

INITIAL STAGES OF TIN ELECTRODEPOSITON FROM SULPHATE-TARTRATE BATHS

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Abstract

Due to the recent interest on tin and tin alloy electroplating, the electrodeposition of tin from sulphate-tartrate baths has been studied in its initial stages. Potentiostatic and potentiodynamic electrochemical techniques have been applied using a three electrode cell and a vitreous carbon electrode. The influence of tartrate, pH and potential in the voltammetric and chronoamperometric response has been analysed and compared with other systems, and the model of nucleation and growth has been obtained. In the experimental conditions of the work, an instantaneous nucleation under diffusion control occurs.

Keywords: tin electrodeposition, sulphate/tartrate bath, nucleation model, critical nucleus.

1. Introduction

The interest of tin and tin alloys has increased in the later years, as possible substitutes for many of the conventional coatings, because tin and tin alloys can be electrodeposited from more benign electrolytes and then minimise the environmental impact. As examples, tin and tin alloys are possible substitutes of toxic chromium and cadmium deposits for decorative and electrical/electronic applications, respectively [1-3]; electroplated pure tin has also been used in the electronic industry as an alternative for tin/lead finishes [4]. Also tin/zinc alloys has been proposed as substitutes of allergenic nickel deposits for decorative and functional coatings [5-8].

Tin has been commercially electrodeposited from acid and alkaline baths [9-11], being the former the more used to obtain bright coatings although involved highly acidic and corrosive electrolytes as sulphuric and fluoride acids. The use of alkanesulphonic acids, particularly methanesulphonic acid [12], and sulphate/complexing agents baths [13-15] appears to show considerable promise as commercial baths for tin and tin alloys.

The recent published studies about tin or tin alloy electrodeposition [12-22] are mainly focused in the study of the additives, the bath compositions and the plating variables which permit to obtain coatings for commercial uses, but only few results about the reduction kinetics of Sn(II) obtained by chronoamperometric techniques were reported [23-26]. In this study, the tin electrodeposition from a sulphate bath using tartrate as chelating agent was investigated by means of potentiodynamic and potentiostatic electrochemical techniques, in order to establish the influence of the electroplating variables in the earlier stages of tin deposit. The model of nucleation and growth of the earlier stages of tin deposits in a sulphate-tartrate bath will be obtained and these results will be compared with those obtained in a sulphate-gluconate bath [26].

2. Experimental

The electrochemical measurements were performed in a three electrode cell using a vitreous carbon electrode as working electrode (area=0.031 cm²), a platinum wire as counter electrode and Ag/AgCl /KCl (3 M) as reference electrode, inserted in a Luggin capillary. All potentials reported in the text are referred to this electrode. An AUTOLAB PSTAT10 was used as potentiostat controlled by a microcomputer. Different sets of voltammetric and chronoamperometric experiments were done. Voltammetric experiments were carried out at 50 mV s⁻¹, scanning at first to negative potentials, and running only one cycle in each experiment. Chronoamperometric experiments were carried out by stepping from an initial potential of -300 mV to the selected final potential, in a wide range.

Chemicals used were SnSO₄, tartaric acid (C₄H₆O₆), sulphuric acid, sodium hydroxide and Na₂SO₄ analytical grade. All solutions were freshly prepared with water, first distilled and then treated with a Millipore Milli Q system. The acidic sulphate bath contained 1 M H₂SO₄ as supporting electrolyte and 0.12 M tartaric acid. The bath at pH 4 and 5 contained 0.9 M Na₂SO₄ as supporting electrolyte and 0.12 and 0.2 M tartaric acid as chelating agent; the pH was adjusted using sodium hydroxide. In all cases the SnSO₄ concentration was 0.01 M. Before each experiment the solution was deaerated

with argon. The working electrode was polished mechanically before each run with alumina powder of 3.75 and 1.87 μm and followed by a short electrochemical conditioning.

3. Results and discussion

Voltammetric study.

