Journal of Applied Electrochemistry **31**: 579–583, 2001.

Effect of pyridine and its derivatives on the electrodeposition of nickel from aqueous sulfate solutions
Part I: Current efficiency, surface morphology and crystal orientation

U.S. MOHANTY[1], B.C. TRIPATHY[2], P. SINGH[2]* and S.C. DAS[1]
[1]*Hydro and Electrometallurgy Division, Regional Research Laboratory (CSIR), Bhubaneswar 751 013, India*
[2]*Department of Chemistry, Murdoch University, South Street, Murdoch, WA 6150, Australia*
*(*author for correspondence)*

Received 21 September 2000; accepted in revised form 19 December 2000

Key words: crystal orientation, current efficiency, deposit morphology, electrodeposition, nickel, picoline, pyridine

Abstract

The effects of pyridine and its derivatives on current efficiency, surface morphology and crystallographic orientations of electrodeposited nickel from acidic sulfate solutions were investigated. The results indicated that the presence of pyridine and picolines had no significant effect on current efficiency. The deposits obtained were smoother, more compact and uniform with picolines than with pyridine. A significant change in surface morphology of the electrodeposits was observed and picolines were found to be better additives than pyridine, 4-picoline being the best. X-ray diffraction revealed that the (200) plane was the most preferred plane and was not affected by the presence of any of these additives in the electrolyte.

1. Introduction

The physical and chemical properties of nickel electrodeposits are affected by the presence of various metallic impurities in the electrolyte [1–5] augmenting simultaneous evolution of hydrogen during nickel ion electroreduction from aqueous solutions [6]. Hydrogen evolution, which is an unwanted reaction during nickel electrodeposition, decreases the cathodic current efficiency (CE) apart from occluding hydrogen into the nickel deposit thereby increasing the internal stress and producing pitted deposits.

Various organic additives are added to the nickel electrolyte to produce bright, levelled and compact deposits [7, 8]. Costavaras et al. [9] studied the effect of some acetylenic and aryl-sulfonic compounds and found that the textures of nickel deposits are related to the nature of unsaturation present in the molecule, which also influences the magnitude of the additive activity. Epelboin et al. [10] and Kaneko et al. [11, 12] have reported the influence of saccharin and aliphatic alcohols and their inhibiting effects on the electrocrystallisation of nickel from a Watts bath. Miluskin [13] demonstrated that thiosemicarbazide derivatives significantly improved the quality of the electrodeposited nickel producing bright and mirror like surfaces with fine crystals. Gao and co-workers [14] studied the effect of 2-butyne-1,4-diol and three other compounds of different oxidation states of sulphur, namely sodium benzene sulphonate, sodium benzene sulphinate and thiosalicyclic acid on the electroreduction of nickel from a Watts bath. They reported that these compounds inhibit electrocrystallization of nickel by adsorbing on the cathode surface.

Pyridine and its derivatives act as corrosion inhibitors [15–17] and levelling agents [18–20]. Volkova [21] studied the adsorption of cationic pyridine derivatives on the dropping mercury electrode. Shimazu et al. [22] observed that bright nickel deposits could be obtained from the solutions containing substituted (hydroxy, formyl and cyano) pyridines together with saccharin. Several workers, including the present authors [23–27], have used pyridine as the cathode polarizer and grain refiner during zinc electrodeposition from acidic sulfate solutions. A decrease in CE during zinc electrodeposition from acidic sulfate solutions in the presence of 2-picoline, 2-cyanopyridine and 4-ethyl pyridine has been reported [26, 27]. Thus pyridine and its derivatives are considered as potential organic additives for metal electrodeposition processes.

This paper reports the effects of pyridine and its derivatives, 2-picoline and 4-picoline on the cathodic CE, surface quality, deposit morphology and the crystallographic orientation of nickel obtained by electrodeposition of nickel from acidic sulfate solutions.

2. Experimental details

2.1. *Apparatus and material*

Nickel electrodeposition was carried out in a rectangular flow cell of dimension 13.2 cm × 8 cm × 6 cm made from Perspex, consisting of separate cathodic and anodic compartments each of dimensions 9 cm × 4 cm × 2 cm separated by a microporous Daramic separator. The cathode and anode, each of area 20 cm^2, were fitted to the respective compartments. Then the two halves with the separator in between were clamped together using Viton O-rings. The anolyte and catholyte were circulated into their respective compartments by separate peristaltic pumps (Cole–Parmer Instrument Company, Australia, model 7553–75) through inlet and outlet ports made from Teflon. One extra port had been provided to each compartment to connect a reference electrode for measuring cathodic and anodic potentials.

