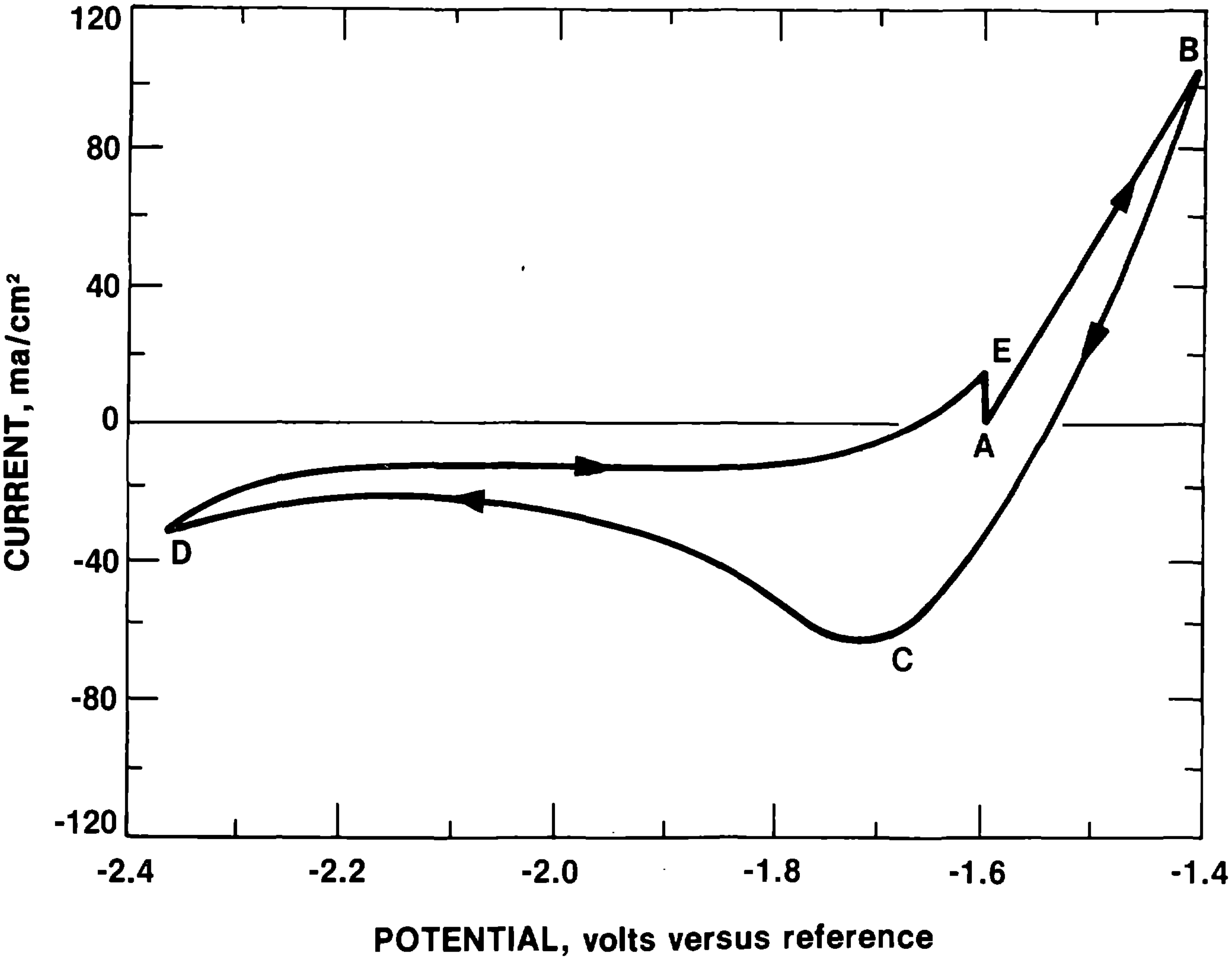

FIGURE 2.—The first cycle of cyclic voltammetric curves for a platinum electrode in molten sodium cyanide-potassium cyanide at 550° C in a helium atmosphere, sweep rate 100 mv/sec.

As has been observed by others (*7-8, 11*), anode (dissolution) current efficiencies, based on Pt^{2+}, were found to be near 100 percent for anodes that had only been used for short periods of time. As more of the platinum dissolves from the electrode, its surface becomes extremely etched. In these cases there was a possibility that pieces of metallic platinum could fall into the bath, resulting in higher apparent anode current efficiencies. This effect was more pronounced at current densities greater than 25 ma/cm^2.

Sweep polarization curves were recorded by scanning the electrode potential in the negative direction from the platinum open-circuit potential using either platinum or vitreous carbon test electrodes in a platinum-containing molten electrolyte. These electrodes were sealed into Pyrex glass tubes to provide a well-defined surface area in contact with the bath. Both electrodes showed a well-defined current plateau for the reduction process under unstirred conditions at the approximate potential expected on the basis of the CV results. This current plateau was shown to be proportional to the platinum ion concentration in the electrolyte and this technique was used throughout the study to monitor the concentration of dissolved platinum.

Even in the helium atmosphere, the platinum plating baths were not stable over long periods of time. The Pt^{+2} complex decomposes slowly and fine particles of platinum settle from the bath. Spectroscopic studies (*1-2*) suggest that platinum can exist in the cyanide bath as a soluble, colorless Pt(O) species. De Haas and Fouche (*1*) have also reported spectroscopic evidence for the existence of a yellow-colored platinum (*1*) cyanide complex. While the role played by the complex chemistry of these baths (*1-2, 10, 12*) to cause this decompositon is not well understood at this time, some evidence for lower oxidation state platinum species in the plating baths has been obtained during this study; further work is in progress to determine the relative significance of these species.

Rhodium

The cyclic voltammetric curve obtained for a rhodium test electrode in a molten cyanide salt bath containing some rhodium is shown in figure 3. Here point A represents the open-circuit potential of rhodium in the bath. From point A to arbitrary point B, a portion of the dissolution region for rhodium metal in the melt is shown. The current response in this region was found to be almost independent of the potential scan rate. The current peak at point C on the curve is due to the reduction of the rhodium ions dissolved in the bath. This peak was shown to in-

