

The study on the influence of aminic additives in the tin electro-deposition process on the carbon steel surface from the alkaline bath

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The present paper discusses the electrodeposition of tin from an alkaline bath of SnCl_2 10^{-1}M without additives and with ethylenediamine, N,N-diethylethylenediamine and ethanolamine additives 10^{-2}M . The investigation of the crystallization processes was made by means of electrochemical methods: the galvanostatic polarization and chronoamperometry. The galvanostatic measurements indicate that the presence of additives shifts the crystallization potential through more negative values. The morphology of metallic deposits were analysed with an Euromex microscope. The chronoamperometric data shows a 3D progressive nucleation for tin electrodeposition from alkaline bath without or with aminic additives.

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1. Introduction

There is an increasing interest in using the tin as a substitute for the conventional deposition because of its more harmless impact on the environment [1-3]. For example, tin and tin alloys are possible replacements of the depositions of chromium and cadmium used with decorative purposes, respectively in applications to electronics [4].

The electrodepositing of the tin can be obtained both from acid and basic baths [5, 6]. Tin acid baths (fluorine-boron acid, sulfate, chlorides, methanesulfonic acid) generally contain additives to inhibit the oxidation of Sn(II) to Sn(IV) [7,8].

Recent studies report the Sn electrodeposition and tin alloys [9, 10]; Au-Sn [11], Sn-Bi [12], Sn-Ag, Sn-Zn, Sn-Cu [13,14], Sn-Pb, Sn-Co [15], and the influence of the additives as: triethanolamine [16], tartaric acid [17], sodium gluconate [18], sodium citrate, ethilenglicol [19], sorbitol [20].

The electrolyte composition has an important role in the determination of the quality of the electrodeposited films [21]. The usage of the additives in the methods of electrodeposition from aqueous solution has some advantages, as the following: metallic shine, the increase of the dimension of the deposited film, modification of the mechanical and physical properties, stress reduction. In addition, the presence of complexant agents in the solution during the processes of electrodeposition increases the life duration of galvanic bath and the adherence of the film to the substrate [22-24].

The low oxidation potential of the tin makes it an electrodic material possible for the oxidative catalytic processes [25, 26]. The tin deposition on the Pt is often used to the electro-oxidation of the formic acid and carbon monoxide for its catalytic effects [27, 28].

To the electrodeposition of the tin on the Pt can occur the formation of some bimetallic compounds $[\text{Pt}_3\text{Sn}]$; $[\text{PtSn}]$ with different catalytic activities. On the other hand, to the electrodeposition of the tin of soluble salts in HCl watery solution, there is formed an instable coat on the gold electrodes. In the case of the Pd electrodes, the absorption of the tin takes place by ionization of the absorbed hydrogen and the irreversible disproportion of Sn^{2+} with formation of the Sn^{4+} and absorbed Sn^0 species.

The present study aims to determine the role of aminic additives in electro-deposition process of tin on the carbon steel surface, using the galvanostatic polarization and chronoamperometry measurements. The morphology of metallic deposits were analysed with an Euromex microscope.

2. Experimental part

The electrodeposition of the tin on carbon steel support was accomplished by using solutions of SnCl_2 10^{-1}M , sodium and potassium tartrat $2 \cdot 10^{-3}\text{M}$, 0.5 g/L gelatin, NaOH (pH=12.5) non-additived and additived with (10^{-2}M) ethylendiamine, N,N-diethylethylendiamine (10^{-2}M) and ethanolamine (10^{-2}M), to the room temperature.

There was used a standard non-divided electrochemical cell, with a working electrode of carbon steel (surface 4 cm^2), an auxiliary electrode of shiny platinum in the form of a plate (surface 1 cm^2), and as a reference electrode was used the calomel saturated electrode (CSE). The working electrode, in carbon steel (C – 0.1% , Mn – 0.4% , Si – 0.035% , Cr – 0.3% . Fe rest) was sanded with metallographic paper of very fine composition, washed with distilled water, degreased with acetone and dried before introducing it in the electrolite solution.

