Pulsed electrodeposition of cobalt and nickel alloy

M. Subramanian*, N. Dhanikaivelu and R. Rama Prabha

The pulsed electrodeposition method was applied for the preparation of Co and Co–Ni alloy. Pulse duty cycles of 5 to 80% at frequencies 10 to 100 Hz with current densities ranging from 2·5 to 7·5 A dm^{-2} were employed. The influence of pulse current density, duty cycle and frequency on the thickness and hardness of the Co and Co–Ni deposit were studied. Corrosion resistance of Co and Co–Ni alloy is compared in the present paper.

Introduction

Ni–Co alloys find applications in a variety of high technology application because of their unique properties: magnetic,[1,2] wear resistance,[3] heat conductivity,[4,5] and electrocatalytic properties.[6,7] These properties are directly related to alloy composition and structure.[8–14] A literature survey indicates that limited systematic work has been carried out in electrodeposition of Co and Co–Ni alloy. Among the few studies published Co electrodeposition has been reported from fluoroborate,[15] nitrate,[16] chloride[17,18] and sulphamate baths.[19] In all these studies only direct current is used. Pulsed current electrodeposition has received much attention in recent years in order to improve the mechanical and chemical properties of the deposit. The advantages of pulse plating are numerous and include the reduction in porosity,[20] lower gas content,[21] high purity, fine grained deposits and deposits having low electrical resistance and good corrosion resistance.[22–26]

In direct current plating, only one parameter is variable, the current or potential. In pulse plating an interrupted current or potential is used. The current may or may not drop to zero between pulses. Three parameters are independently variable in practical pulse plating; pulse current, pulse on time and pulse off time which determine the physical characteristics of the deposits obtained from the given electrolyte. Pulse plating improves the current distribution[25–27] altering the prevailing mass transport conditions[28–31] controlling the microstructure, increasing brightness and decreasing porosity, internal stress and impurities.[32] Kautek et al.[33] have reported decrease in hardness with increasing off time. Suarez et al. were able to improve the throwing power of silver deposit by increasing the off time.[34]

In the present study, a systematic investigation of Co and Co–Ni alloy has been undertaken with the application of square wave pulse. The influence of pulse conditions on the current efficiency, hardness and corrosion resistance have been studied in detail.

Central Electrochemical Research Institute, Karaikudi 630006, India

*Corresponding author, email sanjnamohan@yahoo.com

Experimental

Electrolytes consisting of 0·3 to 0·6M CoSO$_4$, 0·3M boric acid, 0·05M ammonium sulphate and 0·15M NiSO$_4$ were used for the study. The pH of the bath was maintained between 2·5 and 3 using a Testronix pH meter. Temperature of the bath was maintained using a constant temperature thermostat. All the experiments were carried out for 30 min at 45°C. The solutions were freshly prepared using doubly distilled water and Analar grade chemicals. Electrodeposition of Co and Co–Ni alloy on copper cathodes (20 cm^2 area) was carried out using direct current and pulse current. For pulse plating a KRAFT Dynatronix (USA) pulse plating unit model DPR 20-10-5 was used. Surface morphological examinations were carried out by employing a Hitachi S 3000 H scanning electron microscope (SEM). Graphite (from Graphite India) was used as anode for Co deposition and a Ni anode (from Inco Nickie) was used to replenish Ni in Ni–Co deposition.

The procedure for alloy plating consisted of the following sequence of operations:

   (i) mechanical finishing
  (ii) solvent degreasing
 (iii) acid cleaning
 (iv) tap water washing
  (v) rinsing in demineralised water
 (vi) plating
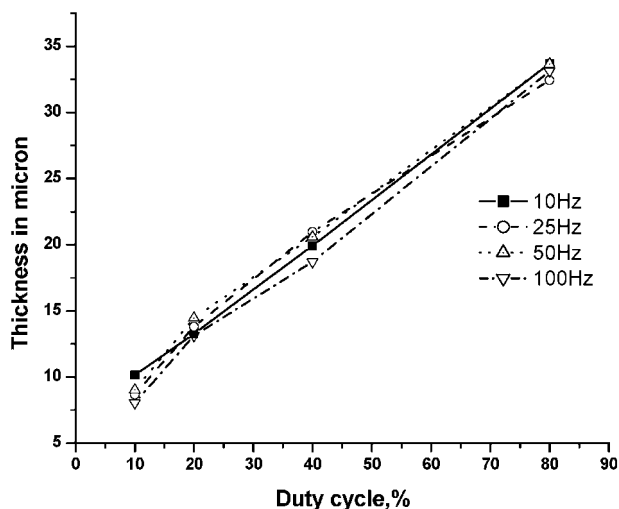 (vii) washing
(viii) rinsing.

