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Electrochemical nucleation of nickel on vitreous carbon electrodes: the influence of organic additives

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The initial stages of the electrodeposition of nickel onto vitreous carbon from ethanol/water chloride solutions was studied in the presence and absence of some organic compounds. The influence of both additives and metal concentration was investigated by cyclic voltammetry, potential step experiments and differential capacity measurements. The role of the additives in the deposition process related to their adsorption, both on vitreous carbon and on vitreous carbon/nickel deposited electrodes, is also discussed.

1. Introduction

The electrochemical phase formation of metals has been extensively studied either by microscopic observation of the electrode surface or by analysing the electrochemical response of the system. The presence of organic compounds in an electrochemical system causes significant changes that affect the nucleation process and growth of a new phase. For this reason many organic substances are used to optimize industrial electrochemical plating processes.

Zinc-nickel is an alloy of considerable technological interest as it improves the deposit properties of zinc coatings. In previous work [1, 2] in our laboratory we studied the characteristics of zinc-nickel deposits obtained from a chloride bath using three organic additives which functioned as brighteners and levelling agents. The objective of the present studies is to explain the deposition mechanism and to examine the influence of each of the additives on nucleus formation and on the growth of electrodeposits. Due to the complexity of the overall process it was planned to electrodeposit separately each one of the two metal constituents in a simple electrochemical system.

The initial stages of this deposition process have been studied on vitreous carbon electrodes in different media [3–5], although most of the papers refer to a Watts type bath, in the absence [6–11] or presence of organic additives [12, 13].

The purpose of this work is the investigation of nickel deposition on a vitreous carbon electrode from a 1.0 M chloride bath at pH 5 and also to analyse the influence of two compounds with different chain length, 4-ethylphenol and 4-nonylphenol, which are representative of an additive used in the bath. The poor solubility of these compounds forced us to use an ethanol-water medium (45%–55%); it has been verified that the general characteristics of the nickel deposition process are the same in an aqueous chloride medium.

2. Experimental details

Electrochemical measurements were made in a conventional three-electrode cell using a Belport 105 potentiostat with *iR* compensation, together with an X-Y Philips PM 8133 recorder and a PAR 175 signal generator. The differential capacity measurements were carried out at 68 Hz with a PAR 5206 lock-in. The morphology of the deposits formed was examined with a scanning electron microscope JEOL/SM 840.

The working electrode was a Metrohm vitreous carbon electrode of area 0.03 cm^2. The electrode was mechanically polished with various grades of alumina on a Metrohm polishing cloth to a mirror-bright finish, then cleaned ultrasonically for 1 min in triply-distilled water. Accurate polishing was necessary to obtain good reproducibility. The electrode was brought in contact with the solution for capillarity (solution meniscus). In the SEM experiments the same quality of vitreous carbon was used.

A saturated calomel electrode, mounted inside a Luggin capillary, was used as the reference electrode and all potentials were referred to this electrode. The counter electrode was a vitreous carbon bar.

All solutions were made with Merck analytical grade reagents and water was treated with a Milipore-Milli Q system. All solutions were freshly prepared and deoxygenated with pure argon prior to each experiment.

3. Results and discussion

3.1. *Nickel deposition*

The study of the nickel deposition process in ethanol-

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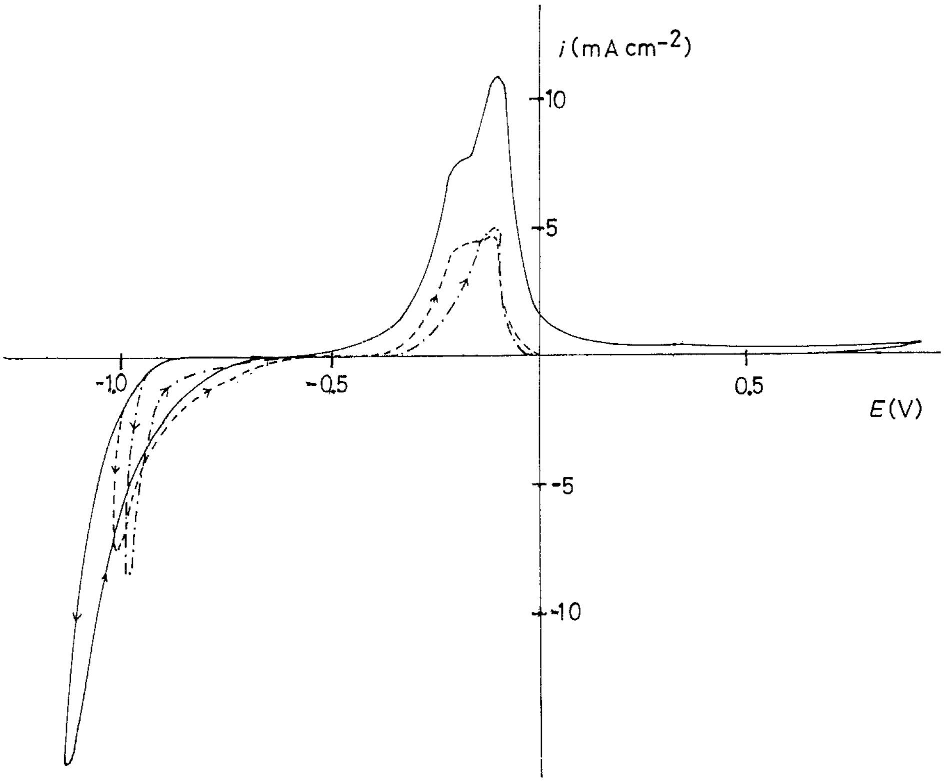

