JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 730–736

Effects of metallic and D2EHPA impurities on nickel electrowinning from aqueous sulphate baths

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Received 4 December 1991; revised 10 November 1992

The presence of metallic and organic solvent impurities in pregnant electrolyte during hydrometallurgical processing causes problems in nickel electrowinning. To overcome these problems, a study on the combined effects of metallic and D2EHPA impurities, on nickel electrodeposition has been carried out. The effects of such impurities on deposit physical appearance, current efficiency, deposit contamination, crystallographic orientation and deposit morphology are discussed. Based on the experimental data and observations, it is possible to achieve smooth and perfect nickel sheet with reasonable current efficiency and purity from the contaminated leach liquors of nickel bearing raw materials being processed in the Regional Research Laboratory, Bhubaneswar. Moreover, the economy of the nickel electrowinning process can be improved by careful selection of experimental conditions.

1. Introduction

Most nickel bearing raw materials contain metallic impurities in various concentrations, along with the easily and economically recoverable metals in appreciable amounts. In hydrometallurgical processing it is found that some of the metal ions from the leach liquors are not completely removed, even after solvent extraction purification steps, and hence contaminate the nickel-pregnant electrolyte. In nickel electrowinning from various leach liquors, it is found that organic solvents such as LIX64N, D2EHPA, Hostreax, etc. also contaminate the pregnant electrolyte during the solvent extraction purification steps. In general, electrolytic nickel operations are found to be very sensitive to the presence of both inorganic and organic impurities. These impurities affect the nickel deposit quality and energy consumption, sometimes drastically, particularly when present in appreciable concentration in the nickel bath. Since little information is available in the literature [1–12], the present study was undertaken.

At the Regional Research Laboratory, Bhubaneswar, different organic solvents are being used to treat various leach liquors of different composition and acidity [13,14]. The individual effects of some metallic, nonmetallic and organic solvent impurities have already been investigated for processing actual leach liquors for the electrowinning of nickel [15–19]. The combined effects of LIX64N and metallic impurities on nickel electrodeposition have been recently reported [20]. D2EHPA (Di-2-ethyl-hexyl phosphoric acid) is normally used to treat leach liquors processed through the acid route. Based on results on the individual effects of some inorganic and D2EHPA impurities, the concentrations of some metal ions, *viz* Cu, Co, Zn and Mn, were reduced to obtain cathode nickel of acceptable purity. This paper describes an experimental study of the combined effects of Mg, Mn, Fe, Al, Zn, Cu, Co and D2EHPA on nickel deposit quality, as a simulation of nickel electrowinning conditions from contaminated solutions.

The effects of various parameters, such as D2EHPA concentration, bath pH, bath temperature and current density have been investigated on deposit physical appearance, current efficiency, deposit contamination, crystallographic orientation and surface morphology. The tolerance limits of D2EPHA and metallic impurities have been identified under different experimental conditions.

2. Experimental details

2.1. *Apparatus and material*

The electrolytic cell used for the laboratory scale investigation was of capacity 250 ml and was fitted with a porcelain diaphragm to control the pH of the anolyte and the catholyte. The duration of electrolysis was 2 h. Hull-cell [21] studies were performed for 30 min in a 250 ml cell. Planar cathodes and anodes of the same dimensions were of stainless steel and lead–antimony alloy (Sb $\sim$ 7%), respectively. The cathodic exposed area for all the experiments, besides those carried out in the Hull-cell, was maintained at

$100\,mm^2$ throughout. The electrolytic solution contained $60\,g\,dm^{-3}$ nickel, $12\,g\,dm^{-3}$ boric acid, and $12\,g\,dm^{-3}$ sodium sulphate. Boric acid and sodium sulphate were used as additives to improve the buffering capacity and the conductivity of the electrolyte, respectively [22–25]. The bath pH was adjusted with dilute sulphuric acid. The stock solutions of metallic impurities were prepared from their respective sulphates. Distilled kerosene was used to dilute D2EHPA to the desired concentrations.

2.2. *Electrolysis*

All the experiments, other than those carried out in the Hull-cell, were conducted at $400\,A\,m^{-2}$ current density, a bath temperature of 305 K and a constant bath pH of 2.5, i.e. standard optimum electrowinning conditions achieved with earlier investigations (Table 1). The required amounts of all metallic and D2EHPA impurities were added to the nickel electrolyte from their respective stock solutions. The cathode was removed from the cell after electrolysis and washed thoroughly with distilled water to remove entrained salt, followed by acetone drying. The cathodic current efficiency was determined from the weight gained by the cathode due to nickel deposition. The favourable current density range for nickel electrowinning was identified by conducting Hull-cell experiments, under different experimental conditions, in the presence of metallic and D2EHPA impurities.

