

Codeposition of copper and tin from acid sulphate solutions containing polyether sintanol DS-10 and benzaldehyde

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Received: 18 August 2008 / Accepted: 22 April 2009 / Published online: 30 April 2009
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Abstract Cu(II) and Sn(II) reduction in acid sulphate solutions containing polyether laprol DS-10 and benzaldehyde (BA) was studied by means of impedance, voltammetric, XPS and XRD techniques. Both additives demonstrate weak surface activity on copper substrate in Cu(II) solutions in the absence of halide impurities. In contrast, their effect is overwhelmingly higher in the Sn/Sn(II) system. The additives induce a significant increase in Sn-electrode impedance and simultaneous strong inhibition of Sn(II) reduction over a wide range of cathodic polarizations. The effects of sintanol and BA in mixed Cu(II) and Sn(II) solutions demonstrate a kind of synergism. Underpotential deposition of tin on foreign (copper) substrate is observed at potentials more positive than the equilibrium potential of the Sn/Sn²⁺ system. Incorporation of tin into the Cu crystalline lattice results in the formation of multiphase material containing pure copper, α -CuSn phase, and intermediate hexagonal *hcp* phase. Formation of the pure tin phase occurs at more negative potentials and results in a strong inhibitive adsorption that manifests itself in the development of a deep voltammetric minimum. The tin content in the coatings depends on BA concentration and, particularly, on the electrode potential.

Keywords Copper–tin alloys · Polyether sintanol · Benzaldehyde · Phase composition

1 Introduction

Various surfactants are widely used in plating baths for the electrodeposition of tin and its alloys. Several polyethers are beneficial additives for producing bronze coatings of high quality. Sintanol DS-10, $C_nH_{2n+1}-O-(C_2H_4-O)_mH$ ($n = 10-12$, $m = 8-10$), known also as Pegepal C in Germany, is a surfactant of this type. Due to its comparatively long alkyl chain C_nH_{2n+1} , Sintanol can act as an inhibitor and as an effective wetting agent. Benzaldehyde (BA), like some other organic substances containing double bonds, aromatic rings, aldehyde groups etc. [1–10] is able to act as a brightener. To improve the operating characteristics of plating baths and the properties of the resulting coatings, certain surfactant combinations are usually applied.

The influence of polyethers on copper deposition has been studied extensively; e.g. [11–16]. According to [13, 14], the effect of Sintanol on the kinetics of both Cu(II) and Sn(II) reduction occurring independently is similar to the effect of other polyethers. Basically polyethers, and in particular Sintanol, in halide-free solutions do not behave like surfactants on copper substrates. In contrast, the inhibition ability of Sintanol on tin has been observed many times [8, 10, 13–20]. According to [16, 21], the length of the hydrocarbon chain is the major factor responsible for the inhibition activity of polyethers on tin, e.g. oligomers of ethylene glycol $HO-(CH_2-CH_2-O)_m-H$ demonstrate surfactant properties only when $m \geq 4$ [21]. Sintanol is a much more powerful surfactant, and its inhibitive effect can be detected even at very low concentrations ($\sim 0.5 \text{ mg dm}^{-3}$) [13].

Benzaldehyde is known as an effective brightener in tin plating. Despite the availability of information related to technological aspects, more detailed data on BA adsorption

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behaviour would still be beneficial. For Cu and Sn codeposition, different effects of BA and similar surfactants on the kinetics of partial processes are known [8, 9]: polarization of Cu(II) reduction becomes more intensive when Sn(II) reduction occurs with some depolarization. Certain aromatic compounds (aldehydes, ketenes) can be reduced in a certain range of potentials, with subsequent chemical transformations [4, 7]. It should be noted that some of the resulting products can also act as the brighteners.

