TIN ELECTRODEPOSITION ON CARBON STEEL. THE INFLUENCE OF THE CONCENTRATION, ADDITIVES AND OF THE METHOD

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abstract: Tin electrodeposition onto carbon steel from $SnCl_2$ solutions at different concentrations was evaluated in the absence and the presence of boric acid, ammonium citrate, tartric acid and sodium chloride. The phase formation of tin film onto a carbon steel electrode was investigated using: linear voltammetry, linear potentiometry, chronoamperometry, normal and differential pulse voltammetry.

key words: electrodeposition; tin film; potentiometry; voltammetry; chronoamperometry.

Introduction

There is an interest, which is more and more accentuated, for the use of the tin as a substitute for the conventional depositions because of its more inoffensive impact upon the environment [1÷3]. For example, the tin and the tin alloys are the possible candidates for the replacement of the chrome and cadmium depositions that are used for some decorative means and in the electronic applications respectively [4].

The electrodeposition of the tin can be realized both by the acid baths and also by the basic baths [5,6]. The tin acid baths (fluoroboric acid, sulphate, chlorides, the methanesulfonic acid) generally contain some additives in order to inhibit the oxidation Sn (II) to Sn(IV) [7]. The tin alkaline baths that contain stannates $[Sn(OH)_6]^{2-}$ present the advantage that there are no additives because the deposition takes place at some very negative potentials, and the parallel formation of hydrogen plays the role of an additive [8]. The main disadvantage is represented by the diffusion of the hydrogen inside the deposited tin layer (fragilization).

The recent studies report the electrodeposition of Sn and the tin alloys [9,10]; Au-Sn [11], Sn-Bi [12], Sn-Ag, Sn-Zn, Sn-Cu [13,14], Sn-Pb, Sn-Co [15], as well as the influence of the additives such as: the triethanolamine [16], the tartric acid [17], the sodium gluconate [18], the sodium citrate, the ethylene glycol [19], the sorbitole [20].

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The composition of the electrolyte has an important role in the determination of the quality of the films subjected to the electrodeposition [21]. The use of these additives in the electrodeposition methods from aqueous solution presents certain advantages such as: the metallic gloss, the increase in size of the deposited film, the modification of the mechanical and physical proprieties, and stress reduction. At the same time, the presence of the complexing agents in the solution during the electrodeposition processes increases the life duration of the galvanic bath as well as the adherence of the film to the base metal [22÷24].

The low oxidation potential of tin makes it a possible electrodic material for some oxidative catalytic processes [25,26]. The depositions of tin on Pt are frequently used for the formic acid and carbon monoxide electrooxidation because of the catalytic effects [27,28].

During the electrodeposition of the tin on Pt, the formation of some bimetallic substances can take place [Pt_3Sn]; [PtSn] with different catalytic activities. On the other hand, for the electrodeposition of the tin from the soluble salts in the aqueous solution of HCl, an unstable layer is formed on the gold electrodes or Pd, the adsorption of the tin takes place by the ionization of the absorbed hydrogen and by the irreversible disproportion of the Sn^{2+} by the formation of the Sn^{4+} and of the absorbed species of Sn^0.

Experimental

The electrodeposition of the tin on the carbon steel support has been realized by using the additive and non–additive solutions of $SnCl_2$, at room temperature. The tin chloride and the additives have been p.a. grade produced by Merck.

We have used a standard one compartment electrochemical cell, with a cylindrical carbon steel working electrode (area = 1 cm^2), a glossy platinum plate auxiliary electrode (area = 1 cm^2), and a saturated calomel electrode (SCE) as a reference electrode.

The working electrode, from carbon steel (Cr 16-18%, Ni 10-15%, Mo 2-3%, Mn 2%, P 0.04%, C 0.035%, Si 0.03%, S 0.03%, Fe balance) has been polished with metallographic paper, washed with distilled water, degreased with acetone and dried before being introduced in the electrolyte solution.

The used devices have included an electronic multimeter 2420 3A SourceMeter, produced by the company Keithley, which can generate and measure the currents and/or the voltages in different stages. The working electrode potential has been read compared to the reference electrode by means of a digital milivoltmeter of type UT30F.