Mechanical finishing

All the specimens were mechanically finished by buffing and polishing. It is important that the operation of finishing was carried out with materials and procedure that were compatible with subsequent plating operations. Thus, before selecting mechanical finishing operations and materials, they were carefully assessed for possible effects during lathe finishing operations.
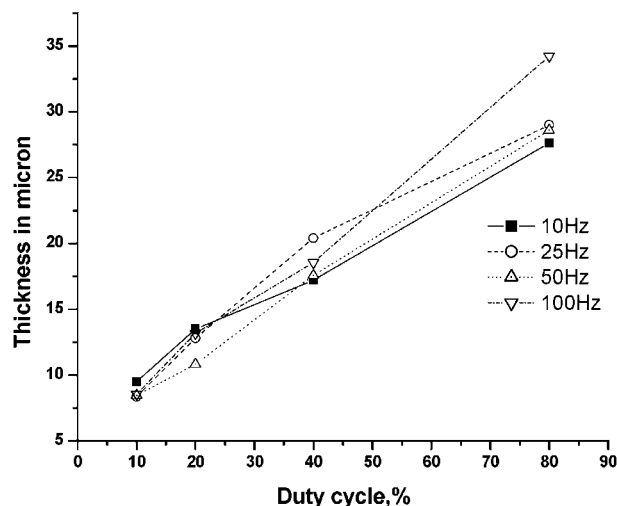
Solvent degreasing

The surface was wiped clean of soils, oils, grease, buffing compounds by a sponge soaked in trichloroethylene.

1 Effect of pulse duty cycle on thickness of Co deposits at 0·6M CoSO$_4$.7H$_2$O

2 Effect of pulse duty cycle on thickness of Co deposits at 0·3M CoSO$_4$.7H$_2$O

The wiping was carried out in one direction to completely remove the soil from the surface.

Acid etching

Acid etching was carried out to remove naturally formed oxide film, and some of the polishing compound, grease, still adhering over the surface, in an acid solution containing 10%HCl for 40 s.

Studies of SEM

Surface morphological examinations were carried out by employing a Htachi 3000H SEM.

X-ray fluorescence spectroscopy (XRF) studies

X-ray fluorescence spectroscopy provides a means of identification of an element by measurement of its characteristic X-ray emission wavelength or energy. This method allows the qualification of a given element by first measuring the emitted characteristic line intensity and then intensity to elemental concentration.

The intensities of the characteristic lines can then be used to calculate concentrations of the various elements present.

The composition of the Co–Ni coatings were examined using an Horiba XRF instrument (model XGT-2700)

X-ray diffraction (XRD) studies

Structural characterisation of the deposit was carried out by XRD using a Phillips Diffractometer Cu K_α (2·2 kW Max) as source.

Surface roughness studies

Surface roughness of the deposit was measured using a Surftest SJ-301 surface roughness tester (Mitutoyo, Japan). The Surftest SJ-301 is a stylus type surface roughness measuring instrument. The stylus of the SJ-301 detector unit traces the minute irregularities of the electrodeposited surface. Surface roughness is determined from the vertical stylus displacement produced during the detector traversing over the surface irregularities. The measurement results are displayed digitally/graphically. The R_a value gives the average roughness of the surface in micrometres.

Electrochemical polarisation studies

These were carried out with the advanced electrochemical system PARSTAT 2273 (Princeton Applied Research, USA) by fixing the potential $+250$ mV from open circuit potental (OCP) and -250 mV from OCP at a sweep rate of 5 mV s^{-1}. The electrochemical experiments utilised a standard three electrode cell. Copper was used as working electrode, platinum as counter electrode and saturated calomel electrode as referance electrode. All potentials are measured with reference to saturated calomel electrode. This method of calculating corrosion resistance is known as the Tafel extrapolation method.

The Tafel calculation gives access to the corrosion current regularly present at the surface of a metal which is in contact with a corroding solution. The corrosion is expressed in loss of metal thickness per year.

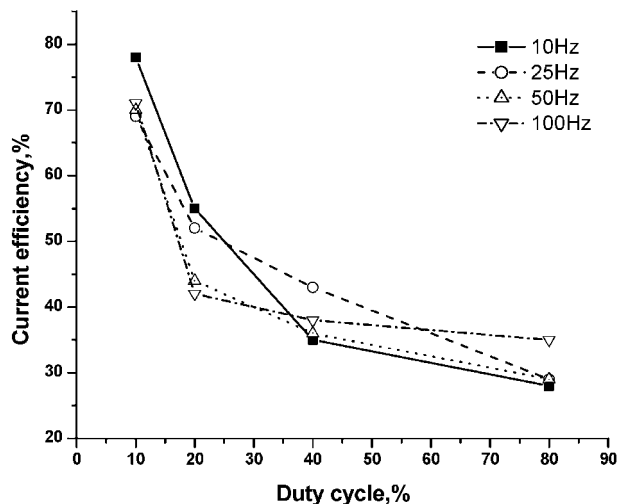The thermodynamical b_a and b_c parameters of the Butler Volmer equation were also determined.

