Effect of Current Densities in Cu-Sn-Zn Electroplating Process on Carbon Substrate Using Less Hazardous Electrolyte

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Abstract. Cu-Sn-Zn ternary alloy coatings was studied from a less hazardous electrolyte containing copper (II) chloride, tin (II) chloride, zinc (II) chloride, reducing agent and complexing agent. In this work, the impact of different current densities on morphology, chemical composition, current efficiency, microhardness and corrosion rate were investigated by method of scanning electron microscope equipped with energy dispersive x-ray spectroscopy, weight gain measurements, x-ray diffraction, and potentiodynamic polarization measurement, respectively. It was discovered that, Cu-Sn-Zn alloys obtained at 30 mA/cm² presents the highest microhardness value. It is also can be concluded that, current densities have a significant impact on the appearance and the surface morphology of Cu-Sn-Zn alloy electrodeposits.

1. Introduction

Electroplating (also known as electrodeposition) is the application of a metal coating to a metallic or other conducting surface by an electrochemical process. It is an electrolysis method which deposits a coating that has a desirable effect. Electroplating is a simple, single-step, and scalable technique for the production of metallic and alloy coatings over different substrates and does not involve high-end infrastructure in most cases [1], [2]. Electroplating process is a method 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 submerged 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 [3].

The main application area of the alloys especially Cu-Sn-Zn deposition are electronic, petrochemicals, energy conversion devices, automotive, clothing and fashion jewelry. In order to produce the excellent production of alloy via electroplating process, the parameters must be controlled
since it has a significant effect on the coating properties, deposition efficiency and hydrogen evolution [4]. Electroplating parameters that can be listed as the applied current density, electrolyte temperature, pH of electrolyte, complexing agent and reducing agent addition, and plating time must be controlled during the process since they determine the characteristics of the coatings. The aim of this work is to provide the less hazardous electrolyte and to study the effect of current density in Cu-Sn-Zn ternary alloys produced via electroplating process.

2. Experimental Details
All solutions in this work were prepared using analytical grade reagents and deionized water. All experiments were carried out in 100 ml electrolytes prepared with deionized water.

2.1. Preparation of substrate
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. The morphology of the substrate is shown in Figure 1. The carbon substrate was heated at 500 °C for 30 to 45 minutes to remove any impurities. The substrate was then degreased in acetone solution. Prior to electroplating, the substrate was activated in 10% sulfuric acid (H₂SO₄) solution to produce a highly clean active surface [5]. After each of these pretreatment process, the substrate was cleaned in distilled water.

2.2. Electroplating of Cu-Sn-Zn
One-compartment cell was used in production of Cu-Sn-Zn ternary alloy via electroplating process. Electroplating process was performed for 15 minutes at room temperature in less hazardous electrolyte containing copper (II) chloride, tin (II) chloride, and zinc (II) chloride. The electrolyte was prepared by adding sodium hypophosphite and sorbitol as reducing and complexing agents, respectively into a solution containing metal chloride as shown in Table 1. Copper sheet was used as an anode and was placed in the same compartment of working electrode. During the plating process, the electrolyte was remained unchanged and no inert gas was used to purge the electrolyte.

2.3. Characterization
The characteristic of Cu-Sn-Zn ternary alloys produced were analysed using SEM equipped with EDX (HITACHI SU1510) to study morphology and chemical composition of Cu-Sn-Zn deposits. The thickness, \( t \) was measured by the following formula:

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

where \( m_2 \) and \( m_1 \) are respectively the mass (g) of alloy plating and substrates; \( A \) is the area (cm²) of the coated specimen; and \( \rho \) is density of alloy (g/cm³). In addition, microhardness of the alloys was measure using a Vickers hardness tester (SHIMADZU HMV-2T) at an applied load of 100 g and 15 s
dwell time. Five measurements were made for each specimen and the average hardness value determined.

Table 1. The composition of less hazardous electrolyte

| Composition          | Concentration |
|----------------------|---------------|
| CuCl₂                | 0.20 M        |
| SnCl₂                | 0.15 M        |
| ZnCl₂                | 0.15 M        |
| Sodium hypophosphite | 0.30 M        |
| Sodium formate       | 0.30 M        |
| pH                   | 2.5 ~ 3.0     |
| Deposition time      | 15 minutes    |
| Temperature          | Room temperature |

2.4. Corrosion test
The polarization investigation was performed using Metrohm Autolab Potentiostat/Galvanostat controlled by computer with NOVA 2.0 software, which uses counter electrode (Pt sheet), reference electrode (Ag) and carbon substrate as working electrode. The potentiodynamic polarization curve known as a Tafel plot, depicts the relationship between potential and corrosion current density. This plot exhibits a linear region, the slope of which is known as the Tafel constants (anodic and cathodic Tafel constants). The intersection of the projection of the linear region of the plot with the open circuit potential (Ecorr) gives the cathodic or anodic corrosion current (icorr). Once icorr is determined, the following equation derived from Faraday’s law was used to calculate the corrosion rate, r:

\[
\text{Corrosion rate, } r = \frac{C \times EW \times icorr}{np}
\]  

where EW is the equivalent weight (g/mol), n is the number of electrons involved, \( \rho \) is density of alloy (g/cm\(^3\)) and C is constant, 3.27 if corrosion rate is in mm/year.

