

Electrodeposition study of the Cu-Zn-Mo system in citrate/sulfate medium

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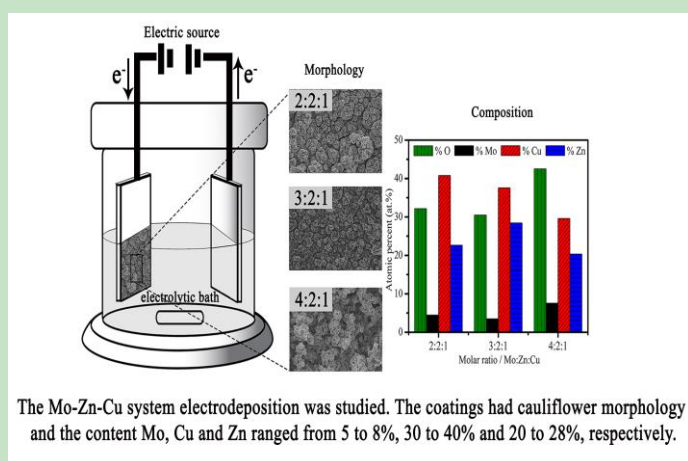
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ABSTRACT: Alloys and composites that contain molybdenum have been studied due to their excellent properties, such as corrosion resistance and catalytic activity. In this work, the parameters for Cu-Zn-Mo system electrodeposition were studied, such as deposition potentials and concentration of electroactive species. The deposition potentials were examined using cyclic voltammetry and anodic linear stripping voltammetry (ALSV), the deposit morphology was evaluated using scanning electron microscopy (SEM) and crystallographic characterization was carried out for X-ray diffraction (XRD). The voltammetry studies indicated co-deposition of the metals in potentials more negative than -1.2 V, and a potential deposition at -1.5 V was chosen. The coatings presented morphology compact with small agglomerated particles with cauliflower structures, and the content of molybdenum, copper, and zinc ranged from 5 to 8%, 30 to 40% and 20 to 28%, respectively.



1. Introduction

Alloys and composites of zinc (Zn) and copper (Cu) commonly called brass have excellent properties such as mechanical strength, malleability and resistance against corrosion; in addition, they are considered to be weakly harmful to the environment^{1,2}. On the other hand, molybdenum (Mo) compounds and oxides are also relevant in terms of their excellent resistance against corrosion and electrocatalytic activities³⁻¹⁰. Therefore, an alloy/composite composed of Cu, Zn and Mo may have applicability as corrosion resistant coating and electrocatalytic material. Methods that use thermal energy, such as thermal spraying¹¹ and melting metal in a vacuum or inert atmosphere¹², are utilized to get these materials, but

both methods are costly and expend a great deal of energy¹³. A reasonable option is electroplating because it is a generally simple technique, inexpensive and broadly utilized in the production of composites, metallic coatings, alloys and semiconductors on different substrates^{14,15}.

Recent research shows the possibility of Mo deposition with Zn and Cu^{14,16-18}. In these studies, the Zn-Mo composite is proposed as a corrosion resistant coating with low danger and environmentally friendly, in contrast to other anticorrosive alloys containing cadmium and chromium. One of the announced methods for getting this material was by potentiostatic deposition at -1.4 V, where an amount of 70% m/m Mo was incorporated on the surface of the coating¹⁴. Kazimierczak *et al.*, in another study,

obtained Zn-Mo coatings with up to 14% Mo and showed that the deposits with more than 1% Mo had amorphous or nanocrystalline characteristics¹⁶. In their turn, Cu-Mo compounds can be used as heat sinks or heat diffusers in electronic devices. Gotou *et al.*¹⁷ studied this system and obtained coatings with up to 22% m/m Mo with amorphous features, regardless of the amount of Mo in the coatings. Thus, a few studies have reported on Cu-Mo and Zn-Mo binary composites; however, there has been no report of Cu-Zn-Mo ternary system obtained by electrodeposition. As previously mentioned, the combination of these three elements could be interesting as a corrosion resistant coating, as with the case of Zn-Cu¹⁹⁻²¹ and Zn-Mo^{14,16,18} alloys and composites. In addition, the introduction of Mo in these coatings should significantly improve the electrocatalytic properties for water electrolysis because the presence of Mo in the iron group's alloys and composites has been described as responsible for the reduction of the overpotential of the hydrogen evolution reaction^{10,22-24}.

