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[54] ELECTROPLATING A GOLD-PLATINUM ALLOY AND ELECTROLYTE THEREFOR

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[51] **Int. Cl.**^{2} **C25D 3/62**; C25D 3/56
[58] **Field of Search** .... 204/43 G, 43 N, 44, 123

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

928,083	6/1963	United Kingdom	204/43 G

OTHER PUBLICATIONS

A. K. Graham et al., Plating, Vol. 2, pp. 148–153, (1949).

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[57] ABSTRACT

An electroplating bath for the deposition of gold-platinum alloys comprising an aqueous solution of alkali metal hexahydroxyplatinate and alkali metal aurate. Preferably, the solution comprises sufficient alkali metal hexahydroxyplatinate to provide from substantially 15 to substantially 25 grams of platinum per liter and sufficient alkali metal aurate to provide from substantially 0.5 to substantially 3.0 grams of gold per liter. The bath is operated at a temperature preferably in the range of from substantially 50°C to substantially 65°C.

6 Claims, No Drawings

ELECTROPLATING A GOLD-PLATINUM ALLOY AND ELECTROLYTE THEREFOR

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of, or under, Contract No. W-7405-ENG-48 with the United States Atomic Energy Commission.

This invention relates to the electrodeposition of gold-platinum alloys.

For the last two decades great impetus to gold plating research has been given by the requirements of the electronics and allied industries that specified thicker coatings of greater hardness, wear resistance, corrosion resistance and lower porosity. Another field which is opening for electrodeposited gold alloys is that of high temperature applications. Electroplated gold-copper alloys have been investigated for this purpose but, in general, a major disadvantage of these alloys is their poor mechanical properties at high temperature. Also, the low-density copper component undesirably decreases the density of the alloy. Of the binary alloys investigated for high temperature use, gold-platinum alloys have been found to be the most suitable. Platinum hardens gold very effectively and also increases its resistance to oxidation and corrosion. Gold-platinum alloys have been used for many years as spinning jets in the viscose rayon industry where they withstand corrosive conditions and severe mechanical conditions for long periods. The gold-platinum alloys are also suitable for use as crucibles for alkaline fusions.

Electrodeposition of alloys involves more complicated processes than the deposition of pure metals. Alloy deposition is much more sensitive to a variety of factors than a single metal. Variables must be controlled much more closely than in a single metal deposition in order to obtain deposits of uniform color, corrosion resistance, composition and appearance. The supporting electrolyte must be chosen so that the reduction potential of the metals will be fairly close. Indeed, it is often difficult to predict the composition of an alloy from that of the electrolyte and from the plating conditions.

Electrodeposition procedures for such gold alloys as gold-copper and gold-silver alloys generally employ cyanide complex solutions. However, metals of the platinum group are not deposited from aqueous cyanide solutions since the cyanide complexes of these metals are so stable that their deposition on the cathode is either impossible, or possible only at very low current densities. Investigations of the deposition of gold-platinum alloys from halide systems were made and reported by A. K. Graham, S. Heiman, and H. L. Pinkerton, *Plating*, Feb. 1949, pp. 148–153. It is stated in the aforementioned article that some of the deposits obtained were extremely dark.

It is among the objects of this invention to provide an electroplating bath and operating conditions for the electrodeposition of gold-platinum alloys of excellent quality and reproducibility.

SUMMARY OF THE INVENTION

It has been found that gold-platinum alloy deposits of consistently excellent quality can be obtained by electrodeposition from an aqueous electroplating bath comprising an alkali metal hexahydroxyplatinate and an alkali metal aurate. The concentration of the alkali metal hexahydroxyplatinate should be sufficiently high

to insure deposition of platinum on the cathode. It has been found that a concentration of alkali metal hexahydroxyplatinate sufficient to provide from substantially 15 to substantially 25 grams of platinum per liter of aqueous solution is eminently suitable for use in the present invention. For best results, an amount of platinum in solution within the range of from substantially 19 to substantially 22 grams per liter is preferred, with the concentration of the alkali metal aurate being adjusted in accordance with the concentration of gold desired in the final deposit. Deposits containing from substantially 15% to substantially 95% gold can be obtained with the baths of the present invention. For high temperature applications, alloy deposits containing from substantially 70% to substantially 85% gold are generally preferred.

