

Influence of variables in nickel-manganese-zinc alloy plating from a sulphate bath

R. KASHYAP, S. N. SRIVASTAVA, S. C. SRIVASTAVA

Department of Chemistry, University of Lucknow, India

Received 8 December 1983

An Ni-Mn-Zn alloy has been satisfactorily electrodeposited from a sulphate bath containing nickel sulphate ($20-23 \text{ g dm}^{-3}$), manganese sulphate ($76-88 \text{ g dm}^{-3}$), zinc sulphate ($18-24 \text{ g dm}^{-3}$), ammonium sulphate (30 g dm^{-3}), thiourea (18 g dm^{-3}) and ascorbic acid (0.8 g dm^{-3}) under various plating conditions, namely, current density $1.0-3.0 \text{ A dm}^{-2}$; temperature $30-45^\circ \text{ C}$; pH $2.7-4.2$ and duration of electrolysis $15-30 \text{ min}$. Semibright, blackish-grey, thin films were generally deposited with the proportion of nickel and manganese in the deposits increasing with increasing current density, temperature and duration of electrolysis. However, the amount of zinc increased as the pH of the solution was raised. The cathode efficiency for alloy deposition increased linearly as the temperature or the pH of the solution was decreased, whereas at any particular pH and temperature it continuously rose with increasing current density or the time of deposition. The cathode polarization shifted to more negative values on increasing the current density and to less negative values at higher pH values and temperatures which consequently lowered the throwing power under the latter conditions.

1. Introduction

Electrodeposition of alloys occupies an important place in modern technology by virtue of the great range and diversity of alloy properties which cannot be met by the use of pure metals. Besides being widely used for decorative and protective purposes, low melting alloys have gained considerable importance recently because of their special potential applications in the computer and electronic industries.

Alloys containing nickel with zinc or manganese are known to possess a high degree of corrosion resistance and good mechanical properties. Ternary thin films of various compositions consisting of nickel and manganese with a third metal have been obtained mainly from sulphate electrolytes [1-8] under different operating conditions. The use of chloride [9], citrate [10] and borate [11] baths to obtain satisfactory deposits has also been recommended. Recently attempts have been made to incorporate selenium into the Ni-Mn electroplates [12, 13] in order to improve the magnetic or mechanical properties of the alloy. The electroplating of iron with nickel and manganese has been

investigated in the presence of some complexing additives [14]. It was thus considered worthwhile to obtain thin alloy films of nickel and manganese with zinc by an electrochemical process from a sulphate bath under different electrolytic conditions.

2. Experimental procedure

A fresh electrolyte solution (225 cm^3) containing sulphates of the three metals together with ammonium sulphate (30 g dm^{-3}), thiourea (18 g dm^{-3}) and ascorbic acid (0.8 g dm^{-3}) was electrolysed for 20 min to obtain thin alloy films detailed descriptions of which are given elsewhere [15]. The alloy films were washed with distilled water and dried. Each film was then peeled off carefully, weighed, and a fixed amount dissolved in dilute nitric acid for analysis. Nickel was estimated gravimetrically as dimethylglyoxime complex. Zinc was estimated titrimetrically using diphenylbenzidine as an indicator, while a colourimetric method [16] was used to determine the manganese content.

The cathode efficiency under various plating

conditions was calculated by the usual method [17] from the deposit composition. The pH of the electrolytic solution was measured using a glass electrode and was adjusted to the desired value by adding either sulphuric acid or ammonia. The cathode potentials corresponding to the hydrogen scale were determined to an accuracy of ± 0.001 V against a standard saturated calomel electrode using an agar-agar bridge drawn into a capillary of approximately 0.1 cm diameter and making a proper contact with the cathode. From the steady value of the e.m.f. of the cathode-calomel electrode combination the potential of the calomel electrode was subtracted to give the required cathode potential. The difference between the potentials attained with and without current flow gave the value of the cathode polarization (η) at a particular plating condition.

Gardam's formula [18]: $N = b/2\rho$ was used to calculate the throwing power (N) from the resistivity (ρ) of the electrolyte and the Tafel slope b of the plot of the cathode polarization against the logarithm of current density.

