

Article

Optimisation of Thiourea Concentration in a Decorative Copper Plating Acid Bath Based on Methanesulfonic Electrolyte

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Abstract: The role of thiourea as an organic additive in the nucleation and growth mechanism was studied for copper deposition and its application in the decorative electroplating and fashion accessory industries. The bath was designed to reduce the environmental and ecological impacts using methanesulfonic acid as electrolyte as an alternative to alkaline cyanide baths. We evaluated the nucleation and growth mechanism of copper exploiting voltametric and chronoamperometric measurements with a brightener concentration ranging from 0 to 90 ppm. We used the Scharifker-Hills model to estimate the type of nucleation mechanism after progressive addition of thiourea. Scanning electron microscope was employed for surface analysis and morphological characterisation of the nuclei. We verified that progressive nucleation is a key step in the obtainment of a shiny and homogeneous copper film, but an excess of thiourea could cause parasitic adsorption reactions on the surface of the substrate. X-ray fluorescence spectroscopy was used for the thickness determination of the copper deposits and the electrodeposition efficiency correlated to thiourea concentration. Finally, the optimal concentration of thiourea was assessed to be 60 ppm for the used formulation of copper plating.

Keywords: electroplating; copper electrodeposition; thiourea; nitrilotriacetic acid; hydroquinone; plating additive; methanesulfonic acid; nucleation and growth; decorative applications; plating industry



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1. Introduction

In the electroplating industry, copper plating is an important treatment and it is often the first and irreplaceable step in the electrodeposition of metal films for both technological [1] and decorative [2] purposes. Copper is an excellent undercoat for subsequent deposits, since it has good capability to compensate substrate defects that could accelerate corrosion, and its deposition can be chemically tailored to obtain levelled, high thickness bright films. The need to deposit small quantities of precious metals in the field of the electroplating industry and fashion accessories necessarily passes from the possibility of depositing copper or copper alloys (bronzes) with high thicknesses, high efficiency and improved corrosion resistance characteristics compared to the past. This need is also fundamental for reducing the environmental and ecological impact for an increasingly eco-sustainable production. This work seeks to improve the copper deposition process, a

basic and fundamental process for the creation of fashion accessories with low environmental impact.

Two basic types of processes are available based on the complexing system used: alkaline (cyanide-based baths) and acid (sulphate and fluoroborate) baths.

Alkaline copper solutions have higher throwing power (uniform deposit thickness on a surface of irregular shape) compared to acid copper solutions. This type of copper baths has low efficiency because of a low metal concentration and high amount of cyanide in the solution. These chemical characteristics avoid the formation of a non-adhering immersion layer of copper at the beginning of the plating process, and they guarantee excellent covering and throwing powers. Unfortunately, the presence of cyanide in alkaline copper plating solutions makes these baths extremely dangerous to handle.

Acid copper baths have a simpler formulation than alkaline ones, because they contain sulphate or fluoroborate, salts such as copper precursors, organic additives and sulfuric or fluoroboric acid, depending on the copper salt. They cannot be plated directly onto active metals, such as zinc or steel, as they will produce non-adhering immersion deposits. Acid copper baths are cheaper and more efficient if compared with alkaline baths. The disadvantage of these baths is their low throwing power which makes necessary a previous deposition of alkaline copper film.

In this work, we studied a new methanesulfonic acid-based copper bath that would be safer for electroplating plant technicians than alkaline cyanide baths, ready to be upgraded in a white bronze deposition bath and eco-compatible [3]. Indeed a coating of bronze commonly followed the copper deposition in nickel-free processes, increasing the corrosion resistance of the final product [4].

We used thiourea (TU) as a brightening agent by performing potentiostatic depositions and focussing on decorative applications. The use of thiourea has been previously adopted by other authors carrying out galvanostatic depositions for technical applications in the electronic sector [5,6]. The action of thiourea during copper deposition was verified exploiting cyclic voltammetry (CV) and chronoamperometric measurements [7–10]. Various depositions using different potentials and amounts of TU were performed to determine the optimal condition to obtain a bright deposit. Chronoamperometric measurements were used to obtain information about the mechanism of nucleation and growth of an electrodeposited film. Current transients have been analysed to obtain information on the type of nucleation (i.e., instantaneous or progressive), ions diffusion coefficient and density of metal nuclei at the electrode surface [11,12]. In this work, we attempted to determine a correlation between the trend of the parameters obtained from the Scharifker–Hills model [13] and the progressive addition of thiourea in an alternative methanesulfonic acid-based copper electrodeposition bath.

