INVESTIGATION AND CHARACTERIZATION OF THE ANODIC AND CATHODIC PROCESSES OF TIN AND SN-AG-CU ALLOYS IN HCL SOLUTIONS

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Lead-free wave soldering applied in modern electronic technology generates growing amounts of drosses containing high proportions of metallic tin, which is usually accompanied by several percentages of silver and copper. The proposed technology targets the extraction of pure tin from this valuable secondary raw material. Although electrorefining in dilute HCl media can offer great advantages, the process may be disturbed by the sensitivity of the anodic dissolution to the conditions and the dendrite formation at the cathode. In order to clarify the processes involved, the mass changes of the electrodes were monitored with high precision without interrupting the current. This technique revealed the disturbing effects caused by Sn(IV) species and the evolved hydrogen gas. Comparing the measured anode potentials to the calculated stability ranges of the Sn species, the practical limits of the anodic current density were estimated. Suitable conditions of anodic dissolution requires controlling the anode potential. The deposited tin is generally loose and dendritic in the entire range of the examined tin and HCl concentrations. However this difficulty can be practically overcome by a patented electromechanical system for compressing the cathodic deposit.

Keywords: tin recycling, soldering dross, electrorefining, hydrochloric acid, anode, cathode

Introduction

Most of the lead-free soldering materials applied in modern electronic industry are tin based alloys containing Ag and Cu (SAC series), although Bi and Sb may also appear as added components [1, 2]. Applying the lead-free alloys in soldering or coating implies a higher rate of copper pick-up by the tin based molten metal bath unfortunately. Therefore, the dross collected regularly from the open surface contains an increased concentration of copper and the bath needs to be refreshed by adding copper-free tin-silver alloy material. In some technologies, the copper concentration of the removed material is even increased by the cooling and partial crystallization. No direct technology has been available for recycling these hazardous secondary tin alloy materials, thus long transportation and conventional tin metallurgy for the reclaiming of the valuable metallic components is currently the only available way of disposal. Electrorefining has also been applied to purify tin, but earlier technology implies special and expensive components in generally sulfuric acid solutions or the inconvenient use of alkaline media at high temperatures [3]. The common H₂SO₄ media imply the difficulties of solution stability, cathode morphology and purity [4]. Pure tin can be recovered directly from soldering waste by electrorefining in a SnCl₂-HCl media [5, 6].

There have been two major difficulties related to the electrorefining of tin in pure acidic aqueous solutions. One of them is the inherently dendritic morphology of the tin crystals deposited at the cathode surface and the other is providing the optimum conditions for the

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dissolution of the anode [5, 6]. As the tin deposition is generally characterized by the formation of long dendrites [7], the rate at which diffusion can supply the ions to the ideally smooth cathode surface must be considerably lower than the rate of charge transfer. Therefore, forced convection should be useful in assuring better deposit morphology and also the required high efficiency of purification. However, efficient solution agitation at the surface of the electrode is difficult and it may disturb the stability of the formed anode slime layer and disperse unwanted particles in the electrolyte. Another way to tackle this difficulty is the application of periodically reversed or interrupted current, or electrodeposition with micro-scale current impulses. Although these techniques have been proved [7] to influence beneficially the crystal form, an adequately dense cathode deposit could only be achieved by mechanical compression [7, 8].

The difficulty of stabilizing the anode processes is caused by the generation of Sn(IV) species instead of the preferred divalent ions of tin. In this case secondary chemical reactions may occur, thus efficiency and stability characteristics of the electrolysis may be impaired. The deposited cathode crystals may be attacked by the reaction:

\[
\text{Sn(IV)} + \text{Sn} = 2 \text{Sn(II)}
\]  

causing re-dissolution of tin already deposited and deterioration of the crystal structure. The chloride medium even enhances this reaction, as it is proven by the results of thermodynamic simulation [5]. In chloride solutions, chloro-complex ions take part, therefore the general form of reaction (1) can be specified according to the following equation:

\[
\left[ \text{SnCl}_y \right]^{4-} + \text{Sn} + (2x - y)\text{Cl}^- = 2\left[ \text{SnCl}_x \right]^{2-x}
\]  