The voltammetric curves reveal, firstly, that in a highly acidic sulphate bath the addition of tartrate ion (fig 1, curve a) does not change the reduction potential of tin, and the electrodeposition takes place around -500 mV as in the absence of tartrate [25]. When the pH is increased to 4 a potential shift to around -700 mV is obtained (fig 1, curve b), revealing that at this pH the complexation of Sn(II) ions by tartrate ions in solution takes place (complexation constants are: $K_1=1.78 \cdot 10^6$, $\beta_2=3.02 \cdot 10^{11}$, at 20°C). Also a significant decrease in the cathodic current is observed. A similar behaviour was observed with a gluconate/sulphuric acid bath and a gluconate/sulphate pH=4 bath, respectively [26]. Reversing the potential in the reduction peak, the response have a shape typical of an electrodeposition process (fig 2), showing a loop with cathodic current greater than that recorded in the preceding negative potential scan.

The anodic scan in the voltammetric curve at pH=4 shows two oxidation peaks instead of the single peak obtained in the highly acidic bath. It is also seen that these two peaks are broader and the anodic currents are much lower. Two peaks were also observed in presence of gluconate at pH=4 [26]. Comparing both media, it is seen that these two peaks are not so well separate in tartrate as in gluconate, and that in tartrate the first peak is more important, meanwhile in gluconate the most important is the second one. The ratio between height of peak I respect to height of peak II increases when the potential scan limit is made more negative (fig 2 and 3). On the other hand, the influence of tartrate is also more important on peak I since this peak becomes more important when tartrate concentration increases (fig 3).

If the potential limit of the cathodic scan is made more negative, a second reduction process around -1000 mV is obtained (fig 3), before the hydrogen evolution takes place. The second reduction process is favoured with the increase of tartrate ion concentration. The shape of the oxidation peaks is not changed.