A voltammetric curve log i versus potential can be processed according to the Tafel method. The Tafel method also gives access to other corrosion parameters such as the zero current potential (corrosion potential), the corrosion current and the polarisation resistance of the sample under study. The Tafel calculation is a complete tool to study the corrosion process at a metal surface.
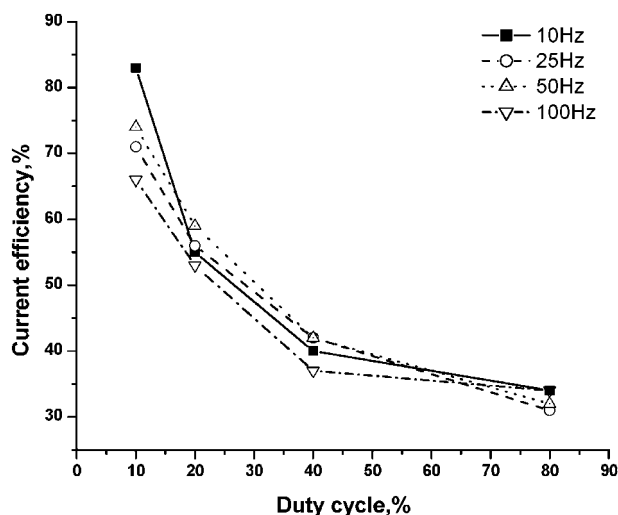
Results and discussion

Effect of duty cycle on thickness of Co deposits

Figures 1 and 2 show the effect of pulse duty cycle on the thickness of the Co deposits obtained at various frequencies. From the data it is observed that the thickness of the Co increases with increase in pulse duty cycle. As duty cycle increases current on time increases and off time decreases. Hence the thickness increases as duty cycle increases. At lower duty cycle, the peak current is flowing for lesser time and also ionic mobility and rate of deposition are less compared to those at higher duty cycle.

Maximum thickness is obtained at 80% duty cycle for higher frequencies (50 and 100 Hz). The same trend is observed when Co concentration is increased from 0·3 to 0·6M (Fig. 2).
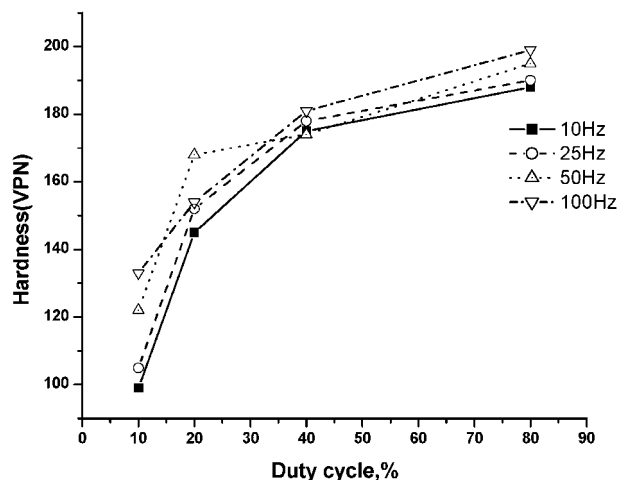
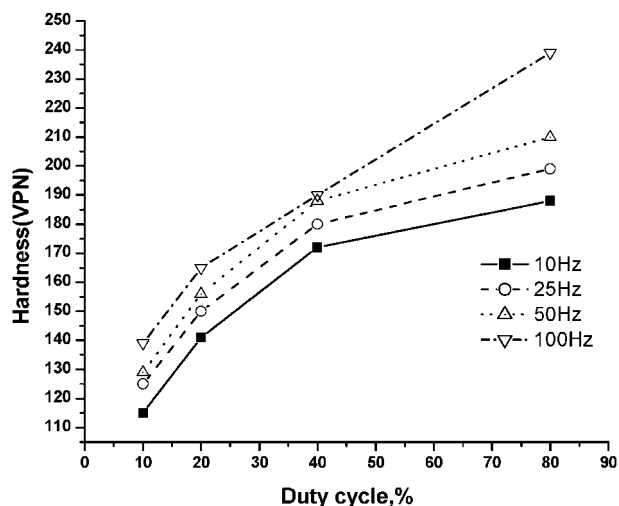3 Effect of pulse duty cycle on current efficiency of Co deposits at 0·3M CoSO₄

