Study of the influence of a bis-glycobenzimidazolone on the reduction of stannous ions

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Abstract

A tin deposit was developed electrolytically on iron plates substrates in an acidic medium comprising metallic tin salts with a bis-glycobenzimidazolone at room temperature. The influence of the additive on the tin coating mechanism was studied by chronopotentiometry and stationary polarization. The morphology and the structure of the deposit were characterized by scanning electron microscopy and X-ray diffraction. The results showed that the deposition process changed in the presence of the bis-glycobenzimidazolone inducing the development of a regular and non-dendritic coating.

Keywords: Coating, tin, electroplating, bis-glycobenzimidazolone, cathodic polarization, SEM, XRD.

1. Introduction

Although tin plating is known since the mid-nineteenth century, the process still has a great interest and its development is still relevant due to good solderability [1-5], the non-toxicity [1, 3, 5] and the corrosion resistance [1-2, 5] of tin coatings. They have a wide field of application and are use in the food industry and the electronic industry [1, 4-7]. Thus, tin coating and its alloys are solicited to replace the deposits of chromium and cadmium [3, 8-10]. In acidic baths, tin deposits are porous, poorly adherent and dendritic with the formation of “whiskers”, thin filaments that grow spontaneously on the surface due to a high deposition overvoltage [4, 6, 9, 11-12]. Initially, lead was often added in the electrodeposition electrolytes to decrease this overvoltage [13]. However, releases from baths containing lead present real environmental problems. To remedy this problem, several authors have suggested the addition of organic compounds [11, 14-15] or surfactants [12,16-17] which can play the same role as lead. Some efforts have been made to develop suitable additives and determine their modes of intervention in the mechanism and in the kinetics of deposition and therefore on the coating properties and structure. These compounds can change the tin voltage reduction, decrease the hydrogen evolution and reduce the surface roughness [2, 6-7, 18]. In this study, we examined the influence of the bisglycobenzimidazolone,[α-ω-N,N’-bis-[3-N-(6-desoxy-3-O-methyl-D-glucopyranos-6-yl)-2-oxobenzimidazol-1-yl)]-decane, in the tinning bath. The effect of this additive on the electrochemical properties of the coating was studied by stationary polarization and chronopotentiometry. The structure and morphology of the deposit were analyzed respectively by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Materials and methods

Solutions of tin sulfate and sulfuric acid were prepared using analytical grade chemicals. The pH was kept at around 1 as in industrial applications and temperature was kept at 22 ± 1 °C. Table 1 contains the electrolytes used, the concentration of 0.1 mole/L being close to industrial conditions. The compound added was α,ω-N,N’-bis-[3-N-(6-desoxy-3-O-methyl-D-glucopyranos-6-yl)-2-oxobenzimidazol-1-yl)]-decane which was synthesized by a method described by Lakhrissi and al. [19]. The structure is shown in Figure 1.
A 200ml cell was used. The substrates were iron plates (1cm^2), mechanically polished down to 1200 SiC paper, degreased in ethanol, etched in dilute sulfuric acid and rinsed with demineralized water prior to the experiment. The electrochemical measurements were carried out using a Potentiostat/Galvanostat/Voltalab PGZ 100 monitored by a personal computer. The reference electrode was Ag/AgCl with all potentials referred. The morphology of the deposits was examined by scanning electron microscopy (SEM) type Quanta 200 [20].

Table 1: Electrolytes compositions.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>SnCl₂(M)</th>
<th>SnSO₄(M)</th>
<th>H₂SO₄(M)</th>
<th>Additive(M)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>0</td>
<td>0.56</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>0</td>
<td>0.56</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>0</td>
<td>0.56</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>1'</td>
<td>0</td>
<td>0.14</td>
<td>0.56</td>
<td>0</td>
</tr>
<tr>
<td>2'</td>
<td>0</td>
<td>0.14</td>
<td>0.56</td>
<td>10⁻⁶</td>
</tr>
<tr>
<td>3'</td>
<td>0</td>
<td>0.14</td>
<td>0.56</td>
<td>10⁻⁵</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.14</td>
<td>0.56</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0.14</td>
<td>0.56</td>
<td>10⁻³</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0.14</td>
<td>0.56</td>
<td>10⁻⁵</td>
</tr>
</tbody>
</table>