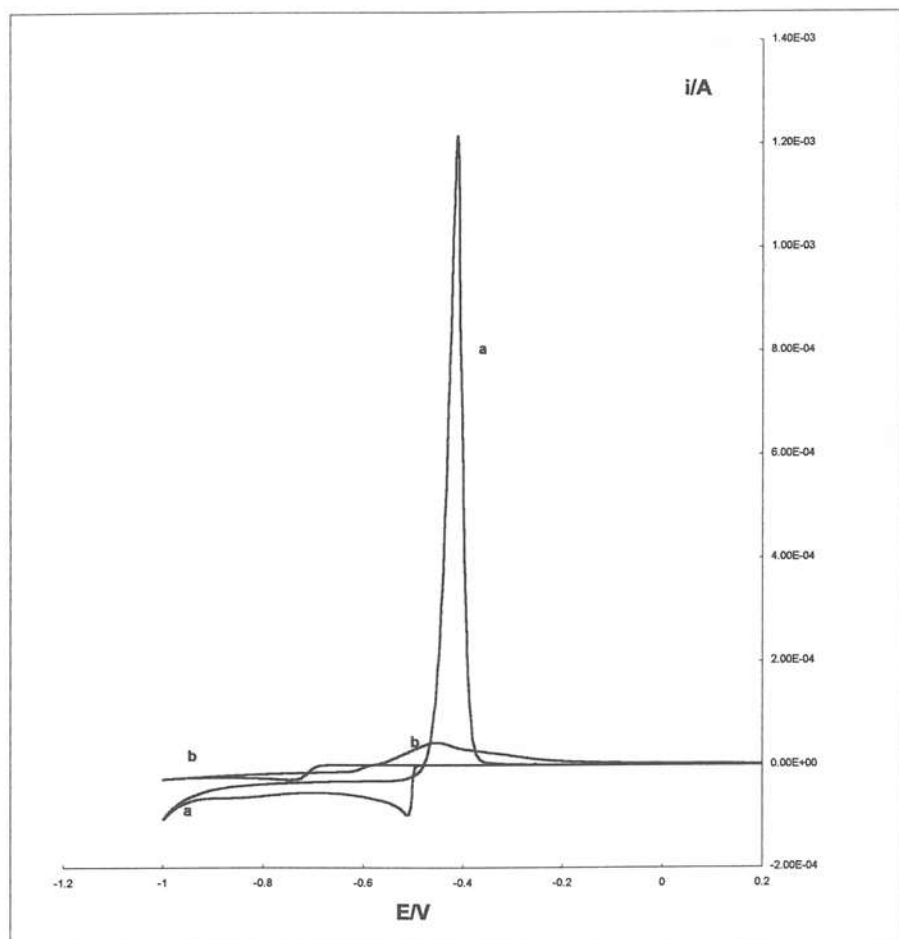


Figure 1. Cyclic voltammograms at 50 mV s^{-1} for solutions: a) 0.01 M SnSO_4 , 1 M sulphuric acid and 0.12 M tartaric acid; b) 0.01 M SnSO_4 , $0.9 \text{ M Na}_2\text{SO}_4$ and 0.12 M tartaric acid, $\text{pH}=4$.

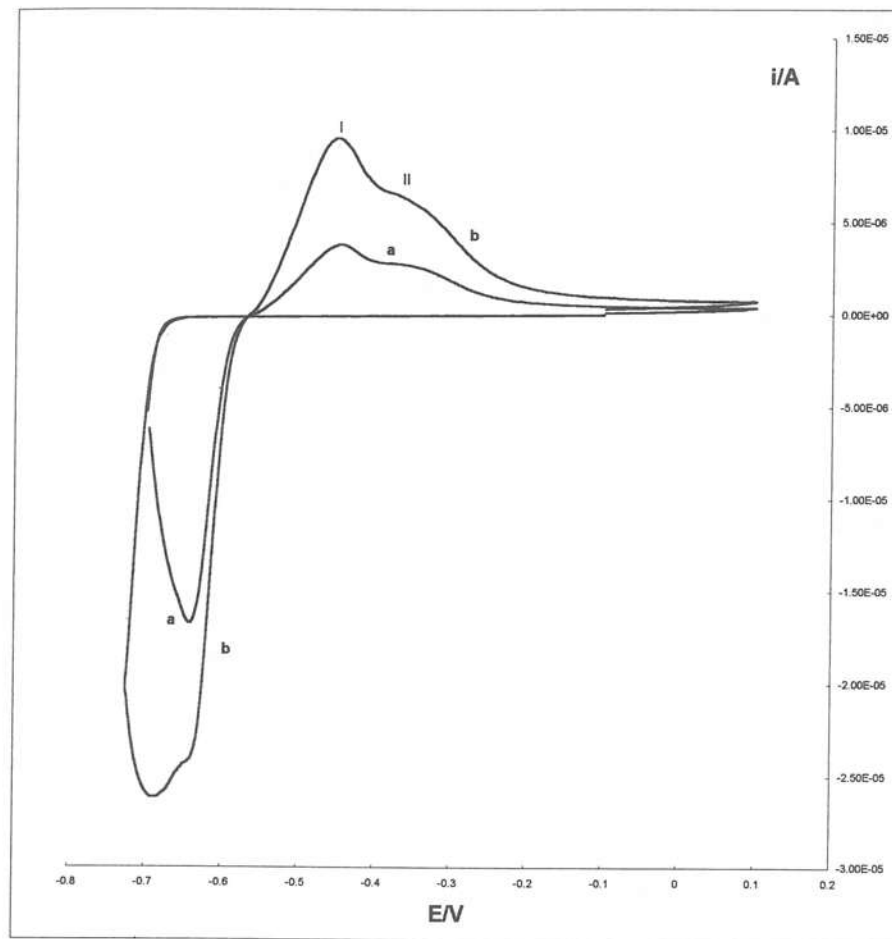


Figure 2. Cyclic voltammograms at 50 mV s^{-1} for solution 0.01 M SnSO_4 , $0.9 \text{ M Na}_2\text{SO}_4$, 0.12 M tartaric acid and $\text{pH}=4$, at low limit cathodic potentials: a) -700 mV ; b) -725 mV .