According to Electrochemical Impedance Spectroscopy (EIS) data [22, 23], adsorption of BA on tin is rather slow. Adsorption parameters continue to change within 2–3 h before steady state is attained. It was also found that adsorbates are more mobile and the reversibility of adsorption–desorption processes is higher in the presence of Sn(II). Comparison of voltammetric and EIS data made it possible to discover a correlation between the double layer capacitance and the exchange current density of metal ion reduction: a gradual decrease in these parameters with exposure time demonstrated one and the same trend [23].

This paper presents the results of a further investigation of simultaneous Cu(II) and Sn(II) reduction in the presence of Sintanol DS-10 and benzaldehyde. It is reasonable to expect that the optimal combination of two additives gives a chance of further improvement of the plating process and the quality of Cu–Sn coatings.

2 Experimental details

Solutions under study contained 0.01 M CuSO₄ (Malinkrodt, USA) 0.01 M SnSO₄ (Fluka, Germany), 1 M H₂SO₄ (high purity) as a supporting electrolyte and different amounts of benzaldehyde (Aldrich, Germany) and Sintanol DS-10 (Orgsintez, Kazan, Russia) with average molar mass of 600. The latter is represented by a mixture of alkylated polyether homologues of general formula C₁₀H₂₁–(C₂H₄O)₁₀–OH. Both organic substances were used as received. Triply-distilled water was used for preparation of solutions, which were deaerated with an argon stream for 30 min or longer. All experiments were carried out at room temperature (20 °C).

Platinum disc (1 cm², voltammetric measurements) or platinum wire (0.36 cm², impedance measurements), both coated with 5–7 μm thick copper or tin, were used as the working electrodes. Codeposition of copper and tin was investigated with the use of copper support. The conventional rotating disc electrode technique with a potential scan rate of 5 mV s⁻¹ was employed for voltammetric measurements. The electrochemical cell for EIS measurements contained an auxiliary electrode fabricated from platinum cylinder (~6 cm²) for *ac* polarization. A conventional Ag|AgCl|KCl (sat) reference electrode was used

in all experiments; electrode potentials reported below are referred to the standard hydrogen electrode scale.

Impedance spectra were collected within the 0.1 Hz to 50 kHz frequency range under open-circuit potential, using a Zahner Elektrik (Germany) IM6 impedance spectrum analyzer. A sufficiently low (5 mV) amplitude of alternating voltage was applied. Each run was started from the maximum frequency and continued for 4–5 min.

For X-ray photoelectron spectroscopy (XPS), the spectrometer ESCALAB MK-II (Mg K_α radiation) was applied. For these experiments, 3 μm thick Cu–Sn samples were prepared by constant potential electrolysis using a rotating disc electrode (1,250 rpm). Analysis results correspond to a 1–2 nm thick external layer. Argon ion bombardment at 5 × 10⁻⁴ Pa was assumed to remove the nanometer-scale surface layer of the electrodeposited Cu–Sn alloy.

X-ray diffraction (XRD) measurements were performed with a Bruker D8 Advance diffractometer equipped with a Göbel mirror as a primary beam monochromator for Cu K_α radiation. Samples for XRD measurements were prepared under potentiostatic mode using a RDE. The grazing incidence technique (X-ray incidence angle of 0.8°) was used to prevent overlap of brass support and deposit reflections in the XRD pattern. The detector scan mode was characterized by 0.02° steps and a sampling time of 8–25 s. Other details of the experimental technique are available elsewhere [24].

3 Results and discussion

Sintanol and benzaldehyde demonstrate different surface activity on copper and tin substrates. According to earlier reports [14, 15], Sintanol has a weak influence on the kinetics of Cu(II) reduction in halide-free solutions. Sintanol addition results in a slight (5–10 mV) increase in cathodic polarization, whereas the limiting current density remains unchanged and obeys the Levich equation. In contrast, Sintanol addition markedly inhibits Sn(II) reduction (decreases considerably the cathodic current density). This takes place over a wide range of cathodic polarizations, including the initial area of limiting current.