2.3. *Deposit analysis*

To determine the purity of the electrodeposited nickel, qualitative EDAX (energy dispersive X-ray analysis) was performed to identify the codeposited/entrained/adsorbed metallic impurities followed by quantitative determination by atomic absorption spectrophotometery. The presence of carbon, oxygen by WDAX (wavelength dispersive X-ray analysis) and sulphur in the electrodeposited nickel sheets were detected using a carbon sulphur analyser. The surface morphology of the deposit sections was examined by SEM. Crystallographic orientations relative to ASTM standard for nickel powders were examined by X-ray diffraction (XRD).

3. Results and discussions

Earlier investigations [15–19] were carried out with different cationic, anionic and organic solvent impurities at different concentrations. The results showed that the current efficiency is not significantly affected (±1%) by inorganic impurities; with organic solvent impurities, however, the current efficiency was drastically decreased. But both inorganic and organic impurities had significant effects on deposit characteristics. For simulation with actual nickel electrowinning conditions and development of an economic and viable process the combined effects of inorganic and organic impurities on deposit characteristics were investigated. The concentrations of some of the metallic impurities in the bath were reduced from their respective tolerance limits (Table 2) in this study.

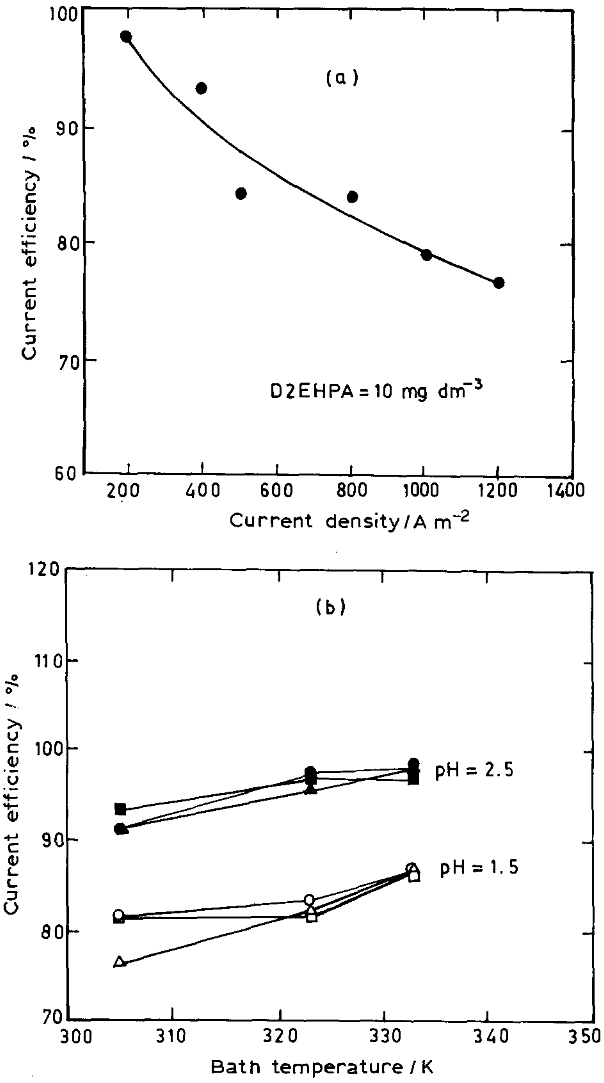

Fig. 1. Effects of (a) current density and (b) bath temperature on current efficiency of nickel electrodeposition in the presence of metallic impurities and D2EHPA. Key for (b): (○, ●) $50\,mg\,dm^{-3}$, (△, ▲) $100\,mg\,dm^{-3}$, and (□, ■) $10\,mg\,dm^{-3}$.

