



Effect of pyridine and its derivatives on the electrodeposition of nickel from aqueous sulfate solutions

Part II: Polarization behaviour

U.S. MOHANTY¹, B.C. TRIPATHY², P. SINGH^{2,*} and S.C. DAS¹

¹Hydro and Electrometallurgy Division, Regional Research Laboratory (CSIR), Bhubaneswar 751 013, India

²Department of Chemistry, Murdoch University, Murdoch, WA 6150, Australia

(*author for correspondence)

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Abstract

The electrochemical reactions occurring during electrodeposition of nickel from acidic sulfate solutions were examined by cyclic and linear sweep voltammetry techniques. The effect of pyridine, 2-picoline and 4-picoline on the electrode polarization behaviour and electron transfer parameter of the cathodic reduction process was also investigated. Strongest electrode polarization was seen with 4-picoline. The order of cathodic polarization was 4-picoline > 2-picoline > pyridine. Kinetic parameters such as Tafel slope, transfer coefficient and exchange current density were determined to analyse the nature of the electrode reactions. The exchange current density for nickel deposition on nickel and stainless steel substrates was in the order 4-picoline < 2-picoline < pyridine.

1. Introduction

Because nickel is an industrially significant metal, the electrochemistry of its electrodeposition has been studied extensively [1–19]. The effects of the addition of relatively small amounts of organic additives in the plating bath on the current efficiency (CE), deposit morphology, crystallographic orientation and polarization behaviour of the cathode during metal deposition are well documented in the literature [2, 3, 5, 12–17, 19].

Maitra et al. [4] studied the effect of halide ions Cl^- , Br^- and I^- on the cathodic polarization of nickel in presence of dicyanamide and other related compounds in sulfuric acid medium. Hoare [8] determined the rate of nickel deposition on a platinum substrate in nickel sulfate solution with and without boric acid using cyclic voltammetric techniques. Nakamura et al. [16] reported the inhibitory effect of saccharin and three kinds of aliphatic alcohols on the electroreduction of Ni^{2+} from Watts bath. They observed synergistic behaviour of the halides and the organic compounds on Ni^{2+} reduction due to their co-adsorption. Gao and coworkers [17] studied the polarization behaviour of nickel in the presence of 2-butyne-1,4 diol and three other compounds of different oxidation states of sulfur (sodium benzene sulfonate, sodium benzene sulfinate and thio-salicylic acid) by linear sweep voltammetry. They found that except for 2-butyne-1,4 diol which showed inhibi-

tory effect all other compounds activated the Ni^{2+} electroreduction. The nickel electrodeposition potential shifted to less negative values in the order thio-salicylic acid > sodium benzene sulfonate > sodium benzene sulfinate. They also found that the crystal size of the electrodeposited metal was inversely related to the deposition overpotential. Das et al. [20, 21] studied the effect of pyridine and its derivatives on electrocrystallization of zinc from acidic sulfate solutions. They found these additives polarized the cathode apart from affecting CE, deposit morphology and crystal orientations.

This work is a continuation of our previous work [22] which reported the effect of pyridine and picolines on cathodic CE and surface morphology and crystal orientation of the nickel electrodeposits. It was reported that these additives had marginal effect on the CE for nickel electrodeposition which was about 96%. However, they affected the surface morphology and crystal orientation of the nickel electrodeposits quite differently. 2- and 4-picolines resulted in smoother, more compact and more levelled deposits as compared to pyridine. These additives were classified as brighteners and grain refiners in the order 4-picoline > 2-picoline > pyridine.

The present paper deals with the effect of these additives on the polarization behaviour of the cathode during the nickel electrodeposition process providing information on the importance of these additives in metal electro-winning.

2. Experimental details

The nickel electrolytes were prepared with reagent grade chemicals and using ultrapure water (Millipore MilliQ system) at room temperature. The solutions used for nickel electrodeposition were of the composition 1.02 M NiSO₄ and 0.08 M Na₂SO₄ with pH 2.5. Stock solutions of 4 g dm⁻³ of each of the additives pyridine, 2-picoline and 4-picoline were made and appropriate volumes were added to the nickel electrolytes during polarization measurements for studying the effect of these additives in the range of 0–40 mg dm⁻³.