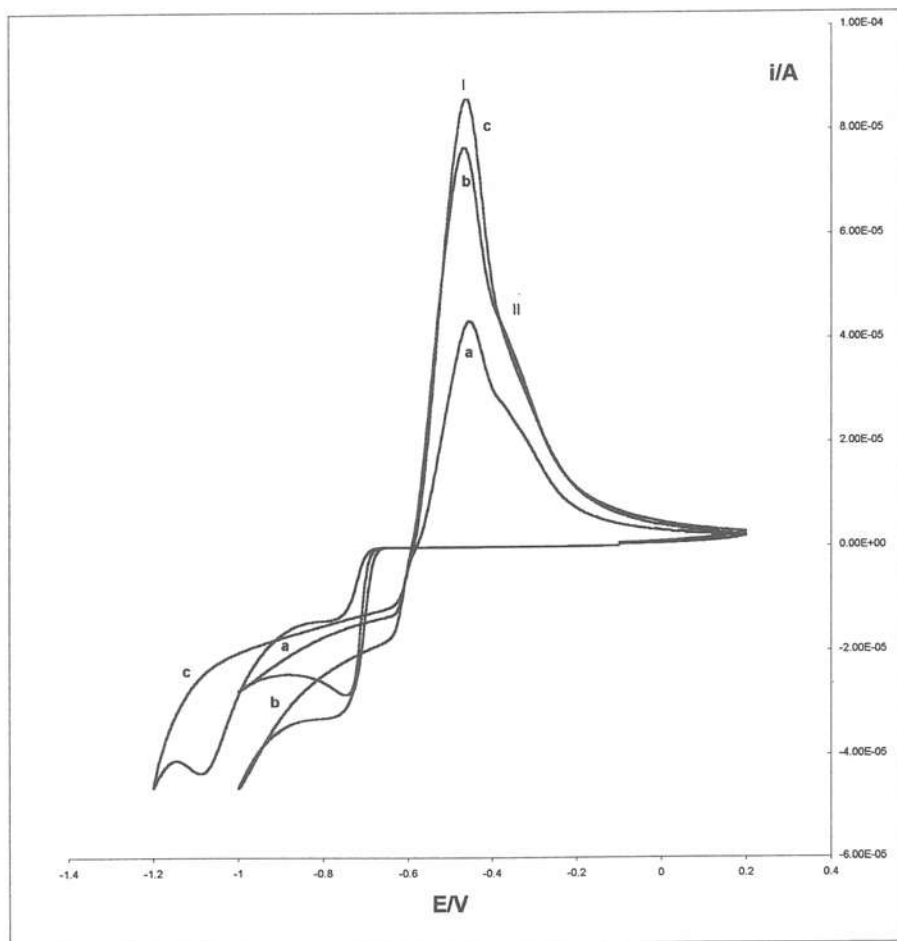


Figure 3. Cyclic voltammograms at 50 mV s^{-1} for different solutions 0.01 M SnSO_4 , $0.9 \text{ M Na}_2\text{SO}_4$, $x \text{ M tartaric acid}$, $\text{pH}=4$: a, c) $x=0.12$, b) $x=0.2$; and different cathodic limits: a, b) -1000 mV , c) -1200 mV .

Previous studies of the aqueous electrochemistry of tin [27 and references cited therein] report data about the hydrolytic behaviour of the stannous ion Sn^{2+} . From these studies the following reaction,



is proposed in H_2SO_4 medium with a constant value of 24.5 at 25°C . The extension of the previous reaction will be more important at $\text{pH}=4$. Then, such as it has been reported in the bibliography for the voltammetric response of other metallic ions [28], a competition between hydroxide ion and the organic tartrate ion to complex Sn^{2+} can explain the two reduction and oxidation peaks observed in figures 2 and 3. In the cathodic scan of figure 3, the first reduction peak appears approximately at the same potential for a sulphate/tartrate bath at $\text{pH}=4$ that for a sulphate/gluconate bath at $\text{pH}=4$ of the same composition [26]. This peak can be attributed to the reduction via SnOH^+ species. The second reduction peak is displaced to more negative potentials in tartrate medium than in gluconate medium. This can be explained because the stability constants of Sn-tartrate complexes are much bigger than those of Sn-gluconate complexes [26]. In the anodic scan of figure 3, the oxidation peak I corresponds to tin oxidation via the formation of Sn-tartrate complexes in solution meanwhile the second oxidation peak II corresponds to tin oxidation via the formation of SnOH^+ species in solution.

