



Improvement of the tin electro-deposition in the presence of sesame oil additive

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Abstract

Tin coatings were electrodeposited on mild steel substrate from acidic sulphate bath. The effect of different electro-deposition parameters including pH, current density, and sesame oil concentration on the Sn coating's properties has been studied. Results show that sesame oil content of coatings has a strong effect on the structure, and morphology of coatings using Scanning electron microscope. Increasing sesame oil ratio in the bath, higher and higher deposition current density increased the Sn content of coatings.

Keywords: Tin, electro-deposition, gravimetry, morphology, additive, kinetic.

Introduction

Tin is one of the metals most often used in the commercial electroplating. It is mainly due to its high corrosion resistance, non - toxicity, and good soldering properties. Such features determine relatively wide application area of the electrodeposited tin as tinplates for food industry (containers and packages), protective coatings for copper in electrotechnical industry, layers improving surface solderability of majority of metals, coatings protecting from the corrosion in aggressive atmosphere, or in manufacturing of printed circuit boards and electronic components [1,2].

Various baths are used for obtaining uniform tin electrodeposits with required quality and morphology. Porous or dendritic deposits are usually obtained. A lead compound is often added to inhibit the reduction of the stannous species and increase the polarization reaction [3]. To avoid pollution problems, organic additives, or surfactants are commonly used to improve the deposit morphology.

The controlled growth of nanocrystals with respect to size and morphology is a pre-industrial manufacturing procedure, and now has become a key aspect of modern material science. Inorganic materials with the same chemical composition may exhibit different properties if their morphologies are different [4]. In general, the morphology of individual nanocrystals or colloidal particles can be controlled by the usage of low molecular mass additives or salts, hydrothermal hydrolysis of amorphous solids, or special crystallization conditions [5,6]. In recent years, organic molecules have been widely investigated as crystal modifiers because they can dramatically influence the morphology of the targeted inorganic crystals if there is molecular compatibility at inorganic-organic interface, such as biological molecules for seashells [7], double-hydrophilic block copolymers as molecular tools for CaCO₃ [8,9], hydroxyapatite [10], and BaSO₄ [11]. Surfactants, an important class of organic molecules with long carbon chains that can affect the morphology and size of targeted products; have attracted great attention as crystal modifiers.

The interest in using natural organic compounds is because of its availability, cost and effect on the environment [12-15]. They pose no detrimental effect on the environment or hazard to human health. A number of natural organic compounds have been identified as good brightening agents in tin electroplating. Examples of these substances sesame oil (SO). These classes of organic compounds are biodegradable and non toxic.

Sesame (*Sesamum indicum*) is recognized as one of the oldest crops in the world. Archeological records indicate that it has been used in India for more than 5000 years [16] and is recorded as a crop in Babylon and Assyria some 4000 years ago [17]. The crop has since spread over many parts of the world including the East African region where it is grown mainly for grains and oil extraction. Sesame has been listed among neglected and underutilized crop species by The International Plant Genetic Resources Institute (IPGRI), as a crop with high potential. A source of excellent vegetable oil, sesame has one of the highest oil contents (35–63%) among oil crops [18-19]. The oil is very stable due to the presence of a number of antioxidants such as sesamin, sesamol and sesamol [20]. Therefore, it has a long shelf life and can be blended with less stable vegetable oils to improve their stability and longevity [20-21].

2. Materials and methods

2.1 Materials and Solutions

The standard bath compositions and deposition conditions for Sn deposits are given in Table 1. The solutions were prepared using distilled water and reagent grade chemicals. The bath temperature for electro-deposition was 298 K. The steel sheets having an exposed area of 1 cm² were used as cathodes. Materials used in this work were of analytical grade. The conventional three-electrode system was used. The potential was monitored against a KCl-saturated Ag/AgCl reference electrode (0.197 V vs. SHE). A platinum plate electrode was used as the counter electrode. Prior to each experiment, the surface of the working was abraded using emery paper up to 1500 grade and then being immersed in pure ethanol, and distilled water, respectively, to remove any surface impurity.

Table 1. The bath composition and deposition conditions.