All the experiments for studying the polarization behaviour (both cyclic and linear sweep voltammetry) were carried out in a glass cell with 100 cm³ electrolyte at 25 ± 1 °C. A stainless steel disk electrode of 3 mm diameter (Austenitic grade 316), and platinum wire of 0.5 mm diameter were used as working and auxiliary electrodes respectively. A saturated calomel electrode (SCE) was used as the reference electrode through a Luggin capillary and all the potentials were reported as such. The surface of the electrode prior to each experiment was polished with 400 and then 1200 grade silicon carbide paper to mirror finish and then rinsed with 1 M HCl followed by ultrapure water.

The cathode potential was scanned in the potential range from 0 to -1100 mV at a rate of 10 mV s⁻¹ using a PAR (model 273A) potentiostat/galvanostat. High purity nitrogen was used to sparge out dissolved oxygen and to maintain an inert atmosphere throughout the polarization studies.

3. Results and discussion

The effect of the additives pyridine, 2-picoline and 4-picoline in the concentration range 0–40 mg dm⁻³ was investigated using cyclic and linear sweep voltammetric techniques.

The nucleation overpotential (NOP) which is the difference between the nucleation potential (E_{nu}) and the cross overpotential were determined from the cyclic voltammograms as reported earlier [22]. NOP is regarded as an indicator of the extent of polarization of a cathode. High NOP values indicate strong polarization

Table 1. Effect of additives on nucleation potential (E_{nu}) and nucleation overpotential (NOP) obtained from the cyclic voltammograms for nickel electrodeposition from acidic sulfate bath

[Additive] /mg dm ⁻³	Pyridine		2-picoline		4-picoline	
	E_{nu} /mV	NOP /mV	E_{nu} /mV	NOP /mV	E_{nu} /mV	NOP /mV
0	-886	-166	-886	-166	-886	-166
10	-910	-190	-926	-206	-928	-208
20	-932	-212	-932	-214	-946	-226
30	-948	-228	-958	-238	-962	-242
40	-962	-242	-966	-246	-976	-256

of the cathode. As can be seen from the data in Table 1, the NOP increases with increase in the additive concentration in the electrolyte. The increase in NOP for a constant additive concentration is in the order 4-picoline > 2-picoline > pyridine. This may be explained in terms of the strong adsorption of the additives on the surface of the electrode. The extent of adsorption appears to be in the order 4-picoline > 2-picoline > pyridine. This is not unexpected because as explained earlier [22] 4-picoline is the strongest and pyridine the weakest base of the three additives. Similar observations have been reported by Gao et al. [15] who investigated the effect of pyridinium-1-propane-3-sulfonate and 1,4-di-(α,β -epoxypropoxy)2-butyne on cathode polarization behaviour during nickel electrodeposition. They also concluded that the extent of the cathodic polarization depended on the degree of adsorption of the additive at the electrode surface. Similar observations were also made by Tooru and Toshia [23, 24] during cathodic polarization of nickel in the presence of pyridine and 3-substituted pyridines.

The cathodic linear sweep polarization curves for nickel electrodeposition on a stainless steel disc electrode in the presence of the additives pyridine, 2-picoline and 4-picoline are shown in Figures 1–3. It can be seen that an increase in the additive concentration progressively increases the reduction potential of Ni²⁺ and the polarization is dependent on the nature of the additive. The cathode polarization is highest for 4-picoline and lowest for pyridine. Similar results were also obtained