3.1. *Deposit physical appearance and current efficiency*

At optimum nickel electrowinning conditions (Table 1), and at constant metallic impurity concentrations, the variations of D2EHPA concentration showed that, in general, cracking and peeling of the deposits started at $50\,mg\,dm^{-3}$. Pin hole formation, nodular growth and deposit dullness were also observed on the electrodeposited nickel surface when the current density was varied from $600–1200\,A\,m^{-2}$ at constant D2EHPA concentration and bath pH. Such changes in the deposit surface are probably due to the cathode surface coverage by D2EHPA causing hindrance to the nucleation. However, there was no significant change in current efficiency up to $100\,mg\,dm^{-3}$ D2EHPA concentration at both bath pHs of 2.5 and 1.5. Based on the physical appearance of the deposit $30\,mg\,dm^{-3}$ D2EHPA can be considered as the tolerance limit at bath pH 2.5. But at lower bath

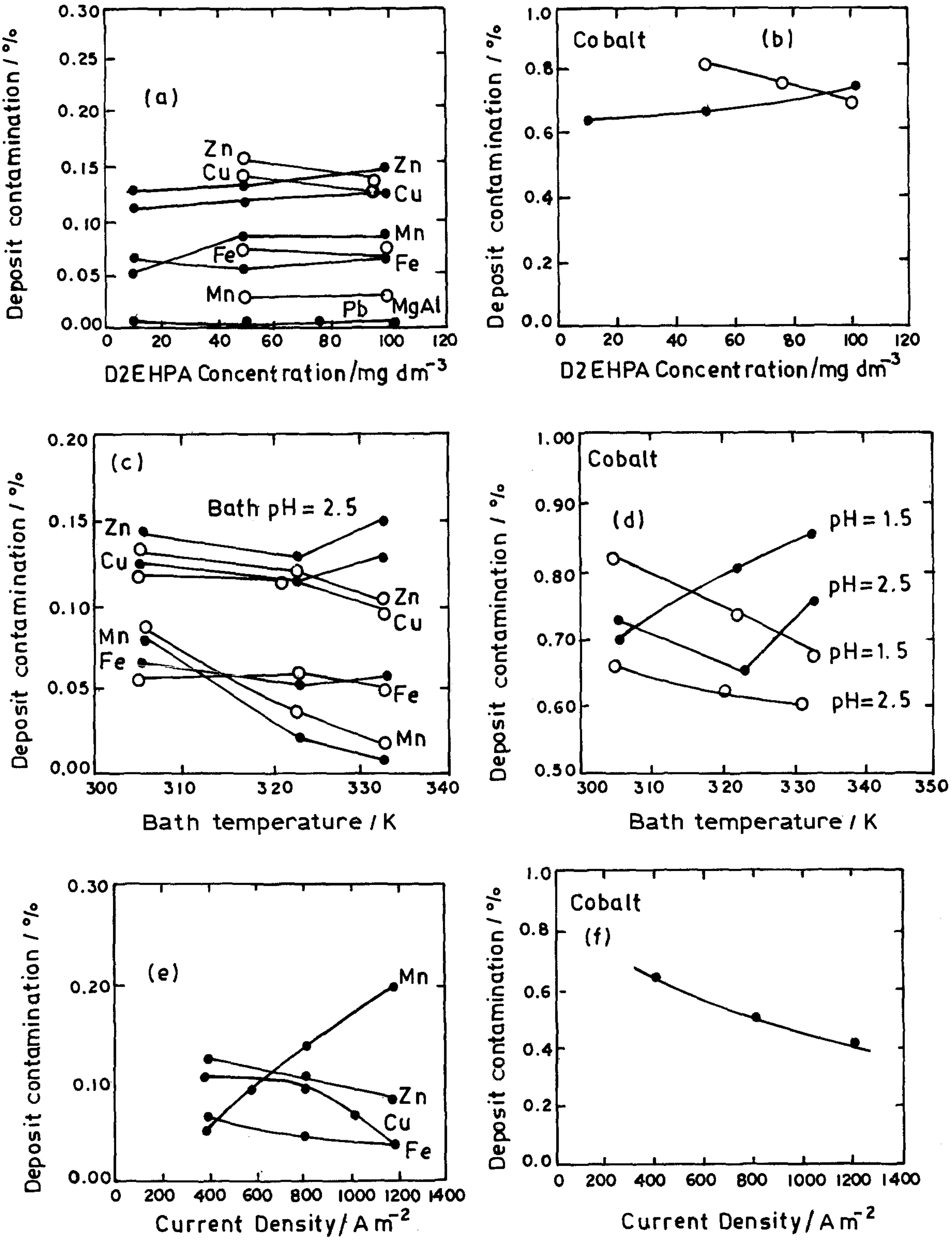

Fig. 2. Effects of different parameters on nickel deposit contamination in the presence of metallic impurities and D2EHPA from aqueous sulphate bath: (a and b) pH: (○) 1.5, (●) 2.5; (c and d) concentration of D2EHPA: (○) 50 mg dm^{-3}, (●) 100 mg dm^{-3}; (e and f) bath pH 2.5, D2EHPA concentration 10 mg dm^{-3}.