5 Effect of pulse duty cycle on hardness of Co deposits at 0·3M CoSO₄

4 Effect of pulse duty cycle on current efficiency of Co deposits at 0·6M CoSO₄

6 Effect of pulse duty cycle on hardness of Co deposits at 0·6M CoSO₄

Effect of pulse duty cycle on current efficiency of Co deposits

The current efficiency decreases when the duty cycle increases from 10 to 80%. This indicates that at lower duty cycles the current efficiency is higher. As the pulse duty cycle increases current efficiency decreases. In pulsed deposition, although the average current is similar to that in dc deposition, the corresponding peak currents are higher when the current is 'on'. Such higher curre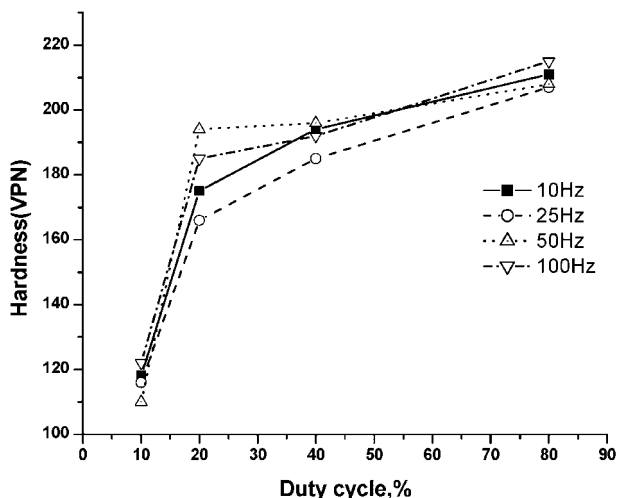nts favour more hydrogen evolution leading to a reduction in current efficiency.[35] This is because the rate of nucleation is also faster at lower duty cycle. In pulse plating, since the pulse current density is usually considerably higher than the corresponding dc density, the population of adatoms on the surface during pulse deposition is higher than during dc deposition resulting in increased nucleation rate.[36] When the duty cycle was increased the on time was also increased and this interferes with the formation of new nuclei. The same behaviour was seen when the concentration of Co varied from 0·3 to 0·6M. The results are given in Figs. 3 and 4.

Table 1 Pulse parameters used for pulse plating of Co and Co–Ni alloy

Duty cycle, %	Pulse frequency and pulse on–off times, ms				Current density, A dm⁻²	
	10 Hz	25 Hz	50 Hz	100 Hz	Peak	Average
5	5–95	2–38	1–19	0·5–9·5	40	2
10	10–90	4–36	2–18	1–9	20	2
20	20–80	8–32	4–16	2–8	10	2
40	40–60	16–24	8–12	4–6	5	2
80	80–20	32–8	16–4	8–2	2·5	2

%duty cycle = (on time/total time) × 100; average current = (on time × peak pulse current)/total time; peak current = average current/duty cycle.

7 Effect of pulse duty cycle on hardness of Co–Ni deposits at 0·6M Co and 0·15M Ni

Effect of pulse duty cycle on hardness of Co deposit

The hardness of Co deposits increases when the duty cycle increases from 10 to 80%. The results are depicted in Figs. 5 and 6. As pulse frequency increases, the hardness is found to increase. During short pulses at higher frequency, a very thin pulsating diffusion layer is formed which leads to enhanced nucleation rates. The reason for a thin pulsating diffusion layer is believed to be that in the immediate vicinity of the cathode the concentration pulsates with the frequency of the pulsating current, decreasing during the pulses and relaxing in the interval between them. Thus, a pulsating diffusion layer exists close to the cathode. If the duration of pulse is short, the diffusion layer does not have time to extend very far into the solution and in particular does not extend to the region where convection takes over the mass transport.[36]
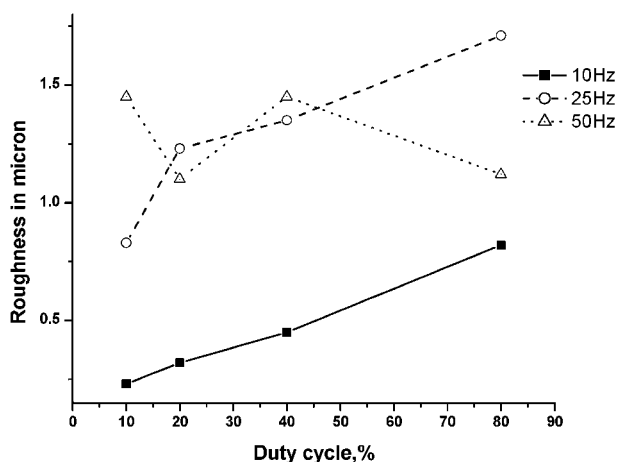
Surface coverage with denser build-up of the fine grained deposits which leads to lower porosity and correspondingly higher hardness values is obtained. Maximum hardness is obtained at a frequency of 100 Hz when the duty cycle is 80%. A similar trend is observed when the concentration of Co is increased to 0·6M.

