

# A comparative study of DC and pulse gold electrodeposits

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Gold deposits were formed on AA 1100 aluminium alloy using a simple chemical pretreatment both by direct current plating (DCP) and pulsed current deposition (PCD) methods. The surface properties of the gold deposits such as adhesion, porosity, surface morphology and corrosion resistance formed by both DCP and PCD methods were compared by analysing them using adhesion and porosity tests, scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). From the analyses, it is observed that the gold film formed by the PCD method has a better corrosion resistance, less porosity and reduced grain size compared to that formed by the DCP method.

**Keywords:** DCP, PCD, SEM, EIS, Corrosion and porosity, Gold, Aluminium

## Introduction

Gold being a noble metal, has a very high resistance to chemical attack. Apart from its chemical stability, owing to desirable electrical properties, gold has been accepted as a versatile material in electronic technology. Gold is widely used for radiation control in Space technology because of its optical stability in space and in pre-launch environments. Also, gold will not undergo sublimation in the high vacuum of Space, so it may not condense and shortcircuit electrical systems or dull optical devices, and therefore gold-plated surfaces are in demand for use in Space research. Electrodeposited thin films of gold are generally porous in nature, which may lead to the formation of corrosion products through the pores. Porosity is the amount of discontinuity in the film responsible for corrosion. The corrosion products will affect the contact resistance degrading the reliability of the connectors. The corrosion of the base metals through porous gold in the electrical contacts has been studied.<sup>1,2</sup> Electrical contacts are generally electroplated with hard gold, which must withstand mechanical as well as chemical wear. The rapid growth of thin film technology has placed many new demands on gold as a microelectronic material.

The pulsed current deposition (PCD) technique is a versatile method for preparing nano-structured metals and alloys<sup>3-7</sup> and composite coatings.<sup>8-12</sup> In recent years, PCD has emerged as a sinecure of modern technology and so, much attention has been paid worldwide because it is a technique that allows the preparation of large, bulk samples with purity, low porosity and enhanced thermal stability. Numerous papers<sup>3-18</sup> have reported the theoretical aspects of pulsed electrodeposition process and the properties of various pulse plated metal deposits on various substrate

metals. Very few papers<sup>19-20</sup> have been published on electrodeposition of gold on various substrate metals by PCD methods. Gold and other metal nano-wires have been prepared using alumina templates<sup>21-23</sup> and electroplating of metals on aluminium and its alloys, other than gold, has also been carried out,<sup>24-33</sup> but studies of pulse plating of gold on aluminium in a single step have not been reported.

Gold plating on aluminium is very difficult because of the presence of a natural oxide film and the number of pre-treatment steps that have to be conducted prior to electroplating. No single step pre-treatment has been reported for direct plating of gold on aluminium and its alloys. It has been the practice to deposit common metals on aluminium and its alloys by modifying the surface, either by the formation of a thick oxide film by anodising or by deposition of zinc/tin from zincating/stannating baths prior to electroplating. Anodised coatings have certain shortcomings. The oxide layer is brittle in nature and forms an insulating layer. Reflectivity is reduced unless high purity metal is used and it has limited corrosion resistance in some environments. In the zincating/stannating process, if the surface of the substrate metal is not homogeneous, an immersion coating of different thickness will be obtained on the matrix and on intermetallic constituents. Good adhesion is achieved only if the plated articles are then heated for about 30 min at 230°C to enable interdiffusion to occur. Also, the deposit obtained from a simple zincate solution will be thinner and more compact. The reproducibility of coatings on aluminium by zincating is critical and special electroplating baths may be necessary for various alloys.

In order to overcome the above drawbacks and to eliminate the number of steps involved in the pretreatment, a novel and simple chemical pretreatment has been developed for electroplating of gold on aluminium. To compare the surface properties of deposits, gold is electroplated directly onto aluminium by both direct

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current plating (DCP) and PCD methods. This paper describes the comparative study of surface properties of DC and pulse gold electrodeposits formed on aluminium.

Experimental

AA 1100 aluminium alloy specimens of size 50×20×0.1 mm were prepared and mechanically polished to obtain a surface roughness of 0.1 μm. The polished specimens were degreased with trichloroethylene and chemically treated in a specially developed simple pretreatment solution containing 10 g dm<sup>-3</sup> zinc chloride, 50% (v/v) ortho-phosphoric acid and 5% (v/v) hydrochloric acid at 30°C for 5 min. After rinsing in deionised water, the specimens were electroplated with gold from a conventional gold bath by DC plating and pulsed current deposition methods. Plating was carried out separately using the same electrolyte and pre-treatment (Table 1).