2.2. *Reagents*

The nickel electrolyte was prepared from analytical grade nickel sulfate ($NiSO_4 \cdot 6\ H_2O$), sodium sulfate ($Na_2SO_4 \cdot H_2O$). Sulfuric acid (H_2SO_4) was used to adjust the electrolyte pH. Pyridine, 2-picoline and 4-picoline were from Aldrich. All the solutions were prepared from ultra-pure Millipore water (Millipore Milli Q system).

2.3. *Electrode preparation*

For electrodeposition and polarisation studies the surface of the electrode prior to nickel electrodeposition was polished with 400 and then 1200 grade silicon carbide paper and then rinsed with 1 M HCl followed by ultra pure water.

2.4. *Electrolysis*

All the electrodeposition experiments were conducted for 2 h at a current density of 200 A m^{-2} by applying current from a regulated power supplier (0–30 V, 5 A, d.c. power supply, Dick Smith Electronics). A precision voltmeter and ammeter were placed in the cell circuit to record the potentials and current. The flow rate of the electrolyte was maintained at 1.8 $dm^3\ h^{-1}$. A thermostat (Grant Selby's, Australia) was used for maintaining the electrolyte temperature at 60 ± 1 °C. The pH of the electrolyte containing 1.02 M $NiSO_4$ and 0.08 M Na_2SO_4 was maintained at 2.5 using dilute H_2SO_4. Stainless steel and lead–antimony (1–5%Sb) were used as cathode and anode, respectively. All the potentials were measured against a saturated calomel electrode (SCE). After electrolysis, the cathode was removed from the cell and thoroughly washed with water and dried. The cathodic current efficiency was calculated from the weight gained by the cathode following electrolysis.

2.5. *Deposit examination*

A Philips PW 1030 X-ray diffractometer was used to examine the nickel deposits to determine their preferred crystal orientations relative to the ASTM standard nickel. The surface morphology of the deposit was examined by scanning electron microscopy (SEM) using a Philips XL20 SE microscope.

3. Results and discussion

3.1. *Nucleation overpotential for nickel electrodeposition*

Nucleation overpotential (NOP) of nickel electrodeposition on stainless steel substrate was determined by using the technique as reported earlier [28]. The pyridine and picolines were found to have a strong effect on the NOP of nickel electrodeposition on stainless steel which shifted towards more negative potentials with increasing additive concentration (Table 1 and Figure 1) in the order 4-picoline > 2-picoline > pyridine. This can be explained in terms of the relative adsorption of these bases on the surface of the electrode. The presence of the conjugative and inductive electron-releasing methyl group in the ring makes picolines slightly more basic than pyridine (pK_b: pyridine 8.59, 2-picoline 8.15, 4-picoline 7.92) [29]. At the working pH of 2.5 all these bases will exist almost exclusively in the protonated form. The order of strengths of adsorption 4-picoline > 2-picoline > pyridine can be rationalized on the basis of the conjugate acids losing a proton after migrating to the electrode surface and becoming adsorbed as the free bases. The adsorption order is the same as the order of base strengths and of localised negative charge on the nitrogen atoms. An additional factor weakening 2-picoline as an absorbent relative to 4-picoline is the presence of the sterically demanding methyl group *ortho* to the nitrogen atom.

3.2. *Nickel electrodeposition potential and current efficiency*

The presence of pyridine, 2-picoline and 4-picoline had very marginal effect on the nickel electrodeposition potential which occurred at −860 ± 5 mV. The CE was also not significantly affected except for the most strongly adsorbed 4-picoline where a 4% decrease was observed at 40 mg dm^{-3} of the additive (Table 1). The decrease in the CE could be attributed to the relative adsorption of the additives, which block the active sites of the cathode surface inhibiting the electrocrystallization of nickel.

