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The influence of a heat treatment on properties of Cu-Zn alloy from a cyanide-free and Zinc sulphate baths

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ABSTRACT

We present an alternative method aiming to reduce the toxicity and the cost of electroplating of Cu-Zn alloy (usually prepared from cyanide baths) while maintaining the decorative qualities and anticorrosive properties of the coating. For this purpose, Cu-Zn alloys were obtained in two steps from non-cyanide electrolytes. First, a copper layer electrodeposited onto a nickel under-layer, followed by a thin layer of zinc from three different simple non-cyanide zinc baths. The Zn/Cu/Ni sandwich system was then subjected to heat treatment at a temperature of 400°C, to ensure the diffusion of zinc into the copper layer to give the desired Cu-Zn alloy structure. The synthesized films were characterized by using X-ray diffraction XRD, scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS). XRD demonstrated that the electrodeposited films are crystalline and present the Cu0.7Zn0.3 phase with preferential (111) orientation. An analysis of XRD patterns revealed that after heat treatment, the Cu-Zn alloys were composed of a predominating α-phase structure. The morphology and composition of the coatings depends on the zinc plating bath type. After annealing, well defined pseudo-spherical Cu-Zn grains were formed covering the entire substrate surface. The EDS analysis indicated the formation of $Cu_{0.7}Zn_{0.3}$ brass alloys, corrosion was studied by impedance spectroscopy. The results showed the feasibility of this low-cost and new route for the preparation of good quality Cu–Zn alloys from cyanide-free electrolytes.

Introduction

Zinc and copper are important materials playing a strategic role in several industrial applications, such as: automotive industry, aeronautics, household appliances, etc. In addition, alloy coatings are very attractive for practice due to their high strength, good plasticity and excellent mechanical properties. There are several methods to obtain these alloys: the physical vapor deposition (PVD), the chemical vapor deposition (CVD), the sputtering, and the molecular beam epitaxy (MBE) techniques are just a few available. These methods have several advantages and are used for specific applications. However, due to certain limitations, such as high capital and high-energy costs, an alternative method is required. Recently, the electrochemical deposition has been used as an alternative technique for producing these structures on different surfaces. Electrodeposition is one of the most commonly used methods for metal and metallic alloy film preparation in many technological processes and the electrochemical processes offer many advantages, including a room-temperature operation, low-energy requirements, fast deposition rates, a fairly uniform deposition over complex three-dimensional objects, low costs and a simple scale-up with an easily maintainable equipment [1-5]. Besides, metal-coating alloys obtained by electrodeposition show better properties than those of pure metals [6, 7].

Cu-Zn alloys (brass) are widely used for decorative purposes [8] as well as for promoting rubber adhesion to steel [9]. Commercial used electrodeposition of Cu-Zn alloys in cyanide baths produces high-quality deposits [10] but causes environmental problems. In addition, there is a need of a rigorous maintenance arises in the use and disposal of cyanide in order to obtain a suitable solution for environmentally safe brass plating [11]. This is why researchers have been looking for an environmentally friendly cyanide-free solution which could be a good substitute without a loss in the quality of coatings [12–15].

Although satisfactory deposition has been obtained in non-cyanide baths with certain operating conditions and bath

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Table 1. Chemical composition of electrolytic bath and conditions for the electrodeposition.

compounds	C_m	S	i	T	t
Na_2SO_4	4 g/l	5×2 cm^2	2 A/dm^2	25°C	03 min
H_3BO_3	5 g/l				
$ZnSO_4$.7H2O	450 g/l				
$Al_2(SO_4)_3$	30 g/l				

compositions, these deposits haven't been used commercially so far, since the films cannot be reproduced, are not well adhered and show unusual colorations [14]. In order to develop an alternative Cu-Zn plating bath that avoids the use of cyanide, we have studied the action of an alkaline bath. In the present investigation, the study of Cu-Zn alloys obtained in two stages separated from non-cyanid electrolytes is reported. The layers were subjected to heat treatment, which favors the diffusion of zinc into copper and makes the production of the Cu-Zn alloy possible. The structural and morphological aspects of the alloys were also examined, corrosion was studied by impedance spectroscopy.

