ELECTROCHEMICAL PROCESSING OF SECONDARY LEAD-TIN ALLOYS

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ABSTRACT

In the course of the studies reported it is found that the composition of lead-tin alloys affects the nature of their anodic dissolution in potassium hydroxide and sulfamic acid solutions. Anodes passivation with oxygen evolution occurs with the increase of the anode potential. It is not possible to separate the metals at the stage of the anodic dissolution studied. The presence of porous areas in the microphotographs of the anodes surface indirectly confirms the proceeding of oxygen evolution. The resulting cathode deposit is in the form of a sponge powder of a dark grey color, easily removed from the surface of the titanium cathode.

Keywords: lead-tin alloy, anodic dissolution, electrolytes, potassium hydroxide, sulfamic acid, polarization curves, passivation.

INTRODUCTION

Currently, secondary tin-containing materials, including lead-tin alloys, are constantly accumulating in the world. The processing of such materials has always attracted the scientists’ interest. There are many ways to process spent lead-tin alloys. The most common method refers to the direct remelting of the alloys aiming to produce a new alloy of a different composition and content of the main components [1]. Methods of chlorination of tin-containing alloys in a chloroform medium or in a dry chlorine current with subsequent tin cementation are also reported [2, 3]. However, the most promising approaches refer to the methods of hydrometallurgy and electrolysis. Aqueous alkaline solutions or molten salts are most often offered as electrolytes and reagents used for dissolution [1, 4 - 6].

The aim of the present research is to establish the electrochemical regularities and the possibility of electrochemical processing of lead-tin alloys using solutions of potassium hydroxide and sulfamic acid.

Preconditions and means of resolving the problem.

A theoretical Model

The anodic dissolution of lead-tin alloys can proceed in alkaline solutions according to the reactions presented in Table 1.

It shows that the dissolution of the alloy in alkaline solutions will begin with dissolution of tin in correspondence with reaction (4). It is followed by the formation of HSnO₂⁻ ions and lead by reaction (6).

The anodic dissolution of tin is described by the following reactions:

\[ Sn + 3OH^- \rightarrow HSnO_2^- + H_2O + 2e; \varphi_0 = -0.91 \text{ V}; \quad (1) \]

\[ Sn + 6OH^- \rightarrow [Sn(OH)_6]^{2-} + 4e; \varphi_0 = -0.92 \text{ V}; \quad (2) \]

\[ HSnO_2^- + 3OH^- + H_2O \rightarrow [Sn(OH)_6]^{2-} + 2e; \varphi_0 = -0.93 \text{ V} \quad (3) \]

The potential values are close. The most negative is the potential of divalent tin oxidation to quadravalent (the last reaction). Therefore, the divalent complex anion
should be more stable in alkaline solutions. Practically, the equilibrium in the solution is as follows:

$$2 \text{HSnO}_2^- + 2 \text{H}_2\text{O} \rightarrow [\text{Sn(OH)}_6]^{2-} + \text{Sn}$$  \hspace{1cm} (4)

Due to the proximity of the equilibrium potentials, the reactions proceed with a higher rate at a lower over-voltage [1, 3]. In alkaline solutions, the formation rate of $\text{SnO}_3^{2-}$ is higher than that of $\text{HSnO}_2^-$. It means that the anodic dissolution is dominated by the tetravalent tin anions. The reduction rate of $\text{Sn}^{2+}$ on the cathode is much higher than that of $\text{Sn}^{4+}$. Therefore, only $\text{Sn}^{4+}$ are present in the cathode layer, where they are discharged to the metal.

The hydrolysis of stannites and stannats produces the hardly soluble acids $\text{H}_2\text{SnO}_2$ (stannite) and $\text{H}_2\text{SnO}_3$ (metastannic). These acids precipitate. As a result, the concentration of tin in the solution is decreased. Therefore, it is necessary to have an excess of NaOH in the solution in order to stabilize it and maintain the required tin concentration. The dissolution in acid solutions of the lead contained in tin alloys when applying an electric current can be considered as a result of electrochemical and chemical alloy dissolutions. The chemical dissolution of lead-tin alloys without their preliminary grinding when using sulfamic acid is insignificant [8 - 11].

The main part of the metals is dissolved due to the action of the electric current, i.e. the process of dissolution is in fact anode dissolution. The start of the alloy dissolution is determined by the standard potential of the more electrically negative metal. As the anode is polarized, the more electrically positive metal passes into the solution, which is shown by reactions (2) and (5) of Table 1.