One of the issues in the electrodeposition of ternary systems is the stability and solubility of the salts used to formulate the deposition baths, which can be achieved by inserting specific complexing agents²⁵. However, aggressive and toxic complexes such as cyanides and chlorides are commonly used in the deposition baths of Zn and Cu alloys²⁶. In the perspective of environmental problems, it is proposed to utilize a complexing agent that stabilizes the electroactive species and is minimally aggressive and toxic. A complexing agent that fits this proposition is citrate; it is nontoxic and forms electroactive complexes with Cu (II) and Mo (VI)

over a wide pH range and with Zn (II) at acidic pH^{14,27,28}.

Considering these facts, the objective of this study was to propose a bath for electrodeposition of the ternary system with Cu (II), Zn (II) and Mo (VI) ions and to verify the conditions for the occurrence of the co-deposition of these three elements. For this, several molar ratios of the ions in the deposition bath were studied using sodium citrate as complexing agent, and morphological, compositional and crystallographic characterizations of the coatings were performed.

2. Experimental

The chemicals used were CuSO₄·5H₂O (> 99%), ZnSO₄·7H₂O (> 99%), Na₂MoO₄ (> 99%) and sodium citrate (Na₃C₆H₅O₇ > 99%), all analytical grade and without any purification. The electrolytic baths were prepared by the dissolution of sodium citrate in ultrapure water treated in the Milli-Q system (18.2 MΩ cm⁻¹), followed by the addition of the salts of the metal ions. According to the work of Kazimierczak *et al.*¹⁶ and Slupska and Ozga²⁹, which correlated the predominant Cu (II), Mo (VI) and Zn (II) species with respect to citrate concentrations and pH in the baths. For that all species to be electroactive in the baths the pH of the electrolyte should be between 3 and 5.5. Therefore, the pH of the electrolytic baths in this work was adjusted to 4 with sulfuric acid. The chemical composition of all baths is shown in **Table 1**.

Table 1. Chemical composition of the deposition baths used.

Baths	[Mo(VI)]/ mol L ⁻¹	[Zn(II)]/ mol L ⁻¹	[Cu(II)]/ mol L ⁻¹	[Citrate]/ mol L ⁻¹	[Mo(VI)]:[Zn(II)]: [Cu(II)]
1	-	0.04	0.02	0.1	0:2:1
2	0.04	-	0.02	0.1	2:0:1
3	0.04	0.04	0.02	0.1	2:2:1
4	0.06	0.04	0.02	0.1	3:2:1
5	0.08	0.04	0.02	0.1	4:2:1

A platinum disk of 0.1 cm² was used as the working electrode in the voltammetric studies. It was sanded in 0.25 μm diamond paste and then remained in sonication for 5 min in isopropyl alcohol before being rinsed with deionized water. The coatings were also produced in 1010 carbon

steel. For this, steel plates with exposed area of 2.6 cm² were used as working electrodes. The plates were treated with 5% sulfuric acid solution to remove the iron oxides. Then, they were rinsed with distilled water and sanded with sandpaper until the granulometry reached 600, and finally

they underwent basic degreasing in NaOH 3.0 mol L⁻¹ for 2 min. An Ag_(s)|AgCl_(s)|Cl⁻ (saturated KCl) electrode and a high surface area Pt grid were used as reference and auxiliary electrodes, respectively.

The voltammetric studies were performed in the potentials range of 1.5 to -1.5 V with a scan rate of 50 mV s⁻¹, three cycles were performed in each measurement. The deposition potentials were evaluated through cyclic voltammetry at different cathodic inversion potentials in the range of -1.0 to -2.0 V with a scan velocity of 50 mV s⁻¹. Electrochemical stripping analyses in the range of -1.0 to 1.0 V were obtained for the coatings deposited in -1.6, 1.75 and -2.0 V in the binary baths of Mo (VI) and Cu (II) (bath 4) and Zn (II) and Cu (II) (bath 5). The stripping analyses were carried out in 0.1 mol L⁻¹ sodium citrate solution at pH 4. The depositions were performed at constant potential in the range of -1.2 to -2.0 V for 1800 s. All measurements were performed at 25° C. The morphologies of the coatings were evaluated using scanning electron microscopy (SEM) with high-resolution field emission using an FE-SEM, ZEISS SUPRA 35, and the composition was analyzed through X-ray dispersive energy (EDX) spectroscopy using a FEI-XL30-FEG with an Oxford Instruments-Link ISIS 300 detector. The structural characterizations were performed using an X-ray diffractometer (Rigaku-DMax2500PC) with Cu K α = 1.5406Å, 40 kV voltage, theta-2theta configuration and a scan angle of 20-80° with a scanning speed of 2°/min.

