JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 508–515

Relation between the presence of inhibitors and deposit morphology in nickel deposition

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Received 22 June 1992; revised 9 November 1992.

Nickel deposition on vitreous carbon from concentrated nickel chloride solutions has been studied. The formation of inhibitors such as H_{ads} and nickel hydroxides has been related to both the shape of the *i–t* transient and the morphology of the deposit. The experimental parameters (pH, nickel (II) and chloride concentration) were varied in order to study the conditions leading to a compact, homogeneous metallic deposit.

1. Introduction

Nickel deposition has been studied in these laboratories at different nickel (II) concentrations in chloride baths both at solution preparation pH and at adjusted pHs [1–4]. Previous results indicate that the deposition of nickel is a complex process in which the inhibition of deposit formation has an important role. The ultimate aim of this work is to study industrial concentration levels starting from simple low concentration systems. Along with the electrochemical work, a systematic morphological study of the deposits has been carried out. It has been established that the deposits obtained at very low overpotentials, with a nickel concentration of the order of 0.5 M, at the pH of preparation, are compact, metallic, and with a growth resembling a 'cauliflower' pattern.

In order to study the range of conditions which permit deposition, without inhibition problems, it was necessary to establish when the inhibition of the process took place and which of the inhibitor-intermediates proposed in the literature [4–11] such as H_{ads} or nickel hydroxides occur under which experimental conditions.

A complete study, in which the acidity of the media and the chloride anion concentration were varied, is now presented. This study shows how these parameters influence the appearance and morphology of the deposit. Furthermore, the concentration range which is available to obtain good deposits in this chloride bath is established.

Moreover interest is centred upon the conditions in which the deposit obtained is similar using both potentiostatic and galvanostatic techniques, because galvanostatic conditions are used in industrial deposition.

2. Experimental details

Voltammetric and potentiostatic experiments were carried out using a Belport 105 potentiostat together with a PAR 175 signal generator and a Phillips PM 8133 X–Y recorder. The galvanostatic measurements were obtained using a PAR potentiostat model 273 controlled by an IBM PS2 model 30. The morphology of the deposits was examined using an Olympus PMGC3 metallographic microscope and a JEOL SM 840 scanning electron microscope.

The solutions were freshly prepared with $NiCl_2.6H_2O$ and NaCl (Merck PA grade); all water used was obtained from a Milipore-Milli Q system. When necessary the pH was adjusted using suitable additions of HCl or NH_4OH. Prior to each experiment all solutions were deoxygenated with argon.

A conventional three-electrode cell was used, the reference being a saturated calomel electrode and all the potentials are reported with respect to this electrode. The working and the counter electrodes were both Metrohm vitreous carbon rods (diameter 2 mm). The working electrode was polished to a mirror finish before each run, using alumina of different grades (3.75, 1.87 and 0.3 μm) and ultrasonically cleaned for 2 min in water. Reproducibility of the experiments depended on the quality of polishing. The working electrode was brought into contact with the solution at the solution meniscus only. In the experiments using a rotating disk electrode (RDE) a Tacussel vitreous carbon rod of 3 mm diameter in a Teflon support was used.

3. Results

A study of the influence of pH, Ni(II) and Cl^- concentrations on the deposition process was carried out in order to find the conditions which lead to deposits with satisfactory appearance and morphology. Moreover, interest was focused on the identification of the species responsible for the inhibition detected under the different experimental conditions and to relate these to the deposit type obtained.