The surface activity of this polyether on copper and tin substrates can be clearly compared using EIS data. Figure 1 shows the relationships between real (*Z'*) and imaginary (*Z''*) impedance components. For the Cu|Cu(II) system, Nyquist plots are arc shaped centred below the abscissa (the behaviour typical for consecutive transfer of two electrons). It is well known that the impedance is highly sensitive to various changes at the electrode surface. We suggest that the increase in |*Z*| up to ~40% induced by Sintanol does not contradict the observation of rather the slight variations of voltammetric response mentioned

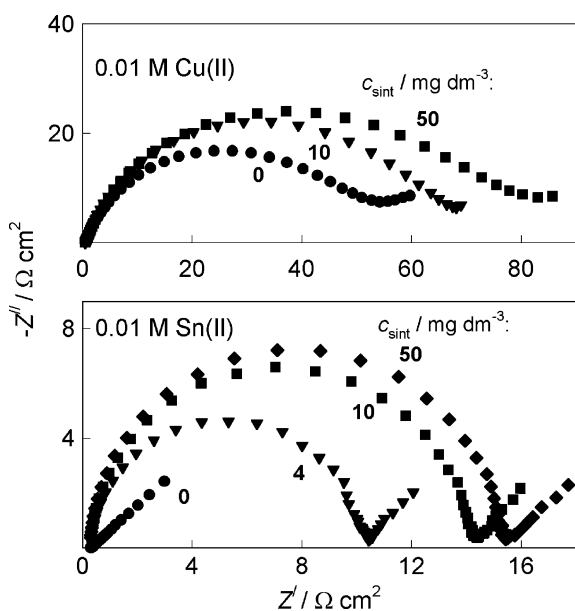


Fig. 1 Nyquist plots obtained for copper (*top*) and tin (*bottom*) electrodes at open-circuit potentials, 0.245 ± 0.002 and -0.239 ± 0.002 V respectively. Concentrations of sintanol (c_{sint}) are indicated near the curves

above. As for the Sn/Sn(II) system, addition of this surfactant does not merely increase the total impedance, but also changes the shape of the Nyquist plots dramatically. In the absence of the surfactant, Nyquist plots are represented by lines of unit slope (typical for diffusion-controlled processes). Sintanol induces the appearance and development of semicircles of various radii, i.e. affects the exchange current density. Quantitative analysis of impedance data employing equivalent circuits is given elsewhere [13, 14].

Benzaldehyde behaviour is similar; its effect on Cu(II) reduction kinetics is weak. However, even millimolar addition of BA changes the shape of the voltammograms of Sn(II) reduction dramatically (Fig. 2). In contrast to the Sintanol effect, two regions of cathodic polarization with different BA-affected features may be designated. The first region lies between the equilibrium potential of the Sn/Sn(II) electrode ($E_{\text{eq}}^{\text{Sn}} = -0.24$ V [11]) and $E \approx -0.45$ V and corresponds to a moderate inhibiting effect of BA. The rate of Sn(II) reduction gradually decreases with BA concentration (c_{BA}), but the intensity of forced convection still affects its effectiveness.

The limiting current densities (i_{lim}) determined at ca. -0.33 V and plotted in Levich coordinates (Fig. 3) may be approximated by straight lines with zero intercept, if c_{BA} is sufficiently low. Application of the Levich equation to the data obtained for surfactant-free solutions gives quite reasonable value of Sn²⁺ diffusion coefficient, $D = 6 \times 10^{-6}$ cm² s⁻¹. However, the slope of the straight lines

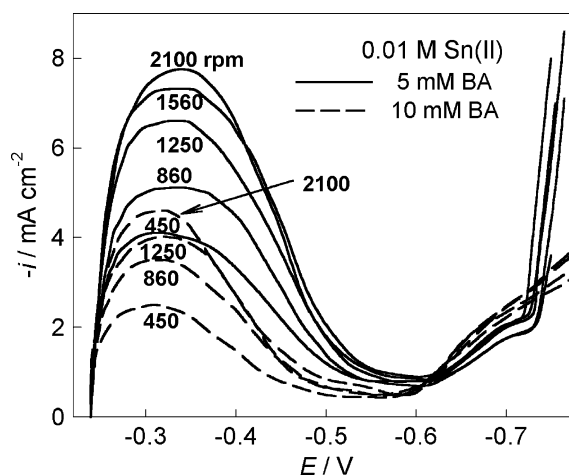


Fig. 2 Voltammograms obtained for 0.01 M Sn(II) solutions with 5 mg dm^{-3} (*solid lines*) and 10 mg dm^{-3} (*dashed lines*) of benzaldehyde. Rotation rate of RDE (revolutions per minute) is indicated near any respective curve

