Evaluation of the Effect of Carbonate Concentration in the Electrodeposition of Copper on Mild Steel Coin Blanks

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Mild steel coin blanks were covered with a thin layer of electrolytic copper, deposited from a cyanide copper bath. The influence of increasing carbonate concentration on the physicochemical properties of the deposits was evaluated. Potassium carbonate was added gradually to the electrolyte to evaluate the structural changes in the electrolytic copper layers. Once reaching the maximum carbonate concentration (400 g/L) additional tests were done to investigate the effect of decreased current on copper plating. The cell voltage decreased as the current density decreased, and the adhesion of the deposit was not enhanced (as seen by SEM and EDS measurements), showing that the incremental addition of carbonate caused substantial problems that are not easily avoidable. The chemical solubilization reactions of air-bearing carbon dioxide and the oxidation of free cyanide ions through dissolved oxygen, evolved in the anodic processes, as well as the anodic oxidation of those ions, contributed greatly to these copper plating inefficiencies. The experiments showed that excessive carbonate in the bath brings more harm than benefit, not only elevating process costs, but also in reducing deposit quality. The optimum conditions were a current of 10 A and a carbonate concentration below 50 g/L.

Keywords: copper plating; carbonate; coin blanks

Introduction

Metal plating is defined as the electrolytic reduction of a metallic element, in ionic form, on the surface of a metallic or electricallyconductive substrate, as a result of the migration of metallic ions (under the influence of an electric current), generally in aqueous solution (although non-aqueous and molten salt processes do exist), with the purpose of protecting the less noble substrate against corrosion, as well as to impart the desired commercial surface finish. In the plating process, an electrolytic cell is used containing an electrolyte (plating bath), consisting of ionic salts of the metal to be plated. The baths are commonly inorganic, such as copper, chromium, tin, nickel, zinc, noble metals (gold, silver, rhodium, platinum, etc.) and alloys such as copper/tin, zinc/iron, zinc/nickel and zinc/cobalt. Plating offers a diversity of finishes, allowing application in decorative (jewelry) and corrosion-resistant applications (tools and automotive parts).^{1,2}

Among the protective processes for mild steel substrates, copper plating occupies a prominent place. In many cases it constitutes a good intermediate layer for subsequent nickel plating. Deposits of copper-nickel-chromium on mild steel provide remarkable protective and decorative properties. The protection of plated copper on iron is cathodic. The copper layer should be thick and compact, which means with minimum porosity, to provide maximum protection.

Copper plating is often used as intermediate layer for further depositing nickel, silver or gold on aluminum and its alloys, zinc and its alloys and high-lead or antimony-containing alloys, on which it would not be possible to plate without compromising adhesion.³

Copper can be plated from solutions with either cupric (Cu⁺²) or cuprous (Cu⁺¹) chemistry. Among cupric baths are the sulfate (the most common), fluoborate and sulfamate. The cyanide baths are cupric.⁴ Sulfate baths have the advantage of lower cost, good chemical stability and relative ease of working as they are less toxic.⁵ In spite of such advantages, cyanide baths continue to be used.⁶⁻⁹ Their deposits are highly adherent, relatively uniform and have finer grains. However, copper cyanide baths are potentially more poisonous, demanding strict safety measures to deal with them.^{9,10}

In order to determine the corrosion resistance of the coatings, samples are subject to (1) neutral salt spray (sodium chloride) testing and (2) the Kesternich test (using sulfurous anhydride, SO_2).

The thickness of the coating (deposited layer) and its properties depend on several factors: the applied current density (or in the context of this work, applied current with a constant plating area), concentration of salts, bath temperature, presence of additives, basis metal condition, bath stirring, pH, etc.^{8,11,12} The amount of plated metal determines the weight and final dimensions of the treated pieces. Therefore, the amount of metal deposited has to be controlled within very restricted tolerances for the final articles to be within their specifications.

Copper cyanide baths

In general, cyanide copper plating baths contain (a) copper (I) cyanide, (b) sodium or potassium cyanide, (c) sodium or potassium hydroxide, (d) sodium or potassium carbonate and (e) Rochelle salts (sodium and potassium tartrate). In practice the formulations vary considerably.^{13,14} Potassium salts are more soluble in water, allowing the use of higher operating current densities.