The equipment used included an electronic multi-meter 2420 3A Source Meter, made by Keithley firm, that can generate and measure currents and/or tensions in different steps. The potential of the working electrode was read against the referential electrode with the help of a digital millivoltmeter of the UT30F type. The electro-deposition was accomplished by galvanostatic polarisation ($v = 5 \mu\text{A}/\text{sec}$), potentiostatic ($v = 5 \mu\text{V}/\text{sec}$). There was used the chronoamperometric method to determine the nucleation mechanism. The morphology of the electrodeposited covers was analyzed with a Euromex microscope.

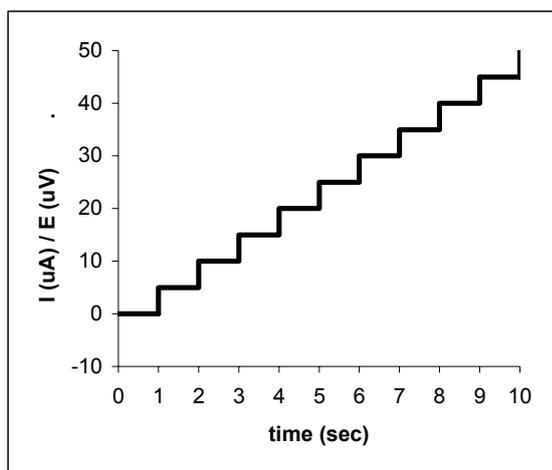


Fig. 1. The generation scheme of the current in galvanostatic methode ($v = 5 \mu\text{A}/\text{sec}$) / potential in potentiostatic methode ($v = 5 \mu\text{V}/\text{sec}$).

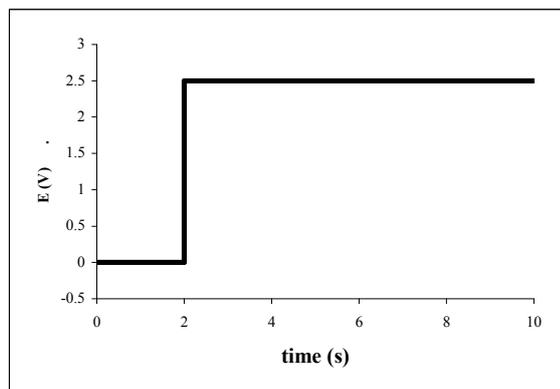


Fig. 2. The generation scheme of the potential in chronoamperometric methode.

3. Results and discussion

3.1. The influence of the additives

The process of electrochemical reduction of the Sn(II) shows some characteristics depending of the used additive. Potentiostatic polarization curves were registered by cathode of the potential from 0 V to -1.5V, in solutions of SnCl_2 0.1M non-additived and additived with

ethylendiamine, N,N-diethylethylendiamine and ethanolamine (Fig. 3).

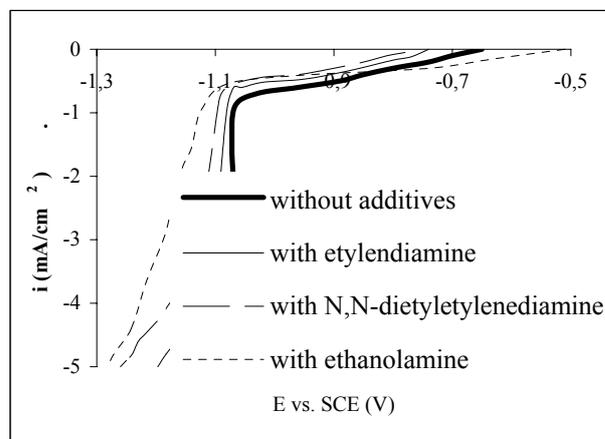
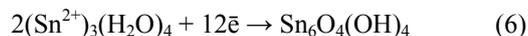
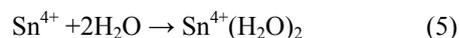
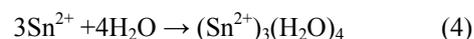
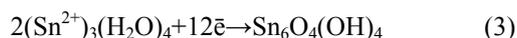


Fig. 3. The potentiograms corresponding to the electrodeposition of the tin from solutions of SnCl_2 0.1M, non-additived and additived with ethylendiamine 0.01M, N,N-diethylethylendiamine 0.01M and ethanolamine 0.01M.