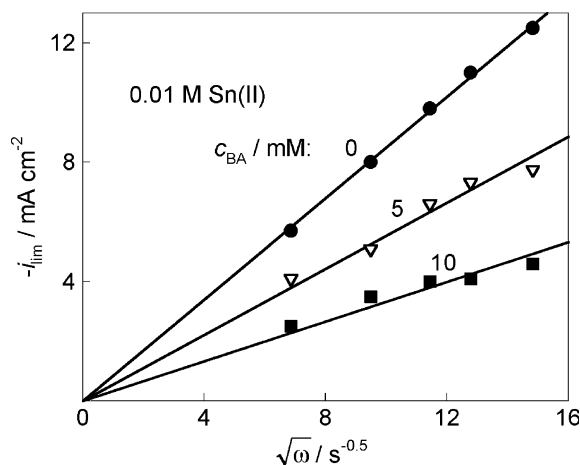


Fig. 3 Plots of limiting current density versus square root of angular rotating rate for 0.01 M Sn(II) solutions with indicated concentrations of BA additive

decreases when BA is added. Similar effects are known for other aldehydes and various polyethers. Different explanations of this observation have been suggested. One of them [1, 2, 7, 17] assumes the formation of a blocking film that retards the migration of ions and creates an additional charge transfer barrier. According to another explanation [17], the surface film drastically reduces the number of sites available for deposition of tin. Basically the latter consideration is based on the concept of partially blocked electrodes [25]. This suggests that the limiting diffusion current can decrease significantly when the dimensions of active or passive sites and the diffusion layer thickness are comparable. Despite the fact that both concepts are supported by experimental data, the mechanism of surfactant behaviour on tin is not yet convincingly clear.

In the second potential interval ($-0.7 < E < -0.5$ V) the inhibiting action of BA is much stronger. In this region the current density attains ca. 1 mA cm^{-2} and no longer depends on the RDE rotation rate. According to [26], the zero-charge potential of tin in $0.01 \text{ M Na}_2\text{SO}_4$ is -0.43 V. We failed to find any data concerning the effect of BA additives on the zero-charge potential. Nevertheless, it can be assumed that the highest surface activity of BA is observed at moderately negative surface charges of the tin electrode.

Tendencies typical of the reduction of individual components are also observed in the case of copper and tin codeposition. When interpreting the voltammetric data one should take into account that the coating composition varies with both electrode potential and solution composition. Figure 4 shows the effect of BA on voltammograms recorded using copper support. Its open-circuit potential in solutions under study is 0.248 ± 0.002 V, close to the equilibrium potential of the copper electrode $E_{\text{eq}}^{\text{Cu}} = 0.245$ V (as estimated in [11] for 0.01 M Cu(II) solutions containing $0.6 \text{ M H}_2\text{SO}_4$). Thus, the first partial process starting at low cathodic polarizations, is the reduction of Cu(II) .

Since $E_{\text{eq}}^{\text{Sn}} = -0.24$ V, the formation of free tin in the coatings is possible only at more negative potentials. This has been confirmed earlier [27] using XPS, voltammetry and chemical analysis. Nevertheless, reduction of Sn(II) starts at ~ 0 V, i.e. at potentials more positive than $E_{\text{eq}}^{\text{Sn}}$. This means that codeposition of Cu and Sn proceeds with a certain depolarization and the formation of binary Cu–Sn phases (*vide infra*). It is clearly seen that the effect of BA is rather weak at $E > -0.2$ V, i.e. when copper is the main component of the coatings, and free tin is absent from it. Voltammetric minima arise at more negative potentials corresponding to the thermodynamic stability of the pure

tin phase, but the width and depth of these minima is weaker as compared to the same features observed for Sn (cf. Figs. 2, 4).

