Electrodeposition and Morphology Analysis of Nickel Nanoparticles from Sulphate Bath

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The electrodeposition of Nickel in the presence of organic compound was studied systematically as function of the nature of the organic additive. The effects of various parameters such as nickel sulphate concentration, bath temperature, current density have been investigated on deposit physical appearance. The tolerance limits and the effect of combined organic additive have been identified under different experimental conditions. We have used scanning electron microscopy (SEM) to characterize the surface morphology of deposits. The SEM pictures show the formation of domain growth of nickel in which nanoparticles are mostly concentrated at domain boundaries and incorporated in the coating matrix to improve the surface mechanical properties. The coatings are found to be highly adherent and uniform by adding calixarene derivative as organic additive at very low concentration. Three-dimensional AFM images confirm that the presence of calixarene derivative improves the surface smoothness. The microhardness measurements were performed and the structure of deposits was examined by X-ray diffraction.

Keywords: Electrodeposition; Ni; Calixarene derivative, Surface morphology; Scanning electron microscopy; AFM

I. INTRODUCTION

The usage of nickel for electroplating has increased substantially in the last two decades and appears likely to grow because of greater consumption in the developing countries of Asia [1–3]. Nickel electroplating has gained major importance as a cheap and versatile surface finishing process for decorative applications [4–23]. Hence, nickel coating by electroplating is of special interest especially in the electronic industry, due to the possession of a combination of properties, such as good corrosion and wear resistance, deposit uniformity, electrical and thermal conductivity [24].

Previous studies of nickel electrodeposition mainly focused on the electrochemical behaviour and on the micrometre-scale morphology of nickel deposits on carbon and various metallic substrates and their dependence on the deposition conditions, such as temperature and stirring, the nature of the substrate and the electrolyte composition [25]. Regarding the latter, in particular the role of boric acid as a component in the widely-utilized Watts electrolyte has been studied, which is conventionally believed to act as a buffer [26].

Electrodeposition involves the reduction at the cathode surface of nickel ions arriving from the electrolyte to produce a deposit. The nickel coating is very thin and, often, so poorly adherent if organic additives are not been added. The presence of tiny amounts of additives or of complexing agents, can have enormous consequences for the resulting microstructure and composition of the deposited materials and hence for their properties. The kinetics and mechanisms of single metal deposition were studied extensively and reaction paths for many systems were established [27–29]. Complexing species play an important role for the discharge mechanism because they change the thermodynamic equilibrium and the rate determining step of the charge transfer reaction at the electrode surface. The additives are not only needed for levelling and superfilling, but they also affect the structure and roughness of the deposits.

Electron microscopy is ideal for examining surface characteristics and structure since it enables high magnifications to be utilised up to ×100 000. The depth of focus is far superior to that of optical microscopy and the resolution possible is of the order of 5–10 Å for the transmission electron microscope and 150–250 Å for the Scanning Electron Microscopy scope [30]. Several groups used the Scanning Electron Microscopy (SEM) or the Atomic Force Microscopy (AFM) to study the effect of additives on the formation and movement of atomic steps during the growth of electrodeposits. In recent study, Ganesh et al. [31] were found that electrodeposition of nickel from a nickel sulphamate bath in the presence of a magnetic field applied at an angle of 45° to the cathode surface produces a nickel deposit with a fine grain structure. Gelatine was added to nickel electroplating bath as organic additive to control the deposition rate, crystallization, leveling and brightness of the deposit [32]. Less knowledge therefore is available on the mechanism of nickel deposition by using organic additives and how deposition conditions affect deposit structure and properties. Nickel electrodeposition exhibits complex potential-dependent growth be-
The aim of the current work is to study the effect of operating conditions and bath additives on the Faradaic efficiency, chemical composition, surface morphology and hardness of nickel deposited. The morphology obtained is dependent on a variety of electrowinning parameters and conditions used for the process.