Experimental

Cathodic polarization curves were galvanostatically obtained in a current density range. The chemical compositions of the solutions used while studying the stability of the baths and taking electro-chemical measurements were given in Table 1. All chemicals used in this work were of analytical grade. Distilled water was used to prepare the solutions and to rinse samples containing electro-deposits.

A vertical rectangular 5 × 2 cm^2 steel plate was used as working electrode [16]. The reason of choosing a steel plate as substrate was among the purposes of the present study: to be able to deposit brass on it for the use in the field of pneumatics where the main application of brass electroplating was on steel. The working surface of the electrode was mechanically polished to mirror brightness and rinsed with distilled water. After polishing, the electrode was cleaned in hot (70°C) NaOH concentrate for 2 min and activated for 30 s in an HCl aqueous solution (1:1) prior to electrodeposition. During all our research work, a layer of Ni was electrodeposited on the working electrodes (steel plate) in a classical two-electrode electrochemical cell (Ni as counter electrode) using the most popular Watts bath; the solution contained 300 g/l $NiSO_4.7H_2O$, 60 g/l $NiCl_2.6H_2O$ and 45 g/l H_3BO_3 (pH = 4.9). Electrodeposition was performed without stirring at about 50°C in a galvanostatic mode at 3 A/dm2 for 6 min. then a layer of Cu was electrodeposited on a steel plate/Ni electrode using a solution containing 250 g/l $CuSO_4$.5H2O and 50 g/l H_2SO_4 (pH = 0.6). Electrodeposition was performed without stirring at about 25°C in a galvanostatic mode at 4 A/dm^2 for 11 min. The Cu-Zn alloy electrodeposition experiments were performed with the solutions shown in Table 1. $ZnSO_4$ bath was chosen in order to produce the coatings. The coatings were produced using the same system and deposition conditions described in Table 1. After the electrodeposition of the different layers, the obtained substrate (steel plate/Ni/Cu/Zn) was annealed at 400°C for 40 min under air ambiance to allow diffusion of zinc into copper thus give the Cu-Zn alloy (cf. Fig. 1).

A JEOL JSM-6300F scanning electron microscope (SEM), with energy-dispersive spectroscopy (EDS) working at 15 kV, was used to examine the surface topography and the elemental compositions of the electrodeposits. For structural characteri-zation, a X-ray diffractometer Bruker AXS D8 Advance operating with 40 kV and 45 mA. The surface roughness was determined with Ambios XP-2 Profilometer, ccorrosion was studied by Electrochemical Impedance Spectroscopy (EIS) at a temperature of 25° C, were obtained in potentiostatic mode with a disturbance signal amplitude of 10 mV in a 0.1 M NaOH solution.

The reagents used in this work: $CuSO_4.5H_2O$ (≥ 98.0%), H_2SO_4 (95.0–98.0%), $NiSO_4.7H_2O$ (99.999%), HCl(37%), KCl (≥ 99.0%), NaOH (≥ 97.0%), Na_2SO_4 (99.0%), $ZnSO_4.7H_2O$(≥ 99.0%) and $Al_2(SO_4)_3$(99.99%) were used as purchased, without further purification.

Results and discussions

Once a copper layer was electrodeposited, the deposition of Zn follows using the same technique. In Fig. 2, SEM micrograph of Zn is presented. Fig. 2 shows plated Zn at the applied current density of 2 A/dm^2: the deposit consists of well-define hexagonally shaped crystals. However, a distinct morphology can be observed for all samples. From the micrograph, it is clear that grains growth direction is parallel to the substrate, and grains are regular and symmetrical with a series of plate-like crystals stacked up mutually. Similar results were obtained by others [18, 19] when they investigated the electrodeposition of zinc in sulphate solutions. The EDS analysis (Table 2) showed the presence of zinc as the predominant element in the coatings.

The XRD pattern of zinc deposits obtained is shown in Fig. 3. XRD pattern exhibits several distinct diffraction peaks: at 2θ = 36.39, 39.12, 43.50, 54.53 and 70.79°, which agree well with the (002), (100), (101), (102), and (110) diffractions peaks of hexagonal zinc (JCPDS no. 00-001-123). The obtained coating was equiaxed still slightly oriented towards the (101) plane, according to the XRD analysis [20].

