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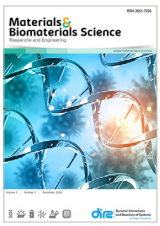

Synthesis and characterization of Cu–Zn alloy by Electrodeposition-annealing route using Zinc chloride bath

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ABSTRACT

Replacement of cyanide in electroplating is a current test. We present an elective strategy intending to decrease the harmfulness and the expense of electroplating of Cu-Zn composite (normally arranged from cyanide showers) while keeping up the beautifying characteristics and anticorrosive properties of the covering. For this reason, Cu-Zn compounds were gotten in two stages from non-cyanide electrolyzÂtes. Initial, a copper layer electrodeposited onto a nickel under-layer, trailed by a slim layer of zinc from straightforward non-cyanide zinc chloride electrolyte. The Zn/Cu/Ni sandwich framework was then exposed to warm treatment at a temperature of 400°C, to guarantee the dispersion of zinc into the copper layer to give the ideal Cu-Zn compound structure. The orchestrated movies were described by utilizing X-beam diffraction XRD, examining electron microscopy and vitality dispersive X-beam spectroscopy (EDS). XRD showed that the electrodeposited films are glasslike and present the $Cu_{0.7}Zn_{0.3}$ stage with particular (111) direction. An examination of XRD designs uncovered that after warmth treatment, the Cu-Zn compounds were made out of a prevailing α-stage structure. The morphology and arrangement of the coatings relies upon the zinc plating shower type. Subsequent to strengthening, very much characterized pseudo-circular Cu-Zn grains were framed covering the whole substrate surface. The EDS examination showed the development of $Cu_{0.7}Zn_{0.3}$ metal composites, consumption was concentrated by impedance spectroscopy. The outcomes demonstrated the achievability of this minimal effort new course for the arrangement of good quality Cu–Zn combinations from sans cyanide electrolytes

Introduction

Zinc and copper are significant materials assuming a vital job in a few modern applications, for example, car industry, flying, family unit apparatuses, and so forth. Likewise, combination coatings are extremely appealing for training because of their high quality, great pliancy and superb mechanical properties. There are a few strategies to acquire these alloys: the physical vapor deposition (PVD), the chemical vapor deposition (CVD), the sputtering, and the molecular beam epitaxy (MBE) procedures are only a couple of accessible. These techniques have a few favorable circumstances and are utilized for explicit applications. Be that as it may, because of specific restrictions, for example, high capital and high-vitality costs, an elective strategy is required. As of late, the electrochemical processes has been utilized as an elective strategy for delivering these structures on various surfaces. Electrodeposition is one of the most usually utilized strategies for metal and metallic compound film arrangement in numerous mechanical procedures and the electrochemical procedures offer numerous favorable circumstances, including a room-temperature activity, low-vitality prerequisites, quick deposition rates, a genuinely uniform affidavit over complex three-dimensional articles, low expenses and a straightforward scale-up with an effectively viable hardware [1-5]. Additionally, metal-covering composites acquired by electrodeposition show preferred properties over those of pure metals [6,7].

Cu-Zn combinations (metal) are generally utilized for beautifying purposes [8] just as for elevating elastic grip to steel [9]. Business utilized electrodeposition of Cu-Zn amalgams in cyanide showers delivers top notch stores [10] however purposes ecological issues. Likewise, there is a need of a thorough support emerges in the utilization and removal of cyanide so as to get a reasonable answer for naturally safe metal plating [11]. This is the reason analysts have been searching for an earth inviting non cyanide arrangement which could

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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				

be a decent substitute without a misfortune in the nature of coatings [12–15].

Although satisfactory deposition has been obtained in non-cyanide baths with certain working conditions and baths structures, these stores haven't been utilized economically up until now, since the film can't be recreated, are not very much followed and show abnormal hues [14]. So as to build up an elective Cu-Zn plating bath that maintains a strategic distance from the utilization of cyanide, we have contemplated the activity of an alkaline bath. In the current examination, the investigation of Cu-Zn alloy got in two phases isolated from non-cyanide electrolyte. The layers were exposed to heat treatment, which favors the diffusion of zinc into copper and makes the creation of the Cu-Zn alloy conceivable. The structural and morphological parts of the aspects of the alloys were likewise analyzed, corrosion was studied by impedance spectroscopy.

