Tutor/s

Dra. Maria Sarret Pons
Departament de Ciència de Materials i Química Física

Dra. Teresa Andreu Arbella
Departament de Ciència de Materials i Química Física

Grau de Química

Treball Final de Grau

Additive-free electrolytic bath for pulse plated AuCu coatings

Recobriments AuCu obtinguts amb corrent polsant a partir d'un bany electrolític sense additius

Josep Boter Carbonell

June 2022

UNIVERSITAT DE BARCELONA

B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

“Hi ha una força motriu més poderosa que el vapor, l'electricitat i l'energia atòmica: la voluntat.”

Albert Einstein

A les Doctores María Sarret Pons i Teresa Andreu Arbella, pel seu esforç i dedicació durant el seguiment de tot el procés i la disposició en la resolució de qualsevol dubte que em sorgís durant el transcurs del treball, i per haver-me donat l'oportunitat de formar part del seu grup de projectes durant aquest semestre.

També voldria agrair a l'estudiant de doctorat Mohamed Amazian El Moussaoui, per la seva bona disposició en ajudar-me durant el transcurs de tot el treball, ensenyar-me el funcionament de tot el laboratori i endinsar-me en el món dels aliatges que per a mi eren desconeguts. He trobat en ell una persona sempre disposada a discutir i donar punts de vista sobre els resultats obtinguts.

Mencionar també a l'empresa Plating Decor Recubrimientos S.L., que va proporcionar la sal d'or necessària per dur a terme el treball. L'or és molt car i sense la seva aportació no hauria estat possible realitzar tants estudis com s'han fet.

Per acabar m'agradaria agrair a tots els professors i professores que he tingut durant el transcurs de la carrera de química, per transmetre la seva passió per aquesta branca de la ciència i compartir el seu coneixement. Moltes d'aquestes ensenyances les he pogut aplicar en aquest treball.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (ODS)

With the rapid evolution of climate change, world governments have been forced to change their climate change strategies. To this end, the ONU created the Sustainable Development Goals (SDGs), which are a set of goals to achieve a sustainable and equitable society.

The field of chemistry has never been viewed favourably on an environmental level, and chemicals have always been associated with pollution. For this reason, for some years now, chemistry has been moving towards a new goal, sustainable chemistry, a new way of working, following the principles of the SDGs.

The SDGs can be classified into 5 broad areas. The area that is most relevant to this work is **Planet**. If the objective of this work, to obtain an electrolytic bath without additives to produce gold for jewellery, can be achieved, this would be a step towards a more sustainable and therefore more eco-efficient industry.

One of the main SDGs that can be addressed through this work is **Ensure sustainable consumption and production patterns** (Goal 12). One of the targets of this goal is to achieve the environmentally sound management of chemicals and all wastes throughout their life cycle, in accordance with agreed international frameworks, and to significantly reduce their release to air, water and land to minimise their adverse effects on human health and the environment. In the course of this work, research is being carried out on how to reduce or eliminate additives, highly polluting organic compounds. If they can be eliminated from industrial processes, this would allow the useful life of cyanide electrolytic baths to be extended and therefore reduce the waste they generate.

CONTENTS

1. SUMMARY

The appearance and properties of gold have made it a very valuable metal since ancient times. It is used in catalysis and electronics, but its most common use is in jewellery. In this field it presents a problem of durability because it is a very soft material that wears out easily. To solve this problem, alloys are mixed with other metals that improve its mechanical and optical properties. This work is based on obtaining a gold-copper alloy of 18 karats (kts) (75% gold).

The gold that is used in jewellery is produced using an electrodeposition technique. Most of the commercial electrodeposition baths are based on cyanide salts, a toxic compound that is harmful to people and the environment. To ensure the correct deposition of all the components of the alloy and to ensure its composition and brilliance, different additives are used, many of which are pollutants when reacting causing a shortening of bath lifetime.

To obtain a bright 18 kts coatings without compromising the stability of the bath, the objective of this work is the optimization of an electrodeposition technique that allows to obtain coatings from electrolytic baths without additives. The pulsed direct current technique is used, which consists of the application of current poles alternated with rest periods, allowing an orderly growth of the deposit. To determine the most suitable parameters of this technique, a pre-pulsating study has been carried out with direct current, including the speciation of the electrolyte. The pre-pulsed studies have allowed to establish which copper complex is more favorable to electrodeposition, which is $[Cu(CN)_3]^{2}$, and the most favorable conditions to carry out the pulsed direct current study have been determined: $[Cu^{+}]$ = 6.86 g/L, $[Au^{+}]$ = 5.00 g/L, $[CN^{-}]$ = 0.40 M, w = 100 rpm, T = 70ºC and j = 2.5 – 5 A/dm^2.

In this work it has been possible to demonstrate that the pulsed direct current technique is effective and allows to obtain gold-copper bright coatings of 18 kts without additives in the bath.

Keywords: gold, copper, alloy, 18 kts, electrodeposition, continuous current, pulsed direct current, additives, jewellery.

2. RESUM

L'aparença i propietats de l'or han fet que des de l'antiguitat es consideri un metall molt valuós. S'utilitza en catàlisi o electrònica, però el seu ús més estès es la joieria. En aquest camp presenta un problema de duresa perquè és un material molt tou que es desgasta amb facilitat. Per solucionar-ho, es fan aliatges amb altres metalls que millorin les seves propietats mecàniques i òptiques. Aquest treball es basa en l'obtenció de un aliatge d'or i coure de 18 quirats (75% d'or).

L'or que es fa servir en joieria es produeix mitjançant una tècnica d'electrodeposició. La major part dels banys comercials estan formats per sals de cianur, un compost tòxic i perjudicial per les persones i pel medi ambient. Per assegurar una deposició correcta de tots els components de l'aliatge i assegurar-ne la composició i la brillantor, s'utilitzen diferents additius, molts dels quals són contaminants i que al reaccionar provoquen un escurçament de la vida útil del bany.

L'obtenció de depòsits brillants i de 18 kts sense comprometre la vida útil del bany és l'objectiu de les empreses dedicades a la joieria. L'objectiu d'aquest treball és l'optimització d'una tècnica d'electrodeposició que permeti obtenir recobriments a partir de banys electrolítics que no continguin additius. S'utilitza la tècnica de corrent polsant que consisteix en l'aplicació de polsos de corrent seguits de temps de repòs, permetent un creixement ordenat del recobriment. Per tal de determinar els paràmetres més adequats per a aquesta tècnica, s'ha fet un estudi previ en corrent continu que inclou l'especiació de l'electròlit. Els estudis pre-polsant han permès establir quin complex del coure és més favorable a l'electrodeposició, el $[Cu(CN)_3]^{2-}$ i s'han determinat les condicions més favorables per realitzar l'estudi de corrent polsant: $[Cu^+]$ = 6.86 g/L, $[Au^+]$ = 5.00 g/L, $[CN^-]$ = 0.40 M, w = 100 rpm, T = 70ºC i j = 2.5 – 5 A/dm^2.

En aquest treball s'ha pogut demostrar que la tècnica de corrent polsant és efectiva i permet l'obtenció de recobriments d'or-coure de 18 quirats brillants sense la necessitat d'utilitzar additius al bany.

Paraules clau: or, coure, aliatge, 18 kts, electrodeposició, corrent continu, corrent polsant, additius, joieria.

3. INTRODUCTION

3.1. THE GALVANIC ELECTRODEPOSITION.

Electrodeposition is a technique widely used to fabricate metallic coatings, due to its low economic cost compared to the other techniques known up to now. This technique consists of using electrical current to deposit the metals on one of the electrodes from a solution of metal ions, either aqueous, organic or a fused salt. The solution may also contain other ions, electrolytes, which do not react, and allow a greater transport of charge through the solution. During the process, a controlled constant current density or potential is applied.

To carry out electrodeposition, at least a two-electrode system is needed (Fig. 3.1.): The working electrode, which acts as a cathode, is composed of a metallic substrate on which dissolved metals are reduced. And the auxiliary electrode, which allows the circuit to be closed, and acts as an anode. Sometimes a reference electrode can be used to monitor the cathode potential.

