

Effect of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ concentration of electrolyte solution on Zn electrode position process

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Abstract:

Zinc electroplating from acidified zinc sulphate heptahydrate electrolytic bath with different zinc content and current density were studied. The weight of the zinc deposition layer increases with the rise of the current density initially and then tends to decrease with the increase of the current density beyond a threshold value of the current density for all bath compositions. An increase of zinc content of electrolytic solution from 120 g/l to 140 g/l retards the process of electroplating and reduces the weight of the zinc deposition layer. The influence of current density and zinc content of electrolytic solution on the relative density of plating layer and current efficiency has been discussed.

Keywords: Electrodeposition, Current density, Current efficiency, Zinc sulphate heptahydrate

Date of Submission: 07-09-2021

Date of Acceptance: 22-09-2021

I. Introduction:

Electroplating is the method of applying a metallic coating to another material by the act of electric current [1]. Electroplated products are widely used in many industries, such as automobiles, ships, aerospace machinery, electronics, etc [2, 3]. Progress in the electrodeposition process has advanced rapidly in a couple of decades and is being dealt with in numerous scientific and technical publications [1-5]. Researches were carried out to achieve different objectives like denser, harder, more corrosion resistance, more wear-resistant, more suitable for subsequent treatment deposition layer, etc. The presence of such a huge number of parameters of research objectives and electroplating parameters prompted this vastness of research publications in recent years [2-9].

Zinc is one of the most used metals for galvanic coating. Although a large number of researches have been carried out in the field of zinc plating to achieve high coating thickness with good adhesion and reasonably low porosity, the achievement of all these properties in plating is still far from complete. At present, a large number of galvanizing electrolytes for zinc plating have been developed. They differ in the reaction of the medium and the state of zinc ions [10, 11]. It is well known that although the zinc deposit from acidified zinc sulphate electrolytic bath is of less bright than the conventional cyanide or chloride zinc plating process, it produces a relatively higher thickness of ductile deposition to the extent of several microns with good adhesion. The aim of this study is to maximize the zinc plating thickness with low porosity (or high relative density) suitable for subsequent homogenization annealing treatment [12]. The effects of zinc concentration of electrolyte and current density on deposition thickness and other characteristics have been studied.

II. Experimental:

The Cu-37wt%Zn alloy wire was prepared from Cu and Zn metal ingots (purity of 99.9 wt %) and drawn into a round wire form of 0.618 mm diameter. Slices of 50 mm lengths were cut from the wire. These specimens were immersed in 20% H_2SO_4 solution to remove oxides and then dipped in 5 g/l of NaOH solution. The substrates were finally cleaned by deionised water and then electroplated with Zn from acidified zinc sulphate heptahydrate electrolytic solution.

The plating process was carried out with various zinc content of electrolytes which were made by dissolving different quantities of zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$). Table 1 displays details of electrolytic bath compositions used for plating of Zn. The pH of the electrolytes was maintained in between 4.0 to 4.5 by adding H_2SO_4 and/or KOH. The plated wire specimens were taken out from the solution after 300 + / - 10 s of plating. The current density was varied. Several specimens were made under the same condition in order to ensure repeatability of results.

The Zn plating thicknesses (δ) were measured by optical microscopy of the cross-section of plated wire specimens and the weight of Zn plating was measured by stripping the Zn plating from plated wire specimens

by dipping in a solution of 32gms of SbCl₃ dissolved 1000cc of HCl [12, 13]. For measurement of Zn deposition, the following formula is used;

$$w = (W_1 - W_2) \dots\dots (1)$$

where, w = weight of plated Zn (g), W₁ = weight of specimen after Zn plating (g), W₂ = weight of specimen after stripping in solution (g).

The relative density of the plated layer is calculated as follows [12]:

$$f = \frac{W_1 - W_2}{W_{th}} \dots\dots (2)$$

where W_{th} is the theoretical weight of plated zinc with thickness δ and can be expressed as;

$$W_{th} = \frac{\pi(d_1^2 - d_2^2)L\rho}{4} \dots\dots (3)$$

Where, d₁ = diameter of plated wire, d₂ = diameter of base wire, L = length of wire and ρ = density of Zn.

The current efficiencies (η) are calculated by;

$$\eta = 100 \times \frac{w}{w_F} \dots\dots (4)$$

Where, w_F is the weight of plated zinc as per Faraday's equation.

