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Effect of organic extractants on the electrocrystallization of nickel from aqueous sulphate solutions

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Abstract

The effect of the presence of commercial organic extractants LIX 84I, Cyanex 272, D2EHPA, Versatic 10 and TBP with or without Mg^{2+} on various electrodeposition parameters for nickel deposition on stainless steel cathode from aqueous sulphate solutions was investigated. The parameters included cathodic current efficiency, deposit morphology, crystal orientation and cathodic polarization. There was no significant variation in the current efficiency in the presence of these additives, but changes were observed in the deposit morphologies and crystal orientations even though all the deposits were bright, smooth and coherent. Changes were also observed in the cathodic polarization behaviour during nickel electrocrystallization in the presence of these additives. The effect of the additives on the electrokinetic parameter, exchange current density (i_0) has also been investigated.

1. Introduction

Nickel is usually recovered by hydrogen reduction or electrowinning from industrial waste and hydrometallurgical leach liquors. The quality of the metal produced by electrowinning is strongly affected by the presence of metallic and organic impurities even at trace levels. These impurities originate either from the starting materials or are built up during the metal recovery process. The effects of such contaminants on nickel electrodeposition have been reported [1–7]. The organic reagents used for the solvent extraction of nickel, a step that usually precedes electrowinning also represent a major source of contamination. The current practice is to remove the residual organic extractants from the electrodeposition baths by absorbing them on solid materials such as activated charcoal. However, trace levels of organic extractants may break through the carbon or still remain in the electrolyte causing detrimental effect on the quality of the electrodeposited metal. Kuzeci et al. [4] have reported that presence of LIX 64N in the electrolytic baths even at very low concentrations, produced pinholed, cracked and blackened deposits. They also noticed a decrease in current efficiency (CE) with an increase in concentration of LIX 64N. The same authors also reported [5] that bright, smooth nickel deposits with CE as high as 96% can be obtained in presence of D2EHPA but cracking, peeling and pitting were observed when the concentration of the extractant exceeded 50 mg L^{-1}. At these concentrations the extractants formed immiscible layer with the aqueous electrolytes.

Mg^{2+} is another contaminant whose effect on the electrocrystallization of nickel is of interest to the mining industry. Relatively high concentrations of Mg^{2+} remain in the hydrometallurgical leach liquors even after the solvent extraction step. The presence of Mg^{2+} has been reported to be both beneficial and harmful [7, 8]. However, the combined effect of Mg^{2+} and the residual extractants is not documented.

This paper reports the results of our investigation of the effect of some commercial solvent extraction reagents, often used in the processing of nickel solutions such as LIX 84I, Cyanex 272, D2EHPA, Versatic 10 and TBP, on the electrodeposition characteristics of nickel from acid sulphate solution containing boric acid. The studies included the effects on the current efficiency, deposit morphology, crystal orientations, cathode polarization and the electron-transfer kinetic parameter, i_0 during electrocrystallization of nickel from aqueous sulphate solutions saturated with the organic extraction reagents in the presence and absence of Mg^{2+}. The solubilities of these organic reagents are given in Table 1.

Table 1. Approximate solubility of the solvent extractive reagents

Organic extractants	Concentration /mg dm^{-3}	Solution pH	References
Versatic 10	70	4.0	[10]
D2EHPA	~30	5–6	[10]
Cyanex 272	2–3	5	[11]
LIX 84I	10	2	[12]
TBP	25–40	2	[12]

2. Experimental details

The rectangular electrolytic flow cell used in this work was similar to that described previously [8]. Ultra pure water [Millipore Milli Q System] was used for preparing solutions. All the inorganic salts used were of analytical grades. The organic extractants LIX 84I was obtained from Henkel, Cyanex 272 from Cyanamid, Versatic 10 from Shell, and TBP and D2EHPA from Mobil. These extractants were used as such without further purification. Before electrodeposition, all the solutions were saturated with the extractants by shaking and equilibrating for about ten minutes using separatory funnels. After equilibration the aqueous phase was settled, separated and then fed to the electrodeposition cell.

