

STUDIES OF ROLE OF ADDITIVES ON ELECTRODEPOSITION OF ZN-MN-MO ALLOY FROM CITRATE BATH

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ABSTRACT

The ternary Zn-Mn-Mo alloys were electrodeposited containing Zinc sulphate 30gL^{-1} , Manganese sulphate 60gL^{-1} , Ammonium molybdate 4gL^{-1} , Citric acid 5gL^{-1} and Starch 1gL^{-1} in presence of one of the following additives: glycine, urea, sulphosalicylic acid, sucrose or thiourea. Smooth, bright grey deposits were formed in presence of these addition agents. Effect of concentrations of these additives on deposit composition, cathode efficiency, cathode polarization and throwing number of the bath were also studied.

KEYWORDS: Additives, Composition, Cathode Efficiency, Polarization, Throwing Number

INTRODUCTION

Few organic substances called additives when present in minute quantities in a particular plating bath often produce smooth, fine-grained and microcrystalline deposit. The additives may profoundly change the form or structure of the deposits as well as well as influencing their physico- mechanical properties. Several such additives are reported to have modified the nature of the electro deposits in three component alloys containing molybdenum or manganese. Effects of addition agents on Ni-Zn-Mn ⁽¹⁾ and Sn-Ag-Cu ⁽²⁾ were also studied. Electrodeposition of Zn from acid based solution ⁽³⁾ and Zn-Mn coating from sulphate bath ⁽⁴⁾ were reported.

A ternary Zn-Mn-Mo alloy electrodeposited from a citrate bath ⁽⁵⁾. An attempt has been done to study the effects of few additives such as thiourea, urea, glycine, sucrose and sulphosalicylic acid on the morphology, the composition of the alloy, the cathode current efficiency, the cathode current efficiency, the cathode polarization and the throwing number during the plating of Zn-Mn-Mo alloy from a citric bath.

EXPERIMENTAL PROCEDURE

Thin alloy films were obtained at 25°C and a pH of 2.05 in presence of various additives such as glycine, urea, sulphosalicylic acid, sucrose and thiourea. Different electrolytic conditions and the procedures adopted for determination of deposit composition and cathode current efficiency have been described elsewhere ⁽⁶⁾. Photomicrographs of the alloy films deposited in presence of the various additives were taken to study the morphological change

The cathode potentials were measured to an accuracy of ± 0.001 V against a standard calomel electrode. The difference between the potentials-attained with and without a definite flow of current recorded on a potentiometer (systronics) at a particular plating condition gave the value of cathode polarization (P). The throwing number (N) in presence of these additives was calculated by using Gardem's formula ⁽⁷⁾ $N = b/2\dot{\rho}$. Here $\dot{\rho}$ is the specific resistance of the electrolytic solution and b the Tafel slope.

RESULTS AND DISCUSSIONS

The effect of additives on the composition of the deposited films has been illustrated in Table 1. The alloy composition also varies with the concentration of the additives. The amount of molybdenum in the deposits has been found to increase in presence of sucrose, urea, sulphosalicylic acid, glycine or thiourea. Zinc by contrast, showed the reverse behaviour. Further, the manganese content increases with the addition of these agents and is more marked with thiourea and glycine. The percentage of molybdenum and manganese decreases and zinc increases on increasing concentration of these additives.

Current Density

The current density within the range studied does not appear to affect significantly the apparent quality of alloy films obtained in presence of the above additives. However the weight percents of the metals change (Table 2).

The general trend in the variation of alloy composition with current density remains the same both in absence and in the presence of these additives. That is the amount of molybdenum and manganese increase as the current density is raised, whereas that of zinc decreases. This might be due to more utilization of current by molybdenum and manganese than zinc at higher current densities.

In presence of urea, molybdenum and manganese contents decrease and zinc content increases at lower current densities such as 2.0 and 3.0 Adm^{-2} but at current density higher than 3.0 Adm^{-2} a reverse behaviour is noticed.