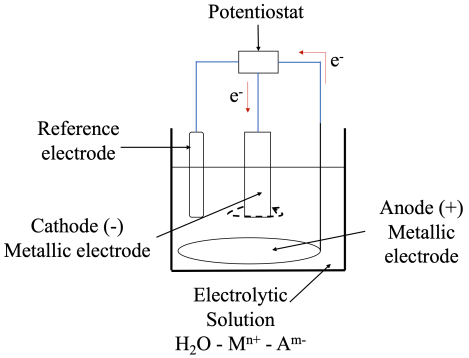

Fig. 3.1. Schematic diagram of a 3-electrode electrochemical cell.

An important factor to consider when electroplating is performed are the properties of the coating. Depending on these, it can be used for different purposes. These properties depend mainly on the structure of the deposit. If a smooth and uniform surface is obtained, the deposit

will show different properties than if a porous and non-uniform surface is obtained. The structure of the deposit will depend on the growth mechanism. There are two general types of growth:

- Layered growth (Fig.3.2.a. and Fig.3.2.b.), where the deposit grows from the formation of discrete layers. Each growth layer will be the structural components of the deposit formed. [1], [2]
- Nucleation growth, (Fig. 3.2.c.) consists of the growth of deposits forming three-dimensional crystals, also known as clusters.[1], [2]

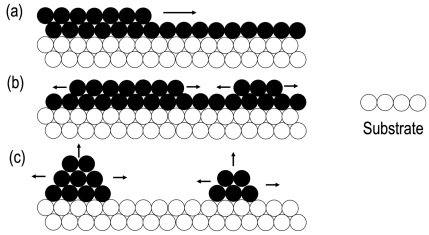

Fig.3.2 Schematic picture of deposit growth mechanisms [2].

In some sectors, such as decoration and jewellery, one of the most important properties is that of appearance. Mostly, the aim is to obtain shiny coatings, for this, it is necessary to obtain smooth surfaces, so that they completely reflect the incident light. To achieve this type of surface, they are preferably obtained from layered growth or small and regular clusters. On the other hand, when growth by nucleation predominates, irregular surfaces are obtained, which scatter the light, obtaining non-shiny deposits. Figure 3.3. shows a diagram of light reflection as a function of the sample surface. [1]

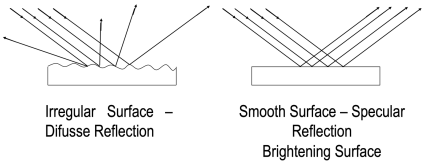

Fig.3.3 Scheme of light reflection as a function of surface shape [2]

When the electrodeposition is carried out, there are some variables that affect the growth mechanism and therefore the structure of the coating.

- **The Electrolytic Bath:** This is the solution containing the metal ions required for the electrodeposition reaction to take place. It also contains other compounds that help

the reaction, such as electrolytic salts, which do not react but increase the transport of charge through ionic conductivity of the solution. Depending on the components and their concentration in the electrolytic bath, the composition and structure of the deposit may vary.

In addition, these baths often contain additives, which are organic compounds at very low concentrations that allow to control the composition and the growth mechanism of the coatings. Different additives can be found classified according to their function:

- Levelling agents, that are absorbed onto the electrode surface, modifying the growth mechanism, and allowing a more orderly growth, and therefore a brighter deposit.
- Surfactants, which favour the hydrogen bubbles, that may form during the electrolysis reaction, to escape and not to adhere to the electrode surface.
- Complexing agents, which form complexes with the metal ions in solution, decreasing the ligand-free cations concentration and, therefore, causing a change in the composition of the deposit obtained.
- pH stabilizers, which allow to control the pH of the electrolyte solution and prevent its variation during the reaction.

Many of the additives used are toxic to the environment, making their subsequent disposal treatment expensive and complex. In addition, they can often react electrochemically, oxidizing or reducing, obtaining compounds that are non-convenient for the bath stability. They are also very difficult to analyse, and their composition is often unknown, since their use is not controlled, and the amount added is controlled from trial-and-error experiments. [1], [3], [4]

Therefore, the main objective of this work is to obtain a bath, which allows to obtain deposits of the desired composition and appearance, without the need to use additives.

- **Current density (j):** The applied current density controls the rate of metal deposition. The higher the current density, the faster the reaction, while the lower the current density, the slower the reaction. The speed of deposition affects the growth mechanism of the deposit, the higher the speed, the more disordered the electrodeposition and therefore the growth by nucleation is favoured, whereas at lower speeds, the growth is ordered and therefore the growth by layers is favoured.

- **Mass Transport:** As the electrical current is applied to the system, the ionic metal molecules move towards the electrode. This movement of the ions is called mass transport. Once at the electrode, these react to form the metal (0). As the reaction proceeds, the number of molecules around the electrode decreases, therefore, a diffusion layer is created between the electrode and the solution. As the diffusion layer increases, it causes the reaction process to become more difficult. As the current density increases, the diffusion layer is caused to grow faster, and the larger ions are deposited in smaller quantities. To control the effect of the diffusion layer, the process must be kept under stirring to keep the diffusion layer constant, and then, mass transport becomes controlled by convection. [2], [5]
- **The substrate:** To achieve a good and durable coating, it is necessary to use substrates that have a good adhesion to the coating metals. For a coating to adhere to the substrate surface and perform its function, its adhesion to the substrate must tolerate mechanical stresses and elastoplastic distortions, thermal stress and displacement from the environment or process fluid. Adhesion depends on a few attributes at the substrate surface, such as its atomic bond structure, elastic moduli and stress state, thickness, purity, and fracture toughness. Furthermore, depending on the substrate and shape used in the electroplating process, a different levelling of the deposit will be obtained, thus varying its mechanical and optical properties. [5]

The electrodeposition technique is widely used to produce coatings, since it allows the production of both functional and decorative, like jewellery, deposits at a low cost.

3.2. GOLD AND ITS ALLOYS.

One of the most used metals in electroplating is gold, especially in decorative coatings, due to its aesthetic properties and its electrical and anticorrosive properties. Its discovery it has been considered one of the most valuable metals and its possession marked people's wealth. Approximately 86 % of the gold produced is used in the jewellery industry, but other uses can also be found, for example in the manufacture of electronic equipment, especially in the manufacture of microprocessors, in oral implants and in coinage, among others. [1], [6], [7]

Gold has great properties, both chemical and physical. It is a good conductor of heat and electricity, and also one of the most ductile and malleable metal that exists. However, pure gold

is very soft, and therefore its use is not recommended because it breaks or wears out very easily. [2], [8]

It is one of the noblest metals known, so it is one of the least reactive metallic elements in its fundamental state. However, gold can form very stable alloys with many other metals. Thanks to its capability of forming alloys, it is possible to vary its properties and therefore obtain harder and more durable gold pieces. The noble metal alloys, such as gold, silver, etc., are classified using karats (kts) system:

Alloys between 12 (50% of noble metal) and 18 (75% of noble metal) kts are considered low-grade alloys used as components in electrical circuits or as catalysts. On the other hand, 18 to 24 (100% of noble metal) karat alloys are considered high grade, mostly used in decorative applications.[8]

The most used metal to alloy with gold is copper (Cu), as it makes it harder. But, can also be found alloys with iron (Fe), nickel (Ni), cobalt (Co), ruthenium (Ru) or silver (Ag) among others. Depending on the alloy, gold pieces can be manufactured with different properties and colours, for example white, pink, blue or even black. [6]

In the decorative industry, one of the most used alloys to make yellow gold, the most common gold, is the alloys of 18 karat gold with copper and other metals to tune its properties.

To proceed with the electrodeposition of gold, three different electrolytic baths can be used: acid, neutral or alkaline. It has been found that the bath that requires the least maintenance and has the longest life duration is the alkaline bath, that is composed of cyanide salts. [6] Cyanide is one of the most toxic compounds for both humans and the environment. The legislation to control the use of this compound is very restrictive. At the industrial level, its use has been decreasing as substitutes have been found that fulfil its function. In the field of gold electroplating, no substitute has yet been found that gives the stability that cyanide gives to the bath and, therefore, it is still widely used.

In this study, we will focus on an 18 kt Cu and Au alloy which apart from having decorative uses, is also of environmental interest, as it can be used in catalysis for the decomposition of some pollutants, like carbon monoxide [9].