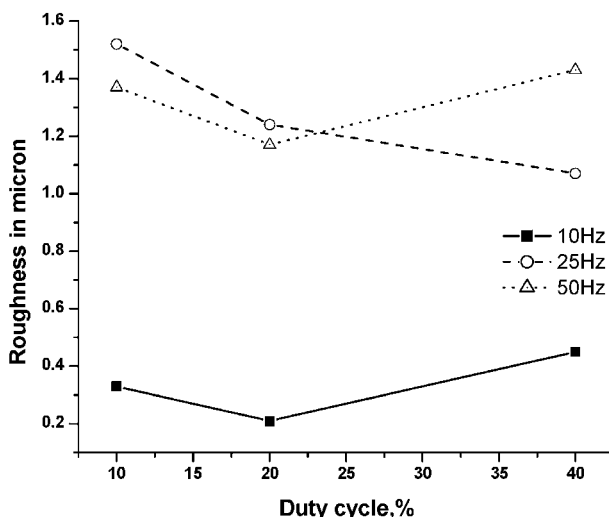## Effect of pulse duty cycle on hardness of Co–Ni alloy

The authors were able to obtain Co–Ni alloy deposits with hardness value of 211 HV at 80% duty cycle. The hardness of Co–Ni alloy is higher than that obtained without Ni. The results are presented in Fig. 7.

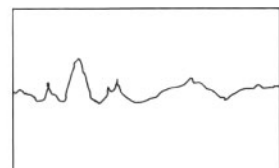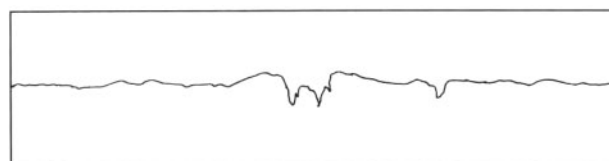

8 Effect of pulse duty cycle on roughness of Co at 0·6M

9 Effect of pulse duty cycle on roughness of Co–Ni alloy

Roughness on Co at 0.6 M

Roughness on Co - Ni alloy at 0.6 M

10 Surface profilograms of Co–Ni alloy and Co

Table 2 Effect of pulse duty cycle on thickness of Co–Ni alloy at 0·6M Co sulphate

Pulse duty cycle	Thickness, μm		
	10 HZ	25 Hz	50 Hz
10	12	11	14
20	11	17	12·5
40	16·5	10·5	14
80	28	16·2	12·3

Table 3 Effect of pulse duty cycle on roughness of Co–Ni alloy at 0·6M Co sulphate

Pulse duty cycle	Roughness, μm		
	10 HZ	25 Hz	50 Hz
10	0·23	0·83	1·45
20	0·32	1·23	1·1
40	0·45	1·35	1·45
80	0·82	1·71	1·12

1: blank Cu; 2: Co–Ni (dc); 3: Co (pulsed current); 4: Co–Ni (pulsed current)

11 Polarisation studies of different alloys in 3·5% w/v NaCl

Effect of pulse duty cycle on thickness of Co–Ni alloy at o·6M CoSO$_4$

As the pulse duty cycle is increased from 10 to 80% the thickness of alloy deposit increases. The results are given in Table 2.