The heat treatment is widely used to form alloys [21, 22]. To understand the effect of heat treatment on the electrodeposited Zn-Cu morphology, thedeposit was examined using SEM Fig. 4). The heat treatment significantly changed the morphology of the deposits, it can be observed that Cu-Zn films covered the substrates completely, the deposits become round-shaped after heat treatment. The morphologies obtai-

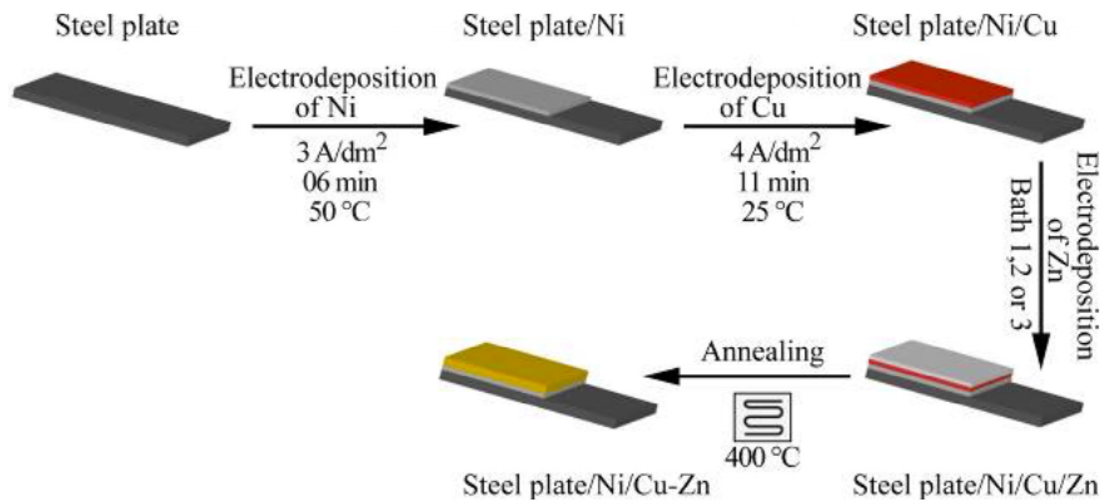

Fig. 1. Steps for depositing Cu/Zn alloy on steel/Ni plate.

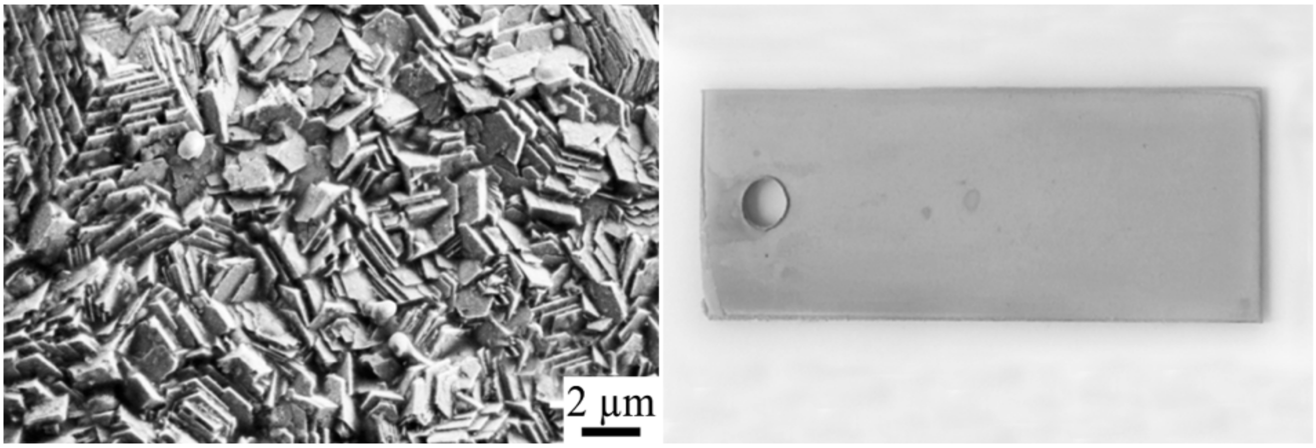

Fig. 2. SEM images of zinc deposits after 3 min of electrolyze onto steel-plate/Ni/Cu substrate and photograph of Zn film obtained before heat treatment.

ned are similar to those obtained with other methods [23]. A heat treatment at 400°C provides the diffusion of zinc into copper to give Cu-Zn alloys.