One of the variables requiring control in the utilization of the baths of the present invention is the pH of the solution. It is important that the electroplating bath be highly alkaline; the pH of the solution should be maintained above substantially 11.0. If the pH of the solution falls below substantially 11.0, the alkali metal hexahydroxyplatinate tends to form a precipitate. Generally, the solutions prepared by dissolving an alkali metal hexahydroxyplatinate and an alkali metal aurate have a sufficiently high pH for use in the present invention, but, if necessary, the pH of the solution can be adjusted before and/or during use by the addition of suitable amounts of water-soluble alkaline acting substances such as alkali metal salts of weak acids, e.g., phosphoric acid, acetic acid or citric acid.

Another variable requiring control is the plating temperature. The temperature affects not only the structure and appearance of the electrodeposited alloys but also their chemical composition. In general, the preferred temperature is in the range of from substantially 50°C to substantially 65°C.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, there is provided an electroplating bath for the electrodeposition of gold-platinum alloys comprising an alkali metal hexahydroxyplatinate and an alkali metal aurate in aqueous solution.

In a specific embodiment of the invention, the aqueous electroplating bath comprises from substantially 15 to substantially 25 grams per liter of platinum as alkali metal hexahydroxyplatinate and gold, as alkali metal aurate, in a concentration sufficient to yield a gold-platinum deposit of the desired composition. Preferably, from substantially 0.5 to substantially 3.0 grams of gold, as alkali metal aurate, is present per liter of solution.

More specifically, there is provided by the present invention an aqueous electroplating bath for the electrodeposition of gold-platinum alloys comprising from substantially 19 to substantially 22 grams per liter of platinum as sodium or potassium hexahydroxyplatinate and from substantially 0.5 to substantially 3.0, preferably from substantially 1.0 to substantially 2.0, grams per liter of gold as sodium or potassium aurate, the pH of the solution being maintained at above substantially 11.0, preferably above substantially 11.5.

The operating conditions suitable for any particular plating application may be readily determined by one skilled in the art. The average cathode current density used will depend upon the alloy desired and on the shape and size of the article to be plated. It is preferable to employ cathode current densities of below substantially 20 amperes/ft^2, preferably substantially 5 to substantially 8 amperes/ft^2, under normal direct current plating conditions, with a deposition rate of from substantially 0.0002 to substantially 0.00025 inch/hr.

Generally, the electrolyte solution is used with insoluble platinum or platinum clad anodes, and it is necessary to replenish the gold and platinum deposited from the electrolyte solution by addition of fresh gold and platinum compounds.

As stated above, it is important that the pH of the solution be maintained above substantially 11.0, and preferably above substantially 11.5, to prevent precipitation of the alkali metal hexahydroxyplatinate. If necessary, water-soluble alkaline substances such as alkali metal salts of weak acids, e.g., potassium phosphate, potassium acetate, or potassium citrate can be added before and/or during use in sufficient quantities to maintain the pH of the solution in the required range. Suitable brightening agents, which are well known in the art, can be added from time to time to maintain the desired physical characteristics of the alloy deposited.

For best results, the electrolyte of the present invention is operated at temperature of substantially 50°C to substantially 65°C.

The following examples are illustrative of the electroplating solutions of the present invention.

EXAMPLE I

A 250 ml. aqueous electroplating solution was prepared containing 21 grams per liter of platinum as $K_2Pt(OH)_6$ and 0.7 grams per liter of gold as $KAuO_2$. The pH of the solution was above 11.5. The bath was operated at a temperature of 55°C. The electrolyte was used to plate clean brass parts. The composition of the deposited alloy was 10% Au-90% Pt. The deposit was found to be smooth.

