A Study of Process Parameters for Zinc Electrodeposition from a Sulphate Bath

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ABSTRACT: *Investigation of process parameters for the electrodeposition of zinc has been carried out using direct current. Cathode current efficiency and deposit thickness were determined by weight measurement method. Influence of current density on the deposition process was also investigated. Bath agitation and cathodic polarisation measurements were used to study the mass transport conditions of the electrolytic bath. Scanning Electron Microscope and Field Emission Gun Scanning Electron Microscopes were utilised to study the morphologies of the deposits. Effect of temperature on the deposition process and deposit morphology was also studied. It was observed that cathode current efficiency (CCE%) was dependent on the current density and bath temperature, while deposit thickness was dependent on current density, bath agitation and time. Temperature and pH changes had marked influence on the morphology of the deposits. Cathodic polarisation studies revealed that bath agitation and composition had significant effect on the limiting current density and hence mass transport of the bath.*

KEYWORDS: *Zinc, Eletrodeposition, Morphology, Sulphate bath, Cathode polarisation, masstransport.*

I. INTRODUCTION

Zinc has found widespread use as the basis of a whole range of sacrificial coatings for ferrous substrates [1]. It is the most commonly used sacrificial coating [2] and can be applied by a variety of techniques, including hot- dipping, metal spraying, cementation, cladding and electrode position [1]. The corrosion characteristics are strongly determined by the texture and microstructure obtained, which in turn depends on the specific deposition procedure employed. The role of electroplating parameters on the formation of different textures and microstructures is well established by several researchers [3] using various approaches, which has effectively lead to the preparation of coatings that differ in their macro and micro-structure, texture density, uniformity and corrosion resistance [4,5]. Also, it is reported [6] that electrodeposited films' texture, apart from the corrosion behaviour, can noticeably affect a variety of properties such as paintability, formability and wear resistance.

A wide variety of plating bath composition has been employed in electrogalvanizing to control the growth of cathode deposits, inhibiting the formation of dendrites and to produce fine-grained, smoother deposits [7]. Electrode position yields grain sizes in the nanometer range when variables such as bath composition, pH, temperature, current density, etc are chosen such that nucleation of new grains is favoured rather than growth of existing grains [2]. Many of the acid type baths utilise zinc sulphate and are normally used to electroplate cast iron and malleable irons. The main disadvantages of the acid type baths are that they are corrosive so care has to be taken to protect operators and equipment and these baths generally exhibit poor current efficiency.

Electroplating normally takes place under a DC regime, however, improved smoothness by means of pulse plating, a periodically interrupted process in which a certain duty cycle of cathodic potential/current is employed [6, 8, 9]. Velinov *et al* [10] found that in the zinc electrocrystallization process two types of inhibition occur, primary and secondary (autoinhibition). They reported that the conditions for cathode deposit formation and consequently crystallite orientation are significantly altered by hydrogen codischarge. In general, the crystalline forms and crystal orientation of metal deposit result from a competition between growth parallel and perpendicular to the deposition substrate, both determined by supersaturation (expressed by cathodic overvoltage), which characterises the process in a complicated manner [7]. A high 'out' growth rate normal to the substrate leads to a fibrous structure whilst an increased rate of lateral growth may lead to the development of large "facets" parallel to the substrate.

The effect of zinc and acid concentration on current efficiency has been reported [11]. According to the authors, increasing the zinc concentration (decreasing the acid concentration) increased the current efficiency in a non-linear fashion and that the highest rate of increase occurred when the zinc concentration was increased from 42 to 50 g/l. This was attributed to increase in zinc deposition reaction rate as the number of zinc ions in

the electrolyte rises. Also, since the number of H^+ ions in solution decreases, the rate of hydrogen evolution reaction is reduced. Both of these factors improve the current efficiency [11]. Indicators of an excellent electrode position bath includes; good current efficiency and throwing power, longevity of the bath, minimal hydrogen evolution, etc. This work therefore seeks to investigate the process parameters suitable for the bath in question to produced zinc electrodeposits with good sacrificial protective properties.