Copper cyanide (CuCN) supplies the necessary copper ions for deposition. This salt is soluble in alkaline cyanide solution, due to the formation of copper cyanocomplexes. When this salt is in excess, the copper is present almost totally in the form of $[Cu(CN)_3]^{-2}$, as it is the most stable among all the formed copper cyanide complexes.^{15,16} In addition, if there is not enough free cyanide in the bath, precipitation of CuCN can take place on the anode surface, forming an adherent layer, causing anode passivation or polarization, which is detrimental

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to the anode dissolution process, reducing the anodic current efficiency. $^{17}\,$

Plating of copper on steel occurs when a potential is applied to the cathode which is below that of iron in the solution. The addition of an excess of cyanide in the copper bath determines the decrease of the "noble" character of the metal (decrease of the reduction potential). That allows one to obtain more adherent copper deposits.¹¹

The potassium hydroxide maintains the pH at a highly alkaline level (>13), avoiding the possibility of free cyanide decomposing to release hydrocyanic acid. The high pH inhibits carbonate formation that would otherwise occur through cyanide reacting with carbon dioxide in the air.

The presence of a certain amount of alkaline carbonates (up to 60 g/L) presents some advantages:^{18,19} (a) increased bath conductivity, (b) buffered bath pH, (c) increased cathodic polarization, thus improving copper adhesion, d) reduced anodic polarization, possibly forming complex carbonates with the metallic ions released by the anode and (e) increased maximum anodic current density.

Electrochemistry of cyanide copper plating

processes^{15,17,18}

Cathodic reactions

The copper plating can be described as follows:

$$K_{2}Cu(CN)_{3} + e^{-} \rightarrow Cu^{\circ} + 2KCN + CN^{-}$$
(1)

evolving, simultaneously, hydrogen gas, according to the following reaction:

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2\uparrow$$
 (2)

Hydrogen gas evolution consumes over 20% of the current used in the plating process.

Anodic reactions

The dissolution of the copper anode is represented by the inverse of the cathodic reaction with cyanide consumption, released at the cathode according to the following reaction:

$$Cu^{\circ} + 2KCN + CN^{-} \rightarrow K_{2}Cu(CN)_{3} + e^{-}.$$
 (3)

Another parallel anodic reaction is oxygen evolution:

$$4OH^{-} \rightarrow 2H_{2}O + O_{2}\uparrow + 4e^{-}$$
(4)

Another important reaction, which takes place at the anode, is the oxidation of cyanide ions into cyanate:

$$\mathrm{KCN} + 2\mathrm{OH}^{-} \rightarrow \mathrm{KCNO} + \mathrm{H}_{2}\mathrm{O} + 2\mathrm{e}^{-} \tag{5}$$

Subsequent cyanate hydrolysis produces bicarbonate and ammonia:

$$\mathrm{KCNO} + 2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{KHCO}_{3} + \mathrm{NH}_{3} \tag{6}$$

The bicarbonate produced reacts with potassium hydroxide producing carbonate:

$$KHCO_3 + KOH \rightarrow K_2CO_3 + H_2O \tag{7}$$

Taken together, anodic cyanide oxidation and the subsequent

cyanate hydrolysis, hydrogen evolution at the cathode and potassium hydroxide consumption, can be summarized as follows:

$$\mathrm{KCN} + \mathrm{KOH} + 2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{K}_{2}\mathrm{CO}_{3} + \mathrm{NH}_{3} + \mathrm{H}_{2}^{\uparrow} \tag{8}$$

With the high alkalinity of the bath, a great part of the ammonia is volatilized so that its concentration is less than 1 g/L. The oxidation reaction of cyanide to cyanate, and the subsequent formation of carbonate are favored at high temperature and at increased anode current density.

