



## Electrodeposition of copper–zinc alloys in pyrophosphate-based electrolytes

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### Abstract

Copper–zinc alloy coatings were deposited on mild steel substrates using pyrophosphate-based electrolytes at room temperature and under continuous current. The use of polyligand electrolytes was also investigated, as well as the influence of organic additives on the composition, morphology and electrochemical properties of the coatings. The results showed that good quality copper–zinc alloy deposits could be produced in pyrophosphate-based polyligand electrolytes, especially with the addition of allyl alcohol.

### 1. Introduction

Electrodeposition of metallic layers is generally practised to modify the substrate surface in order to produce a wide range of useful materials with improved mechanical, decorative, electrochemical, electrical, magnetic or optical properties. Thus, less expensive materials can be used as substrates, making this process economically attractive. Compared to pure metal coatings, alloy coatings obtained by electrodeposition show better properties, since their chemical composition can be varied to the required function.

On the other hand, alloy electrodeposition is more complex than single metal deposition and involves control of several chemical and operational parameters. In practice, these parameters are often chosen empirically. Therefore, it is important to develop a more scientific approach leading to a better fundamental understanding of the codeposition phenomenon. This will lead to improved process performance and reliability, as well as the establishment of new alloy systems.

Simultaneous reduction of two or more cations on the cathode surface can only be achieved if their reduction potentials are similar [1], as shown in Equation 1. Their reduction potentials will depend on the correspondent standard potential,  $E^\circ$ , their respective activities in the solution,  $a$ , and the overpotential,  $\eta$ .

$$E_1^\circ + \frac{RT}{nF} \ln a_1 - \eta_1 = E_2^\circ + \frac{RT}{nF} \ln a_2 - \eta_2 \quad (1)$$

The reduction potentials of metal ions with different standard potentials can be approximated by varying

their activities in solution. This way, high quality metallic alloy coatings are usually obtained by using complexing agents, which diminish the activity of the nobler metallic ion in the solution and allow for their simultaneous deposition [1, 2]. Several papers have described the electrodeposition of different kinds of alloy by means of complexing agents [3–7].

Cyanide has been conventionally used as the complexing agent in Cu–Zn electrolytes [2, 8], despite its high toxicity and the need of a rigorous maintenance and control of its solutions. In the search for alternatives to conventional cyanide electrolytes, several copper–zinc electroplating baths have been proposed [7, 9–13]. Among them, pyrophosphate-based electrolytes are good and economical nontoxic alternatives for copper–zinc alloy electrodeposition [7, 10, 13]. These solutions have high stability and the treatment of wastewater is less expensive than for the cyanide solutions [10, 13]. High quality decorative coatings on different kinds of substrate can be produced at room temperature [2]. The coating composition depends on current density and electrolyte composition. Higher temperatures allow the use of higher current density values but have no significant effect on current efficiency, which is generally close to 100%. Solution stirring increases current density, current efficiency and copper content in the copper–zinc coatings from these electrolytes [13].

However, pure pyrophosphate electrolytes are associated with some problems; the production of hard and dark coatings in long lasting electrolysis, for example [14]. Zinc-rich alloys can only be obtained with lower activity of copper ions and/or higher free pyrophosphate

ligand electrolytes [15]. Thus, the use of polyligand pyrophosphate-based electrolytes is an interesting alternative to overcome these problems [10, 13, 16–18]. In such electrolytes the main complexing agent is the pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) ion. An auxiliary ligand is also added to form a more stable copper-mixed-ligand complex. Consequently, copper reduction is more efficiently inhibited, while zinc reduction is favoured at the cathode. Moreover, control of the alloy chemical composition becomes more effective [10, 14].