When the pH is increased until 5 the reduction potentials are shifted to more negative potentials. The shape of the cathodic scan is the same but the intensity of the reduction peaks is lower. In the anodic scan a third oxidation peak around -200 mV appears at this pH (fig 4), which is more important if a more cathodic limit is reached. The shape and position of this peak III is related to oxidation of the hydrogen that remain adsorbed on the surface instead of to evolve far from the electrode surface. To corroborate this statement the stripping response for two experiments with and without agitation conditions was performed. The agitation of the solution during the deposition process favours the diffusion of hydrogen far from the electrode surface and then the oxidation peak III does not appear in the stripping response.

Chronoamperometric study.

A potentiostatic study of the tin electrodeposition in the bath a $\text{pH}=4$ is made at different electrodeposition potentials. The chronoamperometric curves (fig 5) show a typical shape in the range between -750 and -950 mV , with a maximum for the more negative potentials. From the analysis of the current transients in their raising part, and taking into account the induction time t_0 , a dependence against $(t-t_0)^{1/2}$ is observed (fig 6), indicating that a instantaneous nucleation (IN) under diffusion control at the initial stages of tin electrodeposition takes place [29-31]. When the

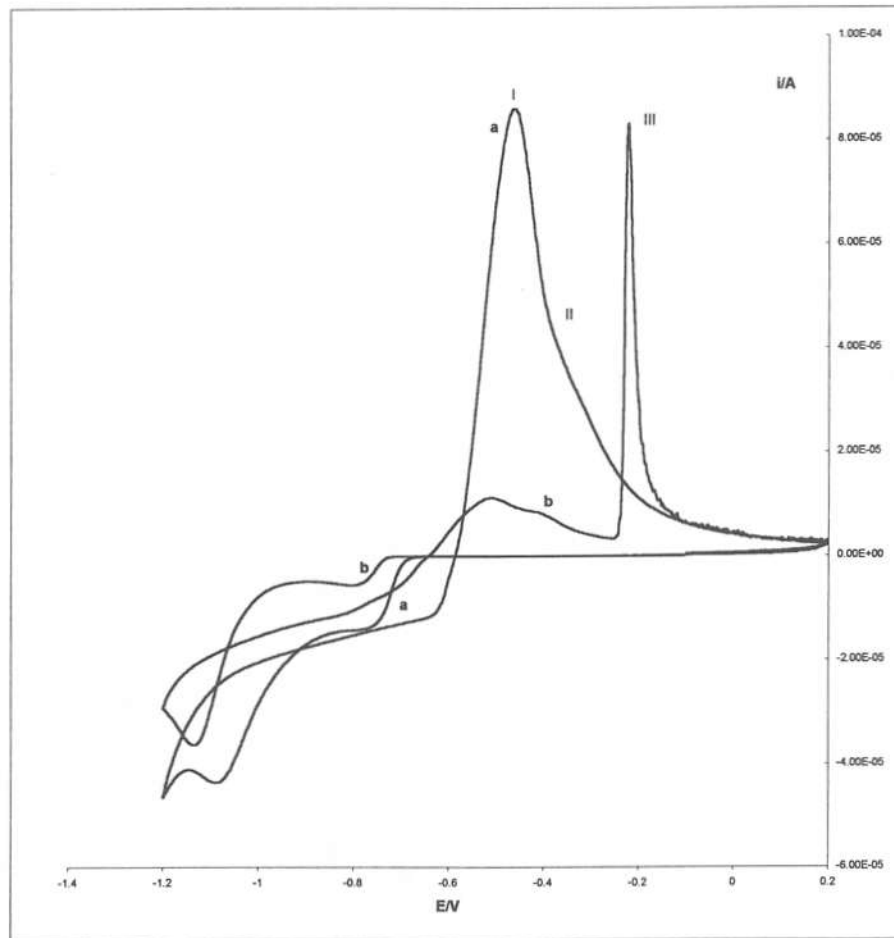


Figure 4. Cyclic voltammograms at 50 mV s^{-1} for solution 0.01 M SnSO_4 , $0.9 \text{ M Na}_2\text{SO}_4$, 0.12 M tartaric acid: a) $\text{pH} = 4$; b) $\text{pH} = 5$.

