

# Study on the electrodeposited Au-Co alloy coating

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## Abstract

Au-Co alloy deposit was prepared by selecting the best component in the bath with citrate the deposit exhibited golden appearance and high percentage of coverage. Good hardness and improving anti-corrosion capability could be achieved by adding 3~4.5%Co element and little rare-earth element to the system, and micro-hardness could increase to 180~190Hv. Optimized bath has stable performance, good throwing power and good covering power. The Scanning Electron Microscope (SEM) illustrated that the deposit was smooth, compact and crystal was nice. It is suited for electrical production; decorative coating, advance electrodeposits and hard-gold deposit.

*Keywords:* Au electrodeposited, Au-Co alloy, citrate

## 1 Introduction

In recent years, gold plating on improving performance and technology research, and other new imitation gold gilded have made great progress [1-4]. Gold alloy coatings due to have good electrical conductivity and stable contact resistance; excellent chemical stability and magnificent golden sheen and is widely used in jewellery, handicrafts, electronics and printed circuit board and other fields [5, 6]. Gold alloy coatings due to have good electrical conductivity and stable contact resistance; excellent chemical stability and magnificent golden sheen is widely used in jewellery, handicrafts, electronics and printed circuit board and other fields [5, 6]. Au-Co alloy coating as a gold alloy coatings have high hardness, this process not only increases the wear resistance of the coating, but also saves the amount of gold. Selection of cobalt sulphate as the main salt of gold-plated can get a uniform appearance, light alloy coatings. Bath composition and process conditions affect the coating was tested on research and routine maintenance of the bath were analyzed and summarized.

## 2 Experimental study

### 2.1 GOLD PLATING PROCESS

Wax → degreasing ultrasonic cleaning → intermediate coating → pickling → cleaning → gilded → activation after treatment.

### 2.2 BATH PREPARATION AND OPEN CYLINDER

Gold salts: 1~3g/L; cobalt sulphate: 0.4~1.5g/L; potassium citrate: 10~20g/L; complexing agents Z1: 10~15g/L; additives Z2: 5~7ml/L; pH value: 3.5~4.5; T: 45~60°C; Jk: 0.15~0.30A/dm<sup>2</sup>; Time: 15~60sec; Time: 15~60sec; the cathode and anode area ratio: 1: 3; cathodic current density:

0.5~1.5A/dm<sup>2</sup>; mixing: cathode swing and bath circulation; filter: continuous filtration; anode: iridium, tantalum and titanium mesh coated electrodes.

Open cylinder: the first two-thirds of water were added into the plating tank, heating 45~50°C, then followed by adding gold salts, conductive salt and various additives and complexing agent. Adjust the pH of the bath with citric acid or potassium hydroxide. The proportion was adjusted to 12 degrees Baume, to plating.

### 1.3 TESTING INSTRUMENTS

- 1) Thickness testing: test using TT230 type coating thickness of coating thickness.
- 2) Appearance characterization: Japanese HITACHI's X-650 scanning electron microscope.
- 3) Coating of gold, Determination of cobalt content: U.S. PerkinElmer Instruments, Inc. Analyst 800 atomic absorption spectrometer.
- 4) PH value determination.

## 3 Results and discussion

### 3.1 THE EFFECT OF PLATING SOLUTION COMPOSITION AND QUANTITATIVE

#### 3.1.1 Gold salts

Gold salts are the main bath salts exist in the form of complex ions into the bath. When gold content is low, the deposition rate is slow; taking a strong current plating, plating is red, not light. If the gold salt content is too low, there will be no coating and burning phenomenon. High gold content, allowing the cathodic current density range is wide, fast deposition rate, but cleaning with water phenomenon is relatively serious, thereby causing loss to the gold salts.

3.1.2 Cobalt sulfate and rare earth metals

Adding sulphuric acid cobalt and rare earth metals gloss coating can improve and enhance the hardness and corrosion resistance, improve the coating protection. Cobalt coating bath of sulphuric acid with increasing cobalt content increases, the hardness increases with increasing cobalt content while. As shown in Figure 1, In the case of cobalt was added, a significant increase in the hardness of the coating, the gold micro-hardness from 88 to 93 increased to between 160 to 190, when the cobalt content than 4wt% after micro hardness increase the speed decreases, the alloy color change. Under normal circumstances, the cobalt content of the alloy coating should desirably be controlled within 4wt%.