II. EXPERIMENTAL

The electrolytic cell used for the electrodeposition of nickel consisted of a 250 ml. The position of cathode and anode was used as described in Hull [33]. A pure nickel sheet (5 cm x 5 cm) was used as anode; the cathode used for electrodeposition was a sheet of copper (2.5 cm x 2.5 cm). The polished copper substrate was degreased with acetone, dipped in acid and finally washed with distilled water and ultrasonically cleaned after electrolys.

A thermostatic bath was used to control the temperature at ±0.01°C. After electrolys, the cathode was washed with distilled water and dried under a stream of air at 105°C during 30 minutes. Dull and bright deposits were obtained without and with organic additives, respectively. The morphology of the deposit was observed by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM).

The electrolyte was a solution obtained by dissolving nickel sulphate, nickel chloride, Boric acid and sodium sulphate in distilled water. Boric acid and sodium sulphate were used to improve the buffering capacity and the conductivity of the electrolyte. All chemicals were analytical reagent grade. The pH was measured by means of Inolab pH-meter from WTW and adjusted to a value of 4.3 through additions of some drops of H2SO4 and NaOH. Magnetic stirring is required to minimize the sedimentation rate and help homogenize the suspension. The electrolysis conditions were bath temperature 50-80°C, current density 1-11 A dm⁻², anode/cathode area ratio 2:1. The electrodeposition was carried out by using regulated DC power supply at various current densities. The Faradaic efficiency was determined from the weight gained by the cathode due to the nickel deposition. The bath compositions for dull and bright deposits are given in Table I and Table II.

The microhardness measurements were performed on a Buchler Microhardness Tester (Micromet 100) by applying 50 g and a loading time of 15 seconds. On average, at least 5 measurements were performed on the surface of each coating. The microstructure of the coatings was also analyzed by means of X-ray diffraction. The grain size can be calculated using the Scherrer formula [34],

\[ \lambda / B \cos \theta = \text{mean grain size}, \]

where \( \lambda \) is the X-ray wavelength, \( \theta \) is the half of diffraction angle 2θ, and \( B \) is the peak half width of X-ray. The Faradaic Efficiency \( (FE) \) was calculated using the following equations:

\[ FE = \frac{W_{\text{exp}}}{W_{\text{th}}} \times 100\%, \]

\[ W_{\text{th}} = \frac{M_i \cdot I \cdot t}{nF}, \]

where \( W_{\text{exp}} \) is the measured weight of the deposit (g), \( W_{\text{th}} \) is the theoretical weight obtained from Faraday law, \( M_i \) is the atomic weight of nickel /g mol⁻¹, \( I \) is the current passed (A), \( t \) is the deposition time (S), \( n \) is the number of electrons transferred in the reduction of 1 mol atoms of nickel \((n = 2)\), \( F = 96485.3 \ C \ mol⁻¹ \), is the Faraday constant.

III. RESULTS AND DISCUSSIONS

Optimum bath composition and conditions of electrodeposition of nickel onto Cu substrates have been given in Table I and Table II. Over 50 samples, coated under different operating conditions were characterized. The effect of current density on the quality of coatings by using the chemical composition of baths cited in (Table II) was investigated. The current densities were varied from 1 to 11 A dm⁻². It has been known that

### TABLE I: Bath chemical composition of dull nickel deposit.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration / g L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>25-350</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>20</td>
</tr>
<tr>
<td>H₂BO₃</td>
<td>10</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>5</td>
</tr>
<tr>
<td>NaC₂H₄NO₃</td>
<td>1.2</td>
</tr>
<tr>
<td>Gelatine</td>
<td>0.88 wt. %</td>
</tr>
<tr>
<td>Calixarene derivative</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### TABLE II: Bath chemical composition of bright and smooth nickel deposit.