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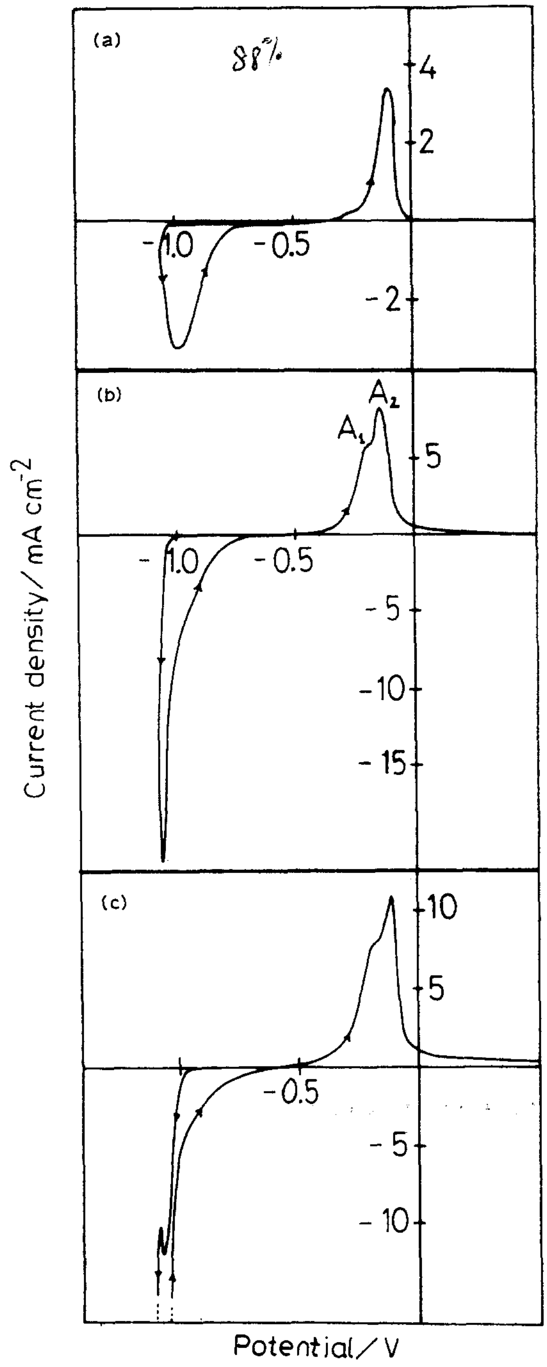

Fig. 1. Cyclic voltammograms of $NiCl_2$ 0.5 M solution (v = 50 mV s^{-1}) at different pH: (a) 2.1, (b) 3.4 and (c) 5.0.

3.1. *Influence of pH*

3.1.1. Voltammetric study. The voltammetric curves obtained for 0.5 M $NiCl_2$ solution and the different pHs studied (Fig. 1) show gradual modifications. Firstly, upon increasing the pH of the medium, the deposition begins at less negative potentials (Table 1). This fact suggests the formation of hydroxylated nickel(II) compounds which favours the deposition process, as has been generally accepted [4, 11, 12 and references therein, 13].

Table 1. Variation of the initial deposition potential in the voltammetric scan with pH of the solution ([$NiCl_2$] = 0.5 m and v = 50 mV s^{-1})

pH	E_d/*mV(SCE)*
0.8	−1030
2.1	−1020
3.0	−1015
3.6	−995
4.4	−960
4.6	−955
5.0	−940
6.5	−930

The voltammogram shows a reduction peak when the pH of the medium is increased (from a pH value of 4). A similar peak has been detected for other experimental conditions (low Ni(II) concentration and pH between 4 and 5) related to an inhibition process arising from the predominance of secondary reactions [2]. When voltammetric holds were carried out in different zones of these voltammetric curves, different kinds of deposits were obtained and growth inhibition was evident for potentials corresponding to the reduction peak.

For all pHs, a double peak was obtained in the anodic scan. This double peak was assigned to the oxidation of nickel deposits with different hydrogen content using the information of Fleischmann *et al.* [14, 15]. The A_2 peak was identified as α-nickel, with minor hydrogen content, and the A_1 peak as β-nickel, with more hydrogen. When the scan was reversed in the initial part of the deposition, α-nickel was predominant in all conditions. Experimental results indicate that the proportion Qβform/Qαform increases for the intermediate pHs studied (3 < pH < 4). These findings may be explained as follows: as the pH is lowered, hydrogen evolution increases and the protons are consumed in this reaction, leaving the hydrogen-lean form of nickel on the electrode. As the pH is increased the discharge potential is lowered and so the rate of hydrogen evolution decreases: the protons, instead of forming hydrogen are included in the deposit, resulting in a relative increase in the hydrogen-richer forms of nickel in the deposit. At the highest pH's due to the very low proton concentration, very little hydrogen is included in the deposit and so the hydrogen-lean forms of nickel increase in dominance again.

At pH 0.8 β-nickel is the dominant form found in the anodic scan; in these conditions the proton concentration is sufficient to produce hydrogen and to obtain hydrogen-rich nickel at the same time.

3.1.2. Potentiostatic study. The deposition process was also analyzed, using potentiostatic methods, relating the form of the *i–t* transients with deposit morphology by optical (OM) and scanning electron (SEM) microscopy.

The *i–t* transients were recorded for $NiCl_2$ 0.5 M at pH's between 0.7 and 6.5. The morphology of the deposit at each pH studied and at different potentials was analysed in order to relate the appearance of the deposit with the possible inhibitors and with the shape of the *i–t* transient.