The principal effects of Sintanol on the kinetics of copper and tin codeposition have been reported in our previous communication [15]. It was established that the addition of relatively high amounts of Sintanol (up to 50 mg dm^{-3}) to solution containing 0.01 M Cu(II) and 0.01 M Sn(II) does not affect the voltammetric response at $-0.2 < E < 0.2$ V. Consequently, this additive is surface-inactive over a wide region of cathodic polarization, where copper deposition prevails. However when $E_{\text{eq}}^{\text{Sn}}$ is approached, the specific voltammetric minimum is developing and becomes more pronounced with increase in Sintanol concentration. This minimum is detectable at already rather low concentrations ($c_{\text{sint}} \sim 2 \text{ mg dm}^{-3}$), and its depth correlates with the Sn(II) concentration in the presence of Sn(IV) [28].

Most of these phenomena are also observed in the presence of both additives (Fig. 5). The splitting of the voltammetric minimum with the subsequent appearance of its duplex structure is a primary point of the further study. It appears that the inhibition ability of the surfactants under study is potential-dependent. The most pronounced inhibition effect predominating at potentials -0.25 to -0.3 V might be attributed to Sintanol, whereas the effect of BA is more pronounced in the vicinity of -0.4 V. Thus, there is an analogy with experimental data obtained for Sn/Sn(II) system and mixed $\text{Cu(II)}\text{--}\text{Sn(II)}$ solutions.

Another possibility is that the inhibition effects become stronger in the presence of both Sintanol and BA (synergistic effect). Specifically, this effect is clearly seen at low cathodic polarizations (see Fig. 5). Cu(II) reduction predominates in this region, and neither Sintanol nor BA, taken separately, demonstrate any inhibition activity. One

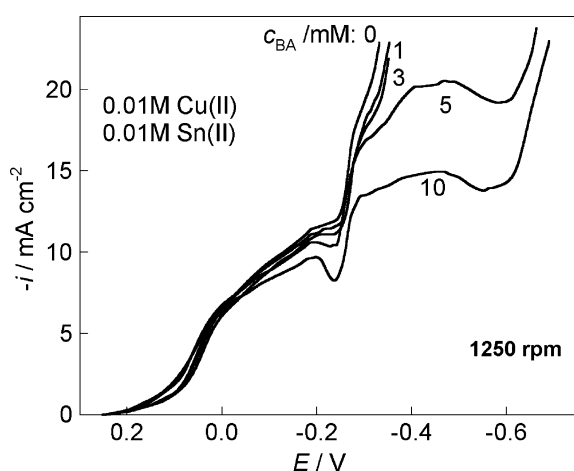


Fig. 4 Voltammograms obtained for mixed Cu(II) and Sn(II) solutions with indicated amounts of BA

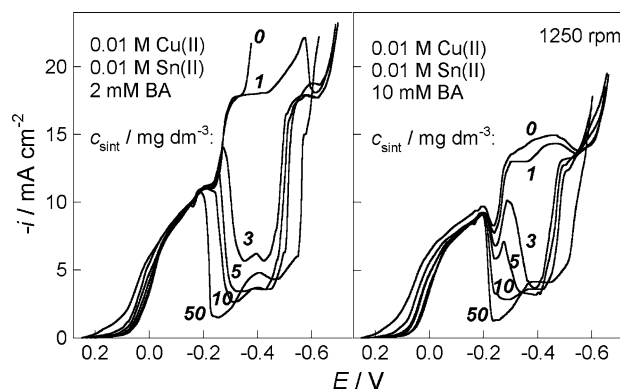


Fig. 5 Voltammograms obtained for mixed Cu(II) and Sn(II) solutions with 2 mg dm^{-3} (left) and 10 mg dm^{-3} (right) of BA and indicated amounts of sintanol

can assume that interaction of adsorbed surfactants and Cu^{2+} or Sn^{2+} ions occurs at the interface. Formation of molecular clusters containing Sintanol, formaldehyde and allyl alcohol have been analysed, and interaction energies have been estimated [10] using semi-empiric quantum chemical simulations. In general co-adsorption of the surfactants should be considered as a complex process governed by many factors, such as electrode potential, solution composition, elemental and phase composition of the coatings, etc.

