

NICKEL-COPPER ALLOY ELECTROFORMING FROM THE CITRATE-SULPHAMATE MIXED BATH

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Electroformed alloys plays an important role as it is characterized by good mechanical properties and improved corrosion resistance. This paper presents the results of electroforming of nickel - copper alloy from a mixed citrate - sulphamate electrolyte. The optimised bath contains:

Nickel Sulphamate	120 g/l
Copper as Copper Sulphamate	6.5 g/l
Sodium Citrate	150 g/l
Boric Acid	20 g/l
Sodium Chloride	5 g/l
pH	3.8
Temperature	308 K

Keywords: Electroformed alloys, nickel-copper alloy and citrate- sulphamate electrolyte.

INTRODUCTION

Electroforming offers the advantage of fabricating metal parts without the multitudinous problems of layout, spring back, die wear, warpage, thinning etc.,. However only few metals and alloys could be electroformed. In recent years there is considerable interest in electroforming of different alloys for various applications [1-10]. Electrodeposited alloys are characterized by their remarkable physical, chemical and corrosion resistant properties. Nickel-Copper alloys are known to be corrosion resistant in several corrosive atmospheres. Several types of solutions have been suggested for the deposition of nickel-copper alloys. The authors [11] described a sulphate - oxalate electrolyte. The authors [12] proposed cyanide solutions while the author [13] used citrate solutions, use of pyrophosphate bath has been advocated as described in [14] and citrate - sulphate electrolyte have been

described in [15-18]. This paper describes the electroforming of nickel-copper alloy from a citrate- sulphamate bath.

EXPERIMENTAL

Copper panels of size 100 x 100 mm were mechanically polished and precleaned using conventional procedures and Hull Cell experiments were carried out in the following electrolyte:

Nickel Sulphamate	120 g/l
Copper as Copper Sulphamate	2.5 - 12.5 g/l
Sodium Citrate	50 - 150 g/l
Boric Acid	20 g/l
Sodium Chloride	5 g/l
pH	3.5 - 4.0
Temperature	308 K

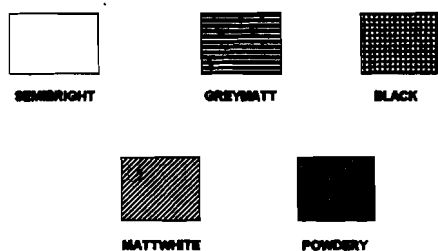


Fig. 1: Code for recording Hull cell pattern

Hull Cell experiments were carried out by changing the concentration of sodium citrate and copper sulphamate to optimise their concentration so as to produce quality deposits. After optimization, electroformed copper-nickel alloy foils were prepared on 100 x 100 mm stainless steel mandrel for the evaluation of hardness and wear resistance of the deposits. The deposit was analysed by dissolving in dilute nitric acid and the copper content was estimated using atomic absorption spectrophotometer. Linear sweep voltammetry was carried out using Bio Analytical System employing a conventional three electrode cell. The hardness of the deposit was measured using LECO micro hardness tester by applying a load of 20 g. Abrasion resistance of the alloy coating was obtained using Erichser Taber Abrasion Tester.

RESULTS AND DISCUSSION

Influence of sodium citrate concentration

Fig. 1. gives the code for recording the Hull cell pattern. Fig. 2. Shows the Hull Cell pattern for different concentrations of sodium citrate by keeping the copper sulphamate concentration at 2.5 g/l as copper. It could be seen from Fig. 2(a). that the deposit is black at a sodium citrate concentration of 50 g/l. As the concentration of

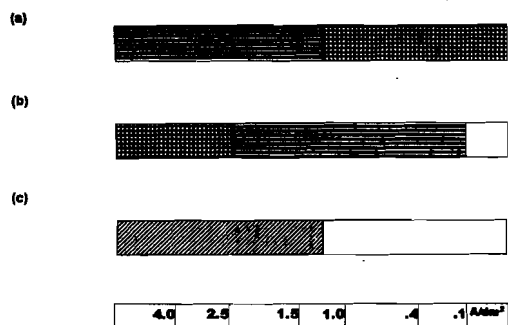


Fig. 2: Hull cell pattern with different concentrations of sodium citrate for the nickel-copper alloy bath containing nickel sulphamate 120 g/l, copper 6.5 g/l, boric acid 20 g/l sodium chloride 5 g/l, pH 3.8, temperature 308 K Sodium citrate in (a) 50 g/l (b) 100 g/l (c) 150 g/l

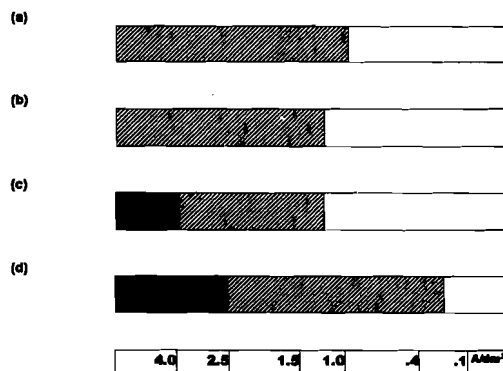


Fig. 3: Effect of copper sulphamate in nickel-copper alloy bath containing nickel sulphamate 120 g/l sodium citrate 150 g/l boric acid 20 g/l sodium chloride 5 g/l, pH 3.8, temperature 308 K Copper sulphamate as copper in (a) 0 g/l (b) 2.5 g/l (c) 6.5 g/l (d) 12 g/l

sodium citrate is increased 100 g/l, greyish deposit at low current density areas and black deposit at high current density areas are obtained as seen in Fig. 2(b).