Cathode Current Efficiency

The variation of cathode efficiency as a function of current density in presence of the above additives has been shown in Table 3, In each case when the concentration of additive is 1.0 gL^{-1} , the efficiency was always high at a given current density then that determined by alloy without an additives. This may be due to the fact that the metal ions near the cathode got quickly removed and diffusion alone was unable to supply sufficient fresh ions in the absence of addition agent but when an additive is used the adequate quantity of fresh ions became available on account of enhanced diffusion due to formation of complexes during the course of electrolysis. Efficiency increases with increasing current density when glycine, sulphosalicylic acid and thiourea was used as an additives and decreases with increasing current density in presence of urea and sucrose. On increasing concentration of additives, the efficiency decreases in each case as less utilization of current for the deposition alloy then that for discharge of hydrogen ions.

Cathode Polarization

The variation of cathode polarization with current density during electrodeposition, both in the presence and in the absence of an additive to the electrolyte has been given in Table 4. The cathode polarization tends to become more negative in presence of urea, sulphosalicylic acid and thiourea and less negative when glycine was used at a given current density. On using sucrose as an additives cathode polarization more negative at lower current densities but at higher current densities it becomes less negative in comparison to values without addition agent. A comparatively high value of cathode polarization may be attributed to the preferential adsorption of these additives. Such adsorption changes the nature of cathode surface by blocking the various growth sites leading to an increase concentration of anions in the vicinity of the cathode and thereby resulting in an increased polarization at a given current density. This increased polarization is responsible for enhancing the formation of new crystal nuclei on the metal surface and as a result the deposit becomes fine

grained but if polarization shifts to highest negative value growth of existing crystallites also increases and deposits become uneven and spongy as in case of thiourea. With increasing current density polarization shifts to more negative value in each case due to increased rate of discharge of metal ions at cathode. Further, it varies linearly with the logarithm of the current density in each case (Figure 1). Furthermore it shifts to more negative as the concentration of thiourea and sucrose is raised from 1.0gL^{-1} to 2.0gL^{-1} the electrolytic bath. Tafel relation holds in their presence. The throwing number calculated from the value of Tafel slope and specific resistance is given in Table 5.

Throwing number found to be higher in case of urea and glycine indicating production of more uniform deposit whereas in thiourea it is very low thus leads to formation of rough deposit. This has also been confirmed by their morphological studies.

Morphology

The physical appearance of the electrodeposits from baths containing these agents at two different concentrations are incorporated in Table 6 and Figure 2. Magnifications of the photomicrographs are 500 times. Photomicrographs of the alloy plates indicate that the addition of 1.0gL^{-1} glycine, urea and sulphosalicyclic acid favours the formation of light grey, smooth, even and fine grained deposits, whereas uneven, dark grey and spotted deposit are obtained in presence of thiourea or sucrose.

When the concentration of addition agent increases from 1.0gL^{-1} to 2.0gL^{-1} , morphology of the alloy plates also changes as is evident from table 6. When the concentration of glycine, sulphosalicyclic acid, or urea is 2.0gL^{-1} in the bath comparatively more light grey, smooth, fine grained deposits are obtained. On the other hand, on increasing concentration of thiourea and sucrose blakish grey, uneven, coarsely crystalline deposits are formed.

Table 1: Effect of the Additives Concentration on the Alloy Deposit Composition at Different Current Densities

Additives	Concentration gL^{-1}	Metal in the Deposit, %		
		Mo	Mn	Zn
None	-	0.30	0.4	99.3
Urea	1	0.40	3.56	96.04
Urea	2	0.32	1.04	98.64
Sucrose	1	1.12	4.40	94.48
Sucrose	2	0.30	0.49	99.21
Sulphosalicyclic acid	1	2.98	5.40	91.62
Sulphosalicyclic acid	2	0.44	0.80	98.76
Glycine	1	3.80	5.40	90.80
Glycine	2	0.24	0.92	98.84
Thiourea	1	2.68	8.60	88.72
Thiourea	2	1.16	2.36	96.48

Bath composition: Zinc sulphate 30gL^{-1} , Manganese sulphate 60gL^{-1} , Ammonium molybdate 4gL^{-1} , Citric acid 5gL^{-1} , Starch 1gL^{-1} , pH 2.05, Temp. 25°C

Table 2: Effects of Current Density on the Deposit Composition in the Absence and in the Presence of Additives at 25°C and a Ph of 2.05

Additives	Metal	Metal (%) in the Deposit at Various Current Densities (Adm^{-2})				
		2.0	3.0	4.0	5.0	6.0
None	Mo	0.20	0.24	0.30	0.48	0.60
	Mn	0.10	0.12	0.40	1.06	1.18