In this work, Cu–Zn alloy coatings with an average thickness of  $1.2 \times 10^{-5}$  m, were produced on mild steel substrates from pyrophosphate-based electrolytes. The effects of the deposition parameters, such as current density and the electrolyte chemical composition on the alloy coating composition, morphology, and electrochemical behaviour were evaluated. The aim of this study was to contribute to a better insight on the behaviour of Cu–Zn electrodeposition from pyrophosphate-based electrolytes in order to attain a more efficient control of the alloy coating properties.

## 2. Experimental details

### 2.1. Cathodic polarization curves

Cathodic polarization curves were galvanostatically obtained in a current density range of 1 to  $1000 \text{ A m}^{-2}$ . Square plates of mild steel AISI 1008 ( $7.40 \times 10^{-5} \text{ m}^2$ ) were used as working electrodes, while a  $1.90 \times 10^{-2} \text{ m}^2$  brass plate (63% Cu, 37% Zn) acted as counter electrode. The reference electrode was a saturated mercury (I) sulphate electrode (SSE).

The polarization curves were obtained in the electrolytes shown in Table 1. In these solutions, bath 1 is the base pyrophosphate bath, where potassium pyrophosphate ( $\text{K}_4\text{P}_2\text{O}_7$ ) is the main ligand. The other components (additives and ligands) were added to this base solution. The organic additives consisted of levelling agents (butynediol and allyl alcohol) and a stress-relieving compound (saccharin). All experiments were carried out at room temperature, under stirring and at pH 8.0.

### 2.2. Alloy electrodeposition experiments

Cu–Zn alloy electrodeposition experiments were also performed in the solutions shown in Table 1. Four

current density values were chosen from the polarization curves previously obtained in order to produce coatings with different compositions: 77, 116, 153 and  $193 \text{ A m}^{-2}$ . The coatings were produced using the same system and deposition conditions described in item 2.1. Plates of mild steel AISI 1008 with an exposed area of  $4.45 \times 10^{-4} \text{ m}^2$  were used as working electrodes.

Each alloy coating was analysed by atomic absorption spectroscopy (AAS) to determine the content of the elements. Partial polarization curves were also plotted by calculating the effective corresponding currents for copper and zinc deposition from the element contents in the alloy coating and the current efficiency [10]. In each case, the partial currents were associated with the corresponding potential response of the total applied current density.

The influence of deposition parameters on the morphology of copper–zinc coatings was analysed by scanning electron microscopy (SEM).

### 2.3. Corrosion experiments

The coatings obtained in the solutions shown in Table 1, at  $116 \text{ A m}^{-2}$ , were electrochemically evaluated by anodic potentiostatic polarization curves. The experiments were performed in a 0.5 M NaCl solution, at pH 5.5 and room temperature. The counter electrode was platinum, while the reference electrode was saturated calomel (SCE).

## 3. Results and discussion

### 3.1. Cathodic polarization curves

Figure 1 presents cathodic polarization curves of steel electrodes in the solutions described in Table 1. The main objective of these experiments was not only to select the current density values to obtain alloy deposits but also to detect the effects of the addition of the auxiliary ligand ( $\text{H}_2\text{PO}_4^-$ ) and/or the organic additives on the cathodic behaviour of the solutions.

The curves in Figure 1 are almost coincident, regardless of the bath composition used. Earlier reports [14, 19] showed that the discharge of metallic pyrophosphate-based complexes might occur as follows:

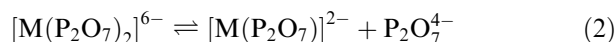


Table 1. Chemical composition of electrolytes ( $\text{mol L}^{-1}$ )

Bath	$\text{CuSO}_4$	$\text{ZnSO}_4$	$\text{K}_4\text{P}_2\text{O}_7$	$\text{KH}_2\text{PO}_4$	Saccharin	Butynediol	Allyl Alcohol
1	0.02	0.20	0.90	–	–	–	–
2	0.02	0.20	0.90	0.07	–	–	–
3	0.02	0.20	0.90	0.07	0.01	–	–
4	0.02	0.20	0.90	0.07	–	0.0058	–
5	0.02	0.20	0.90	–	–	–	0.07
6	0.02	0.20	0.90	0.07	–	–	0.07

