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Effect of pH in Production of Cu-Sn-Zn via Electroplating Using Less Hazardous Electrolyte

Rozainita ROSLEY[1,a*], Suzi Salwah JIKAN[2,b] Nur Azam BADARUZAMAN[3,c] , Misbahul Muneer Abd RAHMAN[1,d] and Hazel Monica MATIAS-PERALTA[2,e]

[1]Centre for Diploma Studies, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia.

[2]Faculty of Science, Technology and Human Development, Universiti Tun Hussein Onn, Parit Raja, Batu Pahat, Johor, Malaysia.

[3]Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia.

[a]rozainita@uthm.edu.my, [b]suzi@uthm.edu.my, [c]azam@uthm.edu.my, [d]muneer@uthm.edu.my, [e]monica@uthm.edu.my

ABSTRACT. Cu-Sn-Zn ternary alloy have been prepared by an electroplating process on carbon substrate from a less hazardous electrolyte containing chloride solution, complexing agent and reducing agent at room temperature. In this study, the effect of pH on deposit composition was investigated in details. pH 9 was found to be the best condition as it was non-acidic and less alkaline solution with composition of $Cu_{54.5}$ $Sn_{32.5}$ Zn_{13}.

Keywords: *Less hazardous, Electrolyte, Ternary alloy, Electroplating;*

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1. INTRODUCTION

Electroplating is both art and sciences. It is an electrodeposition process for producing a dense, uniform and adherent coating, usually of metal or alloys, upon a surface by the act of electric current. This process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. Electroplating is used extensively in a variety of industrial applications as for appearance, protection, special surface properties and engineering or mechanical properties. Process of electroplating is also used for electrical oxidation of anions onto solid substrate, to change the surface properties of an object. Electroplating products are widely used for many industries, such as automobile, ship, air space, machinery, electronics, jewelry, defense, and toy industries.

Alloy can be deposited from two types of plating solutions: the alkaline cyanide copper and formaldehyde [1]. These electrolyte is primarily used for decorative and in electronic applications. Unfortunately, cyanide is one of the most toxic chemicals available and therefore its use carries an extremely high risk to human health and to environment. The use of cyanide salts in plating electrolytes has becomes environmentally disfavored because of ecological considerations including the catastrophic accidental acidification of cyanide, disposal of the exhausted plating bath and waste water treatment are becoming increasingly difficult and expensive, rendering this approach highly unattractive from an industrial perspective [2]. This project have been proposed for use as replacements for the well-known and conventional commercially employed cyanide counterparts and it will reduces the waste treatment costs for destroying cyanide along with fire and liability insurance premiums.

2. MATERIALS AND METHODS

Cu-Sn-Zn alloy were plated by electroplating from a less hazardous electrolyte containing copper (II) chloride, tin chloride and zinc chloride with the help of reducing agent and complexing agent. The details composition and operating condition are given in Table 1. A graphite was used as anode. For coating and morphology studies, carbon was used as cathode. Carbon substrate with dimension 45 mm length, 0.9 mm thickness and 1.8 mm width was heated at 500 ⁰C for 45 min to remove any impurities. The substrate was then degreased in acetone solution. Prior to electroplating, the substrate was activated in 10% sulfuric acid (H_2SO_4) solution to produce a highly clean active surface [3]. After each of these pretreatment process, the substrate were cleaned in distilled water. Plating proses via electroplating was performed for 30 minutes at room temperature in less hazardous electrolyte and was agitated mechanically at room temperature with current density range to 15mA/mm^2.

Table 1 The composition of electrolyte

Composition	Concentration
$CuCl_2$	0.30 M
$SnCl_2$	0.15 M
$ZnCl_2$	0.45 M
Reducing agent	0.45 M
Complexing agent	0.10 M

2.1 Surface morphology and composition analysis. Surface morphology and compositions of the electroplated layers deposited from less hazardous electrolyte bath was investigatedunder scanning electron microscope equipped with energy dispersive X-ray spectroscopy (JEOL, JSM-6380LA). The thickness was measured by the following formula (Eq. 1):

$$t = \frac{(m_2 - m_1)}{A \times \rho} \qquad (1)$$

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

3.1 Effect of pH on composition and morphology. An analytical parameter that can influence the composition of plating layers is pH of the solution bath used. It is proven that the formation constant of a stable metallic complex species is highly pH dependent on which basically determines the availability of effective reducible metallic species in the solutions [4]. In demand to stabilize the solution from precipitation in the alkaline pH range, sodium citrate as complexing agent was added in the chloride solution.