The surface of the zinc plated specimens were analysed in a scanning electron microscope (ZEISS) in order study the surface topography.

Table no 1: Details of composition of electrolytic solutions.

Bath constituents				
	ZnSO ₄ .7H ₂ O (g/l)	KCl (g/l)	Boric acid (g/l)	Average Zn content of bath (g/l)
Bath A	350	15	20	80
Bath B	440	15	20	100
Bath C	530	15	20	120
Bath D	620	15	20	140

III. Results & Discussion:

Figure 1 shows the variation of plating thickness (δ) with current density (CD). The dependence of δ with CD reveals that the plating thickness increases with the rise of current density for all bath compositions. It is observed from figure 1 that for all types of baths, δ does not tend to increase in the same manner with the enhancement of CD particularly, at higher CD. The increase of δ with the rise of CD becomes sluggish when CD is near or above 0.3 A/cm². It can be seen from figure 1 that δ increases with the enhancement of Zn concentration of the bath for any particular value of the CD.

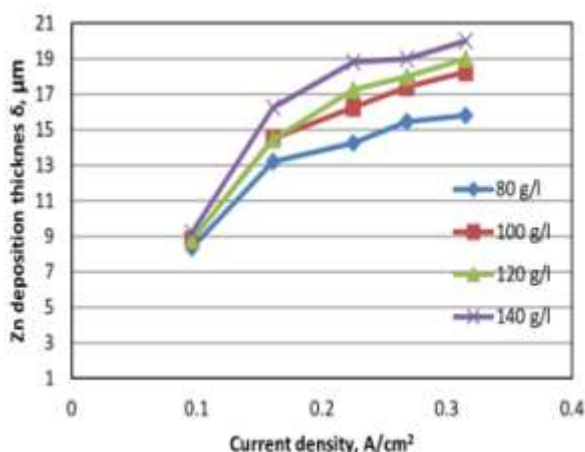


Figure 1 Variation of deposition thickness (δ) with CD for all bath compositions.

It is to be noted that the physical appearance of the plating layer becomes porous, burnt and highly irregular at very high CD. It is often very difficult to measure δ because of irregular character when CD is more than 0.3 A/cm². It is evident from SEM images of figure 2 that surface of plated layer becomes powdery, porous and irregular at CD of 0.315 A/cm² in comparison to 0.096 A/cm² for all concentration of Zn²⁺ in electrolyte composition.