EXPERIMENTAL METHODS AND MATERIALS

1.1 Bath Preparation

Zinc was electrodeposited from additive-free, aqueous solutions composed of standard laboratory reagents. 0.5 litres of deionised water was poured into a beaker and the reagent was added gradually with mild agitation initially and then more vigorously, to enhance dissolution. Measurements of pH were carried out using a HI-8424 digital pH meter, and adjusted accordingly using sodium hydroxide (10 % solution) or concentrated sulphuric acid. The solution was finally made up to 1 litre by adding more water. The whole process was carried out at room temperature (approximately 22^oC). The bath formulation is as follows:

Acid zinc [12]   250 g/l $ZnSO_4.7H_2O$
                   80 g/l Na_2SO_4
                   pH = 2.0-4.4

2.2 Determination of Cathode Current Efficiency and Deposit Thickness

Cathode current efficiency and deposit thickness were measured gravimetrically. Pre-weighed samples after plating were first rinsed immediately in running tap water, immersed in acetone, dried in a stream of warm air and then weighed again to determine the weight gain. Cathode current efficiency and deposit thickness were subsequently calculated using the following formulae:

$$\text{Cathode Current efficiency (CCE)} = \frac{\Delta W}{W_T} - \times 100\% \qquad \textbf{1}$$

Where,

CCE – Cathode current efficiency (%)

ΔW – Change in weight after plating (g)

W_T - Theoretical weight of deposit (g)

Whilst;

$$W_T = \frac{I \times t \times M_{Zn}}{n \times F} \qquad \textbf{2}$$

Where   I = Current (A)
           t = Time (second)
           M_{Zn} = Molecular weight of zinc (g/mol)
           F = Faradays const (96,500 C/mol)
           n = Number of electrons involved in the reaction

2.3 Cathodic Polarisation Studies

Cathodic polarisation studies were conducted for zinc using an ACM Instruments computer controlled potentiostat, model Auto Tafel HP, linked to a personal computer. Each test was carried out on a panel blanked off with chemically inert tape to expose an area of 10 cm^2 (2.5 cm x 4 cm). The counter electrode material was platinum. Each of these different sets of polarisation studies was conducted in order to obtain mechanistic data for metal deposition. The volume of electrolyte was 350 ml.

Two bath compositions were utilized to investigate the mass transport behaviour of zinc electrodeposition and are given below:
           Bath 1- 10 g/l $ZnSO_4.7H_2O$
           Bath 2- 250 g/l $ZnSO_4.7H_2O$

RESULTS AND DISCUSSIONS

3.1 Effect of Agitation

The use of bath agitation is intended to improve the mass transport in the electrolyte and therefore enhance the rate of deposition. However, in terms of cathode current efficiency, bath agitation was found to reduce the current efficiency with increase in agitation. Figure 1 shows that current efficiency of the bath was better without or at lower rates of solution agitation at a constant current density of 5 A/dm2. Since the main reactions at the cathode during electrode position is a competition between zinc reduction and hydrogen evolution, as the limiting current density is approached during zinc deposition, the zinc ion concentration near the cathode is quickly depleted and the cathode reaction shifts from zinc deposition to hydrogen evolution.
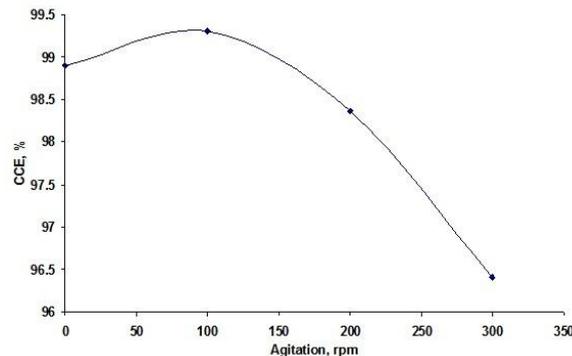
Figure 1 Effect of Bath Agitation on the Cathode Current Efficiency of the Bath at a Current Density of 5 A/dm^2, pH 2.8 and T= 22 ^{o}C.