The composition of Cu–Sn coatings depends on both solution composition and electrolysis parameters. Commercial baths designed for the deposition of yellow bronze contain higher concentrations of Cu(II) and Sn(II) and usually operate under galvanostatic conditions. In this case, applied current densities fall into the potential region of the ascending branch of the voltammogram, i.e. the region of underpotential tin deposition [29]. An example illustrating the surfactant effect on the composition of yellow bronze coatings is given in Fig. 6. It can be seen that BA promotes the enrichment of yellow bronze with tin, and this effect is more pronounced at lower current densities. Similar tendencies can be observed when Cu–Sn samples are fabricated in more dilute solutions under potentiostatic mode (Fig. 7). Two electrode potentials were selected to specify these observations. The first potential value (-0.1 V) corresponds to the region of yellow bronze formation, and the second value (-0.4 V) lies in the region of the characteristic voltammetric minimum (see Fig. 5). It should be noted that the tin content is strongly potential dependent, and the effects of BA are different in these two potential regions. At low cathodic polarization, BA favours accumulation of tin in the coatings. This might be caused by the

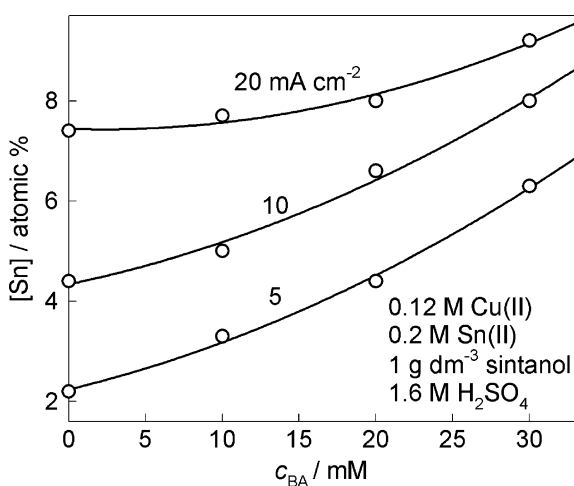


Fig. 6 Tin contents in the coatings obtained at indicated current densities from 0.12 M Cu(II) and 0.2 M Sn(II) solutions with 1 g dm^{-3} of sintanol and indicated amounts of BA. XPS data are presented for coatings with removed ($\sim 30\text{ nm}$) surface layer

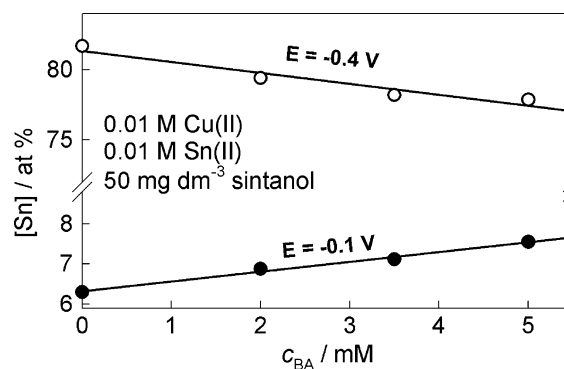


Fig. 7 Tin contents in the coatings obtained at indicated potentials from mixed Cu(II) and Sn(II) solutions with 50 mg dm^{-3} of sintanol and indicated amounts of BA. XPS data are presented for coatings with removed ($\sim 30\text{ nm}$) surface layer

relatively strong inhibition of copper deposition due to the above mentioned synergistic effects. However, the latter tendency is not expected at -0.4 V , when Cu(II) reduction takes place in the region of the voltammetric minimum.