Scharifker–Hills Model

The initial stages of an electrodeposition process are associated with a three-dimensional multiple nucleation mechanism, subsequently the growth and coalescence of the nuclei formed on the electrode surface take place. The growth current of a single hemispherical nucleus depends on the diffusion coefficient, on the concentration of bulk, on the molar charge of the species being deposited and on the molecular weight and density of the deposit [14].

However, in real cases, it becomes necessary to consider the interactions, during nucleation and growth, among multiple nuclei that form simultaneously [15]. The growth of the nuclei occurs on the surface of the substrate extending perpendicularly to it and laterally, along the surface, forming three-dimensional deposits [16]. This process is not part of the two-dimensional process (valid for nucleation in the absence of interactions), which can be treated through Avrami's theorem [17]. In the present work, the Scharifker–Hills model was used. According to the Scharifker–Hills model, two borderline nucleation cases can be treated through two theoretical curves:

- Progressive nucleation:

$$\frac{J^2}{J_m^2} = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367(t/t_m)^2]\}^2 \quad (1)$$

- Instantaneous nucleation:

$$\frac{J^2}{J_m^2} = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2 \quad (2)$$

A method to determine the type of nucleation is the comparison of the dimensionless theoretical curves obtained from Equations (1) and (2) with the experimental values obtained, shown in a plot such as J^2/J_m^2 vs. t/t_m . Where J_m is the maximum current density recorded, and t_m is the time at which J_m occurs.

Different kinetic data of the nucleation mechanism can be obtained by applying the appropriate equation, according to the model.

2. Materials and Methods

The bath used in this work contained 4.62 M methanesulfonic acid (MSA) as the electrolyte, 0.17 M copper(II)–methanesulfonate as copper precursor, 0.1 M nitrilotriacetic acid (NTA) as copper ion complexing agent, 0.09 M hydroquinone (Hyd) as dissolving agent and thiourea (TU) as the organic additive under study in concentrations of 30, 60, and 90 ppm. Hydroquinone was used as a nitrilotriacetic acid (NTA) dissolving agent, as already reported in the literature [18], because the dissolution of NTA in the water/MSA system gave an unstable solution due to the fact of its poor solubility. Electrochemical measurements and depositions were carried out with a Metrohm (Herisau, Switzerland) Autolab mod. μ Autolab type III potentiostat/galvanostat computer-controlled by Nova 2.1.4 software (Metrohm) using Ag/AgCl in saturated KCl reference electrode (0.197 V vs. SHE at 25 °C). All the potentials recorded in this study were related to this reference electrode. Pt wire was used as a counter electrode. The working electrode was a rotating disk (RDE-2) glassy carbon electrode (Metrohm) with a surface diameter of 2 mm, RDE-2 by Metrohm. The glassy carbon electrode was cleaned by an electrochemical treatment based on the following steps [19]:

- OCP measurement;
- Application of a potential of +1.2 V vs. Ag/AgCl/KCl_{sat} for 120 s;
- Rotation at 2000 rpm;
- During electrode rotation, application of 3 voltametric cycles in the range -1/+1.4 V vs. Ag/AgCl/KCl_{sat} at 50 mV/s.

After each electrochemical cleaning, the electrode surface was treated with a polishing cloth and alumina water dispersion (0.3 μ m diameter particles). The surface cleaning was confirmed by the voltametric measurement of the reversible couple $[\text{Fe(II)(CN)}_6]^{4-} / [\text{Fe(III)(CN)}_6]^{3-}$. Each electrochemical measurement and deposition were carried out in a thermostated cell with a set temperature of 25 °C.

Electrodeposition was carried out on glassy carbon buttons with a diameter of 1.5 cm after a previous polishing of the GC surface with polycrystalline diamond dispersion (3 μ m) followed by distilled water rinsing. The electrical contact for the deposition was made using copper tape, applied at the rear part of the GC button.

The morphology of the electrodeposited films was characterised by scanning electron microscopy (SEM); SEM images were recorded with a Hitachi (Tokyo, Japan) SU3800 scanning electron microscope using an acceleration voltage of 10 KeV.