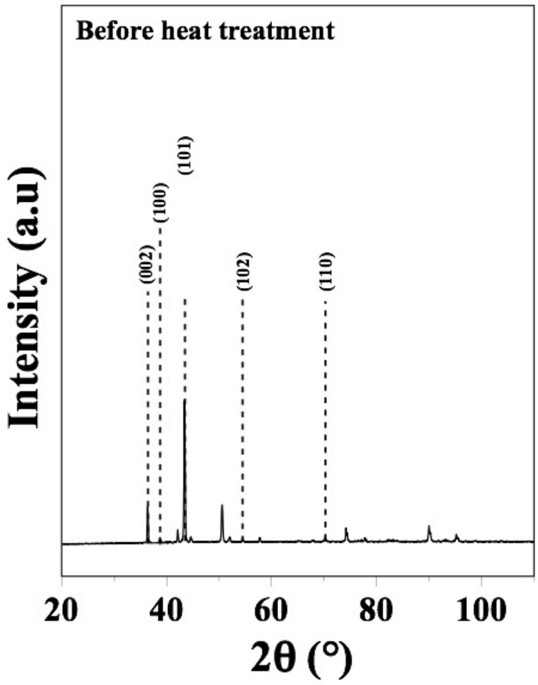

Fig. 3. XRD patterns of zinc layers on steel/Ni/Cu deposited from the bathroom of Table 1.

The surface morphology is traditionally analysed via surface-roughness measurements such as the root-mean-square (RMS) roughness, the average roughness and the peak-to-valley roughness. In brief, the surface roughness Rq (denoted also as RMS) and the mean roughness Ra were calculated using the standard software, the corresponding results were summarised in Table 3. Low surface roughness is obtained from the bath no. 1 (1.19 nm) compared with other two baths. The surface roughness changes with thickness and the variations in the surface morphology for the deposited films are probably due to the deposition conditions.

Fig. 5 shows typical XRD pattern of the obtained deposit. Three peaks at 2θ values of 42, 49, and 72° corresponding to (111), (200), and (220) planes of $Cu_{0.7}Zn_{0.3}$ were observed and compared with the standard powder diffraction card of JCPDS no. 03-065-9062. According to the respective literature, electrodeposited copper-rich Cu-Zn alloys exhibit two phases: the α and β phases [24]. The α phase is a solid solution that has an equilibrium solubility limit of about 35% Zn in Cu with a face-centred cubic structure. The β phase is an inter-mediate phase that has a composition corresponding to Cu-Zn with a body-centred cubic structure.It is obvious from Fig. 5 that XRD pattern of Cu-Zn electrodeposit differs from those of pure Zn and Cu, which indicates that crystalline alloys are also formed after heat treatment.

An analysis of XRD patterns reveals that the Cu-Zn alloy exhibits the corresponding peaks related to the α phase [25]. It should be mentioned that in order to obtain adherent alloys,