Table 4 Effect of duty cycle on percentage composition of Co–Ni alloy

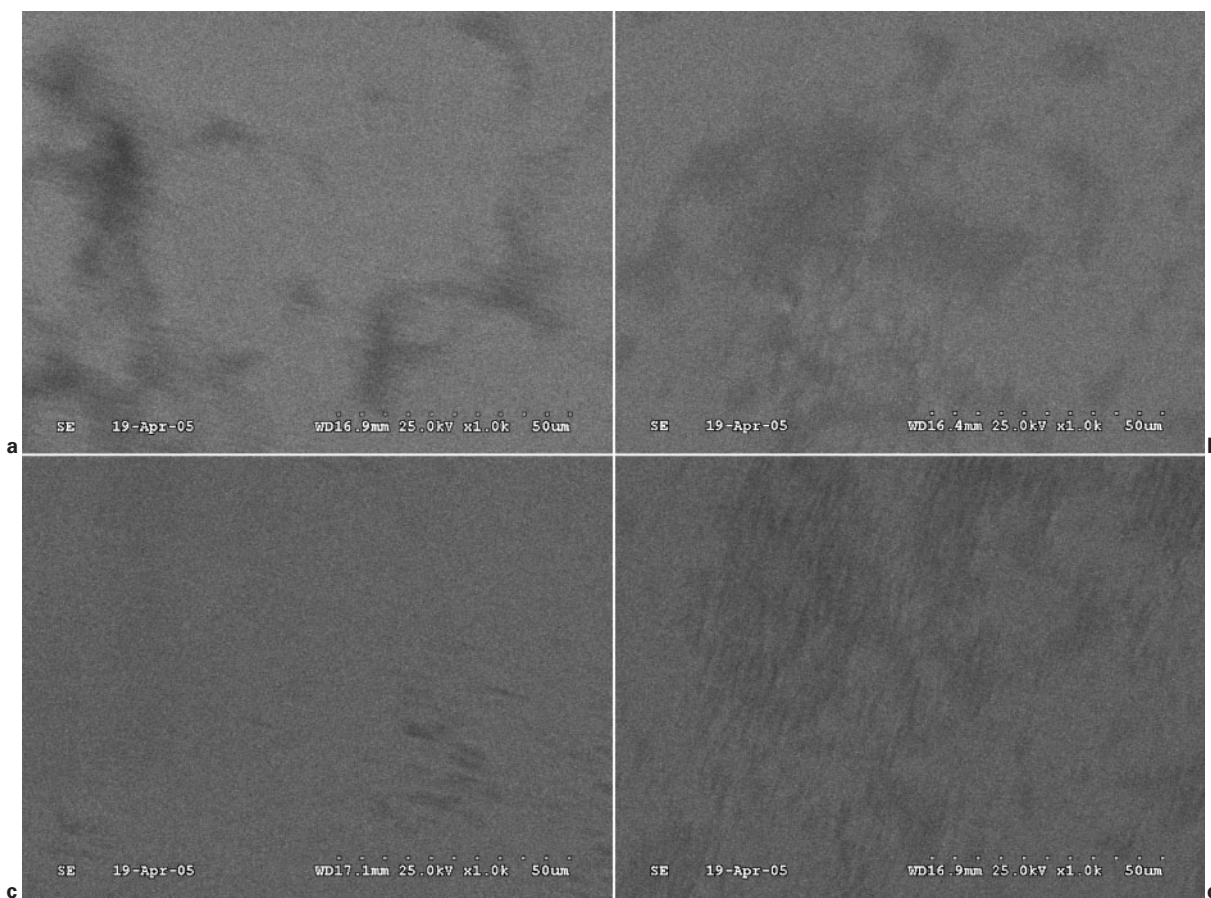| Pulse duty cycle	10 Hz		25 Hz		50 Hz		100 Hz	
	Co	Ni	Co	Ni	Co	Ni	Co	Ni
10	85·70	14·20	82·35	17·64	80·00	20·00	75·29	24·70
20	82·50	17·44	79·30	20·68	75·86	24·10	70·58	29·41
40	78·82	21·17	75·90	24·09	72·94	27·05	65·55	34·40
80	75·29	24·70	72·41	27·58	69·76	30·23	65·55	35·40

Effect of pulse duty cycle on roughness of Co–Ni alloy deposit

Smooth deposits were obtained at lower duty cycle and lower frequency. As the duty cycle and frequency increases the roughness also increases. The same trend is maintained when Co is deposited alone. The results are given in Table 3 and Figs. 8 and 9.