Adding the additives in the electrolyte solution move the potential of crystallization of the tin to values more and more negative; -1.06V for the non-additived solution and respectively -1.07V, -1.09V, -1.11V corresponding to the additived solutions with ethylendiamine, N,N-diethylethylendiamine and ethanolamine.

The main cathodic reactions that take place with the occasion of the electrodeposition of the tin from the alkaline bath are the following:



3.2. Determination of diffusion coefficients

By using the Randles-Sevcik equation there were determined the diffusion coefficients for the Sn^{2+} in all the four solutions:

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

in this equation; n – the number of changed electrodes (2), v – bathing speed of the potential (0.005 V/sec), F –

Fraday constant (96485 C/echivalent), **A** – surface of the electrode (4 cm²), **C** – concentration of the electrolyte solution (0.1 mol/L), **R** – universal gas constant (8.314 J/mol·K), **T** – absolute temperature (K), and **D** is the diffusion coefficient (cm²/sec). Knowing that the temperature was of 25°C (298.15 K), Randles-Sevcik equation can be written in a simplified form:

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

where the constant has the unit (2.687·10⁵ C mol⁻¹L^{-1/2}).

This way, for the four solutions, non-additived and additived with ethylendiamine, N,N-diethylethylendiamine and ethanolamine, the diffusion coefficients are: 2.04·10⁻⁸, 2.75·10⁻⁸, 3.62·10⁻⁸ respectively 4.59·10⁻⁸ cm²/sec.

3.3. Determination of the nucleation mechanism

By using the chronoampermetric method there were lined the transients of current for the η = 10, 30, 50 mV overcharges.