3. Results and discussion

The cathode potential-current density curves for nickel, manganese and zinc, and binary alloys of Ni-Zn, Ni-Mn and Zn-Mn are presented in Fig. 1. The relative position of these curves indicates the feasibility of a ternary alloy formation of these metals. The bath was fairly stable under various plating conditions for a reasonable period of electrolysis.

3.1. Nature and composition of the deposits

Satisfactory deposits in the composition range 5.69–12.39% nickel, 0.12–2.00% manganese, 86.62–94.11% zinc were obtained at current density 1.0–3.0 A dm⁻²; pH 2.7–4.2; temperature 30–45°C. Smooth uniform bright grey thin films were generally deposited at comparatively low current densities (1.0–1.5 A dm⁻²), 30°C and pH 3.7. At higher pH values the deposits became brittle. On the other hand, increasing temperature led to partially powdery deposits.

The influence of different parameters, namely, current density, pH, temperature, duration of deposition and concentration of the constituent

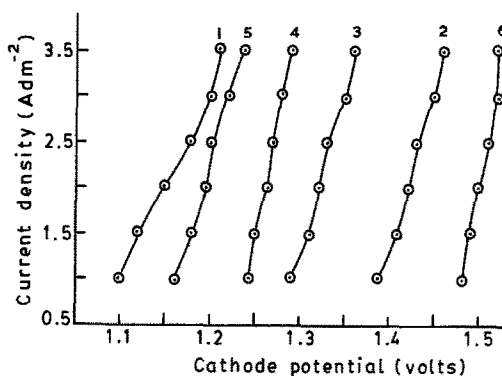


Fig. 1. Cathode potential curves for nickel, manganese, zinc and their binary alloys. Bath conditions: 30 g dm⁻³ ammonium sulphate, 18 g dm⁻³ thiourea, 0.8 g dm⁻³ ascorbic acid, 30°C temperature, pH 3.7. 1 – 20 g dm⁻³ nickel sulphate; 2 – 20 g dm⁻³ zinc sulphate; 3 – 80 g dm⁻³ manganese sulphate; 4 – nickel-zinc: 20 g dm⁻³ nickel sulphate, 20 g dm⁻³ zinc sulphate; 5 – nickel-manganese: 20 g dm⁻³ nickel sulphate, 80 g dm⁻³ manganese sulphate; 6 – zinc-manganese: 20 g dm⁻³ zinc sulphate, 80 g dm⁻³ manganese sulphate.

metals on the alloy composition and the cathode efficiency along with the distribution of total current for the discharge of nickel, manganese, zinc and hydrogen ions in the electrolyte has been represented in Tables 1–4. An examination of Tables 1 and 4 indicates that the percentage of nickel and manganese increases with increasing current density and duration of deposition. This might be due to the gradual utilization of more current by nickel and manganese ions as the current density or time of deposition is increased, as is evident from the analysis of the distribution of total current for the deposition of nickel, manganese and zinc at the cathode. A similar effect on the deposited composition is produced as the temperature is raised (see Table 2) which may be due to the increase in diffusion of the nickel and manganese ions. By contrast, the percentage of zinc increases while that of nickel and manganese decreases with increasing pH of the solution. When the concentration of the metal ion in the electrolyte is increased its percentage in the alloy also gradually increases (see Table 3) at a given current density. An increase in the concentration of a particular metal ion in the plating solution might facilitate the nucleation of that ion in the deposit with the result that its concentration increases as is evident from the examination

Table 1. Effect of current density on deposit composition at 30° C and a pH of 3.7

Current density (A dm ⁻²)	Metal in deposit (%)			Cathode efficiency (%)	Percentage of the current utilized for the deposition of metal			
	Ni	Mn	Zn		Ni	Mn	Zn	H ₂
1.0	6.50	0.24	93.26	66.68	4.78	0.19	61.71	33.32
1.5	7.72	0.40	91.88	67.40	5.73	0.32	61.35	32.60
2.0	8.53	0.56	90.91	67.79	6.36	0.45	60.98	32.21
2.5	9.35	0.72	89.93	68.45	7.03	0.58	60.84	31.55
3.0	10.36	0.90	88.74	69.27	7.88	0.73	60.66	30.73

Bath composition (g dm⁻³): Nickel sulphate, 20; zinc sulphate, 20; manganese sulphate, 80; ammonium sulphate, 30; thiourea, 18; ascorbic acid, 0.8.