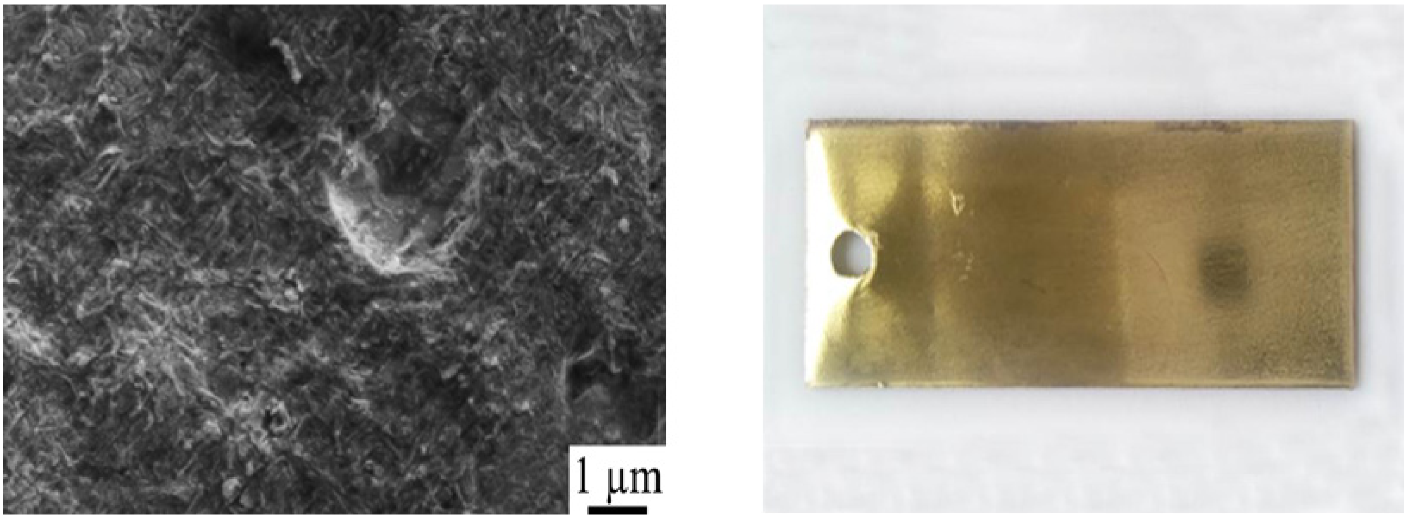

Fig. 4. SEM images of Cu-Zn deposits obtained after heat treatment at 400°C for 1h and photograph of Cu-Zn film obtained.

the heat treatment at 400°C was carried out, which is the most adequate temperature for zinc to get Cu-Zn thin films, but particular care should be taken on annealing. As was reported elsewhere, in single crystals, activation of dezincification (evaporation of zinc) occurred between 673 and 773 K depending on the phase and crystalline orientation [17]. It is known that in α brass a transformation occurs below 400°C and it has been pointed out that this transformation is due to the formation of short-range-order [26].

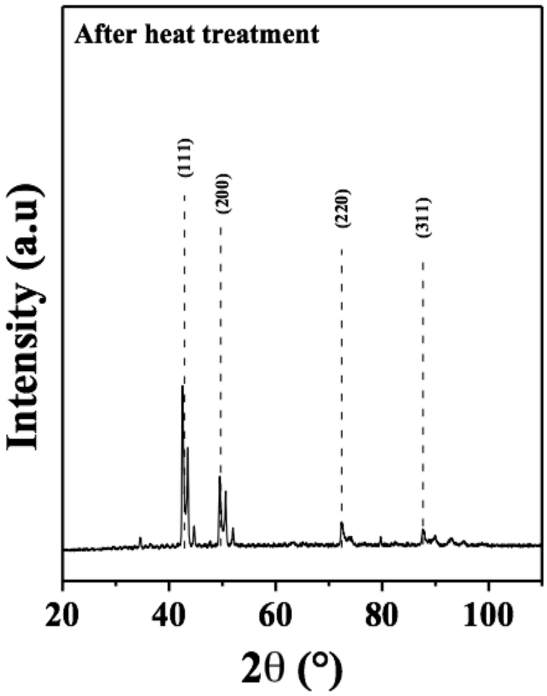

Fig.5. XRD patterns for Cu-Zn deposits obtained after heat treatment at 400°C for 60 min.

In fact, this annealing provides diffusion of zinc within the copper matrix. Zinc atoms are easily diffused as the atomic ray of copper and zinc are approximately identical. So, as is known, alloy coatings can be produced at high temperatures by the inward diffusion of the coating material: they are electrodeposited coatings which are subsequently interdiffused by thermal treatments [27]. Most Zn atoms have been substituted to Cu atoms as we can observe in the EDS results (Table 2). This is true for all alloys obtained with three baths: Zn atoms diffuse in Cu and brass alloys. Thus, substitutional diffusion takes place, which can be attributed to the comparable atomic radius of the elements and the existence of vacancies in Cu crystal lattices.

