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Environmentally friendlier and safer alternatives are required as replacement for highly toxic cyanide baths used by electroplating industries. Glutamate has proved to be an adequate complexing agent in alkaline copper and zinc plating baths due to its capability to form anionic complexes with those metal ions. Consequently, studies with a glutamate-based electrolyte for Cu-Zn alloys deposition are presented. In this work, cathodic polarization experiments on a rotating disk electrode in both static and rotating conditions were carried out using the novel electrolyte with and without the addition of a polymeric cationic surfactant (Polyquaternium-7) in the Cu-Zn-Glutamate system. Galvanostatic experiments, using flat steel electrodes as substrate, were carried...

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# Environmentally friendly electrolyte for the electrodeposition of Cu-Zn alloys

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*Environmentally friendlier and safer alternatives are required as replacement for highly toxic cyanide baths used by electroplating industries. Glutamate has proved to be an adequate complexing agent in alkaline copper and zinc plating baths due to its capability to form anionic complexes with those metal ions. Consequently, studies with a glutamate-based electrolyte for Cu-Zn alloys deposition are presented.*

*In this work, cathodic polarization experiments on a rotating disk electrode in both static and rotating conditions were carried out using the novel electrolyte with and without the addition of a polymeric cationic surfactant (Polyquaternium-7). The deposits were later dissolved by anodic stripping to characterize the electrochemical processes involved in the Cu-Zn-Glutamate system. Galvanostatic experiments, using flat steel electrodes as substrate, were carried out at different current densities with and without additive. These coatings were characterised by SEM, EDS and XRD. Cu-Zn alloys with compositions between 37-83 wt.% of copper were obtained.  $\alpha$ ,  $\beta$  and  $\gamma$  phases were obtained depending on the electrolyte composition and the applied current density.*

**Keywords:** Cu-Zn alloy; glutamate; polyquaternium-7, anodic stripping voltammetry, cathodic polarization

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## 1 Introduction

Copper, zinc and their alloys have been widely and successfully obtained by electrodeposition from alkaline cyanide-based electrolytes for the past hundred years [1–3]. Even though the coatings are satisfactorily employed for corrosion protection, for decorative purposes and as adhesion promoters of rubbers on steel in the tyre industry [4, 5], the high toxicity of the electrolytes and their

negative impact on the environment, triggered the search for an eco-friendly formulations capable of producing good-quality deposits, suitable for a wide variety of applications. Over the years, some alternative cyanide-free electroplating baths have been proposed. [5–13]. Usually, these electrolytes contain a complexing agent preventing copper oxide precipitation at pH values higher than 4. Generally, simple amino acids react with copper forming stable complexes[14, 15], inhibit-

ing copper precipitation in a wide pH range. Glutamic acid, for example, forms negatively charged very stable complexes with  $\text{Cu}^{2+}$  at pH values higher than 4. Based on this, copper glutamate has been used as complexing agent for alkaline copper electrodeposition with successful results [16–18] at  $6 < \text{pH} < 10$ . In recent studies, a zinc glutamate alkaline electrolyte proved to be an adequate zinc plating system as well [19]. Therefore, it was concluded that this complexing agent could be employed in the formulation of a bath for Cu-Zn alloys deposition.

Organic additives are widely used to improve the appearance of electrodeposited metals. Particularly, cyanide replacement in alkaline baths require the addition of levellers and brighteners to maintain the quality of coatings. Levellers from the polyquaternium family came up in the 1930s as antimicrobial agents and later, were employed in cleaning and cosmetics products as hair conditioners [20]. In previous investigations, additives from this family have been used for alkaline copper and zinc plating with successful results [21, 22]. Therefore, it is expected that a leveller from this family could have effect over alkaline brass plating.

Based on preliminary results [23], the experiments of the present work were designed to provide insight into the electrochemical processes that take place in the formulated plating bath. Cu-Zn deposits were produced at different current densities and the influence of an organic additive of the polyquaternium family [20] was evaluated [24–27] to prevent dusty or poorly adherent deposits.

## 2 Experimental

The electrolyte was prepared by dissolution of analytical grade reagents in double-distilled water to attain the following composition: 0.06 M  $\text{CuSO}_4$ , 0.14 M  $\text{ZnSO}_4$  and 0.6 M  $\text{C}_5\text{H}_8\text{NO}_4\text{Na}$ . The pH was

adjusted to 9 by the addition of KOH. For some experiments, the organic additive Polyquaternium-7 (P7), a copolymer of acrylamide and diallyldimethylammonium chloride, was added in a concentration of 30 g/L.

