ELECTRODEPOSITION OF NICKEL-MANGANESE ALLOYS FROM THE SULPHATE BATH

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INTRODUCTION

Electrodeposited nickel-manganese alloys are of interest in the decorative and protective finishing of metals, and in engineering applications as for electroforming. The literature up to about 1963 covers the deposition of these alloys from the sulphate, chloride and pyrophosphate baths and has been discussed in detail by Brenner[1]. The recent work is also confined to the sulphate bath[2-9] including a 5 per cent manganese alloy for electroforming,[10] and there are 2 references relating to the production of alloys containing 0.4 and 2 per cent manganese suitable for electroforming from the sulphate bath[11,12]. These investigations are centred round the effect of addition agents, half cycle rectification current, rotating cathode, ultrasonic vibration, and polarization phenomena.

In addition to the practical aspects, the electrodeposition of manganese alloys is also of theoretical interest from the viewpoint of the low cathode efficiency, inclusion of non-metallic matter in the deposit, and the mechanism of deposition. This work formed part of the general programme on the deposition of binary and ternary manganese alloys from the sulphate bath. An account of the initial studies covering nickel-manganese alloys is presented here.

EXPERIMENTAL AND RESULTS

The bath for plating consisted of nickel and manganous sulphates, ammonium sulphate, and ammonium citrate to prevent a black coating on the anode. A copper-coated platinum cathode and stainless steel anode were used, with a porous diaphragm to separate the catholyte and anolyte. Some results are given in Tables I and II to show the effect of variation in the concentration of the 2 metals on deposit composition, cathode efficiency and potential. The composition and efficiency values were accurate to within $\pm$ 1 per cent and potentials to $\pm$ 10 mv. It was possible to obtain satisfactory deposits, smooth and adherent, dull to bright greyish-white in appearance, in the composition range nickel 7-98 and manganese 1-90 per cent, at an efficiency of 4-85 per cent.

The nickel content in the deposit decreased and the manganese content increased with an increase in the current density and manganese concentration of the solution. The manganese content was high only at a current density of about 16 amp/dm^2 or beyond. The non-metallic matter in the deposit was 1-16 per cent, and increased generally with an increase in the current density. The cathode efficiency increased with an increase in the nickel concentration of the solution and decreased with an increase in the current density. An increase in the manganese content in the deposit was associated with a decrease in the efficiency. The bath could be operated up to 50 amp/dm^2. The variations in the cathode potential with current density were quite marked. Other workers have reported a manganese content up to 94 per cent in the deposit at an efficiency of about 70 per cent, the correlation with the current density and cathode efficiency being similar; the limiting current density was, however, less.

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TABLE I

EFFECT OF NICKEL CONCENTRATION IN SOLUTION ON DEPOSIT COMPOSITION, CATHODE EFFICIENCY AND POTENTIAL

Electrolyte: manganous sulphate 0.25M, ammonium sulphate 75 g/l, ammonium citrate 8 g/l, pH 7.5, temperature 30°C, still plating, bath voltage 2.3-3.8 volts. For each concentration, the first figure under current density gives the manganese and the second the nickel per cent by weight in the deposit, the third the cathode efficiency per cent, and the fourth the cathode potential (—ve sign) in volts on hydrogen scale.

Ni. conc., M	c.d., amp/dm²							
	0.5	1	2	3	4	5	6	8
0.005	7	9	14	13	15	19		
	88	87	86	81	84	81		
	7	7	3	4	3	3		
	0.86	0.90	1.05	1.08	1.18	1.27		
0.01		6	8	9	12			
		88	86	84	81			
		12	9	7	4			
			0.89	0.95	1.00			
0.05	3	4	4	7	8	9		
	94	90	88	82	81	80		
	53	42	37	21	21	23		
	0.76	0.80	0.87	0.93	1.00	1.10		
0.10	2	3	6	7	9	11		
	91	90	90	88	85	73		
	70	56	55	49	38	27		
	0.76	0.82	0.94	1.01	1.13	1.27		
0.20	1	2	3	5	7	7	8	10
	98	96	95	91	88	85	85	83
	85	84	74	65	58	57	47	45
	0.74	0.82	0.91	1.05	1.08	1.16	1.33	1.36

TABLE II

EFFECT OF MANGANESE CONCENTRATION IN SOLUTION ON DEPOSIT COMPOSITION, CATHODE EFFICIENCY AND POTENTIAL

Mn conc., M	c.d., amp/dm²							
	0.5	1	4	12	16	20	30	50
0.05	3	4	7	12	13	13	21	
	96	94	87	76	76	75	65	
	49	37	22	13	16	11	10	
	0.86	0.94	1.22	1.91	1.93	2.54	2.99	
0.10	3	4	9	11	13	15	47	76
	95	93	83	81	80	76	51	21
	53	44	20	14	11	11	10	18
	0.81	0.86	1.21	1.69	1.92	2.16	2.27	
0.25	3	4	8	12	30	47	79	88
	94	90	81	78	63	53	13	7
	53	42	21	10	7	10	27	42
	0.76	0.80	1.06	1.52	1.89	2.48	3.00	
0.50	3	5	9	14	41	71	89	
	94	92	82	77	43	9	9	
	47	37	18	8	9	37	42	
	0.80	0.85	1.12	1.61	2.00	2.96	3.02	
0.75	4	5	10	27	60	80	86	90
	93	92	77	73	40	18	11	7
	47	36	14	9	13	22	39	45
	0.79	0.86	1.16	1.59	1.90	2.59	3.33	

Electrolyte: nickel sulphate 0.05M, bath voltage 2.4-13.0 volts; other conditions as in Table I.

Detailed work is in progress. Preliminary investigations have indicated the possibility of depositing ternary alloys of nickel-iron-manganese from this bath.

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