3. Results and discussion

3.1. Voltammetric studies

The cathodic voltammograms for the baths with 2:2:1, 3:2:1 and 4:2:1 molar ratios of Mo(VI): Zn(II): Cu(II) on Pt are shown in Fig. 1. The peak c1 at 0.15 V and c2 at -0.1 V could be attributed to underpotential deposition (UPD) and bulk deposition of copper from the non-complexed Cu²⁺ ions, respectively³⁰. This is possible because the concentration of citrate (0.1 mol L⁻¹) in these baths was less than the total metal-ion concentration, which is evidence of the occurrence of Mo (VI), Zn (II) and Cu (II) noncomplexed species. It was also observed that peaks c1 and c2 presented higher cathodic currents when the concentration of molybdate was increased in the baths. Since the

molybdenum(VI) citrate complexes are more stable than copper (II) citrate complexes in the pH used, the increase of the concentration of MoO₄²⁺ ions led to a higher concentration of free Cu²⁺ ions in the bath^{31,32}. The increase of the Mo (VI) concentration caused a considerable increase in the peak current c3 in the region of -0.8 V, which was attributed to the deposition of molybdenum oxides/hydroxides (Fig. S1b). The peaks c4 and c5 were due to the reduction of Cu (II) and Zn (II) complexed with citrate, respectively (Fig. S1). The curves in Fig. 1 indicate that the cathodic current in potentials more negative than -1.25 V increased more significantly in the bath with a higher concentration of MoO₄²⁻ (curve 3). This current is due to the evolution of H₂, which is facilitated by the higher amount of Mo oxides/hydroxides deposited that is a catalytic species for hydrogen evolution reaction (HER)³³. In conclusion, an increase of MoO₄²⁻ concentration in the baths facilitates the deposition of molybdenum species; however, it leads to a higher evolution of hydrogen, which can lead to lower deposition efficiency and poor structure of the coatings.

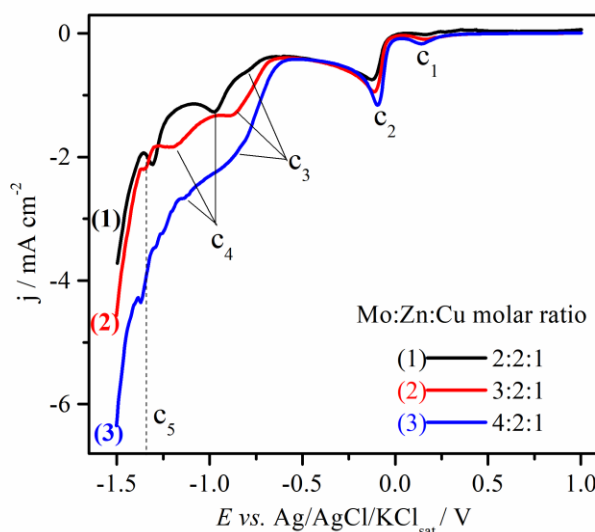


Figure 1. Cathodic voltammograms on Pt for baths Mo: Zn: Cu of molar ratios (1) 2: 2: 1 (bath 6), (2) 3: 2: 1 (bath 7) and 4: 2: 1 (bath 8) at T = 25 °C.

To find the best cathodic deposition potentials, a study was performed on different inversion cathodic potentials in the 2:2:1 Mo: Zn: Cu bath (bath 6), as shown in Fig. 2a. From -1.3 V, the currents were very high due to the HER (graph inserted in Fig. 2a), which made it difficult to visualize the processes; therefore, the study focused on the more positive potential regions.