Operational condition	Quantity	Composition
Anode: Pt	-----	Platine electrode
pH: 1	0.56M	H ₂ SO ₄
Cathode: steel	0.14M	SnSO ₄
Temperature	-----	298 K 303 K
Sesame oil	1mL /10mL ethanol	bath : 50 mL

3. Results and discussion

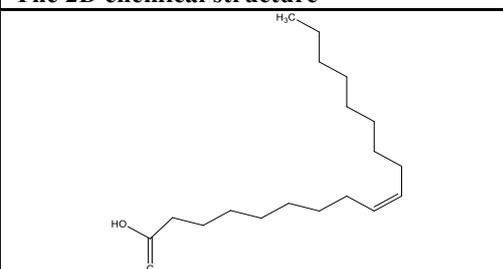
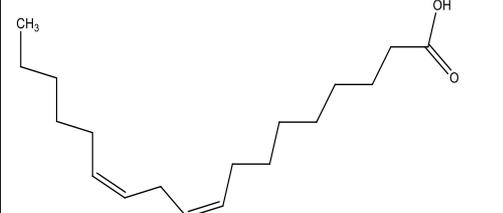
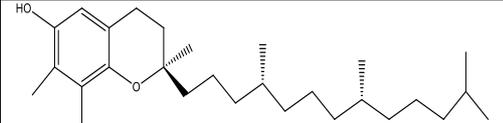
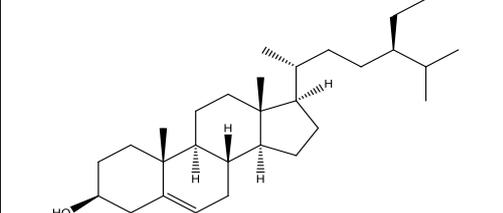
3.1. Sesam oil analysis

Characteristic features of the seed oil revealed a high degree of unsaturation and as determined by gas chromatography reported herein, the major unsaturated fatty acids were linoleic acid (46.9%) followed by oleic acid (37.4%), while the main saturated fatty acid was palmitic acid (9.1%). Sesame seed oil was also found to be rich in tocopherols with a predominance of γ -tocopherol (90.5%). The phytosterol marker β -sitosterol accounted for 59.9% of total sterols contained in sesame seed oil. [22] Their relative percentages are reported in Table 2.

3.2. Cyclic voltammetry

The Cyclic voltammograms registered in stannous solutions were measured in the basic solution (Table 1) with various sesame oil concentrations with a scan rate of 10mV/s (Figure 3) were started from 1.2 V, and then, potential was scanned in the negative direction and reversed at various potentials (from -1.2 to 1.2 V). Electro-deposition of metal on the stainless steel electrode started at potentials of about -0.50 ± 0.04 V, which were much more positive than the values for hydrogen ion reduction in the blank solutions. Course of the curves typical for electro-deposition process was visible during the reverse scan (Figure 3). Characteristic crossover between the branches for the negative and positive sweeps is associated with the nucleation overpotential, since the potential of tin deposition on tin itself is more positive than for the metal deposition on a foreign substrate [23]. Potential of deposit of the tin (peak C₁ and C₂) were dependent on the composition of the bath, while the rate of the process was affected by the concentration of the sesame oil in the bath.

Table 2. The systematic (IUPAC) name, 2D chemical structure of the main constituents of cosmetic linseed oil.

The constituent	The systematic (IUPAC) name	The 2D chemical structure
Oleicacid (C18:1)	(Z)-Octadec-9-enoic acid	
Linoleicacid (C18:2)	(9Z, 12Z)-octadeca- 9,7-dienoic acid	
palmiticacid (C16:0)	hexadecanoicacid	
γ-tocopherol	(2R)-2,7,8-Trimethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]-6-chromanol	
β-Sitosterol	17-(5-Ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,11,12,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3-ol	