To obtain AuCu alloy, the salts of each metal with the cyanide are required. In the case of gold, the salt used for the preparation of the bath is the dicyanoaurate ion ($[Au(CN)_2]^-$). In the copper case, Cu^+ and CN^- can form an equilibrium between four different species and,

depending on Cu/CN ratio, the relative percentage of each complex varies. The compounds that can be formed are: CuCN, $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[Cu(CN)_4]^{3-}$. This implies a problem for the electrolytical system, depending on each of the complexes that can be formed, have a different stability and therefore a different electrochemical behaviour, and that fact may affect the composition of the alloy formed during the electrodeposition process. [10]

The reactions that occur during the electrodeposition [1] of the gold and copper alloy are as follows:

- Cathode (-): Reduction Reaction

$$[Au(CN)_2]^- + 1e^- \rightarrow Au + 2\ CN^- \quad \text{(eq.3.5.)}$$

$$[Cu(CN)_3]^{2-} + 1\ e^- \rightarrow Cu + 3\ CN^- \quad \text{(eq.3.6.)}$$

$$2\ H^+ + 2\ e^- \rightarrow 2\ H_2 \quad \text{(eq.3.7.)}$$

- Anode (+): Oxidation Reaction

$$2\ H_2O \rightarrow 4\ H^+ + O_2 + 4\ e^- \quad \text{(eq. 3.8.)}$$

- Global Reaction:

$$[Au(CN)_2]^- + [Cu(CN)_3]^{2-} + 2\ H_2O \rightarrow Au + Cu + 2H_2 + O_2 + 2H^+ + 5\ CN^- \quad \text{(eq. 3.9.)}$$

To obtain this alloy without the need to use additives that control the composition and surface of the coating, the pulsed DC electrodeposition technique is used.

3.3. PULSED DC ELECTRODEPOSITION.

Unlike the direct current technique, which is the most frequently used technique based on applying a constant current during the whole working period, pulsed DC electrodeposition is based on the rapid alternation of the application of different current density values. This results in electroplating based on cycles of the same amplitude, duration, and polarity. [1], [11]

The use of this technique allows a growth of small and ordered nuclei, so obtaining a levelled deposit, and therefore bright coatings.

Figure 3.4. illustrates the most common DC pulses employed. Each of these cycles is composed of:

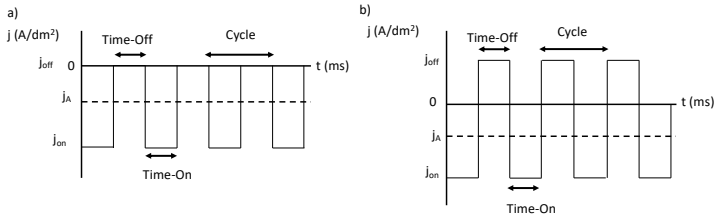

Fig. 3.4. Schematic diagram of the current density applied in the pulsed DC current technique.

- **Time-on (t_{on}):** during which a negative current density is applied (**j_{on}**) to reduce the metals in solution. [5]
- **Time-off (t_{off}):** during which a zero current density is applied (**j_{off}**), that allows the displacement of the metal ions towards the electrode, recomposing the diffusion layer (Fig. 3.4.a.) or a positive current is applied, allowing the redissolution of the deposited metals (Fig. 3.4.b.). [5]

Thus, the **duty cycle (θ)**, is the total time-on applied in each of the cycles and is calculated by equation 3.10. [5], [11], [12]

$$\theta = \frac{t_{on}}{t_{off}+t_{on}} \qquad \text{(eq. 3.10.)}$$

From which the **average current density (j_a)** can be calculated form equation 3.11. This current density would be equivalent to the current density applied in the direct current deposition technique.

$$j_a = \theta \cdot j_{on} + (1-\theta) \cdot j_{off} \qquad \text{(eq. 3.11)}$$

The control of this technique is difficult, because many variables must be controlled, such as the concentration of each of the metals in the bath, the duty cycle, the applied current density, the total charge of the system, etc. For this, a pre-pulsing study at constant DC will be carried out, which will allow us to observe the effect of each parameter on the composition of the deposit to propose the initial selection of pulsed deposition parameters.

After carrying out the study, it is hoped to obtain an optimization of the procedure, which will make it possible to obtain a brilliant coating of the desired composition. In addition, the concentrations of each of the compounds in the solution will be optimized and the amount of cyanide used will be reduced.

4. OBJECTIVES

The main objective of this work is to investigate an electrolytic process which allows the production of 18 kts gold-copper deposits using an additive-free electrolyte, without losing the appearance properties required in jewellery.

To achieve the general objective, the specific objectives are:

- Obtain a speciation analysis of the metal salts in solution to establish the most favourable conditions for the study.
- To carry out a basic electrochemical study to verify the behaviour of the metal species in solution when a constant current is applied. This study must allow to verify the working conditions established by the speciation analysis and to establish the most suitable working conditions.
- Check the effects of the parameters set out in the pulsed current technique on the composition and appearance of the alloys.

5. MATERIALS AND METHODS

5.1. REAGENTS AND MATERIALS.

All the experiments were carried out on different electrolytic baths containing gold and copper cyanide salts. The reagents used in these baths are shown in Table 5.1.

Table 5.1. Information of the reagents used in this study.

Chemical Name	Chemical Formula	Manufacturer	Quality
Copper (I) cyanide	CuCN	Sigma-Aldrich	p.a.
Potassium dicyanoaurate	$K[Au(CN)_2]$	Retrieved by Plating Decor Recubrimientos S.L.	Pure
Potassium cyanide	KCN	Sigma-Aldrich	p.a.

5.2. SPECIES SIMULATION.

To establish the concentration of CN- and Cu+ more favourable to accomplish this work, a simulation of the equilibrium complexes of copper and cyanide, which can be formed at 75ºC, was carried out. For this purpose, the *Spana software*® and its database were used. The concentrations of Cu^+ and CN^- have been determined based on a speciation study.

5.3. CYCLIC VOLTAMMETRY STUDY.

A cyclic voltammetry study was carried out on three solutions at 70 ºC. From each solution, different analyses were performed by varying the concentration of cyanide ions remaining in the solution. Table 5.2. shows the information for each of the solutions.

Table 5.2. Experimental conditions used for the voltammetric study.

nº of solution	$[M^+]$ (g/L)	$[CN^-]$ (g/L)	V_{add} (µL) ($[CN^-]$ (M))
1	$[Cu^+]$ = 3.55	3.43 – 8.55	200 (3.07)
2	$[Au^+]$ = 5.00	4.50 – 39.03	500 (14.50)
3	$[Cu^+]$ = 3.55 $[Au^+]$ = 5.00	4.50 – 29.40	200 (14.50)

Most voltammetries were executed with the following parameters fixed:

- Scan Rate: 50 mV/s
- Electrode rotational speed: 100 rpm
- Working Electrode: Platinum
- Counter Electrode: Platinized Niobium Oxide
- Reference Electrode: Saturated Calomel Electrode (SCE)

The anodic and cathodic limits were varied according to the analysis performed, which will allow us to find the oxidation and reduction peaks in each case. However, most of the cases were made between -2.0 and 2.0 V.

5.4. DEPOSITION STUDY.

The working electrode used in the deposition study was a 1 cm diameter circular iron electrode. Iron is a metal that oxidizes easily, and therefore, it was protected by a film of zinc. Before using it as an electrode, it was treated with a solution of hydrochloric acid (1:1) to oxidize the zinc and remove it from the iron surface.

In addition, before any electrodeposition, the surface had to be cleaned of impurities. For this purpose, the electrode was submerged in a cathodic degreasing solution and a current of 1 A/dm^2 was passed through it for one minute. It was then rinsed with water and placed in an acidic solution. Finally, before being introduced into the working bath, it was rinsed again with water.