A special feature of electrochemically deposited bronze coatings is the presence of various phases being thermodynamically stable only at high temperatures. In addition, our recent investigations [15, 16, 24] demonstrated that Cu–Sn coatings obtained in the presence of some polyethers contain the intermediate hexagonal *hcp* phase. When heated at $350\text{ }^\circ\text{C}$ this phase transforms into $\zeta\text{-Cu}_{10}\text{Sn}_3$. This unusual phase has never been detected in the cast alloys. We associate its formation with underpotential deposition of tin on copper at $E > -0.2\text{ V}$.

The phase composition of bronze coatings demonstrates no substantial changes when BA is added to Sintanol-containing solutions, but the content of the specific phase depends on c_{BA} . Deposits obtained at low cathodic polarization (at $E \sim -0.1\text{ V}$) present a mixture of pure copper, $\alpha\text{-CuSn}$ phase and *hcp* phase (Fig. 8). Despite the fact that the total amount of tin increases with c_{BA} (Fig. 7), the content of *hcp* phase decreases. At the same time, the lustre characteristics of the coatings improve. The latter tendency was also observed in systems with other polyether-containing additives [15, 16, 24].

4 Conclusions

Bright yellow bronze coatings can be deposited from acid solutions containing Cu(II) and Sn(II) sulphates, the polyether Sintanol DS-10 and benzaldehyde as a brightener. Both additives show weak surface activity on copper substrate in halide-free Cu(II) solutions. In contrast, their effect is much higher in the case of the Sn/Sn(II) system, as confirmed by the significant increase

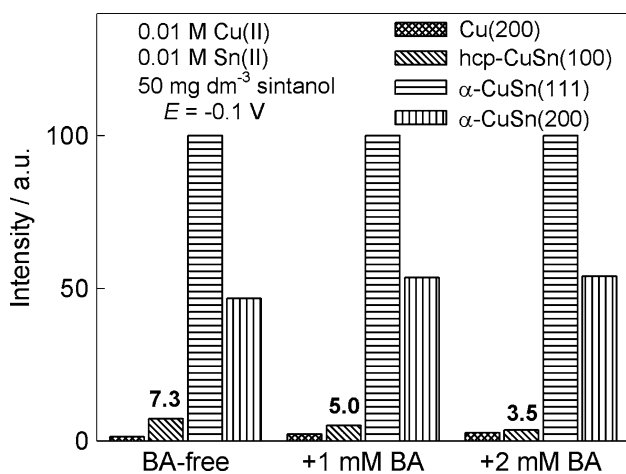


Fig. 8 Phase composition of bronze coatings obtained at -0.1 V from solutions of indicated composition. XRD data are normalized with respect to α -CuSn(111) phase

in the Sn-electrode impedance and the strong inhibition of Sn(II) reduction over a wide region of cathodic polarization.

The tendencies typical for separate (partial) processes remain the same for copper and tin codeposition. At the same time, a synergism in the action of Sintanol and BA is observed. This phenomenon is more pronounced at low cathodic polarization, when Cu(II) reduction predominates.

Voltammetric and XPS data show that codeposition of copper and tin starts at potentials more positive than the estimated equilibrium potential of the Sn/Sn^{2+} electrode. The initial steps of Sn(II) reduction can be considered as underpotential deposition of tin on the foreign (copper) substrate. At subsequent steps tin is depositing as a component of binary Cu–Sn phases, and the coating contains a mixture of pure copper, α -CuSn phase and intermediate hexagonal *hcp* phase.

The formation of a pure tin phase occurs at $E < E_{\text{eq}}^{\text{Sn}}$. This gives rise to strong inhibitive adsorption of Sintanol and benzaldehyde and results in the development of a deep voltammetric minimum. The tin content in the coatings depends on BA concentration and, particularly, on the electrode potential.

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