The methods used for electrode preparation, electrolysis, polarization measurements and deposit examination were similar to our previous paper [8]. Cathodic current efficiency was calculated from the weight difference of the cathode before and after electrodeposition. Polarization measurements were carried out at 25 °C using a PAR model 273A potentiostat/galvanostat for scanning the potential from 0 to −950 mV at a scan rate of 10 mV s^{-1}. The exchange current density (i_0) value for nickel deposition process for each of the systems was calculated from the Tafel plots as reported earlier [9]. A Philips PW 1050 X-ray diffractometer was used to examine nickel deposits to determine their preferred crystal orientations. A Philips XL 20 scanning electron microscope (SEM) was used to examine the surface morphology of the deposits.

3. Result and discussion

3.1. *Cathodic current efficiency*

Table 2 summarizes the CE for nickel electrodeposited from nickel sulphate baths containing Na_2SO_4 (0.084 M) and boric acid (0.194 M) in the presence and absence of various additives. It can be concluded from the results that the presence of any of the investigated organic extractants with or without Mg^{2+} had no effect on the CE, which were approximately 96%. Thus the investigated organic extractants did not have any adverse effect on the CE. Our results appear to contradict the literature report that the presence of LIX 64N or D2EHPA in the nickel sulphate bath caused a reduction in CE [4, 5]. However, this may be because of the excess organic present in the electrolyte producing an aqueous/organic two-phase system in these studies.

3.2. *Cathodic electrodeposition potential*

The nickel electrodeposition potentials are listed in Table 2. As can be seen, the nickel electrodeposition occurs at −0.84 ± 0.02 V vs SCE in the presence and absence of the investigated additives. This suggests that the organic extractants did not have any significant effect on the conductivity of the solution or the double layer at the cathode surface.

3.3. *Crystallographic orientations*

The results of X-ray diffraction analysis of the electrodeposited nickel are given in Table 2. The (200) plane was found to be the most preferred plane irrespective of the presence and absence of the investigated additives in the electrolyte. The order of the preferred crystal orientation of the electrodeposited nickel in the absence of the additives, was (200) > (111). In the presence of D2EHPA additionally a small peak associated with the (311) plane also appeared with an attendant decrease in the intensity

Table 2. Effects of organic extractants on various electrodeposition parameters during nickel electrodeposition on stainless steel electrode from sulphate bath* at pH 2.5

Organic Extractants	[Mg^{2+}] /M	Average CP† /V	CE /%	Crystal planes (*h k l*) Relative peak intensity (I/I_0)			NOP /mV	ΔNOP /mV	i_0 /mA cm^{-2}
				(111)	(200)	(311)			
Nil	–	−0.86	96	62	100	–	−178	0	6.3×10^{-4}
LIX 84I	–	−0.82	93	7	100	–	−170	8	8.0×10^{-3}
Cyanex 272	–	−0.84	95	6	100	–	−203	−25	1.1×10^{-4}
Versatic 10	–	−0.84	95	7	100	–	−170	8	7.2×10^{-3}
D2EHPA	–	−0.83	93	23	100	6	−155	23	8.3×10^{-2}
TBP	–	−0.82	94	7	100	–	−173	5	7.5×10^{-3}
LIX 84I	0.063	−0.84	94	41	100	2	−176	2	3.1×10^{-3}
Cyanex 272	0.063	−0.84	94	38	100	2	−192	−14	7.3×10^{-4}
Versatic 10	0.063	−0.84	95	31	100	2	−178	0	9.2×10^{-4}
D2EHPA	0.063	−0.83	94	47	100	7	−166	12	7.8×10^{-3}
TBP	0.063	−0.84	92	35	100	4	−175	3	1.3×10^{-3}

* $NiSO_4$ = 1.022 M, Na_2SO_4 = 0.084 M and H_3BO_3 = 0.194 M

† CP = cathode potential

of the (111) plane. Although the order of the preferred orientation did not change in the presence of any of the extractants, the intensity of the (111) plane decreased significantly in all the cases. In the presence of Mg^{2+} the order of preferred orientation was (200) > (111) > (311), but the intensity of the (111) plane increased in all the cases irrespective of the type of extractant.