Once the electrode surface has been treated, an electrochemical system is assembled, as shown in Figure 5.1. The devices used are as follows:

- Thermostat – PolyScience
- Rotor – Tacussel CTV01T.
- Potentiostat - Princeton Applied Research VMP2

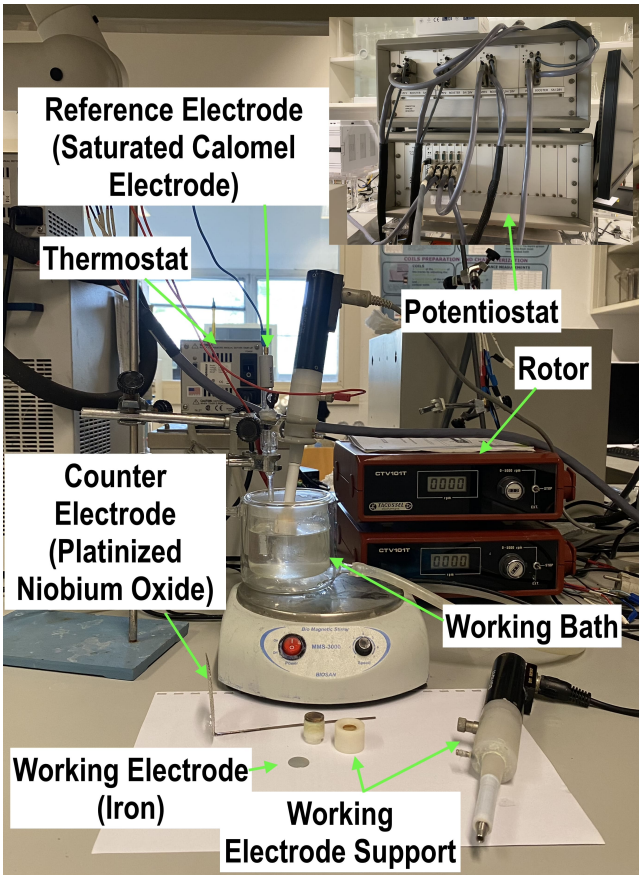

Fig. 5.1. Set-up used during the study.

A test of the working conditions was performed prior to carrying out the pulsed plating study. Table 5.3. shows the experimental conditions used in the DC electrodeposition study.

Each of the experiments were carried out while maintaining the concentration of gold in the solution at 5 g/L and varying the current density.

Table 5.3. Experimental conditions of constant DC parameter control.

	[CN^-] (M)	[Cu^+] (g/L)	w (rpm)	T (ºC)
Experiment 1	0.485	10	100	70
	0.523			
	0.615			
Experiment 2	0.4	6.67	100	70
		6.86		
		7.35		
Experiment 3	0.4	7.12	0	70
			50	
			100	
			250	
	2.90	55	0	
			50	
			100	
Experiment 4	0.4	6.86	10	22
				50
				70

Once the DC electrodeposition study had been completed, the pulsed current study was carried out. To this end, the following conditions are laid down:

- [Cu^+] = 6.86 g/L
- [Au^+] = 5.00 g/L
- [CN^-] = 0.40 M
- w: 100 rpm
- Temperature: 70ºC

This study was carried out by applying a constant DC pulse. The pulses varied according to the duty cycle applied. In this case, the charge applied for each electrodeposit was 2.83 C. This

pulsed current study was achieved by analysing the effect of keeping the working current density (j_{on}) constant, and the effect of keeping the average current density (j_a) constant. In all pulsed current experiments, the duty cycle variance was 10 to 90% in 20% intervals. The duration of each cycle was one second.

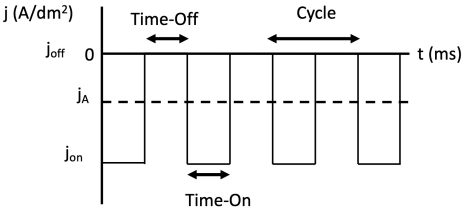

Fig. 5.2. Current diagram applied in the pulsed current study.

5.5. CHARACTERIZATION.

To obtain the composition of each deposit, the X-ray Fluorescence Analysis technique was used, using an X-ray Fluorescence spectrometer (Fischerscope XRAY-XDV). Subsequently, some deposits were analysed with the Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) (Quanta 2000) of the *Centres Científics i Tecnològics de la Universitat de Barcelona* (CCiT-UB) Diagonal.

By using SEM-EDS, microscopic scale images have been obtained of the surface of the deposits.

6. RESULTS AND DISCUSSIONS

6.1. SPECIES SIMULATION.

Copper and cyanide can form different complexes. Depending on which complex is present in solution, it will be electrochemically reactive. The complexes formed are as follows:

- $Cu^+ + CN^- \rightarrow CuCN$[3] log (β) = 15.80 ± 0.15 [3] (eq. 6.1.)
- $CuCN + CN^- \rightarrow [Cu(CN)_2]^-$[3] log ($\beta$) = 23.95 ± 0.01[3] (eq. 6.2.)
- $[Cu(CN)_2]^- + CN^- \rightarrow [Cu(CN)_3]^{2-}$[3] log (β) = 29.33 ± 0.04[3] [4] (eq. 6.3.)
- $[Cu(CN)_3]^{2-} + CN^- \rightarrow [Cu(CN)_4]^{3-}$[3] log (β) = 31.89 ± 0.02[3] [4] (eq. 6.4.)

The CuCN complex is not soluble in water, and the $[Cu(CN)_2]^-$ complex is practically not stable at working temperature (70ºC) and is therefore not found. These two complexes are not of interest for this work, because their condition cannot be considered to react.

As for complexes $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$, in order to compare which complex is more electrochemically reactive, the stability constants of the complexes have to be compared. As can be seen in eq. 6.3. and 6.4., the stability constant of complex $[Cu(CN)_4]^{3-}$ is higher than that of complex $[Cu(CN)_3]^{2-}$. This suggests that complex $[Cu(CN)_3]^{2-}$ will be more reactive and therefore easier to reduce.

The results obtained from the software allow to establish the concentration of each ion in each complex.

First, a simulation of the effect of varying the cyanide in the solution was done when the copper concentration (10.00 g/L) was kept constant. The parameters pH (10.5) and temperature (75ºC) were also previously set, as they were like the working conditions used in this study. The program only allowed certain temperatures to be set. It was decided to study the equilibrium at 75ºC because it was the closest temperature to the working temperature we used (70ºC).

Figure 6.1.a. shows the graph obtained from the simulation with varying cyanide concentrations. The ideal concentration of cyanides to carry out the study is between 0.25 M and 0.85 M, because in this range the $[Cu(CN)_3]^{2-}$ complex predominates and therefore copper will be more prone to reduce.

Then, a speciation simulation was performed by varying the copper (I) concentration, keeping the cyanide concentration (0.4 M) constant. The pH (10.5) and temperature (75 ºC) parameters were also set, as in the previous simulation.

Figure 6.1.b. shows the speciation diagram when the concentration of copper ions was varied. The ideal concentration to carry out the study is between 0.02 M and 0.2 M (1.27 and 12.71 g/L), because of the complex $[Cu(CN)_3]^{2-}$ as the previous speciation.

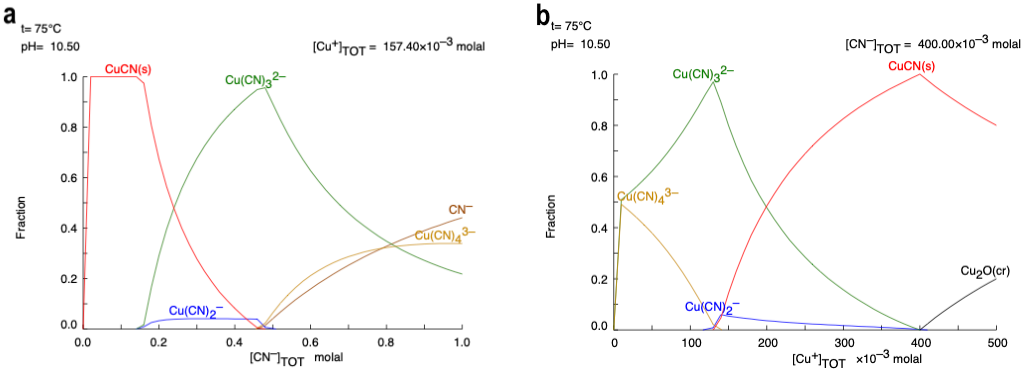

Fig. 6.1. Speciation diagram obtained with Spana software®. a) Variation of cyanide concentration. b)Variation of copper concentration.

6.2. Cyclic Voltammetry Study.

To demonstrate which copper-cyanide complex was the most suitable for the study, a cyclic voltammetry study was performed on three different solutions, prepared from the cyanide salts of the individual metals. The cyanide concentration of each solution is varied by adding two KCN stock solutions. This study was performed at a temperature of 70 ºC, applying an electrode rotation speed of 100 rpm and a scan rate of 50 mV/s.

The first solution was composed of copper(I) and cyanides. The concentration of Cu^+ was 3.55 g/L and the initial concentration of CN^- was 3.43 g/L. The concentration of CN^- was increased to 8.55 g/L, from additions of 200 µL of a 3.07 M KCN solution. Figure 6.2. shows some representative voltammetries that have been obtained from this solution.