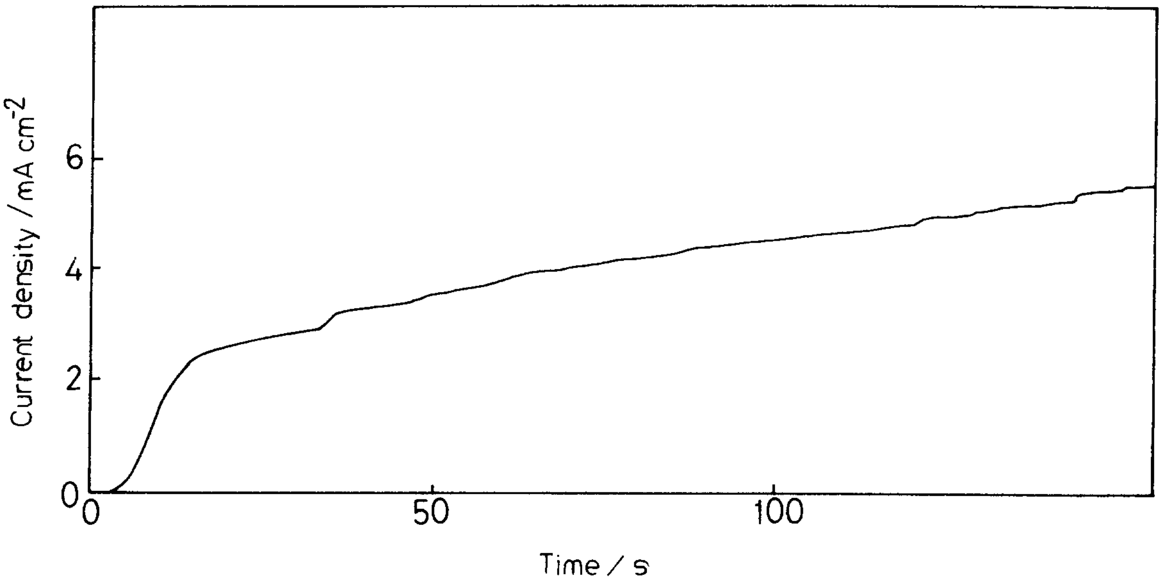

Fig. 2. Potential step transient for nickel deposition in 0.5 M $NiCl_2$ at pH 2.1 from $E_0 = -500$ to -960 mV.

pH<2.3

For solutions of pH < 2.3 *i–t* transients were obtained for which the current increased monotonically to a quasi-steady value for low overpotentials; upon increasing the overpotential the form of the transient changed and the current reached a plateau and afterwards began to diminish slowly. However, for these pHs, hydrogen evolution accompanied the nickel deposition and produced a deformation in the *i–t* curves after a certain deposition time (Fig. 2), which was mainly caused by the presence of hydrogen bubbles, which after generation, desorb off the electrode leading to variations in the effective surface. Obviously, this distortion in the *i–t* transients is more evident at lower pH.

A grey metallic, bright and compact deposit was always obtained, but it was not always uniformly distributed on the electrode, as a consequence of simultaneous hydrogen evolution. SEM study showed it to be 'cauliflower' type and coarse grained (Fig. 3); the grain size was greater than at preparation pH[3].

2.3<pH<4.5

For solutions of 2.3 < pH < 4.5 the form of the *i–t* transients depended on the potential.

For low overpotentials, monotonic *i–t* transients (Fig. 4 curve a) were obtained. Analysis of these curves always revealed a progressive nucleation and three-dimensional growth. The deposit corresponding to these curves was bright, compact and homogeneous all over the electrode. In these curves, sporadic distortions in the transients were observed due to slight evolution of hydrogen bubbles for pH values close to 2.5.

In all cases, the morphology of the deposit was similar (type Fig. 3), but there was a gradual decrease in grain size as the pH of the medium was increased.

These results show that the monotonic increase in the current with time, in the *i–t* transients, was directly related, in the bath studied, with a good deposit, which was compact, homogeneous and 'cauliflower' type.

When the overpotential was increased a decrease in the current was obtained after a certain time (Fig. 4 curve b). This decrease was more pronounced than the fall corresponding to diffusion control and indicated inhibition of the deposition process. Experiments using RDE corroborated this. When the current began to decrease, the deposit darkened and, for the lower pH in this range, small bubbles of gas accompanied the deposition process. The deposits obtained in these conditions were dark and thin-layered (Fig. 5), as a consequence of an inhibition affecting the vertical growth of the deposit.

In some ranges of overpotential a cyclic oscillation was detected in the *i–t* transient (Fig. 4 curve c) following the sudden fall in the *i–t* transient. In these cases, green precipitates were always observed on the deposits. OM revealed these green precipitates formed over the nickel deposit.

When a sudden fall in the current is detected in the *i–t* transient inhibition of the process takes place, indicated by the change in the deposit appearance leading to thin layered deposits.