This could result in the deposition of a mixture of zinc and zinc hydroxide or zinc oxides [13] due to pH increase in the vicinity of the cathode. Also, it is noteworthy that agitation could depolarise the hydrogen evolution reaction and possibly reduce the nucleation rate of zinc on the surface of the cathode. Moreover, the applied current is shared between two processes: zinc deposition and hydrogen evolution [14, 15]. Since the hydrogen over potential and hence evolution in this bath was quite high as was observed during the electrode position process, the main cathode reaction would have been hydrogen evolution. This could be detrimental to zinc deposition as adsorbed hydrogen on the surface of the cathode could hinder zinc nucleation. This could mean a higher current density may be needed to drive zinc deposition. But then, at higher current densities, a larger driving force is required to effect zinc deposition due to possible rise in both anode and cathode potentials with increase in current density [16]. Generally, an improvement in cathode current efficiency with agitation is due to the fact that, agitation helps to prevent the adsorption of evolved hydrogen, which usually sits on the surface of the cathode thereby preventing zinc reduction. The formation of hydrogen bubbles destroyed periodically by stirring the diffuse layer makes it possible for zinc replenishment [14]. As the hydrogen bubbles are swept away, a larger surface area on the cathode becomes available periodically for the deposition of zinc which ordinarily should lead to improved zinc deposition and hence current efficiency. However, this does not appear to be the case in the present investigations. A possible reason could be that agitation was too vigorous to allow sufficient residence time for zinc ions to be reduced on the surface of the cathode. This means, agitation may have been detrimental to the zinc nucleation process in the prevalent conditions.

3.2 Effect of Current Density and Time on Deposit Thickness

In an attempt to optimise conditions for the production of 8 μm thick zinc electrodeposits, a range of current densities were investigated. In each case, maintaining a constant quantity of electricity supplied was crucial to obtain uniform deposit thickness in all the samples. Visually acceptable coatings were obtained within the current density range of 2.0-5.0 A/dm^2.

The experimental results in table 1 show that current density is inversely proportional to time to obtain the same deposit thickness. Increase in current density is accompanied by a decrease in deposition time to obtain 8 μm and vice versa. This is consistent with expectations since at higher current densities, the rate of deposition and deposit build-up is faster. On the contrary, low deposition current densities are associated with small nucleation rates so the layer thickness has to be large enough in order to cover the whole surface of the substrate [6]. This invariably means that lower current densities require longer durations to obtain a particular deposit thickness whilst higher current densities are required to produce the same deposit thickness at a shorter duration. Therefore, for each current density there is corresponding time duration for the production of 8 μm thick

electrodeposits. Possible exceptions would be when either the bath chemistry or other electrodeposition parameters are modified to either enhance or reduce the nucleation and hence deposition rate or reduce/remove reactions in the vicinity of the cathode that are detrimental to metal deposition.

Table 1 Results of the effect of current density and time on the deposit thickness. Bath pH 2.6**.**

Sample	Agitation (rpm)	Current density (A/dm^2)	Deposit thickness (µm)	Time (min.)
27	800	2	8.0	14
27.1	0	2	8.0	14
28	800	2.5	8.0	11
28.1	0	2.5	8.0	11
29	800	3.5	8.0	8
29.1	0	3.5	8.0	8
30	800	4	8.0	7
30.1	0	4	8.0	7

The effect of current density on cathode current efficiency is presented in Figure 2. Changes in current efficiency of the bath appear to be insignificant over a range of current densities between 2.5-4.5 A/dm^2. This is an indication that there was negligible mass transfer resistance or concentration over potential for the range of current densities. Similar observations were reported by Scott et al [16] over a current density range of 100-650 A/m^2.
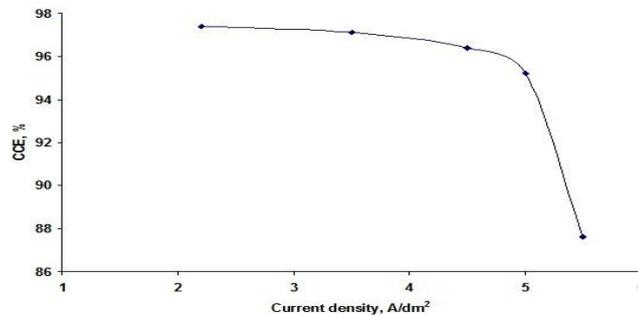
Figure 2 Effect of Current Density on the Cathode Current Efficiency of the Bath at Agitation Rate of 300 rpm, pH 2, Deposition Time 10 min, T= 22 ^{o}C

However, with further increase in current density, the current efficiency decreased significantly. This is attributed to increase in hydrogen evolution [2].