3.4. *Surface morphology*

The presence of organic extractants such as LIX 64N and D2EHPA at concentrations where they form an immiscible phase with the aqueous nickel electrolyte is reported to yield poor quality nickel electrodeposits [4, 5]. This has been attributed to the blockage of the

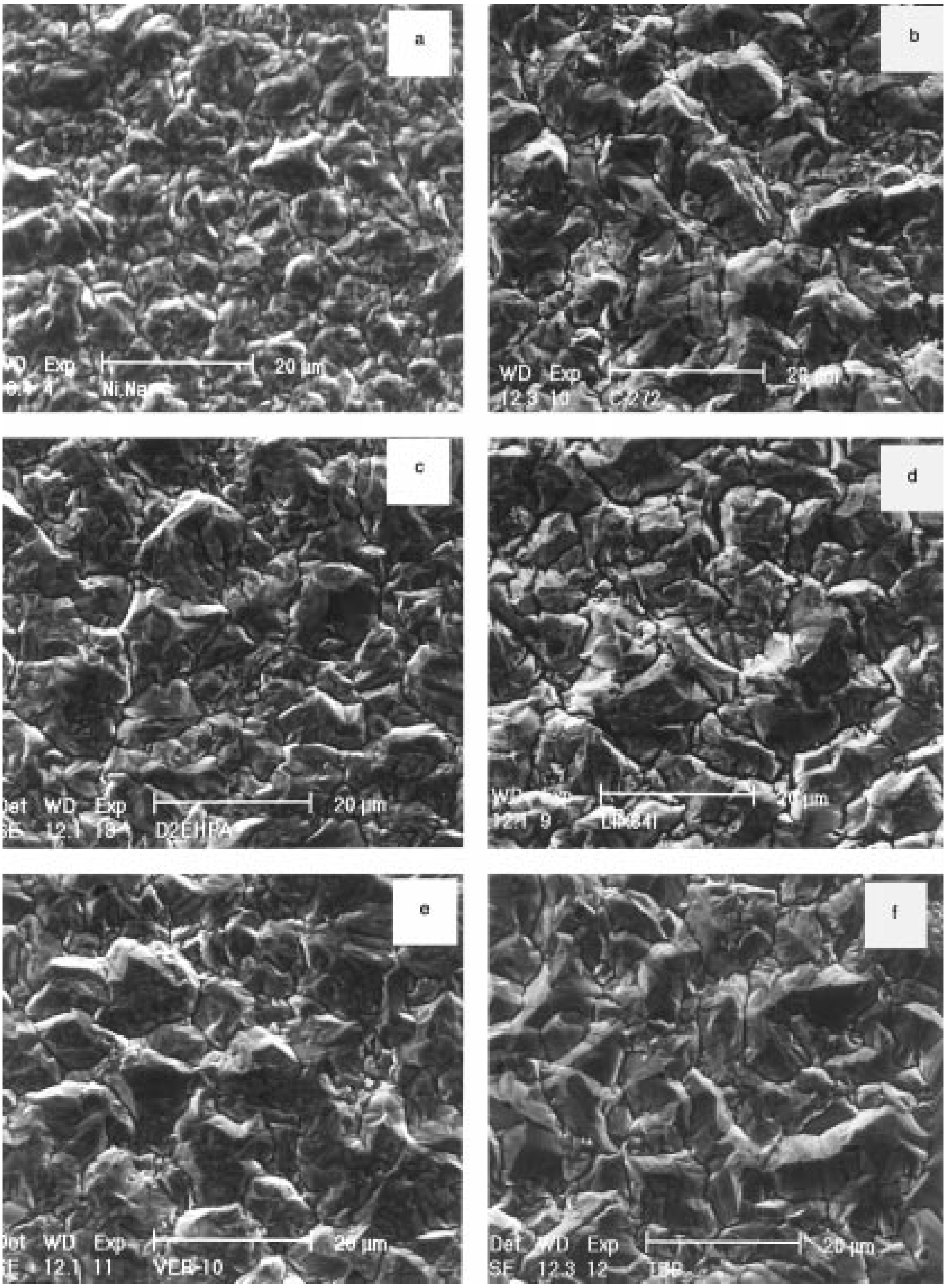

Fig. 1. SEMs showing the surface morphology of the nickel electrodeposits obtained from solutions containing: (a) $NiSO_4$ (1.022 M), Na_2SO_4 (0.084 M) and H_3BO_3 (0.194 M); (b) [a] + Cyanex 272; (c) [a] + D2EHPA; (d) [a] + LIX 84I; (e) [a] + Versatic 10 and (f) [a] + TBP.

cathode surface by the extractants hindering the nucleation process. This could also be caused by small droplets of undissolved reagent, physically attached to the surface of the cathode.

Even though, visually, the nickel electrodeposits were bright, smooth and coherent in all the cases, a close examination of the morphology under the SEM showed that the deposit characteristics were different (Figure 1). It can be seen from Figure 1(a) that in the absence of extractants, round edged crystallites of varying size (in the range 1–7 μm) were randomly oriented. The addition of any of the organic extractants under study increased the size of the crystals to 2–15 μm (Figures 1(b)–1(f)) and the morphologies consisted of bigger crystals surrounded by small crystallites. In some areas there were scattered clusters of crystallites. The presence of D2EHPA and LIX 84I resulted in more rounded crystallites as compared to the other extractants which formed more sharp edged crystals. The addition of Mg^{2+} to the solutions containing extractants decreased the size of the crystallites in all the cases, except that of Cyanex 272 where an increase in crystal size was observed. Overall, all the deposits were smooth, compact and bright indicating that the presence of any of the aforementioned organic extractants with and without Mg^{2+} did not have any gross adverse effect on the quality of the electrodeposited metal.

