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ELECTRODEPOSITION OF THICK COATINGS OF PALLADIUM

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ABSTRACT OF THE DISCLOSURE

Thick adherent coatings of platinum, palladium or alloys of platinum and palladium with other platinum group metals are obtained by passing current through a pair of platinum or palladium electrodes in a molten alkali metal cyanide or cyanide-cyanate bath exposed to air or oxygen at a temperature of from 350° C. to 600° C., then immersing the object to be plated as the cathode.

This invention resulted from work done by the Bureau of Mines of the Department of the Interior, and domestic title to the invention is in the Government.

BACKGROUND OF THE INVENTION

Field of invention

This invention relates to the field of electrodeposition of metals. More specifically, it is related to a method of obtaining thick and adherent coatings of platinum, palladium or alloys of platinum or palladium with other metals from the platinum group.

Description of the prior art

Atkinson, in U.S. Patent 2,093,406 was the first to report the use of molten cyanides to strip platinum group metals from base metal substrates. The use of molten cyanides in the electrodeposition of these metals was established several years later. U.S. Patent 2,929,766 to Withers et al. shows the use of a cyanide bath for iridium plating, and in "Electrodeposition of Several Platinum Metals From Molten Cyanide Electrolytes," Plating, January 1962, Rhoda showed that electrodeposition from cyanide baths allowed plating of platinum and ruthenium as well as iridium on base metals. Rhoda teaches that the cyanide bath must never be exposed to air or oxygen. These prior techniques have not resulted in platinum coatings having the thickness, adherence and lifetime desired and further they have not been applicable to palladium coating. The reason generally given for their latter deficiency is that palladium-cyanide baths have heretofore been unstable above 300° C.

SUMMARY OF INVENTION

Briefly, we have discovered that good coatings of platinum or palladium can be deposited from cyanide baths if the baths are exposed to air or oxygen at a temperature of from 350–600° C.

Accordingly, it is an object of this invention to provide a method for obtaining thick adherent coatings containing platinum or palladium. It is a further object of this invention to provide a method for obtaining thick adherent coatings of platinum or palladium alloyed with other platinum group metals.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The first step of this invention involves the formation of a platinum or palladium cyanide complex. To avoid confusion in the following description, platinum and palladium will be referred to as "primary metal" whereas in the case of alloy coatings, the second platinum group metal which is alloyed with the primary platinum or palladium will be called the "secondary metal." Formation of the primary metal cyanide or cyanide-cyanate complex can be accomplished in several manners using a variety of complexing mixtures of alkali. The primary metal can be dissolved in pure sodium cyanide, or mixture of sodium cyanide and potassium cyanide. An advantage of using a mixture is that it has a lower melting point, for example, a mixture of 53 parts by weight sodium cyanide and 47 parts by weight potassium cyanide has a melting point of 500° C. A still further reduction in bath melting temperature may be achieved through the use of an alkali metal cyanide-alkali metal cyanate mixture. As an illustration, a 50–50 weight percent mixture of sodium cyanide-potassium cyanate melts at about 375° C.

Primary metal can also be introduced into the cyanide bath to form a complex by A.C. electrolysis using two primary metal electrodes or by D.C. electrolysis using a primary metal anode and a cathode of primary metal or another metal.

We have found that it is essential in the preparation of a cyanide complex, from which primary metal can be electrodeposited, to expose the molten bath to air or oxygen either before or during the introduction of primary metal. Further, to ensure the continued and repeated formation of coatings of 5 or more mils in thickness, it is essential that the bath be exposed to air or oxygen at temperatures of 600° C. or less, preferably in the range of from 350–600° C.

Having formed the primary metal complex, the bath may be used immediately, cooled and stored in a desiccator for future use, or it may be added as a supply of complex to another metal.

To plate an object with primary metal, it is immersed as a cathode in an electrolytic bath formed by one of the above-mentioned methods. We have found that refractory or nonrefractory metals can be plated with good results. Thick adherent coatings are easily achieved on many common metallic substrates including stainless steel, carbon steel, nickel, alloys containing nickel chromium and iron such as Inconel and, alloys of molybdenum and tungsten. If the primary metal concentration in the bath is 0.3 weight percent or more, the anode can be of material other than primary metal as for example graphite. The concentration of primary metal in the bath can be determined by weighing the anodes and cathodes before and after each electrolysis or plating period.

Alloys of primary metal with other platinum group metals, i.e. secondary metals can also be electrodeposited. The secondary metal can be introduced into the electrolyte containing primary metal by electrolysis using a secondary metal anode, or an electroylte complex containing the secondary metal can be added to a primary metal complex in any proportion desired. Alternatively, primary metal can be added by electrolysis or in complex form to a bath containing a complex of secondary metal. Once the cyanide or cyanide-cyanate complex of primary and secondary metal has been formed, the object to be plated is made the cathode. The anode composition used during plating will depend upon the desired balance to be maintained in the electrolyte. In this regard, if the anode is graphite, the concentration of both metals will be lowered as plating takes place, whereas if it is of one of the metals, the concentration of that metal will be maintained during electro-deposition. If it is desired that the concentration of both primary and secondary metal is to be maintained, multiple anodes, including at least one of each kind or an alloyed anode can be used.