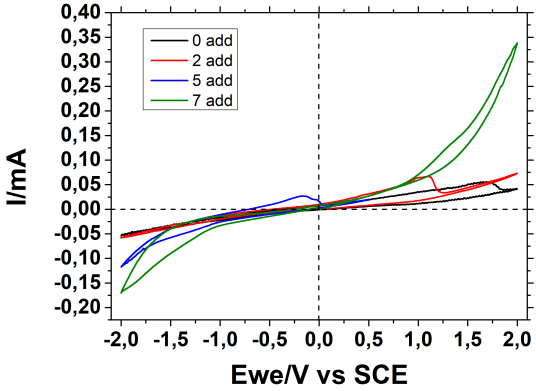

Fig. 6.2. Representative voltammetries obtained for [Cu^{+}] = 3,55 g/L and different cyanide concentrations.

It can be observed that as cyanide ions are added to the solution, the oxidation peak shifts towards more negative potentials. This indicates that more copper is reduced in the outward scan and is therefore easier to oxidise in the return scan. After the 5th addition of cyanide, the oxidation peak starts to shift towards more positive potentials, and the cathodic limit must be increased to -3.0 V. This indicates that the complex in solution is poorly reactive. When compared with the results obtained in section 6.1, at this point the major compound is $[Cu(CN)_4]^{3-}$.

The second solution was composed of gold (I) and cyanide ions. The Au+ concentration was 5.00 g/L, and the initial cyanide concentration was 4.50 g/L. The cyanide concentration was increased to 39.03 g/L, from additions of 500 µL from a 14.50 M KCN solution.

Figure 6.3. shows some of the voltammetries that have been performed on this solution. No oxidation peak is obtained due to the stability of gold (0). As it is one of the most noble metals, it is very stable in the ground state, and therefore does not oxidise easily in this range of potential.

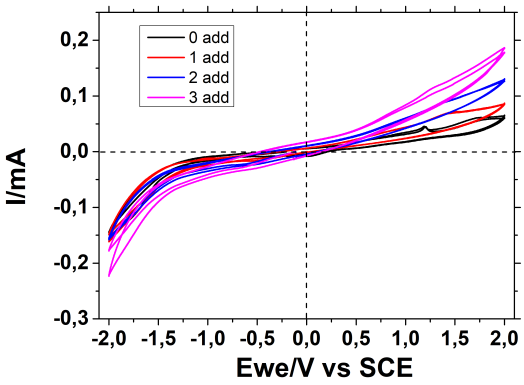

Fig. 6.3. Representative voltammetries obtained for [Au⁺] = 5,0 g/L and different cyanide concentration.

The third solution was composed of Cu^{+}, Au^{+} and CN^{-}. The concentrations of the ions were 3.55 g/L, 5.00 g/L and 4.50 g/L respectively. The cyanide concentration was increased to 29.40 g/L, from additions of 200 µL from a 14.50 M KCN solution.

Figure 6.4. shows some cyclic voltammograms that were performed. In them, the same trend can be observed as in the results obtained from solution one (Fig. 6.2.). This time, no oxidation peak is obtained at negative potentials. This could indicate that the presence of gold hinders the reduction of copper, and therefore, its oxidation.

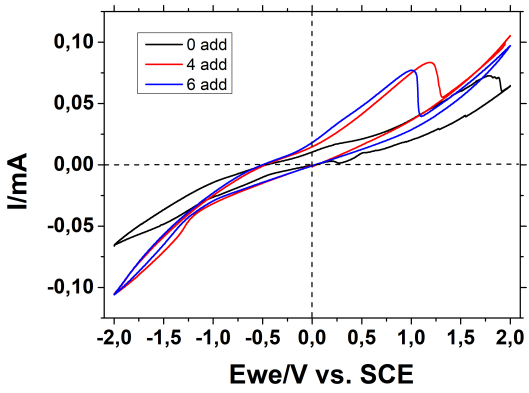

Fig. 6.4. Representative voltammetries obtained for [Cu⁺] = 3,55 g/L, [Au⁺] = 5,0 g/L and different CN^{-} concentration.

6.3. Deposition Study.

The pulsed current electrodeposition is a less studied technique; to understand all the factors that affect its operation, and therefore the result obtained, a direct current study was carried out to understand the effect of the following parameters on the electrodeposition result:

- The concentration of cyanide ions in solution.
- The concentration of copper (I) in solution.
- The rotation speed of the working electrode.
- The working temperature.
- The current density

The concentration of gold was kept constant at 5 g/L during the whole electrodeposition study, because it is the common industrial concentration.

6.3.1. Study of the variation in cyanide ion concentration.

From the results obtained in section 6.1, more specifically from diagram 6.1.a, it was possible to establish which were the most suitable concentrations for carrying out the experiment. Table 6.1. shows the concentrations of cyanide ions used during this experiment, with the relative amount of the complex $[Cu(CN)_3]^{2-}$.

Table 6.1. Cyanide concentrations used in this study and the relative percentage of complex $[Cu(CN)_3]^{2-}$ at each concentration.

Nº of Bath	$[CN^-]$ (M)	$\%_r$ $[Cu(CN)_3]^{2-}$
1	0.48	95.7
2	0.52	84.4
3	0.61	60.7

These concentrations were chosen because the predominant complex in all these cases is the $[Cu(CN)_3]^{2-}$ complex (Fig. 6.1.a.).

As can be seen in the results shown in Figure 6.5., the higher the current density, the higher the percentage of copper in the coating. As the current density increases, the rate of electron transfer reaction increases, and therefore, the ions in the diffusion layer are consumed more rapidly.

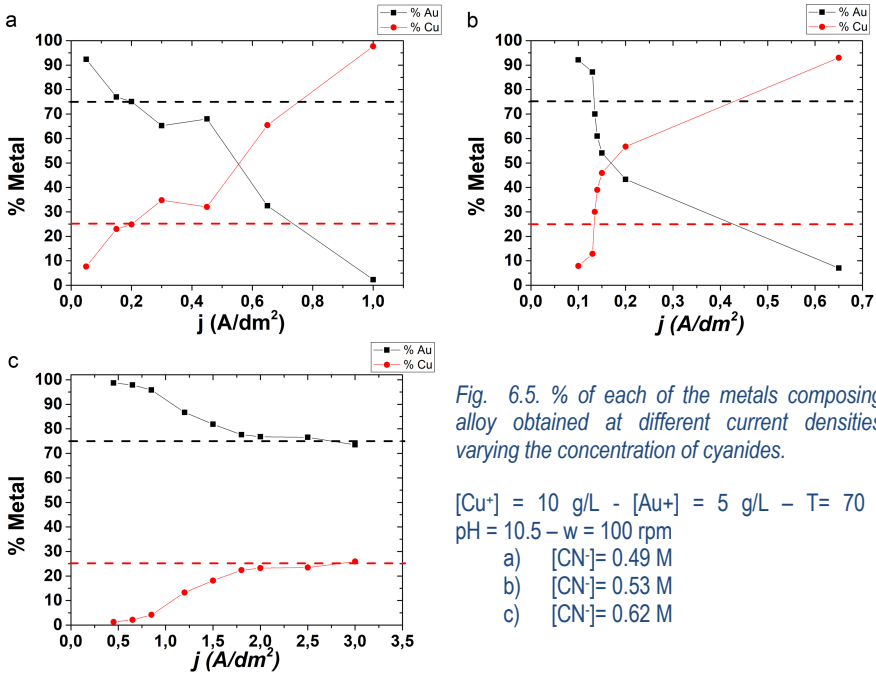

Fig. 6.5. % of each of the metals composing the alloy obtained at different current densities by varying the concentration of cyanides.

[Cu^+] = 10 g/L - [Au+] = 5 g/L – T= 70 ºC - pH = 10.5 – w = 100 rpm

a) [CN^-]= 0.49 M
b) [CN^-]= 0.53 M
c) [CN^-]= 0.62 M

It can also be seen that the higher the relative percentage of complex $[Cu(CN)_3]^{2-}$, the lower the current density required to obtain the 18 kts alloy. In Figure 6.5.a., where the cyanide concentration corresponded to the one with the highest relative percentage of $[Cu(CN)_3]^{2-}$, this current density is 0.20 A/dm^2, whereas in Figure 6.5.c., where the relative percentage of complex $[Cu(CN)_3]^{2-}$ is much lower, a current density of 2.0 A/dm^2 was obtained. However, in this case, a wide range of current densities can be observed (j > 2.0 A/dm^2) where the 18 kts alloy is always obtained.