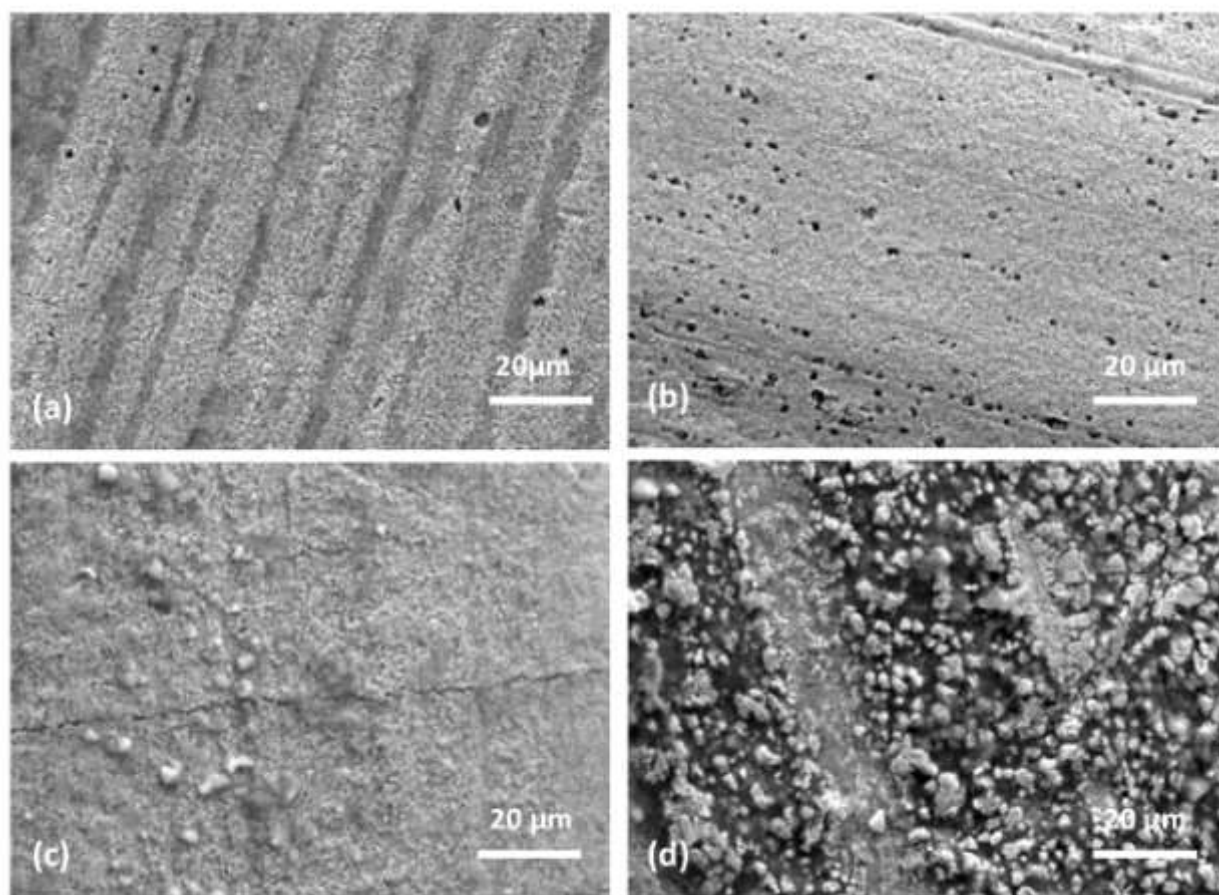


Figure 2: SEM images of electroplated surface (a) bath A at $CD = 0.096 \text{ A/cm}^2$, (b) bath D at $CD = 0.096 \text{ A/cm}^2$, (c) bath A at $CD = 0.315 \text{ A/cm}^2$ and (d) bath D at $CD = 0.315 \text{ A/cm}^2$.

The zinc deposition weight (w) initially increases with the rise of CD for all bath compositions (cf. Figure 3). Zinc deposition weight starts declining with the increase of CD beyond a threshold value of CD for all bath compositions. The threshold point of CD at which w begins to reduce is dependent on the Zn content of electrolytic solution as observed in figure 3. It is evident from figure 3 that for average zinc content of 80 g/l and CD at 0.161 A/cm^2 , the plated weight starts diminishing with the rise of CD, whereas, the same phenomenon is observed when CD is at 0.268 A/cm^2 and average Zn content is 120 g/l.

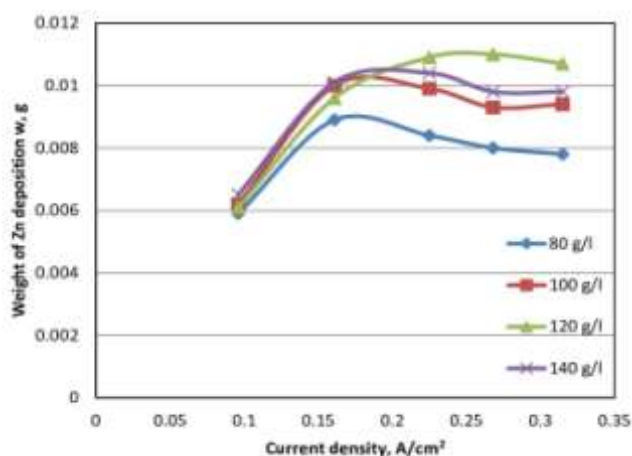


Figure 3: Dependence of Zn plating (w) on CD for all bath compositions.