The thickness of the copper deposits was measured by means of X-ray fluorescence spectroscopy [20,21] using a Bowman XRF (Schaumburg, IL, USA) previously calibrated to certified standards.

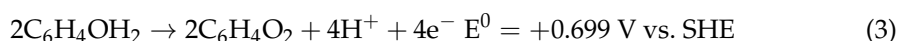
Some preliminary tests were also carried out on a metal electroplated substrate. We used square plates with sides 3 cm long and the following composition, from bulk to top layer: brass (bulk)/Ni (~20 μm)/Au (~0.5 μm).

3. Results

3.1. Voltametric Studies

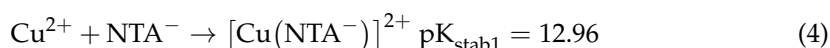
According to the literature, TU is a well-known organic brightener used in traditional copper electrodeposition baths, modifying the kinetics of copper electrodeposition mechanism [7–10]. In this case, thiourea was added in a copper solution that already contained a complexing agent, necessary to tailor copper electrodeposition potential in the case of an upgrade of the bath into a bronze electrodeposition one. From the standpoint of the mechanism with which thiourea modified the copper film formation in the innovative bath developed during this work, cyclic voltammetry was selected to clarify the electrochemical behaviour of copper ions in the absence and presence of thiourea. CV was also useful to select the cathodic potentials applied during chronoamperometric measurements. The voltage range used in cyclic voltammetry measurements (−0.8/+0.5 V) was based on the partial reversibility behaviour of the hydroquinone/benzoquinone couple which would bring a degradation of hydroquinone at scanning potentials over +0.5 V.

The oxidation could be easily explained by the simple redox reaction (Equation (3)):



Moreover, the glassy carbon surface of the electrode would be damaged if the scanning range would overcome +1.5 V in acidic solutions (in this work pH~1) [19,22].

NTA is a copper chelating agent, which at acidic pH values forms univalent complexes and allows for a two-mono-electronic-step mechanism for the reduction of Cu^{2+} ions [23,24] as proposed by Muralitharan et al. In Equations (4)–(6) are shown the chelating behaviour of NTA in acidic solutions and the main reduction mechanism of copper.



The redox behaviour of Cu(II) ions in the presence of MSA, Hyd and NTA is shown in Figure 1a. While Hyd did not alter appreciably neither the redox potentials of the $\text{Cu}^{2+}/\text{Cu}^0$ couple nor the CV signals area, NTA shifted the copper reduction to −0.14 V, slightly reduced the cathodic signal area (reduction MSA–Cu = -2.39×10^{-4} C, reduction MSA–Cu–Hyd–NTA = -2.21×10^{-4} C) and increased the anodic signal area (oxidation MSA–Cu = 4.74×10^{-4} C, oxidation MSA–Cu–hyd–NTA = 7.15×10^{-4} C). The latter was effect caused by a partial anodic degradation of NTA as already reported by Wu et al. [25].

After the voltametric study of the copper electrodeposition solution, increasing concentrations of thiourea were added. In this work, the effects of 30, 60 and 90 ppm of thiourea were tested.

Analysing the red voltammogram in Figure 1b, referring to 30 ppm thiourea in the solution, it was observed that the copper reduction and oxidation peak potentials remained approximately unchanged in the presence of the lowest additive concentration, compared to the dark grey track (absence of TU). Thiourea could interact with both the copper ions as well with the surface of the electrode; its behaviour depended on its molar ratio with the other interacting species present in the solution. In the presence of Cu(II) ions in the solution, thiourea formed stable complexes preceded by a reaction that produced TU–Cu(I) complexes and formamidine disulfide (FDS) as can be explained by Equations (7) and (8) [26].

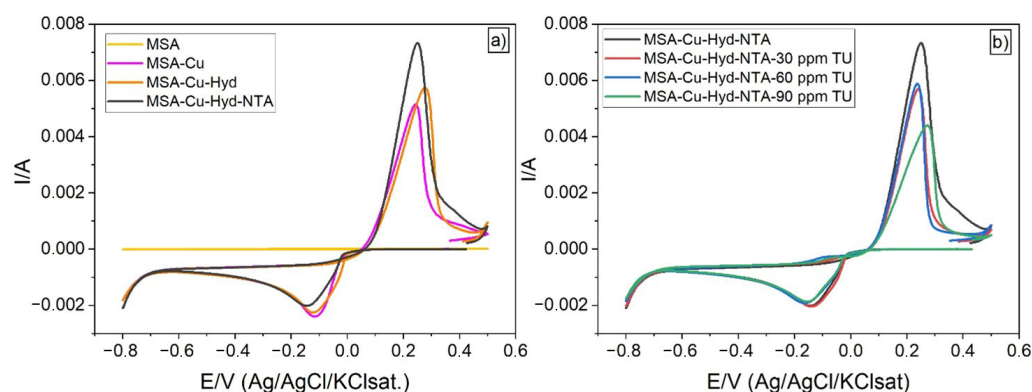
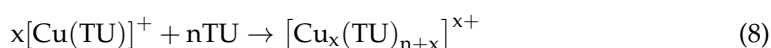