Although the behaviour of the deposition process was similar in the range 2.3 < pH < 4, some differences were significant for different pH values.

For the lowest pH in this range, no inhibition was observed over a large range of potentials. It was necessary to use high overpotentials to observe inhibition of the process, but it was not as pronounced as for the pH of preparation, for which the reduction of current was very pronounced [3].

For pH values > 3 the inhibition was detected at lower potentials.

pH>4.5

For high pH values (pH > 4.5) inhibition of the process was evident from the shape of the *i–t* transients

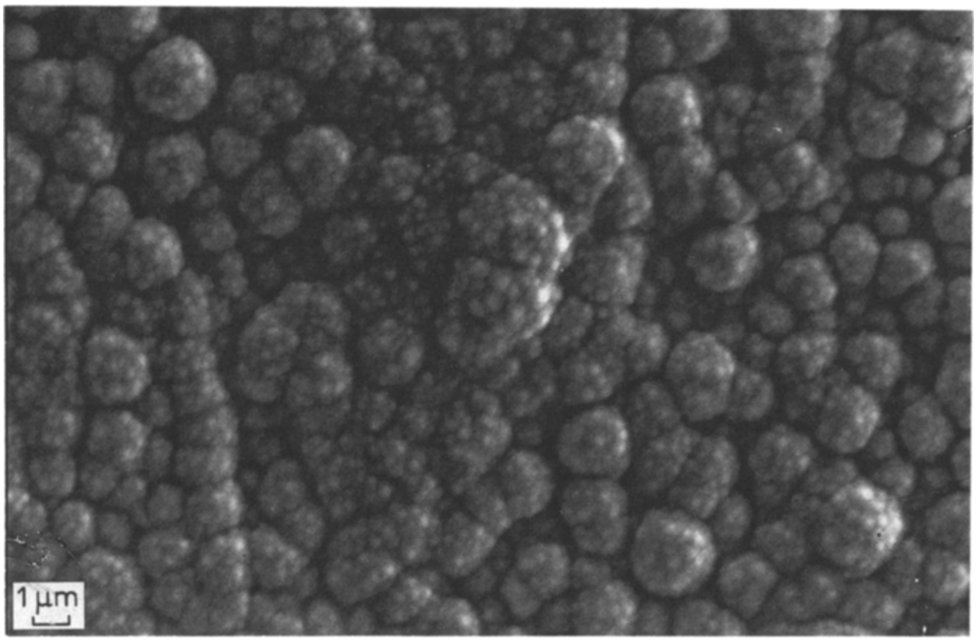

Fig. 3. Scanning electron micrograph of nickel deposition in 0.5 M $NiCl_2$ solution at pH 2.1 by 400 s at −920 mV.

and morphology of the deposits even at very low overpotentials. It was not possible to obtain a monotonic increase of current even changing all conditions and homogeneous and compact deposits were not obtained.

As a consequence of this study it can be concluded that for deposition from 0.5 M $NiCl_2$, a deposit free from inhibition and satisfactory at macroscopic level can be obtained potentiostatically using low overpotentials in the range $2.3 < pH < 4$. In this range for the lowest pH values, the deposit obtained is adequate but the deposition is accompanied by some hydrogen evolution which causes small holes in the deposit surface. On the other hand, around pH = 4 the probability of nickel deposition inhibition increased. These effects were balanced at intermediate pH values; for