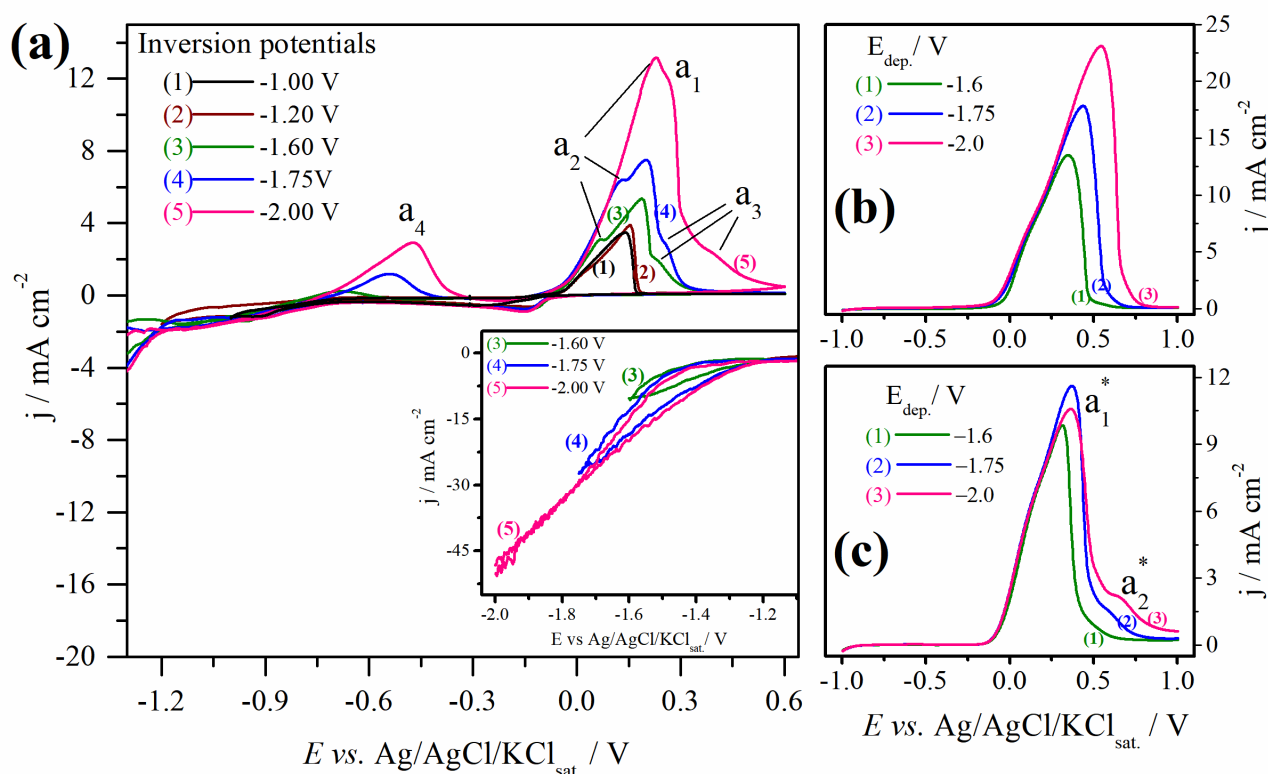


Figure 2. (a) Voltammograms on Pt for bath 3 of 2:2:1 molar ratio of Mo: Zn: Cu at inversion potentials -1.0V (line 1), -1.2 V (line 2), -1.6 (line 3), -1.75 V (line 4) and -2.0 V (line 5). (b) Stripping voltammetry curves for the coatings obtained on Pt in the bath 1 at -1.6, -1.75 and -2.0 V (b) stripping voltammetry curves for the coatings obtained on Pt in the bath 2 at -1.6, -1.75 and -2.0 V at $T = 25$ °C.