Figure 1. CVs of Cu(II)MSA 0.17 M in MSA 4.6 M aqueous solution, $50 \text{ mV} \cdot \text{s}^{-1}$ the scan rate: (a) addition of Hyd 0.1 M and NTA 0.1 M to the copper solution; (b) addition of 30/60/90 ppm of TU to the solution.



In this case, the reduction of copper and the subsequent formation of Cu–TU complexes was, in large part, hindered by two factors: the presence of NTA as copper ligand and the high Cu:TU molar ratio. The reactions reported in Equations (7) and (8) will surely take place in solution, but given the low concentration of TU in our formulation, its action will be mainly due to the fact of its adsorption on the electrode's surface. The further additions of thiourea determined some variations in the cyclic voltammetry of the formulation. In the voltammogram relative to the presence of 60 and 90 ppm of TU, the cathodic signal of copper shifted to -0.16 V , and there was a progressive reduction of the signal area in both the reduction (reduction TU 60 ppm = $-2.11 \times 10^{-4} \text{ C}$, reduction TU 90 ppm = $-2.02 \times 10^{-4} \text{ C}$) and the oxidation peaks (oxidation TU 60 ppm = $5.23 \times 10^{-4} \text{ C}$ and oxidation TU 90 ppm = $4.65 \times 10^{-4} \text{ C}$). In this case, while the moderate shift of the copper reduction potential demonstrated a weak Cu–TU interaction, the main effect can be observed in the decrease in the anodic dissolution signal area. We tentatively attributed this feature to the capability of thiourea and its by-products to adsorb both on the bare glassy carbon surface and on the copper-covered electrode surface. As already proposed by Cofré and Bustos, thiourea tends to adsorb on GC with an electrode coverage proportional to its amount in solution [27], reducing the electrochemically active area. Moreover, Cu–S affinity [9,28] determines the formation of a polymer-like insoluble film from adsorbed TU-species during the nucleation and growth of the copper film [29]. This complex film hinders the electrodeposition and the electro-dissolution of copper and, at sufficiently positive potentials, can be electro-oxidised to produce FDS, S^{-} and CN-containing species [30], which eventually changed the nature of products blocking the copper surface and changed the kinetics of the global anodic reaction. The slowing of the copper anodic dissolution kinetics was the main cause of the reduction of anodic peaks area with the increasing amount of TU in the solution.

3.2. Chronoamperometric Studies

A chronoamperometric study was carried out at three different deposition potentials for copper, based on the voltametric measurements. In this way, we attempted to characterise the nucleation and growth behaviour of copper in an alternative deposition bath with selected amounts of thiourea [7]. The open circuit potential (OCP) is maintained for 10 s, then the potential is stepped at the value of -0.12 , -0.15 or -0.20 V .

The current transients are reported in Figure 2 together with the theoretical curve of instantaneous and progressive nucleation from the Scharifker–Hills model. It is evident that the curves, while following the right trend, did not strictly follow the model. Most of

the curves were above the instantaneous nucleation curve. For this reason, we tried more complex models, such as the Sharifker–Mostany model [31] and Tarallo model [32], but the results were not much different. The same was reported before by many authors that studied the electrodeposition of copper [33–35]. The reasons proposed by the authors for the deviation from the model are due to the assumption by the Scharifker–Hills model that the crystal nucleus is hemispherical and exhibits purely diffusion-controlled growth and can be also the caused by the solution resistance. We suppose that this was also due to the high concentration of copper and the rapidity of the reaction. Similar behaviours were not observed in solutions much more diluted or containing an excess of cyanide, a much stronger complexing agent than NTA.