	Table 2: Contd.,					
	Zn	99.70	99.64	99.30	98.46	98.22
Urea	Mo	0.08	0.16	0.40	0.80	1.12
	Mn	0.08	0.16	3.56	4.44	5.00
	Zn	99.84	99.68	96.04	94.76	93.88
Sucrose	Mo	0.12	0.80	1.12	1.16	1.52
	Mn	0.08	3.36	4.40	5.20	7.60
	Zn	99.80	95.84	94.48	93.64	90.88
Sulphosalicylic acid	Mo	0.88	1.12	2.98	3.48	3.72
	Mn	1.78	3.84	5.40	9.60	10.60
	Zn	97.34	95.04	91.62	86.92	85.68
Glycine	Mo	0.90	2.00	3.80	4.12	4.84
	Mn	2.20	3.89	5.40	11.40	14.40
	Zn	96.90	94.11	90.80	84.48	80.76
Thiourea	Mo	1.44	2.44	2.68	3.20	4.40
	Mn	5.80	7.00	8.60	9.20	9.60
	Zn	92.76	90.56	88.72	87.60	86.00

Bath composition gL^{-2} : Same as given in Table 1.

Additive concentration: 1.0gL^{-1}

Table 3: Effect of Additives on the Cathode Efficiency of Zn-Mn-Mo Alloy as a Function of Current Density

Additives	Concentration (gL^{-1})	Cathode Current Efficiency (%) at Current Density of Adm^{-2}				
		2.0	3.0	4.0	5.0	6.0
None		42.10	41.36	41.10	38.07	37.61
Glycine	1.0	62.02	62.22	64.51	69.60	71.90
	2.0	46.47	45.57	37.10	34.73	36.34
Urea	1.0	48.28	42.42	41.10	40.51	40.41
	2.0	39.41	37.73	37.52	38.51	38.38
Sulphosalicylic acid	1.0	61.13	61.17	62.63	65.34	64.23
	2.0	39.25	38.58	38.54	37.39	37.57
Sucrose	1.0	65.06	58.28	51.30	50.71	50.04
	2.0	40.73	40.66	37.49	37.56	37.24
Thiourea	1.0	75.41	76.94	78.38	79.60	81.53
	2.0	39.43	35.60	36.17	37.25	35.84

Bath Composition: Same as given in Table 1.

Table 4: Effects of Additives on the Cathode Polarization of Zn-Mn-Mo Alloy as a Function of Current Density

Additive	Concentration (gL^{-1})	Cathode Polarization Values at Logarithm of the Current Densities (Adm^{-2})				
		2.0	3.0	4.0	5.0	6.0
None		-1.06	-1.16	-1.25	-1.34	-1.42
Glycine	1.0	-0.96	-1.04	-1.13	-1.15	-1.19
	2.0	-1.05	-1.12	-1.15	-1.16	-1.17
Sucrose	1.0	-1.12	-1.21	-1.26	-1.27	-1.30
	2.0	-1.48	-1.52	-1.55	-1.56	-1.63
Urea	1.0	-1.23	-1.32	-1.40	-1.44	-1.49
	2.0	-1.44	-1.51	-1.55	-1.60	-1.63
Sulphosalicylic acid	1.0	-1.42	-1.49	-1.55	-1.60	-1.63
	2.0	-1.16	-1.24	-1.28	-1.31	-1.32

Thiourea	1.0	-1.52	-1.54	-1.55	-1.55	1.56
	2.0	-1.55	-1.57	-1.57	-1.58	-1.58

Bath composition same as in table 1

Table 5: Table for Specific Resistance, Tafel Slope and Throwing Number in Absence and Presence of Additives

Additives	Concentration (gL ⁻¹)	Specific Resistance Ωcm	Tafel Slope b, V	Throwing Number N, A/cm
None		41.67	0.596	0.00715
Glycine	1.0	25.69	0.524	0.0102
	2.0	16.21	0.393	0.0121
Urea	1.0	25.86	0.526	0.0102
	2.0	20.49	0.407	0.0099
Sulphosalicylic acid	1.0	36.35	0.480	0.0066
	2.0	22.88	0.444	0.0097
Sucrose	1.0	37.04	0.450	0.0061
	2.0	95.72	0.243	0.0012
Thiourea	1.0	47.04	0.073	0.0008
	2.0	50.08	0.100	0.0009

Bath composition : Same as given in Table 1.