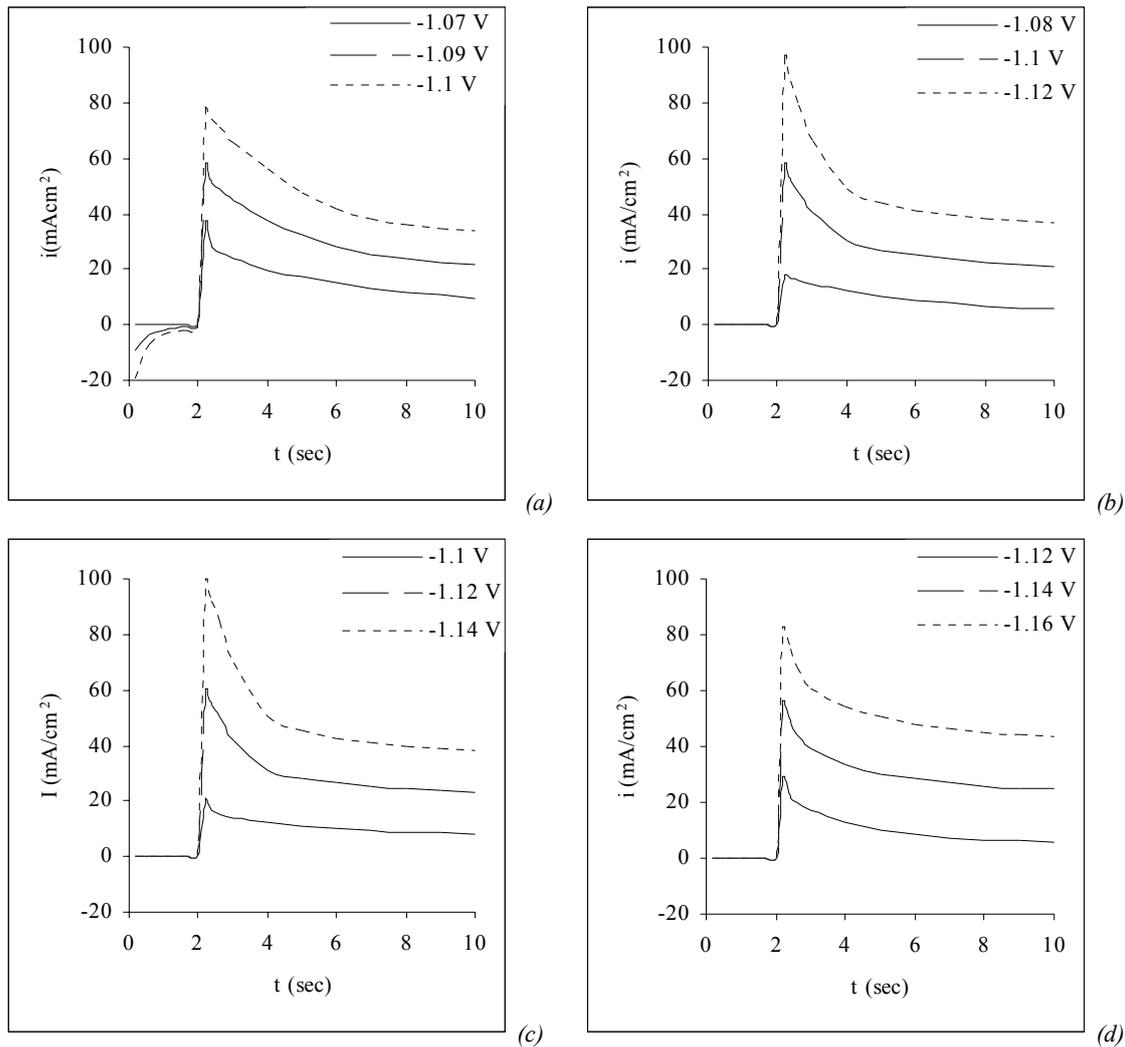


Fig. 4. The corresponding transients for the electrodeposition of tin from solutions of non-additived SnCl₂ 0.1M (a) and additived solutions with ethylendiamine 0.01M (b), N,N-diethylethylendiamine 0.01M (c), and ethanolamine 0.01M (d) to η = 10, 30, 50 mV.

By using the kinetic model of instant and progressive electrodeposition of Sharifker:

$$2D_{inst} \left(\frac{I}{I_{max}} \right)_{inst} = \frac{t}{t_{max}} \exp \left\{ -1/2 \left[\frac{t^2 - t_{max}^2}{t_{max}^2} \right] \right\} \quad (1')$$

$$2D_{\text{prog}} \quad \left(\frac{I}{I_{\text{max}}} \right)_{\text{prog}} = \left(\frac{t}{t_{\text{max}}} \right)^2 \exp \left\{ -2/3 \left[\left(\frac{t}{t_{\text{max}}} \right)^3 - \left(\frac{t_{\text{max}}}{t_{\text{max}}} \right)^3 \right] \right\} \quad (2')$$

$$3D_{\text{inst}} \quad \left(\frac{I}{I_{\text{max}}} \right)_{\text{inst}}^2 = \frac{1,9542}{(t/t_{\text{max}})} \left\{ 1 - \exp \left[-1,2564 \left(\frac{t}{t_{\text{max}}} \right) \right] \right\}^2 \quad (3')$$

$$3D_{\text{prog}} \quad \left(\frac{I}{I_{\text{max}}} \right)_{\text{prog}}^2 = \frac{1,2254}{(t/t_{\text{max}})} \left\{ 1 - \exp \left[-2,3367 \left(\frac{t}{t_{\text{max}}} \right)^2 \right] \right\}^2 \quad (4')$$

here were represented the non-dimensional curves $I/I_{\text{max}} = f(t/t_{\text{max}})$ și $(I/I_{\text{max}})^2 = f(t/t_{\text{max}})$ corresponding to the experimental and theoretic electrodeposition (2D and

respectively 3D) of tin from solutions of SnCl_2 0,1M non-additived and additived with aminic additives.