3.3 Effect of pH

Figure 3 shows that for the range of pH from 2.5-5.0, the cathode current efficiency increased with increase in pH. Similar observations have been reported by other investigators [5] that a decrease of the pH leads to a decrease of the current efficiency. Also in agreement with [3], it can be seen from figures 1, 2, and 3 that majority of current efficiency results produced at pH< 4 shows current efficiencies of less than 100%. However, in Figure 3, at pH> 4 almost all current efficiencies were greater than 100%. A number of reasons may be responsible for current efficiency to be greater than 100%. Apart from the possibility of excellent deposition conditions in the bath, a key reason could be the formation and subsequent codeposition of zinc oxide and hydroxide . It appears, at higher pH values, the formation and consequent codeposition of ZnO and Zn(OH)$_2$ probably occurred due to hydrogen evolution with a resultant increase in pH within the vicinity of the cathode.
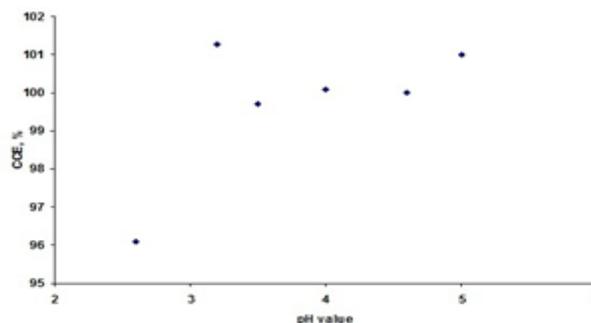
Figure 3 Effect of pH on the CCE of the Bath at a Current Density of 5 A/dm^2, Agitation 400 rpm, Deposition time 6 min., T = 22 ^{o}C

3.4 Effect of temperature

Influence of temperature on CCE shows an increasing linear relationship. This is obvious from Figure 4 as increase in bath temperature from 30 to 40 ^{o}C was accompanied by a corresponding increase in the CCE from 96.0% to 97.4%. Similarly, Scott et al reported [16] that current efficiency increased with increase in temperature from 94.0% at 25 ^{o}C to 97.7% at 50 ^{o}C with a resultant decrease in energy consumption.
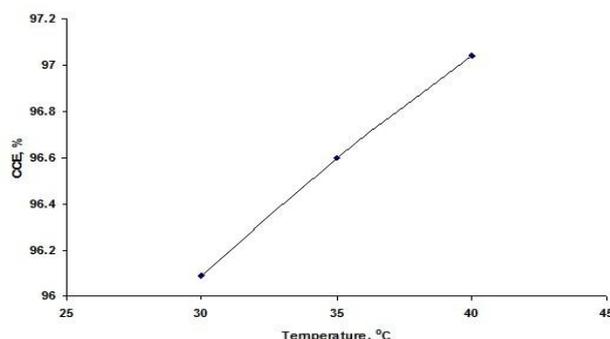
Figure 4 Influence of Bath Temperature on the CCE of the Bath at a Current Density of 3 A/dm^{2},

Agitation 800 rpm, pH 2.6.

The decrease in energy consumption was attributed to increase in current efficiency and a decrease in cell voltage as the temperature rises. At higher temperatures the rate constants of both cathodic reactions increase hence a lower driving force is required [16]. The conductivity of an electrolyte increases with increase in temperature and this is often more pronounced at higher acid concentrations [11].

