



ROLE OF pH AND TEMPERATURE IN ELECTRODEPOSITION OF TERNARY Zn- Mn-Mo ALLOY

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Abstract: Electrodeposition is a process of controlled deposition of materials on conducting surfaces by passing electric current through a solution containing ionic species. Unlike the traditional pure metal coating, electroplating is a cost-effective and an efficient method used for preparation of alloy coatings. Electrolyte deposited alloys can possess certain unique advantageous properties which cannot be found in the coating of any pure metal. There are certain metals that can be deposited only in their alloy form. Molybdenum, Tungsten and Germanium are such examples where they can only be coated by electrodeposition. Electrodeposition of Molybdenum alloy produces hard and protective surface coatings which encourage us to electrodeposit Zn-Mn-Mo ternary alloy from citrate bath and studied the effect of various parameters on the alloy.

This paper is a detailed analysis of the effects of pH and temperature on electrodeposition of Zn-Mn-Mo alloy in a citrate bath containing solution of ions.

Index Terms. Electrodeposition, alloys, temperature, pH.

I. INTRODUCTION

Alloys are generally electrodeposited from aqueous solutions containing constituent metal ions. The process of electrodeposition in aqueous medium has been widely accepted owing to the nontoxic, less expensive nature of the medium. The mechanism of ternary alloy deposition is more complicated than single metal deposition. Electrodeposition of metal is a process in which metal ion after getting rid of its sheath of solvent molecules or complex anions, combines with the equivalent number of electrons to become a neutral atom and gets incorporated into the crystal lattice of the deposit formed on cathode. The process of deposition of metals from aqueous solutions always occurs at a more electronegative potential than the corresponding Nernst or equilibrium potential. (1)

There are various factors which influences the physical appearance of electrodeposits. The electrodeposits are generally considered to be crystalline in structure. The external appearance and physical properties mainly depend on the rate of crystal growth and the formation of nuclei (2). The deposits may be smooth, fine grained, adherent if the plating conditions are such as to favour the rapid formation of crystal nuclei. On the other hand, large crystalline and rough deposits may be produced if the nuclei show a tendency to grow rapidly. The current variables which influence the alloy composition, nature of physical appearances of the deposit as well as the rate of deposition are current density, temperature, pH of the electrolytic solution, concentration of bath constituents, agitation, ions in solution and their concentrations, presence of addition agents, base metal and type of anode. However, no single variation has significant effect on alloy composition or physical properties, a considerable change in any one of the parameters may often require an appreciable change in another parameter to obtain a definite deposit composition .

Hydrogen ion concentration plays an important role in determining the physical characteristics of the deposits and their composition (3). pH variation influences the hydrogen discharge potential, the precipitation of basic inclusions and the composition of the complexes or hydrate from which the metal is deposited. As a general rule, variation of pH should have little effect on the composition of deposits, deposit from bath containing the metals as simple ions, while having a large effect when they are obtained from baths containing the parent metals as complexes with large instability constant.

An increase of bath temperature produces two opposing effects. In the first place, it favours the diffusion of metal ions resulting in the formation of rough or spongy deposits at relatively high current densities. Other effect being an increase in the rate of crystal growth giving it a coarse deposit. Further, hydrogen overvoltage decreases with increasing temperature facilitating the evolution of gas as well as the precipitation of basic salts.

When zinc is co-deposited with the metals like cobalt, nickel, iron, copper and manganese, either of them, helps improve the protective properties of the zinc coating on alloy (4). Such introduction of an alloying element which has a higher corrosion resistance and an improved physico- mechanical properties compared to zinc matrix, creates a possibility of eliminating additional harmful chromatin (5,6). One such element is molybdenum, which has a positive impact on the passivity of stainless steel (7,8).

