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# Copper–zinc electrodeposition in alkaline-sorbitol medium: Electrochemical studies and structural, morphological and chemical composition characterization

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ABSTRACT

The galvanostatic technique was used to analyze the electrodeposition of Cu–Zn on to AISI 1010 steel electrode from an alkaline-sorbitol bath with various proportions of the metal ions in the bath: Cu70/Zn30, Cu50/Zn50 and Cu30/Zn70. Coloration of Cu–Zn films were whitish golden, light golden, golden/gray depending on the $Cu^{2+}/Zn^{2+}$ ratios in the electrodeposition bath, deposition current density ($j_{dep}$) and charge density ($q_{dep}$). The highest current efficiency was ~54.0%, at $j_{dep}$ −1.0 mA cm$^{-2}$ and $q_{dep}$ 0.40 C cm$^{-2}$ in the Cu70/Zn30 bath. Energy dispersive spectroscopy indicated that electrodeposits produced from the bath Cu70/Zn30 showed higher Cu content at lower $j_{dep}$. Also, for same $j_{dep}$ the Cu content increased with $q_{dep}$. Scanning electron microscopy showed that Cu–Zn electrodeposits of high quality were obtained from the Cu70/Zn30 bath, since the films were fine-grained, except the obtained at $j_{dep}$ −20.0 mA cm$^{-2}$ and $q_{dep}$ 10.0 C cm$^{-2}$. Also, these electrodeposits did not present cracks. X-ray analysis of the Cu–Zn electrodeposits obtained at $j_{dep}$ −8.0, −20.0 and −40.0 mA cm$^{-2}$, in each case, with $q_{dep}$ 2.0 and 10.0 C cm$^{-2}$, in the Cu70/Zn30 bath, suggested the occurrence of a mixture of the following phases, CuZn, $CuZn_5$ and $Cu_5Zn_8$. Galvanostatic electrodeposits of Cu–Zn obtained from sorbitol-alkaline baths exhibited whitish golden color, with good prospects for industrial applications, especially for decorative purposes.

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## 1. Introduction

Cu–Zn alloys can be electrodeposited over metal substrates for corrosion protection and/or decorative purposes [1]. Several authors investigated Cu–Zn electrodeposition from cyanide [1–4] and non-cyanide baths [1,5–24], in this last case due to environmental and health concerns. In our laboratory, free-cyanide alkaline Cu–Zn electrodeposition baths using the polyalcohol sorbitol [9] and EDTA [25] as alternative complexing agents have been developed. In the first case [9] it was demonstrated, by voltammetric technique, that $Cu^{2+}$ complexation by sorbitol was beneficial, approaching the $Cu^{2+}$ reduction potential to that of the zincate ion ($[Zn(OH)_4]^{2-}$). This allowed the co-deposition of Cu and Zn and also the color changes of electrodeposits produced potentiostatically took place within a narrow range of applied potentials. Moreover, it was verified that sorbitol prevents the darkening of the Cu–Zn electrodeposits (burning) even in the high hydrogen evolution regions. These observations make sorbitol a potential candidate for replacing cyanide. Despite these promising results obtained from potentiostatic and voltammetric techniques, it becomes important investigate the Cu–Zn electrodeposition, from sorbitol-alkaline bath, using galvanostatic technique, because constant current conditions are nearest to industrial conditions. The aim of the present work is to evaluate the influence of polyalcohol sorbitol as chelating agent on the composition, surface morphology, color and phase structure of Cu–Zn electrodeposits obtained under constant current conditions in alkaline pH.

