

ELECTROPLATING OF NICKEL-COPPER ALLOYS

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Nickel — copper alloy with 30% nickel has Monel like properties with excellent resistance to corrosion and erosion. This alloy deposited over steel substrate has been recommended as a cost-effective replacement for cast Monel for applications in different environments. This paper deals with investigations on the development of a stable bath for electroplating this alloy. A suitable bath is reported on the basis of Hull cell studies, plating experiments, determination of alloy plating efficiency and composition of the plated alloy. Effects of operating parameters on deposition characteristics and deposit properties are also reported.

Keywords: Nickel-copper alloys, hull cell and electroplating.

INTRODUCTION

Nickel-copper alloy with 30% nickel is reported [1] to have resistance to corrosion and erosion even under acidic or alkaline conditions. The alloy deposited over steel substrates has been recommended [2] as a cost effective replacement for cast Monel for applications in different environments.

Copper and nickel are widely separated in the electrochemical series with standard electrode potentials of +0.337 and -0.230 V respectively ; Hence to facilitate alloy deposition, it is essential to bring the deposition potentials close to each other by using complexants and employing suitable metal concentration ratios. There are literature reports regarding the electrodeposition of nickel - copper alloys from electrolytes based on cyanide [3-6] ammonia [7], pyrophosphates [8-10], thiosulphates [11] glycine [12] L-asparagine [13] and citrate [14-19]. Earlier work by Priscott (14) and Elghandour [15] points to the possibility of electrodepositing nickel-copper alloys, from acidic solutions containing citrate. Citrate solutions were used by others also for polarisation studies using rotating disk electrodes [16-18] for investigating the effects of pulse parameters on this alloy deposition [19] and for developing a mathematical model to simulate alloy deposition [20]. This paper deals with investigations for the identification of a stable bath for electroplating nickel-copper alloys.

EXPERIMENTAL

Hull cell experiments were carried out using a 267 ml standard Hull cell. Polished copper cathode pieces and pure

nickel anode were used and a cell current of 1 A was passed for a duration of 5 minutes. Electroplating experiments for evaluation of the current efficiency and alloy composition were performed using platinum foil (75 x 25 x 0.1 m) cathode and nickel anode. The deposits were stripped in 1:1 nitric acid and copper estimated by iodometric titration [21]. Compositions of a few plated samples were estimated by dissolving them and using a Permin Elmer Atomic Absorption Spectrophotometer for the determinations. Current efficiencies were determined from standard equations (2) knowing the mass of deposit and composition of alloy. To ascertain the nature of deposits, plating experiments were also done with cold rolled steel specimens (75 x 25 x 0.3 mm), without or with a cyanide copper strike. Steel or copper panels were used for plating after solvent degreasing and alkaline electrocleaning. Plating on platinum was carried out after degreasing, 1:1 nitric acid dip and alkaline electrocleaning.

Microhardness of electrodeposits (15 µm thick) was measured by the Vicker's method (50 g load) using a PMT - 3 Microscope Hardness Meter of Russian make. Microstructure observations and XRD analysis were resorted to with a Scanning-Electron Microscope (JEOL, JSM-35 CF) and XRD (JEOL JD) instrument respectively.

RESULTS AND DISCUSSION

Hull cell studies

It is well known that the co-deposition of copper with nickel requires the presence of at least one complexant to bring their

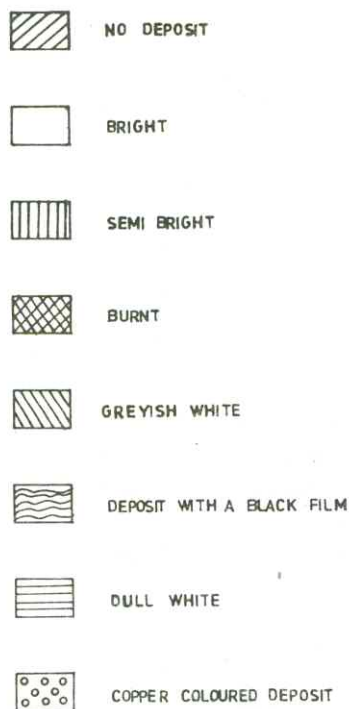


Fig. 1: Codes for representing the appearance of Hull cell panels

deposition potentials close to each other. Hence the effects of adding trisodium citrate and ammonium hydroxide to nickel solutions was experimented upon. It is seen from Figs. 1 and 2, that deposits with bright/semibright/dull white appearance are obtained over the current density range of 0.1-4.0 A/dm² in the presence of trisodium citrate at pH 5.0 and also in the presence of trisodium citrate and ammonium hydroxide at pH 9.0.