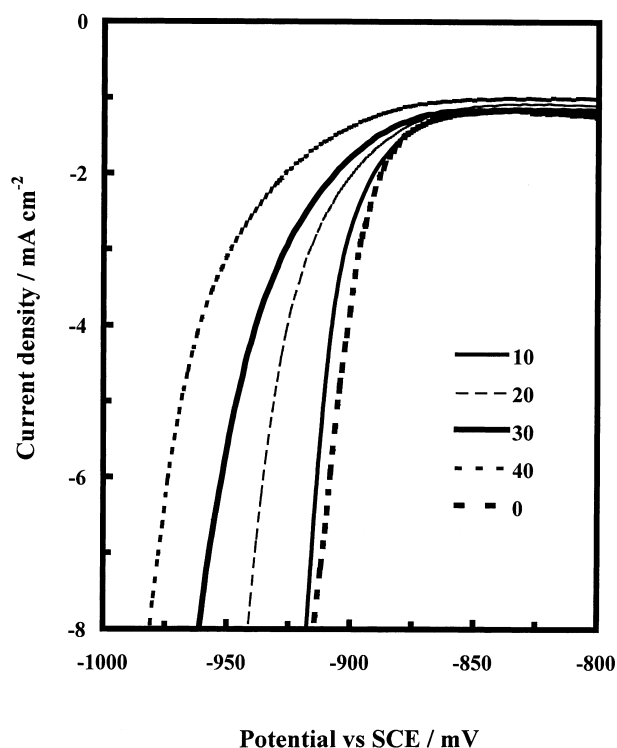


Fig. 1. Effect of pyridine on the linear sweep voltammograms of nickel electrodeposition from acidic sulfate bath. Concentration of pyridine: (••••) 0, (—) 10, (---) 20, (-.-.-) 30 and (---) 40 mg dm⁻³.

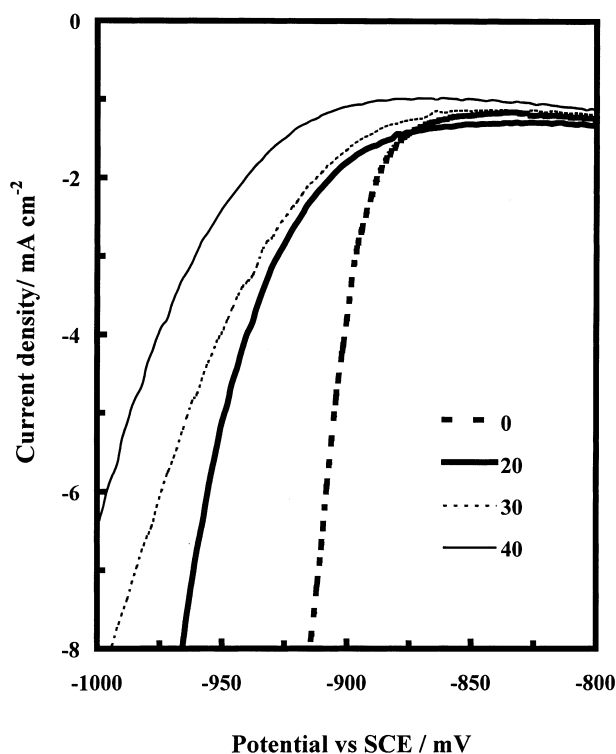


Fig. 2. Effect of 2-picoline on the linear sweep voltammograms of nickel electrodeposition from acidic sulfate bath. Concentration of 2-picoline: (■) 0, (■) 20, (- - -) 30 and (—) 40 mg dm⁻³.

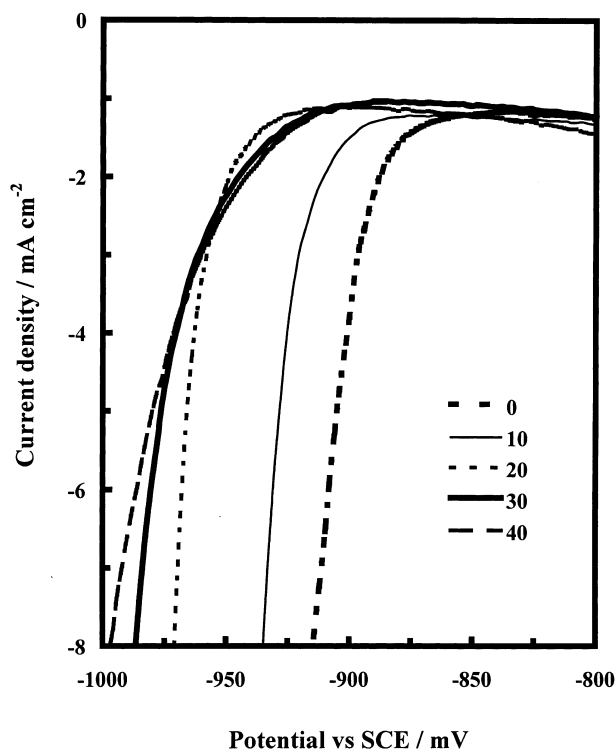


Fig. 3. Effect of 4-picoline on the linear sweep voltammograms of nickel electrodeposition acidic sulfate bath. Concentration of 4-picoline: (■) 0, (—) 10, (· · ·) 20, (■) 30 and (- - -) 40 mg dm⁻³.

for electrodeposition of nickel on nickel substrates in the presence of these additives. This may be attributed to the differences in the adsorption behaviour of the additives on the cathode surface.