3.3. *Surface quality of the nickel electrodeposits*

The pyridine and picolines showed a marked effect on the surface quality of the metal electrodeposits. The

Table 1. Effect of pyridine and picolines on current efficiency, nucleation overpotential and crystallographic orientations

[Additives] /mg dm^{-3}	CE /% (±1%)	NOP /mV (±5 mV)	Crystallographic orientation (*h k l*) Relative peak intensities (I/I_{max})/%			
			(1 1 1)	(2 0 0)	(2 2 0)	(3 1 1)
Pyridine						
0	96	−166	67	100	–	–
2	96	–	40	100	81	69
5	95	–	40	100	67	61
10	95	−190	21	100	2	3
20	95	−212	34	68	100	95
40	94	−242	38	100	82	54
2-picoline						
2	96	–	31	100	4	15
5	95	–	49	100	3	11
10	95	−206	37	100	47	71
20	95	−214	39	100	2	4
40	94	−246	33	100	4	12
4-picoline						
2	96	–	42	100	1	4
5	95	–	32	100	1	4
10	95	−208	40	100	1	2
20	95	−226	42	100	1	2
40	92	−256	34	100	10	33

additives, which adsorb on the electrode surface, are well known to have such an effect [26–28, 30–33]. While the deposit remained almost smooth and uniform up to 5 mg dm^{-3} of pyridine the deposit became increasingly rough at high concentrations, which cracked and tended to peel off from the surface of the electrode particularly at 40 mg dm^{-3}. On the other hand, 2- and 4-picoline produced better quality deposits. Increasing the concentrations of these additives increased the brightness and decreased the pitting. The brightness of electrodeposits may be attributed to the adsorption of these compounds on the cathode surface similar to that reported by Alaune et al. [34] with additives; tetrahydro derivatives of quinaldine, quinoline and isoquinoline.

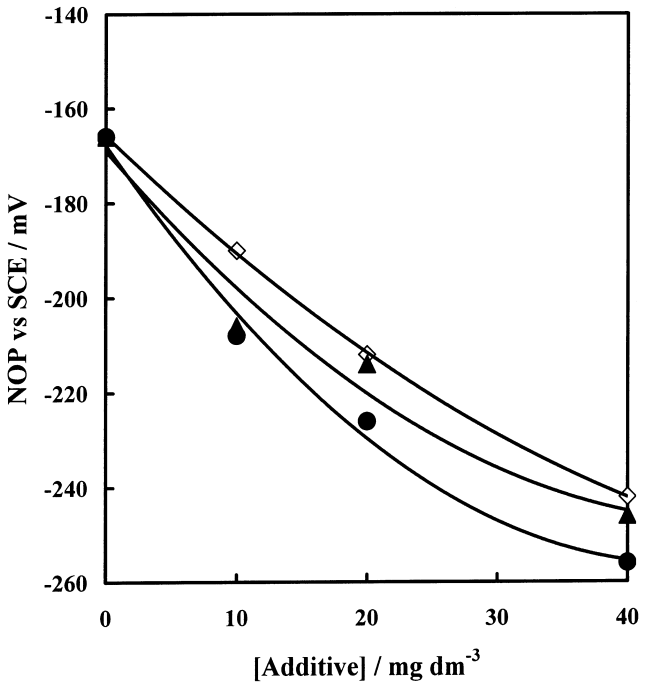

Fig. 1. 1. Effect of additive concentration on nucleation overpotential. Key: (◇) pyridine, (▲) 2-picoline and (●) 4-picoline.

3.4. *Surface morphology*

Figures 2 and 3 show some typical SE micrographs of the nickel electrodeposits obtained in the presence and absence of pyridine and picolines. The deposit obtained from additive free solution consisted of nodular crystallites of nonuniform sizes with some depressions containing relatively smaller nodular growth (Figure 2(a)). The addition of pyridine (2 mg dm^{-3}) produced a compact deposit with fibrous growth of crystallites (Figure 2(b)). Increasing the concentration of the additive to 20 mg dm^{-3} caused the crystallites to grow in the form of irregular blocks (Figure 2(c)). Further increase in the concentration to 40 mg dm^{-3} resulted in smaller size crystals, which were distributed uniformly on the surface (Figure 2(d)). However, the deposit appeared to be less compact as compared to the deposit shown in Figure 2(c).