## 2. Experimental

All the employed chemicals were of analytical grade and double distilled water was used throughout the experiments. The electrodeposition baths for Cu–Zn were freshly-prepared non-cyanide baths, containing: 3.0 M NaOH, variable concentrations of $CuSO_4$ and $ZnSO_4$ and a fixed sorbitol concentration of 0.20 M shown in Table 1. In all baths the total $[Cu^{2+}]+[Zn^{2+}]$ cationic concentration

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**Table 1**
Composition of the Cu–Zn electrodeposition baths.

| Solution | [$CuSO_4$] (M) | [$ZnSO_4$] (M) | [sorbitol] (M) | [NaOH] (M) | molar % of $Cu^{2+}$ and $Zn^{2+}$ | Name |
|---|---|---|---|---|---|---|
| 1 | 0.14 | 0.06 | 0.20 | 3.0 | 70:30 | Cu70/Zn30 |
| 2 | 0.10 | 0.10 | 0.20 | 3.0 | 50:50 | Cu50/Zn50 |
| 3 | 0.06 | 0.14 | 0.20 | 3.0 | 30:70 | Cu30/Zn70 |

was kept constant at 0.20 M. The molar percentages of $Cu^{2+}$ and $Zn^{2+}$ ions were variable.

The working electrode consisted of a 1010 steel disk (0.50 $cm^2$) embedded in epoxy resin. For X-ray diffraction (XRD), scanning electron microscopy (SEM) and semi-quantitative energy dispersive X-ray spectroscopy (EDS) it was employed interchangeable 1010 steel disk electrodes (0.50 $cm^2$) embedded on Teflon®. A Pt plate was the counter-electrode and the reference electrode consisted of Hg/HgO/NaOH (1.0 M NaOH) with an appropriate Luggin capillary. The working electrodes were ground with 600 emery paper, rinsed with water and dried prior the electrochemical experiments.

The Cu–Zn electrodeposits were obtained at distinct constant deposition current densities ($j_{dep}$) in the range shown in Table 2 for each of the baths listed in Table 1. The deposition charge densities ($q_{dep}$) were: 0.4, 1.0 and 2.0 C $cm^{-2}$.

Anodic linear stripping voltammetry (ALSV) was performed for Cu–Zn electrodeposits produced galvanostatically at the various $j_{dep}$ and distinct $q_{dep}$. They were transferred to an electrochemical cell with 1.0 M $NH_4NO_3$ solution and anodic linear stripping voltammetry (ALSV) was performed at a sweep rate ($v$) of 10.0 mV $s^{-1}$. As reported earlier [25] dissolution/passivation of the 1010 steel substrate in 1.0 M $NH_4NO_3$ occurred in the potential range from ∼−0.50 V to +0.40 V, while the Zn and Cu substrates dissolved significantly beyond ∼−0.70 V and ∼−0.20 V, respectively. Therefore, when Zn dissolved, nothing occurred with 1010 steel. However, when Cu dissolved, 1010 steel was passivated. Thus, during dissolution of electrodeposits there was no active dissolution of 1010 steel, which would have contributed significantly to the current efficiency (CE). The 1010 steel was passivated (from ∼−0.50 V to +0.40 V), its contribution to the CE was insignificant, relative to Cu–Zn electrodeposit dissolution. Moreover, the passivation current density was ∼0.25 mA $cm^{-2}$.

XRD patterns were produced with filtered Co Kα radiation (1.78897 Å), using a Siemens D5000 automatic diffractometer set at 40 kV and 20 mA. The diffraction patterns were first collected in a $\omega/2\theta$ scan and then repeated with a $2\theta$ scan (fixing $\omega = 3°$), to achieve a better resolution. SEM photographs were taken with a Leica Stereoscan 440 electron microscope. EDS readings were taken with an Oxford eLX device, EDS Si/Li, with ultrathin Be window. Semi-quantitative chemical analysis of the electrodeposits by EDS was carried out over as much of the electrode area as possible, perpendicular to the surface, without reaching the Teflon ring that surrounded the 1010 steel disk electrode.