The electrodeposition has been realized by the galvanostatic, potentiostatic and cronoamperometric polarization and also by pulses voltammetric methods: the normal pulse voltammetry (NPV) and the differential pulse voltammetry (DPV).

For the potentiostatic method, the steps of potential of 5mV/sec have been applied, while for the galvanostatic polarization, the steps of current of 10μA/sec have been generated. For the methods in pulses we have chosen a basic potential of 0 V and the asccendent pulses have been applied (ΔE = 100 mV) for the method NPV (Fig. 1a), while for the differential pulse method (DPV) the basic potential has increased between the two successive pulses

with $\Delta e = 10$ mV. For both methods, the time between the two pulses and also the duration of a pulse was of 10 seconds (Fig. 1b).

The generation diagramm of the potential in pulses voltammetric methods is presented in the Fig. 1.
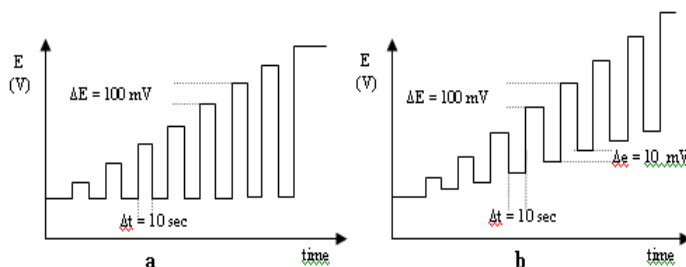

Fig. 1 *The generation scheme of the potential in:*
the normal pulse voltammetry (a), the differential pulse voltammetry (b).

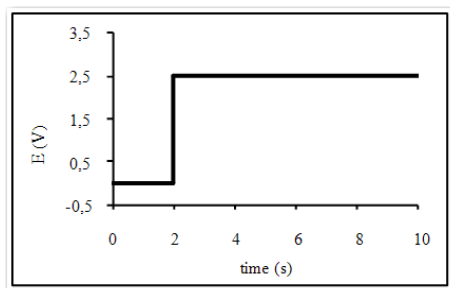The generation diagram of the potential in the chronoamperometric method is presented in Fig. 2:

Fig. 2 *The generation scheme of the potential in the chronoamperometric method.*

Results and discussions

1. The influence of the concentration of the tin ions

The effect of the concentration of the tin chloride, in the range $25 \cdot 10^{-3} - 10^{-1}$ M upon the electrodeposition of tin can be observed in Fig. 3, where the curves of potentiostatic polarization are presented.

The main cathodic reactions that take place at the tin electrodeposition are:

$$2H^+_{(aq)} + 2\bar{e} \rightarrow H_{2(g)} \tag{1}$$

$$Sn^{2+} + 2\bar{e} \rightarrow Sn \tag{2}$$

In the field $-0.25 \div -0.5$ V the cathodic process is the reduction of tin, the reaction (2), while the reaction (1) it take place only as an additional process. In this interval of potentials other secundary processes may occur; a mechanism of the reduction of tin, proposed in the literature [29], is:

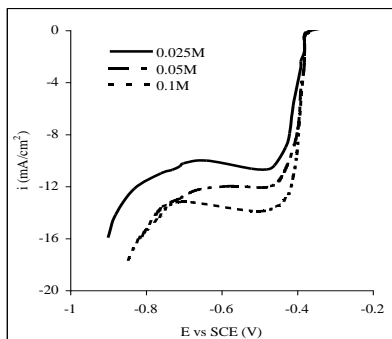The formation of some hydrated stannic complexes:

$$3Sn^{2+}+4H_2O \rightarrow (Sn^{2+})_3(H_2O)_4 \qquad (3)$$

$$Sn^{4+} +2H_2O \rightarrow Sn^{4+}(H_2O)_2 \qquad (4)$$

Fig. 3 *The corresponding voltammograms of the tin deposition from the nonadditive solutions of SnCl$_2$ 0.1M, 0.05M and 0.025M*