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![FIG. 1: Effect of current density on Faradaic efficiency.](image-url)

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electrodeposition under limiting current conditions leads to dendritic or powdery deposits. Therefore, the value of applied current density with respect to the mass transport limited current density is a critical parameter for deposit morphology. As shown in Fig. 1, the Faradaic efficiency ($FE$) increases with increasing current density till reaching a maximum between $6$ and $8$ A dm$^{-2}$. By increasing the current density up to $8$ A dm$^{-2}$, the $FE$ decreased quickly and the coatings obtained were non-uniform, randomly oriented deposit and tended to have some powdery accumulations. Intense bubbles were observed at high densities, it means that hydrogen evolution becomes more prominent. A decrease in the value of the current density of the deposition process enhances density of the surface metal film formation onto copper substrates due to an increase in nucleation rate and a decrease in the radius of the zero nucleation zones. As a result of this, a compact deposit film is formed with a smaller quantity of electrodeposited nickel, and its coarseness and porosity decrease with a decreasing exchange current density.

In this study, the amount of nickel sulphate in each bath was varied from $25$ to $350$ g L$^{-1}$; the current density was fixed at $7$ A dm$^{-2}$ because preliminary results showed that this current density gave bright and smooth deposits. The results are given in Fig. 2. An increase in the bath concentration of Ni$^{2+}$ has also been reported to cause a dramatic increase in the Faradaic efficiency [32], the cathode deposits obtained were silvery white. At higher concentration, the deposits obtained were dull in appearance which can be attributed to the deposition of double salts. In general, the $FE$ was found to decrease after using the concentration of Ni$^{2+}$ more than $150$ g L$^{-1}$. The optimum nickel sulphate concentration was found $150$ g L$^{-1}$ and plating period was $10$ minutes.

In order to illustrate the effect of organic additives on the morphology of coatings, nickel was deposited onto Cu substrates from optimised chemical composition conditions. The bath of nickel plating contains: nickel sulphate $150$ g L$^{-1}$, nickel chloride $20$ g L$^{-1}$, boric acid $10$ g L$^{-1}$, saccharin $1.2$ g L$^{-1}$, gelatine $0.88$ wt. % and $0.05$ g L$^{-1}$ of thioamide calix[4]arene derivative used as organic additive belongs to new class of surfactants which display synergistic properties in their binary mixtures with saccharin on the deposit quality. However, in order to avoid any complexing effects of ammonium in plating bath, sodium sulphate was added at the concentration of $5$ g L$^{-1}$. Almost complete surface coverage was achieved even with current density of $7$ A dm$^{-2}$ at temperature $58^\circ$C. Scanning Electron Microscope (SEM) was used to study the morphology of nickel deposit. SEM micrographs given in Figs. 3(A) and (B) show the structure at the higher magnifications of deposits obtained from electrolyte with chemical composition cited in Table II. As can be seen deposits from Figs. 3(A) and (B), the surface appears smoother with few nod-
FIG. 4: AFM images of nickel coatings. (A) without additive, (B) Calixarene derivative used as organic additive.

