



## Development of a bath for codeposition of copper and platinum

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### Abstract

To improve the mechanical properties of electrodeposited copper, a new bath was developed for the codeposition of copper and platinum. A pyrophosphate bath employing chloroplatinic acid as a source of platinum was investigated at current densities ranging from 1 to 4 A dm<sup>-2</sup> and temperatures from 20 to 60 °C. Bright, shiny and crack-free deposits were obtained at low current densities (i.e., 1–2 A dm<sup>-2</sup>). The amount of platinum observed in the deposits was found to increase with the current density and bath temperature. The Knoop hardness was found to increase with platinum content in the deposits. Corrosion rates measured in solutions of NaCl were found to decrease with platinum content. Deposits containing up to 3.9 wt % of platinum can be obtained by electrodeposition. As compared to electrodeposited copper from the acid bath, the Cu–Pt deposits exhibited a 17% increase in Knoop hardness and a 21% increase in corrosion resistance.

### 1. Introduction

Copper can be easily electroplated and hence it is possible to form complex shapes and seamless objects free of stresses that do not require joining of parts using welding and riveting. This ability to electroform, along with its very high thermal conductivity, makes copper suitable for use in aerospace applications, where the removal of heat (exhausts for hot combustion gases) is desirable. Copper films produced by electrodeposition have very good adhesion properties and exhibit pore free structures of desired thickness [1–3]. Another important feature of copper is its good corrosion resistance. However, copper has relatively low mechanical strength as compared to nickel, which also possesses good heat transfer characteristics.

The most commonly used bath for copper deposition is the acid copper type. The composition of the raw acid bath is given in Table 1. This bath allows production of copper deposits at almost 100% faradaic efficiency [2]. The acid copper bath constituents are inexpensive and the conductivity of the solution is very high, which leads to very low overvoltages [2]. Addition of chlorides and other agents to the raw acid bath results in fine grained, bright deposits with excellent levelling and microthrowing powers. These deposits exhibit hardness ranges on the Knoop hardness scale between 145 and 160 compared to those obtained from the raw acid bath (Knoop hardness number 100–120). The copper cyanide bath

(Table 1), which is an alkaline bath, overcomes some of the disadvantages of the acid copper. Kinetics and growth modes of copper electrodeposition have been discussed in two recent papers [4, 5]. The disadvantages of cyanide baths lie in their toxicity and inability to form thick deposits. The copper pyrophosphate bath (Table 1) which operates at a pH between 8 and 9 has characteristics similar to the acid and cyanide baths [2]. Because the pH is close to neutral, the substrate is not readily attacked by the bath constituents, as is the case with the acid and cyanide copper plating solutions. An important factor is the pyrophosphate to copper ratio. A ratio of 7:1 to 8:1 ensures anode (copper) dissolution and high solution electrical conductivity. The presence of nitrate reduces the amount of hydrogen evolution. The ammonium ions assist in copper anode dissolution. Orthophosphate produced during the hydrolysis of pyrophosphate not only hinders anode dissolution but also acts as a buffer. There is no chemical breakdown of the bath constituents during deposition.

Platinum electrodeposition from platinic and other electrolytes has been reported [6, 7]. Electroless platinum deposition from chloroplatinic acid and hydrazine has also been reported [8]. In a recent paper Baraka et al. [9] have described the electrodeposition of platinum–rhodium alloy on titanium substrates. Although a vast amount of literature exists on electrodeposition of copper alloys, such as tin–copper [10], copper–nickel [11], copper–aluminum [12], copper–zinc [13],

Table 1. Deposition baths for copper

Bath type	Composition	Concentration /g L <sup>-1</sup>	Current density /A dm <sup>-2</sup>	pH
Acid copper	Copper sulfate	150–250	2–5	0.6–1
	Sulfuric acid	45–100		
Copper cyanide	Copper cyanide	19–26	5–10	11–12.2
	Sodium carbonate	15–60		
Copper pyrophosphate	Copper pyrophosphate	50–85	1–8	8–9
	Potassium pyrophosphate	200–350		
	Potassium nitrate	3–6		
	Ammonium hydroxide	4–11 ml L <sup>-1</sup>		

iron–copper [14], copper–indium [15], copper–lead [16], copper–bismuth [17], copper–lithium [18], no published data on copper–platinum electrodeposition is reported.