Another possible reaction is the hydrolysis of cyanide without oxidation: $^{18} \ \ \,$

$$\mathrm{KCN} + 2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{KCOOH} + \mathrm{NH}_{3} \tag{9}$$

The potassium formate formed is very soluble and is quite stable even at high temperatures, and it accumulates in the bath as the electrolysis goes on.¹³

The presence of carbonate in cyanide baths

The alkaline cyanide baths have the disadvantage of suffering gradual carbonate build-up. In other words, even if the baths are not formulated initially with carbonate, this ion is gradually formed in the bath through several mechanisms.¹⁹ The decomposition of cyanide can take place through the absorbed carbon dioxide from the air:

$$2\text{KCN} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + 2\text{HCN}$$
(10)

The hydroxide reaction with the absorbed carbon dioxide from the air, takes place according to the following reaction:

$$2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \tag{11}$$

The cyanide hydrolyzes generating ammonia and formate:

$$\mathrm{KCN} + 2\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{KCOOH} + \mathrm{NH}_{3}^{\uparrow} \tag{12}$$

The formate undergoes gradual chemical and electrochemical oxidation to carbonate:

$$\text{KCOOH} + \text{KOH} \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2^{\uparrow} \tag{13}$$

$$\frac{1}{2}O_2 + \text{KCOOH} + e^- \rightarrow \text{CO}_3^{-2} + \text{K}^+ + \frac{1}{2}\text{H}_2^{\uparrow}$$
 (14)

Finally, there is the cyanide reaction with hydroxide, in the presence of dissolved oxygen:

$$2\text{KCN} + 2\text{H}_2\text{O} + 2\text{KOH} + \text{O}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{NH}_3 \uparrow (15)$$

The first two mechanisms [Reactions (10) and (11)] are the most important in the operation of the cyanide bath. Therefore, all action that avoids absorption of CO_2 restricts the carbonate formation.

According to Geduld,¹⁸ carbonate formation is favored with increasing temperature, mainly for values higher than 71°C. For this reason the bath temperature should be strictly controlled and maintained below this value. Carbonates are also favored with the use of high current densities, which requires a parallel increase of temperature and stirring. As well, carbonates are favored with bath agitation (mainly air agitation) and increased concentration of the bath constituents.

The excessive increase of carbonate content causes several adverse effects in the plating process:^{19,20} (a) reduction of the operating range of the cathodic current density, (b) production of rough deposits, due to the formation of insoluble carbonate particles that are incorporated into the deposits, (c) decreased deposit brightness, (d) increased bath viscosity, which leads to drag-out losses in subsequent rinsing, and (e) decreased cathodic current efficiency.

There are two methods for decreasing the carbonate concentration: solution cooling and chemical precipitation.²¹ The first method involves cooling the bath down to the point where carbonates crystallize. Only baths using sodium salts can be treated by this method, because of the high solubility of potassium carbonate. The second method involves the precipitation of carbonate using calcium oxide, calcium sulfate, calcium or barium hydroxide, and calcium or barium cyanide. Both techniques have advantages and disadvantages and the appropriate choice should be ruled by process conditions.

Brazilian coin standards

Coins circulated in Brazil and other countries are manufactured on a high production scale. These coins can be made of solid alloy blanks (Type I), disks of the "sandwich" or "clad" type (Type II) and plated blanks (Type III).^{22,23}

The United States and now the European Community use the Type II coins, which have advantages such as high security against fraud and counterfeiting due to the uniqueness of the three-layer material and for detectable use in automatic vending machines, mainly for coins of high denomination.

The Type I disks were already the most common in Brazil. In the period from 1899 up to 1998, several metallic alloys and isolated metals were used, *e.g.*, gold, silver, copper alloys (bronze, brass, copper-nickel, bronze-aluminum), nickel, aluminum and stainless steel.²² Type III disks were released in Brazil in July of 1998 as the second generation of "Real^{***} coins. This disk type was issued in the 1970s in Canada. Among the main advantages of Type III disks are:²⁴ (a) a smaller risk of the coating spalling off, as the coins are manufactured with a substrate of mild steel containing less than 10 wt% non-ferrous metals such as copper, nickel and tin; (b) easier to distinguish the face values of the coins for color variety for the elderly and visually deficient; (c) acceptance of the coins with the recommended minimum thickness of the plated layer for use in automatic vending machines and (d) more security against fraud and counterfeiting.