**EXPERIMENTAL**

The model lead-tin alloys were prepared by alloying the corresponding pure metals (Sn and Pb): sample 1 contained 90 % Sn and 10 % Pb, sample 2 - 10 % of Sn and 90 % Pb, These alloys served as anodes. Their surface area was equal to 5.6 cm$^2$. Titanium (VT1-0) plate of a surface area of 5 cm$^2$ was used as a cathode.

Solutions of potassium hydroxide (100 g l$^{-1}$) and sulfamic acid (100 g l$^{-1}$) were the electrolytes applied. The electrochemical cell referred to a 400 mL PTFE

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Table 1. Possible electrochemical reactions occurring at the lead-tin anode [7].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $3\text{OH}^- + \text{Sn} - 2e = \text{H}_2\text{O} + \text{HSnO}_2^-$</td>
<td>-0,91</td>
</tr>
<tr>
<td>2 $\text{Sn} - 2e = \text{Sn}^{2+}$</td>
<td>-0,14</td>
</tr>
<tr>
<td>3 $\text{Sn} - 4e = \text{Sn}^{4+}$</td>
<td>0,01</td>
</tr>
<tr>
<td>4 $2\text{H}_2\text{O} + \text{Sn} - 2e = 3\text{H}^+ + \text{HSnO}_2^-$</td>
<td>0,33</td>
</tr>
<tr>
<td>5 $\text{Pb} - 2e = \text{Pb}^{2+}$</td>
<td>-0,125</td>
</tr>
<tr>
<td>6 $\text{Pb} - 4e = \text{Pb}^{4+}$</td>
<td>0,77</td>
</tr>
<tr>
<td>7 $3\text{OH}^- + \text{Pb} - 2e = \text{H}_2\text{O} + \text{HPbO}_2^-$</td>
<td>-0,502</td>
</tr>
<tr>
<td>8 $6\text{OH}^- + \text{Pb} - 4e = 3\text{H}_2\text{O} + \text{PbO}_2^{2-}$</td>
<td>-0,127</td>
</tr>
<tr>
<td>9 $2\text{H}_2\text{O} + \text{Pb} - 2e = \text{H}^+ + \text{HPbO}_2^-$</td>
<td>0,702</td>
</tr>
</tbody>
</table>

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Fig. 1. Schematic diagram of electrochemical cell for anodic dissolution of lead-tin alloy: 1 - titanium cathode; 2 - silver chloride electrode; 3 - lead-tin anode.
container. All measurements of the anode potentials were done relative to a reference electrode. The circuit of the electrochemical cell is shown in Fig. 1.

The studies were carried out at a temperature of 20°C - 25°C using the electrochemical complex ECC-1012 (developed by IP Tetran LLC, Russian Federation). The polarization and depolarization curves studied were recorded until the maximum current point was reached in both electrolytes.

XSP-104 metallographic microscope was used to obtain the microphotographs of the surfaces of the studied alloys after their anodic dissolution and the cathodic precipitation at the titanium plate. Thus the character of the alloys’ surface change during the anodic dissolution was followed. Information on the structure of the anodic sludge formed was also obtained.

RESULTS AND DISCUSSION

The polarization curve referring to the anodic dissolution of sample 1 in a KOH solution (100 g l⁻¹) is presented in Fig. 2. The active dissolution of the alloy starts at φ ∼ -500 mV and a current of about 750 mA. The anode passivation develops rapidly and is accompanied by oxygen evolution. The complete passivation of the anode occurs at φ ∼ 1300 mV and a current of 1500 mA.

The depolarization curve provides information referring to the mode of the anode dissolution of an alloy of a specified composition when using a KOH solution as an electrolyte. It is necessary to maintain the anode potential at a value not greater than 500 mV at a current of 800 mA - 1200 mA. In this case the transition of lead and tin to the solution occurs almost simultaneously.

The polarization curve of sample 2 in a solution of KOH (100 g l⁻¹) is presented in Fig. 3.

It shows that the active dissolution of the alloy starts at φ ∼ -500 mV and a current of about 1500 mA. The complete passivation of the anode occurs at φ ∼ 1300 mV and a current of 3000 mA. The passivation of the anode is accompanied by oxygen evolution.