## 2. Experimental details

Copper platinum alloy was electrodeposited on to rectangular stainless steel sheets 15 mm by 50 mm. Prior to deposition, the substrates were polished using 240, 320, 480 and 600 grit wet SiC polishing paper successively. The anode was a rectangular sheet of copper measuring 30 mm by 15 mm. Both anode and cathode were rinsed with distilled water and acetone so as to degrease before immersion in the electrolyte. At the conclusion of each experiment the electrodes were rinsed with distilled water and acetone again and then allowed to dry. The deposit weight was determined by difference. The baths used were prepared using distilled water and reagent grade chemicals. All the chemicals used were purchased from Alfa Aesar. Nitrogen gas was bubbled through the electrolyte for about 10 min prior to each experiment to purge the solution of oxygen. Energy dispersive X-ray spectroscopy (EDX) was used to measure the elemental composition of the deposits. Samples were also subjected to Knoop hardness measurements. The samples were polished prior to their mounting on edge in Buehler Sample-Kwik epoxy resin. The polishing step consisted in the application of various grades of polishing paper ranging from 180 to 600 grit. Finally, the samples were polished with 0.5-micron alumina powder. A Knoop indenter was used for 12 s using a load of 10 g. Each sample was indented five times and the average of these measurements is reported.

The corrosion measurements were made using the potentiodynamic polarization method. The desired area of the specimens was exposed in 0.55 M NaCl solution. Nitrogen gas was bubbled through the electrolyte over the course of the reaction. A standard three-electrode reactor using a saturated calomel (SCE) reference electrode was used. Measurements were made using an EG & G model 273 potentiostat/galvanostat, and a CMS 105B basic corrosion measurement system (Gamry Instruments). The corrosion current and the potential were determined using the Tafel and polarization resistance methods.

## 3. Results and discussion

The bath composition and other experimental conditions are listed in Table 2. In preliminary experiments it was found that a solution of pH between 7.5 to 8.0 resulted in the brightest deposits. The deposits appeared to have minimal to no visible surface defects. When experiments were performed at pH greater than 8, weak and powdery deposits were obtained, presumably due to the formation of metal hydroxides. The bath pH was maintained by addition of the requisite amount of pyrophosphoric acid. The pH did not change significantly (maximum decrease of 0.2) over the course of deposition. No spontaneous/galvanic reactions between the Pt ions and the copper substrate were observed. In each of the experiments reported, a total charge of 2500 Coulombs was passed, resulting in deposits of about 2.5 mm thickness. Two sets of experiments are reported below. In one set of experiments, deposition was carried out at current densities of 1, 2, 3, 4 and 5 A dm<sup>-2</sup>, while the temperature was maintained at 20 °C. In another set of experiments carried out at temperatures ranging from 20 to 60 °C, the applied current density was kept constant at 2.5 A dm<sup>-2</sup>.

### 3.1. Influence of current

Each experiment carried out at 20 °C was repeated twice, and for each experiment the anode weight loss and the weight of the deposit produced were noted. The weight of the deposits produced and the loss in weight of the copper anode were estimated to be 0.94 to 1.04 for an experiment conducted at 1 A dm<sup>-2</sup>, respectively. Increasing the current density to 5 A dm<sup>-2</sup> resulted in slightly higher weight of the deposit produced (1.0 g)

Table 2. Bath composition for Cu–Pt deposition\*

Chemical name	Chemical formula	Amount
Copper pyrophosphate	Cu <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	70 g L <sup>-1</sup>
Potassium pyrophosphate	K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	250 g L <sup>-1</sup>
Potassium nitrate	KNO <sub>3</sub>	5 g L <sup>-1</sup>
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	8 mL L <sup>-1</sup>
Chloroplatinic acid	H <sub>2</sub> PtCl <sub>6</sub>	1 g L <sup>-1</sup>
Pyrophosphoric acid	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	As needed

\* For brightest deposits, pH 7.5–8.0.

and somewhat greater loss in the anode weight (1.09 g). Experiment durations of 14 and 3 h were required so as to ensure the passage of a charge of 2500 Coulombs for deposition at current densities of 1 and 5 A dm<sup>-2</sup>, respectively. Deposits obtained at 1 A dm<sup>-2</sup> were found to be very bright, shiny and ductile. The deposits were very similar to those obtained from an acid copper (only) bath. The surface of the deposit in contact with the cathode appeared to have the same morphology as that of the substrate. For example, the small scratches or protrusions present on the surface of the cathode resulted in similar marks on the deposit surface.