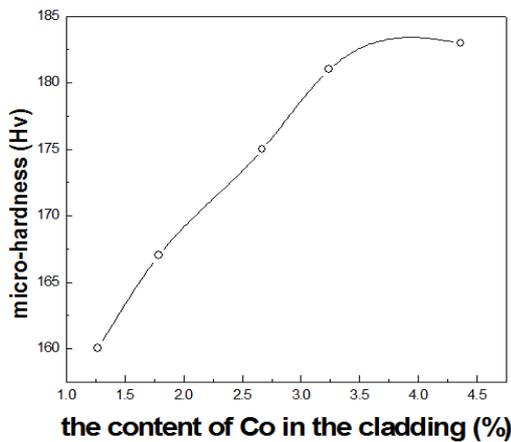


FIGURE 1 Co content with the coating micro-hardness change map

3.1.3 Citrate

Potassium citrate is gilded main conductive salt, but also can be used as an auxiliary complexing agent. Because of citric acid salt and complexing agent additive in Z1 and Z2, reduce the gold, cobalt element to balance the potential difference, in order to achieve total deposits. Maintain stability of the plating solution, improve the cathodic polarization, increased electrical conductivity, reduce energy consumption, promote cell voltage drop. At the same time is also a kind of buffer. Potassium citrate content is too high, affecting the movement of ions, cathodic polarization is too large, the current density decreases; potassium citrate content of less insufficient conductivity, impact adhesion of the gold layer and the underlying particle size of the coating. By the test optimization, potassium citrate concentration in 10~20g, L-1 ideal conductive, complexing properties can be obtained.

3.2 EFFECTS OF PROCESS CONDITIONS ON THE COATING QUALITY AND DEPOSITION RATE

3.2.1 PH value

As shown in Table 1, Figure 2, plating bath pH is too low, hydrogen evolution is serious, low plating efficiency, the

deposition rate is too fast, and easy matt coating surface pinholes and airway. If the pH between 0.5 ~ 4.0, coating deposition rate slows, gas precipitation amount is more, gloss coating apparent slant red; if pH > 6, the precipitation speed slowed sharply, because the Au + mass concentration in plating solution is very low, matt coating surface. Tests showed that pH was able to obtain satisfactory results from 4.0 to 4.5.

TABLE 1 The influence of pH value on the coating appearance

pH	>6	5.0~5.5	4.0~4.5	0.5~4.0	<0.35
Coating appearance	Matt	Golden dark	Bright golden	Shiny reddish	Matt

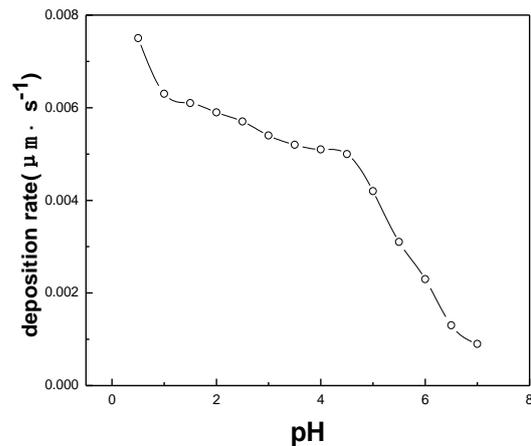


FIGURE 2 Effect of pH on the deposition rate

As shown in Figure 3, as the temperature increases, the coating deposition rate increased rapidly, reaching a high rate in 50~70°C. This is because the high temperature bath will help improve the diffusion of ions migration speed, lower activation energy, while reducing the degree of polarization of cathodic electrodeposition bath when the metal is conducive to improve the electrical ion deposition reaction rate, but the temperature too high as to cause the bath aging and instability. Low temperature, the deposition rate is slow, it is difficult once the quality of the electrodeposition coating, the coating is not bright; temperature is high, the electrodeposition speed is too fast, the coating adhesion is not good. So the control of temperature in 50~60°C can get good coating, high deposition rate [7].

3.2.3 The cathode current density

As shown in Figure 4, the deposition rate increases with increasing current density. When  $J_k < 0.5A/dm^2$ , the cathode current density, more conducive to more positive potential gold deposit, the mass fraction of gold plating up to 98%, failed to effectively render the alloy coating performance; when  $J_k > 3A/dm^2$ , the coating is uneven, rough, which may be the cathode current density is too high, cathodic hydrogen evolution seriously, thus affecting the appearance quality of the coating; when  $J_k > 4A/dm^2$  time, due to the current is too large, the cobalt content is too high, crystallization will

become rough, dark coating, surface dull, too much current will be high potential burning phenomenon. The experimental results show that the cathode current density is generally controlled at 0.5~1A/dm<sup>2</sup> can get a better coating.