Further increase in concentration of sodium citrate leads to the formation of semi bright deposit at low current density areas and matt white deposit at high current density areas as seen in Fig. 2(c). Hence the optimum concentration of sodium citrate is chosen as 150 g/l.

Influence of copper sulphamate

Fig. 3 shows the Hull Cell pattern for different concentrations of copper sulphamate by keeping the concentration of sodium citrate as 150 g/l. It could be seen that at lower concentrations the deposit is matt white and at higher concentrations the deposit is powdery.

Influence of addition agents

Different addition agents such as 1 g/l saccharin, 1 g/l coumarin and 1 g/l 1,2,3 benzotriazole were added to the optimised citrate - sulphamate bath with the aim of producing bright deposits the Hull Cell patterns were prepared. It was found that there was no improvement in the appearance of the deposit.

Chemical analysis of the deposit and bath

Table I shows the copper content in the bath and copper content in the deposit. It could be seen that as the copper content in the bath increases, copper content in the deposit also increases.

Hardness and wear resistance studies

Table II shows the hardness values of the deposit at different concentrations of copper in the bath. As could be seen, the hardness value decreases as the copper content increases. Table III gives the wear index of copper-nickel alloy deposit

TABLE I: Relationship between copper content in the bath and percentage of copper in the deposit

Nickel sulphamate	:	120 g/l
Sodium citrate	:	150 g/l
Boric acid	:	20 g/l
Sodium chloride	:	5 g/l
pH	:	3.8
Cathode current density	:	1 A/dm ²
Temperature	:	308 K

Cu content in bath (g/l)	% of copper in the deposit
2.5	7.18
6.5	12.48
12.5	15.65

TABLE II: Relationship between copper content in bath and hardness of the deposit

Copper content in bath (g/l)	Hardness of deposit (VH)
0.0	292.56
2.5	246.42
6.5	224.42
12.5	192.08

at different concentration of copper in the bath. The wear index of the deposit increases as the copper in the electrolyte increases there by showing the poor wear resistance of the alloy coating.

Voltammetry study

Table IV shows the linear sweep voltammetry data for the nickel - copper alloy system. It could be seen that as the copper content in the citrate - sulphamate bath increases from 2.5 to 12.5 g/l the alloy deposition potential is shifted towards the copper deposition potential. The peak current also increased with the copper content in the bath.

TABLE III: Relationship between copper content in the bath and wear index of the deposit

Copper content in bath (g/l)	Wear index of the alloy deposit Wt loss in g/1000 cycles
0.0	0.006
2.5	0.065
6.5	0.148
12.5	0.267

TABLE IV: Linear sweep voltammetry data

Cu content in bath (g/l)	Nickel content in bath (g/l)	Peak potential (mV)	Peak current (x 10 ⁻³ A)
0.0	30	72	1.47
2.5	30	87	2.13
6.5	30	105	2.40
12.5	30	135	3.58
12.5	—	341	6.80

CONCLUSION

Nickel - Copper alloy electroforming can be carried out from the citrate-sulphamate bath of the following composition.

Nickel Sulphamate	120 g/l
Copper as Copper Sulphamate	6.5 g/l
Sodium Citrate	150 g/l
Boric Acid	20 g/l
Sodium Chloride	5 g/l
pH	3.8
Temperature	308 K

REFERENCES

1. N Atonossov and M Bratoeva, *Interfinish 96*, Birmingham, United Kingdom, September (1996) 127
2. T V Gaevskaya, *Met Finish*, **94(6)** (1996) 100
3. K Hasegawa, *Patent 5,516,594*, assignor to Scovil Japan KK
4. P Leisner, *Interfinish 96*, Birmingham, United Kingdom September (1996) 341
5. E J Podlaha and D Landolt (II), *J Electrochem Soc.* **143(3)** (1996) 893
6. A Watson, *Products Finish*, **61(2)** (1996) 46
7. Y N Sadana and Z Zhang, *Met Finish*, Oct (1987) 49
8. K M Yin and S L Jan, *Trans Met Finish*, **74(2)** (1996) 51
9. A Mayer, *Plat and Surf Finish*, **72(11)** (1985) 76
10. D A Luck, *Trans Inst Met Finish*, **64(3)** (1986) 99
11. R B P Crawford and R D Snyder, *Electroplating Processes*, U S Pat 1,750,092 (1930)
12. H D Hine and W B Cooley, *Trans Amer Electrochem Soc.* **48** (1925) 61
13. O P Watts, *Trans Electrochem Soc.* **84** (1943) 347
14. S K Panickar and T L Ramachar, *J Electrochem Soc.* Japan **25,197 E** 121
15. B H Priscott, *Trans Inst Met Finish*, **36** (1958) 93
16. K Vu Quant, E Chassaing and B Le Veit, *Met Finish*, **83(10)** (1985) 25
17. I Jean Harkans, Chia Hsu Chang, P C Andricacus and E J podlaha, *J Electrochem Soc.* **138(2)** (1991) 411
18. C Madore and D Landolt, *Plat and Surf Finish*, **80(11)** (1993) 73