In the inversion potentials at -1.0 (line 1) and -1.2 V (line 2), only a cathodic and an anodic peak in the range of potentials of -0.25 to 0.25 V were identified as being attributed to deposition and dissolution of Cu. From the potential of inversion of -1.6 V, a peak (a₂) attributed to the dissolution of zinc or zinc-rich phase appeared, and for the more negative potentials (-1.75 and -2.0 V), larger anodic currents were presented, showing the favoring of the deposition of zinc at more negative potentials. The oxidation peaks in the range of 0 to 0.52 V potentials (a₁, a₂ and a₃) that appeared for the inverse potentials -1.6 (line 3), -1.75 (line 4) and -2.0 V (line 5) are attributed to the dissolution of copper and copper-rich phases. It can be concluded from the voltammetric studies that zinc-rich Cu-Zn phases and Cu-Mo composites can be electrodeposited at highly negative potentials simultaneously with the HER from the proposed baths.

The phases related to the anode peaks in the region of potentials of 0.0 to 0.52 V (a₁, a₂ and a₃) cannot be identified only by the voltammograms in Fig. 2a. Therefore, electrochemical stripping

analyses were performed for deposits obtained in the Zn(II): Cu(II) (bath 4) and Mo(VI): Cu(II) (bath 5) binary baths. The coatings were deposited in -1.6, -1.75 and -2.0 V for 5 min on Pt; these curves are shown in Fig. 2b and c, respectively. The stripping curves for the coatings obtained in the bath containing only Zn (II) and Cu (II) presented a shoulder followed by a peak with high anodic current, which was attributed to the dissolution of Cu and Cu-Zn phases. This result enables affirmation that peaks a₁ and a₂ observed in the voltammograms of Fig. 2a were due to the dissolution of Cu-Zn phases formed in potentials more negative than -1.2 V. The attribution of this anodic process to the dissolution of the Cu-Zn is coherent because this process occurs in more negative potentials in comparison to the potential dissolution of the Cu, motivated by the presence of Zn atoms.

Figure 2b shows the stripping curves for the coatings obtained in the bath containing only Mo (VI) and Cu (II). In this voltammogram, one shoulder can be observed followed by the a₁^{*} peak attributed to the dissolution of Cu and a₂^{*} peak

shifted to more positive potentials attributed to the phase dissolution or intermetallic compound formed between Cu and Mo. The shift of the a_2^* peak to more positive potentials compared to the oxidation of Cu is coherent because Mo has passivating characteristics. In turn, this result indicates that the anodic process a_3 in the voltammograms of Fig. 2a is due to dissolution of Cu-Mo phases. The stripping curves confirm the assumption that Cu, Mo and Zn containing intermetallic compounds can be formed from that bath at potentials more negative than the Zn reduction potential, together with HER.

3.2. Physical characterization

Aiming for future applications, the coatings were also produced in 1010 carbon steel and characterized by their morphologies, chemical compositions and crystalline structure. The amount of the Mo, Cu and Zn in the coatings obtained at -1.5 V on 1010 steel in the 2:2:1, 3:2:1 and 4:2:1 molar ratios of Mo: Zn: Cu are shown in Fig. 3. The amount of Cu was the largest of the three metals in the system, varying between 30 and 40% at/at, showing that copper is deposited preferentially in this deposition conditions. However, the increased deposition of Mo-oxidized species with increasing MoO_4^{2-} concentration in the baths directly affected Cu deposition by reducing its content in the coatings. Large amounts of Zn were also deposited, and all coatings that exhibited 20 to 28% of these metal coatings had less than 10% of Mo; on the other hand, they had considerable amounts of oxygen (more than 30% at). From Fig. 3, it is clear that an increase of the Mo content in coatings leads to an increase in the oxygen content, which is independent of the Cu or Zn, indicating that the Mo in the coatings is in the form of oxides. To understand the influence of the deposition potential on the coatings' chemical composition, electrodepositions were performed in a potential range of -1.2 to -1.9 V in the 4:2:1 molar ratio (bath 5) on steel 1010. These data are presented in Fig. 4a without the oxygen contents. It is noticed that the higher Mo contents were deposited at potentials more positive than -1.4 V. However, in comparison to the Cu and Zn contents, the amount of Mo remained almost constant in all deposition potentials, showing that the applied overpotential has little influence on its electrodeposition. On the other hand, both Cu and Zn deposition are strongly dependent on the overpotential applied. At the

potentials more positive than -1.4 V the coatings consisted of approximately 70 to 75% of Cu and between 13 and 15% of Zn, but in more negative potentials, the Zn deposition was favored, becoming the major component with approximately 54% in -1.9 V. Based in Fig. 1, it is possible to infer that copper deposition occurs via kinetically activated regime until the potential near -1.2 V, followed by a diffusion process at more negative potentials. It is agreement the fact that a smaller amount of copper was electrodeposited in more negative potentials. On the other hand, the electrodeposition of zinc was favored in potentials more negative than -1.2 V due this process is activated kinetically. This shows that, depending on the excess potential applied, it is possible to obtain coatings with different compositions. For more positive potentials, Cu rich coatings and for more negative potentials, Zn rich coatings are obtained.