Table 6: Morphology of the Deposited Alloys in Absence and in the Presence of Additives at 4.0 Adm⁻² Current Density

Figure. No.	Additives	Concentration (gL ⁻¹)	Morphology of the Deposit
A	None		Smooth, light grey compact deposit
B	Glycine	1.0	Even, compact, dark grey deposit
C		2.0	Even, dark grey deposit with smaller grain size
D	Urea	1.0	Even, semi bright, large grained deposit
E		2.0	Even, semi bright, smaller grain size
F	Sulphosalicylic acid	1.0	Even, compact, light grey deposit with few large grains
G		2.0	Even, fine, light grey deposit
H	Sucrose	1.0	Even, fine grained, grey deposit
I		2.0	Uneven, blackish grey deposit
J	Thiourea	1.0	Spotted blackish grey deposit
K		2.0	Uneven, coarsely crystalline deposit

Bath composition: Same as given in Table 1

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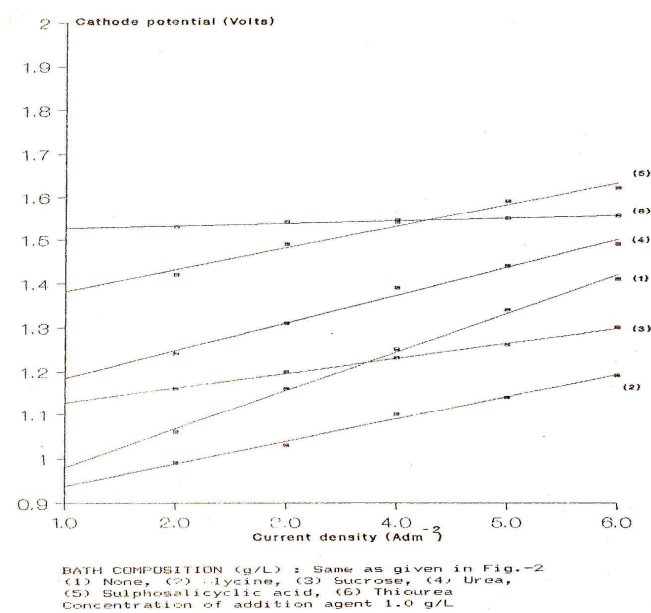


Figure 1



A



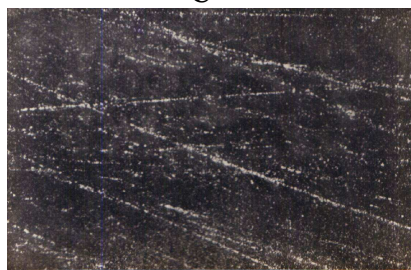
B



C



D



E

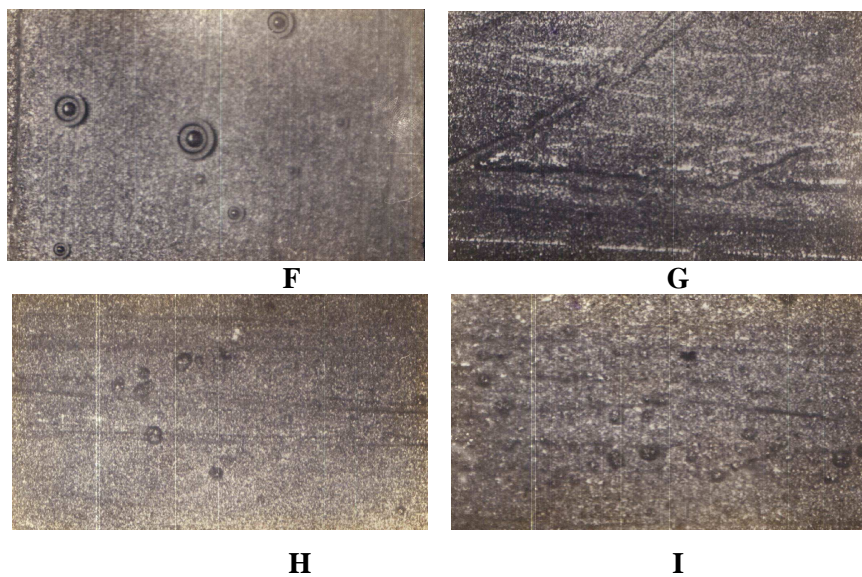


Figure 2