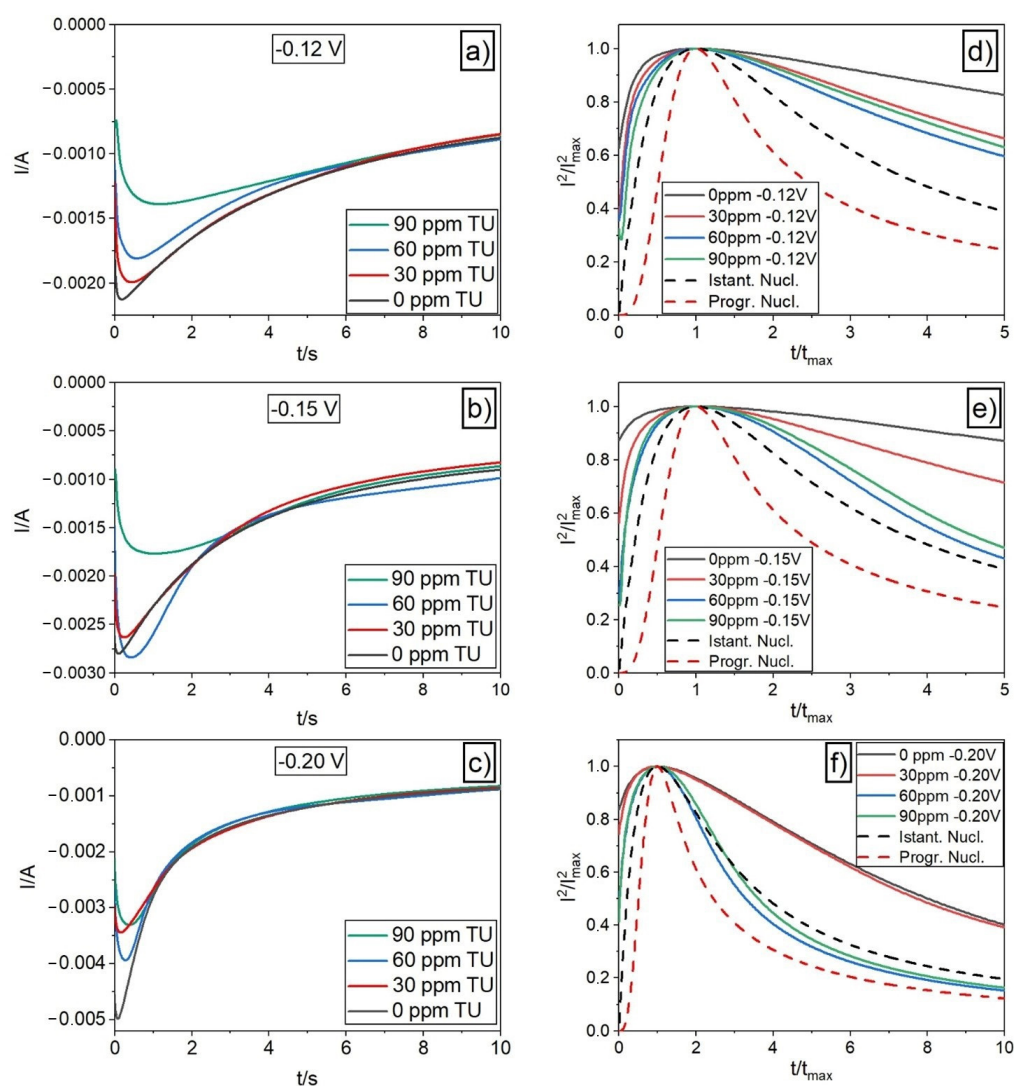


Figure 2. Current transients recorded at various TU concentrations at potentials: (a) -0.12 ; (b) -0.15 ; (c) -0.20 V. (d–f) are the same current transients but normalized with respect to J^2/J_m^2 vs. t/t_m to be able to compare them with the theoretical instantaneous and progressive curves (dashed lines) of the Scharifker–Hills model.

Established with this, we chose to continue to use the Scharifker–Hills model to obtain a qualitative analysis of what was going on in the electrode as done by the other authors.

The measurements reported in Figure 2 allowed for the deduction that the nucleation of copper approaches the progressive mechanism with an increasing concentration of additive and with potentials increasing in absolute value, despite at the concentrations studied, the full progression of nucleation was never achieved. As a general rule, the more

the deposition approaches the progressive nucleation, the more the deposit will be bright and with a mirror finish, which is desirable.