Adhesion tests

All the aluminium specimens electroplated with gold by DCP and PCD methods were subjected to the following tests for evaluation of the adhesion of the coating.

- (i) *Bend test*: The gold plated aluminium alloy specimens were flexed through 180° repeatedly and examined after every 180° bending for any separation of the coating or delamination from the substrate metal.
- (ii) *Heat treatment test*: The DC and pulse gold electrodeposited aluminium specimens were heat treated in a closed furnace at 300°C for 4 h. Then the heat treated samples were immediately quenched in cold water and the surfaces examined.

Porosity test (nitric acid test)

The porosity of the gold coatings formed by both DC and Pulse plating on aluminium samples was tested by treating them in a nitric acid solution. A shallow dish

containing 0.3 dm<sup>3</sup> of concentrated nitric acid was kept at the bottom of the desiccator. The desiccator was sealed and the nitric acid vapours were allowed to equilibrate in the chamber for 30 min. The gold plated aluminium specimens were suspended with threads and placed about 7.5 cm above the liquid surface for 8 h. Then the specimens were removed without rinsing and dried by placing them in an oven at 105°C for 1 h. They were cooled and examined under 10× magnification for blue corrosion products of copper nitrate, which form as crystals that protrude through the gold surface and create discontinuity in the coatings, which allowed the nitric acid vapours to penetrate the gold film.

Electrochemical impedance spectroscopy studies

Electrochemical impedance spectra were recorded by immersing the gold plated aluminium specimens, which act as working electrodes, in a 3 wt-% sodium chloride solution using a computer controlled Thales impedance analyser. A platinum electrode was used as a counter electrode and a calomel electrode as the reference electrode. The reference electrode was connected with the test solution through a salt bridge. AC impedance measurements were carried out in the frequency range of 10 mHz to 100 kHz with an AC modulation at an amplitude of 10 mV above the rest or open circuit potential for gold plated aluminium. The polarisation resistance *R<sub>p</sub>* and double layer capacitance *C<sub>dl</sub>* values for both DC and pulse gold deposits were calculated. Bode impedance spectra were recorded for both DC and pulse gold deposits with and without exposure to 3 wt-% NaCl for 168 h.

Scanning electron microscopy analysis

The surface morphology and porosity of the DC and pulse gold deposits formed on aluminium were studied by SEM analysis. The gold plated aluminium samples were mounted on a sample holder using silver paste and SEM photographs were taken by using a JEOL-JSM-35 LF scanning electron microscope at 25 kV at a magnification of ×1000.

Results and discussion

Adhesion

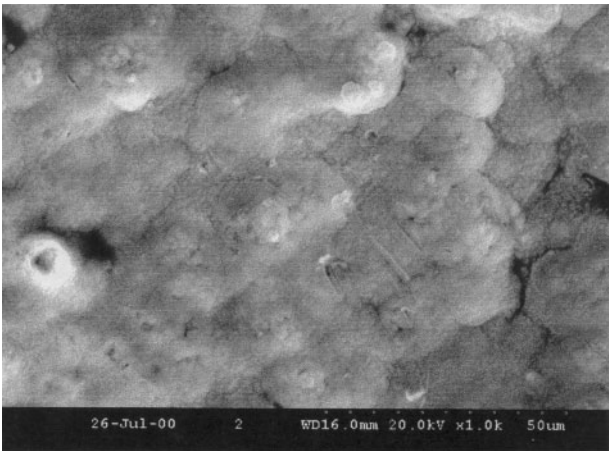
After the bend test, there was no peel-off or separation of the gold coatings formed by DC and pulse plating from the substrate metal. Also, in the heat treatment test, no blisters were observed on the DC or pulse plated gold deposits, which indicates very good adhesion of the gold to the aluminium metal.

Porosity

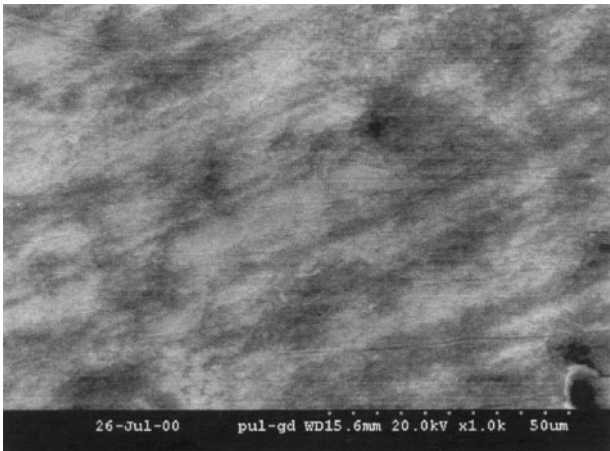
The surfaces of the nitric acid treated DC and pulse gold plated aluminium specimens were examined. A few blisters and green spots were noticed on the DC gold plated aluminium specimen with a gold thickness of 3 μm. However, the pulse gold plated aluminium specimens with a thickness of even 1.5 μm were free of pores. From the data, it was ascertained that the porosity of the pulse plated gold coating is less when compared to that of DC produced gold coating.