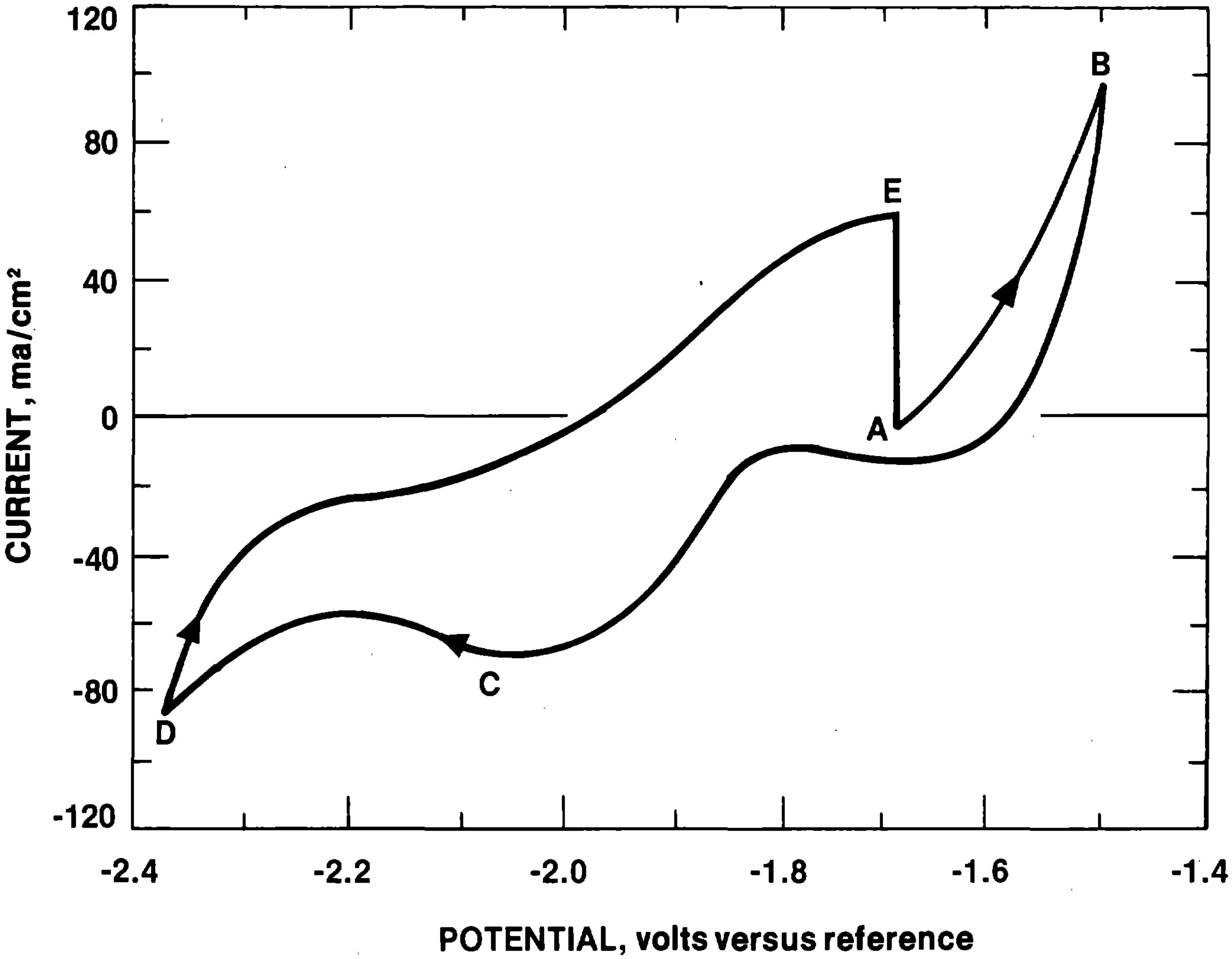

FIGURE 3.—The first cycle of cyclic voltammetric curves for a rhodium electrode in molten sodium cyanide-potassium cyanide at 550° C, sweep rate 100 mv/sec.

crease with increasing scan rate, indicating that the concentration of rhodium available for reduction at point C depends on the rate of diffusion of rhodium ions in the bath. At point D, a significant amount of ionic sodium is being reduced to sodium metal. At point E, rhodium, which had been deposited on the test electrode at potentials more negative than approximately -1.85 v, is being oxidized, producing rhodium ions in the melt. From figure 3 it can be seen that the rhodium deposited at potentials near point C appears to be more easily oxidized (see point E) than the initial rhodium surface (point A). This observed difference in oxidation rates at the same apparent potential indicates that the rhodium surface is covered with some type of inhibiting film at open circuit. The large potential difference between the rhodium open-circuit potential (point A) and the reduction peak (point C) is also indicative of such an inhibiting film.

From the information gained in the CV studies, it was possible to prepare a rhodium-containing bath in the same manner as described in the platinum case. Again, a glass separator was used during the dissolution of rhodium to separate the anode and cathode compartments in order to prevent the sodium metal, formed at the cathode, from reacting with dissolved rhodium ions. Sweep polarization curves were recorded using platinum and vitreous carbon test electrodes in 1-wt-pct-rhodium-containing baths at scan speeds between 5 and 20 mv/sec. These curves were recorded by scanning the potential in the negative direction from the open-circuit potential of a rhodium test electrode. These polarization studies indicated that the reduction of rhodium ions in the bath was diffusion controlled and that the reduction occurred at the same approximate potential predicted by the CV curves. The magnitude of the diffusion limited curve was found to be proportional to the amount of rhodium dissolved in the bath. However, the irreproducibility of the area of the platinum test electrode as well as what may be some irreversibility of the electrodeposition of rhodium on the vitreous carbon and an interference due to sodium codeposition have limited the use of these electrodes for routine in situ analysis of rhodium concentration in the bath.

The optimum potential for the formation of electrodeposits of rhodium, as determined from the slow scan rate traces, appears to be in the region from -2.0 to -2.2 v. At more negative potentials sodium metal will be codeposited with the rhodium, resulting in a porous deposit. Rhodium anode current efficiencies were found to be nearly 100 percent for rhodium dissolution, assuming the rhodium to be present at the +1 ion (*11*). In contrast to the platinum-containing melt, the rhodium plating baths were found to be very stable in the absence of oxygen. When oxygen was inadvertently admitted to the controlled atmosphere enclosure, rapid precipitation of rhodium from the bath was observed, as has been reported previously (*11*).

Additional information regarding requirements for control of the potential during preparation of rhodium plating baths was obtained from cyclic voltammetric studies using the "inert" vitreous carbon test electrode in the rhodium-containing electrolyte. In addition to the problem of codeposition of sodium with rhodium when the potential of the test electrode was scanned more negative than -2.2 v, an additional oxidation wave was observed that cannot be seen in CV traces obtained with a rhodium test electrode. This oxidation current, which was observed in the vicinity of -1.4 v, was hidden by the larger currents due to rhodium dissolution when the soluble test electrodes were used. This oxidation wave observed near -1.4 v is thought to represent the oxidation of rhodium from the + 1 to the + 3 oxidation state. Studies were conducted to determine the nature of this wave and to determine if it would be possible to electrodeposit rhodium from this higher oxidation state in an attempt to eliminate the problem of sodium codeposition at the potential required to prepare rhodium coatings when the + 1 oxidation state of rhodium is present.

First, using a vitreous carbon test electrode, the size of the oxidation wave at -1.4 v was measured as rhodium was electrolytically dissolved in or removed from the bath. The results showed that this diffusion current was linearly related to the concentration of dissolved rhodium. Next, a long-term oxidation of the rhodium-containing electrolyte was carried out in order to convert all of the rhodium in the bath to the + 3 oxidation state. This was accomplished by using a potentiostat to adjust the potential of a graphite electrode in the bulk electrolyte at a value more positive than the oxidation wave. A second graphite electrode contained in a Pyrex test tube (melt-filled) was used as the cathode during the electrolysis.

Periodic cyclic voltammetric scans were recorded at a vitreous carbon electrode as the oxidation progressed. No obvious change was observed in the potential for rhodium reduction, although the reduction current increased with time due to reduction from the rhodium + 3 state, and no additional reduction wave appeared. These experiments show, therefore, that this higher rhodium oxidation state is not desirable for the preparation of rhodium electrodeposits, since a tripling of current is required to produce the same amount of deposit. To prevent the formation of this higher oxidation state, care must be taken to control the potential of the rhodium anode so it is always kept negative to this oxidation wave.

Although spectroscopic studies (*2-3*) have shown that rhodium can exist in both the + 1 and the + 3 oxidation states in the molten cyanide electrolyte, they determined that rhodium wire dissolves electrolytically only as the + 1 ion for current densities of 1.0 to 4.4 ma/cm^2. In the present studies, it has been found that rhodium dissolves exclusively in the + 1 state at currents up to at least 100 ma/cm^2.

Iridium

Figure 4, curve 1, shows a cyclic voltammetric trace for an iridium test electrode in a molten cyanide electrolyte containing dissolved iridium. This CV curve, obtained at a sweep rate of 200 mv/sec, shows some similarities to the curves for platinum and rhodium. The open-circuit potential, point A, is -1.56 v, compared with -1.60 v observed for platinum at the same approximate concentration of dissolved metal. The inflection point observed at B in the iridium dissolution is similar to a smaller inflection ob-