Ammoniacal solutions of nickel containing citrate as complexant were used to examine the effects of adding copper sulphate to these, on the appearance of Hull Cell patterns (Fig. 3). As the copper content of the solution increases, a grayish white region becomes prominent on the Hull Cell plates, indicating this one to be the region corresponding to nickel - copper alloys. With lower copper concentrations, the nickel-like bright layer appears over a wide range whereas high copper concentrations result in coppery looking layers formed at low current densities. These results lead to the conclusions that there is a possibility of formation of nickel-copper alloys over a fairly wide range of current density.

Studies on nature of deposits, alloy composition and cathode current efficiency with solutions of varying compositions

When copper sulphate was added in small quantities to nickel salt solutions containing no complexants, coppery looking deposits were obtained. However with larger amount of

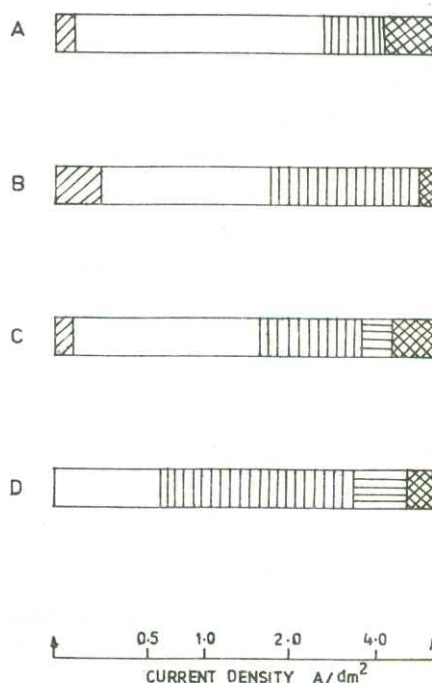


Fig. 2: Appearance of Hull cell panels for nickel plating from various solutions. Cell current 1A, duration 5 minutes

copper sulphate, deposits became dark brown and powdery (Table I) indicating the preferential deposition of copper. This is in conformity with the general inference that codeposition of copper and nickel requires the presence of a complexants which brings their deposition potentials close to each other.

In the presence of trisodium citrate, the pH of a solution composed of copper sulphate and nickel sulphate is not altered appreciably, unlike in the case of one containing no citrate. At 1.0 and 2.0 A/dm² deposition occurs with cathodic current efficiency in the range of 34-63% (Table II). The copper content of the deposit increases with increasing copper concentration in the bath while it shows a slight decrease with current density. Deposits tend to become powdery when the copper concentration is 12 g/l and perhaps, higher.

Nickel-copper alloy deposits were obtained from ammoniacal solutions with efficiencies higher than in the case of acidic solutions (Tables II and III). The deposits have a grayish white colour and at copper sulphate concentration of 8-12 g/l, the copper content of the deposit varied from 29 to 33%.

Electroplating of nickel and nickel-copper alloy was carried out on cold rolled steel panels to ascertain whether coatings of various thickness could be obtained. Results (Table IV) show that when the plating duration is 30 minutes, deposits are well adherent and have a thickness of about 5 μ m. While

