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Elaboration of copper-tin alloys coatings: effect of glycine

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Abstract

Despite the coatings progress, addition of organic additives is limited or restricted in electrolytes with environmental regulations. The electrochemical deposition of Cu-Sn alloy is studied in acidic sulfate electrolyte at pH 1 and room temperature. The present work focuses on the behavior of the copper-tin alloys using glycine as additive to identify the action mechanism of this substance on alloys. Voltammetric analyses display three cathodic and anodic peaks, for Cu-Sn alloys with or without glycine. Alloy composition and their structure are investigated by EDS and XRD. The effect of glycine on copper-tin alloys has been investigated by glow discharge optical emission spectroscopy (GDOES). The SEM images reveal a very specific morphology in the presence of the glycine. A very homogeneous granular surface is obtained, formed by clusters with a decrease of this size. Glycine is a grain refiner to Cu-Sn alloys and the mechanism of electrodeposition of copper-tin alloys is not modified.

Keywords: Electrodeposition, Copper-tin alloys, Electrochemistry, Glycine

1. Introduction

With REACH regulations which tend to restrict the use of nickel salts (restriction of hazardous substances: Nickel Directive 94/27/EC) [1] and the environmental restrictions, several alternatives are investigated to eliminating nickel coatings. Brooman and al. [2] are grouped different solutions into some categories as copper-based alloys. Copper-tin alloys have investigated by our research group [3] and this alloy is recognized as a promising candidate by the industry for their functional properties, and used in technical coatings for its corrosion resistance similar to the nickel's one. Copper and its alloys can be electrodeposited from various electrolytes including aqueous citrate [4], sulfate [5–7], pyrophosphate [8], etc. The sulfate electrolyte is often considered, due to its low cost and low toxicity [5–7, 9-10]. It's necessary to add additives in small quantities [11-15] to improve the quality of deposits and to obtain required physical properties as brightness showned by Survila and al. [18]. In our study, stannous ions (Sn^{2+}) are relatively insoluble in acid electrolyte, that's why adding complexing agents stabilize the copper-tin electrolyte [16-17]. Recently, attention has been paid to substances that can be used in industry with a low toxicity [18]: gelatin falls into this category. Gelatin is a protein obtained by partial hydrolysis of collagen [19]. Consequently, the main components of gelatin reflect the amino acids of the parent collagen. Collagen and gelatin are complex substances which have high molecular weight and composed by various amino acids [20-21]: glycine, proline, hydroxyproline, alanine and glutamic acid. The presence of one additive as gelatin (composed of different amino acids) in the bath limits to the use of others additives, it's a promising choice. Our previous work [3] has shown the influence of gelatin on copper-tin alloys in acidic sulfate electrolyte: the phenomenon of adsorption can be considered. Gelatin is also a grain refiner [3]. In order to understand the influence of gelatin on copper-tin deposits, this objective is to study the influence of the common amino acids present in gelatin, glycine in our case, and to detect this effect to similar to gelatin. Several authors as Kublanovsky or Ballesteros [22-24] used glycine as a complexing agent in the copper electrodeposition in alkaline electrolyte. Actually, adsorption of proteins at solid/liquid interface is an important and challenging interdisciplinary field of the sciences [25]: this process can be exploited in surface treatments [3, 26].Despite these many important contributions to the study of the glycine on metals (Co-Ni [27], Zn [28], Zn-Fe [29]) electrodeposition, no work has been carried out in acidic and more specifically copper-tin electrolyte. The development of copper-tin additive-free baths is a perspective to the future to respect the environmental regulations. The aim of the present work is to detect the effect of the glycine on copper-tin coatings by using the electrochemical techniques of cyclic voltammetry and chronoamperometry in static conditions. The present work also describes the deposition process and interactions with additive similar to gelatin or not. The properties of copper-tin deposits obtained by chronoamperometry are investigated by scanning electron microscopy (SEM), their structure by X-ray diffraction analysis (XRD) and their composition by Glow Discharge Optical Emission Spectroscopy (GDOES).

2. Materials and methods

2.1. Solutions

For the electrodeposition experiments, electrolytic bath are prepared. Table 1 shows the detailed composition of the bath used in this study with operated conditions, determined in our previous works [3, 30]. All solutions are prepared from high quality MilliQ water (18 mΩ.cm).

Table 1: Electrolyte composition and operating conditions for Cu-Sn co-deposition experiments.