The depolarization curve indicates the recommended mode of anodic dissolution of sample 2. It is necessary to maintain the potential at a value not greater than 500 mV at a current of 1500 - 2500 mA.

The microphotographs of the alloys surface show black porosity points on the background of a continuous layer of anode sludge. This indicates that oxygen is released point-wise in the course of its accumulation. Microphotographs of the initial and final surface of sample 1 are given in Fig. 4.

Fig. 2. Polarization (1) and depolarization (2) curves of anodic dissolution of lead-tin alloy (90 % Sn, 10 % Pb) in KOH solution (100 g l⁻¹).

Fig. 3. Polarization (1) and depolarization (2) curves of anodic dissolution of lead-tin alloy (10 % Sn, 90 % Pb) in KOH solution (100 g l⁻¹).

Fig. 4. Initial (A) and final (B) surface (after electrochemical dissolution) of lead-tin alloy with tin content of 90 %, x45.
The polarization curve of sample 1 in a solution of sulfamic acid (100 g l\(^{-1}\)) is presented in Fig. 5. The active dissolution of the alloy starts at \(\phi \sim -2100\) mV and a current of about 200 mA. The passivation of the sample studied develops slowly up to a current of 6000 mA. The anode potential remains negative. The start of the oxygen evolution is recorded at \(\phi \sim -142\) mV and a current of 1600 mA.

The polarization and depolarization curves of sample 1 indicate the joint dissolution of the alloy components. Lead and tin cations pass to the solution simultaneously as there are no extremis points on the depolarization curve corresponding to individual electrochemical reactions.

The anodic dissolution of sample 2 takes place in accordance with the polarization curve presented in Fig. 6. The mechanism of the anodic dissolution of the alloy of a low tin content in the sulfamic acid electrolyte includes the following steps:

- tin is mainly transferred to the solution;
- the alloy surface is enriched with lead;
- lead begins to dissolve from the surface;
- the alloy surface is enriched with tin, etc.

The start of the dissolution of tin from the surface of sample 2 in sulfamic acid electrolyte corresponds to \(\phi \sim -1900\) mV. Lead starts to dissolve upon reaching \(\phi \sim -146\) mV. Oxygen evolution starts at \(\phi \sim -0.142\) mV. The passivation current is equal to 6000 mA.

The resulting cathode deposit in all cases is a mechanical mixture of lead and tin, which is confirmed by the X-ray analysis. The deposit is a spongy, porous, dark grey powder, easily removable from the surface of the cathode. A microphotograph of the cathode residue is shown in Fig. 7.

Spongy, unstable sediments, which are accumulations of small tin crystals, are obtained by electrolysis of stannate solutions containing 0.1 g l\(^{-1}\)-0.2 g l\(^{-1}\) of divalent tin. The sediments are compact in case of electrolysis of solutions containing only four valent tin.

The formation of spongy sediments is explained by the different character of Sn\(^{2+}\) and Sn\(^{4+}\) discharge. The discharge of Sn\(^{2+}\) proceeds without noticeable cathode polarization. As a consequence, the crystals growth at a higher current density precedes the formation of crystallization centers and the formation of spongy sediments.

The process potential of Sn\(^{4+} + 2e \leftrightarrow Sn^{2+}\) becomes more negative with an increase of the current density. Therefore, the quadravalent tin deposition occurs at cathode areas of a lower current density. In this case,
the crystals growth rate is comparable with the rate of formation of crystallization centers, which leads to the formation of a dense precipitation.

CONCLUSIONS

The mode of anode dissolution of lead-tin alloys in potassium hydroxide solution depends on the electrolysis mode, the nature of the electrolyte and the composition of the alloy. Anode passivation occurs as a result of oxygen evolution at $\varphi \sim 1300$ mV. The passivation current depends on the composition of the alloys. The higher the content of lead in the alloy, the higher the current is during the passivation. It is hardly possible to separate the metals at the stage of the anodic dissolution of lead-tin alloys in potassium hydroxide solution.

Two mechanisms of anodic dissolution of lead-tin alloys are established in a solution of sulfamic acid:

- joint anodic dissolution of lead and tin is observed in case of a high tin content of the alloy;
- gradual anodic dissolution of the components proceeds in case of a low tin content of the alloy.

Spongiform cathode sediments are formed under the conditions considered in this investigation. This indicates the presence of divalent tin ions in the near-cathode space. The precipitation is easily removed from the cathode surface.

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REFERENCES