Experimental

Cathodic polarization 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 obtained are similar to those obtained with other methods [23]. A heat treatment

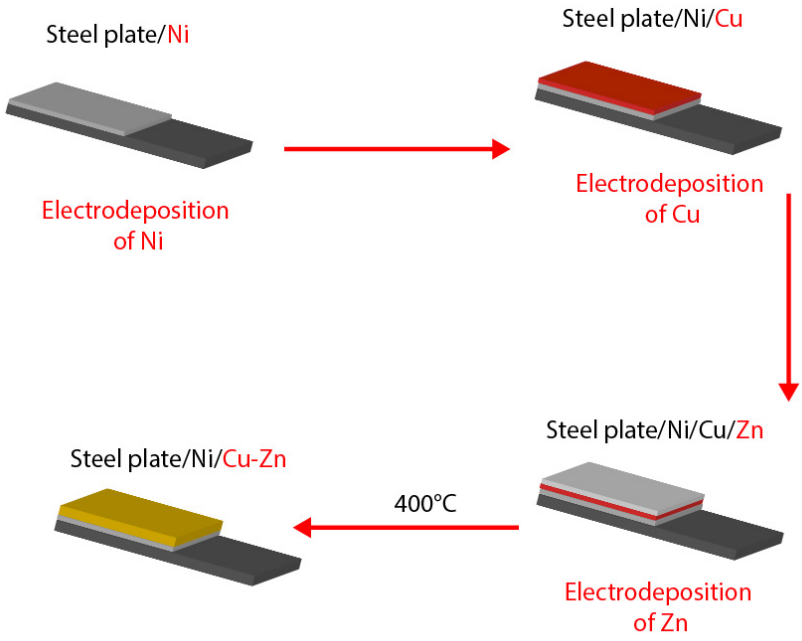

Fig. 1. Steps for elaboration of Cu/Zn alloy.

at 400°C provides the diffusion of zinc into copper to give Cu-Zn alloys.

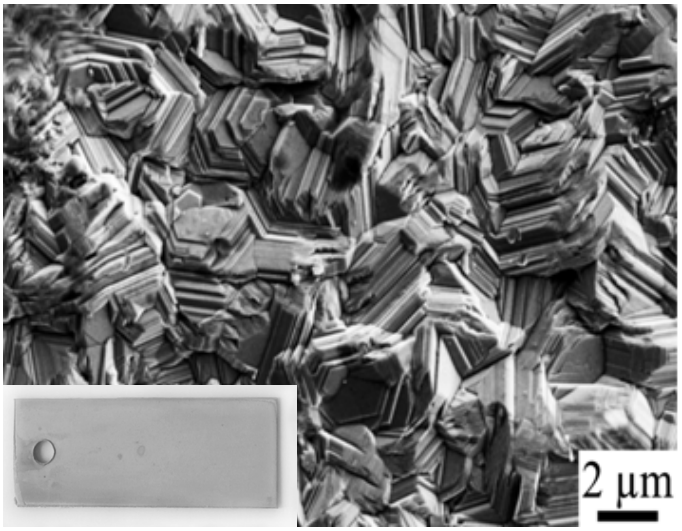

Fig. 2. SEM images of zinc deposits after 3 min of electrolyze onto steel-plate/Ni/Cu substrate and photograph of Zn film obtained before heat treatment.

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.

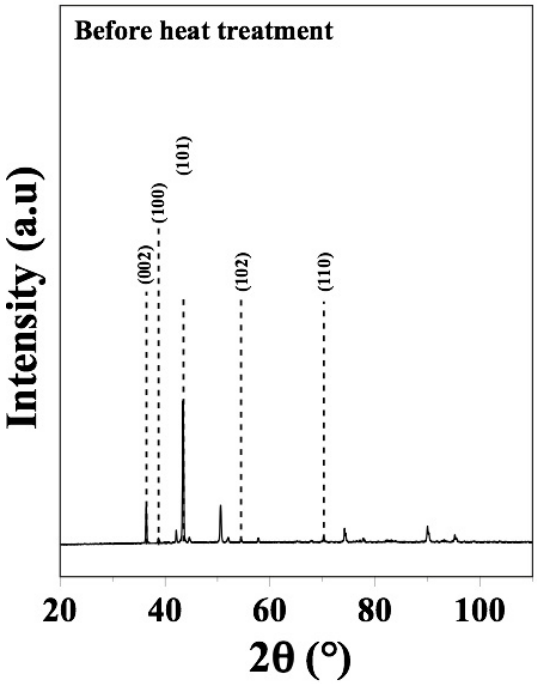

Fig. 3. XRD patterns of zinc layers on steel/Ni/Cu deposited from the bathroom of Table 1.

