

ELECTROFORMING METHOD AND PART OR
LAYER OBTAINED VIA THE METHOD

The present invention concerns an electroforming method for making parts or layers from a gold-based alloy containing zinc, copper and/or silver, and parts or layers obtained via this method. More specifically, the invention concerns a method of this type for depositing thick layers of said alloy, typically of the order of 300 microns, on substrates.

Methods are known for electroplating a gold alloy by electrolysis in an alkaline galvanic bath containing cadmium, in addition to gold and copper. As cadmium is a toxic metal, numerous laws now prohibit the use of cadmium.

In order to overcome this problem, CH Patent No. 680 927 has already proposed replacing cadmium with zinc in the conventional gold alloy (Au, Cu, Cd) electrolytic deposition method.

However, this method only discloses the deposition of gold, zinc and copper alloy layers of the order of 10 microns. Moreover, this document does not give any precise information as to the composition of the final alloy deposited.

It is thus a main object of the present invention to provide a method of electroforming a gold, zinc and copper based alloy part or layer that is free of cadmium, with a thickness of several hundred microns.

It is also an object of the present invention to provide a method of this type that makes layers of this kind with improved hardness while maintaining a good level of ductility.

The invention therefore concerns a method of electroforming a layer of a gold alloy comprising 88 to 94% by weight of gold, x% by weight of copper and/or silver, and 2x% by weight of zinc, x being comprised between 2 and 4, consisting in:

- dipping a metal substrate in an alkaline electrolytic bath containing an anode, said bath containing at least gold salts in the form of potassium gold cyanide, copper salts in the form of copper cyanide and/or silver salts in the form of silver oxide, zinc salts in the form of zinc oxide, sodium cyanide, sodium hydroxide, acid, for example ethylene diaminetetra-acetic acid (EDTA) and a surfactant, said substrate forming a cathode,

- electroforming said layer by creating a voltage between the anode and the cathode to deposit metallic ions on the surface of the substrate,

- interrupting the voltage once the desired thickness of the electroplated layer is reached.

Preferably, the voltage is varied during the step of electroforming said layer, which produces non-homogenous phase α gold crystallisation in the layer at the moment of deposition. This lack of homogeneity reduces the surfaces defects in the deposited layer by a crystalline superstructure.

According to a preferred embodiment of the method of the invention, the voltage between the anode and cathode is reduced in the final phase of the electroforming step in order to increase the concentration of gold in the superficial zone of the deposited layer and thus reinforce the golden colour of the deposited layer.

According to another advantageous aspect of the method of the invention, the electroforming step is followed by a thermal anneal process at between 300° and 700°C for at least 30 minutes and rapid quenching.

It will be noted in this regard that the "liquidus" temperature curve of the Au Zn phase diagram, must not, in any circumstances, be exceeded for the alloy concerned, since during eutectic solidification, from the liquid phase, this would cause solidification in two phases α , β' , which would

result in a marked degradation in mechanical properties after cooling. During this treatment, the crystalline structure of the layer is partially homogenised and then solidified in this forming process by rapid hardening, which prevents intermediate α_1 or α_2 crystalline phases forming for the alloy concerned.

The invention also concerns an electroformed gold alloy part, characterized in that the gold alloy comprises from 88 to 94% by weight of gold, x% by weight of copper and/or silver, and 2x% by weight of zinc, x being comprised between 2 and 4.

According to a preferred embodiment of the invention, the alloy comprises 88% by weight of gold, 8% by weight of zinc and 4% by weight of copper.

Electroforming is performed at a temperature of between 40°C and 80°C.

According to an advantageous embodiment, the surfactant used is a phosphatic ester of a polyglycol alkyl alcohol.

According to the method of the invention, electrolysis is performed in an alkaline galvanic bath with a pH of between 8 and 10, containing approximately 7 to 15 g.l⁻¹ of gold in the form of potassium gold cyanide, approximately 1.5 to 5 g.l⁻¹ of zinc in the form of zinc oxide, approximately 1.5 to 3 g.l⁻¹ of copper or silver in the form of copper cyanide or silver oxide, sodium cyanide, sodium hydroxide, ethylenediamino tetra-acetic acid and its potassium salt and a surfactant.

This electrolysis step is followed by a heat treatment at at least 300°C for at least 30 minutes. This heat treatment is preferably carried out in a reducing atmosphere to reduce the zinc oxide.

Preferably, the galvanic bath further contains a brightener. The brightener is preferably a potassium antimony tartrate combined with potassium hypophosphite or a potassium selenocyanate.

The surfactant is preferably a butyl or nonyl phenol polyglycol phosphatide ester.

The electrolysis is preferably carried out at a temperature of between 60 and 75°C in a galvanic bath whose pH is between 8 and 10.