The diffusion coefficient (D) and the density of the active sites (N) were obtained by means of Equations (9) and (10) which refer to instant nucleation, since the current transients are closer to this trend:

$$D = \frac{J_m^2 t_m}{0.1629(nFc)^2} \quad (9)$$

where n is the number of electrons involved, F is the Faraday constant and c is the molar concentration.

$$N = \frac{1.2564}{t_m \pi k D} \quad (10)$$

where $k = \sqrt{\frac{8\pi c M}{\rho}}$, M is the molar mass of copper and ρ is its density.

The results of these calculations are provided in Table 1. The reduction of the instantaneous nucleation of copper due to the thiourea is supported by the decrease in the nuclei surface density (cm^{-2}) for each deposition potential set of measurements. The shift towards a progressive nucleation produces a lower number of nuclei at the initial stage of the deposition. Our hypothesis on the mechanism of thiourea in the condition studied in this work was reinforced comparing information from cyclic voltammetry and chronoamperometry. The effect of electrode surface inhibition of thiourea observed at 60 and 90 ppm in the CV could also be confirmed by chronoamperometric data in which can be observed a hindering of the copper nucleation at the first steps of electrodeposition. To the best of our knowledge, we supposed that the same mechanism of physio-chemical adsorption of TU and related polymer film on glassy carbon, already observed during voltametric analysis, caused the reduction in the nuclei surface density (cm^{-2}) and the approaching of the progressive nucleation mechanism at increasing TU. Observing this trend, we deduced that the -0.20 V was the best potential for the deposition of copper for this formulation.

Table 1. Kinetic data obtained from the Scharifker–Hills model for the nucleation of copper at various deposition potentials and in the presence of different amounts of TU. The number density of the active sites, N , and diffusion coefficient, D , are reported.

E (V)	TU (ppm)	t_m (s)	$ J_m $ (mA/cm^2)	$D \cdot 10^5$ (cm^2/s)	$N \cdot 10^{-5}$ (cm^{-2})
−0.12	0	0.180	67.83	0.47	27.01
	30	0.445	63.47	1.02	5.05
	60	0.575	57.61	1.09	3.67
	90	1.105	44.27	1.24	1.68
−0.15	0	0.095	89.17	0.43	56.12
	30	0.255	83.85	1.02	8.81
	60	0.415	90.45	1.94	2.86
	90	1.021	56.24	1.84	1.22
−0.20	0	0.08	158.60	1.15	25.02
	30	0.160	109.52	1.09	13.12
	60	0.280	125.38	2.51	3.27
	90	0.370	105.25	2.34	2.66

3.3. Morphological Characterisation

The electrochemical solutions with 0, 30, 60, and 90 ppm of TU were used to produce copper films on a large electrode using the potentiostatic deposition method with an applied deposition potential of -0.20 V, a deposition time of 600 seconds, at a temperature of 25 °C, in the absence of stirring to emulate the chronoamperometric tests condition reported above. The SEM images and pictures reported in Figure 3 allowed for the correlation of the

microstructure of the deposit to the theoretical information obtained by the mathematical model used to analyse chronoamperometric data. The results showed a refinement of the crystallites size up to 60 ppm of thiourea added, while the presence of 90 ppm of TU caused the formation of a copper film with uncontrolled morphology and grain size. As already observed from voltametric analysis, the presence of the highest amount of organic additive caused the random formation of an organic film made of adsorbed TU species. We hypothesised that this film hindered the formation of copper nuclei on the surface of the electrode, promoting the formation of discontinuities in the copper film as can be observed in Figure 3j,k. Moreover, the adsorption of TU species on the growing copper nuclei caused an undefined growth that could not be predicted prior to the characterisation of the film by SEM. From a macroscopic point of view, Figure 3c,f,i,l show the improvement in the aesthetic characteristics of the copper film with the increasing amount of thiourea up to 60 ppm. Adding this concentration of thiourea to the copper bath used in this work, the resulting film obtained was homogeneous and bright, confirming the brightening action of TU and its effect on the nucleation and growth of copper. The results from the concentration of 90 ppm were not suitable for the obtainment of a high-quality copper film from the formulation studied in this work.