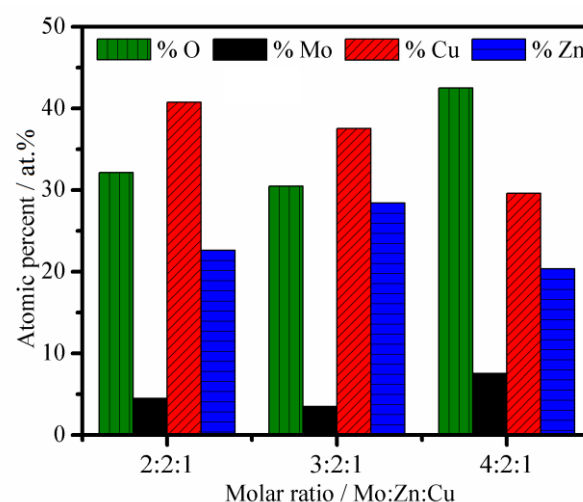


Figure 3. Composition for the coatings obtained in the baths of 2:2:1 (bath 3), 3:2:1 (bath 4) and 4:2:1 (bath 5) molar ratio of Mo: Zn: Cu at -1.5 V on 1010 steel substrate.

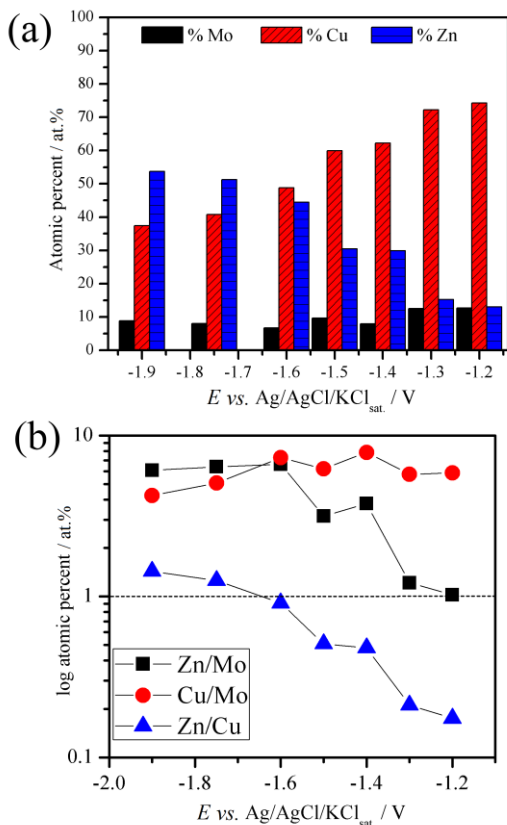


Figure 4. (a) Composition for the coatings obtained in the bath 5 of molar ratio Mo: Zn: Cu 4:2:1 in the range of deposition potentials of -1.2 to -1.9 V. (b) molar ratio between the metals in the coatings obtained in the bath 5 in the range of deposition potentials of -1.2 to -1.9 V on 1010 steel substrate.

The profiles of the atomic ratios between the metals in the coatings are shown in Fig. 4b. Comparing the profiles of the Zn/Cu and Zn/Mo atomic ratios indicates that in the coatings obtained over the entire range of deposition potentials, the ratio values grew following the same pattern. The values of the Zn/Cu ratio in the most positive potentials were less than 1.0 (higher Cu content)

and remained thus until the potential of -1.6 V, where the Cu and Zn contents were similar. In the most negative potentials, Zn electrodeposition was favored, and the Zn/Cu ratio values were greater than 1.0 (higher Zn content). The profile observed for the Zn/Mo ratio was similar to that observed in Zn/Cu, indicating that the behavior of Mo and Cu deposition in relation to Zn deposition is similar; that is, in more positive potentials, Cu and Mo deposition is favored, and a smaller amount of Zn is deposited. According to the Cu/Mo ratio profile, there was a small dependence between Cu and Mo on their deposition, as evidenced by the smaller variation of these values in comparison with the Zn/Mo and Zn/Cu ratios.