As the finest tin crystals are re-dissolved, the cathode loses active surface area and the local current density may increase, resulting in hydrogen evolution. Consequently the acid concentration may drop in such regions and the tetravalent tin ions may start precipitating by hydrolysis. Although in the fresh electrolyte solutions prepared by dissolving metal particles in cc. HCl [5], tin is present in the Sn(II) form, Sn (IV) may arise either because of oxidizing effects from the ambient air or by the irregular conditions of the anode. The former is expressed by the reaction with oxygen:

\[
\left[ \text{SnCl}_x \right]^{2-x} + \frac{1}{2} \text{O}_2 + 2\text{H}^+ + (y - x)\text{Cl}^- = \left[ \text{SnCl}_y \right]^{4-} + \text{H}_2\text{O}
\]  

which is driven by a high thermodynamic force [5]. The precipitation of Sn(IV) species by hydrolysis may cause turbidity. As the HCl concentration drops considerably below 1 mol/dm³ under oxidizing conditions, the formation of hydrated tin-dioxide particles may eventually break up the electrolyte. However, Cl⁻ activity by forming [SnCl₄]⁻ complexes [9, 10] may stabilize the dissolved tin. The redox potential (E) diagrams as functions of the pH or the pCl⁻ values in Figure 1a and 1b show increased stability areas of the Sn(II) and Sn(IV) species in the chloride system compared to the common Sn-H₂O system.
Another source of the generated Sn(IV) species is the anode itself. As shown in Figure 1b, when the potential is higher than the values of the line separating the predominance areas of the Sn(IV) and Sn(II) species in the actual range of HCl concentration marked by the gray area, the anodic dissolution may produce dominantly Sn(IV) species. With the control of the anodic potential, and the corresponding limiting of the anodic current density, the increase of the Sn(IV) concentration can be avoided. However, when the anode is covered with a growing slime layer, maintaining the required current density may imply high anode potentials. As the anode slime contains a high proportion (~50%) of solid tin particles, the anodic process may also be considered involving two consecutive steps. At higher potentials, Sn(IV) ions may be generated primarily, but as they diffuse through the slime layer, they get into contact with the tin particles and Sn(II) may finally arise by reaction (1). However, if the anode slime layer is still thin or loose, the Sn(IV) ions may enter the bulk of the electrolyte. They can also be generated there by reaction (3) if the electrolyte solution is not isolated from the ambient air. As Sn(IV) species reach the cathode of large specific surface area, reaction (1) can significantly reduce the net production of the metal. The origin of the Sn(IV) ions may be indicated by the change in the overall Sn concentration during electrorefining. The major impurities, silver and copper, are virtually indifferent in the anode and retained undissolved in the anode slime. The rest of the practical impurities usually have more negative standard electrode potentials than that of tin, so they may also take part in the anodic process and accumulate in the electrolyte, but they are generally present only in negligible amounts. Thus the change in the bulk tin concentration can be caused by two major effects: (i) oxidation of dissolved Sn(II) species to the Sn(IV) state by air and their reaction with the metal deposited at the cathode; or (ii) hydrogen evolution because of the shortage of available tin ions at the cathode surface at polarized cathode potentials. These effects may both increase the tin concentration in the solution.

The main dangers to the proper operation of the electrolysis are rooted in the conditions of the anode. Its effects are however also detectable in the composition of the electrolyte solution and in the cathodic morphology and current efficiency. The mass changes of the electrodes recorded continuously during the electrolysis may help understand the processes.
1. Experimental procedure