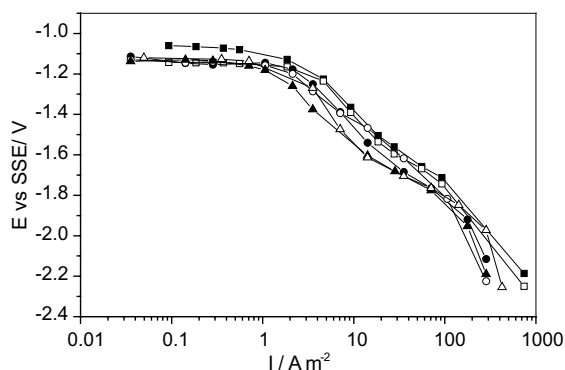
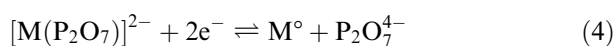
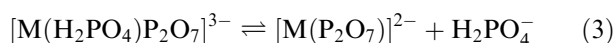


Fig. 1. Galvanostatic polarization curves in the solutions of Table 1. Key: (■) bath 1, (□) bath 2, (●) bath 3, (○) bath 4, (▲) bath 5, (△) bath 6.



It is noteworthy that the electrochemical reaction is the common step on the final dissociation path of both complexes. Therefore, these results show the limitation of the total polarization technique as a unique tool to describe the cathodic process dependence on electrolyte composition.

### 3.2. Alloy electrodeposition

#### 3.2.1. Chemical composition of the coatings

Copper and zinc contents in the coatings produced in the solutions listed in Table 1 were susceptible to the chemical composition of the solution and the current density changes, as can be observed in Figure 2. The solution composition significantly affects the Cu–Zn codeposition process and, apart from the case of deposits obtained in the solution with saccharin (bath 3), the copper content decreases with increase in current density, as already observed [20].

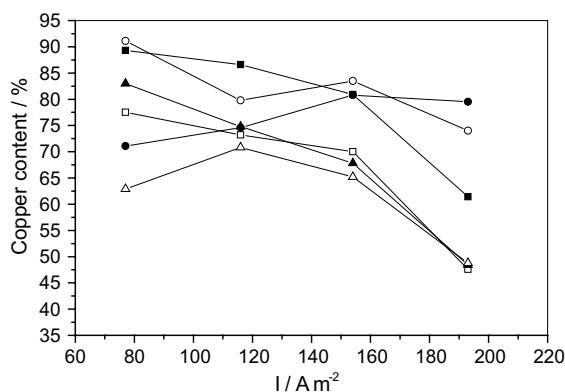


Fig. 2. Copper contents of coatings obtained from the solutions of Table 1. Key: as given in Figure 1.

Figure 2 also shows the effect of monobasic phosphate on the alloy deposition behaviour (bath 2). The coatings produced in this bath show lower copper contents if compared to those obtained from bath 1. The monobasic phosphate ( $\text{H}_2\text{PO}_4^-$ ) ion was added to the base pyrophosphate bath as an auxiliary ligand, sharing a unique coordination sphere when the complex is formed. This is the basic principle of polyligand electrolyte systems: to form more stable copper complexes and to decrease copper activity in the solution [10,14,16–18]. Since the electrochemical step is the same for the discharge of both complexes (Equation 4), the one with the lower dissociation constant would decrease copper activity in the solution more efficiently. If  $K_{D2} = 1.70 \times 10^{-4}$  and  $K_{D3} = 3.57 \times 10^{-5}$  [14] are the dissociation constants for the chemical steps of the copper-pyrophosphate complex and the copper-mixed-ligand complex, respectively (Equations 2 and 3), the higher stability of  $[\text{Cu}(\text{H}_2\text{PO}_4)\text{P}_2\text{O}_7]^{3-}$  becomes evident. This increases the copper deposition overpotential, since an additional energy is required to dissociate the complex before the effective discharge of copper ions on the cathode surface [10, 16].