The coating surface morphologies obtained in the -1.5 V potential are shown in Fig. 5a. They presented a relatively compact structure with small agglomerated particles forming larger cauliflower-like structures; the small, smooth agglomerates on these structures are attributed to the oxides of Mo. The coating obtained in the 3:2:1 bath (Fig. 5b) showed structures similar to that of the 2:2:1 film but with a greater number of smooth structures between and on the grains. In contrast, the coating obtained in the 4:2:1 bath (Fig. 5c) presented less compactness and uniformity in its structure. The variation of the coating obtained in the bath with the higher concentration of Mo can be explained by taking into account the greater evolution of hydrogen that occurs with the electrodeposition of the coatings. This meant that the growth on the substrate was not uniform and compact. The greatest hydrogen evolution from bath 5 is proven by the cathodic voltammetry shown in Fig. 1, in which the cathodic current at -1.5 V related to HER for this bath was considerably higher compared to the currents obtained in the other baths at the same potential.

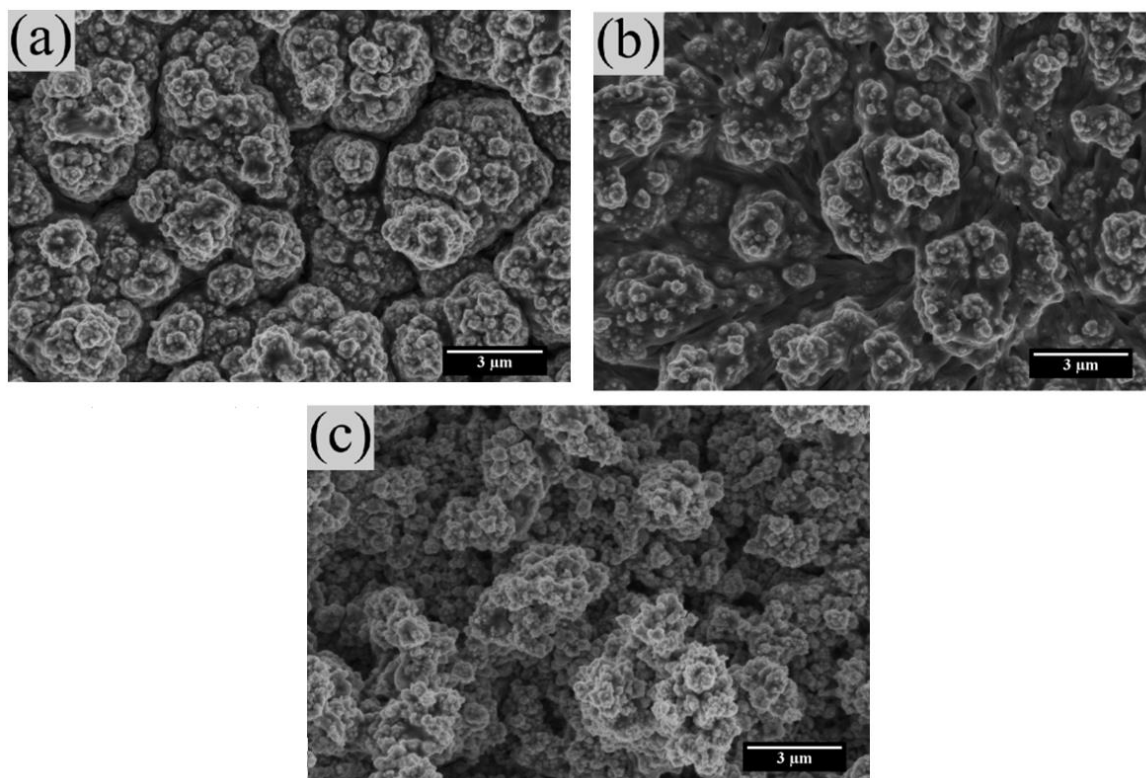


Figure 5. Surface morphologies obtained by SEM for coatings obtained at -1.5 V in baths with Mo: Zn: Cu molar ratio of (a) 2:2:1 (bath 3), (b) 3:2:1 (bath 4) and (c) 4:2:1 (bath 5) on 1010 steel substrate.