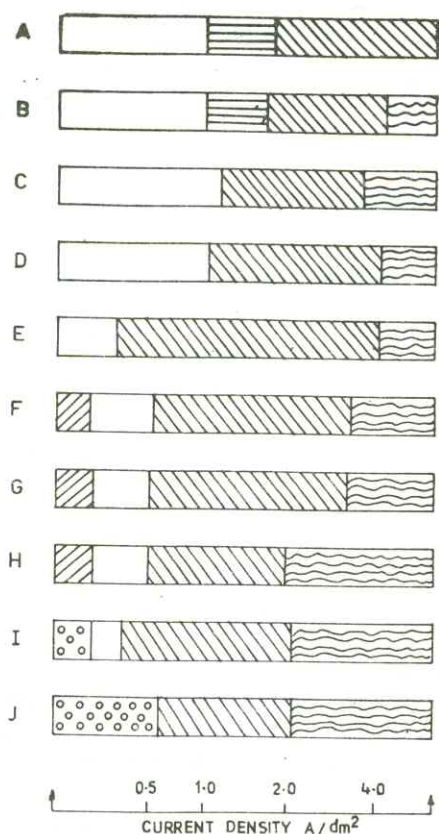


Fig. 3: Effect of addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to solutions with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 50 g/l, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30 g/l, H_3BO_3 30 g/l, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ 50 g/l

pure nickel deposits were semibright but dull white, the alloy deposits were grayish white. When the plating duration was increased so as to get 15 μm thick deposits, it was found that

TABLE I: Effect of copper sulphate addition on deposit appearance

Bath: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 50 g/l, H_3BO_3 30 g/l, 305 K, Still bath

Conc. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (g/l)	pH of solution	Current density A/dm^2	Appearance of deposit
0	4.0	1	Semi bright, white (Nickel coloured)
0	4.0	2	" "
4	2.1	1	Copper Coloured
4	2.1	2	" "
8	1.8	1	Dark brown powdery
8	1.8	2	" "
12	1.7	1	" "
12	1.7	2	" "

TABLE II: Effects of CuSO_4 addition on deposition characteristics of bath

Bath: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 50 g/l; H_3BO_3 30 g/l; $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ 50 g/l

Conc. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (g/l)	Soln pH	Current density A/dm^2	Cu Current (%)	Cathode Current Efficiency (%)	Appearance of deposit
0	5.4	1	—	92	Semibright, white
0	5.4	2	—	91	"
4	4.6	1	13	63	Greyish white
4	4.6	2	11	43	"
8	4.3	1	31	61	"
8	4.3	2	25	40	"
12	4.0	1	55	61	Greyish white powdery
12	4.0	2	52	34	"

adherent white deposits of nickel was produced from solutions of pH 4.0 while from ammoniacal solutions, nickel and nickel-copper deposits showed a tendency to become flaky and powdery, probably because of increased internal stress. To find out if the flaky and powdery nature of nickel-copper deposit was due to initial formation of loosely adherent immersion copper layer, repetition of the experiments were done with the use of copper and cyanide copper struck steel specimens as substrates which also led to the same results. Addition of a stress relieving agent, namely saccharin resulted in the formation of adherent and coherent nickel as well as nickel-copper alloy deposits.

Data on compositions of certain alloy coatings determined by Atomic Absorption Spectrophotometer and Volumetric analysis are included in Table V.

Influence of citrate concentration and operating parameters on nickel-copper alloy deposition

A bath of the following composition was used to study the influence of citrate concentration, pH, current density,

TABLE III: Effects of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ addition on deposition characteristics of bath

Bath: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 50 g/l; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30 g/l; H_3BO_3 30 g/l; $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ 50 g/l
Current density 1.0 A/dm^2 pH = 9

Conc. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (g/l)	Copper content of deposit (%)	Cathode Current Efficiency (%)	Appearance of deposit
0	—	89	Semibright, white
8	29	90	Dull
10	31	89	Greyish white
12	33	83	" "

TABLE IV: Effect of solution pH and plating duration on alloy deposit appearance

Sl. No.	Bath Composition	pH	Duration of plating (minutes)	Appearance of deposit
1.	NiSO ₄ .6H ₂ O 50 g/l NiCl ₂ .6H ₂ O 30 g/l H ₃ BO ₃ 30 g/l	4.0	30	Semibright white
2.	As in (1) + trisodium citrate 50 g/l	4.0	30	" "
3.	As in (2) + NH ₄ OH	9.0	30	" "
4.	As in (3) + CuSO ₄ .5H ₂ O 8 g/l	9.0	30	Greyish white
5.	As in (3) + CuSO ₄ .5H ₂ O 12 g/l	9.0	30	" "
6.	As in (1)	4.0	90	white
7.	As in (3)	9.0	90	Semibright white. Deposit peels off as foil
8.	As in (3) + Saccharin 1 g/l	9.0	90	" "
9.	As in (3) + saccharin 3 g/l	9.0	90	" "
10.	As in (3) + saccharin 5 g/l	9.0	90	Semibright white, No peeling
11.	As in (4)	9.0	90	Greyish white, flaky and powdery
12.	As in (4) Plating on copper substrate	9.0	90	" "
13.	As in (4) Plating after cyanide copper strike	9.0	90	" "
14.	As in (4) + saccharin 5 g/l	9.0	90	Greyish white, adherent
15.	As in (5) + saccharin 5 g/l	9.0	90	" "

temperature and agitation on deposit nature, alloy composition and cathode current efficiency.