This confirms that the process of the inter-diffusion is very important in the phase formation of the electrodeposited Cu-Zn alloy. The diffusion phenomenon was confirmed by visual observations. In fact, during annealing, color changes of substrate were observed: in the beginning of the heat treatment, all substrate surfaces were brick red then, after 30 min, the substrate started turning into yellow and at the end the substrate become yellow, which can be explained by the diffusion of Zn atoms into Cu and formation of the Cu-Zn alloy. The more atoms of Zn diffuse into Cu, the more the color becoming yellow during annealing, thus allowing the formation of yellow brass, with the percentage of copper and zinc about 70 and 30%, respectively.

Table 3. Percentage of Cu and Zn estimated from EDS results.

R_q (nm)	2.253
R_a (nm)	5.057

Table 2. Percentage of Cu and Zn estimated from EDS results.

Before heat treatment		After heat treatment	
Zn (%)	Cu (%)	Zn (%)	Cu (%)
91	07	29	67

The average crystallite size of the particles was calculated from the full width at half maximum (FWHM) of the respective peaks using the Scherrer relation [28]. The values of Dependence of surface roughness the crystallite size and the d-spacing for (111) planes are summarized in Table 4 , which shows that the average crystallite size of Cu-Zn alloys increased from 27.14 nm to 45.32 nm, this result being consistent with the decreasing tendency of FWHM. It could be linked to an increase of the diffusion of zinc into copper, which leads to an improvement of crystallinity.

Table 4. Variations of physicals properties of Zn-Cu films.

2θ (°)	β (°)	D (nm)
42.59	0.157	45.32

The result is represented as a Nyquist graph for frequency values between 100 KHz and 50 mH The Nyquist diagrams obtained are shown in Fig. 6 The impedance diagrams comprise a loop that can be modeled by a parallel circuit (RC). The low-frequency impedance module can be used as a corrosion protection criterion because it includes the different resistances associated with a coated metal: the film's own resistance, the load transfer resistance at the different interfaces as well as the resistance to the diffusion of species. The low frequency impedance module obtained confer a higher degree of protection to the metal in NaCl medium. The higher degree of protection observed can be explained by the nature of the electrolyte. Further tests are to have a better understanding of the mode of protection. anticorrosion of elaborate films.

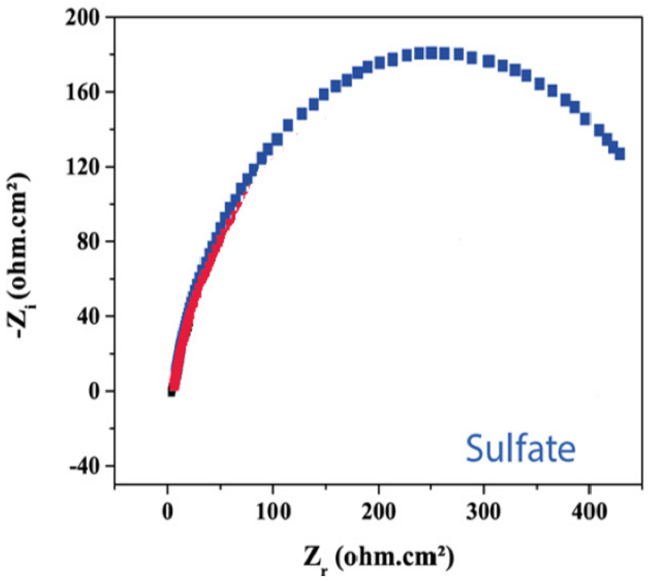

Fig. 6. Potentiodynamic polarization curve and Nyquist diagrams.

Conclusion

Cu-Zn alloys were synthesized using simple low cost galvanostatic electrochemical deposition under optimal conditions. It is possible to plate Cu, Zn and Cu-Zn deposits from an ionic liquid without usage of cyanide electrolytes. The Cu-Zn alloys were electroplated on mild steel substrates in two step followed by heat treatment. First, Cu layers were deposited and then Zn layers. The thermal treatment at 400°C was used to allow the diffusion of zinc into copper to obtain the alloy. The heat treatment significantly changed the morphology of the deposits. The coatings produced from presented a good visual aspect and an adherent alloy, with a percentage of copper and zinc about 70 and 30%, respectively.

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Conflicts of interest

Authors declare no conflict of interests.

Notes

The authors declare no competing financial interest.

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