The cathodic reduction is determined by the processes:

$$2(Sn^{2+})_3(H_2O)_4+12\bar{e}\rightarrow Sn_6O_4(OH)_4 + 6H_2 \qquad (5)$$

$$Sn^{4+}(H_2O)_2+4\bar{e}\rightarrow SnO_2+2H_2 \qquad (6)$$

By using the **Randles-Sevcik** equation has been determined the diffusion coefficients for the Sn^{2+}, in the three solutions:

$$i_p = 0.4463\ n\ F\ A\ C\ (n\ F\ v\ D\ /\ R\ T)^{1/2} \qquad (I)$$

in this equation, n – the number of changed electrons (2), v – the potential scanning speed (0.005 V/sec), **F** – the constant of Faraday (96485 C/equivalent), **A** – the area of the electrode (4 cm^2), **R** – the universal constant of the gases (8.314 J/mol·K), **T** – the absolute temperature (K), and **D** is the diffusion coefficient (cm^2/sec). Knowing that the temperature was of 25°C (298.15 K), the equation Randles-Sevcik can be written in a simplified form:

$$i_p = (2.687 \cdot 10^5)\ n^{3/2}\ v^{1/2}\ D^{1/2}\ A\ C \qquad (II)$$

where the constant has the unit (2.687·10^5 C·mol^{-1}·L$^{-1/2}$).

So, for the three solutions of concentrations 0.1M, 0.05M and 0.025M, the diffusion coefficients are: 5.8·10^{-6}, 19.9·10^{-6} and respectively 55·10^{-6} cm^2/sec. We can observe that at the same time with the increase of the concentration; this is determined by the reach of a supersaturating concentration in the electric double layer for the Sn^{2+} ions at the same time with the increase of the concentration; this also justifies the increase of the current densities.

From Fig. 3 we can observe that at the same time with the increase of the concentration of SnCl$_2$ there also takes place a gradual increase of the cathodic current, and at the same time with the movement towards the more negative potentials, the depolarization by hydrogen also increases.

2. The influence of the additives

The process of electrochemical reduction of the Sn(II) shows some characteristics depending on the chemical composition of the electrolytic bath, respectively depending on the used additive.

The curves of potentiostatic polarization have been registered by the cathodic scanning of the potential form 0V la −1.5V in the solutions that are only made up of some additives and in the solutions 0.025M SnCl₂ + additives (boric acid, ammonium citrate, tartric acid or the mix of the three components and NaCl). The addition of the additives to the solution of electrolyte had not significantly moved the crystallization potential of tin (Fig. 4).

In all four cases, by additivation of the SnCl₂ solution, we did not observe a significant movement of the crystallization potential of the tin deposit away from −0.40 V, which corresponds to the non-additive solution.
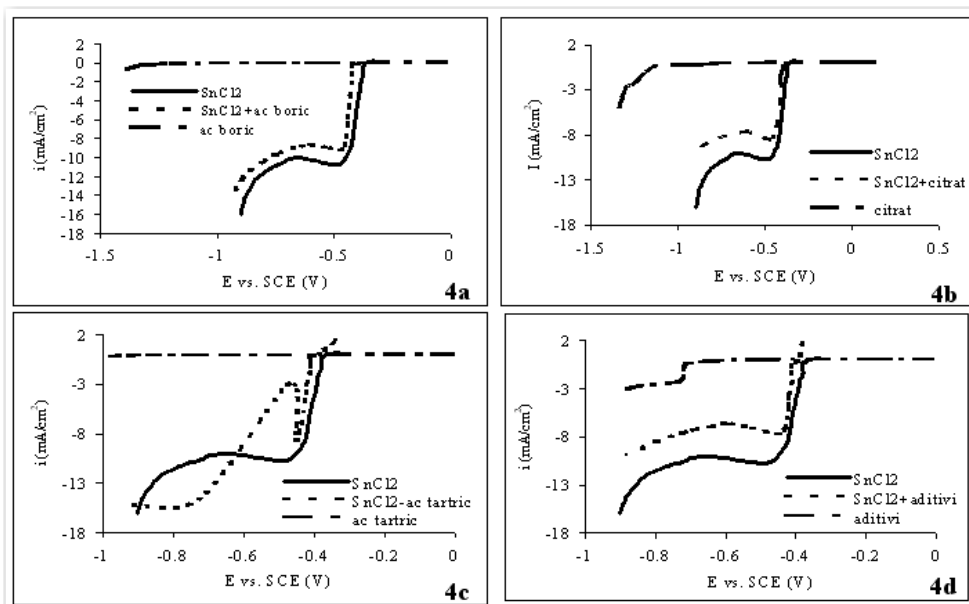