3.5. *Polarization studies*

Figures 2 and 3 show typical cathodic polarization (I/V) behaviour during nickel electrodeposition from nickel sulphate solutions of composition of interest to this work. The presence of the peak ‘A’ in these figures shows that the electrodeposition of nickel is preceded by hydrogen evolution, which is consistent with the literature reports [13–18]. The effect of the additives on the I/V profile appears to be small.

By using the techniques reported earlier [8] the nucleation potential (E_n) and the crossover potential (E_{co}) were determined. For each of the systems the nucleation overpotential (NOP), which is the difference between E_n and E_{co} was then calculated and recorded in Table 2. The NOP value for the electrolyte in the absence of the additives is -178 mV. The relative effects of the additives can best be seen by comparing the shift in the NOP from the base line value of -178 mV. This shift is recorded in Table 2 as ΔNOP.

It can be seen from Table 2 that addition of each of the organic extractants except Cyanex 272 changes the NOP to less negative values, that is, ΔNOP is positive, indicating depolarisation. In the case of Cyanex 272, the NOP changes to more negative potential (ΔNOP, negative), indicating that this material does polarize the cathode. The ΔNOP value for Cyanex 272 was most negative (-25 mV) and for D2EHPA was most positive ($+23$ mV). The presence of Mg^{2+} in combination with these extractants has somewhat levelling effect on the ΔNOP values.