3.5 Morphological changes

Surface morphologies of zinc electrodeposits are presented in Figures 5-7. Since zinc occurs in only one (hexagonal) crystalline form, the morphological features usually observed (moss, sponge, platelets, boulders) must originate from different arrangements of hexagonal units [17]. The predominant crystallographic orientations reported on zinc electrodeposits produced from acid sulphate baths without additives are usually the randomly preferred orientations. Deposit properties of zinc are largely dependent on the texture and surface morphology of the electrodeposits. A typical surface morphology of zinc produced from the bath is shown in Figure 5. These morphologies can be tailored with changes in electrodeposition parameters such as current density, temperature, pH, hydrodynamics of catholyte flow [18], impurities and the presence of certain additives.
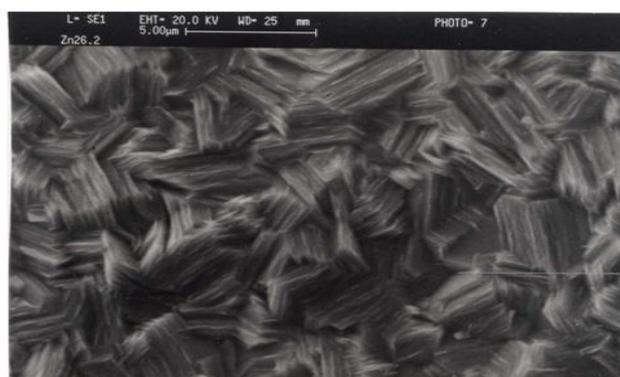
Figure 5 SEM Micrograph of Zinc Electrodeposit from the Bath at a Current Density of 3 A/dm^{2}, Agitation 800 rpm and pH 2.6**.**

3.6 Morphological changes with pH

Electrodeposits were produced with pH variation in the range of 2.6-5.0 at a current density of 3 A/dm^{2}. Such variations had no significant effect on the thickness of the electrodeposits. However, pH changes seem to have some effect on the morphology and preferred orientation of the electrodeposits. As can be seen from Figure 5 deposits obtained from a solution of pH 2.6 generally consisted of zinc platelets with the usual random orientations associated with zinc electrodeposits from acid sulphate baths. However, at a higher pH value of about 5, the morphological features changed slightly from those observed at pH 2.6. Figure 6 shows

that the random orientation initially observed in Figure 5 seems to have transformed to more of a combination of lateral stacking sequence of zinc crystals and zinc platelets aligned almost perpendicular to the cathode.
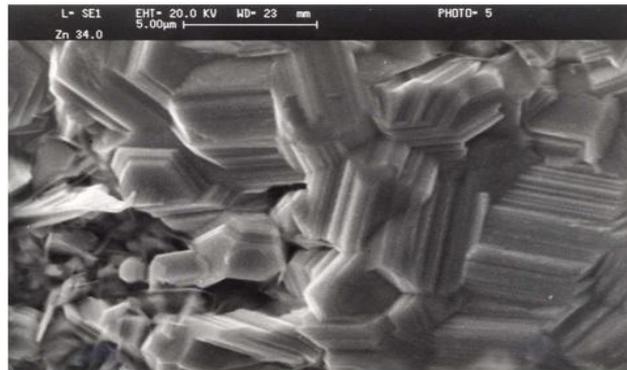
Figure 6 SEM Micrograph of Zinc Electrodeposit from the Acid Bath at a Current Density of 3 A/dm^2, agitation 800 rpm and pH 5