The presence of 2-picoline (2 mg dm^{-3}) in the electrolyte resulted in the crystallites growing in the form of colonies of irregular shape throughout the surface (Figure 3(a)). Further increase in the concentration of 2-picoline progressively produced more compact deposits, for example, at 40 mg dm^{-3} a highly compact deposit was obtained (Figure 3(b)). As can be seen from Figure 3(c) and 3(d), 4-picolines produced the best deposit of all. In this case the deposits tended to be highly compact with more uniform growth of the crystallites.

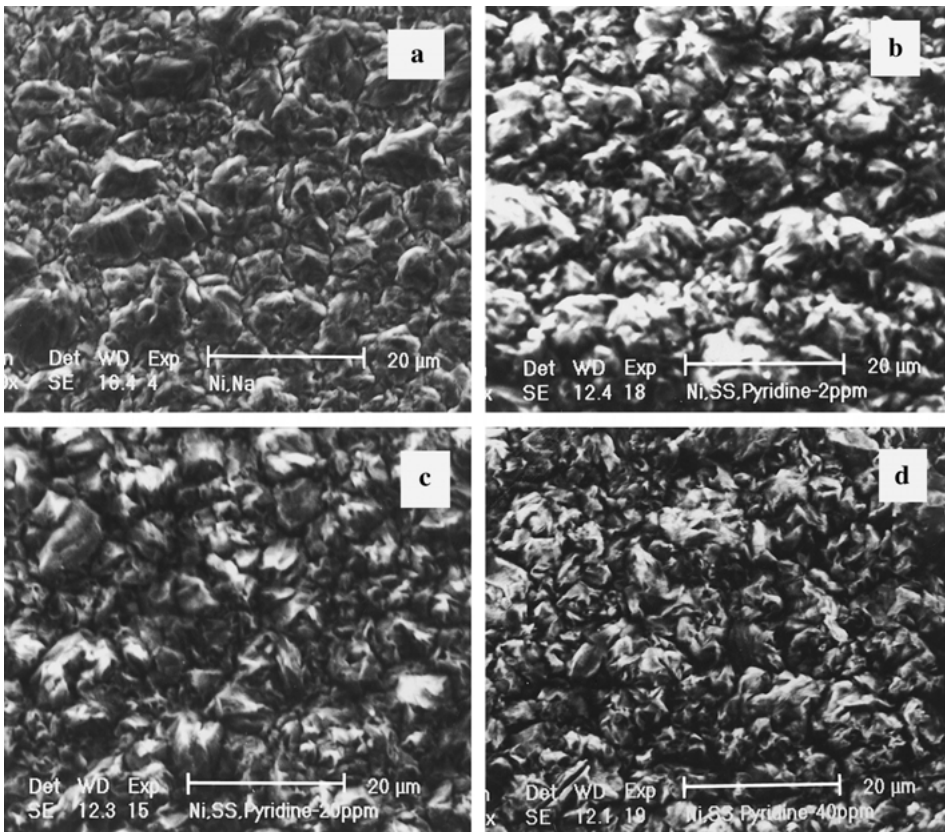

Fig. 2. SE micrographs of nickel electrodeposits from acidic sulfate solutions. (a) Blank, (b) pyridine (2 mg dm^{-3}), (c) pyridine (20 mg dm^{-3}) and (d) pyridine (40 mg dm^{-3}).