While introduction of molybdenum to zinc coating can prove to be an advantage, there is an issue with obtaining a homogenous deposit while using a relatively higher molybdenum content (9,10). This study on ternary Zn-Mn-Mo alloy coatings allowed us to determine a basic bath composition along with an appropriate range of the plating parameters (11). Further observations revealed that deposition of bright and homogeneous coatings was only possible in a relatively narrow plating solution pH range, cathodic current density, temperature, and at stable hydrodynamic conditions. Such parameters have a strong influence on plating process of the alloy Zn-Mn-Mo (12,13). As the pH and temperature of plating solution are important parameters for electrodeposition of alloy, the aim of this paper was to analyse the effect of pH and temperature on the chemical composition, morphological features and protective properties of alloy.

II. EXPERIMENTAL PROCEDURE

Electrolysis of the solution was carried out in an electrolytic cell (14). The cell was assembled from a 0.3 cm thick Perspex sheet (15.5 x 3.5 x10) by cementing the joints with chloroform. A platinum wire sealed in a narrow glass tube was used as an anode. Stainless steel panel (5cm x2cm), sealed on a glass sheet of similar size with Araldite was used as cathode. To avoid uncertainties of cathode surface area, its edges were covered with Araldite. An effective surface area of 10 cm² was thus obtained and in this way a uniform current density was maintained at the cathode. Before each deposition it was properly cleaned, dried, dipped in carbon tetrachloride and again washed and dried. Doubly distilled water was used for preparing the various solutions throughout this work.

The electrolytic cell and electrodes were thoroughly cleaned before use. The cell was filled with 225ml of fresh electrolytic solutions and then placed in a water thermostat to provide temperature control. After inserting the electrodes in position, the electrolysis was carried out for 30 minutes under different plating conditions at current density at 2.0-6.0 Adm⁻². D.C. stabilised power supply was utilized to ensure a constant flow of current during the deposition process. The pH of the solution was measured by pH meter 510 from Systronics instrument, and was adjusted to the desired value by adding 0.5N sodium hydroxide solution at room temperature. Thermostatic bath was used to control the bath temperature (15,16).

The films deposited at the cathode were washed with distilled water, dried and then scratched carefully. A fixed amount (50mg) of alloy was dissolved in 50 ml distilled water containing 2-3 drops of H₂SO₄ for analysing its various metal constituents. Manganese and Molybdenum were estimated by usual colorimetric methods while the amount of zinc was determined titrimetrically using diphenyl benzidine as an indicator (17). The cathode potentials were measured to an accuracy of ±0.001 V against a standard calomel electrode. The bath chemistry and operating conditions for electrodeposition of Zn-Mn-MO alloys are listed in Table 1.

III. RESULTS AND DISCUSSION

3.1 Effect of pH

The effect of variation in pH values on the alloy composition, cathode current efficiency and the distribution of total current utilized for the deposition of molybdenum, zinc and hydrogen ions at 25^oC is given in Table II. It is clear from the table that percentage of molybdenum and manganese in the deposits increases with the increasing pH of the solution while that of zinc decreases under similar conditions. Since the metal of relatively higher position in the oxidation reduction potential series are chemically more active than those at a lower position. It will plate out of solution with difficulty and if hydrogen ions are present in the electrolytic bath, ions of a metal lower than hydrogen in the e.m.f. series would be deposited more easily than the ions of those metals which lie above hydrogen. Hence, with the increasing pH of solution the deposition of molybdenum and manganese will be facilitated. On the other hand, zinc with relatively more positive potential than hydrogen would plate out of solution more slowly in comparison, thereby resulting in a decrease of its content in the deposited film as the pH is increased. A variation in pH may also affect the equilibrium between various metal complexes present unequally with corresponding changes in the deposit composition. An examination of Table IV which represents the effect of pH on the cathode potential during electrodeposition at current density of 4.0 Adm⁻², shows that the value of the cathode potential becomes more negative as the pH of the solution is raised from 2.0 to 2.015 as in figure 1. This may be due to the corresponding decrease in the availability of hydrogen ions at higher pH values. Consequently, more current will be utilized for the deposition of alloy than that for the discharge of hydrogen ions provided by ionisation of the solvent.