The effect of pH was studied by keeping current density (15 mA/mm^2) and metals concentration constant respectively as shown in Table 1. A 10% of sodium hydroxide was added slowly to achieve desired pH. At lower pH, a coarse layer coating was obtained which turn into smooth layer at higher values of pH. Fig. 1 shows the variation of compositions of deposited alloy in pH range from 1.0 to 14.0. It is clear that, composition of Cu was decrease slowly from 96.7% to 54.5% by increasing pH from 1.0 to 9.0. However, with increasing the values of pH, both Sn and Zn content of the alloy increase from 3.3% to 81.8% and from 2.7% to 13.0%, respectively. The local pH of the substrate was increased with the increasing the value of pH solution. The higher pH values of the substrate perhaps are due to the faster recovery of H^+ ion on the surface of substrate [5]. This process causes the development of hydrogen bubbles and rapid depletion of H^+ ions around the substrate and causes Cu penetrates in the form of CuOH, so that easily to precipitates. It was observed that at pH9, composition of Cu, Sn and Zn was 54.5, 32.5 and 13%, respectively. This value was almost similar with Miralloy composition (Cu_{51} Sn_{33} Zn_{17}) which has earned widespread acceptance as an excellent alternative to nickel for a broad range of applications.

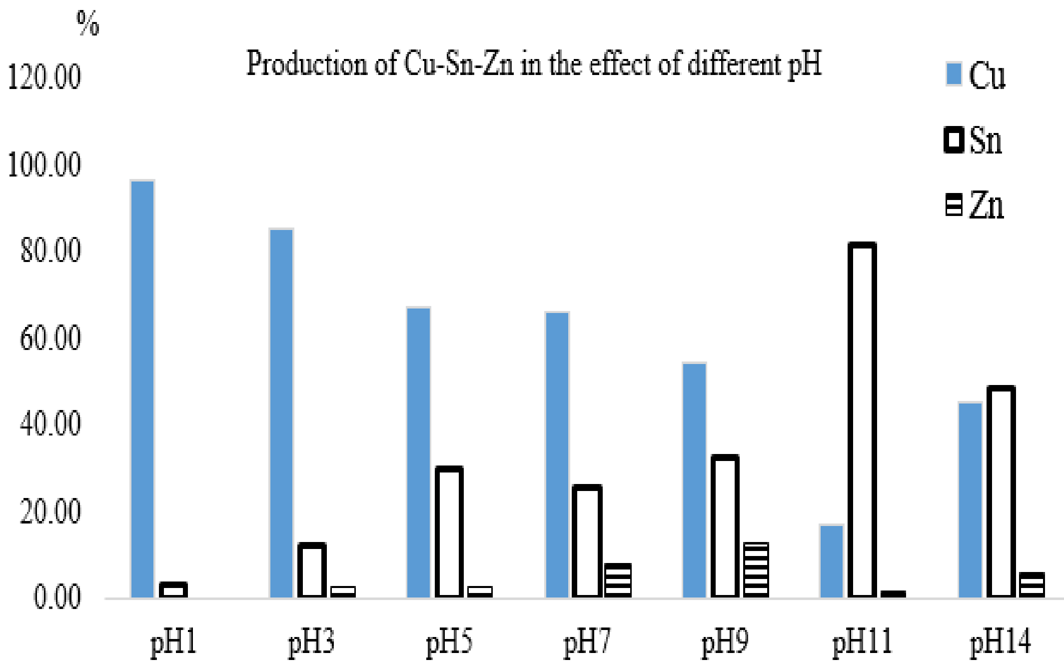

Fig. 1 Production of Cu, Sn and Zn in the effect of different pH

The effect of pH on the surface morphology of Cu-Sn-Zn ternary alloy layers was studied using scanning electron microscope. The layers that electroplated from less hazardous electrolyte at several pH and at constant current density are presented in Fig 2. The morphology for pH 1 exhibit a spongy and cauliflower surface in appearance and continuous deposits with the presence of both large and small grains simultaneously. This phenomenon indicate an abnormal growing during deposition process. However, by increasing the value of pH, the morphology change to coarse and porous in appearance. The change of the surface appearance was justified by the hydrogen evolution and stimulus the electrochemical conditions. Fig 3 shows the energy dispersive X-ray spectroscopy spectra of Cu-Sn-Zn plating layer for the study on the effect of different pH deposited at 15 mA/mm^2.

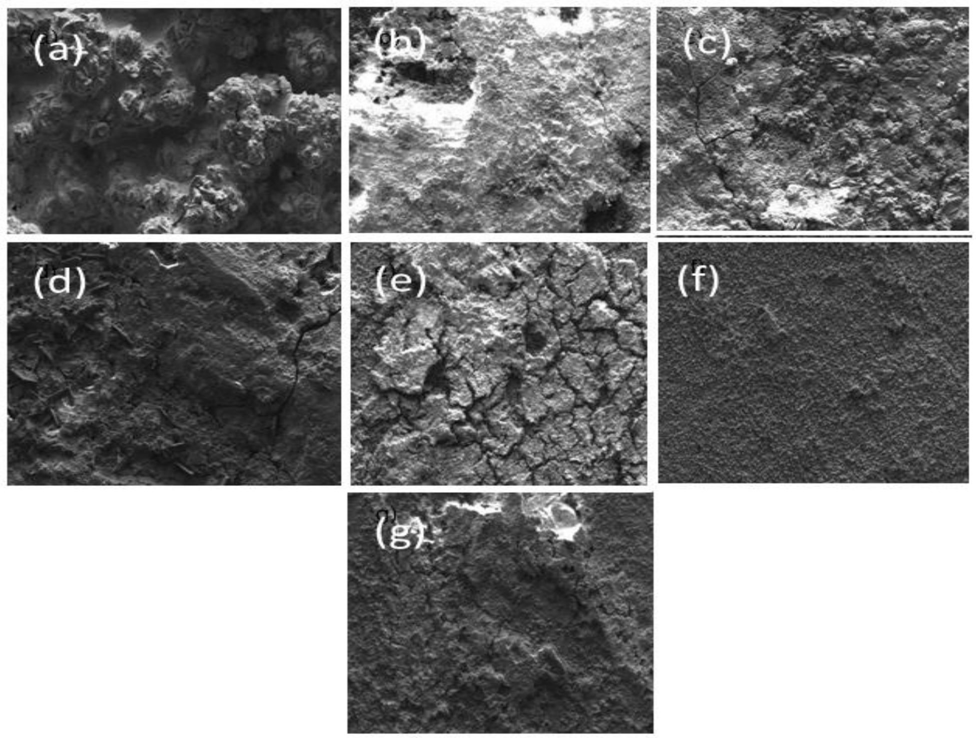

Fig. 2 Effect of pH on the surface morphology of Cu-Sn-Zn alloy coating at pH (a) 1.0, (b) 3.0, (c) 5.0, (d) 7.0, (e) 9.0, (f) 11.0 and (g) 14.0 deposited at 15 mA/mm^2