The baths used at the Brazilian Mint are: a) cyanide copper for R0.01 and R0.05 coins and (b) cyanide copper/tin for R0.10, R0.25 and R1.00 coins (in the latter case, only the ring). The R0.01 and R0.05 coins have a 35-µm layer of copper specified, with SAE 1006/1008 mild steel blanks as substrates.

The decision to use cyanide baths is ruled mainly by the quality of the deposits that can be obtained. Another relevant argument is that this bath type is well known and practiced at the main mints of the world. Copper and bronze deposits were selected mainly to obtain coins with a beautiful appearance and different from the previous series (made of stainless steel).

The present work is a contribution to the study of parameters of copper plating on mild steel aimed at evaluating the quality of the coating obtained. The coating choice for the R\$0.01 coin was made for its handling simplicity, at the lowest cost and to the smallest work

scale. Besides, most of the conclusions obtained in this study can be applied to the line of copper/tin baths, as the excess carbonate formation in that bath also brings problems in the production line. First, we evaluated the influence of carbonate concentration on some variables of the copper plating process, including cell voltage for a given current density, anodic and cathodic efficiencies and the direct influences on the quality of the copper layer obtained under different situations. Secondly, in a bath with high carbonate concentration, a series of plating experiments was performed with decreasing values of applied current.

Experimental

Raw material

An alkaline copper cyanide bath was used, formulated initially with a low carbonate concentration, which was increased by external additions to each experiment. The concentrations of other components were not varied. No additives were added to the bath. Table 1 shows the initial composition.

Copper plating was done on R\$0.01 blanks (mild steel alloy SAE 1006 or SAE 1008) with the following characteristics: (a) individual weight (g): 2.25 \pm 0.07; (b) outer diameter, *d* (mm): 16.63 \pm 0.05; (c) thickness in the center, *h* (mm): 1.30 \pm 0.04; (d) thickness in the border (mm): 1.54 \pm 0.15. The chemical analysis of the disks is given in Table 2. Small OFHC copper cylinders were used as anodes in titanium baskets. The chemical analysis of the anodes is also shown in Table 2.

Table 1—Initial bath composition of copper plating tests

| Component | Concentration |
|---|---------------|
| Copper (as CuCN) | 24.5 g/L |
| Potassium cyanide (KCN) | 12.0 g/L |
| Potassium hydroxide (KOH) | 13.0 g/L |
| Potassium carbonate (K ₂ CO ₃) | 20 g/L |

* Time: 4.46 hr; temperature: 60°C

Table 2—Chemical analysis of raw materials used in the plating process

| Mild Steel Blank | | Copper anode | |
|------------------|-------------|--------------|--------------|
| Element | wt% | Element | wt% |
| С | 0.06 - 0.08 | Cu | 99.95 (min.) |
| Mn | 0.24 - 0.45 | 0 | 0.004 (max.) |
| Р | 0.04 (max.) | Pb | 0.002 (max.) |
| S | 0.05 (max.) | S | 0.003 (max.) |
| Si | 0.10 (max.) | Fe | 0.006 (max.) |
| | | Sb | 0.002 (max.) |
| | | Ni | 0.002 (max.) |
| | | Bi | 0.003 (max.) |

^{**} The "Real" is the primary currency denomination in Brazil, and is symbolized as "R\$."

Reaction system

Figure 1 shows a schematic diagram of the equipment used in the copper plating. It consists basically of a support, a tank for the copper bath (50 L capacity), a rotating barrel with a rotation speed control (with capacity for 1 kg of pieces (cathode) to be coated), and a temperature control. Cell voltage was monitored with a digital multimeter. For bath circulation, a magnetic pump was used. The cylindrical copper anodes were contained in two titanium baskets and immersed on either side of the plating barrel. In the literature,^{4,19} the anode area needs to be at least twice that of the cathode. In this work, the anode area was three times the cathode area. For the electrocleaning step (accomplished prior to plating), the same rotating barrel was used in a cell made out of polypropylene containing the cleaner. For heating, a Teflon[®]-coated electrical-resistance heater was used.