Cathodic polarization was carried out in a three-electrode cell both in absence and in presence of P7 using a vitreous carbon rotating disk electrode (RDE) as working electrode (0.283  $\text{cm}^2$ ) and Ag/AgCl (sat) electrode as reference electrode. All the electrochemical potential values in this work are expressed in this scale. The counter electrode was a platinum wire. The potential was swept from open circuit potential to a cathodic potential ( $E_c$ ) at 50 mV/s. Once  $E_c$  was reached, potentiostatic deposition was performed for 2 minutes. Afterwards, the deposits were dissolved by anodic stripping, sweeping the potential from the open circuit potential (OCP) to 1 V in the same electrolyte. The electrochemical tests were performed using an AUTOLAB PGSTAT 204 potentiostat/galvanostat controlled by Nova 2.0 software and the temperature was kept at  $60 \pm 0.5^\circ\text{C}$  using a FRIGOMIX 1495 thermostat.

Galvanostatic deposits (GD) were obtained on steel electrodes (25  $\text{cm}^2$ ) (Q-panel QD-36). The substrate was cathodically cleaned in a solution of NaOH (100 g/L) applying 0.1 A at  $50^\circ\text{C}$  for 1 minute and using a 304 stainless-steel anode. Then it was pickled in  $\text{H}_2\text{SO}_4$  10 % v/v for 1 minute at room temperature, washed with distilled water, ethanol and dried with warm air. The experimental conditions are presented in *Table 1*. The electrolysis time was set to maintain constant the cathodic charge at 13.6 C/ $\text{cm}^2$ .

The morphology and chemical composition of the GD were characterized by SEM using a Quanta200 FEI microscope (Tungsten filament source) equipped with an EDS detector.

Tab. 1: Experimental conditions for GD of Cu-Zn alloys

Sample identification	Additive P7 (g/L)	Current density (j, A/cm <sup>2</sup> )
1	0	0.032
2	0	0.048
3	0	0.064
4	30	0.032
5	30	0.048
6	30	0.064

Internal stress measurements were carried out using the bent strip technique with a Specialty Testing & Development Co. plating cell and nickel-iron alloy test strips (PN:2042B). Current density (CD) and deposition time were set to obtain a deposit thickness (t) of 3 µm according to the recommendations given in the standard procedure. Afterwards, the test strips were washed with distilled water, ethanol and fast-dried with a warm air jet. The total number of spread increments of the strip legs (U) was measured with PN 683 deposit stress analyser. Finally, internal stress (S) was calculated using Eq. 1:

$$S = \frac{U K M}{3t} \quad (1)$$

where M is the ratio between the elasticity modulus of the deposit and that of the substrate (0.81) and K is the calibration constant of the substrate (39.94 Nm<sup>-1</sup>).

XRD measurements were performed with Philips 3020 goniometer and a PW 3710 controller with CuKα radiation (λ = 1.54 Å) and a nickel filter. The detector was swept between 10° and 100° with a 0.04° step and 2 seconds per step.

### 3 Results and discussion

#### 3.1 Electrochemical characterization

Cathodic polarization curves in static conditions for the electrolytes without and with P7 are presented in *Figure 1*. The addition of P7 to the bath produced a drop in the current density caused by the adsorption of the additive on the surface of the cathode. This phenomena has been described by several authors in a wide variety of combinations of metals and additives [28, 29]. Moreover, the curve with P7 at 0 RPM shows a diffusion-limited current density of -0.01 A/cm which is not observed for the electrolyte without additives.

When the electrode was rotating at 1500 RPM, the peak was displaced ~0.1 V towards more cathodic potentials (*Fig. 1*). This effect is in agreement with Dow et al. [24] that established that quaternary ammonium-based additives are more effective under strong forced convection hydrodynamics.

*Figures 2-5* show anodic stripping voltammetry curves. For  $E_c = -1$  V, two anodic peaks (A1 and A2)

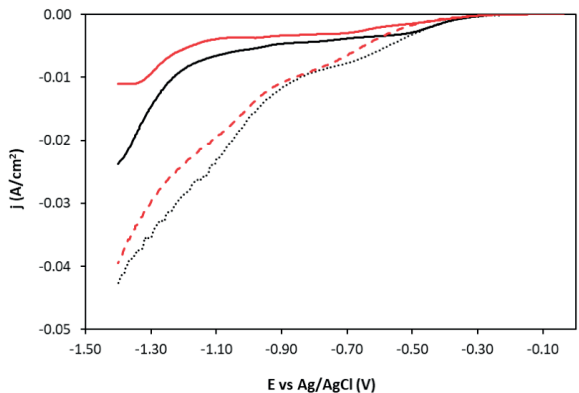


Fig. 1: Cathodic polarization curves for the electrolytes without additive at 0 RPM (black continuous), 1500 RPM (black dotted) and with P7 at 0 RPM (red continuous), 1500 RPM (red dotted).