The kinetic parameters Tafel slope (b), transfer coefficients (α) and exchange current density (i_0) for nickel electrodeposition on stainless steel and nickel substrates were calculated from their respective cathodic linear sweep polarization curves using the same method as described earlier [25, 26]. The results are given in Table 2. The additives affected the Tafel slopes only slightly which remained in the vicinity of 120 mV decade⁻¹. Several authors [27, 28] have reported the value of Tafel slopes around 120 mV decade⁻¹ from nickel chloride and perchlorate solutions at different temperatures in the pH range of 4–6. Davison and Harrison [29] have also reported the value of Tafel slope to be around 114 mV decade⁻¹ from sulfate solutions on a hanging mercury drop electrode using linear sweep voltammetry in the pH range 5–6. Likewise, it was found that pyridine and picolines had virtually no effect on the transfer coefficients for nickel electrodeposition, both on nickel and stainless steel substrates. This indicates that these additives had no effect on the symmetry of the electron transfer reaction. However, the effect of the additives is more clearly reflected in the variation of the i_0 values. A decrease in i_0 value with increase in concentration is seen for all the additives, which may be attributed to the adsorption of the additives on the cathode surface thereby lowering the rate of electron transfer reaction. The decrease in i_0 values on both stainless steel and nickel substrates was found to be in the order 4-picoline > 2-picoline > pyridine. It was also found that the i_0

Table 2. Effect of additives on the kinetic parameters b , α and i_0 for nickel electrodeposition from acidic sulfate bath

[Additive] /mg dm ⁻³	b /mV decade ⁻¹		α		i_0 /mA cm ⁻²	
	A	B	A	B	A	B
Pyridine						
0	-105	-110	0.56	0.53	7.4×10^{-3}	5.8×10^{-2}
10	-103	-119	0.57	0.49	5.0×10^{-3}	5.2×10^{-2}
20	-119	-125	0.49	0.47	2.6×10^{-3}	5.0×10^{-2}
30	-101	-118	0.59	0.50	1.0×10^{-3}	3.0×10^{-2}
40	-105	-117	0.56	0.50	1.0×10^{-3}	1.5×10^{-2}
2-picoline						
10	-119	-128	0.49	0.46	6.4×10^{-3}	4.0×10^{-2}
20	-118	-130	0.50	0.45	4.6×10^{-3}	3.3×10^{-2}
30	-120	-130	0.49	0.45	3.4×10^{-3}	2.0×10^{-2}
40	-109	-127	0.54	0.46	9.5×10^{-4}	9.4×10^{-3}
4-picoline						
10	-110	-128	0.53	0.46	6.3×10^{-3}	4.0×10^{-2}
20	-113	-119	0.52	0.49	3.3×10^{-3}	2.3×10^{-2}
30	-128	-119	0.46	0.49	2.0×10^{-3}	1.2×10^{-2}
40	-110	-166	0.53	0.35	7.5×10^{-4}	7.5×10^{-3}

A = nickel deposition on stainless steel.
B = nickel deposition on nickel.

values are strongly dependent on the nature of the substrate. As noted in Table 2 the i_0 values for nickel substrate are one order of magnitude higher than those for stainless steel.

The effect of adsorbates on the electrode kinetics of metal electrodeposition processes is a well known phenomenon. For example Stanković [30] who studied the effect of Fe(II) on the kinetics of copper deposition found that the exchange current densities decreased with increasing concentration of Fe(II) ions in the electrolyte. The possible explanation given by the author was based on the electrostatic cation adsorption effects, in which the presence of an adsorbate altered the double layer structure and decreased the rate of an electrochemical reaction. The same author [31] has also reported a decrease in the corresponding exchange current densities with increasing concentrations of Cl^- ions during copper deposition from acidic sulfate solutions. Tripathy et al. [25, 26] have observed a decrease in i_0 values for triethylbenzyl ammonium chloride and quaternary ammonium bromides while studying the kinetics of zinc deposition from acidic sulfate solutions.