We tried to adhere to the procedures practiced at the Brazilian Mint, only varying the current densities of the electrocleaning and copper plating, thereby taking into consideration the difference in production scales.

Experimental procedure

Using an analytical scale, a 1-kg load of disks of mild steel was weighed. The disks were subsequently washed with distilled water (60°C) to remove the water-soluble coating present to protect the disks during storage and transport. The scale was also used to weigh out 11 kg of metallic copper cylinders as anodes.

After draining the water, the disks were transferred to the rotating barrel for electrocleaning (cleaner concentration, 100 g/L; temperature, 55°C; current, 2.5 A; time, 2.5 min). They were then thoroughly rinsed with distilled water (60°C). Before going to the next step, the barrel was thoroughly washed with running water and finally with distilled water to eliminate any trace of degreasing solution.

The washed blanks were then pickled in a 12-g/L solution of hydrochloric acid for five minutes at room temperature to remove any adherent oxides. They were then rinsed with distilled water (60°C). The washed blanks were transferred quickly to the rotating barrel for copper plating. After pickling, the blank surfaces were chemically active, and vulnerable to rapid oxidation. The barrel was sealed and then immersed in the cyanide copper bath, maintained at 60°C. The current density was fixed at the pre-established value, based on the calculated plating time and disk surface area to achieve the desired plate thickness.



Figure 1—Outline of the electrolytic system for copper plating.

In a first series of experiments, the carbonate (as K_2CO_3) concentration was varied in the bath (20 to 400 g/L), while the concentration of KCN and soluble copper were fixed (Table 1), as were the applied voltage (10 V) and the weights of the blanks and copper cylinders (anodes). The anodic current density used was 0.143 A/dm². Taking into consideration the copper layer thickness practiced at the Brazilian Mint (7.4 wt% of copper), the applied current (10 A), and a current efficiency of 70%, the plating time can be calculated for 1.0 kg of blanks:

74 g Cu = 2.372 g/A·hr × 10 A × 0.7 × $t \rightarrow t \approx 4.46$ hr,

which is similar to the value used at the Brazilian Mint. In another series of experiments, the carbonate concentration of (400 g/L) was fixed, and the applied current was varied (4 to 10A), which required that we re-calculate the plating time according to the formula above.

During the plating process, an hourly sample (5 mL) of the bath was collected for analytical control. The cell voltage was recorded every 30 min. During the plating process the volume of the bath was also corrected by adding distilled water to account for evaporation. Before starting each experiment the analysis of the previous experiment was considered to verify the corrections needed to maintain proper bath composition.

After plating, the blanks were quickly removed from the barrel and thoroughly rinsed with hot water (60°C) and then dried with the help of a dryer. They were weighed without delay, and kept afterwards in a desiccator under vacuum, for further thermal treatment. Four plated blanks were selected for analysis in the scanning electronic microscope (to be discussed later). The same washing, drying and weighing procedures were used for the copper cylinder anodes.

Thermal treatment was performed at the Brazilian Mint, in an annealing oven purged with oxygen-free nitrogen. The flow of reducing gas was then adjusted enough (30 m³/hr) to prevent rusting of the blanks. The annealing temperature was 250°C. The objective of the thermal treatment was to refine the grains, forming an interdiffusion layer and rendering the plated blanks less susceptible to corrosion.

The final finishing step (polishing and drying) was also accomplished at the Brazilian Mint, in a small-load polishing machine, used for such tests. The blanks were put inside of the reservoir of the polishing machine with water, polishing soap and 10 kg of stainless steel spheres. Soon afterwards a thorough rinsing was done with distilled water. The procedure was repeated, but this time with citric acid instead of soap. After the washing operation, the blanks were put inside of a clean cloth bag and dried in a centrifuge.

Cathodic (ε_C) and anodic (ε_A) current efficiency calculations Using the following formulas the cathodic and anodic efficiencies, for each copper plating test, were calculated:

Cathodic efficiency,
$$\varepsilon_C = \frac{D_D - D_S}{2.372 I_C t}$$
 (16)

where:

 D_D = weight of the blanks with the copper layer (g); D_S = weight of the blanks without the copper layer (g); 2.372 = electrochemical equivalent for Cu⁺¹ reduction in cyanide bath (g/A-hr);

 I_c = cathodic current (A) and t = plating time (hr).