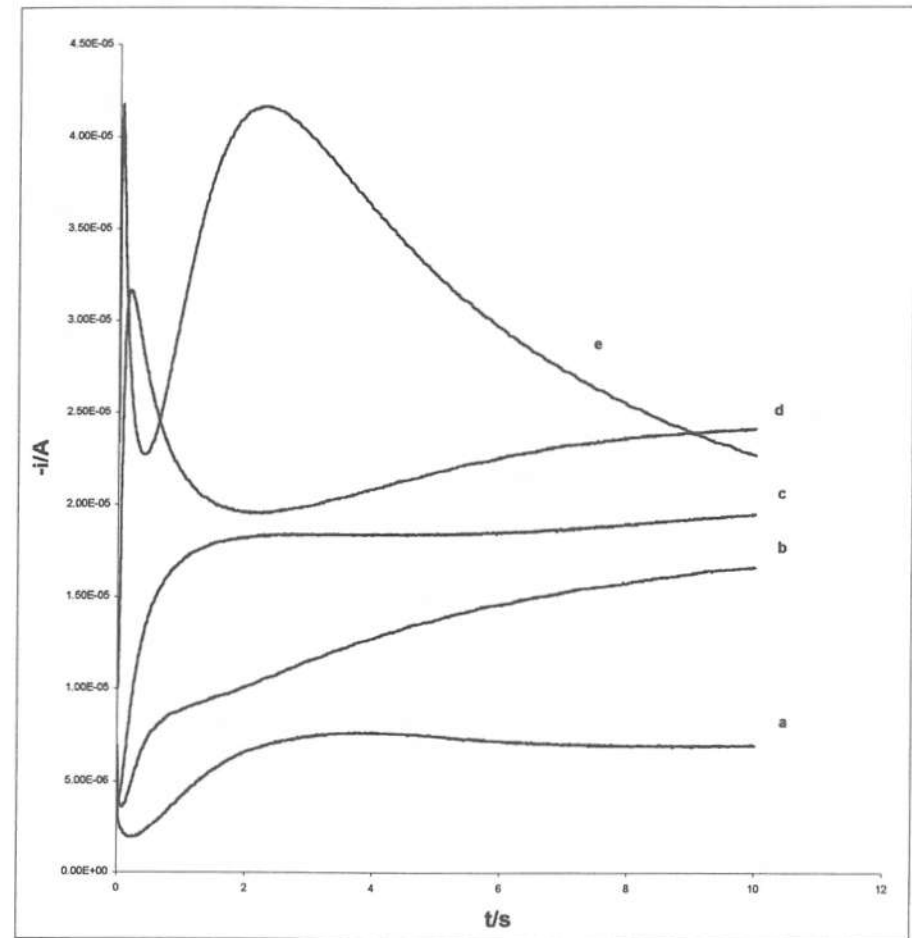


Figure 5. Potentiostatic transients for solution 0.01 M SnSO_4 , $0.9 \text{ M Na}_2\text{SO}_4$, 0.12 M tartaric acid, $\text{pH} = 4$. The potential step transients were made from $E_0 = -300 \text{ mV}$ to: a) -750 , b) -775 , c) -850 , d) -900 , e) -1000 mV .