Fig. 2: Anodic stripping voltammetry curves without additive for  $E_c = -1$  V at 0 RPM (black continuous) and 1500 RPM (red dotted)

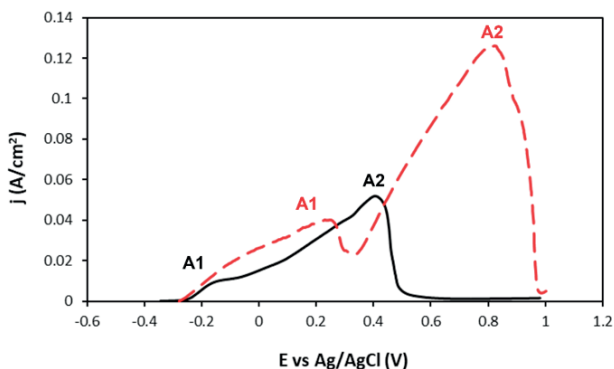
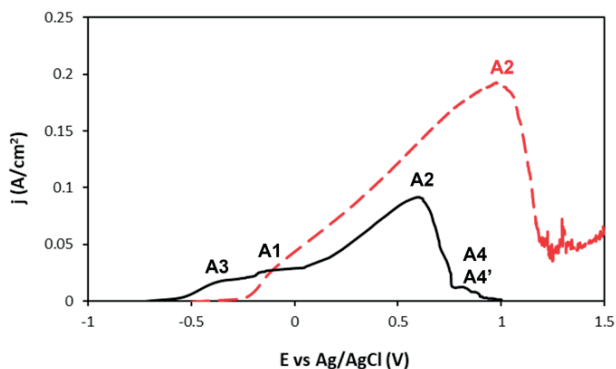
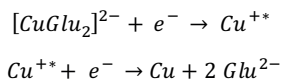


Fig. 3: Anodic stripping voltammetry curves without additive for  $E_c = -1.4$  V at 0 RPM (black continuous) and 1500 RPM (red dotted)



were registered both at 0 and 1500 RPM for the electrolyte without P7 (Fig. 2). Comparing  $E_c$  with standard potentials for copper and zinc, it is expected that only copper deposits at -1 V, and therefore, these anodic peaks can be assigned to the dissolution of Cu in a two-step mechanism [16]:



where  $Cu^{+*}$  stands for some complex formed between  $Glu^{2-}$  and  $Cu^+$ .

For  $E_c = -1.4$  V at 0 RPM, additional peaks were registered during anodic stripping: A3 at -0.36 V

and A4/A4' between 0.82 and 0.88 V. These peaks disappear and only A2 was observed at 1500 RPM (Fig. 3). The latter could indicate that the processes represented by peaks A3 and A4/A4' involve soluble species which are removed from the cathode surface as the electrode rotates. The dissolution mechanism of Zn in alkaline media has been extensively studied in the past [30, 31], showing this is a complex process involving various soluble ions and precipitates. The appearance of these peaks for  $E_c = -1.4$  V and their splitting tendency indicate that they could be related to Zn oxidation process and that more than one Zn-Glu soluble species and/or Zn oxides/hydroxides may be involved in this process [19].

Fig. 4: Anodic stripping voltammetry curves with P7 for  $E_c = -1V$  at 0 RPM (black continuous) and 1500 RPM (red dotted)