(17)

where:

 A_A = weight of the anodes before starting the copper plating process;

 $\varepsilon_{C} = \frac{A_A - A_D}{2.372I_A t}$

 A_D = weight of the anodes after finishing the copper plating process;

 I_A = anodic current (A) and

t =plating time (hr).

Anodic efficiency,

The efficiencies can also be calculated using the following formula:

$$\varepsilon_{C} = \frac{V(C_{o} - C_{t})}{\frac{1}{nF}} \times \frac{1}{\int_{0}^{t} I(t)dt}$$
(18)

where:

V = electrolyte volume (L);

 C_o = copper concentration in the electrolyte at the beginning of the plating process (mol/L);

 C_t = copper concentration in the electrolyte at the end of the plating process (mol/L);

F = Faraday constant (96,490 Coulomb/mol);

n = number of electrons involved in the reduction and oxidation reactions;

I =current (A).

Calculation of the energy consumption (kW-hr/kg)

Using the following formula the energy consumption was calculated for the copper plating, taking into consideration the carbonate concentrations:

Energy consumption =
$$E \frac{nF}{M \cdot \varepsilon_c} \cdot \frac{100}{3,600}$$
 (kW-hr/kg) (19)

where:

E = cell voltage (V);

n = number of electrons involved in the reduction of cuprous ions.

M = gram-atoms of copper (63.5 g);

F = Faraday constant (96,490 Coulomb/mol);

 ε_{C} = current efficiency (%).

Analytical methods

The potassium salts (carbonate, hydroxide and cyanide) were analyzed by classic titration methods. In the case of the carbonate, the warm sample was treated with 0.25 mol/L barium chloride, precipitating the carbonate ions in the form of $BaCO_3$, which was then cooled and filtered. The precipitate was suspended in water and titrated with 0.25 mol/L hydrochloric acid using methyl-orange as an indicator. The cyanide was titrated with 0.1 mol/L silver nitrate, using potassium iodide as an indicator. The KOH content was determined by titration with 0.25 mol/L hydrochloric acid solution, the pH being monitored with a pH meter. Copper was analyzed by atomic absorption spectroscopy.

Scanning electron microscopy (SEM) was used to analyze the surface topography of the copper layer and the thickness of those layers. The equipment used was a Leica 5440 SEM. The surface analysis provided information on the copper layer porosity, the presence of precipitates and surface uniformity. For these studies, two

plated blanks were separated from each experiment, one without and the other with thermal treatment. In the analysis of layer thickness, the homogeneity of the copper layer was observed in order to verify the existence of occlusions and the presence of powdery deposits (or the lack thereof). Six blanks from each experiment, three without thermal treatment and three with thermal treatment were taken for such analysis. As one of the objectives was to measure the thickness of the copper layer, each lot of three blanks was submitted to a transverse cut, leaving 1/3 of the coin. The other 2/3 of the blanks was immersed in a resin and the group was dried and later polished to expose the metallic surface of the transverse cut. They then received a very thin silver surface coating, using a metallizer, as the resin was not conductive.

Results and discussion

Variation of bath composition with plating time

From the chemical analyses of the bath a very small variation of the concentration of each constituent was observed during each copper plating test, bearing in mind the constant replacement of water as it evaporated. That observation is applied not only for the series of experiments where the concentration of carbonate was varied (Fig. 2) but also to those where the plating current was varied (Fig. 3).

Cathodic (ε_{c}) and anodic (ε_{A}) efficiencies

Figure 4 shows the effect of increasing the carbonate concentration on the anodic and cathodic current efficiencies, while Fig. 5 shows the effect of increased current on those efficiencies. The plating efficiency decreased with increasing carbonate concentration, while the efficiency increased with increasing current (or current density, given the constant plating area of the coin blanks.).

Energy consumption

Figures 6 and 7 show the effects of carbonate concentration and of current on energy consumption, respectively. The energy consumption decreased with increasing carbonate concentration. Similarly, by fixing the carbonate concentration at 400 g/L, the energy consumption was reduced at lower currents.