Table 1 Composition of plating bath with conditions for DCP and PCD

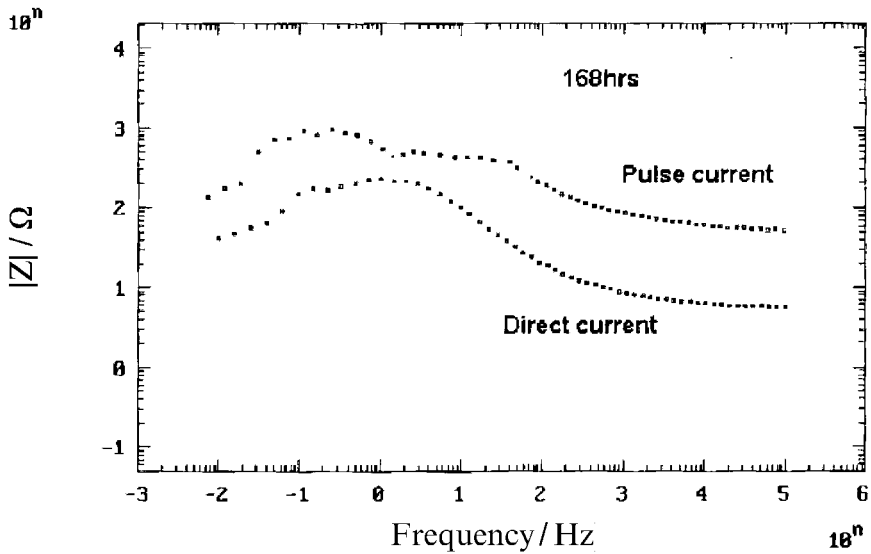
Gold electroplating bath	
Potassium gold cyanide	10 g dm <sup>-3</sup>
Citric acid	40 g dm <sup>-3</sup>
Sodium citrate	40 g dm <sup>-3</sup>
pH	4.0
Direct current plating (DCP)	
Current density	1 A dm <sup>-2</sup>
Plating time	10 min
Temperature	30°C
Thickness	3 μm
Pulsed current deposition (PCD)	
Average current density	1 A dm <sup>-2</sup>
Peak current density	5 A dm <sup>-2</sup>
Pulse 'on' time	20 ms
Pulse 'off' time	80 ms
Pulse duty cycle	20%
Pulse frequency	10 Hz
Temperature	30°C
Plating time	5 min
Thickness	1.5 μm



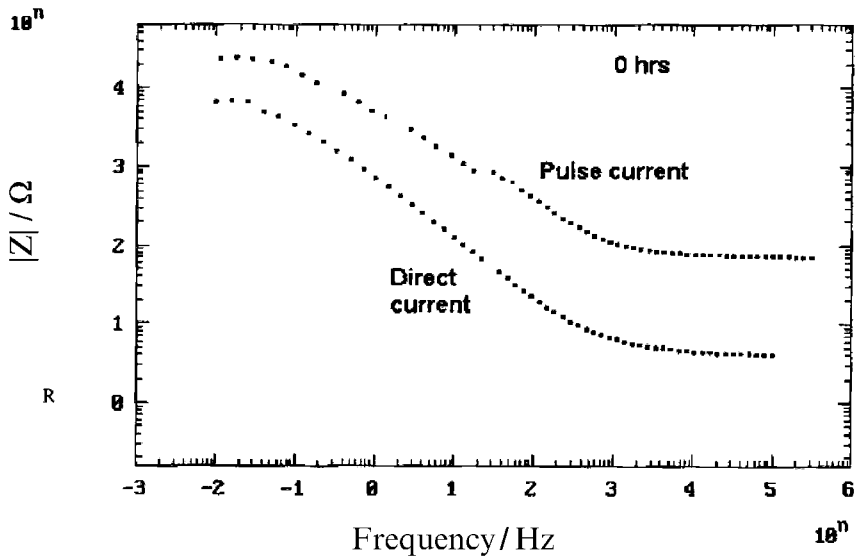
1 Scanning electron micrograph of DC gold plated aluminium