pH, i.e. 1.5, higher concentrations of D2EHPA can be tolerated. Moreover, it was observed that the effects of D2EHPA on deposit physical characteristics were much less pronounced than those of LIX64N [20].

In general the current efficiency was found to gradually decrease with increase in current density up to 1200 A m^{-2} (Fig. 1(a)). But the current efficiency was found to be almost constant in the current density range 400–800 A m^{-2}. At 200 A m^{-2} the current efficiency was remarkably high but the deposit physical appearance was affected slightly. The deterioration of the nickel deposit due to cracking, peeling, nodular growth and dullness started at a current density of 600 A m^{-2}.

The investigations performed at higher bath temperature, i.e. > 305 K, revealed that there was little effect on current efficiency (Fig. 1(b)) and physical

Table 1. Optimum nickel electrowinning conditions from aqueous sulphate bath

Electrolyte	Nickel 60 g dm^{-3} Boric acid 12 g dm^{-3} Sodium sulphate 12 g dm^{-3}
Bath pH	2.0–2.5
Bath temperature	305 ± 2 K
Current density	400 A m^{-2}
Electrolysis duration	2 h
Diaphragm	Porcelain P80, 3 mm thick
Current efficiency	96%
Cell voltage (V)	4.5 V
Deposit	Smooth, bright and perfect sheet

appearance of the electrodeposited nickel at different D2EHPA concentration and at a path pH of 2.5. But at pH of 1.5 there was a significant increase in the current efficiency at higher temperature, particularly at 333 K at both the D2EHPA concentrations i.e. 50 and 100 mg dm^{-3} studied. But the deposit physical appearance was found to be poor with cracking, peeling and pitting. This was possibly due to faster kinetics and non-uniform nucleation. Under similar experimental conditions investigations with the Hull-cell indicated that, at bath pH of 1.5, the working current density range can be extended and the tolerance limit of D2EHPA can be enhanced, as nickel deposit quality was not affected. Moreover, higher bath pH and higher bath temperature were favourable for nickel electrodeposition with regard to deposit physical appearance over a wide current density range.

3.2. *Deposit contamination*

The quantitative determination of codeposited/entrained/adsorbed impurities in the nickel deposits shows that besides the added metallic impurities the nickel deposit was also contaminated with lead, oxygen and sulphur. The lead contamination is perhaps from anode corrosion and carbon, oxygen, and sulphur from the nickel electrolyte. The presence of carbon and oxygen in both the upper and lower surfaces of electrodeposited nickel sheets was

Table 2. Tolerance limits and deposit contamination of different impurities during nickel electrowinning

Impurities	*Concentration in bath*/mg dm^{-3}	*Concentration in deposit*/%
(i) Individual effects of metallic and D2EHPA impurities		
Mg	500	0.006
Mn	250	0.14
Al	5	0.005
Zn	100	0.35
Co	500	1.72
Fe(II)	5	0.02
Fe(III)	100	0.17
Cu	100	0.05
D2EHPA	30	–
(ii) Combined effects of metallic and D2EHPA impurities		
Mg	500	< 0.0001
Mn	220	0.04
Al	5	< 0.0001
Zn	30	0.14
Co	180	0.61
Fe(II)	5	0.02
Fe(III)	10	–
Cu	30	0.095
D2EHPA	30	–