The electrolysis can be achieved with a current density typically of the order of 1.0 A.dm⁻².

The electrolysis is followed by a heat treatment carried out at a temperature higher than 300°C for a time of typically between 30 minutes and 1 hour. This heat treatment includes rapid air cooling, which can be obtained, for example, in a band furnace. The heat treatment is performed under a reducing atmosphere.

We will now describe an example of the electrolytic deposition according to this embodiment of the invention and the method of preparation for the same.

In this deposition example, there is an 18 carat gold alloy, free of toxic metals or metalloids, in particular free of cadmium, with a pale yellow colour 2N, with a hardness of between 200 and 300 HV 0.005, ductile in particular for thicknesses of between 40 and 350 microns, with excellent brilliance and with a very high level of resistance to wear and tarnishing.

This deposition is obtained by electrolysis in an electrolytic bath followed by a heat treatment at 300°C for 30 minutes under a reducing atmosphere.

The electrolysis is performed in an electrolytic bath containing the following compounds:

Example:

- Au in the form of KAu(CN)₂: 11 g.l⁻¹
- Cu in the form of CuCN: 2.5 g.l⁻¹
- Zn in the form of ZnO: 2.5 g.l⁻¹

- NaCN: 20 g.l⁻¹
- NaOH: 5.5 g.l⁻¹
- KHCO₃: 5 g.l⁻¹
- K₄[EDTA]: 5 g.l⁻¹
- H₄[EDTA]: 5 g.l⁻¹
- PH: 8
- Temperature: 70°C
- Current density: 1 A.dm⁻²
- Wetting agent: 0.2 mg.l⁻¹ phosphatide butyl phenol polyglycol ester
- Potassium selenocyanate : 10 mg.l⁻¹
- EDTA = ethylene diaminotetra-acetic acid

In this example, the electrolytic bath, contained in a polypropylene or PVC container with thermal insulation, has a pH of between 8 and 10 and is at a temperature of 70°C. The bath is heated using quartz, PTFE, porcelain or stabilised stainless steel immersion heaters. The bath has a density of between 16 and 30 g.cm⁻³ at 20°C. Good cathode rod movement and electrolyte flow must be maintained. The anodes are made of platinum plated titanium or stainless steel.

The electrolysis is performed with a current of between 1 and 2 A.dm⁻². These conditions provide cathode efficiency of 100 mg.A.min⁻¹.cm⁻² with a speed of 0.5 micron.min⁻¹.

Of course the present invention is not limited to the example illustrated but can be subject to various variants and alterations which will be clear to those skilled in the art. In particular, the bath can contain traces of silver and the following metals: In, Cd, Zr, Se, Te, Sb, Sn, Ga, As, Sr, Be, Bi.

Moreover, the wetting agent may be of any type that can wet in an alkaline cyanided medium.

CLAIMS

1. Method of electroforming a layer of a gold alloy containing 88 to 94% by weight gold, x% by weight copper and/or silver and 2x% by weight zinc, x being comprised between 2 and 4, consisting in:

- dipping a metal substrate into an alkaline electrolytic bath
5 containing an anode, said bath containing at least gold salts, in the form of potassium gold cyanide, copper salts in the form of copper cyanide and/or silver salts in the form of silver oxide, zinc salts in the form of zinc oxide, sodium cyanide, sodium hydroxide, acid and a surfactant, said substrate forming a cathode,
- 10 - electroforming said layer by creating a voltage between the anode and the cathode to deposit metallic ions on the surface of the substrate,
- interrupting the voltage once the desired thickness of the electroplated layer is obtained.

2. Method according to claim 1, characterized in that the voltage is
15 varied during the step of electroforming said layer.

3. Method according to claim 2, characterized in that the voltage is decreased in the final phase of the electroforming step to increase the concentration of gold in the superficial zone of the deposited layer.

4. Method according to any of the preceding claims, characterized
20 in that the electroforming step is followed by a thermal anneal process of between 420° and 700°C for at least 30 minutes and a rapid hardening process.

5. Method according to any of the preceding claims, characterized in that the surfactant is a butyl phosphatide or nonyl phenol polyglycol ester.

25 6. Method according to any of the preceding claims, characterized in that the electroforming is performed at a temperature of between 40° and 80°C and preferably between 60 and 75°C.

7. Electroformed part made of gold alloy, characterized in that the gold alloy is made up of 88 to 94% by weight gold, x% by weight copper and/or silver, and 2x% by weight zinc, x being comprised between 2 and 4.

8. Electroformed part according to claim 7, characterized in that
5 the alloy is made up of 88% by weight gold, 8% by weight zinc and 4% by weight copper.

9. Electroformed part according to claim 7 or 8, characterized in that the gold in said alloy is essentially formed of phase α gold.