Monitoring the electrolytic cell voltage

The cell voltage is the potential difference between anode and cathode and it usually refers to non-equilibrium conditions, when current flows through the cell. Figure 8 shows the cell voltage with time as a function of the carbonate concentration in the bath. As expected, with increasing carbonate concentration, the cell voltage decreased as a result of increasing the electrolyte ionic strength. However, that increase in ionic strength reduced the current efficiency. In other words, the competing reactions involved in carbonate formation "consume current," reducing the efficiency of the electrode processes of interest, increasing energy consumption. Figure 9 shows that the cell voltage also decreased when the applied plating current decreased.

Change in appearance of the copper plated blanks with applied current

Figure 10 clearly shows the appearance of the copper-plated mild steel blanks for each of the currents tested (CO₃⁻² = 400 g/L), compared with the unplated substrate (left photo). It is clear that the copper layer degraded when the applied current was reduced, rendering the blanks useless for coin minting operations. Only the samples produced at a current of 10 A measured up to the appearance of R\$ 0.01 coins in circulation.



Figure 2—The concentration of the bath constituents in the tests for evaluating the influence of carbonate concentration on the copper plating: (1) 20 g/L, (2) 50 g/L, (3) 100 g/L, (4) 150 g/L, (5) 200 g/L, (6) 250 g/L, (7) 300 g/L, (8) 350 g/L and (9) 400 g/L. I = 10 A.



Figure 3—The concentration of the bath constituents in the tests for evaluating the influence of current intensity on the copper plating: (1) 10 A, (2) 8 A, (3) 6 A and (4) 4 A. $[CO_3^{-2}] = 400 \text{ g/L}.$



Figure 4—The effect of carbonate concentration on the current efficiencies (ϵ_c = cathodic efficiency and ϵ_A = anodic efficiency). I = 10 A.



Figure 6—Energy consumption in the plating tests varying the carbonate concentration. I = 10 A.



Figure 5—Effect of current intensity on the current efficiencies (ϵ_c = cathodic efficiency and ϵ_A = anodic efficiency). [CO₃⁻²] = 400 g/L.





JOURNAL OF APPLIED SURFACE FINISHING



Figure 8—Cell voltage in the tests where the carbonate concentration was varied. I = 10 A.



Figure 9—Cell voltage in tests varying the current intensity. $[CO_3^{-2}] = 400 \text{ g/L}.$



Figure 10—Surface aspect of the mild steel blankets plated with copper under different current intensities, compared to the original blanks. $[CO_3^{-2}] = 400 \text{ g/L}.$

Analysis of the plated copper surface

Figure 11 shows the copper layer surface obtained as a function of the carbonate concentration in the bath. At a concentration of 50 g/L (Fig. 11a), the copper layer appears quite uniform with no evidence of porosity. However, with increasing carbonate concentration in the bath, significant morphologic changes were noted in the copper layers, with porosity observed, starting from values of 300 g/L (Fig. 11f). At 350 g/L of carbonate (Fig. 11g), a precipitate of calcium carbonate was observed (Point A). That was also confirmed by EDS analysis (Fig. 12). Further, increasing the carbonate concentration to 400 g/L (Fig. 11h) led to complete loss of copper adhesion. Significant exfoliation of copper occurred just by merely handling the plated coin blanks.

When the current was reduced from 10 to 8, 6 and 4 A at a carbonate concentration of 400 g/L, it was completely detrimental to copper adhesion. In the worst case, at a current of 4 A, non-adherent copper was produced, as seen in Fig. 10.

The photo in Figure 13 (left) shows areas of a blank whose copper layer (Current = 6 A) exhibits defects (Area A), which was also confirmed by EDS analysis (Fig. 13, right). On the other hand, Fig. 14 shows the formation of copper flakes (Current = 4 A) that, with stirring of the bath, spalled off the coin blank, accumulating in the bottom of the plating cell.