The crystal structures were evaluated using X-ray diffraction (XRD) and are shown in Fig. 6. The phases were identified with the aid of the crystallographic data patterns.

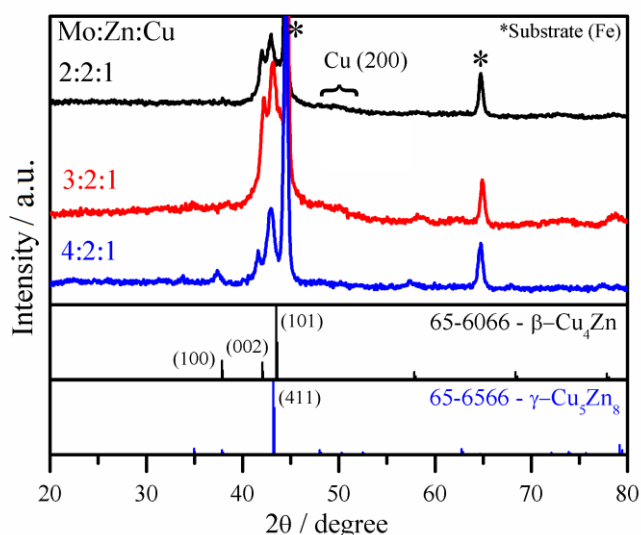


Figure 6. X-ray diffraction patterns for coatings obtained at -1.5 V in baths of Mo: Zn: Cu molar ratios of 2:2:1 (bath 3, black line), 3:2:1 (bath 4, red line) and 4:2:1 (bath 5, blue line) on 1010 steel substrate.

For all coatings, two phases of the Cu-Zn alloy were identified, β -Cu-Zn (PDF # 65-6066) and γ -Cu-Zn (PDF # 65-6566). The equilibrium phase diagram for Cu-Zn alloys shows that Cu-rich phases, such as α -Cu-Zn (99-70% Cu) and β -Cu-Zn (with up to 48% Zn), and Zn-rich phases, such as γ -Cu-Zn (Cu_5Zn_8 , with up to 66% Zn) and ε -Cu-Zn₅, are possible to obtain through electrodeposition²¹.

The identified β -Cu-Zn and γ -Cu-Zn phases are consistent with composition data shown in Fig. 3, where all coatings contained 30 to 50% Cu and 25 to 35% Zn. However, no peaks of Mo or oxidized species of this metal were observed, although these coatings had up to 8% of Mo, indicating that the electrodeposited Mo species are totally amorphous. On the other hand, diffraction patterns showed significant irregularity in background intensity, most evident in the range of 2θ from 50° to 53° . This irregularity was attributed to the diffraction of plane (200) of the Cu with low crystallinity, which might have been caused by the introduction of amorphous Mo into the lattice of this metal. According to Gotou *et al.*¹⁷, molybdenum can be introduced into the crystal lattice of the copper, causing an enlarging of lattice space and leading to

an amorphous structure. Therefore, the Cu-Zn-Mo coatings obtained in this work were a mixture of Cu-Zn intermetallic phases and copper-molybdenum amorphous composites, as well as Mo oxides with fully amorphous characteristics.

4. Conclusions

In this work was studied the parameters for electrodeposition of the system Cu-Zn-Mo in citrate baths. The voltammetric profiles indicate that binary phases of Cu-Zn and Cu-Mo can be formed in potentials more negative than -1.2 V together with hydrogen evolution. The morphologies of the coatings obtained in the potential of -1.5 V were compact and presented small agglomerated particles forming larger cauliflower structures, and Mo, Cu and Zn in these coatings ranged from 5 to 8%, 30 to 40% and 20 to 28%, respectively. Compositional analysis and XRD patterns showed that no ternary phases were formed, but rather a mixture of intermetallic Zn-Cu phases and Mo-Cu amorphous composite, as well as Mo oxides with totally amorphous characteristics.

5. Acknowledgments

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See **Supplementary information**.

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