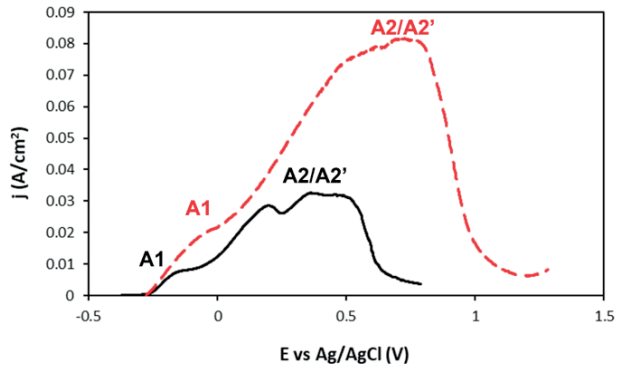
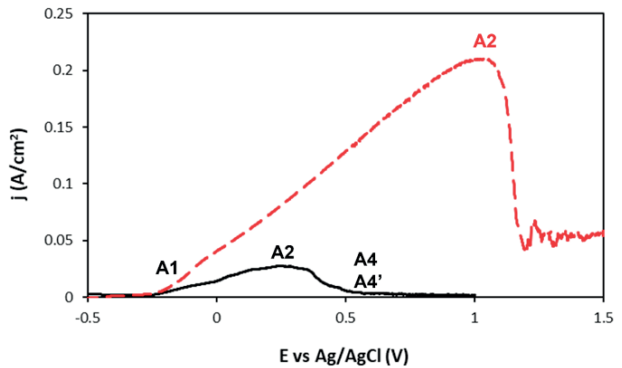


Fig. 5: Anodic stripping voltammetry curves with P7 for  $E_c = -1.4V$  at 0 RPM (black continuous) and 1500 RPM (red dotted)



Figures 4 and 5 show the anodic stripping curves of the deposits obtained for the electrolyte with P7. When  $E_c = -1V$ , A2 splits in 2 peaks in presence of the additive at 0 and 1500 RPM. This behaviour has been observed in Cu-glutamate and Cu-ammonia electrolytes and has been attributed to the disproportionation of  $Cu^+$  ions on the metallic surface producing  $Cu^{2+}$  ions [16, 32]. The latter was not observed for  $E_c = -1.4V$ , indicating that a different deposit is obtained at more cathodic potentials for both 0 and 1500 RPM.

As it was discussed in the cathodic scanning, the additive produced a drop in the current density and consequently, in the amount of material deposited. Hence, the Figure 6 show the images

of the deposits obtained on the RDE at the end of each cathodic polarization. Particularly, samples obtained at 1500 RPM were bright and properly levelled, indicating that the effectivity of this additive depends on convection [27]. Also, the changes in coloration support the hypotheses that the two metals are codepositing when the cathode is polarized to  $-1.4V$ .

### 3.2 Galvanostatic deposits

The appearance of the GD (Tab. 1) can be seen in Figure 7. The samples 1, 2 and 4 were similar in brightness and colour, but sample 3 presented yellow areas. Samples 5 and 6 resulted dark and powdery.

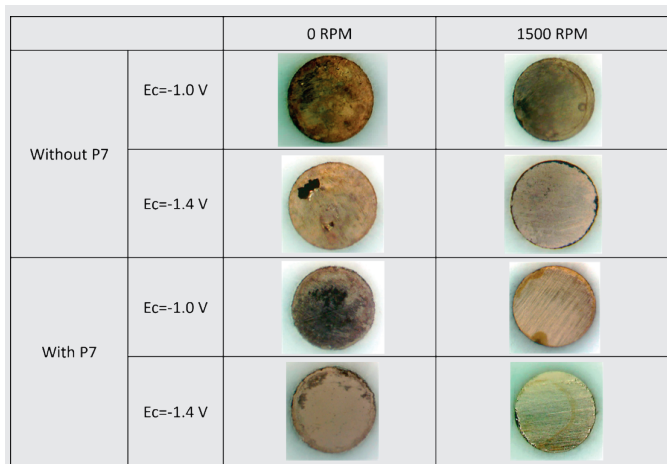


Fig. 6: Deposits obtained on the RDE at the end of each cathodic polarization with and without P7