3.2 Effect of temperature

Attempt has been made to study the influence of variation of temperature on alloy composition, cathode current efficiency and distribution of total current for the deposition of molybdenum, manganese, zinc and hydrogen ions from the present bath and the results are consolidated in Table III along with the effects being projected in Figure 2. It has been observed that molybdenum and manganese contents in the deposits decreased with the increasing temperature. Zinc by contrast, showed reverse behaviour which might be due to the increase in diffusion of the zinc ions with increase in temperature. At temperature greater than 30^oc and a pH of 2.05, no deposition was observed. Table IV represents the variation of the cathode potential with temperature at a pH value of 2.05 and at current density of 4.0 Adm⁻². An increase in temperature at a particular current density and pH of the solution causes the cathode potential to become less negative, this may be due to a decrease in the apparent thickness of the diffusion layer immediately adjacent to the cathode surface with increasing temperature of the electrolyte. Consequently, the diffusion coefficient of the depositing ions increases, as a result of which the cathode potential attains a less negative value. During deposition of the alloy, most of the current is utilized to deposit the metal ions and the rest is consumed for the discharge of hydrogen ions. The total cathode current efficiency continuously increases with increasing pH of the electrolytic solution at current density of 4.0 Adm⁻² as shown in figure 1. A similar behaviour was also observed when the temperature of the solution is decreased (figure 2). This indicates that relatively more current is utilized for the deposition of alloy than for the discharge of the hydrogen ions provided by the ionization of the solvent as the pH is increased or temperature is decreased

CONCLUSION

In this study Zn–Mn–Mo alloy coatings were electroplated from citrate-containing aqueous solutions. The effects of pH and temperature on the chemical composition, cathode current efficiency and surface morphology of the coatings were determined. The following conclusions were made:

As the pH is increased from 2.0 to 2.15 (at $T = 25^{\circ}\text{C}$), the cathode current efficiency for deposition of the three metals, and deposition rate increases.

Molybdenum and Manganese content in the deposited alloy increases with increasing pH whereas Zinc decreases.

It has been observed that molybdenum and manganese contents in the deposits decreases with increasing temperature. Zinc by contrast, shows the reverse behaviour.

The morphological features of alloy plating consist of the colour grey, even fine-grained compact deposits are favoured by decreasing the pH values or increasing the temperature on the other hand, the deposits become uneven, blackish grey crystalline deposit at lower temperatures and increasing pH.

The best alloy plating out of all the conditions introduced above was obtained at the following conditions:

1. pH value of 2.05
2. Temperature at 25°C

At the said conditions, we were able to witness a smooth and compact deposit which could be suitable for decorative and protective purposes

Table I. Bath composition and deposition conditions.

Bath composition			Deposition conditions	
1	Zinc sulphate	30.0 gL ⁻¹	pH	2.0 - 2.05
2.	Manganese sulphate	60.0 gL ⁻¹	Temperature	20 - 35 ^o C
3	Amm.molybdate	4.0 gL ⁻¹	Current density	2.0 -6.0 Adm ⁻²
4	Citric acid	5.0 gL ⁻¹	Duration of deposition	20 - 50 min.
5	Starch	1.0 gL ⁻¹		
6	Anode	Platinum		
7	Cathode	Stainless steel		

Table II. Effect of pH on deposit composition at current density 4.0 Adm⁻² and pH 2.05

S. No	pH	Metal in deposit %			Cathode current efficiency	Percentage of current utilized for deposition of			
		MO	Mn	Zn		MO	Mn	Zn	H ₂
1	2.0	0.16	0.20	99.64	30.09	0.10	0.07	29.93	69.90
2	2.05	0.30	0.40	99.30	41.10	0.25	0.20	40.65	58.90
3	2.10	0.40	1.12	98.30	41.84	0.34	0.46	41.04	58.16
4	2.15	1.40	3.92	94.68	59.41	1.66	2.76	54.99	40.59

Bath composition: Zinc sulphate 30.0 gL⁻¹, Manganese sulphate 60.0 gL⁻¹, Amm.molybdate 4.0 gL⁻¹, Citric acid 5.0 gL⁻¹, Starch 1.0 gL⁻¹, Temperature 25^oC, Current density 4.0 Adm⁻²