The raw materials for the anodes were selected according to practical reasons. The compositions of the SAC type soldering alloys generally used by the large electronic companies also in Hungary are characterized by a silver concentration of 2.5–4% and a copper content of 0.1–0.9% some producers may apply a metallurgical treatment to their soldering dross. By cooling the spent soldering bath to low temperatures much of the original copper content can be removed by fractional crystallization. In this way the secondary dross – purchased by the scrap collectors – may reach as high levels as 9–10%. Therefore we have examined the behavior of tin alloys representing a large variety in the SAC group: Sn999, SnCu1, SnCu9Ag3, SnAg3. The compositions of the examined electrolytes were 5, 10, 20 and 40 g/dm³Sn and 1 mol/dm³HCl. The elemental compositions of the anode materials are given in Table 1. Cathodes were cast from pure tin.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Ag</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Sb</th>
<th>Zn</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn 99.9</td>
<td>0.009</td>
<td>&lt;0.01</td>
<td>0.003</td>
<td>0.004</td>
<td>&lt;0.0005</td>
<td>0.001</td>
<td>0.002</td>
<td>0.003</td>
<td>99.97</td>
</tr>
<tr>
<td>SnCu1</td>
<td>0.028</td>
<td>0.246</td>
<td>1.061</td>
<td>0.0183</td>
<td>0.001</td>
<td>0.002</td>
<td>0.001</td>
<td>0.002</td>
<td>98.62</td>
</tr>
<tr>
<td>SnAg3</td>
<td>3.34</td>
<td>0.205</td>
<td>0.152</td>
<td>0.021</td>
<td>0.0014</td>
<td>&lt;0.002</td>
<td>0.005</td>
<td>0.007</td>
<td>96.25</td>
</tr>
<tr>
<td>SnCu9Ag3</td>
<td>2.83</td>
<td>0.01</td>
<td>9.04</td>
<td>0.011</td>
<td>0.0038</td>
<td>0.001</td>
<td>0.0017</td>
<td>0.008</td>
<td>86.42</td>
</tr>
</tbody>
</table>

The experimental system capable of in-situ recording of the mass changes of the electrodes is shown in Figure 2. The electrode (of 6X6 cm active surface area) was hung on a positioning adapter with a thin polyamide thread. The current is conducted by a thin flexible cable, so as not to interfere with the mass measurement. The data acquisition system was designed to record beside the actual mass readings the detected values of the current, the cell voltage, the electrode potential vs. a calomel reference electrode. This setup was used for short term measurements (5 min) with fresh electrodes. For testing the behavior of the cell on a longer run, the in-situ mass measurement was not used, because for longer runs some mechanical intervention was needed to prevent the growing dendrites from reaching the anode. In this case, the electrodes were supported firmly and periodical cathode compression was applied every 5 minutes. The electromechanical compressing system [8] has been developed for laboratory and pilot scales. The cell applied in the laboratory experiments is shown in Figure 3, also illustrating the cathode crystals at the start and the finish of the compression period. The cathode compression system and the current supply were controlled by a special electronic device developed in our laboratory, based on micro-processing units. The system characteristics were recorded continuously by a data acquisition system consisting of an AD interface (NI-USB6212) and a data processing program specifically developed using the NI-LabView software.
2. Experimental results and discussion

The electrode processes are clearly indicated by the continuously recorded masses of the electrodes. The buoyancy force in the electrolyte solution of the given composition was automatically corrected by an algorithm built in the computerized data processing system. The correlation is based on the density values of Figure 4, preliminarily determined.
The anodic process is demonstrated by the decreasing mass of the electrode. As shown in Figure 5a, the dissolution rates of the freshly prepared Sn99.9 (technically pure tin) anodes are proportional to the time elapsed after the start of the current and also to the applied anodic current density. With the high sensitivity of mass measurement, relatively slight further changes in the mass could also be detected after the current was switched off (Figure 5b). It can be interpreted as an indirect proof for the assumed reaction of the Sn(IV) species with the metallic tin in the anode or in the produced slime layer. The effect is stronger after the electrolysis runs with higher anodic current densities. It can also be noted that in this case there is a progressive increase, as the amount of Sn(IV) generated does not only depend on the amount of electric charge transmitted, but also on the potential of the anode.