Nickel Sulphate	50 g/l
Nickel Chloride	30 g/l
Copper Sulphate	12 g/l
Saccharin	5 g/l

An increase in the concentration of trisodium citrate decreases the copper content of the alloy and the cathode current efficiency (Fig. 4). The deposits have a coppery tinge for a 30 g/l citrate concentration in the bath, whereas with 50-100 g/l citrate grayish white deposits with 19-33% copper are obtained (Table VI). This shows the essential role of trisodium citrate in facilitating the codeposition of nickel, the less noble metal, along with copper.

Uniformly grayish white deposits with 29-38% copper were obtained at 81-88% cathode current efficiency at pH 8.0 - 10.0. Deposits obtained from solutions of lower pH values were nonuniform in appearance. It is also seen that copper percentage and current efficiency increase with an increase of pH from 6.0 to 10.0 Table VII, Fig. 5).

The effects of operating current density on the nature of deposit, copper content of the alloy and cathode current

efficiency are shown in Fig. 6 and Fig. 8. Coppery coloured deposits with high copper contents are obtained at current densities less than 0.75 A/dm² whereas the influence of current density on metal content is far less pronounced in the current density range of 0.75-2.0A/dm². The preferential deposition of copper, the more noble metal, at lower operating current density is as expected for a regular alloy plating system.

Increase in operating temperature or agitation of the bath is normally known to result in an increase in metal concentration in the diffusion layer which, in turn, will lead

TABLE V: Alloy comparison by AAS and volumetry

AAS Method					
Absorbance		Concentration		Copper (%)	Copper % (volumetry)
Nickel	Copper	Nickel	Copper		
0.410	0.281	6.21	3.34	34.97	34
0.562	0.182	8.52	2.26	20.96	21

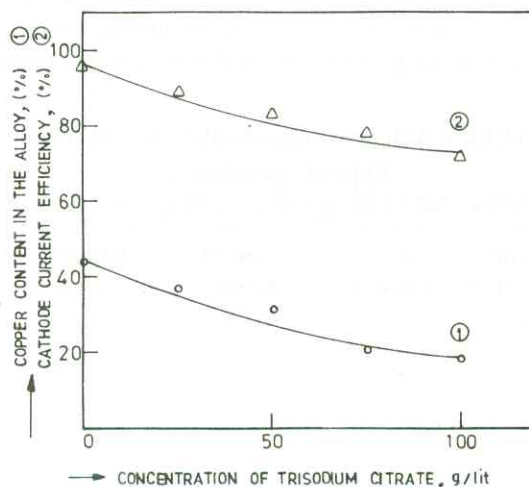


Fig. 4: Influence of citrate concentration on deposit composition and deposition efficiency
Bath composition: As in Table VI

TABLE VI: Influence of trisodium citrate on nickel-copper alloy deposition
 Bath: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 50 g/l; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30 g/l;
 H_3BO_3 30 g/l; $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 12 g/l; Saccharin 5 g/l;
 pH 9.0; Current density 1 A/dm²

Conc. of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_4$ 2 H ₂ O g/l	Copper in deposit (%)	Cathode current efficiency (%)	Appearance of deposit
0	44	96	Greyish with copper tinge
25	37	89	" "
50	33	83	Greyish white
75	21	78	" "
100	19	72	" "

to an increase in the percentage of the nobler metal in the case of regular alloy plating systems. This is confirmed by the observations that the deposited alloy is copper coloured and has high copper percentage when the bath is operated at 330 K or 305 K with agitation (Table VIII).