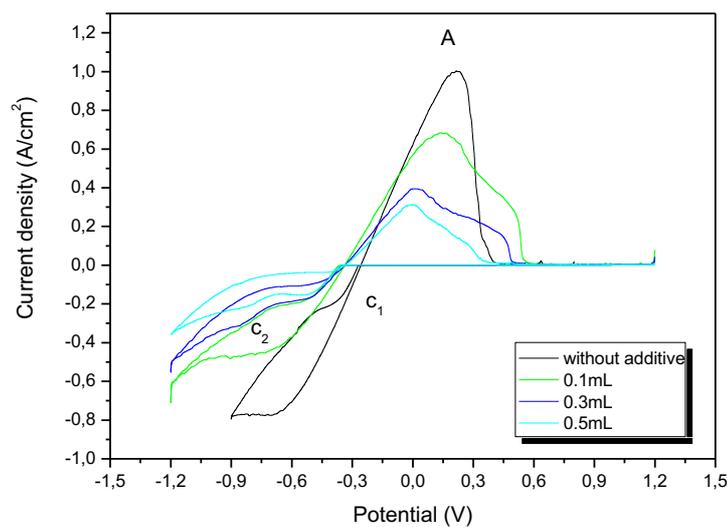


Figure 3: Cyclic voltammetric curve of the electro-deposition and dissolution of Sn on a steel substrate, produced in solutions of 0.14 M SnSO₄+ 0.56 M H₂SO₄, without and with different sesame oil concentration; at 25.0 mV .S⁻¹

In the presence of this additive, the strengthening of deposit of tin has been observed, while the process inhibits in function of the increase in the concentration of the sesame oil in the bath. It has been confirmed by the area of the double peak anodic (mark in the sweep to the rear, to the potential of -0.4V) corresponding to the formation of ions Sn (II) from the metal already tabled. Cathode currents observed at potentials Below - 0.75 V (C₂ to Figure3) have been attributed to the evolution of hydrogen. [24].

3.3. Current density effect

The current densities are also an important plating parameter and should be controlled properly .To understand the effect of sesame oil on the coating rate, varying the current density applied by the chronopotentiometry method for 10 min, and calculating the ratio of the electro-deposition of tin with and without sesame oil. The results are showing in figure 4. In the case of the bath with sesame oil additive, the plating rate increases continuously with the increase of the current density and reaches a maximum at 15 mA / cm² and after this value, the deposition rate deteriorates when the current density increases. The second bath, without additive show a similar behavior, i.e., the plating rate increases with current density, while there is a decrease in the deposition rate after 15mA / cm² .On the other hand, higher current densities can lead to a release of hydrogen [25]. In addition, it is clear that a great improvement of the electro-deposition rate in the presence of sesame oil additive by comparing with the case without additive. It is interesting to note that both solutions have similar plating rates (19 μ.m / h) for a current density of 20 mA / cm², and pinholes are more frequent in the films deposited at current densities higher [25]. It may be noted that the presence of this additive has a good effect on the appearance of electrolytic tin deposit.

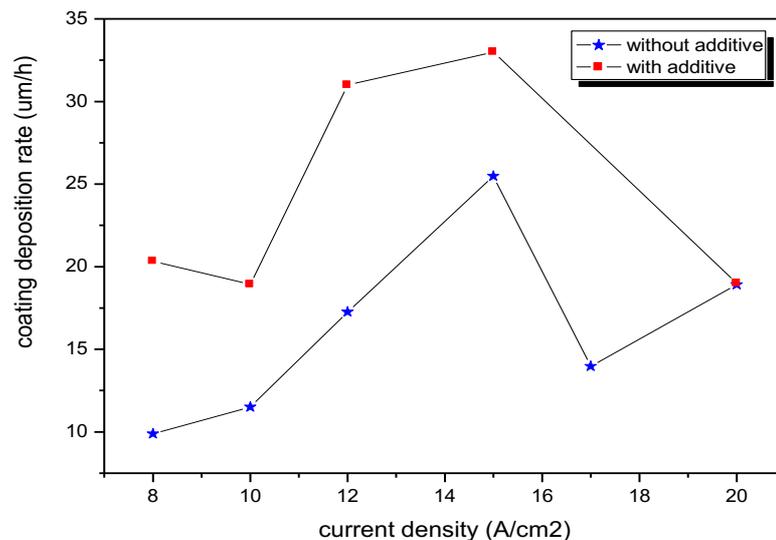


Figure 4. Current density effect in electro-deposition rate with and without additive.