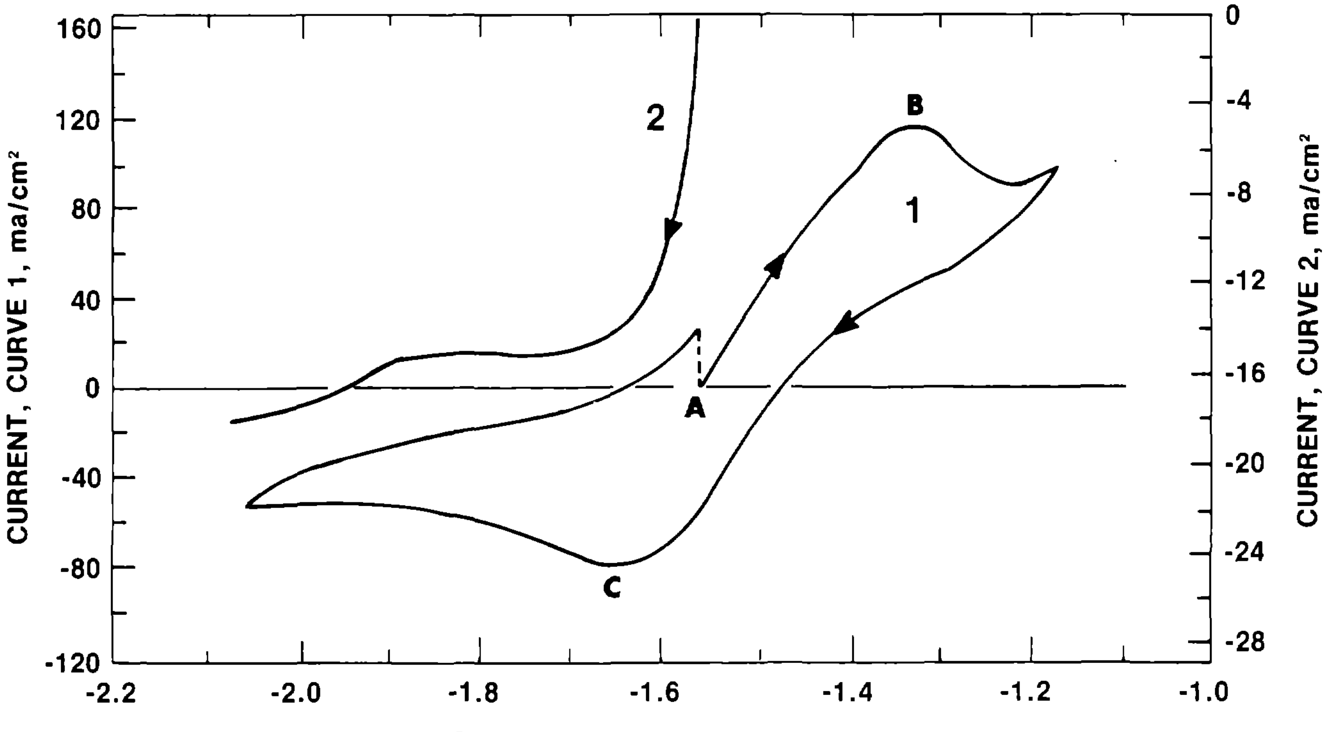

FIGURE 4.—Cyclic voltammetric curve (1) for an iridium electrode in molten sodium cyanide-potassium cyanide at 550° C, sweep rate 200 mv/sec; slow sweep rate polarization curve (2) showing the diffusion current for iridium reduction in the presence of dissolved iridium, sweep rate 20 mv/sec.

served for rhodium during multiple cycle voltammetric curves. This passivation may be due to the formation of a poorly conducting film of either iridium cyanide or polymerized cyanogen (*7*), which may slowly dissolve in the molten electrolyte. The reduction peak, point C, is -1.64 v for iridium compared with -1.70 v observed for platinum. The current observed for a sweep polarization experiment for an iridium test electrode, scanned in the negative potential direction at 20 mv/sec (fig. 4, curve 2), shows that the reduction of iridium from the iridium-containing molten cyanide electrolyte occurs without apparent difficulty, and at the potential predicted from the CV curves. However, the magnitude of the diffusion limited current has been found not to be a dependable measure of iridium dissolved in the bath.

A 1-wt-pct-iridium-containing melt was prepared by the same techniques as those used for the platinum and rhodium baths; that is, with an ion-conducting glass tube to separate the cathode compartments from the bulk melt that contained the anode and by potentiostatic control of the iridium anode during dissolution. Initial attempts at electrodepositing coatings, however, resulted in irreproducible deposits and widely varying current efficiencies. A series of experiments was performed, using iridium cathodes and anodes, to determine the conditions that give the greatest current efficiencies and yield-quality deposits. The desirable oxidation state of the iridium in the bath for the electrodeposition of coatings is assumed to be the +3 form (*7. 11*).

For the 1-wt-pct-iridium-containing molten cyanide electrolyte, it was determined that a cathode current density of approximately 10 ± 2 ma/cm² gave the best quality iridium deposits without requiring electrolyte agitation. Using this fixed cathode current density, a series of iridium deposits were prepared for a range of anode current densities. The total charge passed during each deposition was sufficient to replace at least one-half of the iridium content of the bath. The results of eight experiments are shown in figure 5. At low current densities, the anode and cathode current efficiencies are very low. The cathode current efficiency is near 80 percent for anode current densities between 35 and 90 ma/cm². The anode current efficiency is near 100 percent at current densities from 20 to 50 ma/cm², then decreases at higher current densities, becoming equal to the cathode efficiency in the region of 90 ma/cm². Equal cathode and anode current efficiencies are desirable in order to maintain a constant bath composition. The primary cause for not attaining a measured current efficiency of 100 percent for the anode and cathode reactions is thought to be due to the formation of other (higher and lower) oxidation states at the cathode and anode (*2, 7*). However, the reduced anode current efficiency at high current densities may be caused by the oxidation of cyanide ion to form cyanogen gas (*7*). This oxidation reaction could produce irreversible changes in the bath composition. Thus, for iridium deposition, anode current density should be maintained at less than 50 ma/cm². It should be noted that the current efficiencies shown in figure 5 would undoubtedly change if some other cathode current density had been selected.

A similar study was conducted (*7*), which found that a cathode current density of approximately 10 ma/cm² resulted in the highest current efficiencies (at an unspecified anode current density), but that the anode cur-

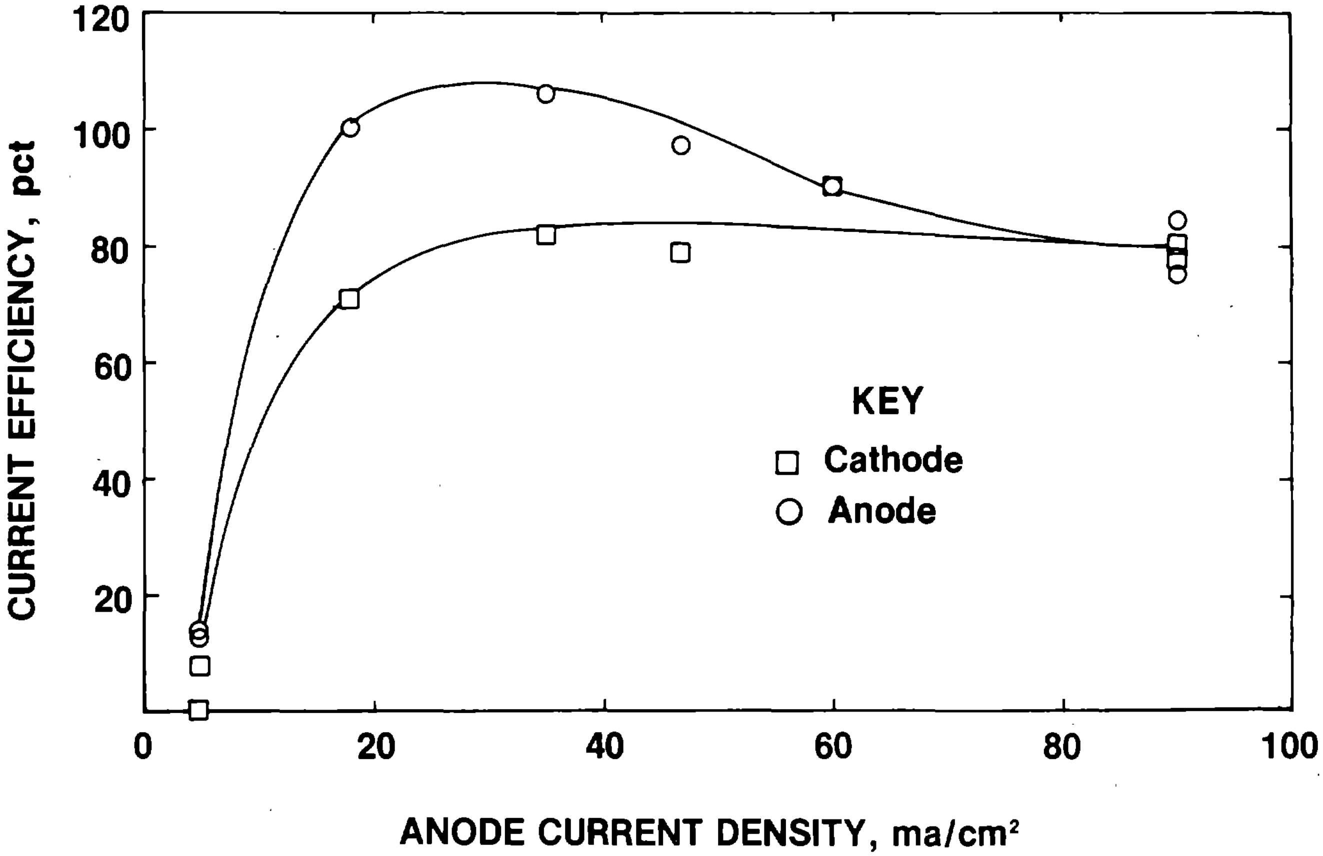

FIGURE 5.—Iridium dissolution (anode) and deposition (cathode) current efficiencies as a function of anode current density.

rent efficiency reached a maximum of 60 percent at 40 ma/cm^2 (at an unspecified cathode current density). In addition, the results (*7*) showed that both anode and cathode current efficiencies dropped off as baths aged. This reduction in current efficiency with time was not observed in the present studies. It is possible that insufficient charge was passed during the experiments reported (*7*) to establish a reproducible, steady-state mixture of the various oxidation states of iridium in the bath. If insufficient charge was passed, the true effect for a specific current density may not be accurately reflected in the resulting current efficiencies.