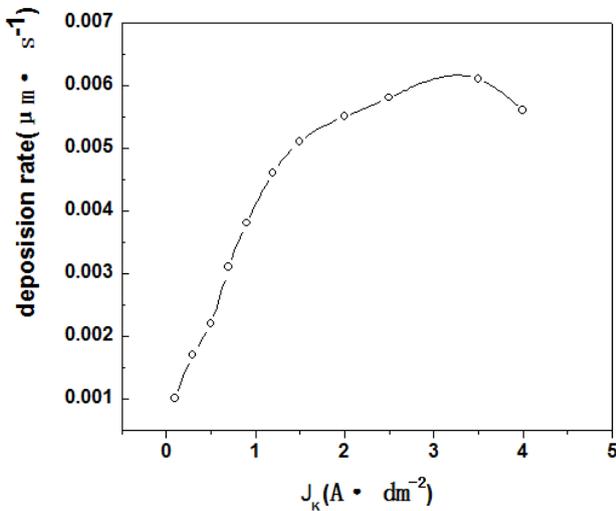


FIGURE 3 Effect of temperature on the deposition rate

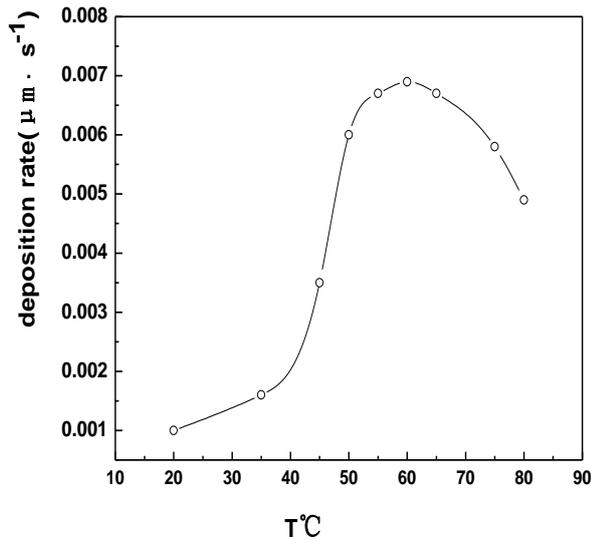


FIGURE 4 Effects of current density on the deposition rate

### 3.3 GOLD - CHARACTERIZATION OF COBALT ALLOY COATINGS

#### 3.3.1 The appearance of the coating

Coating on the surface of the SEM photos shown in Figure 5 and Figure 6, as can be seen from figure crystalline coating fine, evenly distributed, smooth surface.

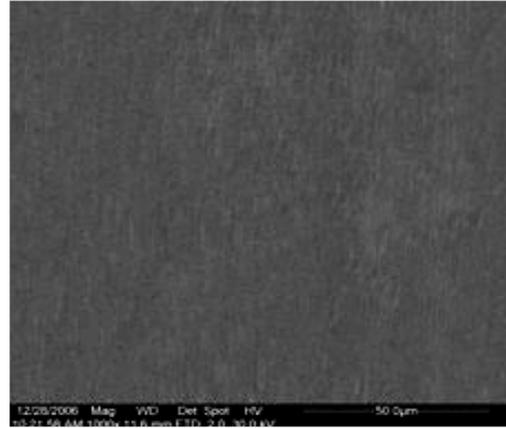


FIGURE 5 The 1000×11.6mm SEM picture of Au-Co Electrodepositing surface

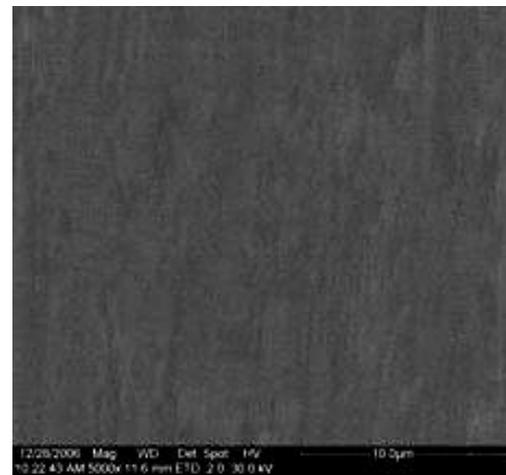


FIGURE 6 The 5000×11.6mm SEM picture of Au-Co Electrodepositing surface

#### 3.3.2 Coating thickness

Using TT230 type coating thickness test coating thickness, coating thickness between 0.05~0.3μm. Because the coating is too thin, the coverage is not enough; coating is too thick, the high cost of electroplating. Coating deposition rate is 0.001~0.007μm · s<sup>-1</sup>, under appropriate process conditions and bath formulations, depending on the length of time the bath, the plating 10~20s, can achieve the proper coating thickness.