Fig. 4 *Cathodic voltamogramms of tin electrodeposition from SnCl₂ 0.025M + 10⁻³M boric acid (4a), SnCl₂ 0.025M + 10⁻³M ammonium citrate (4b), SnCl₂ 0.025M + 10⁻³M tartric acid (4c), SnCl₂ 0.025M + 10⁻³M tartric acid + 10⁻³M ammonium citrate + 10⁻³M boric acid + 5·10⁻³M NaCl (4d).*

3. The influence of the electrodeposition method

Knowing that the electrodeposition of a metal or of a metallic alloy is influenced by the generation scheme of the current or of the tension, has been studied by a comparison the electrodeposition of the tin by the potentiostatic method (Fig. 5a), galvanostatic (Fig. 5b), the normal pulse voltammetry (Fig. 5c) and the differential pulse voltammetry (Fig. 5d).
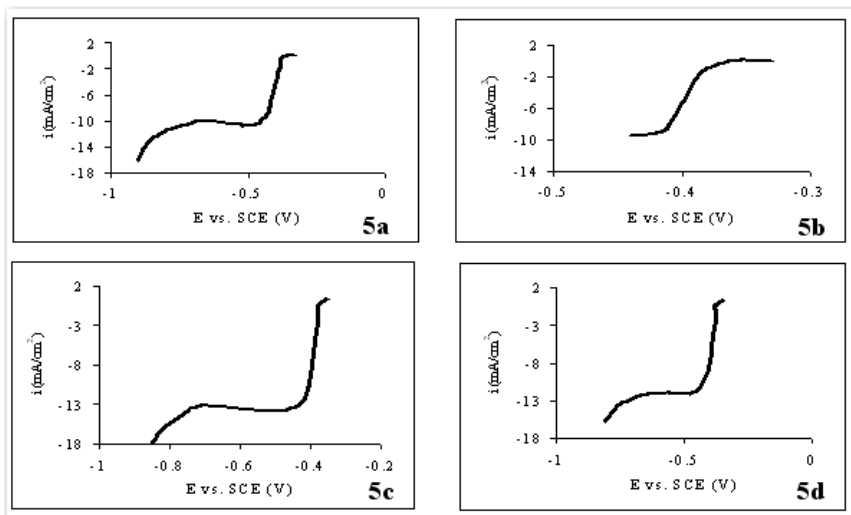
Fig. 5 *Cathodic curves coressponding to tin electrodeposition from SnCl$_2$ 0.025 M: potentiostatic (5a), galvanostatic (5b), NPV (5c) and DPV (5d).*

We can observe from the Fig. 5 that under the practical aspect there is no big differences between the crystallization potentials of tin, obtained for the three methods (potentiostatic, NPV and DPV). But, by the galvanostatic deposition, the crystallization potential is slightly moved towards more positive values (-0.36 V). The closeness of the crystallization potential to the reversible one (-0.35 V) indicates a more powerful interaction metallic deposit-base metal. In the same time, by the galvanostatic method, we can obtain the deposit with the biggest thickness and the best adherence.

By using the chronoamperometric method, we have traced the current transients for the overpotentials of η = 20 mV (E = –0.38 V), η = 40 mV (E = –0.40 V), η = 60 mV (E = –0.42 V).
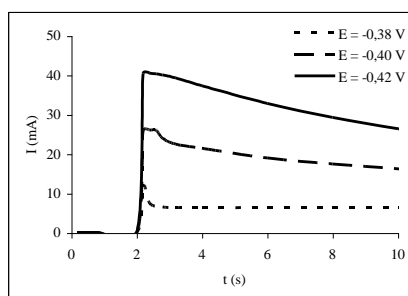

Fig. 6 *The current transients that correspond to the electrodeposition of tin from SnCl$_2$ 0.025M at E = -0.38V, E = -0.40V, E = -0.42V.*

By using the kinetic model of instantaneous and progressive electrodeposition of Sharifker [30]:

$$\left(\frac{I}{I_{max}}\right)^2_{inst} = \frac{1,9542}{t/t_{max}}\left\{1-\exp\left[-1,2564\left(\frac{t}{t_{max}}\right)\right]\right\}^2 \qquad (III)$$

$$\left(\frac{I}{I_{max}}\right)^2_{prog} = \frac{1,2254}{t/t_{max}}\left\{1-\exp\left[-2,3367\left(\frac{t}{t_{max}}\right)^2\right]\right\}^2 \qquad (IV)$$

where: I, I_{max} represent the current and maximum current respectively; t, t_{max} represent the time and maximum time corresponding to the transient current from chronoamperommetry.