The average platinum concentration of 0.25 wt % (average) was observed as shown in Figure 1. Two data points corresponding to the two platinum content values obtained for duplicate experiments are shown. The average of the two platinum content values is also plotted and connected with corresponding data points from other experiments. The surface of the deposits that was exposed to the electrolyte was found to be smooth. Deposits produced at 2 A dm<sup>-2</sup> were neither as bright nor as ductile as the copper deposits obtained from the acid bath. An average platinum content of 2.35 wt % was estimated. Again, the surface of the deposits in contact with the cathode seemed to be an imprint of the substrate surface. The surface exposed to the electrolyte had some spots where signs of nonuniform deposition were visible. The deposits produced at 3 A dm<sup>-2</sup> were found to have a platinum content of 3.2 wt % (average); however, they were dull in appearance. They also appeared to be brittle in comparison to copper deposits obtained from an acid bath. This can be explained by noting that at high current densities, overvoltage at the cathode causes excessive hydrogen evolution. Pitting and islands of overplating were also noticeable on the deposit surface. The surface of the deposits exposed to the electrolyte had numerous areas where overdeposition was clearly visible especially around the edges. At edges and sharp corners, the current density is known to be much higher than at the centre, leading to extremely high overvoltages and, thus, higher incidences of non-uniform deposition.

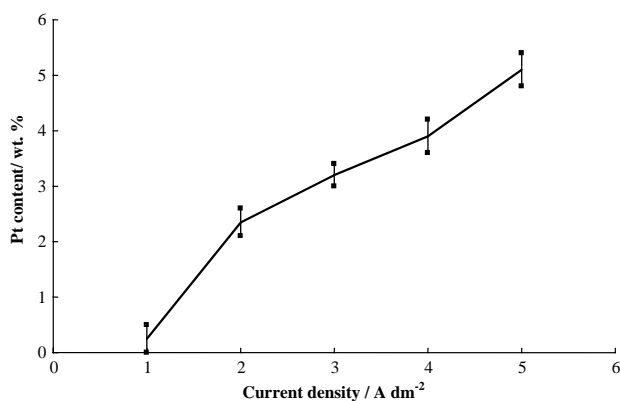


Fig. 1. Platinum content against current density (deposition temperature 20 °C).

Deposits produced at 4 A dm<sup>-2</sup> were much less bright and very brittle in comparison to those obtained at lower current densities. The deposits had a platinum content of 3.9 wt % (average). The deposits produced at 5 A dm<sup>-2</sup> had a relatively high platinum content of 5.1 wt % (average) but were flaky and powdery. Figure 1 is a plot of the platinum content against current density of various deposits obtained at 20 °C. The data clearly show that an increase in current resulted in a concomitant increase in the platinum content. The chloroplatinum ion used as a source of platinum has a more positive redox potential (0.73 V vs NHE for PtCl<sub>6</sub><sup>-</sup>/PtCl<sub>4</sub><sup>-</sup>) than that of copper (0.34 V vs NHE for Cu<sup>2+</sup>/Cu). Hence, an increase in the platinum content with current (potential) is attributed to activation control of the reaction.

### 3.2. Influence of temperature

An increase in the platinum content of deposits with temperature for experiments conducted at 2.5 A dm<sup>-2</sup> was observed (Figure 2). An increase in the bath temperature from 20 to 60 °C resulted in a corresponding 27.6% increase in the platinum content. The data also support the earlier inference that the rate of deposition is activation controlled. Increase in temperature under these conditions is expected to favour deposition of the less active element.

### 3.3. Knoop hardness

The hardness value of the deposits was found to increase with the applied current, reach a maximum value of 130 at 3 A dm<sup>-2</sup> and then decrease significantly with further increase in current (Figure 3). Although, the inclusion of platinum in the deposits results in enhanced strength, and the platinum content is observed to increase with current density, one-to-one correspondence between the platinum content and hardness is not observed for the following reason. As the current density is increased, more brittle deposits are produced presumably due to inclusion of hydrogen (visual observation of deposits).

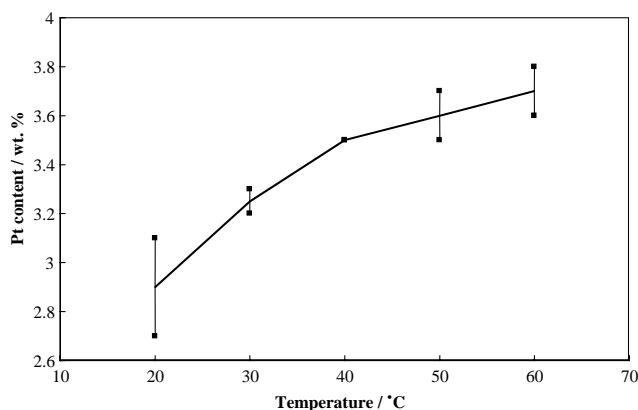


Fig. 2. Platinum content against deposition temperature (current density 2.5 A dm<sup>-2</sup>).