Chemicals	Concentrations	Function
Sulfuric acid (H_2SO_4)	0.6 mol/L	Supporting electrolyte
Sodium sulfate (Na_2SO_4)	0.5 mol/L	Background electrolyte
Copper(II) sulfate ($CuSO_4.5H_2O$)	0.04 mol/L	Source of Cu^{2+} ions
Tin (II) sulfate ($SnSO_4$)	0.04 mol/L	Source of Sn^{2+} ions
Glycine (when added)	1 g/L	additive
pH	1.05 ± 0.03	
Conductivity	127 ± 5 mS cm^{-1}	
Temperature	25 °C	

The glycine (Gly) is a simplest amino acid found in the structure of gelatin: H_2NCH_2COOH. Glycine exists under three different forms in aqueous solutions depending on the pH value [31-32].

In this study, the bath is an aqueous acidic sulfate electrolyte with the pH value is equal to 1. Glycine is the cationic form, positively charged as H_2G^+. The copper and tin species are also cationic form: Cu^{2+} and Sn^{2+}. In the electrolyte, the glycine protonation and the metallic species, positively charged, induce the repulsive forces: the formation of complexes is not involved.

2.2. Material

The substrate is a platinum disk with an area S = 0.33 cm². The platinum substrate is an inert material and is chosen to avoid the influence of the substrate during the mechanism of electrodeposition [3, 32]. Before each measurement, the working electrode (substrate) is etched with 10% sulfuric acid for 30 s and rinsed carefully with distilled water.

For an industrial approach, the substrate is modified to be close to industrial reality. It's not possible to using platinum substrate in industries that's why copper-tin alloys are studied on steel and brass substrates. Platinum is an inert material, while steel is active. The nature of the substrate is specified for each experiment to avoid confusion and a section of the influence of the substrate is created. For theses substrates, the preparation of the surface is different: the substrate is etched with acetone for 15 s and then, with 50% sulfuric acid for 1 minute and rinsed carefully with distilled water.

2.3. Methods

2.3.1. Electrochemistry

Electrochemical experiments were performed in a one-compartment three-electrode cell connected to a PGZ-301 Radiometer potentiostat controlled by VoltaMaster 4 software. The working electrode is a platinum disk with an area S=0.33 cm². The expose surface area is etched with sulfuric acid and ultrasonically cleaned prior to all experiments. A saturated mercurous sulfate electrode (MSE) is used as reference, and all potentials refer to this scale. A platinum disk is used as a counter electrode.

2.3.2. Characterization of samples

Scanning electron microscope (SEM) pictures allow identifying the morphological coatings of copper-tin alloys with an Environmental FERI Quanta 450 W microscope model. These coatings are also characterized by X-Ray Diffraction (XRD) on a D8 Advance Bruker, with Cu Kα radiation. X-ray diffraction analyses are performed to determine the formation of alloys or not with or without glycine. All these experiments are performed in addition to GDOES (Model JobinYvon HORIBA GD Profiler) depth profiles in order to understand the electrodeposition mechanisms of copper-tin alloys and observe the influence of the glycine (Gly).

3. Results and discussion

3.1. Influence of glycine on electrodeposition process

Cyclic voltammetry study is realized in the -0.1V to -1.5V vs. MSE potential range onto platinum substrate from solution described in table 1 in the presence ([Gly] = 1g/L) and absence of glycine. The potential scan is initiated in the negative direction from the open circuit potential (E_{ocp}) at scan rate of 10 mV.s^{-1}. Fig.1 presents cyclic voltammograms obtained without and with glycine. All voltammograms present the following characteristics: a negligible cathodic current is observed from the E_{ocp} to -0.6 V vs. MSE, this suggests no reaction in this potential range. After, from -0.6 V vs. MSE, the reduction of metallic elements begins: the reduction of copper at E = -0.72 V vs. MSE (I_c) and the reduction of tin at E = -0.98 V vs. MSE (II_c), identified in our previous work [3]. Glycine addition to the electrolyte doesn't modify the current density of the peaks I_c equal to -1.3 mA/cm² (at E = -0.72V vs. MSE) and II_c equal to -2.5 mA/cm² (at E = -0.98 V vs. MSE). When glycine is added, the hydrogen reaction occurs at a more negative potential (E = -1.33 V/MSE). When the scan direction is reversed in the switching potential, three anodic peaks, I'_a, II'_a, and III'_a appear at potentials of -0.9 V, -0.33 V and -0.28 V vs. MSE, respectively. The first peak I'_a is attributed to oxidation of tin. The other peaks could be due to oxidation of copper-tin alloy and copper free species. But in our previous work [3], this observation is already present for the copper system. These anodic peaks could be due to complexes between glycine and copper, copper species (free complex ions and adsorbed state) in different phases, or oxidation platinum surface.