In the case of Figure 6.5.b., the 18 kts alloy was not obtained, because with a very small interval of current densities the composition of the deposit varied greatly.

Figure 6.6. shows a comparison of two deposits with the same composition. The deposit shown in Figure 6.5.a. was obtained at a very low current density, 0.15 A/dm^2, so the growth mechanism obtained in this case was layered, resulting in a bright sample. In contrast, the deposit shown in Figure 6.5.b. was obtained at a much higher current density, 2.5 A/dm^2, which resulted in a faster growth, predominantly nucleation growth, resulting in a dull sample.

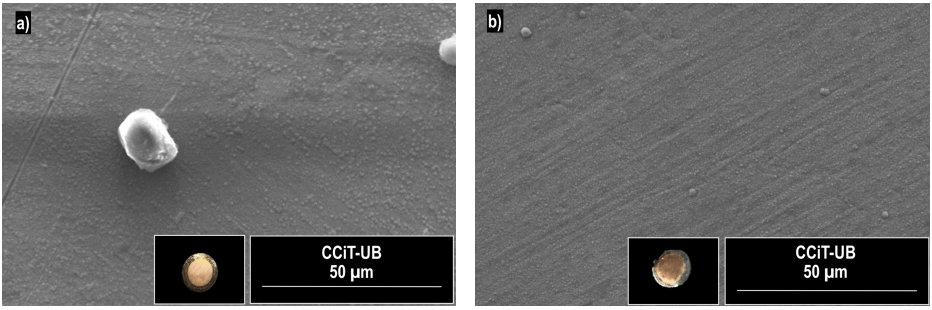

Fig. 6.6. Comparison of macroscopic and microscopic images of two deposits with approximate the same composition (75% Au – 25 % Cu) .

a) [CN-]= 0.485 M - j = 0.15 A/dm^2 b) [CN-]= 0.615 M – j = *2.5 A/dm^2*

Although the interest of this work is to obtain shiny 18 kts gold deposit, working at such low current densities, the deposition time is likely to be very high. Therefore, working at such low current densities cannot be considered a viable option.

6.3.2. Study of the variation in copper (I) ion concentration.

In this study, the copper concentration was varied, keeping the concentration of cyanide and gold ions in the bath constant. To establish the working concentrations, the results obtained in Figure 6.1.b. were used. The established working concentrations were as shown in Table 6.2.

Table 6.2. Copper concentrations used in this study and the relative percentage of complex $[Cu(CN)_3]^{2-}$ at each concentration.

Nº of Bath	$[Cu^+]$ (g/L)	$\%_r$ $[Cu(CN)_3]^{2-}$
1	6.67	84.8
2	6.68	86.1
3	7.37	91.2

Figure 6.7. shows the results of this study. As in section 6.3.1., there is a tendency for the copper composition of the deposit to increase as the current density increases. In addition, it is also observed that the higher the relative percentage of $[Cu(CN)_3]^{2-}$, the lower the current density required to obtain the 18 kts.

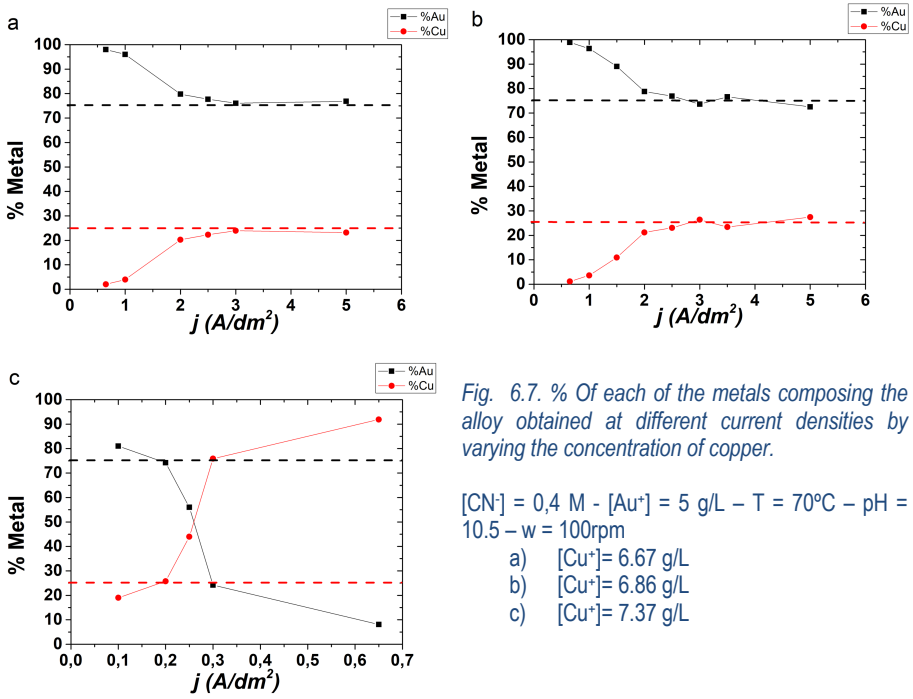

Fig. 6.7. % Of each of the metals composing the alloy obtained at different current densities by varying the concentration of copper.

$[CN^-]$ = 0,4 M - $[Au^+]$ = 5 g/L – T = 70ºC – pH = 10.5 – w = 100rpm

a) $[Cu^+]$= 6.67 g/L
b) $[Cu^+]$= 6.86 g/L
c) $[Cu^+]$= 7.37 g/L

As can be seen in Figures 6.6.a. and 6.6.b., which are the representation of the results obtained at lower copper concentrations (lower relative percentage of $[Cu(CN)_3]^{2-}$) a wide range is obtained at high current densities, from 2 to 5 A/dm^2, where the desired alloy is obtained. This will allow to work with a wide range of applied intensities when applying pulsed current.

When operating at a current density of 0.65 A/dm^2 and a copper concentration of 7.37 g/L, a deposit with a gold spiral in the middle is obtained due to the rotation. So, it was decided to carry out a study of the effect of this on the composition and shape of the deposit.

When the concentration of copper in the solution is reduced, the concentration of cyanides is also indirectly reduced, as less cyanides are needed to complex the copper and obtain the complex of interest.

Another problem resulting from the reduction of the copper (I) concentration is that the aging of the bath (100 mL) was very fast, thus obtaining results that did not match the expected results.

An SEM-EDS analysis of some of the alloy obtained was also carried out and the results are shown in Figure 6.8. in comparison with the macroscopic images.

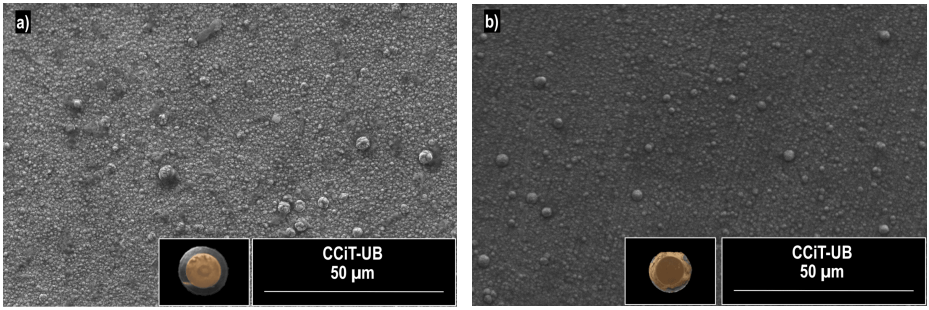

Fig. 6.8. Comparison of macroscopic and microscopic images of two deposits with approximate the same composition (75% Au – 25 % Cu).

a) [Cu^+]= 6.67 g/L - j = 2.5 A/dm² b) [Cu^+]= 6.86 g/L – j = 3.5 *A/dm²*

The deposits shown in Figure 6.8. are both 18 kts coatings. Although they have the desired composition for the study, their appearance is not of interest, because neither of them is bright. Both were obtained at high current densities, 2.5 and 3.5 A/dm² respectively, which results in rapid and disordered deposit growth, creating an irregular surface, and therefore do not reflect light.

But, at the same time, it could be interesting to use it in applications where the physical aspect is not important for example in catalysis [11].