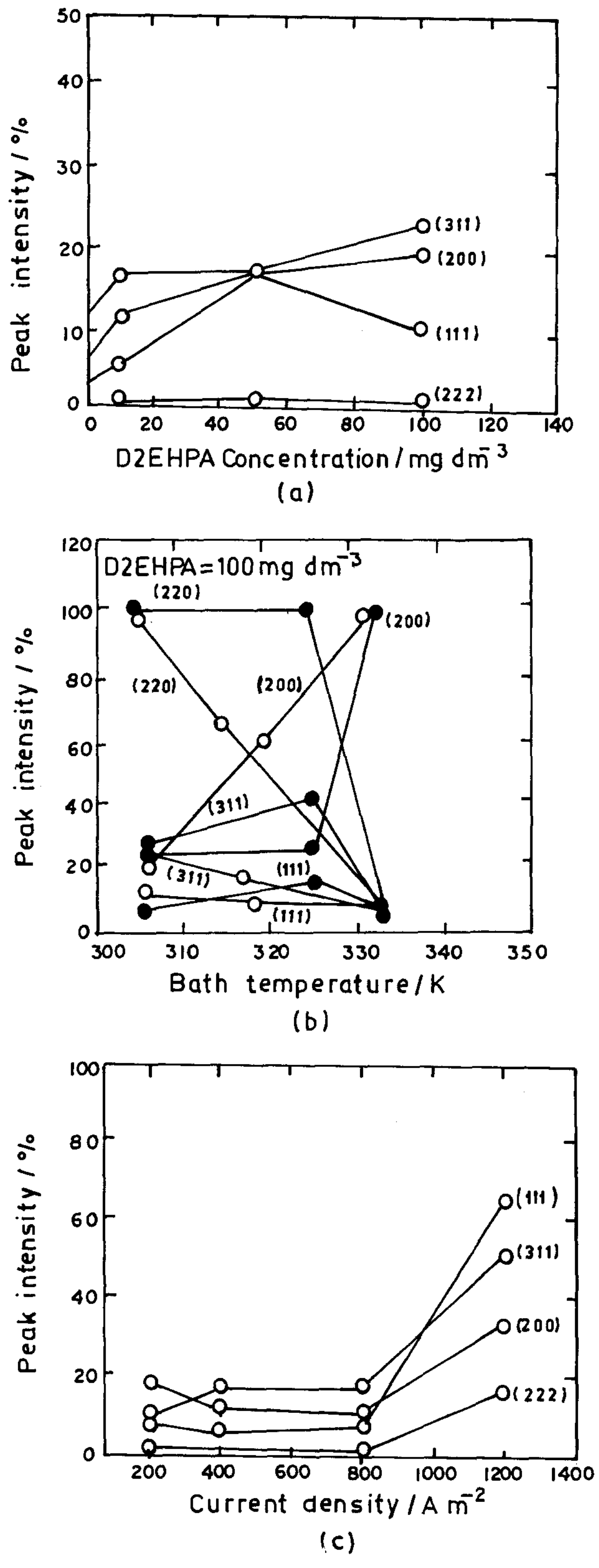

Fig. 3. Effect of various parameters on peak intensity at different crystallographic orientations of nickel deposits: (a) D2EHPA concentration, (b) bath temperature, and (c) current density. Key: (○) pH 2.5 and (●) pH 1.5.