3. Results and discussion

3.1. Cathodic current efficiency (CCE)
Production of Cu-Sn-Zn alloy via electroplating are connected by hydrogen evolution. According to Faraday’s Law, cathodic current efficiency was estimated from the cathode's weight gain. Figure 2 shows the current efficiency obtained from various current densities range from 10 to 50 mA/cm\(^2\) in Cu-Sn-Zn alloy production via electroplating. As the current density is further improved, the percentage of cathode current efficiency of the electroplating process increased slightly from 79.66 % to 88.31 %. However, as the applied current density increased by more than 30 mA/cm\(^2\), the cathode current's efficiency steadily decreased to 84.85 %. This is indicative of hydrogen evolution at a high current density, which contributes to powdery deposits. As illustrated in Figure 3, hydrogen evolution is also the reason for the deposition rate increase steadily up to ~87.83 mm/h and decreases beyond the current density of 30 mA/cm\(^2\). The rose in the evolution of hydrogen may interrupt the deposition rate of the electroplating process.

3.2. Surface morphology and composition analysis
Figure 4 (a) to (e) presents the scanning electron microscope micrograph of carbon substrates coated with Cu-Sn-Zn alloy after electroplating process at various current densities. In this study, the plating process was varied at 10, 20, 30, 40 and 50 mA/cm\(^2\). The morphology of the scanning electron microscope reveals that the nucleation rate is low resulting in a rough, less dense, less compact and more porous at lower current densities which is from 10 mA/cm\(^2\) to 20 mA/cm\(^2\). These poor qualities of deposits are expected as due to the longer time for metal nuclei to grow [6]. Meanwhile, as shown in Figure 4 (c) to
(e), scanning electron microscope images of the deposited Cu-Sn-Zn alloy surface at the higher current density, produced deposits with compact, fine and small-grain metals.

Figure 2. Cathode current efficiency of Cu-Sn-Zn ternary alloy produced in various current densities at pH electrolyte 2.5 ~ 3.0 and deposition time of 15 minutes.

Figure 3. Deposition rate of Cu-Sn-Zn ternary alloy produced in various current densities at pH electrolyte 2.5 ~ 3.0 and deposition time of 15 minutes.

Figure 5 exhibits the composition of Cu-Sn-Zn alloy coatings on carbon substrate achieved at various current densities. The study shows how the compositions of Cu, Sn and Zn significantly depends on the current density applied in the electroplating process. The composition of the Cu-Sn-Zn alloy coatings in the influence of current density was characterized by EDX with mapping analysis. As shown in Figure 5, it is clear that the deposited alloy on carbon substrate comprises of copper, tin and zinc for all samples regardless of current density. Initially, as the applied current density increased from 10 mA/cm², the weight percentage of copper gradually reduced slightly from 88.45 to 82.78 %. However, as the applied current density is increased more than 30 mA/cm², the percentage of copper is drastically reduced from 82.78 to 63.42 %. Meanwhile, the weight percentage of tin and zinc are slightly improved as the applied current density was further increased to 50 mA/cm².
3.3. Microhardness
The effect of current density on microhardness is shown in Figure 6. It can be observed that the microhardness increases with current density up to 30 mA/cm\(^2\) and then it decreases. This can be expected because when the deposition current density is very low, in this work is less than 30 mA/cm\(^2\), the deposits has a lesser number of nuclei and hence a higher grain growth is favored. As the current density increase further, the formation of nuclei increases with the applied current due to higher energy. This phenomenon refines the grain size and a rise in microhardness is observed. However, beyond a certain current density (30 mA/cm\(^2\)), a decrease in microhardness is observed. This observation shows that at higher overpotentials, the hydrogen evolution also takes part in deposition process due to the concentration depletion of ionic species at solution/cathode surface. The hydrogen ions are adsorbed giving porous microstructure, which lowers the microhardness of the coatings.

Figure 4. Surface morphology of electrodeposits prepared from Cu-Sn-Zn ternary alloy produced in various current densities at pH electrolyte 2.5 ~ 3.0 and deposition time of 15 minutes (a) 10 mA/cm\(^2\), (b) 20 mA/cm\(^2\), (c) 30 mA/cm\(^2\) (d) 40 mA/cm\(^2\), (e) 50 mA/cm\(^2\)

Figure 5. Element composition of Cu-Sn-Zn ternary alloy produced in various current densities

Figure 6. Average microhardness of Cu-Sn-Zn ternary alloy produced in various current densities
densities at pH electrolyte 2.5 ~ 3.0 and deposition time of 15 minutes.

3.4. Electrochemical corrosion behaviour of Cu-Sn-Zn alloys.

Figure 7 shows the electrochemical results of corrosion test on Cu-Sn-Zn alloys produced via electroplating using less hazardous electrolyte in various current density. Overall, it is clear that the corrosion potential of Cu-Sn-Zn alloys plated using low current density is more noble than Cu-Sn-Zn alloys plated using high current density.

![Figure 7. Tafel polarization curve of Cu-Sn-Zn ternary alloy produced in various current densities at pH electrolyte 2.5 ~ 3.0 and deposition time of 15 minutes.](image)

4. Conclusion

The outcomes of various experimentation lead to the conclusion:

- Cu-Sn-Zn ternary alloys is successfully electroplated using less hazardous electrolyte (which is simple, non-toxic, and environmentally friendly).
- Microhardness of Cu-Sn-Zn ternary alloys increases with increasing current density up to 30 mA/cm² and then, drops with the further increase in current density due to the porous microstructure of the alloys.
- Corrosion potential of Cu-Sn-Zn ternary alloys at low current density (lower than 30 mA/cm²) is more noble than Cu-Sn-Zn ternary alloys produced at high current density.

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