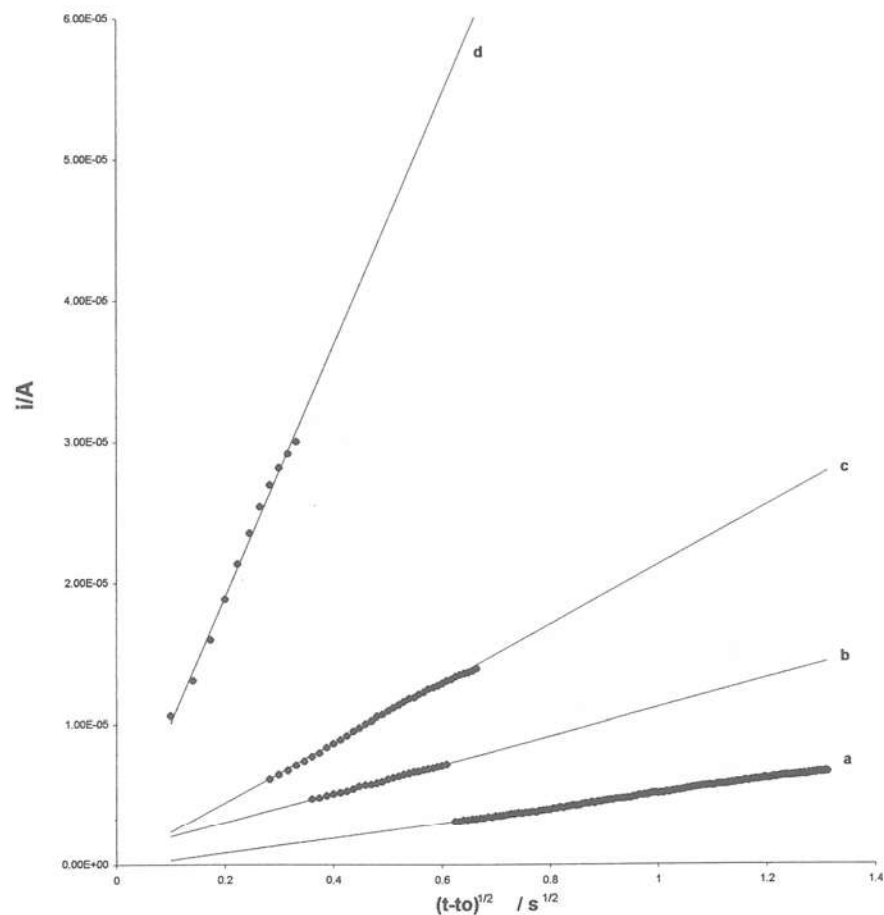


Figure 6. Plot of i vs. $(t-t_0)^{1/2}$ for the curves a-d in figure 5.

deposition potential is more negative than -950 mV a second maximum is obtained in the current transient curves, related to the second electrodeposition process observed in the voltammetric study.

Using the corresponding expression for a IN process under hemispherical diffusion control (eq 1) [29-32], and from the experimental values for the slopes of i vs. $t^{1/2}$, the density of nuclei N^* can be calculated (table 1).

$$I = k t^{1/2} \tag{1}$$

$$k = \frac{\pi z F M^{1/2} (Dc)^{3/2} A N^*}{\rho^{1/2}}$$

In eq 1 the following parameter values have been used: $\rho = 7.3 \text{ g/cm}^3$, $z = 2$, $M = 118.69 \text{ g/mol}$, $F = 96485 \text{ C/mol e}^-$, $D = 1 \cdot 10^{-5} \text{ cm}^2/\text{s}$, $c = 1 \cdot 10^{-5} \text{ mol/cm}^3$ and $A = 0.031 \text{ cm}^2$.

When $\ln N^*$ is plotted against the potential or the overpotential, a good linear correlation is obtained (fig 7). From the slope of this plot and according to equation 2 [33-35],

$$\frac{d \ln J}{d \eta} \approx \frac{d \ln N^*}{d \eta} = \frac{zF}{RT} N_{crit} \tag{2}$$

the critical nucleus size is determined, resulting in a value between 0 and 1. This result is in agreement with others studies that also have determined very low values for the critical nucleus size in electrodeposition [35-39]. The explanation to this result is that the electrode surface active centres play the role of the critical nucleus [40]. Then, when the necessary overpotential is reached, nucleation occurs at these centres without any additional barrier for nucleation, and the growth of the nucleus proceeds immediately.