Table III. Effect of temperature on deposit composition at current density 4.0 Adm⁻² and pH 2.05

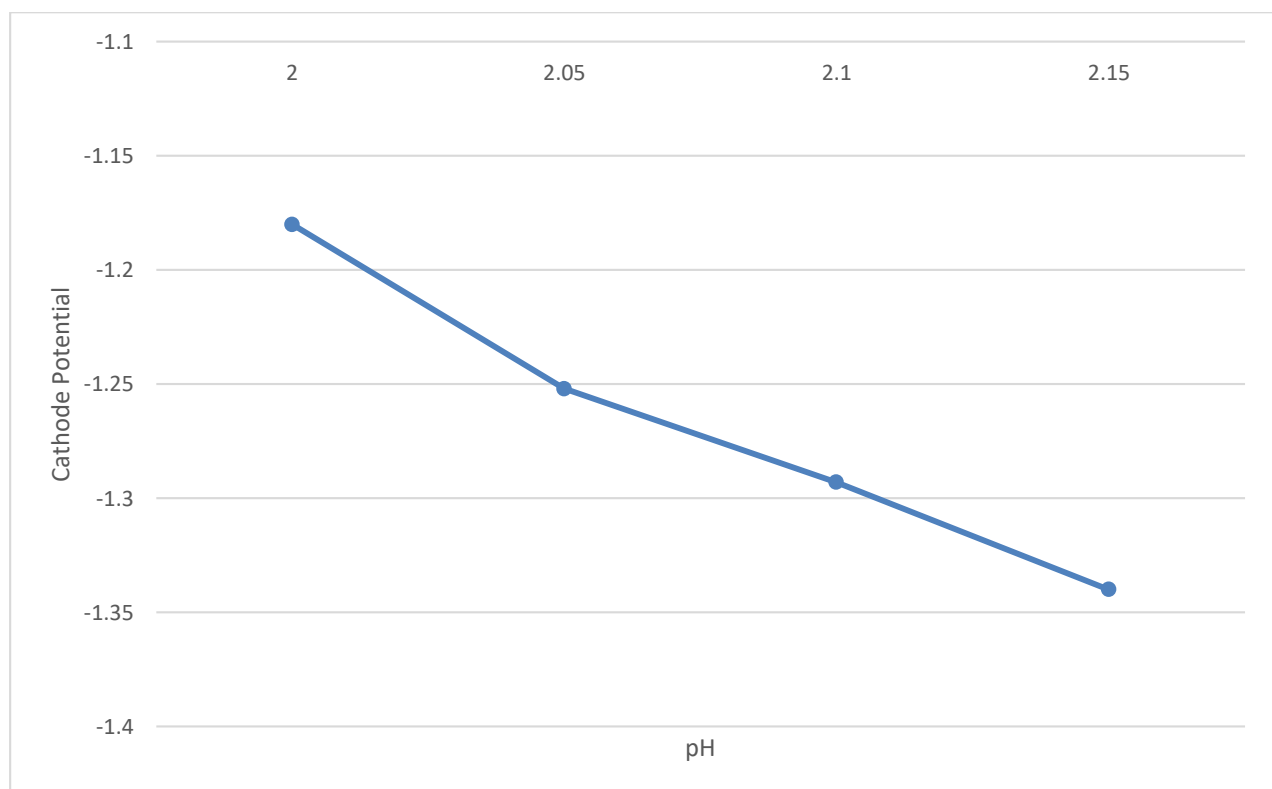
S. No	Temperature	Metal in deposit %			Cathode current efficiency	Percentage of current utilized for deposition of			
		MO	Mn	Zn		MO	Mn	Zn	H ₂
1	20 ^o c	0.88	2.32	96.8	47.64	0.85	1.21	45.58	52.36
2	25 ^o c	0.30	0.40	99.30	41.09	0.25	0.20	40.64	58.91
3	30 ^o c	0.24	0.22	99.54	31.18	0.15	0.08	30.95	68.82
4	35 ^o c	-	-	-	-	-	-	-	-