Other studies have yielded additional information regarding this complex, but not completely understood, system. Cyclic voltammetric studies with a vitreous carbon test electrode have indicated the presence of only one electrochemical redox couple in the iridium-containing molten cyanide salt; the reduction part of which represents the reduction of dissolved Ir^{3+} ions to iridium metal. Long-term oxidation of the bath with a graphite electrode results in an apparently higher oxidation form of iridium that cannot be reduced directly to iridium metal. On the basis of these studies, as well as the current density-current efficiency study described earlier, it is apparent that several competing reactions involving iridium can occur at the electrodes, the significance of each being dependent upon the current density. At low anode current density the observed low anode current efficiency is apparently due to oxidation of the preferred +3 iridium state to some higher oxidation state or the dissolution of iridium metal to the +1 or +2 state. At higher anode current densities the dominant reaction is the dissolution of the iridium anode as the +3 ion. At the cathode, two competing reactions may occur; the iridium +3 ion may be reduced to iridium metal, or the iridium in a higher oxidation state may be reduced to the +3 state, resulting in overall apparent current efficiencies always less than 100 percent.

These conclusions are consistent with the results of spectroscopic studies (*3*) where, by infrared and diffuse reflectance measurements, it has been shown that at very low current density of 1 ma/cm^2, iridium dissolves electrolytically as Ir^+ and, as the current density is increased, the likelihood of the reaction of iridium metal being oxidized to the +3 state increases. Harding (*7*) also suggested that the Ir^{3+} ions in the melt may be oxidized to a higher oxidation state, probably the +4 state, on the basis of cyclic voltammetric studies of iridium in molten sodium cyanide baths.

Palladium

Palladium studies were initiated by attempting to prepare a palladium plating bath by the same techniques as were used for platinum; that is, with an ion-conducting glass tube to separate the anode and cathode compartments, and by potentiostatic control of the anode. It was found, however, that the current efficiency for palladium dissolution was strongly dependent on the amount of palladium dissolved in the bath. For palladium concentrations up to $\simeq$ 1 wt-pct in a fresh bath, the apparent dissolution current efficiency for the assumed formation of Pd^{2+} was determined to be nearly 200 percent for a dissolution current density of 12 ma/cm^2. With further increases in the palladium concentration the current efficiency progressively decreased until an efficiency of near 100 percent was reached for palladium concentrations $\geqslant$ 2 wt-pct.

Cyclic voltammetric studies using a palladium test electrode and a range of scan speeds, 10 mv/sec and faster, in a bath containing some palladium showed both the oxidation current of the palladium as well as the current peak that represents the reduction of palladium ions dissolved in the bath during the positive-going part of the sweep plus the small contribution from palladium initially in the bath. This cyclic voltammetric study indicates that palladium is readily dissolved and redeposited from this bath if the palladium is present in the bath in the proper oxidation state. At a slow scan speed of 2 mv/sec, the oxidation of the palladium test electrode is observed but only the diffusion-limited current for the reduction of the dissolved palladium can be observed on the trace. Slow scan rate cyclic voltammetric studies using a vitreous carbon test electrode showed that baths with low ($\leqslant$ 1 wt-pct) palladium concentration exhibit an oxidation current that increases in size with increasing palladium concentration. However, no reduction current is observable on the scans and no palladium deposits can be prepared from the bath. With continued addition of palladium above 1 wt-pct by electrochemical dissolution of palladium metal, the oxidation wave measured at a vitreous carbon test electrode attains a maximum value and a reduction wave begins to appear. This reduction wave corresponds to the potential observed in the rapid scan rate cyclic voltammetric studies for palladium reduction, and this reduction must be observable before palladium coatings can be electrodeposited.

The oxidation current observed at the vitreous carbon electrode has been attributed to a palladium-containing species that is readily converted to the Pd^{2+} ion by oxidation at an inert electrode. Periodic cyclic voltammetric traces recorded during a long-term oxidation of this bath at a graphite working electrode at -1.2 v showed that the oxidation current continuously decreased, while at the same time the normal palladium reduction current increased. Also, it was found during these experiments that, for a given weight of total palladium in the bath, the sum of the currents observed at the vitreous carbon electrode, due to the oxidation and reduction of palladium, is a constant. Since the current efficiency for palladium deposition is consistent with a two electron process,

$$Pd^{2+} + 2e = Pd^{\circ}, \tag{3}$$

it appears that the oxidizable palladium species must be present in the melt in a zero-valence state. The fact that the oxidizable species cannot be reduced over the potential range available in the melt also indicates a zero oxidation state. Evidence for the existence of this unusual oxidation state has been reported in spectroscopic studies (*1*). The examination of palladium metal species in the quenched alkali cyanides showed that palladium species can exist in +2, +1, and zero oxidation states.

A cyclic voltammetric trace for a palladium test electrode in a bath from which palladium could be electrodeposited, and a slow sweep rate polarized curve, recorded using a vitreous carbon electrode, are shown in figure 6. For the cyclic voltammetric trace, the potential was scanned at 100 mv/sec about the open-circuit potential, point A. Point C represents the reduction of Pd^{2+} ions in the melt, while the current at point B represents the dissolution of the palladium test electrode plus some contribution due to the oxidation of the Pd(O) species in the bath.

The formation of this zero-oxidation-state palladium species is believed to be due to an indirect reaction of the palladium ion with an impurity in the molten cyanide, probably the cyanate ion (OCN^-). The reagent-grade NaCN and KCN salts used to prepare the plating baths are known (*9*) to contain cyanate ion at $\simeq$ 1 wt-pct. The mechanism by which the reaction between cyanate ion and palladium ion is thought to occur is discussed later in this section.

Although cyclic voltammetric studies have shown that heating a palladium-containing bath in air results in the conversion of all the unknown species of palladium to the