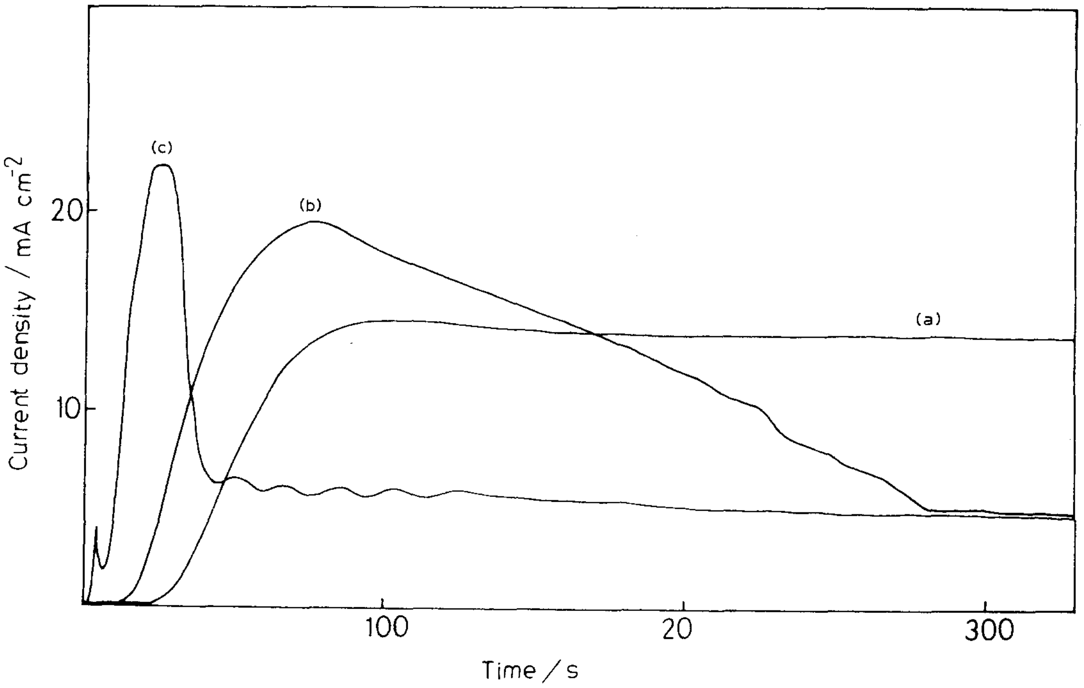

Fig. 4. Potential step transients for nickel deposition in 0.5 M $NiCl_2$ solutions at pH 3.0. Curve a: −940 mV; curve b: −960 mV; curve c: −1015 mV.

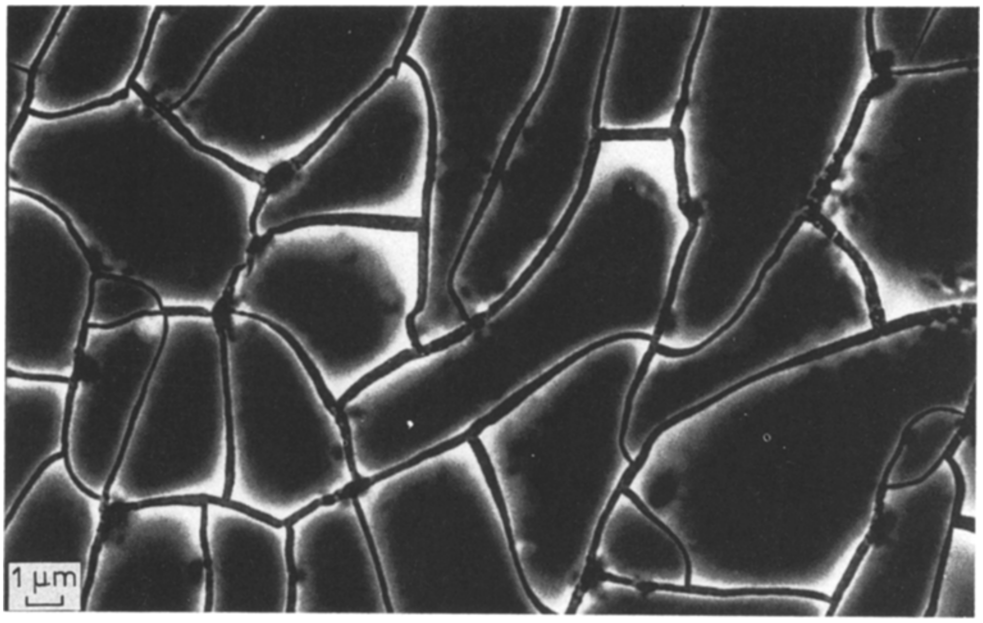

Fig. 5. Scanning electron micrograph of nickel deposition in 0.5 M $NiCl_2$ solution at pH 3.0 obtained by 450 s at − 1040 mV.

this reason, pH = 3 was selected to study the influence of different parameters. At this pH the range of potentials for which the deposition was free from inhibition processes is greatest and when inhibition began to appear it was less pronounced than at higher pH values.

In these conditions, the influence of Ni(II) and Cl^- concentrations was analysed.

3.2. *Influence of Cl^- concentration*

Since in the chloride bath used the better deposits were obtained from a solution of pH around 3, it was decided to analyse the influence in these conditions of high chloride concentration. The modification of the process was analysed at various points after the controlled addition of sodium chloride until a total chloride concentration of 4 M was obtained: an electrochemical study was made for all chloride concentrations.

At high Cl^- concentrations reproducibility was a serious problem. It seemed that the presence of high chloride concentrations modified the initial stages of the process, thus affecting the substrate and the initial nickel (II) species.

In voltammetric studies using more negative limit potentials, in systems with high chloride concentration, it was possible to obtain a current efficiency close to 100%. Similarly, voltammetric stripping revealed that the increase in chloride ions favoured the formation of the more hydrogenated forms of nickel.