Figure 15 shows SEM photos of plated copper surfaces from tests with carbonate concentrations of 20, 50, 300 and 350 g/L, after thermal treatment. For the low carbonate concentration (20 g/L)

(Fig. 15a), after thermal treatment, a surface was obtained where the grains were very defined. At 50 g/L (Fig. 15b), a decrease in grain size was evident along with the appearance of depressions, which got worse as the carbonate concentration increased further.

Determination of copper layer thickness

Figure 16 shows a cross section of a copper plated mild steel blank (10 A, 20 g/L CO_3^{-2}) where the thickness of the copper deposit is indicated on both faces of the blank. The deposit obtained was quite compact and homogeneous, with uniform thickness. In that particular case, the carbonate concentration was at the lowest value studied (20 g/L) and the blank did not undergo subsequent thermal treatment. When a thermal treatment was applied to that same blank, the copper layer was still more homogeneous, albeit with a smaller thickness, as shown in Fig. 17. The thickness decrease is explained by the interdiffusion of the copper layer with the mild steel substrate.

When the carbonate concentration was 150 g/L, the copper deposit became deformed compared to the previous profile (Fig. 18), on one of the blank faces. This irregularity would actually present a matte surface, which would require a subsequent mechanical polishing. Such a mechanical treatment would remove copper, altering the final thickness of the copper deposit and also causing porosity in that deposit.

Increasing the carbonate concentration to 350 g/L (Fig. 19) severely affected the copper deposition process, obliterating deposit adhesion and rendering the subsequent coin minting operation unworkable.



Figure 11—Copper plated layer (I = 10 A) obtained under different carbonate concentrations in the bath: (A) 50 g/L, (B) 100 g/L, (C) 150 g/L, (D) 200 g/L, (E) 250 g/L, (F) 300 g/L, (G) 350 g/L and (H) 400 g/L (magnification: $5000 \times$).



Figure 12—EDS analysis of the copper layer for detecting the precipitated calcium carbonate (point A D figure 11g).



Figure 14—Photo of the mild steel blank surface with deficient covering of that surface with lamellar and non-adherent copper deposit under 4 A current intensity (magnification: 1000x).





Figure 13—(left) Photo of the mild steel blank surface with poor surface coverage with plated copper (6 A current), with areas showing the mild steel substrate (A) without copper deposit (magnification: 1000x); (Right) EDS analysis of the same blank surface where picks of metallic iron are observed, indicating that part of the substrate area was not covered with electrolytic copper.

JOURNAL OF APPLIED SURFACE FINISHING



Figure 15—Photos of the blanks surface covered with copper under different carbonate concentrations (I = 10 A), after thermal treatment at 250 °C under nitrogen atmosphere: (A) 20 g/L, (B) 50 g/L, (C) 300 g/L and (D) 350 g/L (magnification: 5000x).



Figure 16—Cross-section of copper plated mild steel blank (I = 10 A and $[CO_3^{-2}] = 20 \text{ g/L}$) before thermal treatment (magnification: 200x).



Figure 17—Cross-section of copper plated mild steel blank (I = 10 A and $[CO_3^{-2}] = 20 \text{ g/L}$) after thermal treatment (magnification: 200x).



Figure 18—Cross-section of copper plated mild steel blank (I = 10 A and $[CO_3^{-2}] = 150 \text{ g/L}$) before thermal treatment (magnification: 200x).



Figure 19—Cross-section of copper plated mild steel blank (I = 10 A and $[CO_3^{-2}] = 350 \text{ g/L}$) before thermal treatment (magnification: 200x).

Conclusions

Copper plating on mild steel coin blanks at low carbonate concentrations produced pieces where the copper layer was homogeneous. In addition, that low concentration increased the cathodic and anodic current efficiencies for the copper plating process. However, as the carbonate concentration increased in the bath, other adverse factors began to harm the operation of the copper plating process. One of the most harmful effects was the compromising of the copper adhesion, as evidenced by scanning electronic microscopy of the cross section of the copper plated blank. Further, in most of the tests at high carbonate concentrations, the copper deposits showed increased porosity. As the carbonate particles (as $CaCO_3$) adhered to the blank surface, surface irregularities formed to produce a non-uniform and matte copper surface.

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