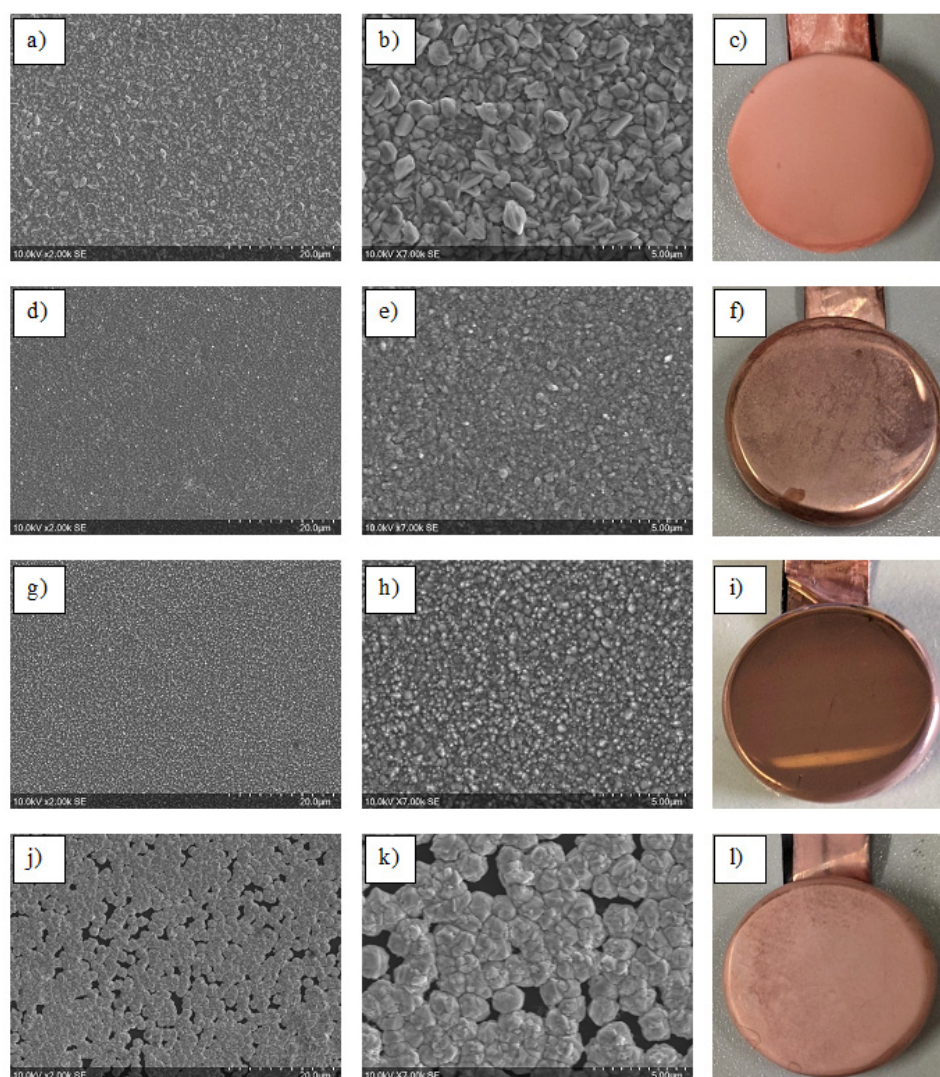


Figure 3. (a,d,g,j) SEM characterisation 2k \times magnification; (b,e,h,k) 7k \times magnification) and (c,f,i,l) sample photographs of the copper film obtained with various amount of TU: 1—0; 2—30; 3—60; 4—90 ppm. Electrodeposition parameters: 600 s, -0.20 V, 25 $^{\circ}$ C.

3.4. Film Thickness Characterisation

The obtained copper films were analysed using XRF spectroscopy to obtain the metal's film thickness. The measurements were conducted in three different spots for each sample.

The reduction of the thickness value with increasing TU concentration (Table 2) confirmed the suppressing behaviour of thiourea on the copper growth, which is the result of its effect on the nucleation mechanism. Compared to the value obtained without the addition of thiourea, the copper film thicknesses obtained adding 30 and 60 ppm were very similar, and also similar were the aspect of the as deposited copper surfaces. The further addition of TU to 90 ppm in the solution caused a drastic reduction in the thickness which confirms our hypothesis on the formation of an electrodeposition-hindering TU-derived organic film based on the morphological analysis of this sample and the voltametric analysis of the deposition solution.