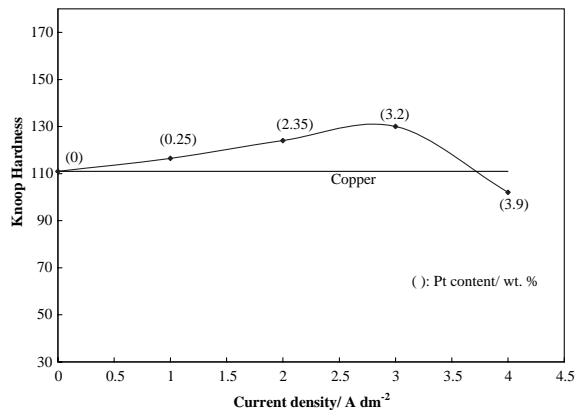


Fig. 3. Knoop hardness against current density (deposition temperature 20 °C).

In addition, hydroxide formation and local increase in pH as a result of hydrogen evolution may also contribute to the formation of brittle deposits. The embrittlement due to hydrogen retention is the mitigating factor for reduction in hardness for deposits produced at 4 A dm<sup>-2</sup>. About 17% enhancement in hardness of deposits produced at 3 A dm<sup>-2</sup> over the corresponding value of copper film produced from an acid bath was observed. A significant increase in the Knoop hardness with temperature was observed (Figure 4). Deposition at higher temperatures resulted in enhanced platinum content and, since experiments were conducted at a relatively moderate current density of 2.5 A dm<sup>-2</sup>, no significant hydrogen evolution or embrittlement due to hydrogen inclusion was observed. As compared to a copper film, a 23% increase in the Knoop hardness of Cu–Pt deposits was noted.

### 3.4. Corrosion measurements

For each data set reported, experiments were conducted using duplicate deposits produced under constant current conditions. The data reported represent averages of the results of each set of replicate experiments. The

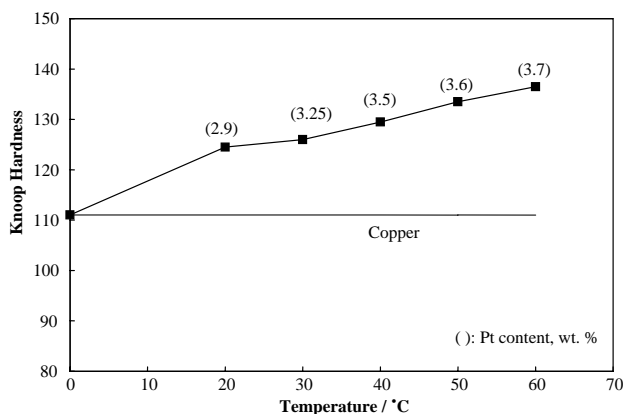


Fig. 4. Knoop hardness against deposition temperature (current density 2.5 A dm<sup>-2</sup>).

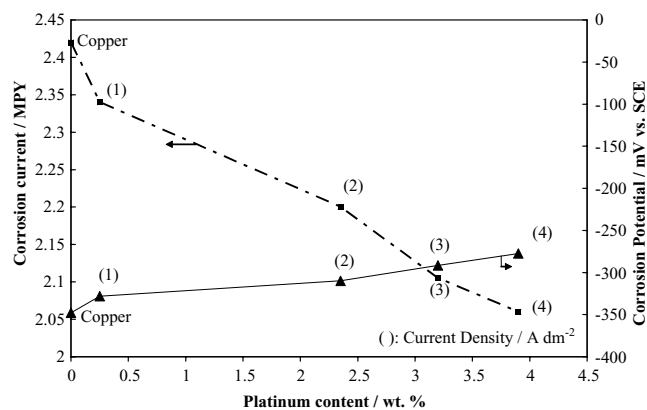


Fig. 5. Corrosion rate and potential against platinum content.

corrosion rate and corrosion potential for electrodeposited copper film (from acid bath) as determined by the potentiodynamic polarization method were found to be 0.06 mm per year, and -348 mV vs SCE. The data calculated using either the Tafel or polarization methods were found to be nearly identical.

Figure 5 shows a plot of corrosion rate vs platinum content for experiments carried out at 20 °C and current densities ranging from 1 to 4 A dm<sup>-2</sup>. The data show that the corrosion rate decreases with platinum content, and the maximum decrease over the corrosion rate of a copper film was found to be 15%. It is also observed that corrosion potential becomes nobler with increase in the deposit platinum content.