Fig. 1. Cyclic voltammogram of $NiCl_2$ 0.5 M; v = 100 mV s^{-1}. Different limit potentials: (—·—) −990 mV, (– – –) −1015 mV, (——) −1140 mV.

water medium (45 : 55) containing different Ni(II) concentrations in the range 0.01–0.5 M (in all cases, the chloride concentration is maintained at 1.0 M by means of a suitable addition of NaCl) was performed using cyclic voltammetry, potential step experiments and differential capacity measurements.

3.1.1. General behaviour. Figure 1 (continuous line) shows a cyclic voltammogram for a high Ni(II) concentration on a vitreous carbon electrode. A clear deposition process is observed when the scan is reversed and two close peaks are obtained for the dissolution of electrodeposited nickel. The exact location of the anodic peaks depends on such factors as sweep rate and cathodic limit potential. When the cathodic limit potential is increased, the oxidation process becomes more difficult and when the scan rate is decreased a small oxidation peak is observed, probably due to the passivation of the nickel surface.

Thus, the 0.5 M $NiCl_2$ solution permits analysis of the nickel dissolution process, since in these conditions the Ni(II) deposition is not totally irreversible. The assignation of oxidation peaks is difficult, but different voltammetric experiments have been carried out to observe the stripping of the electrodeposit obtained in this medium. For very low cathodic limit potential (> −990 mV) only one oxidation peak was observed in the anodic scan. When the cathodic limit was increased slightly a new oxidation peak was obtained at more negative potentials (Fig. 1). These voltammetric results indicate that the different forms of nickel observed in aqueous media [10] are also formed in this ethanol-water solution. Thus, the oxidation peak at more positive potentials seems to correspond to a α-solid solution of H in Ni, whereas when the limit is made more cathodic, more hydrogen ions are reduced at the nickel surface, β-solid solution of H in Ni could be formed and the second peak seems to correspond to β-Ni solution. Also in this medium, when the electrolytic nickel deposit is exposed at the rest potential in the solution, the first oxidation peak decreases while the second increases (Fig. 2).

For a very low cathodic limit (−800 mV) holds of different duration were carried out before reversing

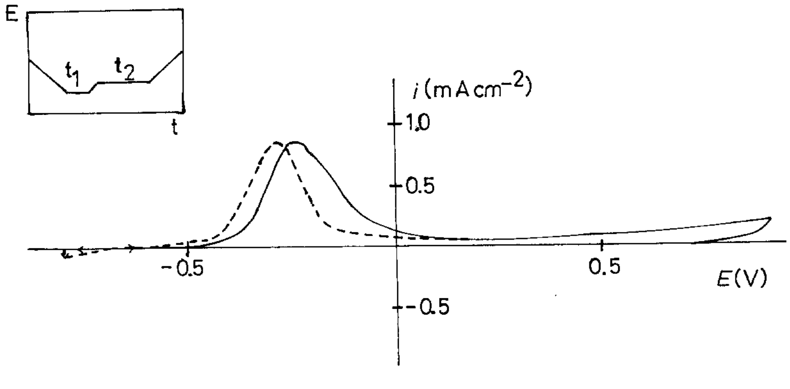

Fig. 2. Cyclic voltammogram of $NiCl_2$ 0.5 M; v = 100 mV s^{-1}: (– – –) t_1 = 1 min at −790 mV and t_2 = 0; (——) t_1 = 1 min at −790 mV and t_2 = 4 min at −680 mV.