2 Scanning electron micrograph of pulse gold plated aluminium



3 Comparative Bode impedance diagram of DC and pulse gold plated aluminium after exposure to 3% NaCl for 168 h



4 Comparative Bode impedance diagram of DC and pulse gold plated aluminium without exposure

Table 2 Polarisation resistance  $R_p$  and double layer capacitance  $C_{dl}$  values for the DC and pulse gold electrodeposits with and without exposure to 3 wt-% NaCl

Plating method	Time of exposure to NaCl/h	$R_p/\Omega$	$C_{dl}/F$
DC	168	215.1	$7.7 \times 10^{-4}$
Pulse	168	406.8	$4.0 \times 10^{-4}$
DC	0	553.8	$3.7 \times 10^{-4}$
Pulse	0	683.9	$1.2 \times 10^{-4}$

Scanning electron microscopic studies

The surface morphology and porosity of the gold deposits formed on aluminium by DC and pulse electrodeposition were studied by SEM analysis. Figure 1 is a SEM micrograph of the DC gold plated aluminium surface and Fig. 2 is that of the pulse gold plated aluminium surface. No pores were found in the SEM of the aluminium surface plated with gold by PCD, whereas a large number of pores were observed in the SEM photograph of the DC gold plated aluminium surface. Also, the SEM of the pulse gold plated aluminium surface has a greater surface density than the DC gold plated aluminium surface. Therefore, in the case of pulse current deposition, the porosity of the deposit is very much decreased. Also pulse plating permitted a thinner gold deposit (1.5  $\mu\text{m}$ ) than the DC gold deposit (3  $\mu\text{m}$ ) resulting in a saving of gold and a reduction of weight.

The grain size of the pulse gold deposit was smaller compared to that of the DC gold deposit. In pulse plating, the peak current density is higher than the average current density. So an increase in peak current leads to a decrease of grain size. The decreased porosity and denser packed surfaces are a direct result of the fine grain size in the pulse plated gold deposits. This decrease in porosity achieved by pulsed plating is possibly due to the desorption of hydrogen during the ‘off’ time of the pulse cycle, because porosity is related to the presence of hydrogen bubbles on the surface during deposition.

Electrochemical impedance spectroscopic studies

Figures 3 and 4 show the comparative Bode impedance plots of DC and pulse gold plated aluminium with and without exposure to 3 wt-% NaCl for 168 h. The points in the figures represent the experimental data whereas the solid line represents the best fits obtained by Nonlinear least squares fit (NLLSF) technique. The impedance responses of both DC and pulse gold deposits with and without exposure to NaCl are characterised by well defined curved line spectra.

From the impedance spectra (Figs. 3 and 4), it can be inferred that the impedance of the pulse gold electrodeposit was higher than that of the DC gold deposit, which indicates that the corrosion resistance of pulse gold deposited aluminium specimens is greater than that of DC gold plated aluminium. Similar behaviour was also observed in the DC and pulse gold plated aluminium after exposure to 3 wt-% NaCl for 168 h. However, the impedance of gold plated aluminium specimens after exposure was found to be low compared to that of the specimens without exposure, which indicates that the gold plated aluminium surfaces

had undergone corrosion as a result of exposure to NaCl.

The calculated  $R_p$  and  $C_{dl}$  values of the DC and pulse gold plated aluminium specimens with and without exposure to NaCl are presented in Table 2. From this table, it is clear that the pulse gold plated samples have high  $R_p$  values and low  $C_{dl}$  values, compared to those of the DC gold plated aluminium samples with and without exposure to NaCl, which indicates the corrosion resistance of pulse gold deposits is greater than that of DC gold deposits. However, the DC and pulse gold plated aluminium samples with exposure have low  $R_p$  values and high  $C_{dl}$  values compared to those of samples without exposure. It can also be assumed that the gold plated aluminium samples have undergone corrosion during exposure to 3 wt-% NaCl for 168 h.

Conclusions

- 1. A single step pre-treatment method was used for electroplating of gold on aluminium.
- 2. Reductions in power consumption, time and cost were obtained using this method.
- 3. The gold deposits formed on aluminium by both DCP and PCD methods showed very good adhesion.
- 4. The pulse gold deposited aluminium surfaces have better corrosion resistance than the DC gold deposited aluminium surfaces.
- 5. The pulse gold plated aluminium surfaces have less porosity, smaller grain size and high surface density compared to DC gold plated aluminium surfaces.
- 6. Also, the use of pulse current results in a saving in gold, as well as reduced weight, power consumption, time and cost.

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