Figure 6 shows a plot of the corrosion rate and corrosion potential against temperature. As compared to the data shown in Figure 5, a greater increase in the corrosion resistance and corresponding enhancement in the corrosion potential is observed for the experiments. The deposits produced using a current density of 2.5 A dm<sup>-2</sup> and a temperature of 60 °C showed the maximum decrease (21%) in corrosion rate over the corresponding rate for a copper film obtained from an acid bath. Data in Figures 5 and 6 suggest that platinum inclusion in the copper film imparts corrosion resistance. In addition, the current density used for electrodepo-

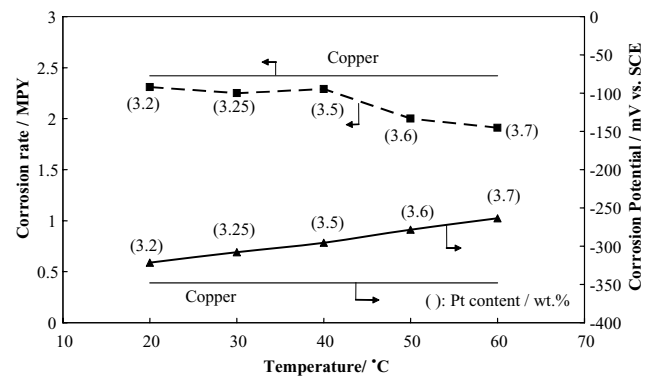


Fig. 6. Corrosion rate and potential against deposition temperature (current density 2.5 A dm<sup>-2</sup>).

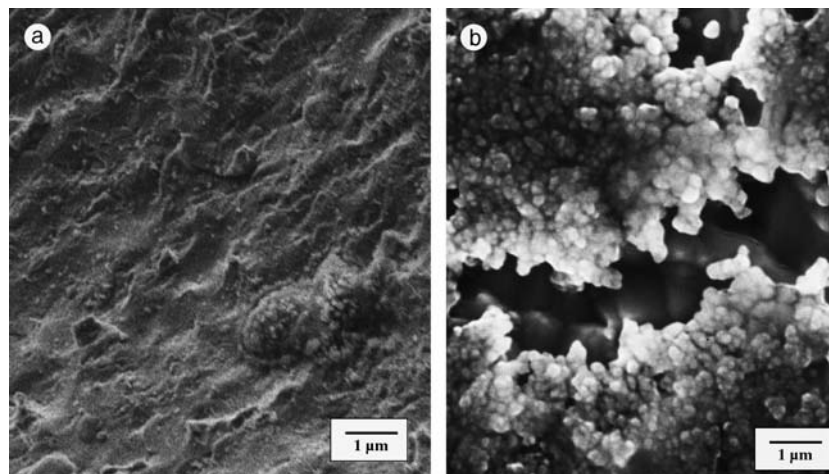


Fig. 7. SEM photomicrographs of CuPt deposits obtained at (a)  $2.5 \text{ A dm}^{-2}$  and (b)  $4.0 \text{ A dm}^{-2}$ . (Deposition temperature  $20 \text{ }^\circ\text{C}$ ).

sition also influenced the morphology and structure of the deposit which, in turn influences the corrosion rate.

Figure 7(a) and (b) are photomicrographs of the deposits obtained at  $2.5$  and  $4.0 \text{ A dm}^{-2}$ . The deposit produced using the lower current density of  $2.5 \text{ A dm}^{-2}$  is observed to be free of cracks in comparison to the one obtained at  $4.0 \text{ A dm}^{-2}$ . Deposits produced at current densities greater than  $2.5 \text{ A dm}^{-2}$  are nodular, relatively nonuniform and show signs of overdeposition. The deposits produced at  $4 \text{ A dm}^{-2}$  and  $20 \text{ }^\circ\text{C}$ , which contain  $3.9 \text{ wt } \%$  (average) platinum, have slightly higher corrosion rates than for deposits containing  $3.7 \text{ wt } \%$  (average) platinum obtained at  $2 \text{ A dm}^{-2}$  and  $60 \text{ }^\circ\text{C}$ . Deposits produced at higher current densities (Figure 7(b)) contain surface defects which lead to a lowering of the corrosion resistance. However, due to higher platinum content, the corrosion rate is observed to decrease albeit gradually with the current at which the deposits were produced.

#### 4. Summary

It has been shown that the plating bath developed in this study can be used to produce Cu–Pt deposits which have significantly greater mechanical strength and higher corrosion resistance than that of a copper deposit obtained electrochemically using an acid bath without additives.

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