The relevant anode potentials are shown in Figure 6. The values are measured vs. a calomel reference electrode and transformed according to the expression of the reference potential:

$$\text{Hg}_2\text{Cl}_2 + 2e = 2\text{Hg} + 2\text{Cl}^-,$$

$$E = 0.283 \text{ V} \quad (c_{\text{Cl}^-} = 1 \text{ mol/dm}^3)$$

Figure 4. Densities of the electrolyte solutions as functions of the composition at 25 °C

Figure 5. Changes in the masses of the Sn99.9 anodes during (a) and immediately after (b) electrolysis with different current densities (40 g/dm³ Sn, 25 °C)
to be expressed vs. the standard hydrogen electrode (SHE). Figure 6 shows the potential values developing on different anode materials at relatively low (500 A/m²) and high (2000 A/m²) current densities in electrolyte solutions of low (10 g/dm³) and high (40 g/dm³) tin concentrations. The latter settings represent less favorable conditions for the anodic process.

![Figure 6](image_url)

*Figure 6. Measured potentials of different anode materials at different current densities and tin concentrations in the electrolyte (1 mol/dm³ HCl, 25 °C)*

The potentials do not show much change during the first 5 minutes of the electrolysis. Generally, the dissolution of the anodes alloyed with silver can take place at the lowest potentials, however copper seems to hinder the reaction. Especially at higher current densities, the anodic dissolution requires higher potential in the electrolytes of higher tin concentration. At the lowest examined current density, the anodes made of different materials, work at virtually the same potential.

The alloying elements influence the phase composition and the texture of the anode produced by casting. If the cooling rate is normal, copper may appear in the form of Cu₆Sn₅ intermetallics dispersed in the α-Sn solid solution type matrix. Silver is prone to form larger aggregates of the segregating Ag₃Sn phase [12]. Dissolution of the anode is not uniform
over the active surface. The solid solution and the primary crystalline tin phases, especially in the preferred orientation are preferentially dissolved. Thus the originally smooth surface becomes gradually rougher and some particles of the intermetallics and the matrix metal may drop out. The increasing surface area reduces the effective current density in a galvanostatic operation, which results in lower overpotentials. This mechanism is corroborated by the experienced higher mass of the anode slime, containing larger particles in the case of the silver containing anodes. The typical structure of the anode slime produced from the SnCu8Ag3 type anode material is shown in Figure 7.

![Figure 7](image.png)

**Figure 7. The structure (a) and EDAX spectra (b) of the typical components in the anode slime generated from the SnCu9Ag3 material**

The area marked with No. 1 in Figure 7 indicates the virtually homogeneous Sn-Cu crystals, whereas the area marked with “2” shows the segregated fibrous Sn-Ag phase. The metallic content in the anode slime makes this by-product valuable, although selective extraction of the contained metals requires a special processing technology. The elemental analysis of the slime gives 44% total tin concentration, with 31% copper and 6.7% silver beside minor concentration of other impurities.

The results referring to the changing masses of different anodes in electrolytes of low and high Sn concentrations in the electrolyte (Figure 8) indicate that at high Sn concentrations the anodic dissolution partly takes place by generating Sn(IV) species even at relatively low anodic current densities. The resulting mass change is consequently less.
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Figure 8. Measured mass changes of different anodes in electrolytes containing low (a) and high (b) concentrations of tin (1 mol/dm$^3$HCl, 25 °C)

The unfavorable anodic reaction at high anode potentials resulting in the generation of Sn(IV) species can be normally compensated by the secondary reaction in the slime, but there is virtually no such layer present at the surface of the anodes in the first 5 minutes of the operation. The Sn(IV) may thus escape to the bulk of the solution and reaching the cathode surface, they may cause re-dissolution by Eq. (1). As also seen, copper alloying deteriorates the conditions.

The cathodic process should be associated with a continually increasing mass of the electrode. However, Figure 9 shows that in electrolytes of low tin concentration the decreasing cathode masses were recorded after the start of the electrolysis. It is especially so at higher apparent current densities (Figure 9b). The current density for the cathode can only be expressed referring to the original geometric surface area. The fresh and smooth starting cathode is quickly covered by separately growing crystals of deposited tin, thus the actual surface area is increasing until a virtually stable form is reached. The initial decrease in the observed cathode mass is caused by the evolution of hydrogen gas. As demonstrated by Figure 10, the small bubbles are stuck at the gradually changing surface of the cathode and they are released slowly. Later, the cathode surface becomes rougher, the cathode potential may also rise under galvanostatic conditions and the hydrogen evolution stops. Subsequently the tin deposition is predominant. At high applied apparent current densities it happens considerably later.
Figure 9. Measured mass changes of the cathode in electrolytes containing different levels of Sn concentration at low (a) and high (b) apparent cathodic current densities (1 mol/dm³ HCl, 25 °C).