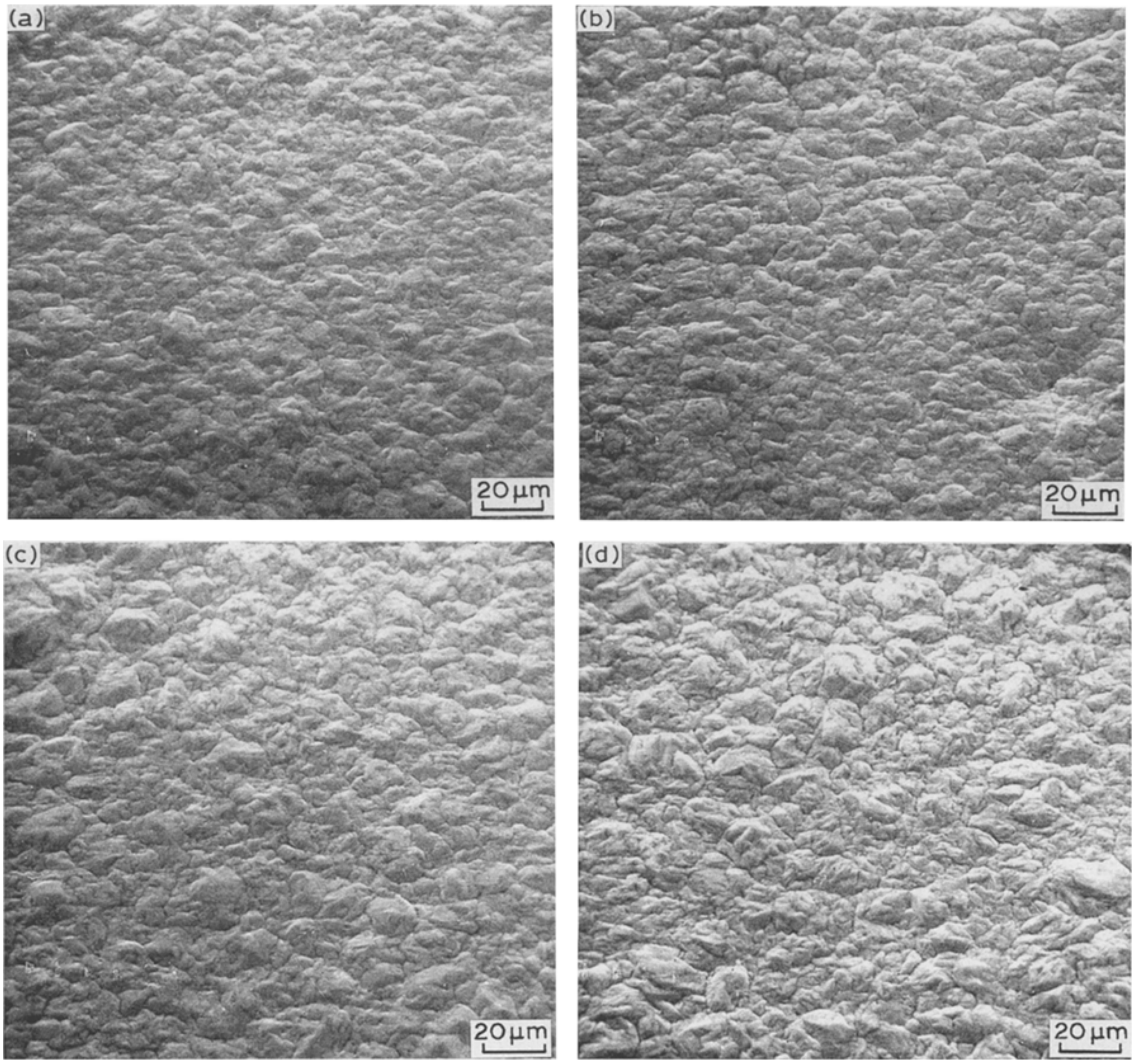

Fig. 4. SEM photomicrographs of nickel deposits under different experimental conditions. Metallic impurities, D2EHPA 100 mg dm^{-3} and (a) bath pH 2.5, temp. 305 K; (b) bath pH 2.5, temp. 333 K; (c) bath pH 1.5, temp. 305 K; and (d) bath pH 1.5, temp. 333 K.

detected as clear spots by WDAX. This indicates the interaction of the D2EHPA with depositing ions. The incorporation of sulphur is advantageous, as it increases the anode limiting current density and anode efficiency, when used in electroplating/forming/refining operations.

The contamination due to Mg, Al, and Pb is insignificant ($\sim$ 0.0002%). The results of deposit contamination with variation of different parameters are presented in Fig. 2. The nickel deposit contamination slightly increased due to Zn, Mn, Co, and Cu, when the D2EHPA concentration was varied from 10–100 mg dm^{-3} at bath pH 2.5. But at bath pH 1.5 the contamination of the nickel decreased only slightly except for Mn (Fig. 2(a) and (b)). This was probably due to the strong complexing nature of D2EHPA with specific metallic ions at lower bath pH and, therefore a changing electrochemical behaviour.

Higher bath temperatures up to 333 K (Fig. 2(c) and (d)) at D2EHPA 50 mg dm^{-3} and pH 2.5 resulted in deposits with less impurities while at 100 mg dm^{-3} D2EHPA contamination due to Zn, Co, Fe and Cu is greater at 333 K. The Mn contamination was reduced significantly with increase in bath temperature at both the D2EHPA concentrations. This was possibly due to greater adherence of Mn to the lead anode as MnO_2. At constant bath temperature and pH and variation of current density from 400–1200 A m^{-2} it was found that there was a gradual decrease in contamination with Zn, Cu, Fe and Co. Only Mn contamination increased with the increase in current density, probably because of the onset of the anodic limiting current density for MnO_2 deposition (Fig. 2(e) and (f)).