6.3.3. Study of the effect of varying the electrode rotation rate.

In this case, the influence of the electrode rotation rate on the composition of the deposit was analysed. The rotation of the electrode, in addition to causing a movement of the electrode, was responsible for the agitation of the bath, allowing the control of the diffusion layer.

First, the effect of electrode rotation was studied on a bath that partially simulated the concentration conditions of one of the commercial baths. When working at a Cu^{+} concentration of 55 g/L, at a current density of 0.20 A/dm^2, an alloy containing 18.76% gold and 81.24% copper is obtained at a rotation rate of 100 rpm. As the rotation rate of the electrode decreases, no deposit was formed. In contrast, when no rotation was applied to the electrode, this time an alloy containing 98.10% gold and 1.90% copper was obtained.

Then, the study was carried out with a copper concentration to 7.12 g/L and working at a current density of 0.65 A/dm^2. When working at a rotational rate of 100 rpm, a heterogeneous deposit with a loop in the middle was obtained. The gold composition of the spiral was about 90% gold and 10% copper. As the rotational rate changes, the composition of this spiral remains constant, while the composition at the edge of the deposit varies with the rotational rate. In Figure 6.9., the composition of the deposition around the spiral can be observed as the rotational rate is varied. As the rotational rate increases, the gold composition of the coating decreases.

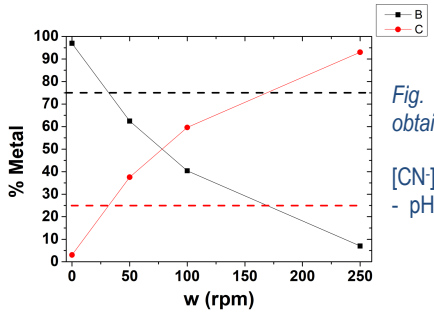

Fig. 6.9. % Of each of the metals composing the alloy obtained at different electrode rotation rate.

[CN^{-}] = 0.4 M - [Au^{+}] = 5 g/L – [Cu^{+}] = 7,12 g/L – j = 3 A/dm^2 - pH = 10,5 – T = 70 ºC

6.3.4. Study of the effect of temperature.

By studying the effect of the bath temperature on the composition of the coating, it was observed that increasing temperature the amount of gold in the deposit decreased. Figure 6.10. shows the alloy compositions obtained at three different temperatures.

This could be because as the temperature increases, the ions in solution move at a faster speed, increasing the rate of the reaction, causing the reaction mechanism to change and the less noble metal, in this case copper, could be deposited more easily.

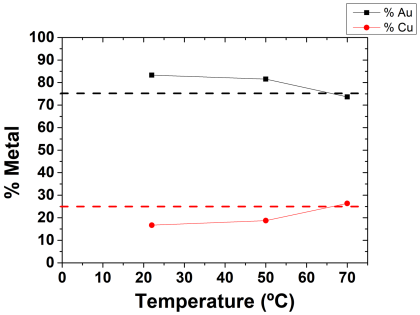

Fig. 6.10. % Of each of the metals composing the alloy obtained at different temperatures

[CN^-] = 0.4 M - [Au^+] = 5 g/L – [Cu^+] = 6.86 g/L – j = 3 A/dm^2 - pH = 10,5 - w = 100rpm

6.3.5. Pulsed DC study.

After studying the parameters involved on the electrodeposition, it was possible to establish the working conditions for a pulsed current electrodeposition study. From the experiments carried out, shown in sections 6.3.1 to 6.3.4, it can be concluded that the optimum conditions for the pulsed current study are the following:

- [Cu^+] = 6.86 g/L
- [Au^+] = 5.00 g/L
- [CN^-] = 0.40 M
- Rotation Rate = 100 rpm
- Temperature = 70ºC

These conditions are chosen because from 2.5 to 5 A/dm^2 the alloy composition is always close to 18 kts, as seen in the section 6.3.2.

The pulsed current experiments allow to study the effect of the duty cycle on the alloy composition. Then, the effect of both the working current density (j_{on}) and the average current density (j_a) is studied. In all cases, the time-off current density (j_{off}) is kept at 0 A/dm^2.

6.3.5.1. Study of the effect of duty cycle at a constant working current density (j_{on}).

This experiment was carried out to understand the behavior of ions in solution when no current was applied to the system. For them, a constant working current density (j_{on}) of 3 A/dm^2 was set, in the middle of the stability range of the alloy, and the studies were carried out varying the duty cycles from 10 to 90%.

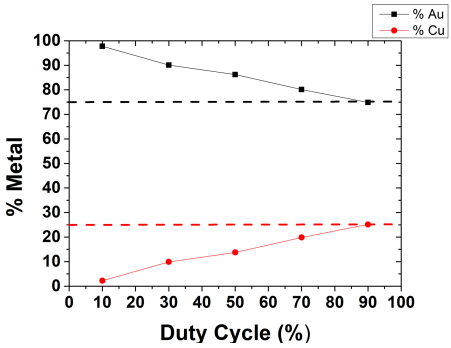

Fig. 6.11. % Of each of the metals composing the alloy obtained at a constant j_{on} and different duty cycles.

[CN^-] = 0.4 M - [Au^+] = 5 g/L - [Cu^+] = 6.86 T = 70ºC - pH = 10.5 - w = 100rpm - g/L – j_{on} =3.0 A/dm^2

Figure 6.11. shows the decrease of % of gold with the increase of the duty cycle. This is because more gold ions can reach the electrode and be reduced during time-off period. At lower time-off, they do not have enough time to move towards the electrode and therefore, less gold ions react.

6.3.5.2. Study of the effect of duty cycle at a constant average current density (j_a).

In this study, the duty cycle was varied from 10 to 70% at three different medium current densities, 2.5, 3.0 and 5.0 A/dm^2, all of which were within the zone of stability of the alloy when a constant current is applied.

Figure 6.12. shows the results obtained in this experiment. The % of gold of the alloy decreases with a duty cycle increase.

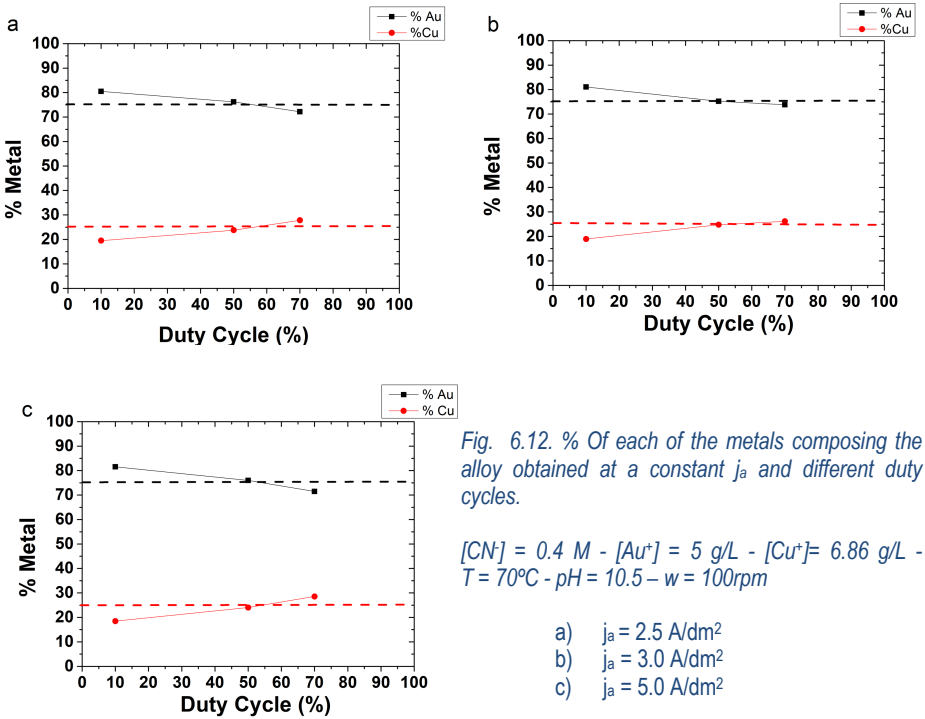

Fig. 6.12. % Of each of the metals composing the alloy obtained at a constant j_a and different duty cycles.

[CN^-] = 0.4 M - [Au^+] = 5 g/L - [Cu^+]= 6.86 g/L - T = 70ºC - pH = 10.5 – w = 100rpm

a) j_a = 2.5 A/dm^2
b) j_a = 3.0 A/dm^2
c) j_a = 5.0 A/dm^2

Figure 6.13. shows a comparison of some deposits obtained with a macroscopic and a microscopic image. A practically smooth surface is obtained, which allows the light to bounce and therefore shine.