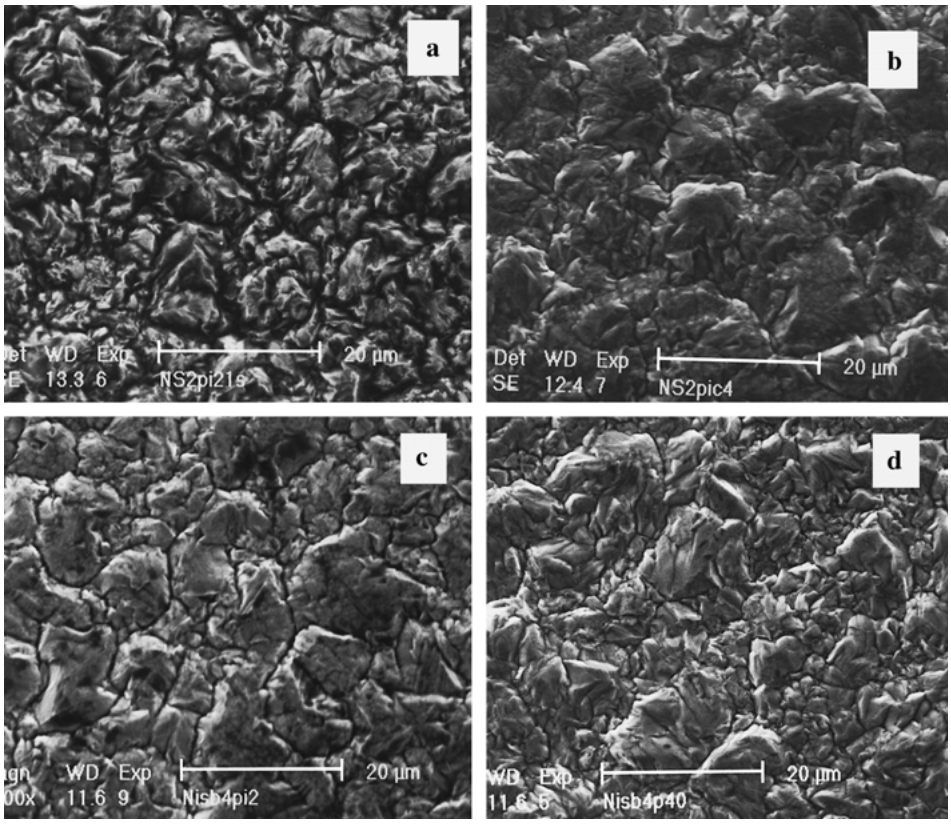

Fig. 3. SE micrographs of nickel electrodeposits from acidic sulfate solutions. (a) 2-picoline (2 mg dm^{-3}), (b) 2-picoline (40 mg dm^{-3}), (c) 4-picoline (2 mg dm^{-3}) and (d) 4-picoline (40 mg dm^{-3}).

3.5. *Crystal orientation*

Table 1 shows the effect of the pyridine and picolines on the orientations of the different crystallites in the nickel electrodeposits. The deposit obtained from the additive free solution had only (200) and (111) planes, the (200) plane being the most preferred. The introduction of the pyridine to the electrolyte resulted in two new crystal planes (220) and (311). Thus addition of 2 mg dm^{-3} of pyridine resulted in (200) (220) (311) (111) as the preferred crystal orientation pattern. Increasing the concentration to 10 mg dm^{-3} caused a significant fall in the peak intensity of (220) and (311) crystal planes. At 20 mg dm^{-3} the order of the preferred orientations was found to be (220) (311) (200) (111) which changed to (200) at 40 mg dm^{-3}.

The addition of 2-picoline produced slightly different crystal orientation pattern. At a concentration of 2 mg dm^{-3} the order of preferred orientation was (200) (111) (311) (220). But when its concentration was increased to 10 mg dm^{-3}, the order changed to (200) (311) (220) (111). At higher concentrations (i.e., beyond 10 mg dm^{-3}), the crystallite growth in the direction of (220) and (311) were inhibited. These marked changes in the crystallographic orientations are reflected in the observed deposit morphology which was smooth and compact.

The addition of 4-picoline produced virtually similar results as with 2-picoline except for small variations in the peak intensities. The deposits obtained with 4-picoline were brighter, more levelled and more compact than those with 2-picoline.

4. Conclusions

The following conclusions could be drawn from the study:

(i) The presence of pyridine, 2-picoline and 4-picoline has only a marginal effect on the CE of nickel electrodeposition.
(ii) The presence of the additives has a strong influence on the preferred orientations of the electrodeposited nickel.
(iii) The presence of 2- and 4-picolines results in smoother, more compact and more levelled deposits as compared to pyridine.
(iv) The additives act as brighteners and grain refiners in the order 4-picoline > 2-picoline > pyridine.

Acknowledgements

The authors thank P. Fallon for assistance in SEM, K. Seymour for XRD and T.B. Issa for general assistance throughout the work. The authors (Mohanty, Tripathy and Das) thank Dr R.P. Das for encouragement. The financial support of the Australian Government in carrying out a part of this work is also acknowledged.