3.7 Morphological changes with temperature

Increase in temperature was observed to have some effect on the crystal orientation of the deposit. With increasing temperature, the lateral stacking sequence of crystal orientation appears to have transformed from the usually random orientations (see Figure 5) to that with the edges of the crystals perpendicular to the surface of the substrate (see Figures 7 and 8). Also, at about 35 ^{o}C, onset of white patches was noticed as particles on the edges of zinc crystal (see Figure 7). As the temperature increased to 40 ^{o}C, the white patches became conspicuous on the surface of the deposit as obvious in Figure 8. The observed improvement in cathode current efficiency with increase in temperature as earlier mentioned and shown in Figure 4 is probably as a result of such growths and consequent incorporation in the electrodeposits thereby increasing the weight gain and hence cathode current efficiency values.
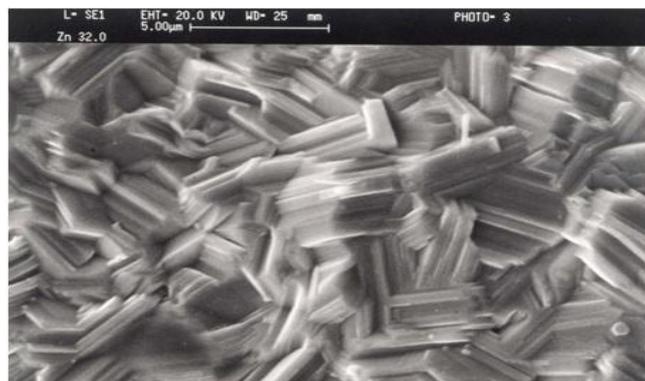
Figure 7 SEM Micrograph of Zinc Electrodeposit Produced at a Current Density of 3 A/dm^2, Agitation 800 rpm, pH 2, T = 35 ^{o}C**.**
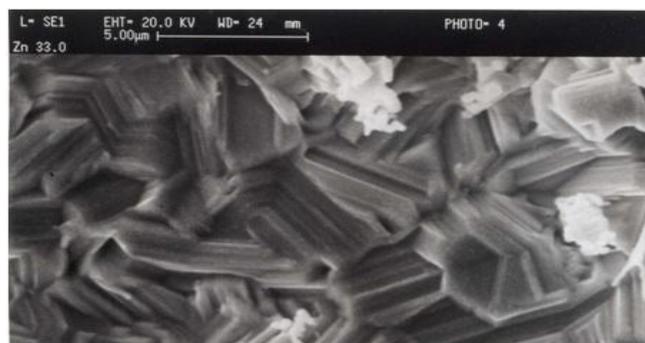
Figure 8 SEM Micrograph of Zinc Electrodeposit Produced at a Current Density of 3 A/dm^2, Agitation 800 rpm, pH 2, T = 40 ^{o}C.

3.8 Cathodic polarisation studies

Cathodic polarisation studies were carried out on mild steel to aid a mechanistic understanding of zinc electrodeposition. Mild steel panels were polarised from their open circuit potential. Both dilute and concentrated baths were used. Dilute electrolytes were employed in order to achieve well-defined deposition behaviour in the polarisation curves as opposed to solutions with high zinc levels where metal reduction peaks are less clear [19].

Figure 9 shows a pair of cathodic polarization curves from the dilute bath and another pair from the concentrated bath both with and without agitation. It is obvious from this figures that current density increased for all the investigations carried out in the presence of bath agitation. It appears zinc deposition did not occur until the potential was about −1130 mV vs. SCE. A gradual increase, depending on the concentration of Zn^{2+}, with steep activation is
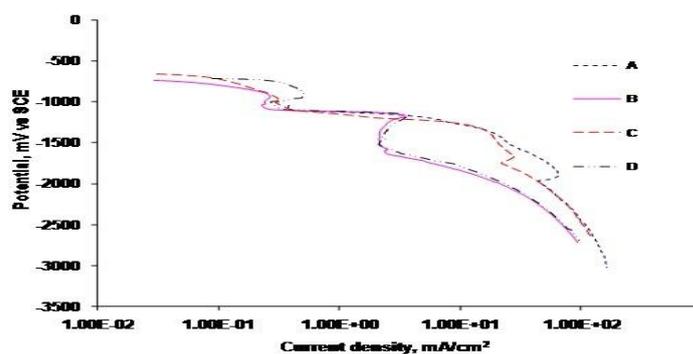
Figure 9 Cathodic polarisation of zinc baths containing 250 g/l $ZnSO_4.7H_2O$ (A) agitation (B) Without agitation. Bath with 10 g/l $ZnSO_4.7H_2O$ (C) without agitation (D) agitation.

Then observed in a short range of potential and then diffusion control appears to take over at higher potential values. However, for the investigations without agitation, the zinc deposition current appears to be very low. This is an indication that for the bath compositions and deposition conditions investigated here, agitation was favourable for the zinc deposition reaction due to enhanced mass transport. Similar improvements in mass transport and hence zinc deposition current densities have previously been reported [4].

CONCLUSIONS

Cathode current efficiency and deposit thickness were generally dependent on current density, agitation and bath temperature. Solution agitation was slightly detrimental to the current efficiency of the bath. Temperature and pH had marked influence on the deposition process. At higher temperatures, patches of white deposits thought to be oxides of zinc were observed.

For similar deposit thicknesses, plating time was inversely proportional to current density. Cathodic polarisation studies revealed that bath agitation had significant effect on the limiting current density and hence mass transport of the bath.

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