Effect of Different Complexing Agent on Surface Morphology and Microstructure of Cu-Sn-Zn Coatings Electrodeposited From Less Hazardous Electrolyte

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Abstract. In the present work carbon was electrochemically coated with Cu-Sn-Zn ternary alloy coatings from an electrolyte containing copper chloride, tin chloride and zinc chloride. The morphology and chemical composition of the deposits were examined by means of scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS), respectively. The results exhibited that Cu-Sn-Zn coatings with 5,5-dimethylhydantoin as complexing agent contain a large amount of copper. It is found that sodium formate was the suitable complexing agents in production of Cu-Sn-Zn ternary alloy due to its uniform and smoothly depositions coated on substrate.

1. Introduction
Electroplating is the process in which layers of material are coated on top of substrate due to the application of an electric current to the system. The substrate is immersed in an electrolyte containing metal salts which when dissolved is the source of the positively charged metal cations to be deposited. A negative charge is then applied to the substrate which acts as the cathode attracting the metal cations towards the substrate. The metal cations are reduced and deposited at the substrate surface. Brass is electroplated from a mixed copper and zinc, bronze, speculum alloy can be electroplated to achieve some of advantages of each constituent and good corrosion protection. In industry, soldering of Cu-Sn-Zn alloys are commonly formed as a result of interfacial reactions that occur between the solder (Sn-Zn) and the copper as substrate [1]. Electroplating of alloy is used extensively in a variety of industrial applications including electroforming, electrorefining, and as an undercoat for other deposits to protect basis metal or to promote adhesion, soldering and printing rolls [2].

Copper and its alloy have many technical applications based on their properties to be applied such as electrorefining, automotive and electronics for the purposes of appearance, special surface protection and mechanical properties. Cu-Sn-Zn ternary alloys exhibit better cyclability, due to the nanostructured nature of Cu-Zn alloys and large capacities due to the high capacity of Cu-Sn alloys [3]. These ternary alloys are more attracting than binary copper alloy from a decorative view, because the deposits obtained from the ternary alloys present better mechanical resistance. These alloys also can be electroplated from alkaline cyanide solution and the acid sulphate solution bath. The most common bath used in the electronic applications is cyanide solution while for the purpose of decorations and appearance applications the acid sulphate solutions was chosen [4]. The use of cyanide salts in the electroplating of Cu-Sn-Zn has turn out to be environmentally disfavoured because...
of the ecological considerations [5][6]. Hence, in this paper, the effect of different complexing agents was studied on the microstructures properties of Cu-Sn-Zn ternary alloy produced with less hazardous electrolyte via electroplating.

2. Experimental

2.1 Substrate preparation
All solutions in this work were prepared using analytical grade reagents and deionized water. All experiments were carried out in 250 ml electrolyte prepared with deionized water. The electrolyte was prepared by adding reducing agent and complexing agent, respectively into a solution containing CuCl$_2$, SnCl$_2$ and ZnCl$_2$, which were chosen as the source of copper ions, zinc ions and tin ions. The substrate used was carbon with dimension 45 mm length, 0.9 mm thickness and 1.8 mm width was served as cathode and graphite was act as anode. Substrates were heated at 500 °C for 45 minutes to remove any impurities. The substrates were then degreased in acetone solution. Prior to electroplating, the substrates were activated in 10% sulfuric acid (H$_2$SO$_4$) solution to produce a highly clean active surface [5]. After each of these pre-treatment process, the substrate was cleaned in distilled water.

2.2 Electrodeposition of Cu-Sn-Zn
Plating processes via electroplating was performed for 30 minutes in less hazardous electrolyte containing copper chloride, tin chloride and zinc chloride with the help of reducing agent and complexing agent as shown in Table 1. The bath was agitated mechanically with current density range from 0.5 to 4 A dm$^{-2}$. The solution bath was placed on the heater with the temperature monitored by a contact thermometer. The electrolyte pH was adjusted with sodium hydroxide acting as a buffer and agitation was set constantly.

| Composition          | Function          | Concentration |
|----------------------|-------------------|---------------|
| CuCl$_2$             | Cu metal source   | 0.17 M        |
| SnCl$_2$             | Sn metal source   | 0.13 M        |
| ZnCl$_2$             | Zn metal source   | 0.23 M        |
| Sodium hypophosphite | Reducing agent    | 0.45 M        |
|                      | Complexing agent  | 0.20 M        |
| pH                   |                   | 7 – 9         |
| Temperature          |                   | 45 – 55 °C    |
| Plating time         |                   | 30 min        |

2.3 Surface morphology and composition analysis.
In order to study the surface morphology and compositions of the electroplated layers deposited from less hazardous electrolyte bath, scanning electron microscope (SEM) equipped with energy dispersive x-ray (EDX) spectroscopy (JEOL, JSM-6380LA) were used. The thickness was measured by the following formula:

$$t = \frac{(m_2 - m_1)}{A \times \rho}$$

(1)
Where \( m_2 \) and \( m_1 \) are respectively the mass of alloy plating and substrates; \( A \) is the area of the coated specimen; \( \rho = \Sigma \rho w \) (\( w \) is the mass fraction of Cu, Sn and Zn in alloy).