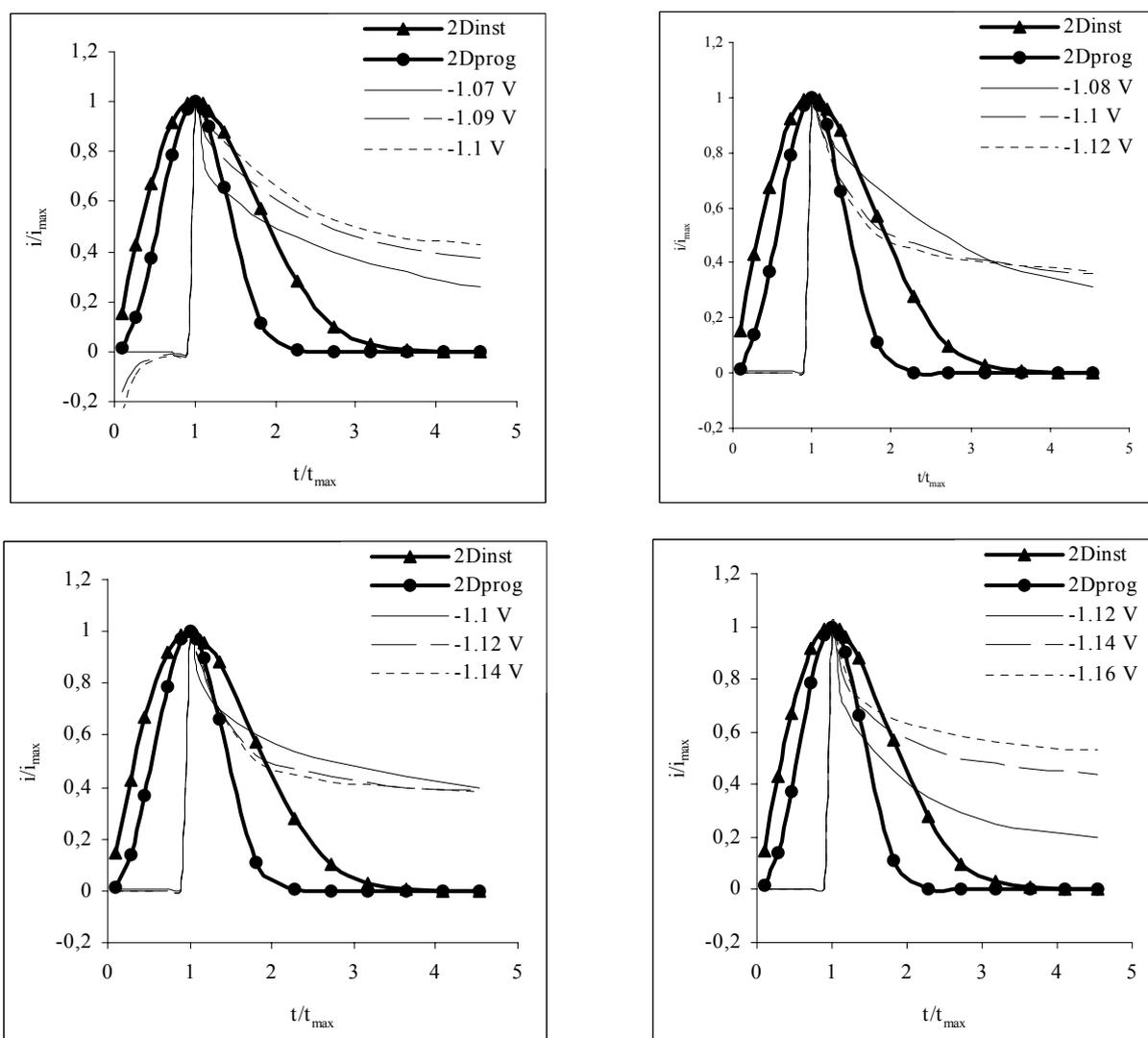


Fig. 5. Representation of the non-dimensional curves $(I/I_{\text{max}}) = f(t/t_{\text{max}})$ corresponding to the experimental and theoretic electrodeposition of tin from solutions of SnCl_2 0.1M non-additived and additived with aminic additives, by 2D instant and progressive electrodeposition.