4. Conclusions

- (i) The additives cause cathode polarization in the order 4-picoline > 2-picoline > pyridine.
- (ii) The exchange current density for nickel deposition on nickel and stainless steel substrates is in the order 4-picoline < 2-picoline < pyridine.
- (iii) The i_0 values are an order of magnitude higher on nickel than on stainless steel substrates.

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References

1. R.K. Dorsch, *J. Electroanal. Chem.* **21** (1969) 495.
2. J. Amblard, I. Epelboin, M. Froment and G. Maurin, *J. Appl. Electrochem.* **9** (1979) 233.
3. M.Y. Abyaneh and M. Fleischmann, *Trans. Inst. Met. Finish.* **58** (1980) 91.
4. A. Maitra and K. Bhattacharya, *J. Ind. Chem. Soc.* **57** (1980) 854.
5. M.Y. Abyaneh, M. Berkem and M. Fleischmann, *Trans. Inst. Met. Finish.* **60** (1982) 114.
6. M. Fleischmann and A. Saraby-Reintjes, *Electrochim. Acta* **29** (1984) 69.
7. A. Saraby-Reintjes and M. Fleischmann, *Electrochim. Acta* **29** (1984) 557.
8. J.P. Hoare, *J. Electrochem. Soc.* **134** (1987) 3102.
9. S.K. Gogia and S.C. Das, *Metall. Trans.* **19B** (1988) 823.
10. C. Kollia, N. Spyrellis, J. Amblard, M. Froment and G.M. Maurin, *J. Appl. Electrochem.* **20** (1990) 1025.
11. S.K. Gogia and S.C. Das, *J. Appl. Electrochem.* **21** (1991) 64.
12. R. Albalat, E. Gomez, C. Muller, M. Sarret and E. Valles, *J. Appl. Electrochem.* **21** (1991) 709.
13. E. Gomez, C. Muller, R. Pollina, M. Sareet and E. Valles, *J. Electroanal. Chem.* **333** (1992) 47.
14. E. Kuzeci, R. Kammel and S.K. Gogia, *J. Appl. Electrochem.* **24** (1994) 730.
15. C. Gao, Y. Lu and R. Liu, *Plat. Surf. Finish.* **44** (1994) 83.
16. Y. Nakamura, N. Kaneko, M. Watanabe and H. Nezu, *J. Appl. Electrochem.* **24** (1994) 227.
17. C. Gao, Y. lu, S. Yue and H. Wang, *Trans. Inst. Met. Finish.* **77** (1999) 75.
18. B.C. Tripathy, S.C. Das, P. Singh, G.T. Hefter and D.M. Muir, *J. Appl. Electrochem.* **31** (2001) 573.
19. B.C. Tripathy, P. Singh, D.M. Muir and S.C. Das, *J. Appl. Electrochem.* **31** (2001) 301.
20. S.C. Das, P. Singh and G.T. Hefter, *J. Appl. Electrochem.* **19** (1996) 219.
21. S.C. Das, P. Singh and G.T. Hefter, *J. Appl. Electrochem.* **27** (1997) 738.
22. U.S. Mohanty, B.C. Tripathy, P. Singh and S.C. Das, *J. Appl. Electrochem.* **31** (2001) 579.
23. S. Tooru, *Chem. Express* **7** (1992) 809.
24. S. Tooru, I. Toshia, N. Kohyo, N.K. Gijutsu, *Konkyusho Hokoku* **43** (1994) 17.
25. B.C. Tripathy, S.C. Das, P. Singh and G.T. Hefter, *J. Appl. Electrochem.* **28** (1998) 915.
26. B.C. Tripathy, S.C. Das, P. Singh and G.T. Hefter, *J. Appl. Electrochem.* **29** (1999) 1229.
27. R.C.V. Piatti, A.J. Arvia and J.J. Podesta, *Electrochim. Acta* **14** (1969) 541.
28. T. Hurlen, *Electrochim. Acta* **20** (1975) 499.
29. W. Davidson and J.A. Harrison, *J. Electroanal. Chem.* **44** (1973) 431.
30. Z.D. Stanković, *J. Electrochem. Soc.* **128** (1981) 1862.
31. Z.D. Stanković, *Electrochim. Acta* **29** (1984) 407.