EXAMPLE II

An aqueous electroplating solution was prepared as in Example I, except that the concentration of gold present (as $KAuO_2$) was 2.8 grams per liter. The electrolyte was used to plate clean brass parts. The bath was operated at a temperature of 65°C. A current of 0.2 ampere was employed. The composition of the final deposit was 30% Pt-70% Au. The deposit was found to be of excellent quality.

EXAMPLE III

A 250 ml. aqueous electroplating solution was prepared containing 20 grams per liter of platinum as $K_2Pt(OH)_6$ and 1.55 gram per liter of gold as $KAuO_2$. The pH of the solution was above 11.5. The bath was operated at a temperature of 53°C and 0.4 ampere was used to plate a clean brass panel. The final deposit contained 37.5–38% Pt.

EXAMPLE IV

A bath containing 2.0 g/lAu (as $KAuO_2$) and about 20 g/l Pt as $K_2Pt(OH)_6$ operated at 53°–55°C and a current of 0.2 amperes produced a deposit containing 55% Pt.

The electroplating solutions illustrated in the above examples can also be prepared with other alkali metal hexahydroxyplatinates, particularly $Na_2Pt(OH)_6$, and with other alkali metal aurates, particularly $NaAuO_2$. However, from a long range stability standpoint, the potassium salts are preferred.

Alloy deposits containing from substantially 15% to substantially 95% gold can be obtained by using electroplating baths similar to those illustrated above. For best results, the concentration of the alkali metal hexahydroxyplatinate should be such as to provide from substantially 15 to substantially 25 grams, and preferably from substantially 19 to substantially 22 grams, of platinum per liter of solution, with the concentration of the alkali metal aurate being adjusted to provide the desired concentration of gold in the final deposit. Generally, varying the concentration of the alkali metal aurate to provide from substantially 0.5 to substantially 3.0 grams of gold per liter of solution will yield gold-platinum alloy deposits within the composition range contemplated by the present invention providing a constant current density is used. Thus, to maintain a specific alloy composition, the platinum and gold contents in the bath must be carefully controlled as well as the current density.

Although the invention has been described with reference to specific examples, it will be appreciated that various modifications and changes will be evident to those skilled in the art without departing from the true spirit and scope thereof. Thus, it is not intended to limit the invention except by the terms of the following claims.

What I claim is:

1. An aqueous electrolyte solution for the electrodeposition of gold-platinum alloys comprising an alkali metal hexahydroxyplatinate and an alkali metal aurate and wherein the pH of the solution is above substantially 11.0.

2. An electrolyte solution as claimed in claim **1** wherein the alkali metal hexahydroxyplatinate is selected from the group consisting of sodium hexahydroxyplatinate and potassium hexahydroxyplatinate, and the alkali metal aurate is selected from the group consisting of sodium aurate and potassium aurate.

3. An electrolyte solution as claimed in claim **1** wherein the concentration of the alkali metal hexahydroxyplatinate is sufficient to provide from substantially 15 to substantially 25 grams of platinum per liter of solution.

4. An electrolyte solution as claimed in claim **1** wherein the concentration of the alkali metal aurate is sufficient to provide from substantially 0.5 to substantially 3.0 grams of gold per liter of solution.

5. An electrolyte solution as claimed in claim **1** wherein the alkali metal hexahydroxyplatinate is potassium hexahydroxyplatinate in a concentration sufficient to provide from substantially 19 to substantially 22 grams of platinum per liter of solution and the alkali metal aurate is potassium aurate in a concentration sufficient to provide from substantially 0.5 to substantially 3.0 grams of gold per liter of solution.

6. A process for the electrodeposition of gold-platinum alloys which comprises electrolyzing an aqueous electrolyte solution as claimed in claim **1** at a temperature between substantially 50°C and substantially 65°C.

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