We have represented the non-dimensional curves $(I/I_{max})^2 = f(t/t_{max})$ that correspond to the experimental electrodeposition of the tin from $SnCl_2$ 0.025M to E = –0.42V, and the theoretical curves for the instantaneous and progressive electrodeposition.
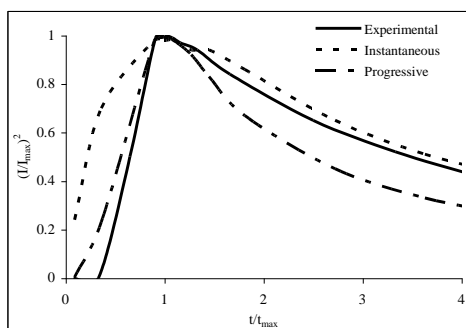

Fig. 7 *The representation of the non-dimensional curves $(I/I_{max})^2 = f(t/t_{max})$ corresponding to the experimental electrodeposition of the tin from $SnCl_2$ 0.025M to E = -0.42V, and the theoretical curves for the instantaneous and progressive electrodeposition.*

As we can also observe from Fig. 7, we can affirm that the electrodeposition of tin on the carbon steel electrode, in the given experimental conditions, takes place taking into consideration an instantaneous kinetics of nucleation.
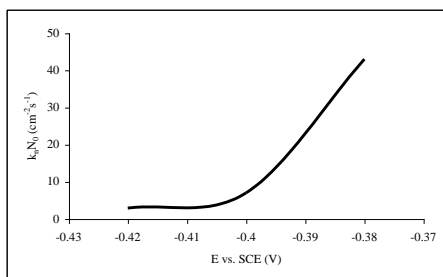

Fig. 8 *The variation of the nucleation rate, k_nN_0 in the same time with the increase of the cathodic overtensions of electrodeposition.*

By determining the nucleation rate by the formula (V) we can observe from Fig. 8 that the nucleation rate, k_nN_0 decreases in the same time with the increase of the cathodic overpotentials of electrodeposition (Fig. 8).

$$k_n N_0 = 0,2898 \frac{1}{8\pi c_0 V_m^{1/2}} \frac{zFc_0}{I_{max}^2 t_{max}^3}^2 \qquad (V)$$

where: c_0 is concentration of the $SnCl_2$; V_m is molar volume; z is the number of the changed electrons; F is the Faraday number.

The parameters of the electrodeposition process are presented in Table 1.

Table 1 The parameters of the electrodeposition.

Potentiostatic method		Chronoamperometric method c = 0.025 M				
c (M)	D (cm^2/sec)	E (V)	η (V)	I_{max} (mA)	t_{max} (s)	$k_n N_0$ ($cm^{-2}s^{-1}$)
0.1	$5.8 \cdot 10^{-6}$	-0.38	0.02	11.91	2.2	$43 \cdot 10^6$
0.05	$19.9 \cdot 10^{-6}$	-0.40	0.04	26.1	2.4	$7 \cdot 10^6$
0.025	$55 \cdot 10^{-6}$	-0.42	0.06	40.53	2.4	$2.9 \cdot 10^6$

Conclusions

We can observe that at the same time with the increase of the concentration it also takes place a decrease of the diffusion coefficients, this thing being determined by a reached supersaturating level of the concentration in the electric double layer for the ions Sn^{2+}, thing that also justifies the increase of the current densities.

The addition of additives do not move the crystallization potential and it presents the advantage of getting some uniform and compact deposits with a much better adherence of the layer.

We have observed that under the practical aspect there are no big differences between the crystallization potentials for the deposition of the tin, determined by the four methods (–0.40 V in the potentiostatic methods, NPV and DPV and –0.38 V in the galvanostatic method).

The chronoamperometric method indicates an instantaneous nucleation mechanism, this thing also being confirmed by the decrease of the nucleus rate in the same time with the increase of the deposition overtension.

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