Interestingly, it is observed from figure 3 that w reduces when Zn concentration of the electrolytic solution is raised from 120 g/l to 140 g/l for all values of CD. Clearly, the enhancement of Zn concentration above 120 g/l does not attribute to the rate of ionic activity in the electrolytic solution. A higher concentration of $ZnSO_4 \cdot 7H_2O$ in the electrolyte solution increases the viscosity of the solution to such an extent that diffusion of Zn^{2+} becomes slow [3, 5]. This phenomenon is particularly prevalent when the average Zn content of the electrolytic solution is increased from 120 g/l to 140 g/l. The higher viscosity with the zinc content of 140 g/l induces hindrances to the passage of ions in the solution in electrolysis process. This phenomenon leads to lower diffusivity of Zn^{2+} with higher Zn content in the electrolyte, and the deposition layer becomes porous, irregular, and powdery at higher CD, as seen in figure 2d. At very high Zn content in the bath, there are too many metal ions in the electrolyte which can trigger increased precipitation of metal hydroxide and further hinders the deposition of metal ions in the cathode [8]. Hence, the deposition of Zn exhibits a significant fall.

Calculations of relative density (f) from equation (3) at various CD and Zn content of electrolytic solution reveal that f decreases with an increase of CD for all values of Zn content of electrolytic solution as shown in figure 4. This suggests that the presence of porosity enhances as CD increases. The process of entrapment of porosity during the electrodeposition process and the other defects in the plating layer increase significantly when the average Zn content reaches 140 g/l. Accordingly, f falls more steeply with the increase of current density at Zn content 140 g/l in comparison with other baths.

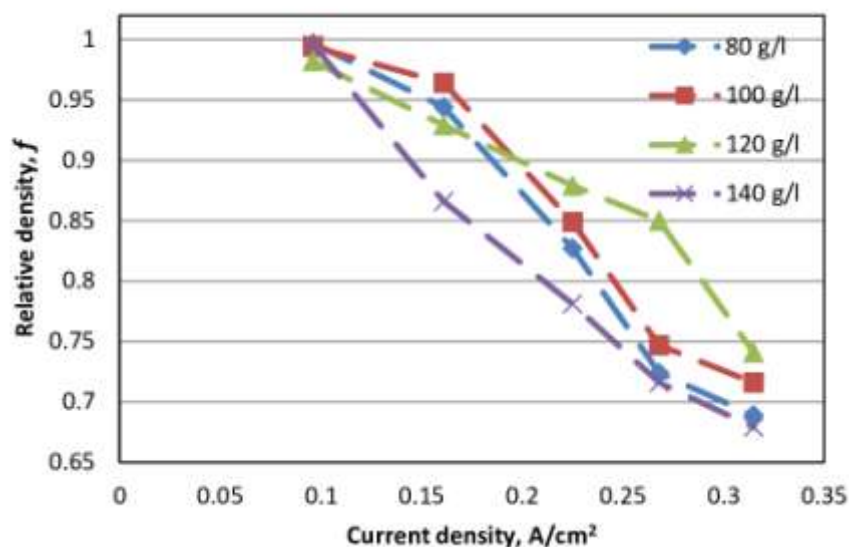


Figure 4: Relative density versus CD for all bath compositions.

Figures 5a to 5d display the dependence of current efficiency (η) with CD at various bath compositions. It is evident that η falls with an increase of CD for all bath compositions. It is observed that the η reduces below 60% at CD 0.12 A/cm² for bath A, whereas, it becomes 60% at CD 0.2 A/cm² for bath D.