The electro-deposition tin is performed in an acid bath, but the degree of the acidity influence on the quality of the plating and tin plating rate. Thus, the solution pH is a very important factor in the electro-deposition, indeed, it affects both anodic and cathodic reactions and various phenomena associated with the structure and composition of the metal-solution interphase. The major phenomena include; adsorption, potential zero charge, structure of the double layer, structure of ions species in the solution and the ionic strength of the solution. [26]. The figure 5 shows the case of two electro-deposition rate, with and without additive function of pH. It may be noted that the two curves have similar behavior and that the increase pH medium does encourage the electro-deposition rate which means that the acidity is more favorable for the electro-deposition. However, it appeared that the electro-deposition rate in case of the solution containing sesame oil is improved over that obtained without additive.

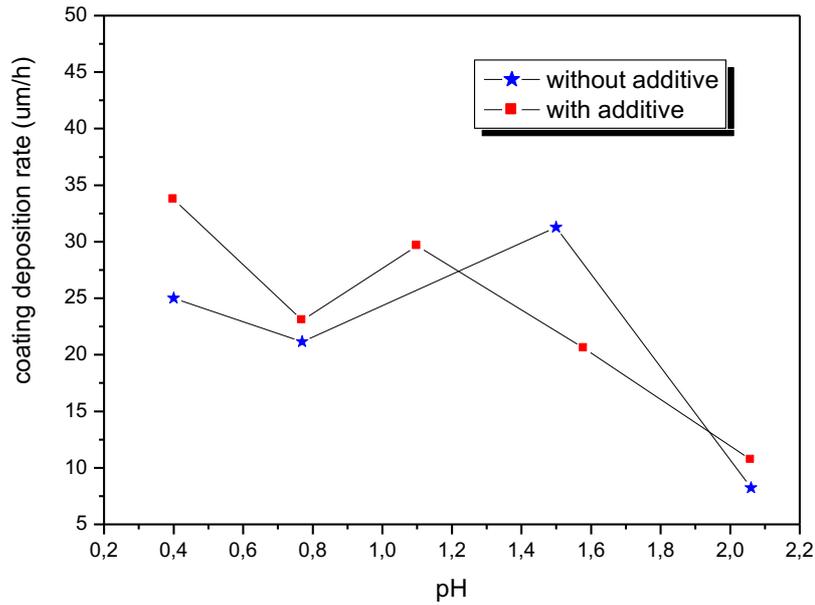


Figure 5: Additive concentration effect on electro-deposition rate.

3.4. Morphology of tin electro-deposition

A study of SEM surface images of the Sn electrodeposits was carried out to establish the relationship between the absence and presence of sesame oil in the Sn electro-deposit morphology. Figure 8 and Figure 9 show SEM micrographs of Sn electrodeposits produced potentiostatically at -550mV , without and with additive respectively, was determined. It is noted that the obtained deposits, without additive were porous and dendritic and had an irregular form (Figure 8 a-b). By contrast, in the presence of SO additive, the obtained deposit was more regular, non-porous, smooth (Figure 9 c-d). The use of this additive allows to obtain deposits, made of tin, spanning glossy, which can act coverings. The disappearance of the spaces between the stacks and fineness of the deposit suggests that the presence of sesame oil additive improves the corrosion resistance of the coatings.