3. Results and Discussion

The morphologies of the Cu-Sn-Zn ternary alloy on carbon substrate in the study of the effect of different complexing agents were examined by SEM presented in Figure 1(a-d). It is clearly shown that the grain structures of the Cu-Sn-Zn deposited on carbon is strongly affected by the type of complexing agents. In the deposition of Cu-Sn-Zn developed with sodium formate as complexing agent as shown in Figure 1(a), the large agglomerates were observed. These large sized granules are composed of strong hydrogen and sodium oxylate generated by decompositions of sodium formate [7]. In the production of Cu-Sn-Zn ternary by using sodium acetate as complexing agent as presented in Figure 1(b), the obtained deposits is rigorous and it was perpendicular to the surface. This can be explained by the presence of carbonic acid function in its structure that are produced by the decompositions of sodium acetate. Sodium acetate also acts as buffer to keeps a relatively constant pH level of electrolyte and to stabilize the metal ions in alkaline bath [8]. Figure 1(c) shows the surface morphology of Cu-Sn-Zn ternary alloy deposited in the presence of D-sorbitol in electrolyte as complexing agent. The deposits is regular and becomes denser due to refining actions of D-sorbitol [4]. In this work, 5,5-dimethylhydantoin was selected as one of the complexing agent to be studied in the effect on the properties of microstructure Cu-Sn-Zn alloy. 5,5-dimethylhydantoin (DMH) is the most in demand available as complexing agent for metal electroplating with heterocyclic structure organic molecule and gives a good solubility and stability in alkaline solution. Its derivatives also acts as more stable complexing agent for metal ions [9]. As seen in Figure 1(d), fine deposits were obtained with 5,5-dimethylhydantoin compared to others complexing agents. However, the presence of porosity was also noticed for each study. This was due to the release of hydrogen gas at working electrode during electroplating process even though a continuous stirring supposed to prevent such condition. Hence, it will produce a less homogenous and less durable surface finish [10].

![Figure 1. SEM micrographs of Cu-Sn-Zn layers deposited from electrolyte containing (a) sodium formate, (b) sodium acetate, (c) D-sorbitol and (d) 5,5-dimethylhydantoin as complexing agent in production of Cu-Sn-Zn ternary alloy via electroplating.](image-url)
Figure 2. Atomic compositions of Cu-Sn-Zn coatings electrodeposited from electrolyte with different complexing agents.

Figure 3. Thickness of Cu-Sn-Zn Ternary Alloy Deposited in The Effect of Different Complexing Agents

The compositions of Cu-Sn-Zn deposited on carbon by using different complexing agents was investigated using energy dispersive x-ray (EDX) analysis. As illustrated in Figure 3, the content of Cu deposited with 5,5-dimethylhydantoin as complexing agent is relatively high (95.27 %). This is because Cu\(^{2+}\) is easier to obtain electrons provided by reducing agent in depositing of Cu-Sn-Zn alloy on carbon substrate. However, the deposition Zn with the same complexing agent is relatively low, which is only 0.52 %. The presence of Zn in smaller amount in the deposited alloy with respect to amount of Zn in the electrolyte might be due to the thermodynamic instability of alloy system. The amount of Cu and Sn deposited in electroplating using sodium formate and sodium acetate are in the same range, on average containing approximately 85 % and 3.5 %, respectively. Cu-Sn-Zn deposited
via electroplating with D-sorbitol as complexing agent exhibit almost similar content as white bronze which are 68.22% Cu, 26.18% Sn and 5.68% Zn, respectively. However, the obtained deposits were mostly powdery.

Complexing agents affects not only on the coating surface morphology but also the thickness of Cu-Sn-Zn deposited layers. Figure 3 demonstrates the relationship between the types of complexing agents and Cu-Sn-Zn ternary alloy coating thickness. It is noticeable that Cu-Sn-Zn ternary alloy is easily electrodeposited on carbon substrate with sodium formate and sodium acetate as complexing agent. The deposits obtained were brownish and uniformly coated on substrate. However, the deposits obtained on carbon with D-sorbitol and 5,5-dimethylhydantoin as complexing agents, were powdery and tended to peel off from the substrate.

4. Conclusion
Cu-Sn-Zn ternary alloy coatings may be successfully achieved by electrodeposition from less hazardous electrolyte with addition of appropriate complexing agent. The addition of proper amounts of sodium formate to the electrolytic bath results in the formation of uniform, and smooth Cu-Sn-Zn ternary alloy coating.

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6. References
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