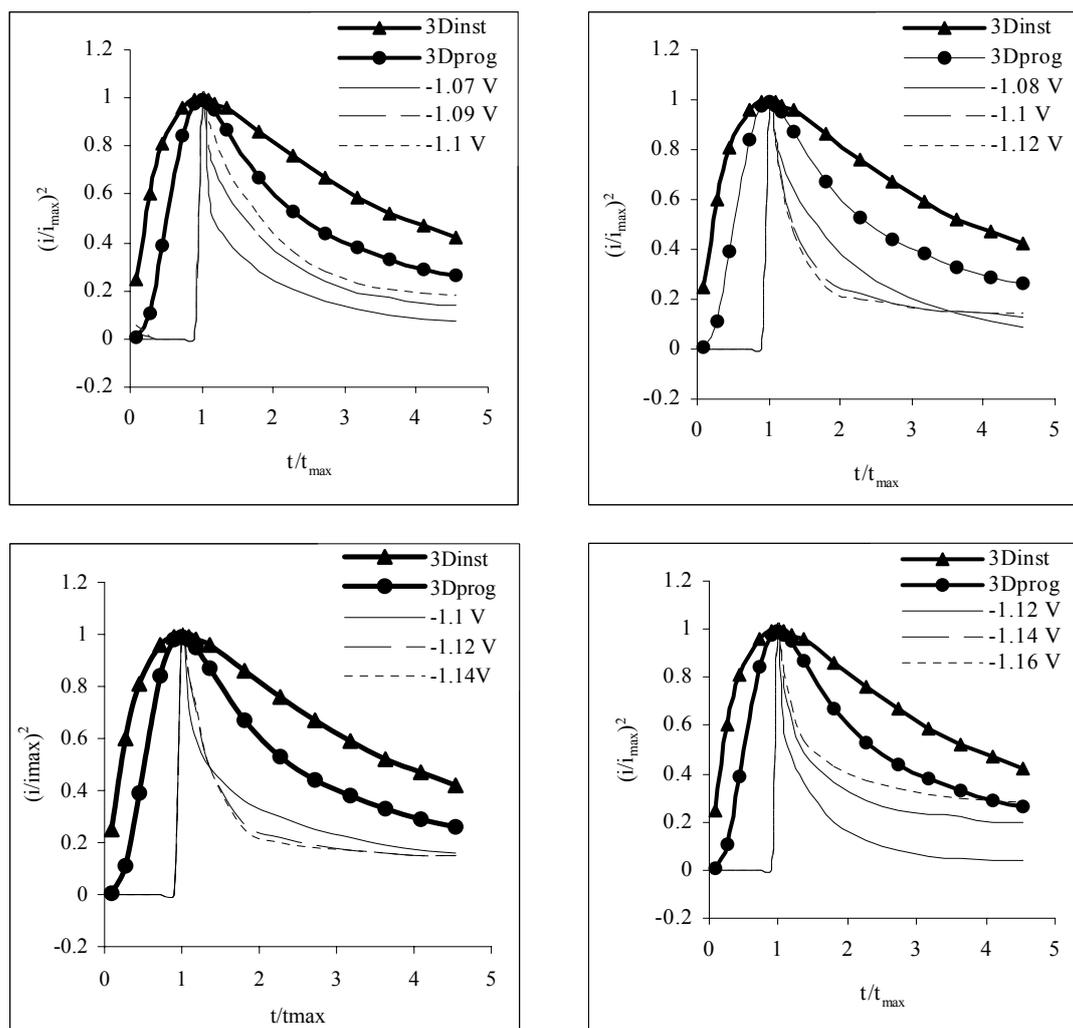


Fig. 6. Representation of the non-dimensional curves $(I/I_{max})^2 = f(t/t_{max})$ corresponding to the experimental and theoretic electrodeposition of tin from solutions of SnCl_2 0.1M non-additived and additived with aminic additives, by **3D** instant and progressive electrodeposition.