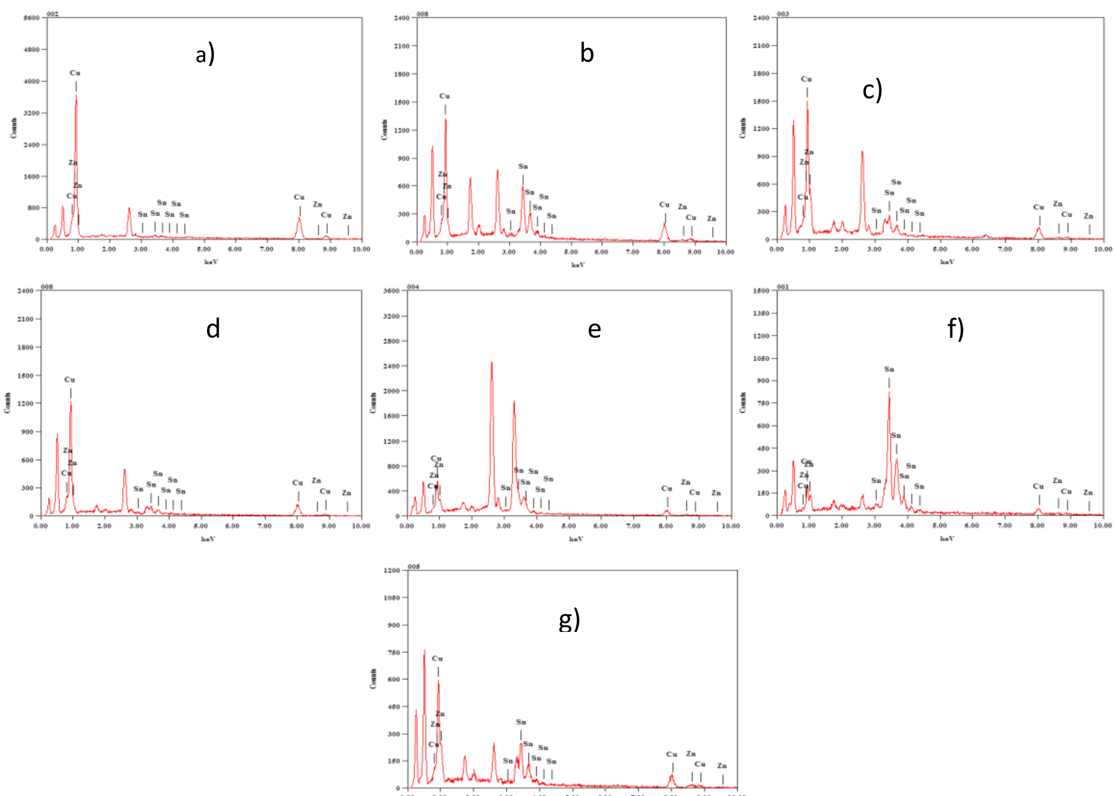

Fig. 3 EDS spectrum of Cu-Sn-Zn alloy coating at pH (a) 1.0, (b) 3.0, (c) 5.0, (d) 7.0, (e) 9.0, (f) 11.0 and (g) 14.0 deposited at 15 mA/mm^2

4. SUMMARY

Cu-Sn-Zn ternary alloy was successfully plated on carbon substrate. It was recognized that the pH of electrolyte has significant influence in composition of alloy and on the overall plating process. As in this studies, the optimum pH was found at pH 9 which gave the similar composition of Miralloy at non-acidic and less alkaline solution.

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REFERENCES

[1] Z.A. Hamid, A.A. Aal, New environmentally friendly noncyanide alkaline electrolyte for copper electroplating, Surf. Coatings Technol., 203 (2009) 1360-1365.

[2] A. Liu, X. Ren, B. Wang, J. Zhang, P. Yang, J. Zhang, M. An, Complexing agent study via computational chemistry for environmentally friendly silver electrodeposition and the application of a silver deposit, R. Soc. Chem. Adv., 4 (2014) 40930-40940.

[3] R. Wu, T. Yin, Z. Leng, G. Du, X. Guo, M. Zhang, J. Zhang, The process of electroplating with Cu on the surface of Mg-Li alloy, Surf. Coatings Technol., 225 (2013) 119-125.

[4] C. Srivastava, S.K. Ghosh, S. Rajak, A.K. Sahu, R. Tewari, V. Kain, G.K. Dey, Effect of pH on anomalous co-deposition and current efficiency during electrodeposition of Ni-Zn-P alloys, Surf. Coatings Technol., 313 (2017) 8-16.

[5] M. Haerifar, M. Zandrahimi, Effect of current density and electrolyte pH on microstructure of Mn-Cu electroplated coatings, Appl. Surf. Sci., 284 (2013) 126-132.