Adding glycine causes no modification in the deposition process. A slight shift towards more negative values is observed in the presence of glycine for the hydrogen evolution. On the basis of these results, glycine has not effect on the mechanism electrodeposition of copper-tin alloys. This indicates the absence of interfacial modifications in glycine presence during electrodeposition [3].

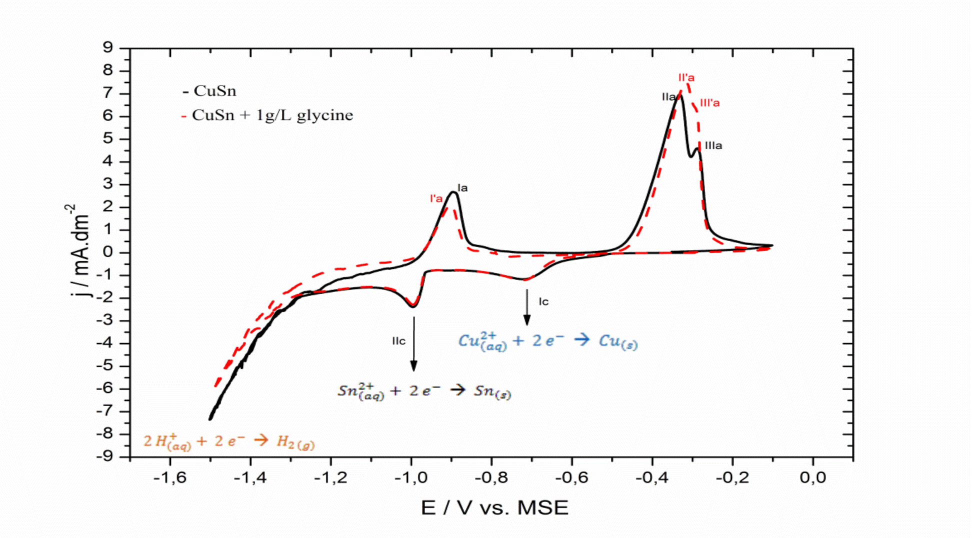
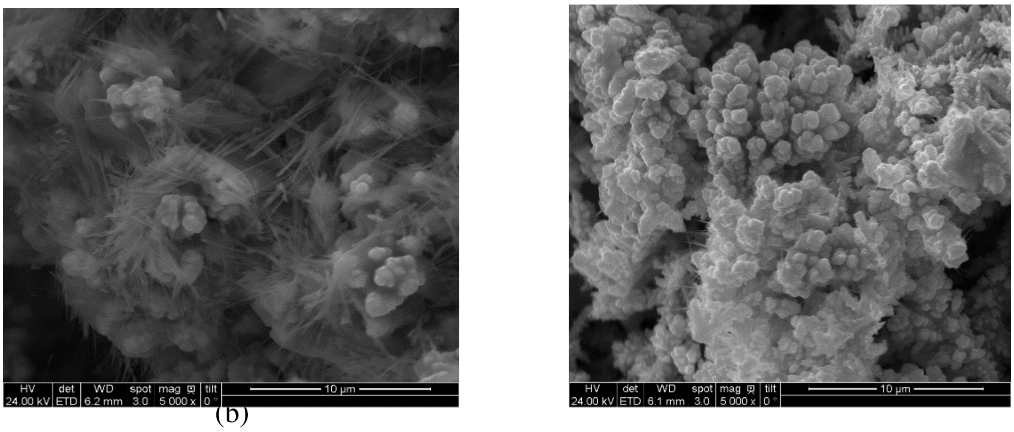


Figure 1: Cyclic voltammograms of copper-tin deposition with composition of the solution: H_2SO_4 0.6M, Na_2SO_4 0.5M, $CuSO_4$ 0.04M, $SnSO_4$ 0.04M without glycine (—) and with 1g/L glycine (---).

3.2. Morphology of Cu-Sn deposits

Scanning electron microscopy (SEM) images are obtained from copper-tin alloy deposited on a polycrystalline platinum disk substrate. Copper-tin coatings are deposited by polarization at a potential of -1100 mV vs. MSE over a period of 15 min for SEM analyses in the absence of glycine (fig. 2(a)) ant the presence of 1g/L glycine (fig. 2(b)).



(b)

Figure 2: SEM micrographs of copper-tin deposit obtained for 15 min at −1100 mV/MSE, from an electrolyte containing (a) no additive, (b) 1 g/L of glycine on platinum substrates.