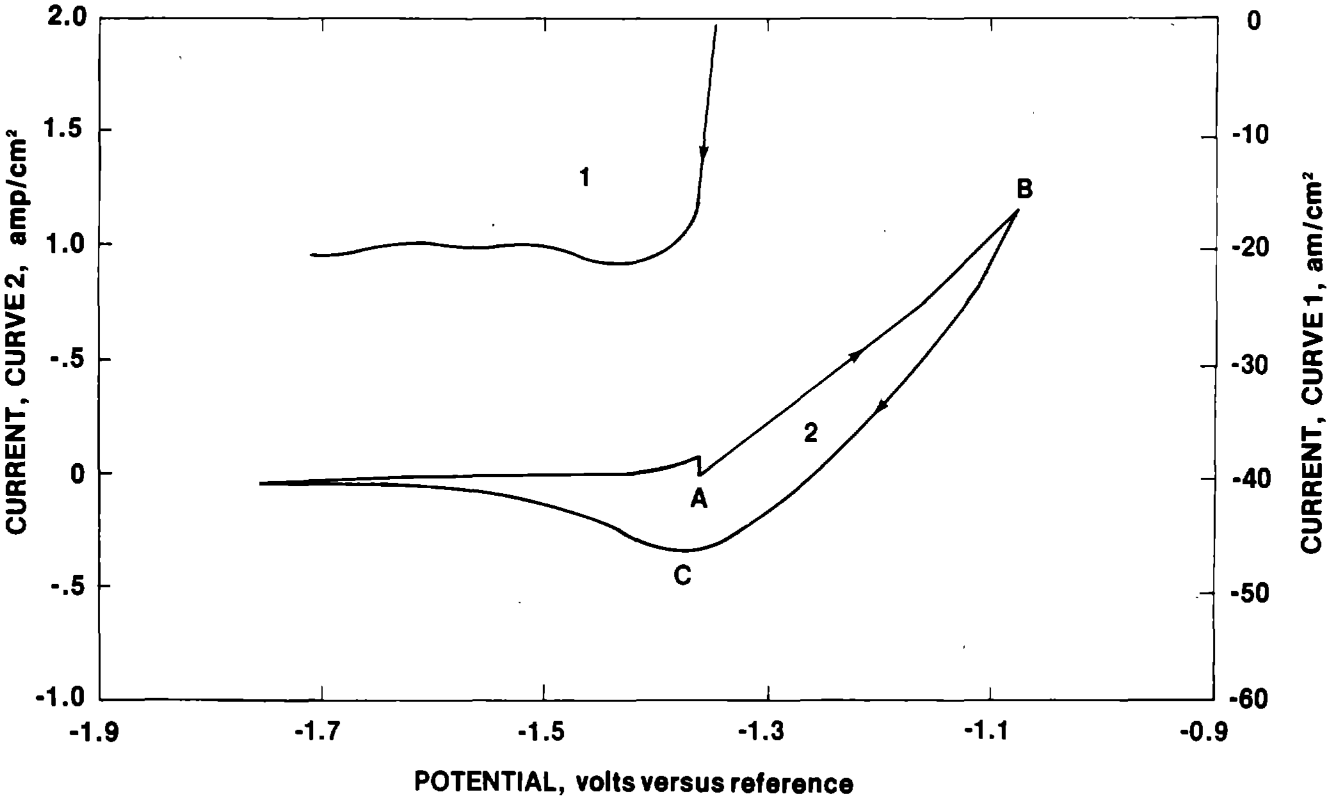

FIGURE 6.— Polarization curve (1), recorded at 5 mv/sec with vitreous carbon test electrode, showing the diffusion current for palladium reduction in the presence of dissolved palladium in molten sodium cyanide-potassium cyanide at 550° C; cyclic voltammetric curve (2) for palladium electrode for a sweep rate of 100 mv/sec.

+ 2 oxidation state, as seen in earlier Bureau of Mines (*11*) studies, this is not a desired operating condition due to the rapid decomposition of the palladium-containing cyanide bath in air. One method that showed some promise to stabilize the palladium plating bath was the addition of selected chemical reagents.

De Haas and Fouche (*1*), in their spectroscopic studies, showed that sodium dicyanamide, $NaN(CN)_2$, was an oxidizing agent in the molten cyanide electrolyte. Because of that study (*1*), a series of experiments were conducted to determine if the addition of $NaN(CN)_2$ oxidant to a palladium plating bath would produce an increase in the concentration of the desired plating form of palladium (+2) species in the melt through oxidation of the soluble palladium (O) species, and to determine if the palladium (+2) complex could be stabilized.

Sodium dicyanamide was added in small increments to an equimolar NaCN-KCN molten bath with no palladium present. When a total of 1.6 wt-pct $NaN(CN)_2$ had been added, a reduction current was observed at a vitreous carbon test electrode at a potential of -1.60 v versus the silver-silver chloride reference electrode. This reduction current increased as additional increments of $NaN(CN)_2$ were added. After 2.7 wt-pct $NaN(CN)_2$ was added, palladium ($\leq$1 wt-pct) was then added electrolytically and a reduction current was observed at a vitreous carbon test electrode at -1.35 v, which corresponded to the potential previously observed for palladium reduction in a cyanide electrolyte with no $NaN(CN)_2$ added. Furthermore, when the potential of the test electrode was moved positive to the open-circuit potential, after having been held at a sufficiently negative potential, a stripping peak on the CV trace was observed. This peak represents the current due to the oxidation of palladium metal that had been electrodeposited on the vitreous carbon test electrode surface. After quenching and remelting of the bath, no changes in the open-circuit potential of the vitreous carbon test electrode or the stripping peak area were observed, indicating a relatively stable palladium-containing bath. However, when coatings were electrodeposited from this palladium-containing bath and also from a second bath prepared in a similar manner to which 1.9 wt-pct $NaN(CN)_2$ had been added, the cathode current efficiencies were only 29 and 19 percent, respectively.

When increasing amounts of $NaN(CN)_2$ were added to the palladium-containing melt in several increments, the CV traces recorded at a vitreous carbon test electrode showed that the open-circuit potential became more positive, and the total current as indicated by the CV wave increased slightly; however, there was essentially no change in stripping peak size. It is clear that even though the $NaN(CN)_2$ appears to increase the stability of the bath and to increase the palladium that is reducible at a vitreous carbon electrode, either most of the palladium present is not reducible to the metallic state, as evidenced by the low cathode current efficiencies or, perhaps, the reduction of $NaN(CN)_2$, that was observed at -1.60 v can occur at a measurable rate at -1.35 v. Also, some of this low current efficiency may be the result of corrosion of the palladium by the $NaN(CN)_2$; initial open-circuit corrosion rates of palladium in the presence of excess $NaN(CN)_2$ were observed to be as great as 25 ma/cm^2.

In another series of experiments, electrochemical measurements to determine the effects of disodium cyanamide, Na_2NCN, on the cyanide melt were conducted. The Na_2NCN was expected to act as a reducing agent in the melt (*1*). When small increments of the Na_2NCN were added (total $\simeq$ 1 wt-pct) to an equimolar KCN-NaCN melt, an oxidation current response was observed on a CV curve at -1.30 v, using a vitreous carbon test electrode. This potential is near that observed for palladium reduction in a normal cyanide melt. As in the case of $NaN(CN)_2$ additions, the measured current (in this case, an oxidation current) increased with Na_2NCN additions.

An experiment was conducted to show that Na_2NCN can function as a reducing agent in the presence of Pd^{2+} in a molten cyanide bath. In this test, a palladium-containing ($\simeq$ 0.59 wt-pct) molten cyanide bath was subjected to a long-term oxidation using a graphite working electrode as described earlier. After 12,920 microequivalents (µeq) of charge was passed, most of the palladium present had been converted to the Pd^{2+} state (for a 45.870 g equimolar NaCN-KCN containing 0.269 g (5,060 µeq) of Pd). Increments of Na_2NCN were then added to the bath. The ratio of Pd^{2+} to Pd° in the bath as a function of added Na_2NCN was monitored by measuring the oxidation and reduction currents observed at a vitreous carbon test electrode. Table 1 shows the results for six additions of Na_2NCN to the palladium-containing, preoxidized bath. The concentrations of Pd^{2+} and Pd°, given in the table as the chart recorder wave heights of the reduction and oxidation currents measured using the vitreous carbon electrode, changed in opposite directions as the Na_2NCN was added. Approximately twice as much Na_2NCN as expected was required to lower the concentration of Pd^{2+} to a small value. However,the decrease in the amount of Pd^{2+} present was directly related to the increase in the level of Pd° in the bath. That the sum of the heights of the oxidation and reduction waves was observed to be a constant (in this case 4.50 cm at a given current measurement sensitivity) is somewhat surprising, and seems to indicate that the diffusion coefficients for the two species are very similar.

TABLE 1.—Reduction of Pd^{2+} to Pd^o in a molten NaCN-KCN bath produced by additions of disodium cyanamide

Na_2NCN[1] added, µeq (cumulative)	[2]Pd^{2+}	[2]Pd^O	$\frac{Pd^{2+}}{Pd^O}$
0	3.21	1.28	2.51
1,093	3.00	1.50	2.0
3,093	2.04	2.46	.83
5,418	1.65	2.85	.57
8,255	.59	3.91	.15
10,650	.29	4.20	.07
17,742	0	4.50	0

[1] Based on equivalent weight equals formula weight divided by 2.

[2] Observed current in arbitrary units (centimeters of recorder displacement).

These studies serve to illustrate the complicated chemistry of the molten cyanide electrolyte. Spectroscopic studies of these electrolytes (*1, 9-10*) have determined that a number of reactions that control the oxidation states of many platinum-group metals occur in these systems. When an electric current is passed through the molten alkali cyanide electrolyte during the dissolution of a platinum-group metal, if the anode potential becomes too positive, cyanogen gas, $(CN)_2$, will be generated. This gas can react with the cyanide ion to generate the dicyanamide ion through the reaction (*10*),

$$(CN)_2 + CN^- = N(CN)_2^- + C, \qquad (4)$$

and an electrochemical equilibrium between cyanamide ion and dicyanamide ion can be expected (*10, 12*),

$$N(CN)_2^- + 2e- = NCN^{2-} + CN^-. \qquad (5)$$

The electrochemical equilibrium (equation 5) could then control the amounts of palladium present in the electrolyte in the +2¢ and zero-oxidation states (*10, 12*),

$$Pd(CN)_4^{4-} + N(CN)_2^- = Pd(CN)_4^{2-} + NCN^{2-} + CN^-. \qquad (6)$$

The reaction (equation 6) is in agreement with the results observed in the experiments described earlier where cyanamide and dicyanamide were added to the palladium-containing electrolyses.