The organic compounds added to the solutions in Table 1 (baths 3 to 6) strongly affect the alloy deposition process (Figure 2). Saccharin addition to the electrolyte containing the auxiliary ligand (bath 3) disturbs its complexing characteristics. Figure 2 shows an increase in the copper contents of the coatings obtained in bath 3, as compared to those produced in bath 2, mainly at higher current densities. This fact can be attributed to instability of the polyligand complex in the presence of this brightening agent, causing an increase in the activity of copper ions. To the best of our knowledge, there are no data in the literature concerning the effects of saccharin on this kind of mixed complex. For this reason, a more detailed investigation must be carried out to better understand this issue. Similar results were obtained for coatings produced in the solution containing butynediol (bath 4), also suggesting a decrease in the stability of the copper mixed complex due to the presence of this additive.

The addition of allyl alcohol to the base solution, with and without monobasic phosphate (baths 5 and 6), provided a great reduction in copper contents in the coatings, as compared to those obtained in the base solution. Although proposed as a levelling agent, very few data concerning the effects of allyl alcohol on copper–zinc alloy electrodeposition can be found in the literature. Vagarlyuk et al. [21] indicated that copper (1)-allyl alcohol complexes may exist in acid medium. However, despite the lack of information on the formation of such complexes in basic medium, our results suggest that the presence of allyl alcohol would decrease copper activity in the solution due to the formation of a new complex. In addition, different and more stable complexes (or mixed complexes) could be formed, combining allyl alcohol and pyrophosphate ligands.

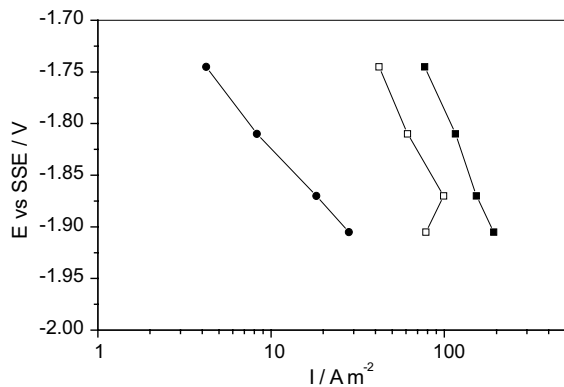


Fig. 3. Partial polarization curves of alloy electrodeposition in base pyrophosphate solution (bath 1). Key: (■) total, (□) copper and (●) zinc.

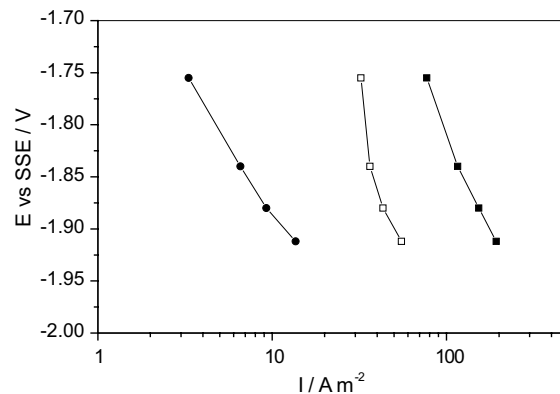


Fig. 5. Partial polarization curves of alloy electrodeposition in pyrophosphate + monobasic phosphate solution containing saccharin (bath 3). Key: (■) total, (□) copper and (●) zinc.