3. Results and discussion
3.1. Cathodic polarization
3.1.1 Influence of SnCl₂ concentration

Figure (2) shows the cathodic polarization curves performed in tin chloride at concentrations ranging from 0.014 to 0.1 M. We note that the current intensity increases with the concentration of SnCl₂. This result allows us to confirm that the peak obtained corresponds to the stannous ions reduction. [21] These curves show three areas: An increase in the current at a voltage between -0.35 V and -0.43 V attributed to the reduction of tin:

\[
\text{Sn}^{II} + 2e^- \rightarrow \text{Sn} \quad (1)
\]

A more detailed mechanism is proposed in the literature with the formation of hydrated stannic complexes [22]

\[
3\text{Sn}^{II} + 4\text{H}_2\text{O} \rightarrow (\text{Sn}^{IV})(\text{H}_2\text{O})_4 \quad (2)
\]
\[
\text{Sn}^{III} + 2\text{H}_2\text{O} \rightarrow \text{Sn}^{IV}(\text{H}_2\text{O})_2 \quad (3)
\]
\[
2(\text{Sn}^{IV})(\text{H}_2\text{O})_4 + 12e^- \rightarrow \text{SnO}_3\text{(OH)}_4 + 6\text{H}_2 \quad (4)
\]
\[
\text{Sn}^{IV}(\text{H}_2\text{O})_2 + 4e^- \rightarrow \text{SnO}_2 + 2\text{H}_2 \quad (5)
\]

This increase is followed by a cathodic plateau due to diffusion of tin, and finally the hydrogen evolution:

\[
2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_2(g) \quad (6)
\]
From Figure 2, in the case of industrial conditions, where the concentration of stannous ions is high (0.1 mol / L), the cathodic current density applied to obtain a good quality of deposit must be less than 6 mA / cm$^2$, the diffusion current of stannous ions. The application of such currents involved a low deposition rate. To increase the kinetics, it is desirable to apply a much higher current density. At -15 mA / cm$^2$, the deposition rate becomes appreciable. However, this leads to saturation of the Sn$^{2+}$ ions concentration in the double layer and a significant evolution of hydrogen involving dendritic, porous and burned coatings (Photo 1). To remedy this problem, the addition of surfactants to the bath appears to be very interesting alternative. It has been proposed by many authors. Thus, we considered the addition of a bis-glycobenzimidazolone (Figure 1) to our electrolyte.

Photo1: Deposit performed at -15 mA /cm$^2$ in electrolyte 1

3.1.2. The effect of the addition of α,ω-N,N’-bis-[3-N-(6-desoxy-3-O-methyl-D-glucopyranos-6-yl)-2-oxobenzimidazol-1-yl]-decane

Stationary current-voltage curves for the three electrolytes 1, 2 and 3 are grouped in Figure (3). In the presence of the additive (Fig. 3, curves 2, 3), we find that the cathodic current decreases indicating a deceleration of the reduction process. On the other hand, we notice a depolarization of the hydrogen reduction with a shift towards more cathodic values. When changing the stannous salt, from SnCl$_2$ to SnSO$_4$, we see the same evolution (Figure 4). Thus, our additive would act independently of counterion of the salt. To better visualize the reduction peak in the latter case, we diluted the electrolyte. The decrease in the reduction current of tin depending on the additive reaches a limit at a concentration of $10^{-3}$ mol/L of bis-glycobenzimidazolone with the kinetics of the reduction of tin at that point being controlled by diffusion [9,23, 24] (Fig. 5).
3.1.3. The effect of pH
Figure (6) shows the cathodic polarization curves plotted with the electrolyte (3) for different values of pH. We see a rapid increase in current when the pH decreases. This confirms the role played by hydrogen reduction in the deposition of tin. To control the deposition kinetics, the pH must be as high as possible without causing precipitation in the bath. In our case, it would be in the order of pH 3.
3.2. Chronopotentiometry study