When the primary metal is palladium, optimum plating conditions for both the single metal and alloys are temperatures of from 350° to 600° C. depending upon the mixture of cyanide salts used, cathode current densities in the range of from about 3–20 ma./cm., anode to cathode area ratios of from about 1/1 to 2/1, and total platinum group metal ion concentration, including secondary metal in the case of alloys, of about at least 0.2 percent by weight.

When the primary metal is platinum, optimum plating conditions for both single metal and alloy coatings are temperatures of from 500–600° C. depending upon the mixture of molten salts used and the reduction in melting point of the bath as electrolysis continues, cathode current densities of from about 5–30 ma./cm.^{2}. depending upon temperature and the concentration of metal in the electrolyte, anode to cathode area ratio of from 1/1 to 2/1 and total platinum group metal ion concentration, including secondary metal in the case of alloys of at least 0.2 percent by weight.

These conditions represent preferred but not critical parameters in the electrodeposition of platinum, palladium and their alloys with other platinum group metals. The critical step is the exposure of the cyanide bath to air before or during the introduction of platinum or palladium into the bath. This exposure need not continue during the plating step. In fact, as long as the bath has been previously exposed, plating may take place with the continual formation of metal-cyanide or cyanate complex in the absence of air or oxygen, at generally increased cathode efficiencies.

The following examples will serve to more specifically illustrate the invention. In each example the substrates were rounded on the edges and tips by grinding and filing, washed in trichloroethylene or ethyl alcohol, rubbed with wet pumice, washed with distilled water and ethyl alcohol, and dried in warm air. No other pretreatments are necessary as with other prior art platinum group metal plating techniques.

Example 1.—Two hundred and thirty (230) grams sodium cyanide were placed in a silicon carbide crucible and heated in air to 600° C. A palladium anode and a molybdenum cathode were inserted into this melt and electrolyzed at cathode current densities of 7–20 milliamperes per square centimeter for 30-minute periods until a concentration of 0.2 percent metal ion concentration had built up. At that point a smooth, adherent, coherent deposit of palladium formed on the cathode at a current efficiency of 28 percent. The cathode was rotated to lessen possible stratification of metal in the electrolyte and to form a more uniform deposit. At a current density of 4–10 ma./cm.^{2}, a deposit of palladium five mils thick was formed by repeated electrolyses on the same cathode substrate. At 600° C. the bath could be operated for up to 10 hours before decomposition of the electrolyte and subsequent metal precipitation resulted in lower cathode current efficiencies.

Example 2.—A 50–50 weight percent mixture of sodium cyanide-potassium cyanide was placed in a fused quartz crucible and heated in air to 560° C. Palladium metal was then introduced into the electrolyte by D.C. electrolysis using a palladium anode and a palladium cathode at a current density of 20 ma./cm^2. After a buildup of approximately 0.3 percent palladium in the electrolyte, an adherent, coherent deposit could be formed on molybdenum at a bath temperature of approximately 450° C. At this temperature a deposit 4.5 mils in thickness formed on molybdenum at a cathode current efficiency of over 55 percent. Electrolysis was continued for over 20 hours with no indication of electrolyte deterioration.

Example 3.—A 50–50 weight percent mixture of sodium cyanide-potassium cyanate was heated in air to 475° C. Palladium metal was introduced into the electrolyte by D.C. electrolysis using a palladium anode and a palladium cathode at a current density of 10–20 ma./cm.^{2}. After a buildup of approximately 0.5 weight percent palladium in the electrolyte, adherent, coherent deposits of palladium were formed on molybdenum at a cathode current efficiency of 31 percent. Adherent, coherent deposits 2 mils in thickness were formed at cathode current efficiencies up to 61 percent.

Example 4.—A 50–50 weight percent mixture of sodium cyanide-potassium cyanide mixture containing 0.9 percent palladium formed as in Example 2 was heated to 375° C. An indium anode was substituted for the palladium anode and D.C. electrolysis continued at 15 ma./cm.^{2} until a coating 2 mils in thickness formed on the molybdenum cathode. X-ray analysis of the coating indicated a surface composition of approximately equal percentages of palladium and iridium.