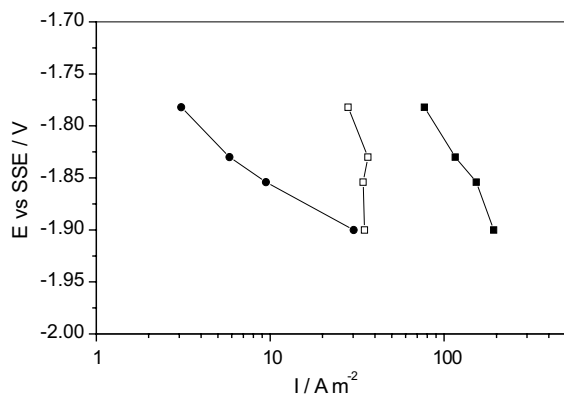


Fig. 4. Partial polarization curves of alloy electrodeposition in pyrophosphate + monobasic phosphate solution (bath 2). Key: (■) total, (□) copper and (●) zinc.

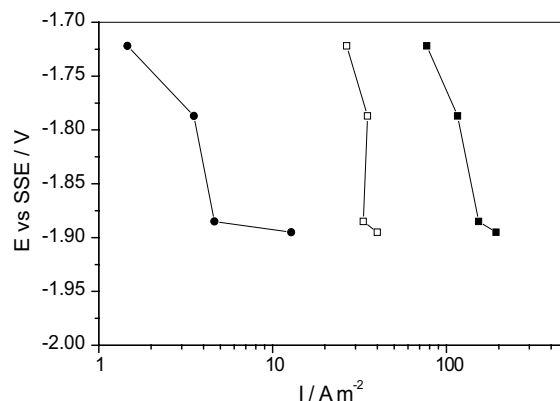


Fig. 6. Partial polarization curves of alloy electrodeposition in pyrophosphate + monobasic phosphate solution containing butynediol (bath 4). Key: (■) total, (□) copper and (●) zinc.

### 3.2.2. Partial polarization curves

The literature states that the chemical dissociation step of the copper-mixed complex is the one mainly responsible for the increase in the copper deposition overpotential [16]. Actually, this effect can be experimentally observed by plotting the partial polarization curves, taking into account the mass contribution of each alloy element and their corresponding current efficiency for all the electrodeposition conditions. Figures 3 and 4 show the partial polarization curves for baths 1 and 2 in Table 1, respectively. The copper partial polarization curve for bath 1 (Figure 3) is near the total curve, indicating that the alloy is rich in copper. On the other hand, for the solution also containing monobasic phosphate (bath 2), the copper partial polarization curve is more biased and far from the total curve (Figure 4). Therefore, the increase in the overpotential for copper deposition, caused by the formation of copper-mixed complex, inhibits copper deposition. However, this phenomenon only represents an enhancement of zinc deposition at high current densities. Lower current efficiencies found at low current densities suggest that  $H_2$  evolution may be favoured under these conditions.

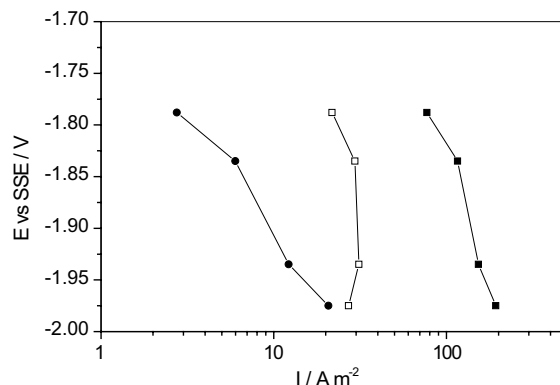


Fig. 7. Partial polarization curves of alloy electrodeposition in base pyrophosphate solution containing allyl alcohol (bath 5). Key: (■) total, (□) copper and (●) zinc.