As one can observe from Figs. 5 and 6, one can affirm that the electro-deposition of the tin on the carbon steel electrode, in the given experimental conditions, takes place after a progressive kinetic of **3D** nucleation, both in absence and presence of aminic additives.

3.4. The analysis by microscopy of the electrodeposited films

By using a Euromex, Holland microscope, there was analyzed the surface morphology of the carbon steel both before the electrodeposition and after the electrodeposition of the tin from SnCl_2 0.1M non-additived and additived with aminic additives solutions.

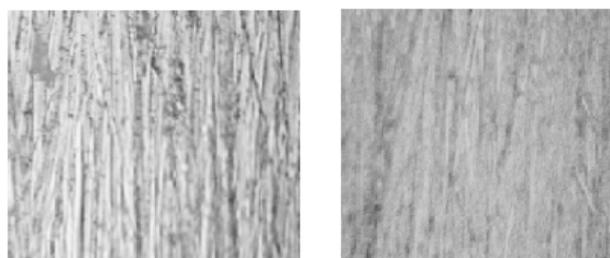


Fig. 7. The surface of the carbon steel (a) before the electrodeposition and (b) covered with Sn from the non-additived SnCl_2 10^{-1}M solution.

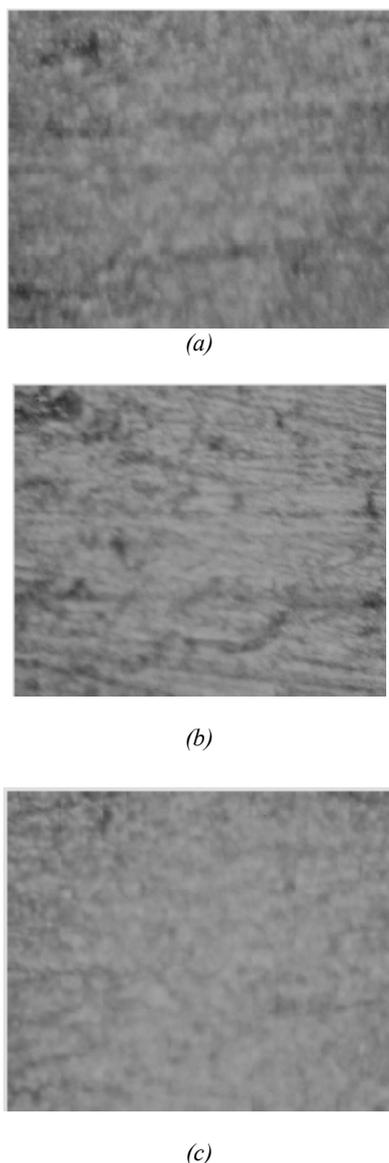


Fig. 8. The surface of the carbon steel covered with Sn from the SnCl_2 0.1M solution additived with (a) ethylenediamine, (b) N,N-diethylethylenediamine and (c) ethanolamine.

The microscopic analysis of the electrodeposited tin covers, indicate their superior density in the presence of the ethanolamine and slightly lower in the presence of ethylenediamine, N, N-diethylethylenediamine and respectively in the absence of additives.

4. Conclusions

One can observe that once with the addition of additives (ethylenediamine, N,N-diethylethylenediamine and ethanolamine) there takes place a movement of the crystallization potentials towards values more and more negatives once with the growth of the diffusion coefficients, this is, most probably, because of the formation of some ion complex of Sn^{2+} with the additive molecules.

The crystallization potential is out of place because of the adding of additives and presents the advantage of obtaining some even, dense depositions with a better adherence to the undercoat.

There has been observed that under practical aspect there are no big differences among the tin crystallization potentials, determined through the two methods (-1.07 V in the potentiostatic method and -1.06 V in the galvanostatic method). The chronoamperometric method indicates a progressive 3D nucleation mechanism.

The microscopic analysis shows a decrease of density in the electrodeposited films in the presence of additives, in the following order: ethanolamine > ethylenediamine > N,N-diethylethylenediamine and the films deposited on the carbon steel surface from non-additived alkaline solution

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