With regard to the potentiostatic studies, the *i–t* transients revealed a different behaviour at high chloride concentrations from that observed for $[Cl^-]$ = 1 M. The potentiostatic curves, even at low overpotentials, lose their monotonic current increase and the *i–t* transients (Fig. 6) were spread out at intervals. The deposit obtained in these lower potentials never had the ‘cauliflower’ appearance, being black, loose and fine-grained.

The presence of higher chloride concentration did not substantially modify the beginning of the process, but slightly advanced it. At high chloride concentrations a modification in the form of the initial reactant (a chloro-hydroxylated nickel complex) may take place, which results in more reactive species.

The results indicate that the deposit is better using $NiCl_2$ 0.5 M and pH 3 when the chloride concentration is only that corresponding to the nickel salt used.

3.3. *Influence of nickel(II) concentration*

When the experimental conditions of pH and Cl^- concentration were related to the kind of deposit obtained in 0.5 M $NiCl_2$ solutions, the concentration of nickel (II) was diminished but the conditions for which inhibition processes were not detected (low overpotentials, pH = 3 and 1 M chloride concentration) were maintained.

For 0.1 M $NiCl_2$ and $[Cl^-]$ = 1 M (adjusted with NaCl), the behaviour was similar to that observed for 0.5 M, in both the voltammetric and potentiostatic results. For low overpotentials, the usual *i–t* transients and deposit related to them (compact, grey metallic, homogeneous) were obtained and the morphology was as expected (cauliflower type). So the deposit obtained was satisfactory for Ni(II) concentrations in a range of 0.1–0.5 M for $[Cl^-] = 1$ M.

On the other hand, when Ni(II) concentration was increased to 1 M using $NiCl_2$ 1 M in no case was a monotonic *i–t* transient obtained, even at very low overpotentials.

The voltammetric study for 1 M $NiCl_2$ showed that the more hydrogenated forms of nickel were also favoured, in a similar way to low nickel(II)/high chloride concentration.

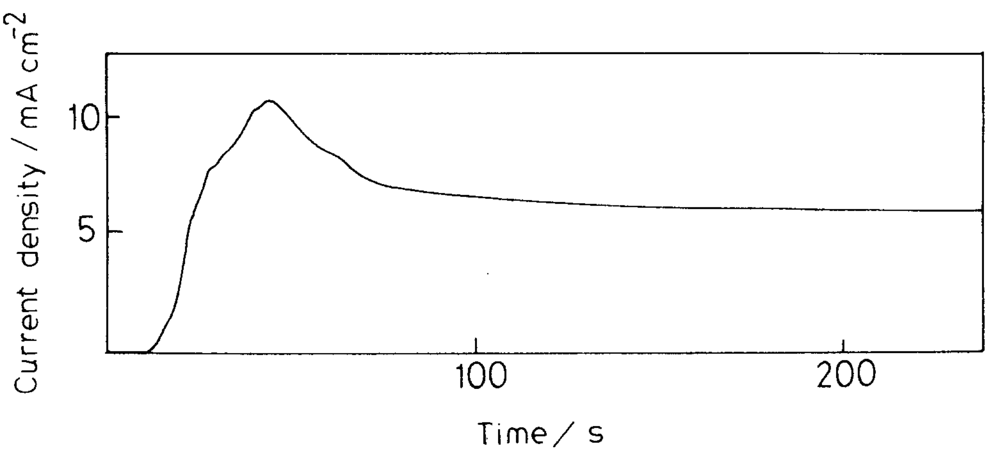

Fig. 6. Potential step transient for nickel deposition from 0.5 M $NiCl_2$ + 3.0 M NaCl at pH 3.0 from $E_0 = -500$ to -890 mV.

3.4. *Galvanostatic study*

The galvanostatic curves obtained for $NiCl_2$ 0.5 M at pH = 3 are shown in Fig. 7. *E–t* transients were obtained corresponding to a nucleation and growth process: the typical nucleation peak followed by a steady potential. A high overpotential was necessary to begin the deposition process; when this potential had been achieved the nucleation began and deposition continued at a steady value depending on the current applied: more negative as the current density increased. When the current was below 3 mA cm^{-2} the deposit obtained at high deposition times was metallic, compact and homogeneous. A morphological analysis by SEM showed that the deposits were, in this case, 'cauliflower' type, although at comparative conditions the grain size was smaller than that obtained using the potentiostatic technique.

For high current densities ($i > 5$ mA cm^{-2}) the transient form continued showing the nucleation peak but did not have a stabilization potential, possibly due to hydrogen production. Galvanostatic deposition in these conditions led to a dark deposit, related to the inhibition processes observed in potentiostatic experiments.