Table 2. Effect of temperature and pH on deposit composition at 2.0 A dm⁻² current density

Temperature (° C)	pH	Metal in deposit (%)			Cathode efficiency (%)	Percentage of the current utilized for the deposition of metal			
		Ni	Mn	Zn		Ni	Mn	Zn	H ₂
30	3.7	8.53	0.56	90.91	67.79	6.36	0.45	60.98	32.21
35	3.7	8.74	0.64	90.62	66.32	6.38	0.50	59.44	33.68
40	3.7	9.14	0.76	90.10	65.62	6.59	0.59	58.44	34.38
45	3.7	9.75	1.48	88.77	65.24	6.98	1.13	57.13	34.76
30	2.7	10.36	0.76	88.88	70.45	8.01	0.63	61.81	29.55
30	3.2	9.14	0.64	90.22	69.08	6.94	0.52	61.62	30.92
30	4.2	7.92	0.52	91.56	66.99	5.84	0.41	60.74	33.01

Bath composition: Same as for Table 1.

Table 3. Effect of metal concentration in the bath on deposit composition at 30° C, pH of 3.7 and 2.0 A dm⁻² current density

Concentration of metal sulphate (g dm ⁻³)	Metal in deposit (%)			Cathode efficiency (%)	Percentage of the current utilized for the deposition of metal				Bath composition (g dm ⁻³)
	Ni	Mn	Zn		Ni	Mn	Zn	H ₂	
Nickel									
20	8.53	0.56	90.91	67.79	6.36	0.45	60.98	32.21	MnSO ₄ - 80; ZnSO ₄ - 20
21	8.74	0.64	90.62	67.81	6.52	0.51	60.78	32.19	(NH ₄) ₂ SO ₄ - 30
22	9.14	0.64	90.22	68.09	6.84	0.51	60.74	31.91	thiourea - 18
23	9.55	0.72	89.73	68.14	7.15	0.58	60.41	31.86	ascorbic acid - 0.8
Manganese									
76	8.33	0.52	91.15	67.77	6.22	0.41	61.14	32.23	NiSO ₄ - 20; ZnSO ₄ - 20
80	8.53	0.56	90.91	67.79	6.36	0.45	60.98	32.21	(NH ₄) ₂ SO ₄ - 30
84	8.53	0.58	90.89	67.79	6.36	0.46	60.97	32.21	thiourea - 18
88	8.94	0.64	90.42	68.07	6.69	0.51	60.87	31.93	ascorbic acid - 0.8
Zinc									
18	8.74	0.84	90.42	68.08	6.54	0.67	60.87	31.92	NiSO ₄ - 20; MnSO ₄ - 80
20	8.53	0.56	90.91	67.79	6.36	0.45	60.98	32.21	(NH ₄) ₂ SO ₄ - 30
22	8.13	0.52	91.35	67.75	6.07	0.41	61.27	32.25	thiourea - 18
24	7.92	0.44	91.64	67.73	5.91	0.35	61.47	32.27	ascorbic acid - 0.8

Table 4. Effect of duration of electrolysis on deposit composition at 30° C, pH of 3.7 and 2.0 A dm⁻² current density

Time (min)	Metal in deposit (%)			Cathode efficiency (%)	Percentage of the current utilized for the deposition of metal			
	Ni	Mn	Zn		Ni	Mn	Zn	H ₂
15	8.33	0.44	91.23	67.78	6.21	0.35	61.22	32.22
20	8.53	0.56	90.91	67.79	6.36	0.45	60.98	32.21
25	8.94	0.58	90.48	67.99	6.68	0.46	60.85	32.01
30	9.55	0.72	89.73	68.20	7.16	0.58	60.46	31.80

Bath composition: Same as for Table 1.

of the distribution of total current utilized by different ions for their deposition.