One possible explanation for the continuing decomposition of the palladium bath is that the dicyanamide ion is removed from the equilibrium (equation 6) by a polymerization process (*10*). The reaction in equation 4 is not thought to be occurring in present studies because care was taken to not allow the potential to become sufficiently positive to cause cyanogen generation.

In the present studies it was observed that the freshly prepared cyanide electrolyte is corrosive to palladium metal, so that the electrolyte as prepared appears to contain dicyanamide ion. As mentioned in the "Experimental Techniques" section, the electrolyte was prepared by an initial melting in air. This procedure is known to cause the formation of cyanate and carbonate ions (*9*). While no substantive study of the mechanism for the formation of carbonate ion during the oxidation was found, a reasonable overall reaction might be

$$3\,OCN^- = N(CN)_2^- + CO_3^{2-}. \qquad (7)$$

Another route to the formation of dicyanamide ion has been suggested (*12*) that may also explain the observed decomposition of the palladium and platinum containing electrolytes.

$$Pt(CN)_4^{2-} + 3CN^- = Pt(CN)_4^{4-} + N(CN)_2^- + C \qquad (8)$$

and

$$Pd(CN)_4^{2-} + 3CN^- = Pd(CN)_4^{4-} + N(CN)_2^- + C \qquad (9)$$

The reactions given in equations 8 and 9 are reasonable in that carbon has been determined to be present in the plating bath decomposition products.

While the addition of $NaN(CN)_2$ appears to decrease the rate of precipitation of palladium metal from the bath, it also appears to be the cause of the low cathode current efficiencies observed when coatings are produced from these baths. Based on the electrochemical studies, using cyclic voltammetry and slow sweep rate polarization, on the findings from the experiments to stabilize the palladium plating baths by chemical means and on the melt preelectrolysis studies, the best method for preparation of palladium plating baths seems to be to use a helium atmosphere and an ion-conducting glass tube to separate the anode and cathode compartments during palladium dissolution. Salt preparation must include the preelectrolysis of the cyanide bath (in a helium atmosphere) using an inert electrode and, in contrast to the other platinum-group metal baths, the premelting of the salts in air is not desired as this has been shown to increase the concentration of cyanate ions, a bath inpurity. Palladium plating baths prepared in this manner are still found to decompose slowly, with metallic palladium precipitating from the bath.

Future studies are planned to evaluate palladium plating baths prepared using electrolytes purified by the techniques used by Lessing (*9*). However, if the reaction given in equation 9 is a correct and significant reaction, it may not be possible to prepare a stable palladium-containing molten alkali metal cyanide electrolyte.

COATINGS

Substrates

Substrates selected for electrodeposition studies included copper, Monel, Inconel, molybdenum, 316 stainless steel, and a series of iron-chromium alloys. Substrates usually were in the form of small coupons, often 2.54 by 1.27 cm, with a small hole drilled in one end. A wire passed through this hole supported the coupon in the molten salt bath and provided an electrical contact while the coupon was immersed in the melt. The first step of substrate preparation involved mechanical polishing of the coupons through 600 grit paper followed by degreasing in trichloroethylene. Molybdenum and Inconel were chemically etched before plating while the iron-chromium alloys were electropolished to a bright finish. Effects of various surface preparations were not too significant. Roughness of the substrate was reflected in deposits only when the thickness of the coating was less than about 10 µm.

Plating Parameters

Platinum coatings were electrodeposited on all of the substrates at current densities of 2 to 10 ma/cm^2, with no bath agitation. Cathode and anode current efficiencies were found to be near 100 percent for electrodeposition from a 1-wt-pct-platinum-containing bath. Coatings from the 1-wt-pct-platinum baths were smoother than those obtained from 3-wt-pct-platinum-containing baths; coatings prepared at higher current densities appeared slightly rougher than those at lower current densities. Proton-induced X-ray emission (PIXE) and Auger-electron spectroscopy (AES) analyses of the surface of various coatings have shown carbon as a small ≈3-percent impurity. Analysis of coatings electrodeposited on copper and Monel substrates show rapid diffusion of copper through platinum during the plating process. For the other substrates used, no substrate alloying elements were detected in the platinum coatings.

Rhodium coatings were prepared from 1-wt-pct-rhodium-containing baths on Fe-5-wt-pct Cr, Inconel, and Monel. Although rhodium was adherent to the Fe-5-wt-pct Cr and Monel substrates, it was not very adherent to Inconel as the coating could be peeled off. Current densities were approximately the same as those for platinum, again with no bath agitation, resulting in current efficiencies close to 100 percent.

Adherent iridium coatings were electcrodeposited on Fe-5-wt-pct Cr and Inconel coupons from a 1-wt-pct-iridium-containing melt under unstirred conditions. As discussed previously, earlier Bureau of Mines work (*11*) had indicated that agitation of the molten salt by cathode rotation was required for high-quality deposits. Slow scan rate polarization studies have shown that the shape and position of the current-voltage response were not altered by agitation, and cyclic voltammetric curves at the vitreous carbon were not significantly affected. However, it was found that anode and cathode current densities must be very carefully controlled to maintain constant bath composition due to competing nondissolution and nondeposition reactions occurring at the electrodes.

Palladium coatings were electrodeposited on Inconel at current densities of about 3.5 ma/cm^2. The current efficiency was low, however, which may be due to poor adherence of palladium to Inconel. Electrodeposition from the same bath at a palladium cathode resulted in current efficiency of 70 percent. Examination of the coatings by optical microscopy showed small metallic pieces of palladium in the coating. The instability of the palladium plating bath noted earlier causes fine particles of palladium to precipitate slowly from the bath and these can be trapped in the coating, resulting in a rough deposit.

Cementation Reactions

Some substrates, such as the Fe-Cr alloys, were found to quickly attain the platinum open-circuit potential upon being lowered into a platinum-containing melt. To determine the cause of this constant potential, electropolished samples of Fe, Cr, and Fe-Cr alloys, containing 5, 10, 13, and 18 wt-pct Cr, were exposed to a platinum-free molten cyanide bath. Analysis of Fe-5-wt-pct Cr samples after exposure to the molten bath either at open circuit or used in repetitive cyclic potential sweeps revealed surfaces that were enriched in chromium. In other experiments, the open-circuit potentials of the alloys in the platinum-free molten alkali metal cyanide salt bath were measured and all metals except chromium were found to be negative with respect to the potential required to deposit platinum. Interestingly, the measured open-circuit potential became more negative as the amount of chromium increased in the alloys. As a result, corrosion or cementation reactions occur in platinum-containing melts, the rate of which increases with increasing chromium content of the alloy. This cementation is undesirable because as iron is depleted from the surface, the platinum is deposited in small islands, resulting in a nonadherent deposit. To prevent this, it was found that the cathode could be lowered into the bath and held at a potential negative to the open-circuit potential for that alloy until the cathode was completely covered with platinum. Then, since corrosion reactions could no longer occur, the potential was then moved to the normal deposition potential.

Coating of Large Vessel

Several attempts were made to prepare platinum coatings on large surfaces. As an example of a large-scale plating problem, the inside of a 316 stainless steel 1-liter pressure vessel was coated with platinum. The vessel, shown in figure 7, had an inside surface area that was 50 times larger than any surface coated previously in this program, and required the development of procedures to handle large quantities of the molten salt. In order to fully coat the upper sealing surface of the vessel body, a temporary lip was welded to vessel. The inner surfaces were sandblasted and then chemically etched. Using a 0.5-wt-pct-platinum-containing melt at 570° C in the helium atmosphere, the vessel was coated with 15 µm of platinum during a 3-hour deposition period. The top of the pressure vessel and the upper portion of the thermocouple well were each coated to a thickness of approximately 6.2 µm. The lower portion of the thermocouple well was coated to a thickness of approximately 20 µm.