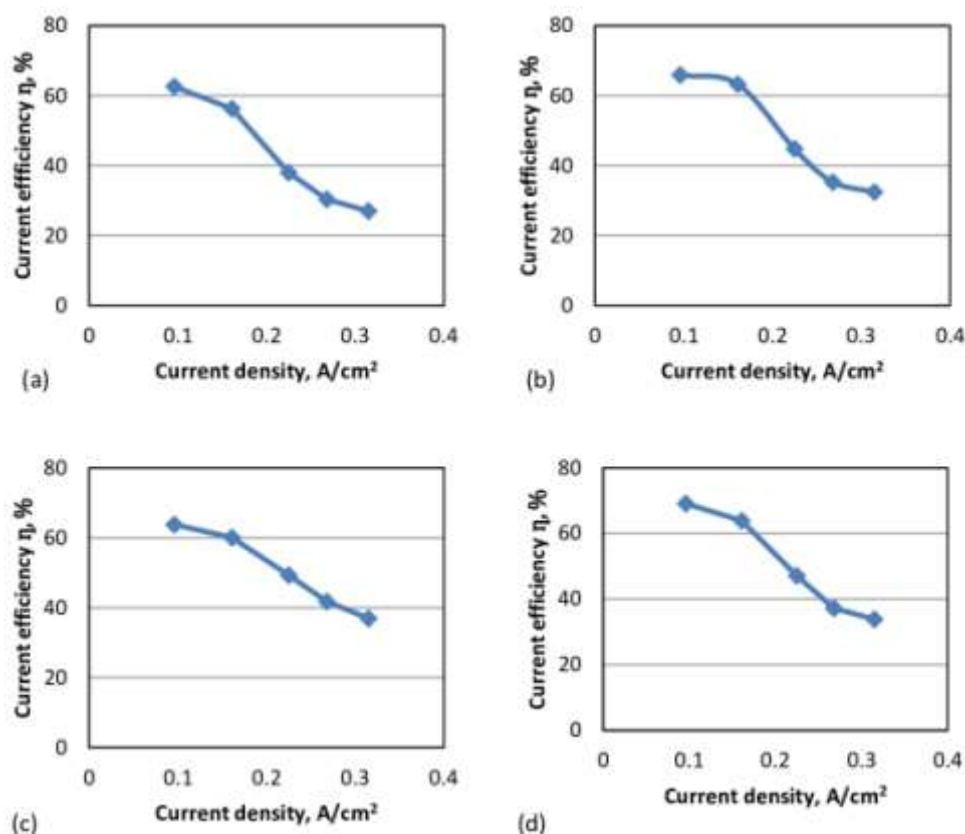


Figure 5: The Plot of current efficiency (η) against current density, (a) Bath A, (b) Bath B, (c) Bath C (d) Bath D.

It is usually assumed that the increase of $ZnSO_4 \cdot 7H_2O$ concentration in the bath would increase the concentration of Zn^{2+} in solution and thereby would always enhance the deposition process of Zn. Clearly, the present experiments indicate that an increase of zinc content of electrolyte solution above 120 g/l does not ensure the enhancement the weight of the deposition layer and its characteristics. Therefore, the increase of CD and zinc content of the bath should be carefully chosen in such a way that current efficiency and relative density do not adversely affect the plating layer characteristics. Relative density less than 0.9 can pose serious problems in protective properties and subsequent annealing treatment [12]. The openness of the plating layer deteriorates the protective properties.

The zinc content of the bath can play an important role in current efficiency. It is evident from figures 5a and 5c that for CD at $0.225 A/cm^2$ and average Zn content at 80 g/l, η is 38 %, whereas, it increases to 49.3 % when average Zn content of bath is increased to 120 g/l. It is to be noted that η again falls to 47.1 % when the average Zn content of the bath further raised to 140 g/l (cf. Figure 5d). This suggests that increasing Zn content does not enhance η linearly and there exists a limiting point beyond which the increase of zinc ions in electrolytic bath reduces the current efficiency.

It is apparent that the onset of many other reactions takes place at the electrodes when η is less than 60 %. This means that a large part of the current is used in the side reactions of the reduction of hydrogen, hydroxyl, and sulphate ions. Because of a large amount of hydrogen gas evolution at the cathode at η less than 60 %, OH^- ions are abundant at the cathode surface. This phenomenon leads to much higher local pH in the vicinity of the cathode surface than the bulk solution pH, resulting in a quick alkalization of metal/solution at interface [11, 14].

IV. Conclusions:

The zinc plating thickness increases with the rise of current density for all values of Zn concentration of the bath. The zinc deposition weight enhances with the increase of current density in the initial stage for all values of Zn concentration. When CD crosses a threshold value, the weight of plating starts to reduce. The threshold value of CD depends on the Zn concentration of the electrolyte. The enhancement of Zn content in the electrolyte from 120 g/l to 140 g/l has resulted in a decrease in deposition weight. It is observed that the zinc plating layer becomes powdery, porous, and irregular when current density is near or above $0.3 A/cm^2$.

The current efficiency does not maintain a linear relationship with CD for all values of zinc concentration of bath. It is found that η falls sharply beyond a limiting value of CD which depends on the zinc content of the electrolytic solution.

Acknowledgement: The author would like to thank Prof. J.D. Majumder, Dept. of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur, India for the use of SEM facility.

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P. S. Basak. "Effect of ZnSO₄.7H₂O concentration of electrolyte solution on Zn electrode position process." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 14(9), (2021): pp 10-15.