3.2. Cathode efficiency

Owing to the simultaneous discharge of hydrogen ions and other metal ions the cathode efficiency was always found to be less than 100%. The cathode efficiency for the deposition of a single metal was found to be 4.27–9.83% for nickel, 0.09–1.55% for manganese, 56.18–62.39% for zinc and 63.89–72.63% for the alloy under similar conditions. The total efficiency increases linearly as the temperature is decreased from 45 to 30° C as indicated in Table 2 at a given current density. A similar behaviour (see Table 2) is also observed with decreasing pH of the solution ranging from 4.2 to 2.7. However, at any particular pH and temperature it continuously rises as the current density or the duration of electrolysis is increased. This means that comparatively more current is utilized for the deposition of the alloy than that

for the discharge of hydrogen ions provided by the ionization of the solvent as the current density or the time of deposition is increased (see Tables 1 and 4). Furthermore, when the concentration of either nickel, manganese or zinc is increased in the bath, the total efficiency remains almost constant at any particular current density (see Table 3).

3.3. Cathode polarization

Table 5 represents the variation of cathode polarization with current density during electrodeposition of the alloy in the temperature and pH ranges of 30–45° C and 2.7–4.2, respectively. It is observed that the cathode polarization shifts to more negative values as the current density is increased at a given temperature and pH of the electrolyte solution. With increasing current density the diffusion of the metal ions becomes insufficient to keep pace with their discharge at the cathode and as such more hydrogen ions are simultaneously discharged. The cathode polarization

Table 5. Variation in cathode polarization with temperature and pH at different current densities

Temperature (° C)	pH	Cathode polarization $\eta(V)$ at current densities (A dm ⁻²)				
		1.0	1.5	2.0	2.5	3.0
30	3.7	-0.922	-0.931	-0.942	-0.947	-0.955
35	3.7	-0.915	-0.920	-0.926	-0.931	-0.937
40	3.7	-0.913	-0.919	-0.924	-0.929	-0.933
45	3.7	-0.908	-0.917	-0.922	-0.928	-0.932
30	2.7	-0.934	-0.944	-0.952	-0.962	-0.967
30	3.2	-0.930	-0.937	-0.944	-0.949	-0.956
30	4.2	-0.913	-0.918	-0.925	-0.932	-0.939

Bath composition: Same as for Table 1.

Table 6. Data for resistivity, Tafel slope and throwing power at various temperature and pH values

Temperature ($^{\circ}\text{C}$)	pH	Resistivity, ρ ($\Omega\text{ cm}$)	Tafel slope b (V)	Throwing power (N)
30	3.7	15.97	0.0625	0.001 96
35	3.7	14.31	0.0538	0.001 88
40	3.7	13.70	0.0486	0.001 84
45	3.7	13.33	0.0478	0.001 79
30	2.7	16.53	0.0692	0.002 09
30	3.2	16.21	0.0666	0.002 05
30	4.2	15.80	0.0615	0.001 94

Bath composition: Same as for Table 1.

thus changes to a more negative value. This may also account for the observed increase in cathode efficiency under similar conditions. Further, polarization has been found to attain comparatively less negative values at higher temperatures probably due to an increase in the diffusion coefficient of the depositing ions. This finally results in making the cathode polarization less negative. Similar behaviour is also observed when the pH of the bath is raised which may be due to the corresponding decrease in the availability of hydrogen ions to carry current at any particular current density.

3.4. Throwing power

The throwing power has been calculated from the values of the Tafel slope and the resistivity at various pH values and temperatures. The results are listed in Table 6. It is seen to decrease as the temperature or pH of the bath is increased. This suggests that relatively low temperature and pH should favour more uniform coatings. This is confirmed in practice.

Acknowledgement

One of the authors (R.K.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for the award of a Junior Research Fellowship during the tenure of which the present work has been carried out.

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