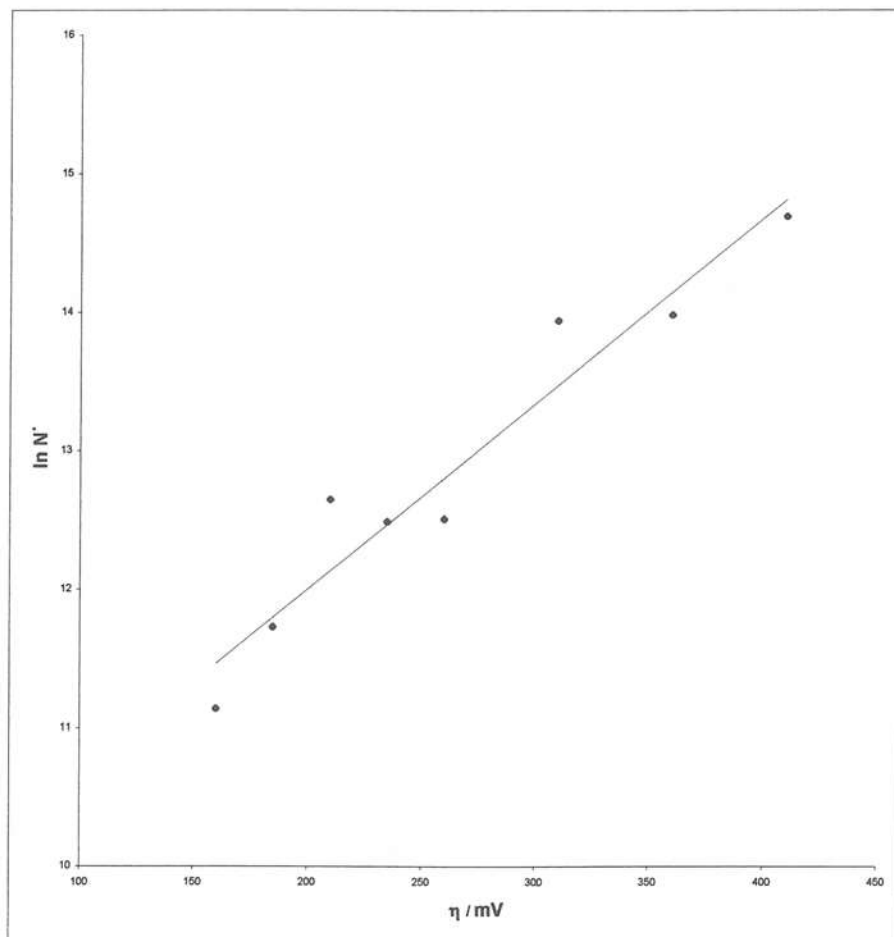


Figure 7. Plot of $\ln N^*$ vs. overpotential, η , for values on Table 1.

Table 1 Nuclei density, N^* , at different overpotentials, η , for tin electrodeposition in a sulphate-tartrate bath.

$-E / \text{mV}$	t_0 / s	η / mV	$k / \text{A s}^{-1/2}$	N^* / cm^2
750	0.32	160	$5.3 \cdot 10^{-6}$	$6.92 \cdot 10^4$
775	0.08	185	$9.6 \cdot 10^{-6}$	$1.25 \cdot 10^5$
800	0.06	210	$2.40 \cdot 10^{-5}$	$3.13 \cdot 10^5$
825	0.05	235	$2.03 \cdot 10^{-5}$	$2.65 \cdot 10^5$
850	0.04	260	$2.08 \cdot 10^{-5}$	$2.71 \cdot 10^5$
900	0.01	310	$8.68 \cdot 10^{-5}$	$1.13 \cdot 10^6$
950	0	360	$9.00 \cdot 10^{-5}$	$1.18 \cdot 10^6$
1000	0	410	$1.84 \cdot 10^{-4}$	$2.40 \cdot 10^6$

$$\eta = E_0 - E = -590 - E$$

4. Final comments

The reduction of tin is shifted to more cathodic potentials in a tartrate bath at pH=4-5, because of the chelating action of tartrate. The electrodeposition process in the initial stages occurs through an instantaneous nucleation and diffusion control. From the calculated nuclei density and its dependence on the overpotential, a critical nucleus size of 0-1 is obtained, indicating that the atomistic model of nucleation will be more realistic for its description, and that the electrode surface active centres play the role of the critical nucleus.

Acknowledgements

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