Similarly some experiments were made using a solution with high chloride ion content. In these cases, the transients were similar, but upon increasing the current density in the galvanostatic transient, a second rounded peak appeared. This was probably related to the inhibition observed as a consequence of chloride adsorption. In these conditions only very low current densities gave 'cauliflower' deposits and, on increasing the current density, thin-layered deposits, which showed inhibition effects, were produced.

So, the production of the same kind of deposit was possible both potentiostatically at low overpotentials

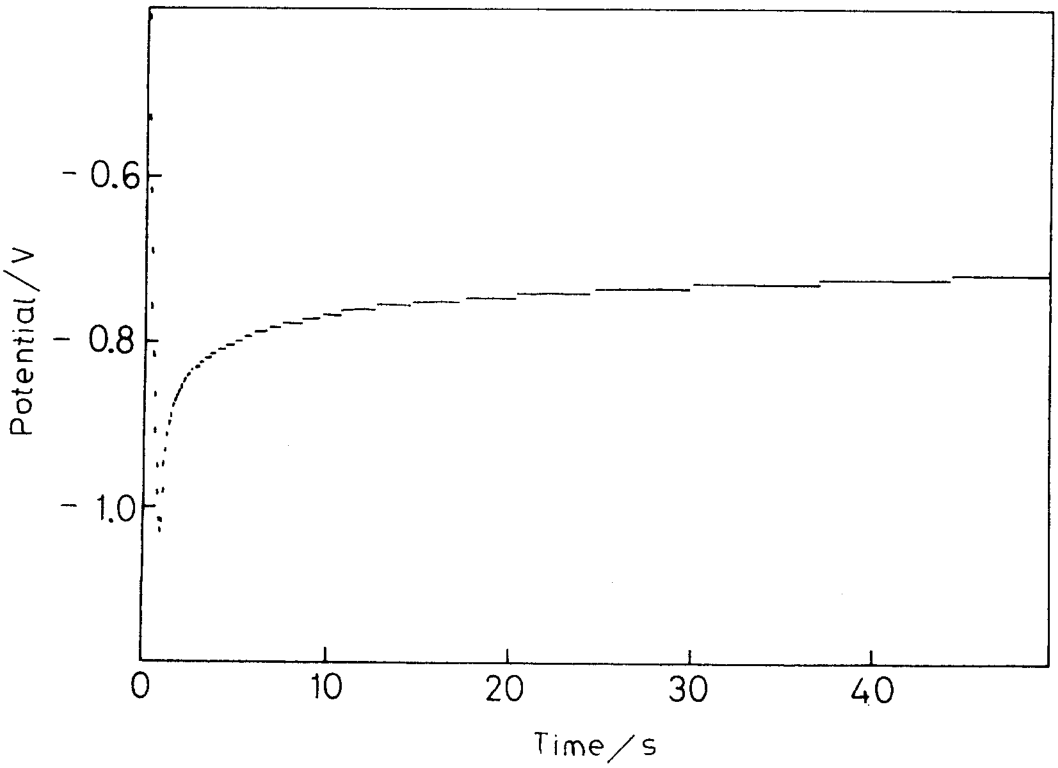

Fig. 7. Galvanostatic transient for nickel deposition from 0.5 M $NiCl_2$ at pH 3.0. Current density: 0.4 mA cm^{-2}.

and galvanostatically at low current densities. Although the galvanostatic techniques are more generally used, they did not lead to markedly better deposits. When the current densities (galvanostatic) or overpotentials (potentiostatic) were increased, the deposits obtained remained similar.

4. Discussion

Results on the influence of pH show a gradual change of the behaviour of the deposition process depending on the acidity of solution.

For $pH < 2.3$, the *i–t* transients do not show a sudden decrease in the current in all cases, but they present distortions due to the screening effect of hydrogen bubbles, since in these conditions the hydrogen can evolve by means of the direct electronation of protons on the freshly deposited nickel. It is known that this reaction is not possible at these potentials on vitreous carbon.

This effect led to non-uniform distribution of the nickel deposits over the electrode surface. However, at microscopic level the deposits corresponded to a cauliflower pattern, with a normal vertical growth.

In these experimental conditions the inhibitory effect attributed to hydrogen in the literature leads to the destruction of the deposit as a consequence of gas evolution.

For this reason the term 'inhibition' of deposition will not be used in this discussion, since, although simultaneous hydrogen evolution takes place leading to deposits which are not useful at the macroscopic level, the deposition process may continue indefinitely with satisfactory morphology of the deposits at the microscopic level.

For the intermediate pH range ($2.3 < pH < 4.5$) an inhibition of the process was always observed to varying extents. This inhibition was observed at lower overpotentials as the pH of the medium increased.