References

1. M.R. Thomson, *Trans. Am. Electrochem. Soc.* **42** (1922) 79.
2. D.T. Ewing, A.A. Brouwer and J.K. Werner, *Plating* **39** (1952) 1343.
3. J.K. Dennis and J. Fuggles, *Trans. Inst. Met. Fin.* **46** (1968) 185.
4 A. Geneidy, W.A. Kochler and W. Machu, *J. Electrochem. Soc.* **106** (1959) 394.
5. D.R. Srivastava and K.S. Nigam, *Surf. Technol.* **10** (1980) 343.
6. R.K. Dorsch, *J. Electroanal. Chem.* **21** (1969) 495.
7. G.T. Rogers, M.J. Ware and R.V. Fellows, *J. Electrochem. Soc.* **107** (1960) 677.
8. S.A. Watson and J. Edwards, *Trans. Inst. Met. Finish.* **34** (1957) 167.
9. T.A. Costavaras, M. Froment and A.H. Goff, *J. Electrochem. Soc.* **120** (1973) 867.
10. I. Epelboin, M. Froment and G. Maurin, *Plating* **53** (1960) 102.
11. N. Kaneko, N. Shinohara, Y. Itoh and H. Nezu, *Bunseki Kagaku* **40** (1991) 655.
12. Y. Nakamura, N. Kaneko, M. Watanbe and H. Hezu, *J. Appl. Electrochem.* **24** (1994) 227.
13. A.S. Miluskin, *Zashch.Met.* **29** (1993) 275.
14. C. Gao, Y. Lu, S. Yue and H. Wang, *Trans. Inst. Met. Finish.* **77** (1999) 75.
15. R.S. Dubey, S.N. Upadhyay and J.S. Choudhary, *J. Electrochem. Soc.* (India) **42** (1993) 239.
16. Kirk-Othmer, 'Encyclopedia of Chemical Technology', Vol.7, 'Corrosion and Corrosion Inhibitors' (Wiley-Interscience, New York, 1982), p.135.
17. P.N.S. Yadav and R. Wadhawani, *Trans. SAEST* **28** (1993) 134.
18. H.C. Brown, *Trans. Inst. Met. Finish.* **43** (1969) 63.
19. W. Gundel and W. Strauss, *US Patent* 2876 177 (1959).
20. N. Hackerman and H. Haeshe, *J. Electrochem. Soc.* **105** (1958) 191.
21. V. Volkova, *Nature* **185** (1960) 743.
22. T. Shimuzu, T. Ishizuka and N.K. Gijatsa, *Ken Kyusho Hokoku* **43** (1994) 1724.
23. L.E. Cambi and G. Devoto, *Atti Accad Linced* **15** (1932) 27.
24. V.D. Grigorev and N.I. Fulman, *TSVETNYE Metally/Non-Ferrous Metals* **15** (1974) 14.
25. K.N. Srinivasan and S.V.K. Iyer, *Bull. Electrochem.* **6** (1990) 35.
26. S.C. Das, P. Singh and G.T. Hefter, *J. Appl. Electrochem.* **26** (1996) 1245.
27. S.C. Das, P. Singh and G.T. Hefter, *J. Appl. Electrochem.* **27** (1997) 738.
28. B.C. Tripathy, S.C. Das, G.T. Hefter and P. Singh, *J. Appl. Electrochem.* **27** (1997) 673.
29 G. Aylward and T. Findlay, 'SI Chemical Data', 3rd edn (Jacaranda Wiley, Brisbane, 1994), p.96.
30. V.I. Lakshmanan, D.J. MacKinnon and J.M. Brannen, *J. Appl. Electrochem.* **7** (1977) 127.
31. B.C. Tripathy, I.N. Bhattacharya, P. Gopalkrishna and S.C. Das, *Trans. Indian Inst. Met.* **51** (1998) 303.
32. B.C. Tripathy, S.C. Das, G.T. Hefter and P. Singh, *J. Appl. Electrochem.* **28** (1998) 915.
33. B.C. Tripathy, S.C. Das, P. Singh and G.T. Hefter, *J. Appl. Electrochem.* **29** (1999) 1229.
34. Z. Alaune, Z. Talaykyte and L.T. Mokshu, *Akad.Darb (Sec. B)* **31** (1971) 65.