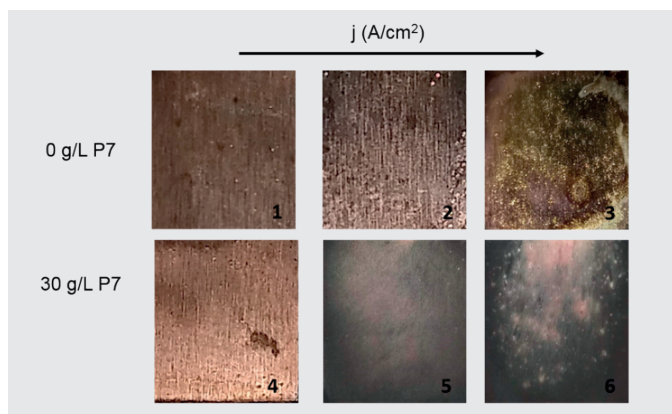


Fig. 7: Galvanostatic deposits obtained in the conditions shown in Table 1

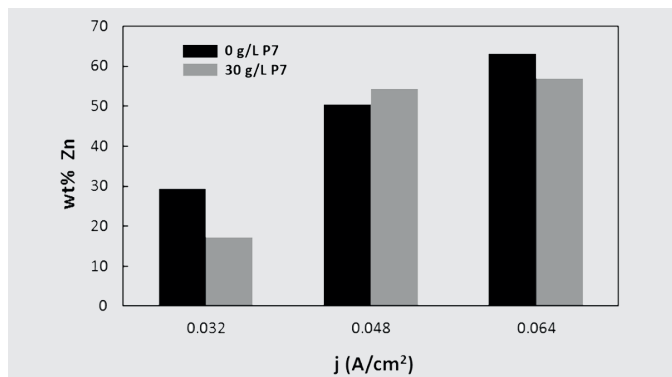


Fig. 8: Composition of the GD determined by EDS



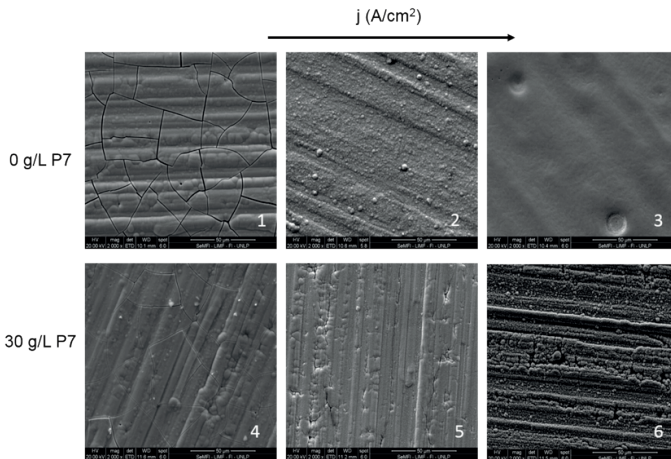


Fig. 9: SEM images of GD at 2000X

The composition of the deposits was determined by EDS and is presented in *Figure 8*. As expected [33], a raise in  $j$  favoured the deposition of the less noble metal (Zn) since the electrode potential becomes more cathodic and the deposition of Cu is limited by mass transport. The addition of P7 modified the zinc content of the deposits, reducing it for the extreme tested values and increasing it for  $0.048 \text{ A/cm}^2$ .

*Figure 9* shows SEM images of the surface of the samples 1-6 at 2000X. Sample 1 presented a globular morphology copying the substrate surface. Cracks were observed all over the coating. This have also been observed for copper coatings obtained from a glutamate-based electrolyte [16] and in Cu-Zn deposits generated with different non-cyanide electrolytes [23, 34]. The same microstructure with smaller grains was found in sample 2 whereas the surface of sample 3 was covered with a smooth, crack free coating.

When P7 was added to the electrolyte, the appearance of cracks was diminished at  $0.032 \text{ A/cm}^2$  and the globular morphology was less notorious at

$0.048 \text{ A/cm}^2$ . However, the effect was inverse for sample 6 which showed a marked globular morphology in comparison with sample 3.

The diminishment of the cracks in the coating observed for sample 4, led to the hypotheses that P7 might influence the internal stresses of the deposits. Then, the internal stresses of the coatings were determined at  $0.032$  and  $0.064 \text{ A/cm}^2$ . The results are presented in *Table 2*. For  $j=0.064 \text{ A/cm}^2$  no difference was detected in  $S$  despite the increase in the Cu content of the alloy in the sample produced with additive. When the coating was obtained at  $0.032 \text{ A/cm}^2$  with P7, higher %Cu and  $S$  were measured although less cracks have been observed by SEM.