After the temporary lip was removed, the vessel was tested in hydrochloric acid at high temperature and pressure to determine the corrosion resistance of the coating. Subsequent examination of the coating showed many small corrosion spots, apparently due to porosity of the platinum coating on the vessel body and the top portion of the thermocouple well. The lower portion of the well was free of corrosion, due either to the thicker platinum coating (20 versus 6.2 µm) on that portion or because the current density used in coating this area was smaller than that used for the remainder of the vessel (2 versus 6 ma/cm^2), resulting in a less porous coating. In addition, the thermocouple well was new, while the vessel body initially showed severe pitting from use in earlier work, and this may have resulted in a less adherent platinum coating. The study does show, however, that the procedures and conditions used for coating small test coupons can be adapted to coat much larger objects.

Coating Within Small Holes

There has been considerable interest in applications of platinum metal coatings for use in glass fiber production.

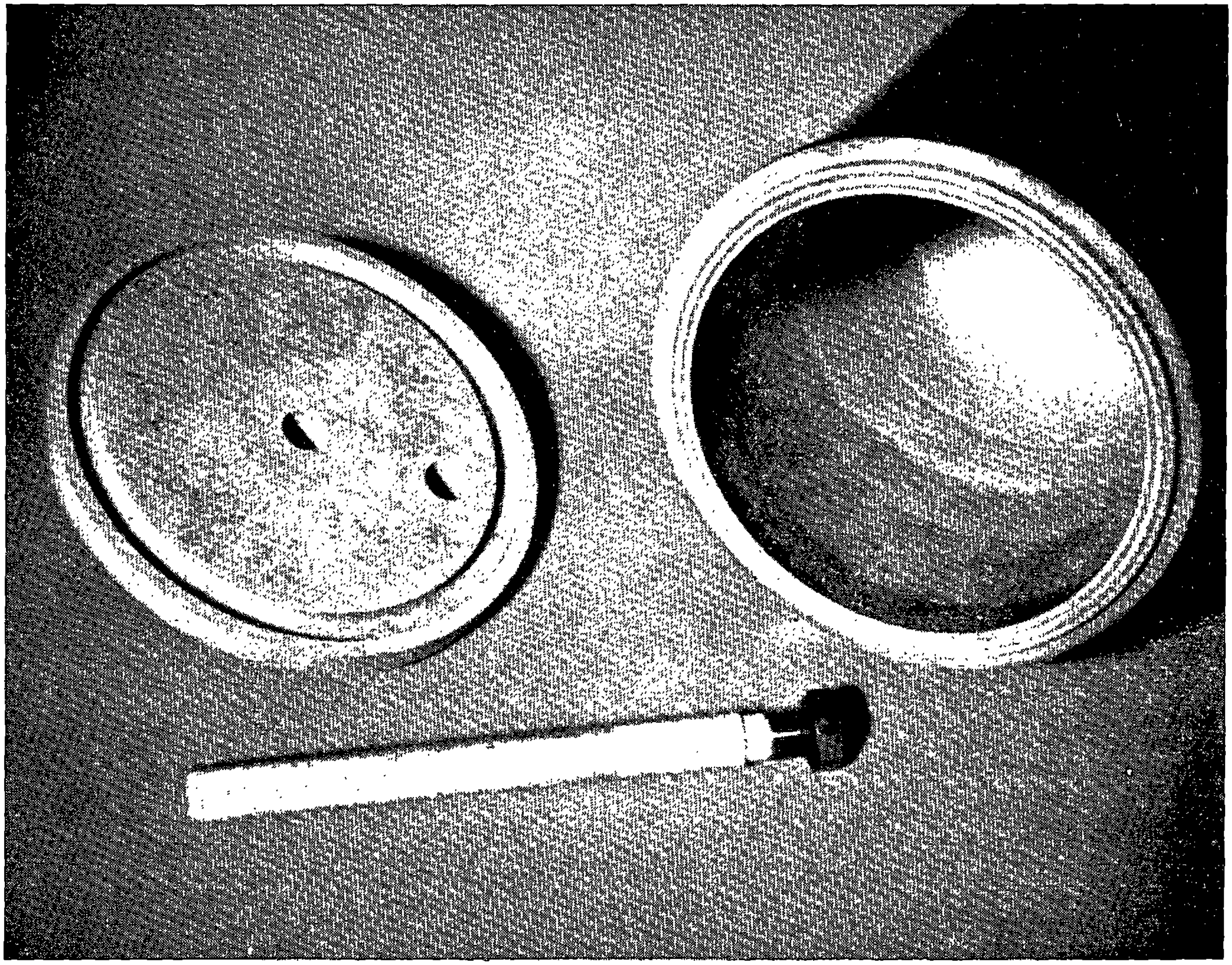

FIGURE 7.— One-liter pressure vessel, top and lid after electrodeposition of platinum coating.

In one application, test coupons of a cobalt-base superalloy material were coated with platinum. The 0.6-cm-thick test coupons were cut from a large-diameter fiberglass production crucible that had many small-diameter holes (≈30 μm) for fiberglass extrusion. In use, the small diameter holes become enlarged due to oxidation, rendering the crucible useless. This application was also of interest since no method was known to permit coating the inside surface of the holes.

Electrodeposition of a uniform coating on the alloy, including coating the inside surfaces of the small diameter holes without allowing dendrite growth to close the holes, was accomplished using a current-reversal plating technique. This technique involved adjusting the potential of the piece to be coated to a value at which platinum deposition occurred for a given period of time, and then stepping the potential to a more positive potential for a shorter period of time, where stripping (dissolution) of the deposit could occur. The dissolution current density at elevated surface areas, such as dendrites, was higher than at smoother areas of the coatings, so that the dendrites dissolved at a faster rate to produce a smoother, more even coating.

The test coupons were subjected to a temperature of 1,200° C in an air environment and then examined for corrosion resistance. Examination of the coupons revealed that while the flat surfaces were sufficiently covered with platinum, the surfaces of the inside of the holes were not completely covered. Scanning electron photomicrographs of the inside surface of a hole of a sectioned, noncoated test coupon showed surface features suggesting that the nonadherence problem was due to carbide or nitride impurities left on the surface where the holes were formed by ion-beam melting under kerosine. The platinum-containing molten cyanide bath was found to have very good throwing power, since the inside of the holes were covered with a thick platinum deposit except in areas where the impurities were on the surface.

SCANNING ELECTRON MICROSCOPY

To better correlate plating parameters with oxidation or corrosion resistance desired for a specific coating application, a study was initiated utilizing the scanning electron microscope (SEM) to determine the effects of various plating parameters on the grain size and porosity of the deposits. In the initial study, ≈ 50-μm-thick platinum coatings were electrodeposited on Inconel substrates from a 1-wt-pct-platinum bath using a series of direct-current-plating current densities up to the diffusion limited current and by using several current-reversal cycle lengths.

Figure 8 shows SEM photomicrographs of three platinum coatings prepared by direct current plating at current densities equal to complete, one-half, and one-quarter diffusion limited current. The diffusion limited current for this bath was experimentally found to be equal to 12 ma/cm^2 in the absence of bath agitation. The smallest average grain size was found for the coating prepared at a current density equal to one-half the diffusion limited value (8B). While the other two coatings appear to have similar grain sizes, the coating prepared at one-quarter of the diffusion limited value (8C) exhibits better packing of the grains, and fewer pores are visible. Because gas transport through the coating is expected to occur predominantly via grain boundaries or through pores, the most protective coating of the three should be the one prepared at one-quarter the diffusion limit, 8C, although the one prepared at one-half the diffusion limit, 8B, would be expected to show greater ductility and better impact resistance. In any case, to provide long-term protection, these coatings would probably have to be at least 75 μm thick.