On the basis of the investigations carried out, conditions found most suitable for depositing nickel-copper alloy with 25-35% copper are as follows:

Nickel Sulphate	50 g/l
Nickel Chloride	30 g/l
Copper Sulphate	12 g/l
Saccharin	5 g/l
Boric acid	30 g/l
Trisodium citrate	50 g/l
pH	8.0-9.0
Current density	0.75-1.50 A/dm ²
Temperature	303-318 K
Anode	nickel

TABLE VII: Effects of solution pH on nickel-copper alloy deposition

Bath : $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 50 g/l; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30 g/l;
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 12 g/l; H_3BO_3 30 g/l; $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ 50 g/l; Saccharin 5 g/l; 305 K Current density 1 A/dm²

Solution pH	Copper in deposit (%)	Current Efficiency (%)	Appearance of deposit
4	29	84	Bright but black at edges
6	24	80	" "
8	29	81	Greyish white
9	33	83	" "
10	38	88	" "

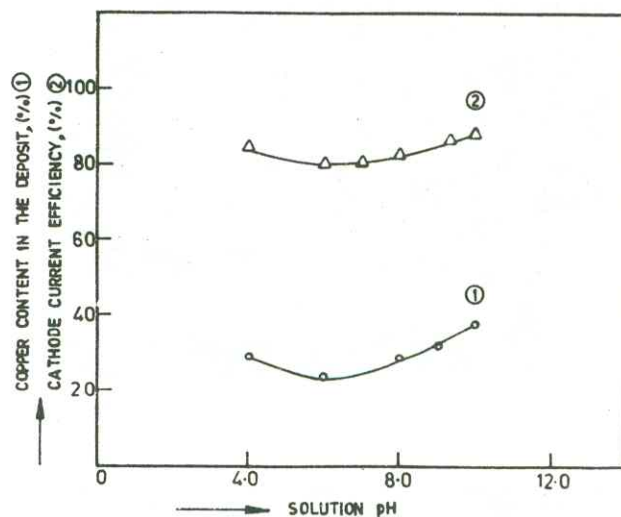


Fig. 5: Influence of solution pH on deposit composition and deposit deposition efficiency
 Bath composition: As in Table VII

Properties of electrodeposited nickel and nickel-copper alloys — A comparison

The nickel-copper alloy electrodeposits have microhardness higher than that of pure nickel electrodeposits (Table IX). An alloy with 28% copper has a microhardness of 397 V, compared to 362 for pure nickel.

Fig. 7 is a comparison of microstructure of deposits of nickel-copper alloy and nickel. A pattern of uniform crystalline structure is evident in each case, the grain size

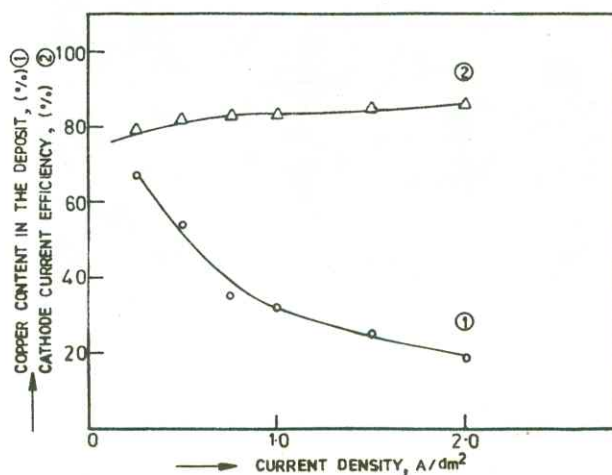


Fig. 6: Influence of current density on deposit composition and deposition efficiency
 Bath composition: As in Table VIII