The surface profilograms of Co–Ni alloy and Co are given in Fig. 10.
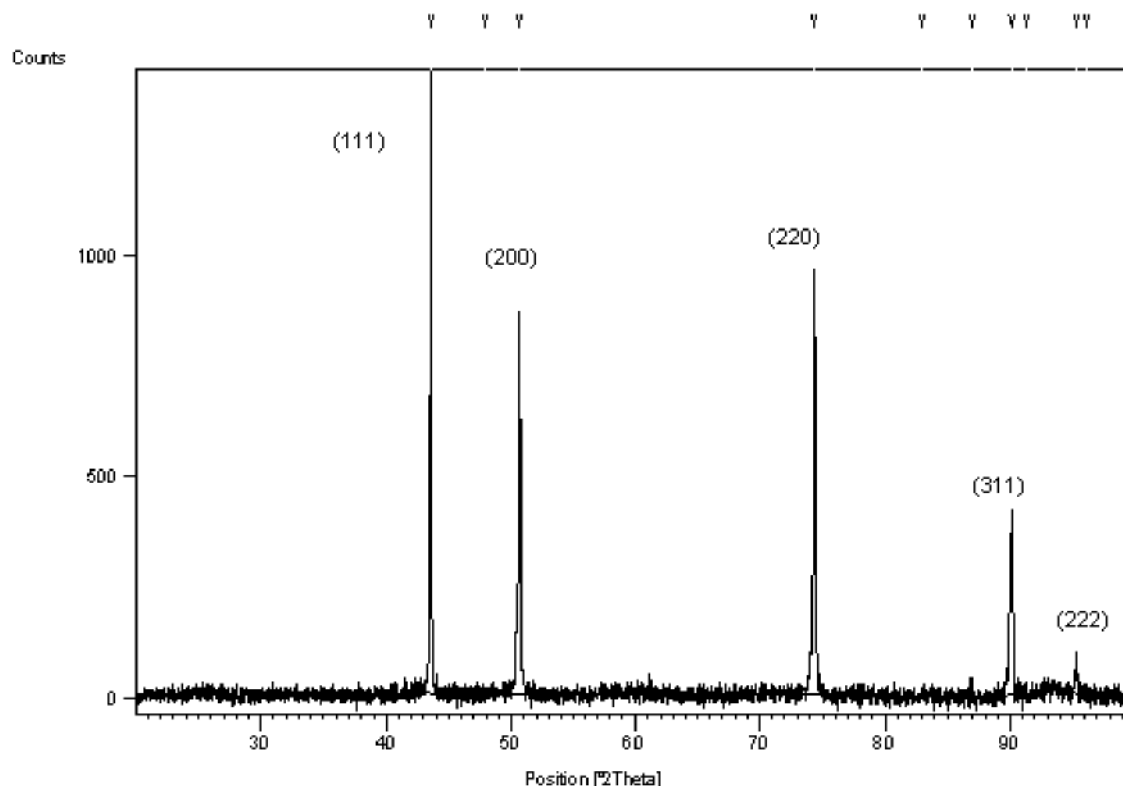
Effect of pulse duty cycle on percentage composition of Co–Ni alloy

Analysis of the deposit using XRF indicates that the percentage of Co is higher than Ni under all of the plating conditions. This is expected because Co–Ni is an anomalous type of deposition. Anomalous deposition is characteristic of a system where the less noble metal is deposited preferentially. In the case of Co–Ni, Co being less noble is preferentially deposited. The results are given in Table 4.

12 Scanning electron micrographs of *a* Co deposition at 0·3M *b* Co deposition at 0·6M, *c* Co–Ni deposition at 0·3M and *d* Co–Ni deposition at 0·6M

13 X-ray diffractogram of Co–Ni alloy at 10% duty cycle

Corrosion resistance of dc and pulse plated Co–Ni alloy

Corrosion resistances of Co and Co–Ni alloy were compared by electrochemical polarisation studies. The results are given in Fig. 11 and Table 5. From the table it is seen that Co–Ni alloy shows higher corrosion resistance than Co. This is probably because by using pulse current finer grained compact and less porous deposits tend to be obtained than by using dc current.

SEM studies

Images of SEM pulse plated Co and Co–Ni are given in Fig. 12. These show that smooth, compact and fine grained deposits were obtained when pulse current was used.

Studies of XRD

The results show that the alloy exhibits face centred cubic structure and (111) growth orientation with significant (200), (220) and (311) reflections as well. The results are given in Fig. 13. Grain sizes were determined using Scherrer's formula

$$D = 0.9\lambda / B\cos\theta$$

where D is the grain size, B is the broadening of the diffraction line measured at half of its maximum intensity in radians, θ is the diffraction angle and λ is the X-ray wavelength (1.5406 Å) used. The calculated average grain size is 1.59 to 3.59 nm; the higher grain size is attributed to preferred orientation along (220) plane.

The preferred growth orientation was determined using texture coefficient TC_{hkl}. This factor can be calculated by using

$$TC_{hkl} = \frac{I/I_0}{1/N\{\sum [I/I_o]\}}$$

where TC_{hkl} is the texture coefficient of the plane, I_{hkl} is the measured intensity of the (hkl) plane, $I_{o(hkl)}$ corresponds to the recorded intensity in the JCPDS data file and N is the number of preferred directions of the growth. The TC_{111} was found to be 0.659. This indicates that the Co–Ni film has strong reflex along (111).

Conclusions

Based on the above studies it can be concluded that a maximum current efficiency of 83% in Co–Ni deposition is obtained at 10% duty cycle and smooth fine grained deposits are obtained at the lower duty cycle. The percentage composition of Co is higher than Ni in all the conditions because it is an anomalous type of deposit. Co–Ni alloy has a better corrosion resistance in these studies than Co alone.