Without additive in the electrolyte, dendritic growth on preferential locations is present on deposits (fig. 2(a)). The structure of this deposit is formed in elongated shapes likened to needles, which is characteristic of tin whiskers [33-35]. The copper-tin deposit consists of large grains resulting in a rough surface. Addition of 1 g/L of glycine (fig. 2(b)) produces a smooth deposit surface with finer grains compared to the samples without glycine. With additives (fig. 2(b)), the Cu-Sn deposit is homogeneous over the platinum surface. SEM micrographs (fig. 2) reveal to the morphology of copper-tin coatings. According results of Sürme and al. [36], 54.5% Sn containing alloys have some morphological irregularities, confirmed by this study. The glycine doesn't influence the mechanism of electrocrystallization. This observation is confirmed by results obtained by EDX. Actually, chemical analyses of cathodic deposits are performed via energy dispersive spectroscopy. Results from this characterization showed the presence of glycine doesn't modify the proportion of metallic elements in deposits: the weight percent of copper is 56 % and the weight percent of tin is 44%. This Cu-Sn content produce surface finishes from grey. These results are in accordance with different studies of Low and Walsh [37] and Sürme and al. [36] which was also investigated the some electrodeposition characteristics of copper-tin alloys. In conclusion, glycine acts as a grain refiner agent on copper-tin alloys promoting the nodular formation.

3.3. Structure of Cu-Sn deposits

The deposits are examined by X-ray diffraction (XRD) to determine the formation of preferred alloys with glycine. Fig. 3 shows that the addition of glycine in the standard electrolyte doesn't change the preferential crystalline orientation and stoichiometry balance remains Cu_6Sn_5 for all specimens. XDR patterns detect any compound of copper and tin alone without additive. This could be due to the formation of crystallite composite in the extreme surface of deposits: the whiskers of tin, for example, confirmed by SEM micrographs. The intensity of these peaks disappears with adding glycine. Glycine doesn't modify the formation of Cu_6Sn_5 alloy and minimize the formation of copper compound and tin compound at the surface of samples.

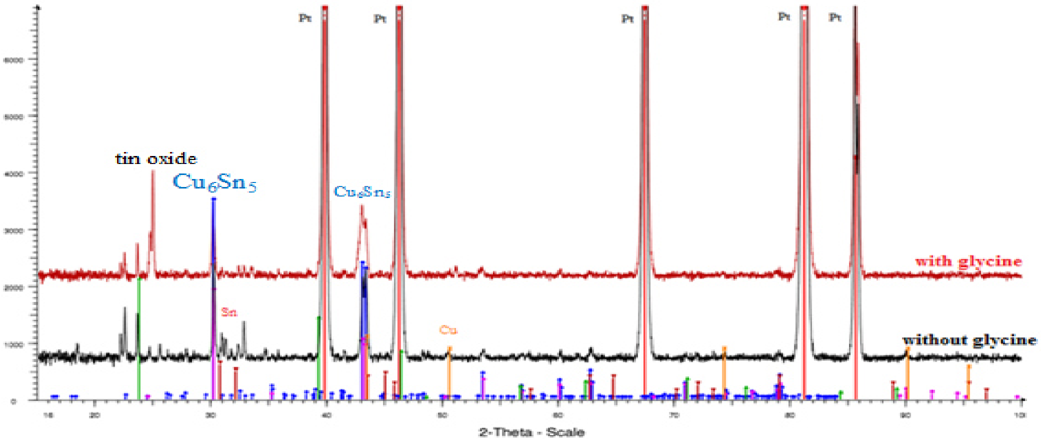


Figure 3: XRD diffraction patterns obtained for the solutions of copper-tin alloys without glycine (-) and with glycine (-).

3.4. Influence of the substrate

For an industrial application, substrates such as steel or brass are widely used. Therefore, the SEM images and GDOES profiles are investigated to determine the formation and the composition of the alloys in presence of glycine. The SEM micrographs characterize the morphology of coatings obtained by chronoamperometry on steel substrate (fig. 4). Figures 4a and 4b look very similar. The results show that with glycine, the deposit is homogeneous, less rough and covers over the surface.