The change in the appearance of the deposits that occurred at different deposition times according to the pH and the overpotential was related to the inhibition. This inhibition causes the decrease in the current in the *i–t* transient, due probably to adsorption of species that obstruct the vertical growth, since in these conditions the deposits obtained were always thin-layered.

Adsorbed species may be present in these conditions over the freshly deposited nickel as nickel hydroxides or H_{ads}, which have been proposed as typical inhibitors of nickel deposition.

The presence of H_{ads} has been proposed from a secondary reaction of Ni(I) intermediate [9, 10 and references therein].

$$\mathrm{Ni(I)} + H^+ + e^- \longrightarrow \mathrm{Ni(I)} + H_{ads}$$

or

$$\mathrm{Ni(I)} + H_2O + e^- \longrightarrow \mathrm{Ni(I)} + H_{ads} + OH^-$$

since the direct electronation of protons is unimportant [16] when the hydrogen-ion concentration in the solution is low.

The dynamics of H_{ads} species formed depends on the experimental conditions (pH and overpotential). At lower pH in this range they are more likely to evolve to hydrogen gas, producing the few bubbles observed, which produce a few distortions in the *i–t* transients and are responsible for the existence of small holes in the deposit. The inhibitory effect produced by H_{ads} was evident only when the overpotential was increased sufficiently.

As the pH increases, the possibility of detachment of hydrogen diminishes and H_{ads} remains adsorbed on the deposit. When H_{ads} is sufficient, the deposit darkens and the current in the *i–t* transient falls.

As a consequence of H_{ads} formation a sudden increase in local pH at the interface can cause, at this intermediate pH, the local precipitation of nickel hydroxides on the nickel deposit. This local precipitation takes place at low times and low overpotentials as the pH increases. This was confirmed by the green coloration of the deposits observed both macroscopically and microscopically. By optical microscopy, green precipitates were also evident on the deposits.

Inhibition was observed only at high overpotentials for the lowest pH. The extension of the reaction must be significant to cause sufficient variation of local pH to produce an inhibition due to nickel hydroxides. In these conditions, experiments made using an RDE showed that this inhibition of hydroxides was not observed, due to the renewal of the solution at the interface, thus eliminating, in part, local pH variations. These results however show the participation of hydroxides in the inhibition even at relatively low pHs.

The darkening of the deposit related to H_{ads} formation always occurred before the formation of green toned deposits directly assigned to the nickel hydroxide precipitation.

In the chloride bath used nickel hydroxide formation prevented homogeneous nickel deposition for $pH > 4.5$, as occurs for other nickel baths studied, in which it was not possible to obtain a coherent deposit of nickel with solutions of $pH > 5$ [5].

On the other hand, varying chloride and nickel concentration shows the influence of other species such as chloride anions. The shape of the *i–t* transient for which a monotonic increase in current is not obtained under any conditions, and the type of deposit (dark and fine-grained), suggest that some chloride is adsorbed on the freshly deposited nickel, which hinders further growth. Moreover, when the Ni(II) concentration was increased using $NiCl_2$ 1 M, a deformation in the *i–t* transients was observed. In this case a greater chloride ion concentration is present and the possible inhibition by chloride observed on the nickel surface may cause the distortion of the *i–t* transient. However, increase in Ni(II) concentration counteracts the other inhibition processes observed for $NiCl_2$ 0.5 M, which may be partially overcome at relatively high overpotentials.

5. Conclusions

(i) In the bath studied, the optimal deposition conditions are $NiCl_2$ 0.5 M, pH around 3 and low overpotentials or low current densities.

(ii) It is possible to obtain the same kind of deposit using both potentiostatic and galvanostatic techniques.

(iii) When inhibitors are absent in the deposition process a metallic deposit of nickel which is compact, homogeneous and bright is obtained, whose morphology is of 'cauliflower' type.

(iv) There is a direct relation between the morphology of the deposits and the shape of the *i–t* transients and the presence of inhibitors during the deposition process.

(v) The inhibitors H_{ads} and nickel hydroxides are directly related. The predominance of their influence is a function of the pH of the medium and the overpotential applied.

(vi) Although chloride ions seem to facilitate the initiation of the deposition process, growth inhibition is always observed at high chloride concentrations.

Acknowledgements

The authors are grateful to the Comisión de Investigación Científica y Técnica (Project PB 90–0437) for financial assistance, and to Servei de Microscopia y Espectroscopia of the University of Barcelona for the SEM studies. Not least we wish to thank Drs C. Muller, W. G. Proud and M. Sarret for their helpful comments in the preparation of this paper.

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