The cathodic polarisation data were used to calculate the electrokinetic parameters i_0 as reported earlier [9]. These data are also included in Table 2. Although it is not possible to use these data to propose a definitive model for the effect of the additives on the rates of electron transfer, one point is clear, the additive which shows the highest negative ΔNOP (Cyanex 272) has the least i_0 value. Likewise, the additive which has the highest positive ΔNOP (D2EHPA) has the highest i_0 value. This

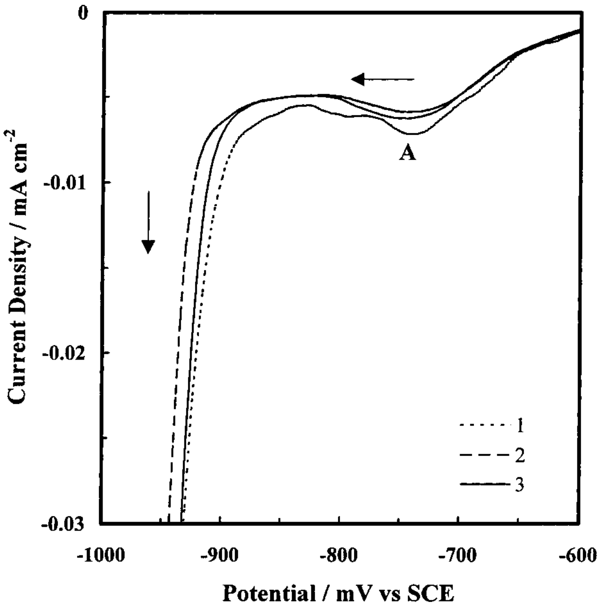

Fig. 2. Cathodic polarization for nickel deposition from 1.022 M nickel sulphate solution at pH 2.5 containing Na_2SO_4 (0.084 M) and H_3BO_3 (0.194 M). Key: (- - - - -) blank, (– – –) [blank] + Cyanex 272 and (——) [blank] + $MgSO_4$ (0.063 M).

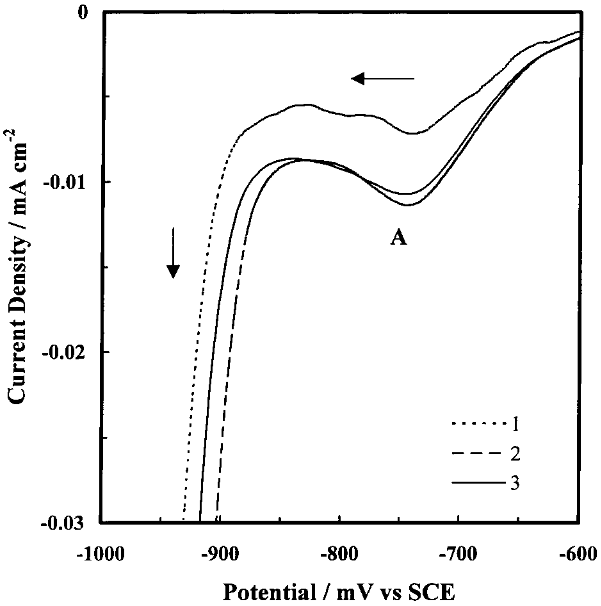

Fig. 3. Cathodic polarization for nickel deposition from 1.022 M nickel sulphate solution at pH 2.5 containing Na_2SO_4 (0.084 M) and H_3BO_3 (0.194 M). Key: (- - - - -) blank, (– – –) [blank] + D2EHPA and (——) [blank] + $MgSO_4$ (0.063 M).

could well be related to the degree of adsorption of these reagents on the cathode surface. Clearly, further work is needed to understand their relationships quantitatively.

4. Conclusions

The following conclusions can be drawn from the present investigation:

(i) The presence of dissolved organic extractants such as LIX 84I, Cyanex 272, Versatic 10, D2EHPA and TBP at saturation level concentrations in the electrolyte have no adverse effect on the current efficiency and visual deposit quality. Bright, smooth and coherent nickel deposits are produced with larger crystallite size.

(ii) The addition of Mg^{2+} together with the organic extractants noted above also produces bright, smooth and coherent nickel deposits with smaller crystallite size except Cyanex 272 where an increase in crystallite size is observed.

(iii) The nucleation overpotential values indicate that all the extractants except Cyanex 272 are cathode depolarisers for nickel electrodeposition. D2EHPA is the strongest depolariser of all the investigated organic extractants.

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