The effects of the organic compounds on the Cu–Zn electrodeposition process from the solutions in Table 1 (baths 3 to 6) can be observed in Figures 5 to 8. The presence of saccharin (bath 3) gives rise to a copper partial polarization curve slightly closer to the total curve, especially at high current densities, if compared to

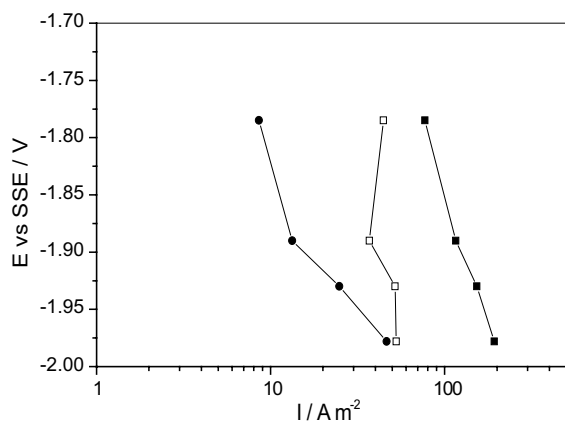


Fig. 8. Partial polarization curves of alloy electrodeposition in pyrophosphate + monobasic phosphate solution containing allyl alcohol (bath 6). Key: (■) total, (□) copper and (●) zinc.

bath 2. This indicates that saccharin affects the copper-mixed complex stability in the solution. Simultaneously, a small depolarization effect can be observed on the zinc curve, only at low current densities. At high current values, however, an opposite effect is verified, probably due to an increase in  $H_2$  evolution.

In Figure 2 it was shown that the presence of butynediol (bath 4) led to an increase in copper content in the alloy coatings. This was associated with changes in the dissociation of the mixed complex, allowing free copper deposition. In principle, one could expect a copper partial polarization curve closer to the total curve. However, the presence of butynediol caused no significant changes in such curves (Figure 6), as compared to that obtained without the additive (Figure 4). This unexpected result can be explained by taking hydrogen reduction into account. Since butynediol adsorbs on the substrate surface and catalyses the hydrogen reduction [22], the current efficiency decreases [10]. Thus, although copper deposition was enhanced, the observed decrease in current efficiency brought about a copper partial curve at the same polarization levels as obtained in bath 2. Moreover, this phenomenon inhibits zinc deposition, which accounts for the shift of the zinc partial polarization curve towards lower current values (Figure 6).

In both baths containing allyl alcohol (baths 5 and 6), as the current increases, copper partial polarization curves are shifted to more negative potentials (Figures 7 and 8). By contrast, zinc partial polarization curves are depolarised and closer to the copper ones, mainly at high current values. This effect is accentuated if the solution also contains  $H_2PO_4^-$  (Figure 8). As already shown, the presence of this additive seems to increase the stability of the pyrophosphate-based copper complexes, thus favouring zinc deposition. These results corroborated our assumption concerning the formation of a new mixed and more stable copper complex containing allyl alcohol, which would decrease copper activity in the solution more efficiently. However, a

more detailed investigation needs to be carried out in order to fully support this hypothesis.

### 3.3. Morphology of coatings and corrosion experiments

The morphological features (Figure 9) and the corrosion resistance of copper–zinc alloy coatings (Figure 10) are now presented and correlated to the results discussed before. Figure 9(a) shows that irregular and coarse coatings are produced in the base pyrophosphate solution (bath 1). Their corrosion behaviour is similar to that of pure zinc, with open circuit potential  $E_{oc} = -1.025 V$  and active dissolution in NaCl 0.5 M (Figure 10). The zinc content in these coatings was always lower than 20% (Figure 2), which may indicate zinc enrichment at the surface coating. The use of the base pyrophosphate bath seems to produce alloy coatings with the desired composition only at the beginning of the process [14, 23]. Subsequently, as the electrolysis continues, hydrogen reduction and the low buffer capacity of  $HP_2O_7^{3-}$  ions cause a pH increase on the cathode surface. As a consequence, the interfacial activity of  $P_2O_7^{4-}$  ions increases, as well as the stability of the copper-pyrophosphate complex, allowing for a local enhancement of Zn deposition. By X-ray diffraction analysis, Ishikawa et al. [23] confirmed the presence of nickel hydroxide hydrate in Cu–Ni coatings obtained in pyrophosphate solution. Therefore, the deposition of zinc hydroxide compounds on the electrode surface cannot be neglected.