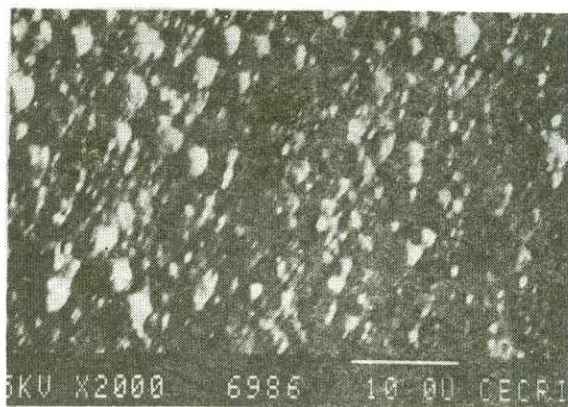


Fig. 7(a) Nickel

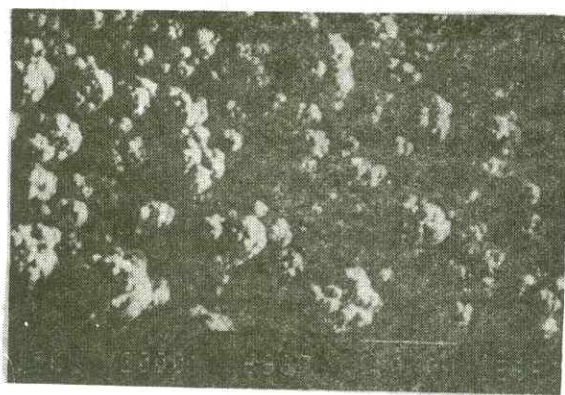


Fig. 7(b): Nickel-copper alloy (copper 29%)

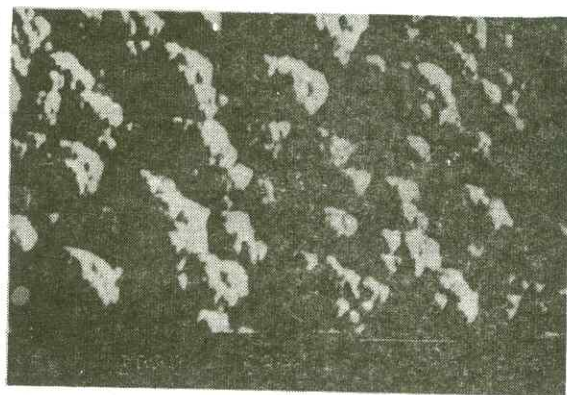


Fig. 7(c): Nickel-copper alloy (copper 37%)

Fig. 7: Microstructure of nickel and nickel-copper alloy deposits

showing an increase with an increase in copper content of the alloy.

The X-ray diffraction pattern of nickel and copper electrodeposits (Fig. 8) show the characteristics peaks for nickel and copper [22]. The patterns obtained for two typical nickel-copper alloys (Fig. 9) depict sharp diffraction peaks

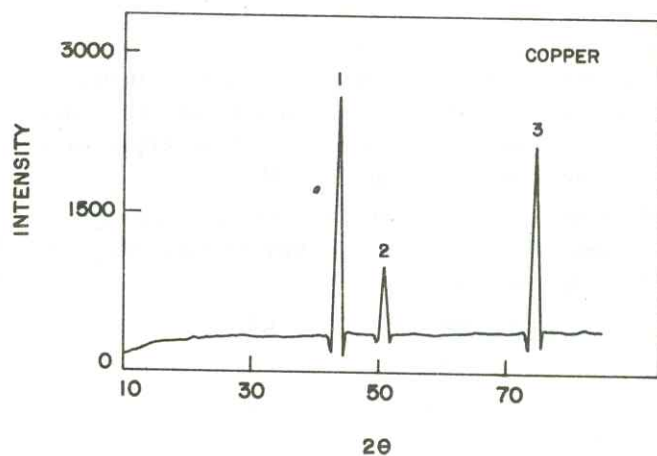
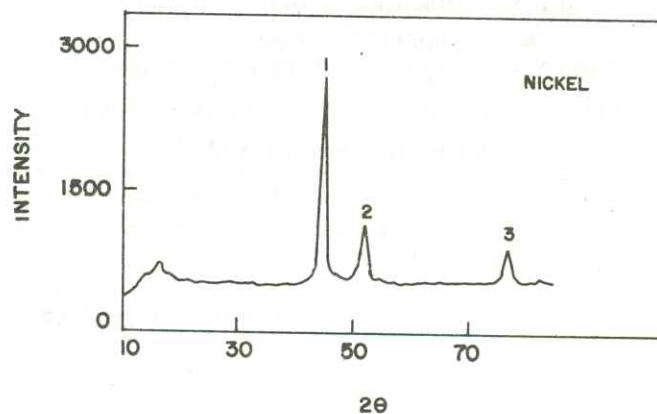