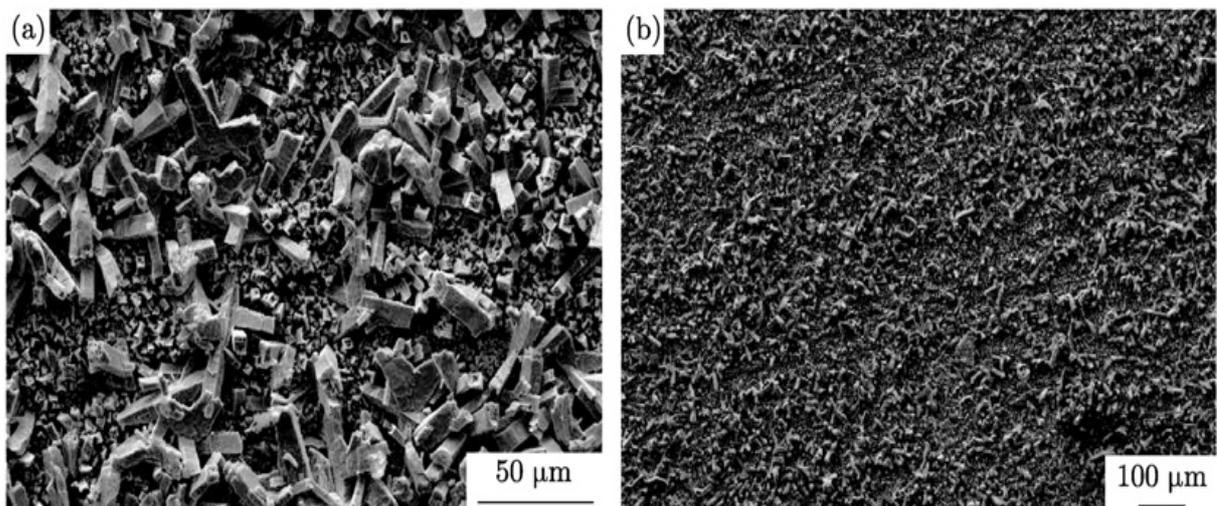


Figure 8: SEM images of tin deposits obtained under the current density of 15 mA/cm^2 at 25°C from the additive-free bath.

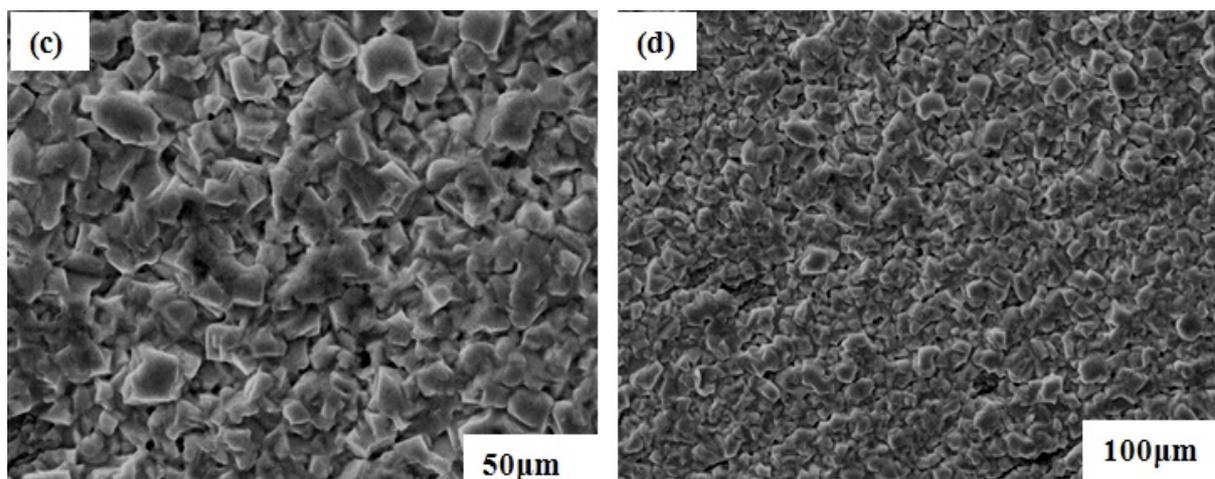


Figure 9: SEM images of tin deposits obtained under the current density of 15 mA/cm² at 25°C in the presence of 0.3 mL the sesame oil bath.

Conclusion

Electro-deposition of tin from acidic baths in the absence and presence of sesame oil additive was investigated. Cyclic voltammetry measurements indicated that SO is not electroactive. In addition, in the presence of SO, four peaks were observed, two in the cathodic range and two in the anodic range. It is also found that the reduction of Sn²⁺ ions runs under diffusion control and the hydrogen evolution was affected by the presence of the additive and the nature of the working electrode. In addition, it is shown that the electro-deposition rate of tin and the cathodic current efficiency increased with SO. The morphology of tin deposits showed that the obtained electrodeposits became regular, smooth and dense in the presence of SO.

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