Bath composition: same as in Table II

Table IV. Variation of cathode potential at different PH and different temperature

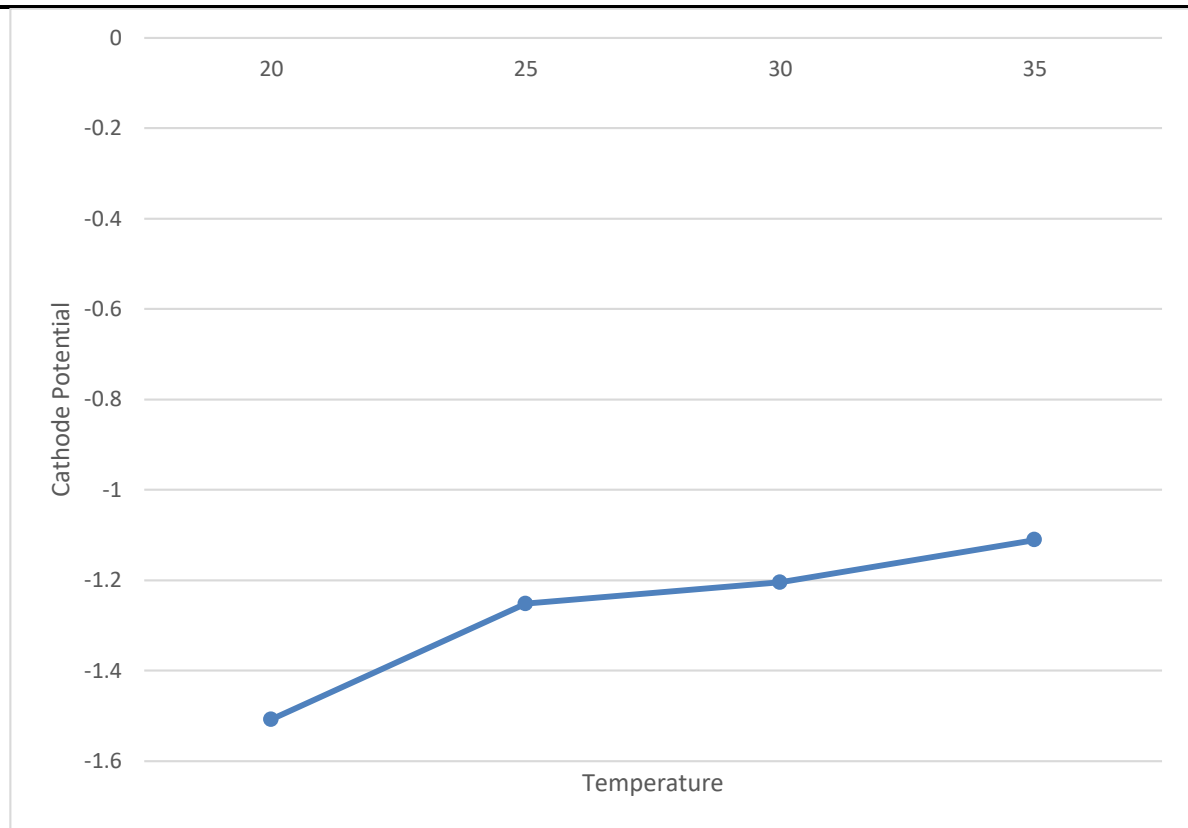
S. No	pH	Cathode Potential	S No.	Temperature	Cathode Potential
1	2.0	-1.180	1	20 ⁰ c	-1.508
2	2.05	-1.252	2	25 ⁰ c	-1.252
3	2.10	-1.293	3	30 ⁰ c	-1.205
4	2.15	-1.340	4	35 ⁰ c	-1.111

Bath composition: same as in Table II



Bath composition: same as in Table II

Figure I. variation of cathode potential at different pH



Bath composition: same as in Table II

Figure II. variation of cathode potential at different temperature

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