It can also be seen that in some cases there are holes in the surface. This is due to the formation of hydrogen during the reduction process. When working at such high current densities, the protons in the medium are also reduced to form hydrogen gas (E=0.0V vs. SHE), giving off gas bubbles. The way the working electrode was arranged in this study (horizontally) did not allow the hydrogen bubbles to escape and remain attached to the electrode, which caused some variations in the potential reading and reduced the area of the electrode.

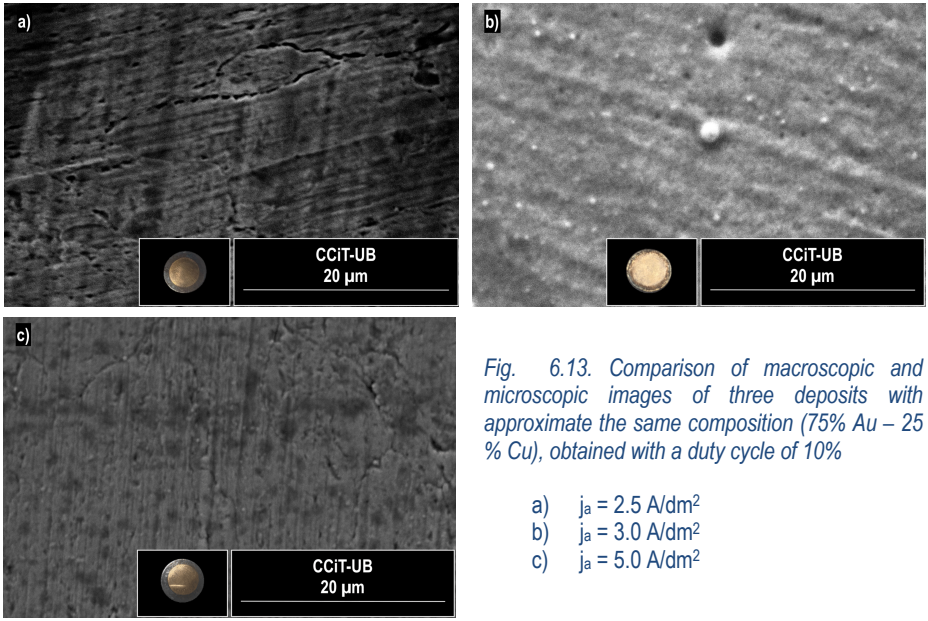

Fig. 6.13. Comparison of macroscopic and microscopic images of three deposits with approximate the same composition (75% Au – 25 % Cu), obtained with a duty cycle of 10%

a) j_a = 2.5 A/dm^2
b) j_a = 3.0 A/dm^2
c) j_a = 5.0 A/dm^2

6.3.6. Comparison of the surface of pulsed current and direct current deposits.

To understand the difference in appearance between the deposits obtained from the direct current technique and those obtained from the pulsed current technique, it is necessary to compare the appearance of the surface at the microscopic level. Figure 6.6.b. and Figure 6.13.b. show the SEM image of two 18 kts deposits. Both were obtained at a current density of 3 A/dm^2. The difference between the two coatings is the technique used to obtain them.

The deposit in Figure 6.6.a. was obtained from the application of constant direct current, whereas the deposit in Figure 6.13.b. was obtained by the pulsed current technique with an average current density of 3 A/dm^2.

By observing the appearance of each of the deposits obtained, their brightness has increased in comparison to the deposits obtained at the same current density but at direct current. This is because, even when working at high current densities, by working with very small-time intervals, it allows the creation of micro clusters that grow in an orderly manner, resulting in a smooth and therefore shiny surface.

7. CONCLUSIONS

The work carried out in this project concludes that 18 kts gold and copper alloy can be obtained from the electrodeposition technique using a bath without additives.

The speciation study allowed us to understand which are the predominant species with different concentrations of Au^+, Cu^+ and CN^-.

From the voltammetric study it has been possible to establish which species are more favourable to electrodeposition at the working temperature used, which is $[Cu(CN)_3]^{2-}$.

With the constant DC study varying the different process parameters, it has been possible to establish the most suitable conditions for starting the pulsed current deposition study:

- $[Cu^+]$ = 6.86 g/L
- $[Au^+]$ = 5.00 g/L
- $[CN^-]$ = 0.40 M
- Rotation Rate= 100 rpm
- Temperature= 70ºC
- j_a = 2.5 – 5 A/dm^2

From the pulsed current study, it has been possible to analyze the influence of the pulse current density, both instantaneous and average, and the duty cycle. These initial results demonstrate that bright 18 kts AuCu coatings can be obtained without the use of additives.

The pulsed current also allows to reduce the Cu^+ concentration of the bath, which implies an indirect reduction of the CN^- concentration. This leads to obtain less polluting and safer baths, since CN^- is toxic both for the environment and for people.

8. REFERENCES

[1] M. Paunovic and M. Schlesinger, *Modern electroplating.* Wiley, 2010.

[2] M. Paunovic and M. Schlesinger, *Fundamentals of Electrochemical Deposition*, 2n Edition. Hoboken, New Jersey: A John Wiley & Sons, INC., 2006.

[3] M. An, "Mechanism of additives in electroplating of Sn-Zn alloy," *Plating and surface finishing*, vol. 86, no. 5, pp. 130–132, 1999.

[4] K. Boto, "Organic additives in zinc electroplating," *Electrodeposition and Surface Treatment*, vol. 3, no. 2, pp. 77–95, Mar. 1975, doi: 10.1016/0300-9416(75)90048-6.

[5] J. W. Dini, *Electrodeposition : the materials science of coatings and substrates*. Noyes Publications, 1993.

[6] W. Giurlani *et al.*, "Electroplating for Decorative Applications: Recent Trends in Research and Development," *Coatings*, vol. 8, no. 8, p. 260, Jul. 2018, doi: 10.3390/coatings8080260.

[7] M. Fleischer, "The abundance and distribution of the chemical elements in the earth's crust," *Journal of Chemical Education*, vol. 31, no. 9, pp. 446–455, Sep. 1954, doi: 10.1021/ed031p446.

[8] B. Hammer and J. K. Norskov, "Why gold is the noblest of all the metals," *Nature*, vol. 376, no. 6537, pp. 238–240, Jul. 1995.

[9] X. Liu, A. Wang, T. Zhang, D.-S. Su, and C.-Y. Mou, "Au–Cu alloy nanoparticles supported on silica gel as catalyst for CO oxidation: Effects of Au/Cu ratios," *Catalysis Today*, vol. 160, no. 1, pp. 103–108, Feb. 2011, doi: 10.1016/j.cattod.2010.05.019.

[10] J. H. Kyle and G. Hefter, "A critical review of the thermodynamics of hydrogen cyanide and copper(I)–cyanide complexes in aqueous solution," *Hydrometallurgy*, vol. 154, pp. 78–87, Apr. 2015, doi: 10.1016/j.hydromet.2015.03.012.

[11] H. Babaei, M. Khosravi, M. Sovizi, and A. Khorramie, "The Influence of Effective Parameters on Optimizing the Electrochemical Deposition Rate of Au-Cu Alloy with High Thicknesses for the Production of Hallow Gold-Jewelry Artifacts with Pulsed Current (PC) on A Silver Substrate," *Analytical & Bioanalytical Electrochemistry*, vol. 11, no. 9, pp. 1270–1288, 2019.

[12] M. S. Chandrasekar and M. Pushpavanam, "Pulse and pulse reverse plating—Conceptual, advantages and applications," *Electrochimica Acta*, vol. 53, no. 8, pp. 3313–3322, Mar. 2008, doi: 10.1016/j.electacta.2007.11.054.

9. ACRONYMS AND SYMBOLS

- Au: Gold
- AuCu: Gold-Copper alloy
- CN: Cyanide
- Cu: Copper
- DC: Direct Current
- E: Potential
- j: current density
- kts: karats
- M^{+}: Metallic Ion
- p.a.: Pratical Grade
- SCE: Saturated Calomel Electrode.
- SR: Scan Rate
- SEM-EDS: Scanning Electron Microscope- Energy Dispersive X-ray Spectroscopy
- T: Temperature
- t: time
- V: Volume
- w: Electrode rotation rate
- [ ]: Concentration