3.3. *Crystallographic orientations*

The presence of (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) orientations is indicated in all the nickel deposits, obtained under different experimental conditions. Therefore, the nickel structure is, as usual, face centred cubic (f.c.c.) as reported by others [8,26] in the presence of metallic and D2EHPA impurities also. The preferred orientation was found to be (2 2 0) in most of the electrodeposited sheets obtained in the presence of metallic and D2EHPA impurities. The relative intensities were calculated with respect

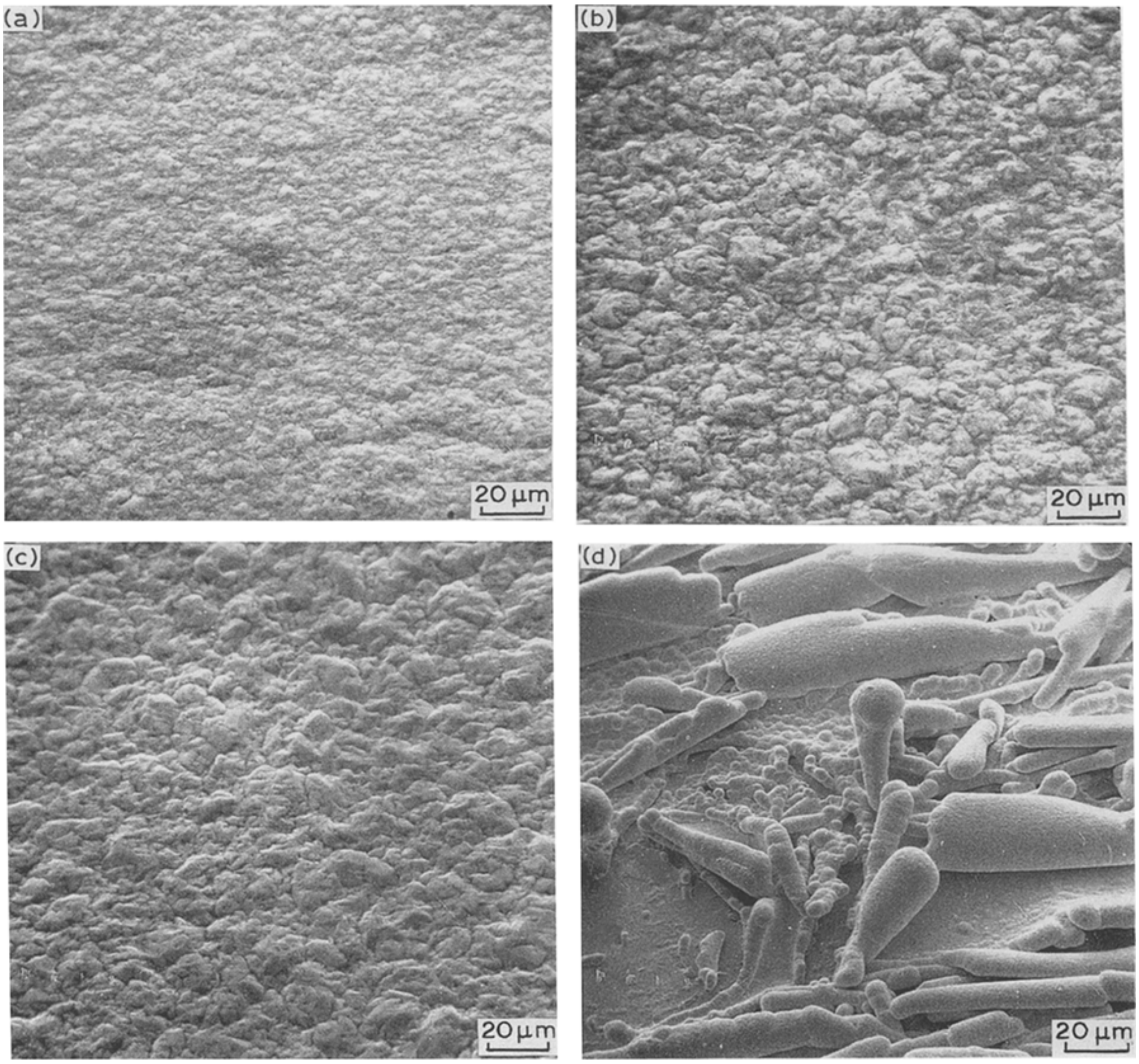

Fig. 5. SEM photomicrographs of nickel deposits under different current densities. Metallic impurities, D2EHPA $10\,mg\,dm^{-3}$, bath pH 2.5, temperature 305 K and current density (a) 200, (b) 400, (c) 800 and (d) $1200\,A\,m^{-2}$.