Table 2. XRF analysis of the copper films' thickness obtained from the solutions with 0, 30, 60 and 90 ppm TU by potentiostatic deposition.

TU (ppm)	Cu Thickness (μm)
0	1.58 ± 0.03
30	1.38 ± 0.03
60	1.46 ± 0.06
90	0.98 ± 0.03

3.5. Copper Deposition on Metal Substrate

Finally, we performed some preliminary tests of the studied baths on a metal substrate before the industrial scale-up and the use in a pilot plant. The substrates presented the following composition from the bulk to the top layer: brass(bulk)/Ni ($\sim 20 \mu\text{m}$)/Au ($\sim 0.5 \mu\text{m}$). The depositions were performed with a potential of -0.20 V in the presence of 30, 60 ppm and 90 of TU. Photos and SEM micrographs of the samples are reported in Figure 4. The best grain refinement and macroscopic appearance was again obtained in the presence of 60 ppm of thiourea (Figure 4b).

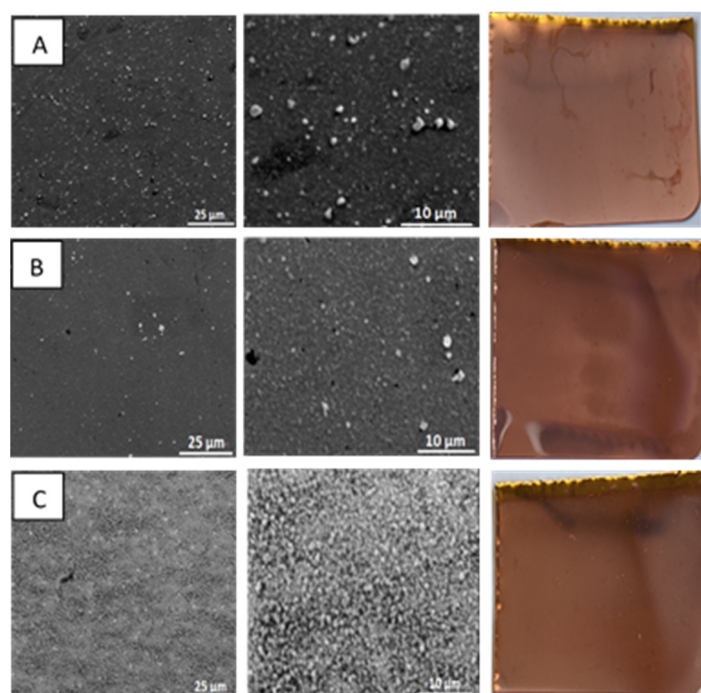


Figure 4. Electrodeposition of copper on brass/Ni ($\sim 20 \mu\text{m}$)/Au ($\sim 0.5 \mu\text{m}$) substrate performed with a deposition potential of -0.20 V vs. Ag/AgCl/ KCl_{sat} in the presence of (A) 30 TU; (B) 60 TU; (C) 90 ppm TU.

4. Conclusions

In this work, we evaluated the optimal deposition potential and TU concentration for a new copper deposition formulation designed as an alternative to alkaline cyanide baths. The action of TU as a brighter agent was confirmed and assigned to the adsorption of the molecule on the electrode's surface, limiting the deposition process. The effect due to the complexing behaviour was discarded due to the low concentration of TU. By means of chronoamperometries, we found that the best potential for the deposition was -0.20 V with a TU concentration of 60 ppm. Higher concentrations of TU worsened the deposition probably by the formation of a film. The current transient did not follow very well the Scharifker–Hills model, as well as other models, but following the path of other authors, we used it as a qualitative tool to drive the deposition to a progressive process. After the electrochemical characterisation, some samples were produced and analysed with SEM for the morphological characterisation. We found a grain refinement of the coating and an improvement of its aesthetic appearance increasing the thiourea amount up to 60 ppm. Morphological analysis also highlighted the formation of a copper film with an uncontrolled growth in the presence of 90 ppm of TU, reasonably due to the adsorption of an excess of TU species on the cathode surface. The increment of adsorbed TU species at the increasing amount of dissolved TU in solution was also confirmed by XRF data, which reported a reduction in copper thickness going from 0 to 90 ppm of TU. Finally the formulation was tested even on a electroplated metal sample to verify that it could be suitable for an industrial application. We found that the developed bath was suitable for decorative applications in the fashion electroplating industry.

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