### 4 Electroplating fault diagnosis and repair

In "Hull Cell" Based on experiments and experimental results on small groove, study concluded coating defects that may occur. It's a detailed analysis of the reasons, in a simple and intuitive form proposed repair methods and measures, as shown in Table 2.

TABLE 2 Electroplating fault repair

Electroplating failure	Fault diagnosis	Repair methods
No alloy plating or "off gold" phenomenon	<ol style="list-style-type: none"> <li>1. In the process of electroplating power supply connection</li> <li>2. Master of salt in the plating solution concentration is low</li> <li>3. The base material surface with oil or wax excrement</li> <li>4. Before plating workpiece passivation membrane</li> <li>5. Improper treatment before plating or plating passivation</li> <li>6. Contaminated with cyanide plating solution</li> <li>7. In the plating solution mixed with chromic acid oxidation impurities, etc</li> </ol>	<p>Check the power supply circuit and a joint of Yin and Yang and corrected</p> <p>Replenish the gold content of the bath and add a certain amount of conductive salt</p> <p>Improve the oil removal to wax concentration and temperature, increasing trichloroethylene ultrasound degreasing</p> <p>Strengthen the activation treatment before plating, reducing plating pieces of residence time in the air</p> <p>Check gilded before plating process, strengthen pre-coating process</p> <p>Adjust pH value, heating, stirring to remove cyanide</p> <p>Adjust pH value, add ferrous salt precipitation reduction after high pH</p>
Coating roughness	<ol style="list-style-type: none"> <li>1 bath cloudy</li> <li>2 gilt plating has been rough before</li> <li>3 cathodic current density is too high</li> </ol>	<p>Filter bath added main salt</p> <p>Check gilded before plating process, strengthen pre-coating process</p> <p>Reduce the cathode current density and add a certain amount of conductive salt</p>
Coating color bleak	<ol style="list-style-type: none"> <li>1 gold content is too low</li> <li>2 cathode current density is too low</li> <li>3.pH not in the specified range</li> <li>4 temperature is too low</li> </ol>	<p>Add gold salt bath and add a certain amount of conductive salt</p> <p>Based on results of the analysis appropriate to add gold and conductive salt bath</p> <p>Adjust the solution pH value</p> <p>To improve the bath temperature process specification</p>
Coating redness	<ol style="list-style-type: none"> <li>1 solution of copper impurities</li> <li>2 gold content is too high</li> <li>3 temperature is too high,</li> <li>4 the cathode current density is too high</li> </ol>	<p>Add a certain amount of complexing agent to copper ions masking</p> <p>Fill gold-plated lower concentration of water, and the appropriate adding amount of conductive salt and complexing agent</p> <p>Add cold water to cool and adjust the electrolyte temperature to 50°C, and appropriate additional main salt</p> <p>Reducing the current density, adding gold and conductive salt bath</p>
Coating hair green	<ol style="list-style-type: none"> <li>1 the solution containing silver or other impurities</li> </ol>	<p>Added conductive salt and complexing agent mask interference ions.</p>
Plating solution was muddy brown	<ol style="list-style-type: none"> <li>1 complexing agent is too low</li> <li>2 bath aging has a lot of impurities</li> <li>contaminated plot</li> </ol>	<p>Need to supplement the complexing agent and conductive salt</p> <p>Need to filter in removing impurity, clean up the amount of gold plating tank recovery solution</p>

## 5 Conclusions

Gold - cobalt alloy plating optimum conditions are: pH value: 3.5 to 4.5; temperature: 45~60°C; cathodic current density: 0.5~1.5 A/dm<sup>2</sup>; gold plating the mass fraction of about 96.5%, the coating thickness is between 0.05~0.3μm.

Appropriate process conditions can be prepared gold - cobalt alloy plating, the coating hardness, surface bright and

compact, fine crystal, which was the golden color. Can effectively improve coating performance, cost savings, and has broad application prospects.

Coating and plating quality problems can be solved through appropriate technical methods to achieve safe and efficient production of gold plating.

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