Example 5.—A 50–50 weight percent mixture of sodium cyanide and potassium cyanide was heated in air at 450° C. It was then electrolyzed in air at 450° C. using a palladium anode and molybdenum cathode for a period of 4.5 hours at a cathode current density of 15 ma./cm.^{2}. The cathode current efficiency was calculated to be 15%. An argon atmosphere was then substituted for the air atmosphere. It was discovered that continuation of electrolysis in the inert atmosphere at the same temperature resulted in a cathode current efficiency of 95 percent.

Example 6.—Two hundred thirty (230) grams of sodium cyanide were placed in a crucible and heated at about 600° C. in air. A platinum anode and a tungsten cathode were inserted into this melt and electrolyzed at cathode current densities of 30–40 milliamperes per square centimeter (ma./cm.^{2}) for successive 30 minute periods. The cathode was rotated at approximately 120 r.p.m. At the beginning of the second period or within one hour operating time with this electrolyte, a smooth, dark grey deposit approximately 0.1 mil thick formed on the cathode.

Example 7.—Platinum was introduced by electrolysis using a platinum anode and cathode into a molten bath containing 230 grams of sodium cyanide. The bath was exposed to air at about 600° C. and the platinum addition was continued for 45 minutes. The total platinum introduced during that period was 0.28 weight percent. This bath was then operated in air at about 600° C. with a platinum anode and molybdenum cathode at 30 ma./cm.^{2} cathode current density. After 2 hours and 45 minutes, a deposit 0.5–1.0 mil thick had formed on the cathode at a current efficiency of 40.3 percent. After 2 additional hours electrolysis on a fresh molybdenum cathode, a deposit 1.5–2.0 mils thick formed at a current efficiency of 60.5 percent.

Example 8.—A bath of the type used in Example 6 was heated in air at about 600° C. Platinum was electrolytically introduced using a platinum anode and a platinum cathode at anode and cathode current densities of 10 ma./cm.^{2} and 30 ma./cm.^{2} respectively in an air atmosphere and at a temperature of 600° C. After a period of 3 hours it was found that the melting point of the bath was lowered considerably enabling a plating operation in a temperature range of from 525–555° C. and a cathode current density of 10 ma./cm.^{2}. After plating for 4 hours it was found that platinum was depositing on the cathode at the rate of 0.5 mil per hour.

Example 9.—A cyanide bath of the type used in Example 6 was heated in air at about 600° C. Platinum was introduced using a platinum anode and platinum cathode at anode and cathode current densities of 10 and 30 ma./cm.^{2} respectively for 3 hours at 600° C. in air. Then an Inconel sheathed thermocouple was substituted as the cathode. The temperature was held in a range of from 500–575° C. cathode current densities at from 10–20 ma./cm.^{2} and anode current densities of 5–10 ma./cm.^{2}. After 4 hours the thermocouple was coated with a 2 mil thickness of platinum.

Example 10.—A cyanide bath of the type used in Example 6 was heated in air at about 600° C. Platinum was introduced under the same conditions as in Example 9 until a platinum concentration of 2.0 percent was obtained. A solid Inconel rod was immersed in the electrolyte as the cathode for 11 hours at 500° C. in air at a cathode current density of 10 ma./cm.^{2} and anode current density of 5 ma./cm.^{2}. Use of a platinum anode maintained the platinum concentration in the electrolyte at over 2.0 weight percent. At the end of the plating period the rod had a 5 mil thick platinum coating. Since then the coated rod has resisted oxidation by air at temperatures of 1200–1300° C. for over 400 hours.

Example 11.—A platinum electrolyte was formed as in Example 9 and 5 weight percent ruthenium was added to the electrolyte in the form of a ruthenium/cyanide. At a temperature of 550° C. and a cathode current density of 10 ma./cm.^{2}, a platinum alloy was plated out which varied in ruthenium concentration from 2 to 7 percent.

Though the invention has been described in terms of the preferred embodiments and examples disclosed herein, it will readily be appreciated by those of ordinary skill in the art that many modifications and adaptations of the invention are possible without departure from the spirit and scope of the invention as claimed hereinbelow.

What is claimed is:

1. A method of electroplating a thick adherent coating of palladium on a metal substrate comprising

(a) forming a molten bath of approximately a 50–50 weight percent mixture of sodium cyanide-potassium cyanide at a temperature of about 560°;

(b) immersing a palladium anode into said molten bath;

(c) electrolytically dissolving the anodic palladium into said bath in the presence of air or oxygen;

(d) electroplating said dissolved palladium onto a cathode composed of said metal substrate after said bath builds up to approximately 0.3 percent palladium, said electroplating being carried out at a temperature of about 450° C., in the presence of air or oxygen; the thickness of said palladium plating being at least 4.5 mils.

2. The method of claim **1** wherein said metal substrate is a member of the group consisting of stainless steel; carbon steel; nickel; alloys containing nickel, chromium and iron; alloys of molybdenum and alloys of tungsten.

3. The method of claim **1** wherein said metal substrate is a refractory metal.

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