Another coating was prepared for SEM examination using the current-reversal technique with a plating cycle of 200 seconds and a dissolution cycle of 20 seconds (fig. 9B). For comparison, a higher magnification of the coating shown in figure 8C is also shown in figure 9A. These coatings have approximately equal grain sizes. However, the coating prepared using current reversal shows considerable etching of the crystal faces and rounding of the edges. The thicker coatings of the platinum metals that have been prepared using current reversal techniques

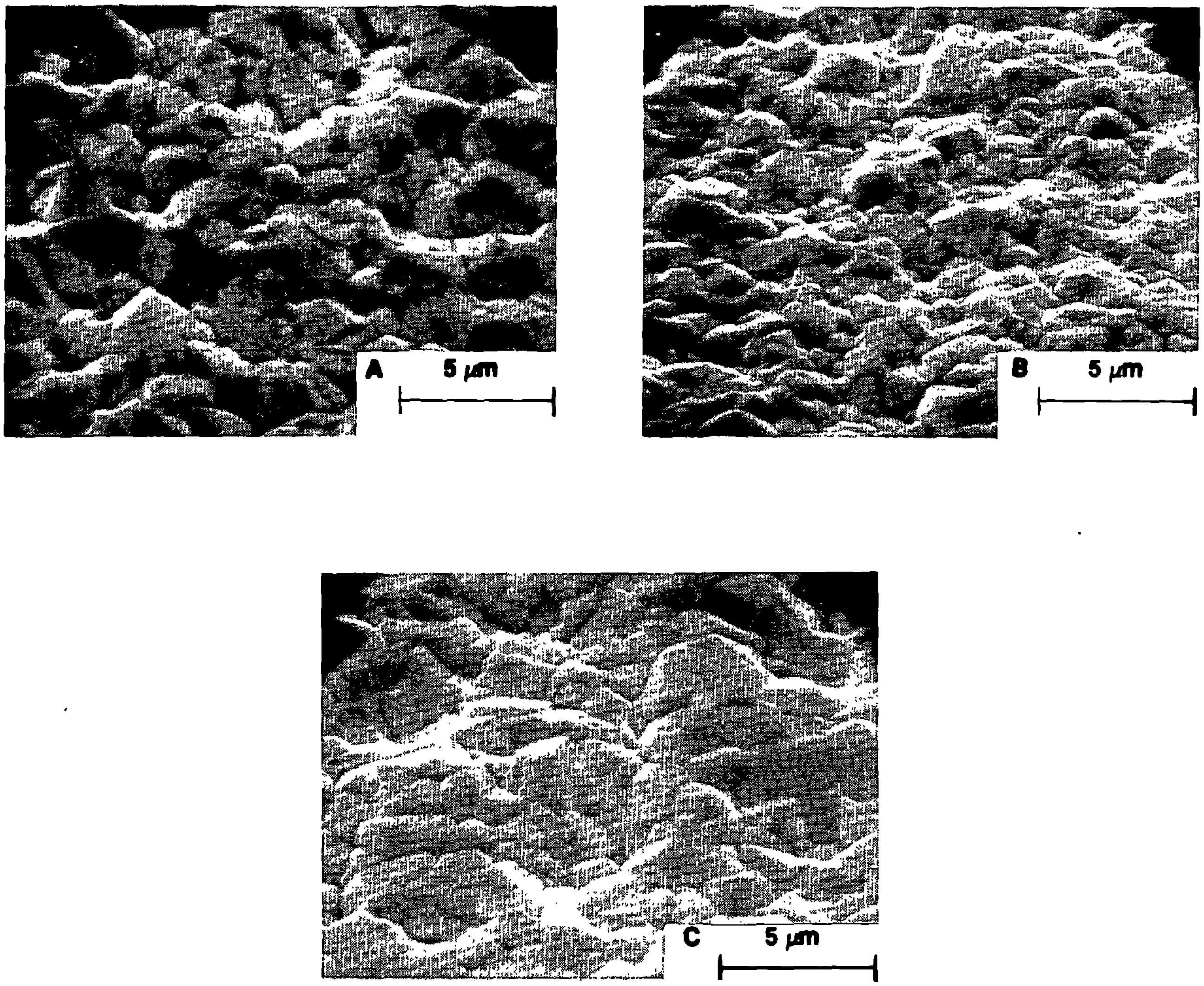

FIGURE 8.—Scanning electron photomicrograph of platinum coating electrodeposited at (A) diffusion limited current, (B) one-half diffusion limited current, and (C) one-quarter diffusion limited current.

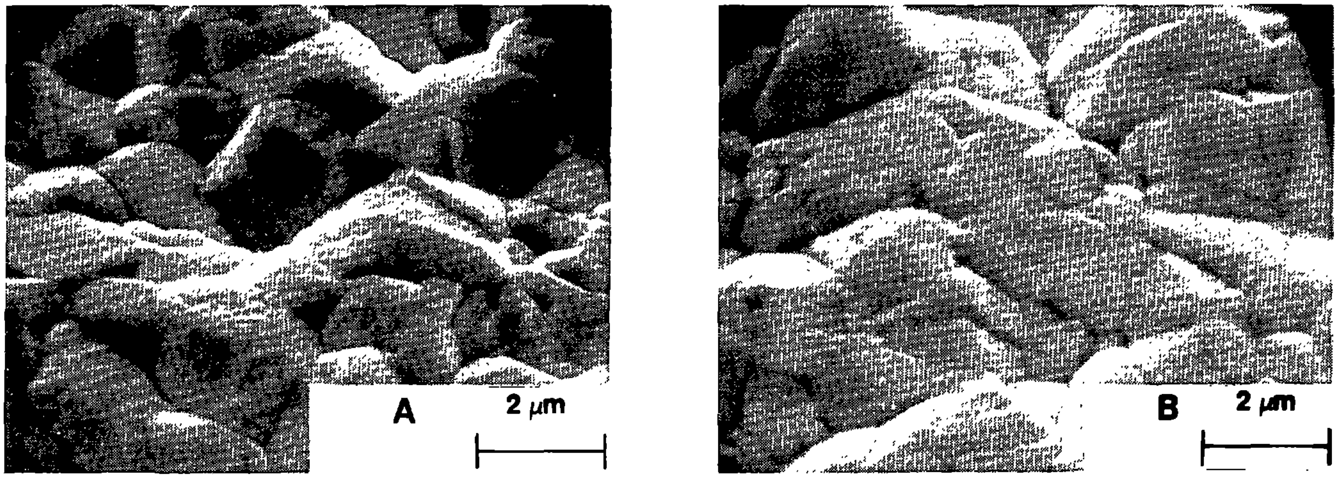

FIGURE 9.—Scanning electron photomicrograph of platinum electrodeposited by (A) direct current plating and (B) current reversal—200-sec deposition, 20-sec dissolution cycles.

show similar crystal structures. Current reversal techniques have been found to be a useful method to prepare smooth, uniform coatings of the platinum metals, provided that the cycle times used are sufficiently long to insure that a well-defined concentration gradient is developed during the deposition portion of the cycle. As an example of what can occur when the cycle time is too short, an SEM photomicrographic examination of a platinum coating prepared using a 20-second reduction, 2-second oxidation cycle showed the coating to be composed of large, separated islands of platinum rather than a continuous coating, indicating that the cycle time in this case was too short.

SUMMARY

By the use of experimental electrochemical techniques, the discrepancies reported by various researchers concerning the requirement for the presence or absence of oxygen to prepare platinum-group-metal-containing molten cyanide plating baths have been resolved. It has been found that, by carefully controlling the potentials at which the dissolution and deposition reactions occur and by preventing the cathodic reaction product formed during initial plating bath preparation from reacting with platinum-group metal ions dissolved in the bath, plating baths of Pt, Rh, and Ir can be prepared and operated in an oxygen-free atmosphere. Coatings of these metals can be electrodeposited at good current efficiencies, with iridium deposition requiring very careful control of the current densities.

Although plating baths of palladium can be prepared in helium, a reaction in the molten alkali cyanide melt causes the palladium ion to be rapidly converted to palladium metal. An electrolytic purification procedure prior to dissolution of palladium in the melt reduces the rate of this reaction. Even with this purification step, the palladium-containing molten cyanide plating bath slowly decomposes, causing the formation of finely divided palladium metal. Though much of this metal settles to the bottom of the crucible, some finely divided particles are found codeposited in the palladium coatings prepared from these baths. This decomposition process also occurs with the platinum-containing electrolytes, but at a very much slower rate.

Smooth, adherent coatings of Pt, Ir, and Rh have been prepared on a variety of substrates including copper, Monel, molybdenum, and stainless steels. While platinum and iridium were found to also be adherent to Inconel, rhodium coatings could readily be peeled off. Investigation into applications for the thick, protective platinum metal coatings is continuing. Applications studied so far have shown that the procedures and conditions used for coating the small test coupons can be adopted to coat much larger objects. In addition, platinum-group metal coatings show promise for application in industries that handle molten glass. Most importantly, since the plating baths for these metals may be prepared and operated under the same oxygen-free atmosphere, this allows for the development of methods to electrodeposit thick coatings of the more useful platinum-group metal alloys.

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