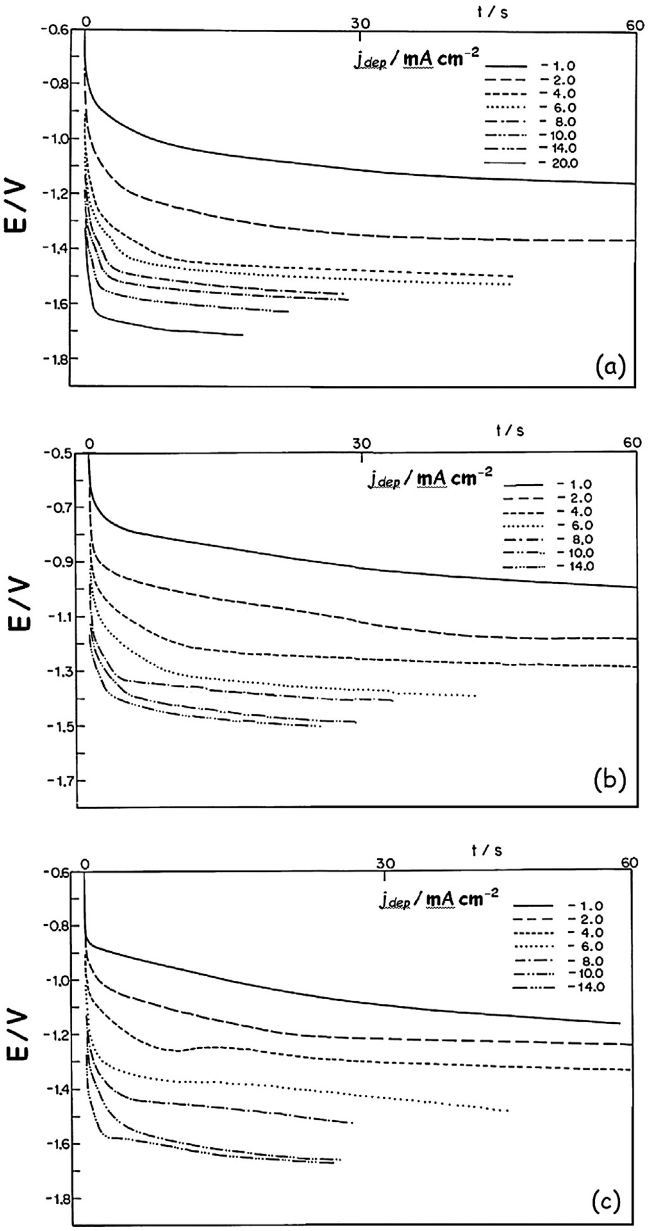

**Fig. 1.** Typical potential ($E$) *vs.* time ($t$) transients at several $j_{dep}$, indicated in figures, for the electrodeposition of Cu–Zn from baths containing 0.20 M sorbitol + 3.0 M NaOH and different Cu/Zn molar ratios: (a) Cu30/Zn70; (b) Cu50/Zn50; (c) Cu70/Zn30.

## 3. Results and discussion

### 3.1. Electrochemical investigation of the Cu–Zn electrodeposition

Fig. 1(a)–(c) shows typical galvanostatic transients (($E$) *vs.* ($t$)) of Cu–Zn films electrodeposited on 1010 steel substrate from three different $Cu^{2+}/Zn^{2+}$ molar ratios in an alkaline bath containing sorbitol as the $Cu^{2+}$ complexing agent, with a total concentration of the two cations of 0.20 M. The galvanostatic technique was used to analyze the influence of $j_{dep}$, $q_{dep}$ and bath composition on the Cu–Zn electrodeposits.

Typical $E$ *vs.* $t$ transients obtained from Cu–Zn baths were analyzed from the reached potential regions and also from the $H_2$ evolution overpotentials for Cu, Zn and 1010 steel substrates reported in the previous voltammetric analysis for these baths, found in Ref. [9]. Fig. 1(a)–(c) shows that for $j_{dep}$ in the range from −1.0 mA $cm^{-2}$ to −4.0 mA $cm^{-2}$, the potential did not reach the potential region for HER on Cu–Zn electrodeposits in the time scale of the experiment, except for Cu30/Zn70 bath and $j_{dep}$ of −4.0 mA $cm^{-2}$. This potential region, as it was analyzed in [9], starts at a great extent at *ca.* −1.40 V. These results led to infer that the 1010 steel substrate could not be totally covered by Cu–Zn

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