More refined coatings are obtained in bath 2 (Figure 9(b)), which should improve their electrochemical behaviour. Indeed, Figure 10 shows that these coatings are nobler ( $E_{oc} = -0.420 V$ ) than those produced in bath 1, in spite of their lower copper contents (Figure 2), due to the increase in the overpotential for the discharge of copper ions, as already seen in Figure 4. Moreover, a more efficient buffer capacity of  $H_2PO_4^-$  ions could stabilize the interfacial pH and hinder the surface zinc enrichment observed in coatings from bath 1. Consequently, deposits from bath 2 have uniform bulk composition. Ishikawa et al. [23] observed that the use of a buffer substance in Cu–Ni pyrophosphate electrolyte improves Ni deposition, even though no significant effect was detected on the copper partial polarization curve.

Interesting results were also obtained with the coatings produced in baths 3 to 6. For instance, coatings obtained in the solution containing saccharin (bath 3) and butynediol (bath 4) present irregular, large and coarse grains (Figure 9(c)). In particular, coatings obtained from bath 4 show cracks, probably due to  $H_2$  reduction, which seems to be catalysed by the butynediol. This would increase the hardness of the coatings and cause fragile fractures on their surface [10]. The morphological characteristics of the deposits obtained in baths 3 and 4 are reflected by their inferior corrosion performances, compared to those coatings obtained in the absence of additives (bath 2) (Figure 10).

