Co-Deposition of Cu-Sn-Zn Alloy from An Alkaline Cyanide Solution

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ABSTRACT
The electrodeposition of ternary Cu-Sn-Zn alloy by using the alkaline cyanide solution was produced in this study. The electroplating process was performed at 65°C in a slightly stirred solution. The effect of current densities of 5, 10, 15 and 20 mA/cm\textsuperscript{2} that applied in bath composition on the composition of deposit were investigated. The surface morphology of ‘cauliflower’ was appeared under SEM investigation. The presence of Cu-Sn-Zn alloys was detected via XRF with an existence of small impurities.

Keywords:
Electroplating, Cu-Sn-Zn alloy

INTRODUCTION
Copper-tin-zinc(Cu-Sn-Zn) alloy electrodeposits put forward an outstanding corrosion protection for metals by merging the barrier protection of copper, tin and the galvanic protection of zinc, without the bulky corrosion product associated with wholly zinc deposits. The alloy coating also gives a brighter color and enhanced properties. It is therefore not surprising that a number of applications of Cu-Sn-Zn alloy deposits have been known and well recognized [1].

Cu-Sn-Zn coatings have been utilized on the chassis of electrical and electronic apparatus and on critical automotive parts such as fuel and brake line components. Other possible applications include car body panels, where the trend is towards lengthening corrosion warranties, and the aerospace industry where the absence of corrosion is of supreme importance. Few patents [2] covering the deposition of such alloys from cyanide solutions probably the first known significant publication on Cu-Sn-Zn coatings. There are also publications on such coatings via electroless method [3].

EXPERIMENTAL METHODS
Copper was occupied as cathode in this study. Copper sheet were cut into smaller pieces with a dimension of 40 mm x 45 mm x 1.3 mm. The pieces were highly polished and finally were cleaned by using ultrasonic method.

The full details of the bath formulation and preparation are described in patents [2] on the invention of the plating system. Table 1 shows the formulation used to obtain Cu-Sn-Zn alloy in this study

<table>
<thead>
<tr>
<th>Table 1: Bath formulation used for Cu-Sn-Zn coatings</th>
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<tbody>
<tr>
<td>Chemicals</td>
</tr>
<tr>
<td>CuCN</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>Na\textsubscript{2}Sn(OH)\textsubscript{6}</td>
</tr>
<tr>
<td>NaCN</td>
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The pH of the plating solutions is usually between 13 and 14. The solution was also gently stirred throughout the electroplating operations. The bath was operated from anodes made from graphite and highly polished copper as cathode. The electroplating experiments were carried out at temperatures of 65°C and the operating current densities of 5, 10, 15 and 20 mA/cm\textsuperscript{2}. The corresponding plating conditions are reported with the results. Deposition was carried out for sufficient time to give about 60 microns thick deposits. The SEM and XRF were used to analyze the composition and thickness of the coating

RESULTS AND DISCUSSION

XRF Analysis
Each electroplated substrate was analyzed via XRF and the result was listed in Table 2.
Table 2: XRF analysis of the deposited Cu-Sn-Zn alloy

<table>
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<tr>
<th>Current Density (mA/cm²)</th>
<th>Deposit Composition (wt%)</th>
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<tbody>
<tr>
<td>5</td>
<td>55.99% Cu, 31.75% Sn, 09.88% Zn, 02.39% C</td>
</tr>
<tr>
<td>10</td>
<td>57.16% Cu, 24.01% Sn, 12.04% Zn, 06.79% C</td>
</tr>
<tr>
<td>15</td>
<td>61.46% Cu, 27.01% Sn, 11.53% Zn</td>
</tr>
<tr>
<td>20</td>
<td>56.68% Cu, 30.69% Sn, 12.62% Zn</td>
</tr>
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</table>

From Table 2, Cu-Sn-Zn co-deposit was successfully obtained from all current density applied during electroplating process. In accordance to this result, the existence of each constituent of the alloy for each current density can be compared as shown in Figure 1.

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Figure 1: Weight of Cu-Sn-Zn vs current density

Instead of Cu-Sn-Zn presence, some samples portrayed a small percentage existence of carbon. This impurity was originated from the graphite anodes.

SEM Analysis
Under the SEM investigation in Figure 2(a)-(d), all electroplated samples portrayed the infamous ‘cauliflower’ morphology. The cauliflower appearance looks rougher and bigger when the current density increases. The presence of porosity was also noticed for each current density applied. This was due to the release of hydrogen gas at the cathode during electroplating even though a continuous stirring suppose to prevent such condition. Hence, it will also result in a less homogen and less adorable surface finish.

Figure 2: Surface morphology of Cu-Sn-Zn coating at current density of (a) 5 mA/cm², (b) 10 mA/cm², (c) 15 mA/cm², and (d) 20 mA/cm².

CONCLUSION
As a conclusion, approximately 60 microns thickness of Cu-Sn-Zn alloy was successfully deposited on a copper substrate. An average coating composition of 55 – 60wt% of copper, 25 – 30wt% of tin and 10 – 12 wt% of zinc was able to be obtained. Cauliflower appearance was detected under SEM analysis where the morphology became rougher with the increment of the current density

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