Tab. 2: Internal stress of Cu-Zn alloys

Sample identification	$S$ (MPa)	% Cu
1	25.2	70.7
3	18.0	36.9
4	32.4	82.8
6	18.0	43.0



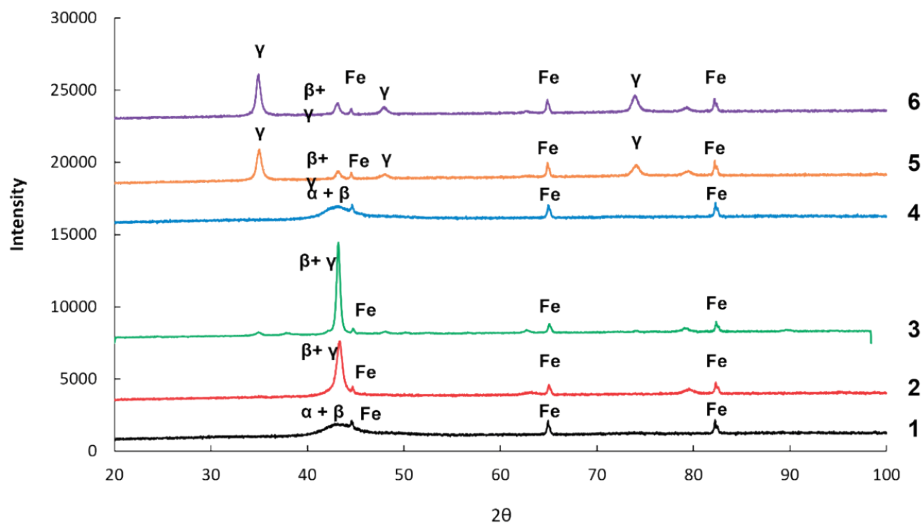


Fig. 10: XRD patterns obtained for GD deposits

Figure 10 shows the XRD spectra of the GD from Table 1. Neither metallic zinc nor metallic copper was detected, indicating that Cu-Zn alloy is present in all the deposits, being  $\alpha$ ,  $\beta$  and  $\gamma$  phases of brass the main components. Coatings 1 and 4 presented a wide peak at approximately  $43^\circ$  which may correspond to overlapping of phases  $\alpha$  and  $\beta$  signals. All the samples showed the characteristic peaks of the substrate (Fe;  $45^\circ$ ,  $65^\circ$  and  $82^\circ$ ). Samples 2, 3, 5 and 6 presented three other peaks: a sharp one at  $43^\circ$  with higher intensity than the two small shoulders found at  $63^\circ$  and  $80^\circ$ . These peaks are consistent with the presence of  $\beta$  and  $\gamma$  phases. The sharp peak at  $43^\circ$  was more notorious in deposits 2 and 3 than in samples 5 and 6, which presented three additional peaks at  $35^\circ$ ,  $48^\circ$  and  $74^\circ$ , corresponding to  $\gamma$  phase. Hence, the difference in texture can be attributed to additive effect. This is consistent with the findings reported by Özdemir et al. for Cu-Zn alloys deposited from citrate baths [35]. There is a marked influence of  $j$  in the composi-

tion and phase distribution of the deposits. The additive P7 favours the deposition of  $\gamma$  phase with orientation (222) ( $35^\circ$ ) and inhibits the deposition of  $\beta + \gamma$  phases ( $43^\circ$ ).

According to Brenner,  $\alpha$  and  $\beta$  phases have contents of Cu between 50 and 100 % and correspond to yellow and reddish alloys while  $\gamma$  phase usually contains 32.5-41.5 % Cu. Compositions of alloys not included in those ranges correspond to mixtures of phases (Fig. 11) [33]. The findings reported in this work are consistent with the data provided by the author.

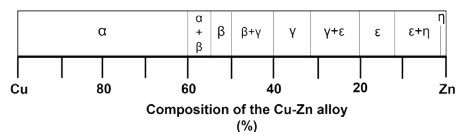


Fig. 11: Phases vs composition of Cu-Zn alloys taken from "Electrodeposition of alloys. Principles and practice. Volume 1" by A. Brenner

## 4 Conclusions

A stable cyanide free electrolyte for brass deposition was obtained and tested.

Cu-Zn alloys were successfully electrodeposited from a mild alkaline electrolyte containing glutamate as complexing agent. Composition of the alloys were between 17 and 63 wt% of Zn.

The addition of polyquaternium additive P7 produced a drop of the cathodic current density which is indicative of the levelling effect of the additive by its adsorption on the surface of the cathode. Also, P7 modified the zinc content of the deposits.

XRD studies showed that current density and the presence of the organic additive strongly influenced the phases and textures of the coatings obtained during electrodeposition, particularly the appearance of peaks corresponding to  $\gamma$  phase at higher current densities.

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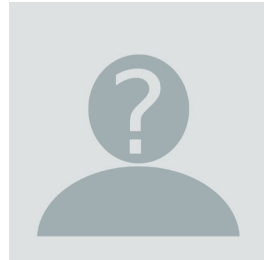
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