Fig. 8: X-ray diffraction patterns for nickel and copper deposits

TABLE VIII: Effects of operating parameters on alloy deposition characteristics

Bath: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 50 g/l; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30 g/l;
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 12 g/l; H_3BO_3 30 g/l;
 $\text{Na}_2\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ 50 g/l; Saccharin 5 g/l; 305 K

Current density A/dm ²	Solution pH	Temp K	Agitation	Cu in deposit (%)	Current Efficiency of deposit (%)	Appearance of deposit
0.25	9	305	—	67	79	CC
0.50	9	305	—	54	82	"
0.75	9	305	—	35	82	GW
1.00	9	305	—	33	83	"
1.50	9	305	—	25	85	"
1.00	9	305	MG	71	86	CC
1.00	9	305	VA	90	88	"
1.00	9	318	—	34	85	GW
1.00	9	330	—	50	86	CC

MG — Mild agitation; VA — Vigorous agitation;
 CC — Coppery coloured; GW — Greyish white

TABLE IX: Microhardness of nickel-copper alloy deposits

Copper content of alloy (%)	Alloy deposit microhardness V ₅₀
0	362
12	376
28	391
37	424

indicating the crystalline nature of the deposits. The patterns are similar to those for nickel but the peaks are seen slightly shifted along the 2θ axis. This indicates the existence of nickel-copper alloy as a solid solution. Proper indexation of the diffraction peaks [23] gives average 'a' values (Table X) of 3.5390 Å and 3.5665 Å respectively for nickel-copper alloys with 29% and 37% copper, the values being intermediate between those reported (22,24) for nickel (3.515 Å) and 21% nickel - 79% copper alloy (3.5950 Å).

CONCLUSION

A suitable bath composition consisting of nickel sulphate, nickel chloride, copper sulphate, boric acid, trisodium citrate and saccharin has been identified for producing smooth, uniform looking and adherent nickel-copper alloy deposits.

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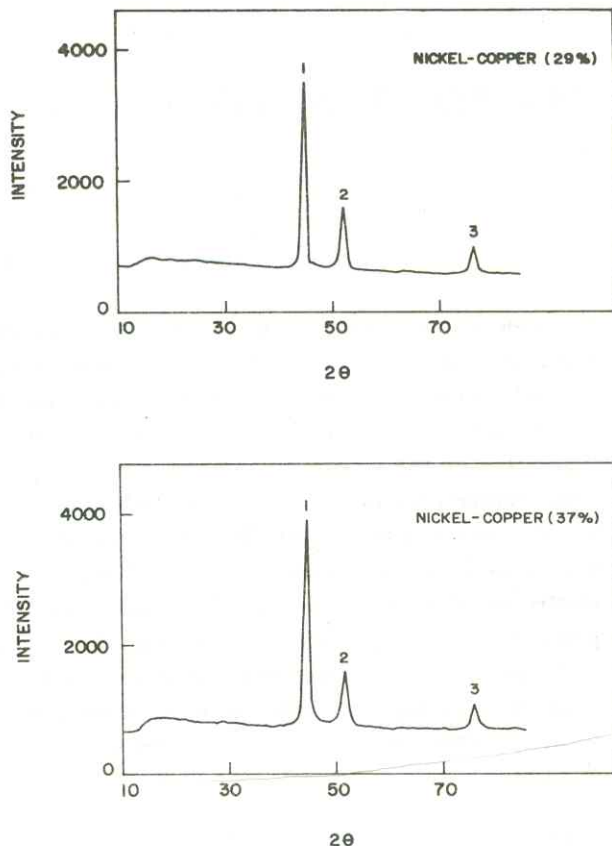


Fig. 9: X-ray diffraction patterns for nickel-copper alloy deposits

TABLE X: Data on XRD analysis

Cu content of alloy (%)	Miller indices h k i	2θ	d	I/I ₀	a ⁰ (Å)
29	1 1 1	44.300	2.043	100	3.5386
	2 0 0	51.600	1.770	46	3.5400
	2 2 0	76.000	1.251	28	3.5385
37	1 1 1	43.900	2.061	100	3.5698
	2 0 0	51.200	1.783	40	3.5660
	2 2 0	75.400	1.260	27	3.5638

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