The trace of the curves $E = f(t)$ at a current density equal to -15 mA/cm$^2$ with the electrolytes (1), (2) and (3) shows the stabilization of the potential at -453 mV for electrolyte (1) at -458 mV for electrolyte (2), whereas it reaches -476 mV in the case of electrolyte (3). This potential drop after the addition of the additive could be attributed to partial blocking of the surface by its adsorption (Fig. 7). The same trend is observed when changing the metal salt, from SnCl$_2$ to SnSO$_4$ (fig.8). Furthermore, we found that the potential stabilization increases with the current as was expected (Fig.9).

**Figure 6:** pH effect on the tin reduction.

**Figure 7:** Chronopotentiometric curves produced with electrolytes: 1, 2, 3. $I = -15$ mA/cm$^2$

**Figure 8:** Chronopotentiometric curves produced with electrolytes: $1'$, $2'$, $3'$. $I = -15$ mA/cm$^2$
3.3 Characterization of tin deposit

3.3.1. Morphology

The coatings obtained without additive have a burned appearance. The SEM observations show a porous, irregular and dendritic surface (photos 2 and 4). In contrast, the coatings obtained from the electrolyte (5) containing the bis-glycobenzimidazolone at a concentration of $10^{-3}$ M and at the same current density have a uniform and regular surface (photos 3 and 5). Nevertheless, we find that the grain size is smaller for coatings elaborated without additive. Indeed, a high deposition rate promotes germination (photos 6 and 7).

![Photo 2](image1)

**Photo 2**: SEM images of Sn coating obtained at $I = -15$ mA/cm$^2$ with electrolyte 1

![Photo 3](image2)

**Photo 3**: SEM images of Sn coating obtained at $I = -15$ mA/cm$^2$ with electrolyte 5

![Photo 4](image3)

**Photo 4**: SEM images of Sn coating obtained at $I = -15$ mA/cm$^2$ with electrolyte 1

![Photo 5](image4)

**Photo 5**: SEM images of Sn coating obtained at $I = -15$ mA/cm$^2$ with electrolyte 5
3.3.2. XRD analysis
The X-ray patterns of Sn coatings performed at -15 mA/cm² in electrolytes 1 and 5 with JCPDS file of tin (N°. 4-673) are shown in Figure 10 [25]. They all exhibit a tetragonal structure. The coating deposited from electrolyte 1 (without additive) showed a (200) preferred orientation whereas the layer deposited from bath 5 with bis-glycobenzimidazolone presented a (101) preferred orientation. One of our studies conducted in the presence of the bis-glycobenzimidazolone showed strong preferential orientation in the direction (112) [2]. This change in the preferential direction of tin deposit growth in the presence of the additive could also explain the improvement of the coating quality.

![Photo 6: SEM images of Sn coating obtained at I = -15 mA/cm² with electrolyte 1](image1)

![Photo 7: SEM images of Sn coating obtained at I = -15 mA/cm² with electrolyte 5](image2)

**Figure 10:** (a) X-ray diffraction patterns of coatings deposited from electrolyte 1 (b) X-ray diffraction patterns of coatings deposited from electrolyte 5 (c) Reference pattern of tin (JCPDS file 4-673)
Conclusion

A new additive, the bis-glycobenzimidazolone was used in tin electrodeposition from stannous solutions. Electrochemical investigation showed that this additive decreases the cathodic current and increases the overvoltage for hydrogen evolution. The coating deposited from electrolyte without additive presented a (200) preferred orientation whereas the layer deposited from the bath with bis-glycobenzimidazolone presented a (101) preferred orientation. These observations may explain the improvement of the coating surface. Indeed, the deposits made in the presence of the additive are less porous, more uniform and regular.

References


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