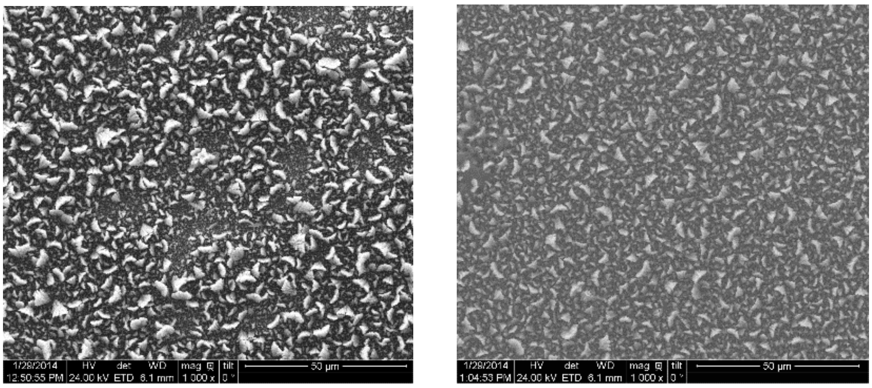
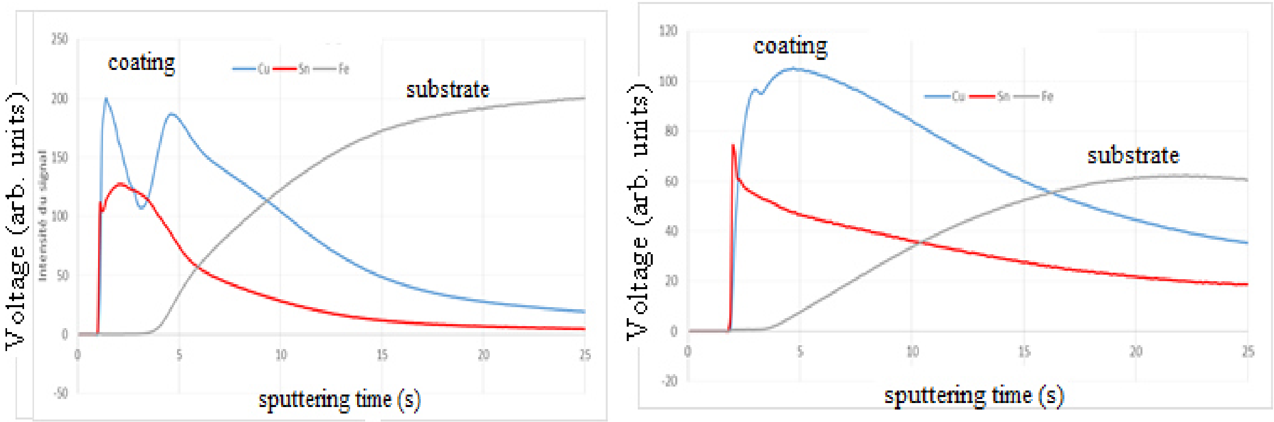


Figure 4: SEM micrographs of copper-tin deposit obtained for 15 min at –1500 mV/MSE, from an electrolyte containing (a) no additive, (b) 1 g/L of glycine on steel substrates.

The composition of coatings on steel substrates is investigated using the glow discharge optical emission spectroscopy (GDOES) technique. So, the effect of glycine on copper-tin alloys are studied on steel substrates (Fe) illustrated in figure 5. The signals of copper and tin characterize the coating part and the signals of iron are related to the substrate part. The coating/substrate interface is defined as the position where the Fe signal increase. Examination of this profile indicates without glycine two layers of copper at the coating surface and at the coating/substrate zone. This result confirm results obtained by SEM (whiskers of tin in the surface) and by XRD measurements (presence of copper-tin alloy and copper phases). Profile shows that without glycine (fig. 5a), there is the presence of two layers of copper which can be explained by the presence of copper alloy as Cu_6Sn_5 and Cu single crystal form (confirmed by previous XRD results). Other copper-tin alloys with glycine (fig. 5b), elements appear homogeneously distributed on the layer deposit. It reveals a homogeneous distribution characteristic of the formation of alloy, confirmed by XRD results. Glycine enhances the formation of the copper-tin alloy.



(a) (b)

Figure 5: GDOES profiles for (a) copper-tin alloys and for (b) copper-tin alloys with 1g/L of glycine.

Conclusion

In order to improve properties of copper-tin alloys, coatings elaborated with glycine in acidic sulfate electrolyte have been investigated by electrochemical analysis and characterizations. Various techniques are used to evaluate properties of copper-tin alloys and to determine the effect of glycine on deposits.

Results obtained by electrochemical analyses show that the behavior of glycine doesn't affect the electrocrystallization process of copper-tin alloys. At acidic pH, the protonation form of glycine can't be due to the phenomenon of complexation. Adsorption is also not detected. Therefore, the SEM micrographs show that glycine has a grain refining effect as well as leveling properties on electrodeposits of copper and copper-tin alloys. XRD measurements prove that glycine enhances the formation of copper-tin alloys and in particular Cu_6Sn_5. The GDOES profiles present the distribution of the detected elements versus the sputtering time. Profile with glycine indicates that the distribution of elements of the alloy is uniform. Adding glycine play a role on the structure of copper-tin alloys, confirmed by results obtained by XRD technique.

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