Figure 10. The initial structure of the cathode deposit influenced by the evolved gas bubbles (2000 A/m², 10 g/dm³ Sn, 1 mol/dm³ HCl, 25 °C).

This irregularity is however absent if the Sn concentration in the electrolyte is 20 g/dm³ at least. The initial hydrogen evolution has little direct effect on the current efficiency but it is mostly unfavorable because of blocking a significant fraction of the active cathode surface when the initial tin deposition takes place. Thus the morphology of the produced
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Cathode deposit is also affected by these conditions. Because of the irregular contact with the substrate, the metal deposit is formed with a typical spongy structure.

The characteristic deposit structures obtained with the experiments of 5 min duration with the various tin concentration and apparent current density settings are arranged in Figure 11.

![Figure 11. Cathodic deposits obtained with different apparent current densities in electrolytes of varied tin concentrations (1 mol/dm$^3$ HCl, 25 °C)](image)

A consistent or recurring evolution of hydrogen may also raise concern about the stability of the tin chloride solution because of the decreasing acidity and the danger of Sn(IV) hydrolysis. Although at higher than optimum apparent current densities, hydrogen bubbles do not interfere with the initial deposition, but the fast charge transfer associated with the sluggish ion transport [7] produces long dendrites and needle crystals, which is also undesirable.

The longer-term electrolysis may also involve the gradual change in the distribution of dissolved tin among its species. The iodometric analysis results of solution samples taken regularly during an 8h long run are plotted in Figure 12. The cathodic current efficiency – measured by removing the deposit every hour – referring to the whole time of electrolysis was ~95%.
Figure 12. The change of Sn concentration during electrorefining (SnCu1 anode, 1000 A/m², 1 mol/dm³ HCl, 25 °C)

As the current efficiency is close to the theoretical value and virtually no Sn(IV) species are found in the electrolyte, it may be assumed that the anodic process was run under favorable conditions. The slime layer – and the metallic particles in it - developed during the extended process could eliminate the generated Sn(IV) species and aerial oxidation could be considered negligible.

Conclusions

The specially designed experimental cell equipped with in-situ continuous mass measurement of the electrodes could indicate the principal processes taking place at the anode and the cathode during the initial stage of the tin electrorefining in chloride solutions. It has shown, that the tin anode is dissolving undisturbed in a wide range of current densities, however the distribution of dissolved tin among the possible Sn(II) and Sn(IV) species may vary. The presence of Sn(IV) ions was indirectly indicated by the mass changes. High currents are possible at significantly increased anode potentials, especially on anodes containing copper alloying. Controlling the anode potential is therefore primarily important in providing optimum conditions for the procedure. The anode slime is composed of a large proportion of metallic particles, especially with silver containing anodes. These particles may be efficient in eliminating the generated Sn(IV) species and help assure the desired overall anodic process of producing Sn(II) species. The experiments have pointed out the initial evolution of hydrogen at the cathode, especially in electrolytes of low tin concentration (< 20 g/dm³) and high (> 1000 A/m²) apparent current densities. Hydrogen bubbles stuck on the surface of the cathode may also deteriorate the developing structure of the tin deposit. The anodic slime not only contains a high proportion of metallic tin, but also collects – beside copper – the valuable silver content of the anode alloy. Therefore it is considered as an important by-product beside the cathode tine of high purity. The process is
stable under optimum conditions and electromechanical cathode compression can assure trouble-free operation over a long period of time without human supervision. The system of cathode compression, however may be further developed and the anode slime processing may be integrated with the electrorefining procedure. In that way this new technology can be attractive for practical implementation at the sites of electronic producers.

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