Table 5 Corrosion studies

Substrate	Condition	E_{Corr}, mV	I_{Corr}	Corrosion rate, mpy
Copper		−201.1	5.027 mA	2.253
Co–Ni on Cu	dc 2 A dm^{-2}	−478.7	12.08 mA	5.070E-3
Co on Cu in pulse current	Pulse 2 A dm^{-2}, 20% duty cycle	−419	1.748 mA	733.1 E-3
Co–Ni on Cu in pulse current	2 A dm^{-2}, 20% duty cycle	−478.8	781.7 nA	327.7 E-3

References

1. F. Prasal: US patent 3 274 079, 1966; *Chem. Abstr.*, 1967, **66**, 16032k.
2. F. Friemel: East German patent 52 869, 1966; *Chem. Abstr.*, 1967, **67**, 17376h.
3. M. Jato: Jpn patent 74 33723, 1974; *Chem. Abstr.*, 1975, **82**, 91774n.
4. S. Ichioka and T. Koda: Jpn patent 75 02377, 1975; *Chem. Abstr.*, 1975, 83, 87387s.
5. V. B. Singh and V. N Singh: *Plat. Surf. Finish.*, 1976, **63**, (7), 34.
6. C. C. Hu and C. Y. Weng: *J. Appl. Electrochem.*, 2000, **31**, 499.
7. C. C. Hu and A. Bai: *J. Appl. Electrochem.*, 2001, **31**, 565.
8. F. Maurel, B. Knosp and M. Backhaus-Ricoult: *J. Electrochem. Soc.*, 2000, **147**, 78.
9. C. C. Wang, K. S. Goto and S. A. Akbar: *J. Electrochem. Soc.*, 1991, **138**, 3673.
10. W. Schwarzacher and D. S. Lashmore: *IEEE Trans. Magn.*, 1996, **32**, 3133.
11. S. S. Djokic and M. D. Maksimovic: in 'Modern aspects of electrochemistry', (ed. J. O'M Bockris), No. 22, 417; 1992, New York, Plenum Press.
12. T. Osaka: *Electrochem. Acta*, 1999, **44**, 3855.
13. T. Osaka, M. Takai, K. Ohashi, M. Saito and K. Yamada: *Nature*, 1998, **392**, 796.
14. E. M. Kakuno, D. H. Mosca, I. Mazzaro, N. Mattoso, W. H. Schreiner, M. A. B. Gomes and M. P. Cantao: *J. Electrochem. Soc.*, 1997, **144**, 3222.
15. K. M. Yin: *J. Electrochem. Soc.*, 1997, **144**, 1560.
16. E. Beltowska-Lenman and A. Riesenkampf: *Surf. Technol.*, 1980, **11**, 349.
17. Y. M. F. Marikar and K. I. Vasu: *Chem. Era*, 1970, **6**, 5.
18. G. Sotirova, I. Petrova and S. Amryanov: *Galvanotech. Sym.*, 1985, **7**, 382.
19. S. I. Berezian. R. M. Sageeva. L. G. Sharapova and V. G. Shtyrlin: *Zashch. Met.,* 1986, **22**, 267.
20. J. Scoyer and R. Winand: *Surf. Technol.*, 1977, **5**, 169.
21. T. Shimada: Jpn patent 62 19979, 1987.
22. Y. Y. Wang, C. S. Tung and C. C. Wan*: Met. Finish.*, 1980, **78**, (9), 21.
23. C. A. Snavely: *Trans. Electrochem. Soc.*, 1947, **92**, 537.
24. N. Ibl: *Surf. Technol.*, 1980, **10**, 81.
25. C. J. Raub and A. Knodler: *Plat. Surf. Finish.*, 1978, **65**, (9), 32.
26. N. M. Osero: *Plat. Surf. Finish.*, 1986, **73**, (3), 20.
27. N. Masuko, T. Osaka and Y. Ito (eds.): 'New trends and approaches in electrochemical technology'; 1996, New York, John Wiley & Sons.
28. S. I. Kwak, K. M. Jeong, S. J. Kim and H. J. Sohn: *J. Electrochem. Soc.*, 1996, **143**, 2770.
29. N. Ibl: *Surf. Technol.*, 1980, **10**, 81–104.
30. D. T. Chin: *J. Electrochem. Soc.*, 1983, **130**, 1657.
31. M. Datta and D. Landolt: *Surf. Technol.*, 1985, **25**, 97.
32. H. Y. Cheh: *J. Electrochem. Soc.*, 1971, **118**, 551.
33. M. Halmdienst, W. E. G. Hansal, G. Kaltenhauser and W. Kautek: *Trans. IMF*, 2007, **85**, (1), 22.
34. C. Suarez, E. Chavez, J. A. Diez, H. Grande and R. Guixa: *Trans. IMF*, 2007, **85**, (1), 46.
35. G. Devaraj: *Plat. Surf. Finish.*, 1996, **83**, (6), 62.
36. J. C. Puippe and F. Leaman (eds.): 'Theory and practice of pulse plating', 1st edn, 1–247; 1986, Orlando, FL, AESF.
37. B. Subramanian, S. Mohan and S. Jayakrishnan: *Surf. Coat. Technol*, 2006, **201**, 1145.