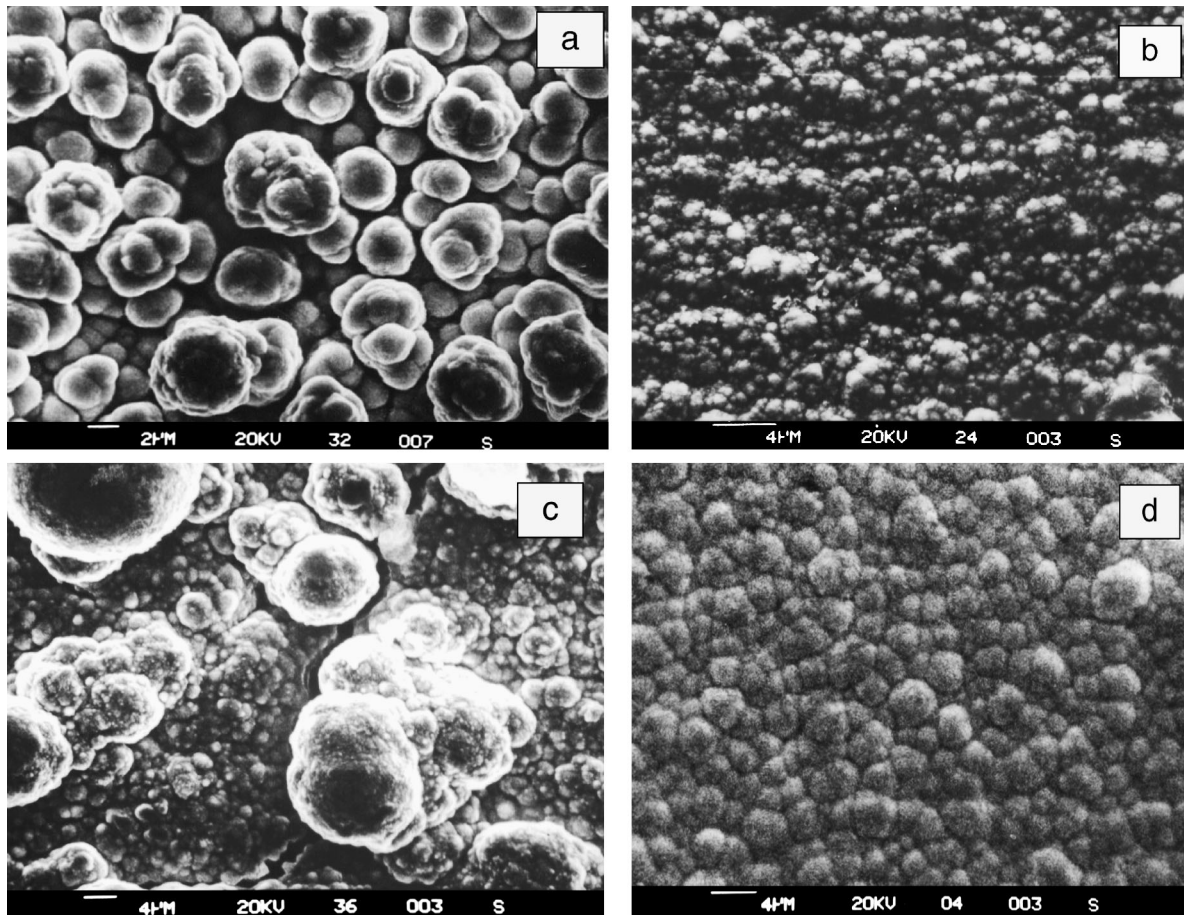


Fig. 9. Morphology of coatings from the solutions of Table 1: (a) bath 1; (b) bath 2; (c) bath 4; (d) bath 5.

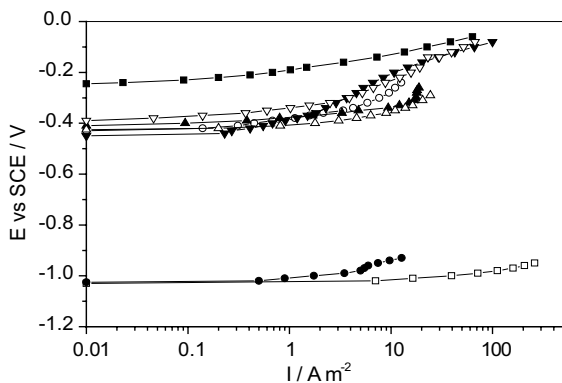


Fig. 10. Anodic polarization curves of coatings produced in the solutions of Table 1. Electrolyte: 0.5 M NaCl, pH 5.5, 25 °C. Key: (■) copper, (□) zinc, (●) bath 1, (○) bath 2, (▲) bath 3, (△) bath 4, (▼) bath 5 and (▽) bath 6.

The deposits produced in solutions with addition of allyl alcohol (baths 5 and 6) have a more regular and refined topography, with small grains and without cracks (Figure 9(d)). These coatings also showed the best corrosion performance (Figure 10). Shinier and more uniform coatings than those produced in the polyligand electrolyte (bath 2) were obtained by direct addition of allyl alcohol to the base pyrophosphate solution (bath 5). This suggests that allyl alcohol may

act not only as a levelling agent, but also affects alloy electrodeposition behaviour. It has already been verified by the partial polarization curves (Figure 7). Furthermore, this result also indicates that allyl alcohol may be used as a new and efficient auxiliary ligand to produce a more stable copper-pyrophosphate-based complex.

#### 4. Conclusions

Copper–zinc alloy coatings can be produced in pyrophosphate solutions, with different chemical compositions and current density conditions. The properties of the coatings may be improved by using an auxiliary ligand and/or a proper organic additive. The use of monobasic phosphate as an auxiliary ligand produces stable copper complexes and homogeneous coatings. On the other hand, the addition of saccharin and butynediol affects the stability of copper complexes and the quality of the coatings. The addition of allyl alcohol improves the morphology of the coatings, as well as their corrosion resistance, with or without monobasic phosphate in the electrolyte. This organic compound seems to act not only as a levelling agent, but also as a new and efficient auxiliary ligand, since it directly affects the copper partial polarization curve. This fact may be attributed to an increase in the stability of pyrophosphate-based copper complexes.

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