to the preferred orientation. The results of X-ray scanning showed that the peak intensity values changed with change in experimental conditions (Fig. 3). Some interesting changes in peak intensities of some of the orientations were observed with variation of experimental conditions. In general, the preferred orientation changed to (2 2 0) at 333 K and pH 2.5 and 1.5. Moreover, the (2 2 2) peak became significant at $1200\,A\,m^{-2}$ current density. At bath pH 2.5 and 1.5 peak intensities were found to increase with increase in D2EHPA concentration from $10–100\,mg\,dm^{-3}$ except the (1 1 1) orientation, where there was a decreasing tendency. Higher bath temperature (333 K) caused a decrease in peak heights at bath pH 2.5 and 1.5 except for the (2 0 0) orientation, where it became the preferred orientation. The peak intensities were higher at low and very high current densities. Moreover, the peak height values gradually increased with increase in current density from $800–1200\,A\,m^{-2}$ for all the crystallographic orientations.

3.4. *Surface morphology*

Some typical SEM photomicrographs showing the surface morphology of deposits obtained under different experimental conditions are shown in Figs 4 and 5. In general, it was observed that the impurities in the bath changed the deposit morphology with change in electrowinning bath condition. At bath pH 1.5 the increase of crystal size and greater compactness was observed. But at higher bath temperatures, i.e. 333 K, the surface morphology changed significantly at both pH 2.5 and 1.5 with a nonuniform increase in the crystal size. The gradual change in surface morphology with increasing current density from $200–1200\,A\,m^{-2}$ is shown in Fig. 5.

At $200\,A\,m^{-2}$ the crystallite size decreased significantly. This microcrystallinity is also reflected by the deposit brightness. At high current density the surface roughness increased, which was also observed in the physical appearance of the deposit. At a current density of $1200\,A\,m^{-2}$ nodular crystals of irregular size and shape were observed. This was possibly due to faster nucleation with change in the deposition kinetics.

4. Conclusions

The following conclusions can be drawn from this study:

(i) It is possible to achieve bright, smooth, and perfect nickel sheet with ~ 96% current efficiency and >99% metal purity at optimum nickel electrowinning conditions in the presence of metallic and D2EPHA impurities.

(ii) The deposit physical appearance is affected significantly at bath pH 2.5 and D2EHPA $>50\,\text{mg}\,\text{dm}^{-3}$ by cracking, peeling and pitting. At lower pH the bath can tolerate slightly greater D2EHPA concentrations. Moreover, up to $100\,\text{mg}\,\text{dm}^{-3}$ of D2EHPA there is an insignificant change (±1%) in current efficiency at bath pH 2.5 and 1.5.

(iii) The major contamination of the nickel deposit is due to cobalt, because of its similar electrochemical behaviour. Lead from the anode and carbon and sulphur from the electrolyte also contaminated the deposits to some extent, along with other metallic impurities added to the bath. The deposit contamination was found to decrease with decrease in pH from 2.5 to 1.5.

(iv) There is no change in nickel crystal structure in the presence of metallic and D2EHPA impurities from f.c.c., as all crystallographic orientations are present. But the peak height values changed with change in nickel bath condition and experimental conditions. In most of the deposits, (2 2 0) is the preferred orientation. The (2 0 0) became the preferred orientation at 333 K. At $1200\,\text{A}\,\text{m}^{-2}$ current density, the (2 2 2) peak was significant.

(v) The surface morphology changed with change in experimental conditions, particularly at higher D2EHPA concentration, higher bath pH and high current density.

(vi) Based on the experimental data the tolerance limit of D2EHPA has been identified under different experimental conditions for perfect, smooth, and bright nickel sheet, which can be easily stripped from the cathode surface.

(vii) It is possible to develop a viable and economic process for nickel electrowinning from solutions contaminated with metallic and D2EHPA impurities by careful control of the process parameters.

Acknowledgements

We are grateful to the Director and Head, Hydro & Electrometallurgy Division, of RRL(B) and German Academic Exchange Service (DAAD) Bonn, Germany for their encouragement to complete this project. Also financial assistance in the form of DAAD fellowship provided to SKG for placement at this institute is gratefully acknowledged.

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