ules present on them. This may be attributed to the presence of sufficiently surfactant complex ions at the cathode which on reduction gives smooth deposition of nickel. The quality of nickel deposits depends on the concentration of non-ionic surfactant. At low organic levels, a rise in its concentration increases its adsorption onto the copper substrate and so blocks more of surface. The calixarene compound, 5,11,17,23,29,35-Hexakis-t-octyl-37,38,39,40,41,42-hexakis (N-phenylthiocarbamoyl methoxy) calix[6]arene, was shown in our previous paper to form a cage complex with Ni\(^{2+}\) selectively [35]. In the current work, it was applied in catalytic amounts: 0.05 g were dissolved by protonation in 2 mL of 2 M H\(_2\)SO\(_4\) containing 50 v% dichloromethane at 318 K, then 0.1 mL of the clear solution was added to the sulphate bath. Complex formation with Ni\(^{2+}\) prevented the precipitation at the trace concentration. The effect of the calixarene in the electroplating is discussed in terms of its cationic complex with Ni\(^{2+}\), bearing protonated nitrogen atoms. By comparing with similar acetonilide structures [36], the first protonation constant is estimated to be log \(K_{ca. 5}\) in aqueous solution. Thus, the complex would bear a charge higher than +2 at the applied pH, facilitating the migration to the cathodic surface compared with uncomplexed Ni\(^{2+}\). Upon reduction of Ni\(^{2+}\), the calixarene can again form a complex. Chemisorption of the calix[4]arene derivative at metal surfaces takes place through its sulfur atom with electron transfer by the loosely bound electrons in the S=C \(\pi\) bond. The thioamide groups of the adsorbed calixarene derivative are oriented towards the solution and can be protonated by H\(^{+}\) ions that are in the vicinity of the electrode. The observed influence of the surfactant and calixarene derivative on the growth morphology of nickel deposits was attributed to their effect on surface diffusion. Surfactant is added to the bath to ensure that hydrogen gas bubbles, which form on the work piece, are easily liberated by solution agitation. The role of substrate structure was also investigated and it was found that organic additives adsorbed preferentially at defect sites.

A weak deposit and some powdery accumulations were obtained from electrolyte with chemical composition cited in Table I. The morphology and crystal structure can be modified in absence of organic additives. From SEM images shown in Figs. 3(C) and (D), it would seem that the morphology of deposit has more number of nodules and the surface is not smooth significantly, although the micro-cracks may have become slightly bigger. On other hand, by increasing the current density of the deposition process can produce a porous deposit due to hydrogen co-deposition. The phenomenon can be explained by the fact that the hydrogen evolution is more dominant than the reaction of nickel deposition when organic additives are not added. Further evidence for comparatively smoother surface of deposits can be obtained from the comparison of AFM images shown in Figs. 4(A) and (B). These images were obtained for nickel coatings deposited on mild copper coupons using the chemical bath composition cited in Table I and II. It is clear that deposits have different surface roughness values due to the different growth patterns. Three-dimensional AFM images in Figs. 5(A) and (B) show that the presence of calixarene derivative as organic additive improves the surface smoothness. The
roughness value obtained for the coatings from Figs. 5(A) and (B) are respectively 198.6 and 12.5 nm. These results confirm the effect of calixarene on the deposits morphology, the coatings results in smoother surface.

XRD studies of the deposited films were done. The conditions of deposition are mentioned in Table II. The deposit along Ni(200) as the intensity of peak is double in comparison to Ni (110) in case of Ni film. The morphology and crystal structure can be modified in presence of the organic additives. Single peaks at a 2θ value of 52.034°, 61.14°, 9.74°, 114.75° and 123.16° are seen for both deposit (Figs. 6(a) and (b)). Therefore, there is apparition of two peaks at 70.27° and 75.46° for the smooth deposit using bath composition cited in Table II. In order to investigate the calixarene compound effect on the surface morphology of nickel deposit, several samples were grown by varying the additive concentration. When the concentration of calixarene derivative decreases, the surface quality becomes rough. This shows the effect of the organic additive used as surfactant.

The grain sizes calculated from full width at half maximum (FWHM) of the peaks are 11.5 and 13.5 nm. The deposition of nickel from the sulphate bath cited in Table II leads to smooth, adherent and hard deposit. The micro-hardness values are around 535 and 601 VHN. However, the hardness in the case of coatings obtained from sulphate bath without organic additives (Table I) decreased approximately to 190 VHN.

### IV. CONCLUSIONS

We have carried out electrodeposition of nickel onto Cu substrates using nickel sulphate bath in the presence of organic additive. Electrolyte composition has been shown to have a significant effect on the morphology of the deposits. Our results show that the use of calixarene derivative as organic additive leads to very fine grain and smooth deposit as opposed the micro-cracks may have become slightly bigger to a layer type growth in its absence. Three-dimensional AFM images show that the presence of calixarene derivative improves the surface smoothness.

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