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, 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.

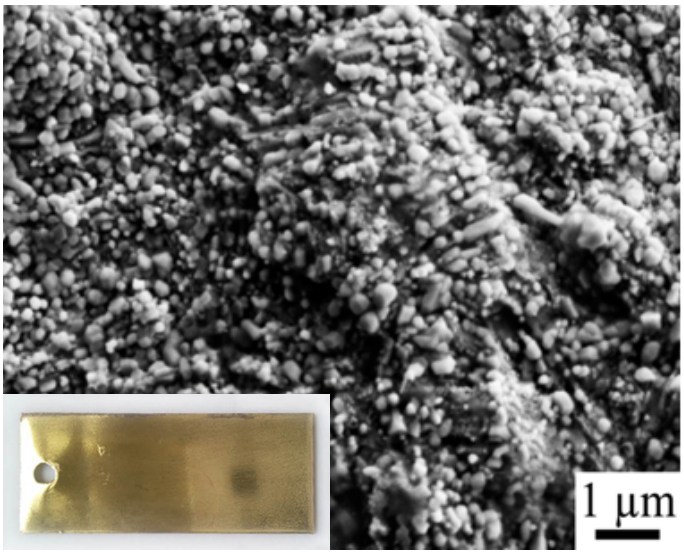

Fig. 4. SEM images of Cu-Zn deposits obtained after heat treatment at 400°C for 1h and photograph of Cu-Zn film obtained.

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].

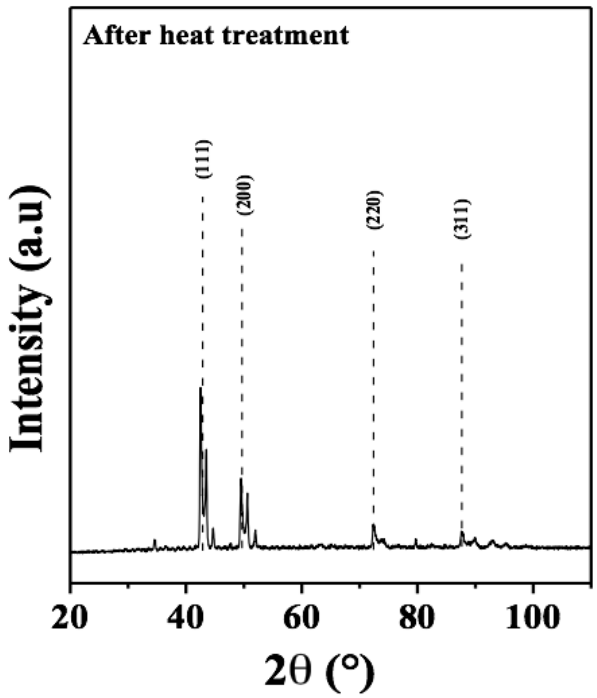

Fig.5. XRD patterns for Cu-Zn deposits obtained after heat treatment at 400°C for 60 min.

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)	1.198
R_a (nm)	3.751

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)
42.45	0.314	27.14

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 dif-

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

Before heat treatment		After heat treatment	
Zn (%)	Cu (%)	Zn (%)	Cu (%)
93	04	21	75

ferent 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.

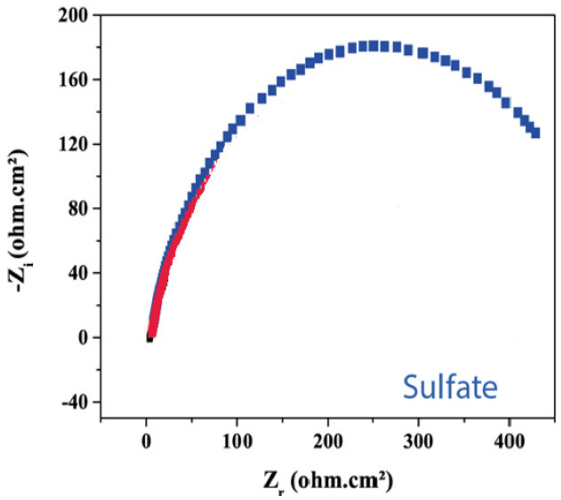

Fig. 6. Potentiodynamic polarization curve and Nyquist diagrams.

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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