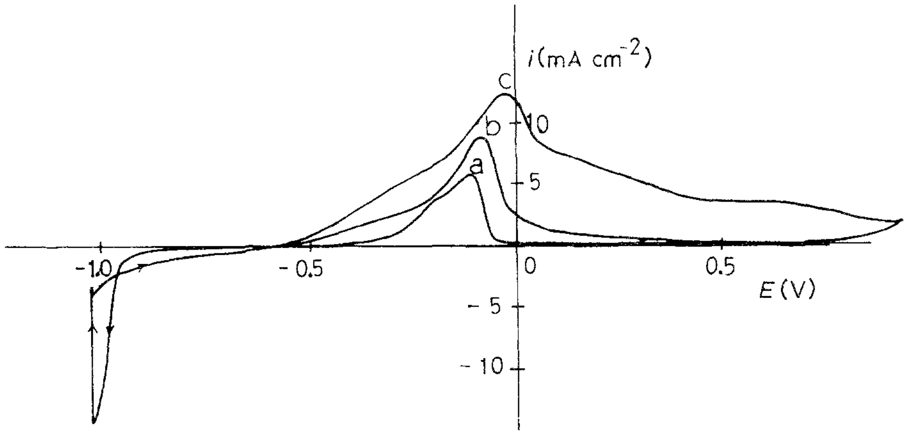

Fig. 3. Influence of hold time during a hold at -1028 mV. $NiCl_2$ 0.5 M: (a) 0 s, (b) 30 s and (c) 120 s. $v = 100\,mV\,s^{-1}$.

the voltammetric scan and successive oxidation peaks were obtained for different holding times, showing that the deposition is a complex process for long deposition times (Fig. 3).

When the Ni(II) concentration is decreased, the voltammetric curves reveal the initial stages of deposition and the process becomes more irreversible. At 0.1 M Ni(II) concentration, in the anodic sweep, only a small oxidation peak appears and this peak does not appear at 0.01 M, contrary to that observed in other ethanol-water compositions [4]. Figure 4a shows a voltammogram obtained for 0.01 M of Ni(II). On the forward sweep, there are two reduction peaks; a nucleation loop is observed when the scan is reversed at the foot of the two reduction peaks. Two nickel reduction peaks have also been observed on a Pd electrode [14], but this phenomena has not been previously reported for a vitreous carbon surface.

Since most authors suggest that the deposition of nickel passes through the formation of an adsorbed complex [15, 16], this possibility was checked by means of differential capacity measurements, in the absence of faradaic processes. The adsorption of different species was tested by comparison of the curves obtained with the supporting electrolyte only (1.0 M NaCl) and those solutions containing different $NiCl_2$ concentrations, keeping the whole chloride concentration at 1.0 M (Fig. 5). At this chloride concentration, the results show that the capacity decreases proportionately with increasing Ni(II) concentration. This fact is probably due to the adsorption of a nickel-chloride complex on the vitreous carbon electrode, and deposition process could arise from these complexes.

3.1.2. Potential step experiments. To analyse the initial stages of deposition, potential step experiments were carried out and i–t transients recorded in each case. The potential was stepped from -0.5 V, where no electrode reaction occurs, to more negative values. The i–t response obtained for high Ni(II) concentrations is shown in Fig. 6. Two close current maxima were obtained with different time values, characteristic of a nucleation and growth process. With increasing overpotential, the current increases and reaches the peak more rapidly, as is usual in these cases. When the first peak is analysed by means of the BFT model (Bewick, Fleischmann and Thirsk) [17, 18], the reduced plot is in agreement with that expected for the poten-

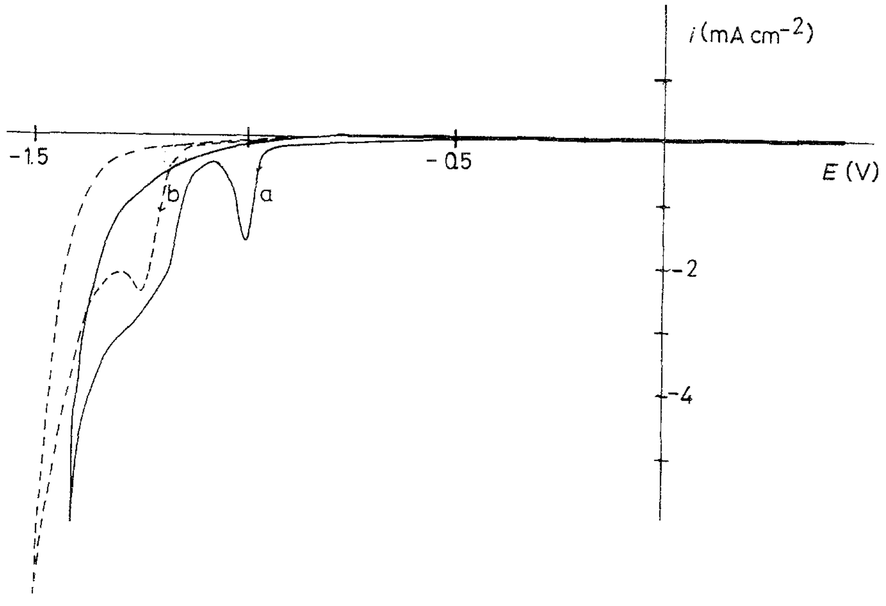

Fig. 4. Cyclic voltammogram of $NiCl_2$ 0.01 M and NaCl 0.98 M; $v = 50\,mV\,s^{-1}$. (a) Free electrolyte, (b) solution containing 4-nonylphenol 2.5 g dm^{-3}.

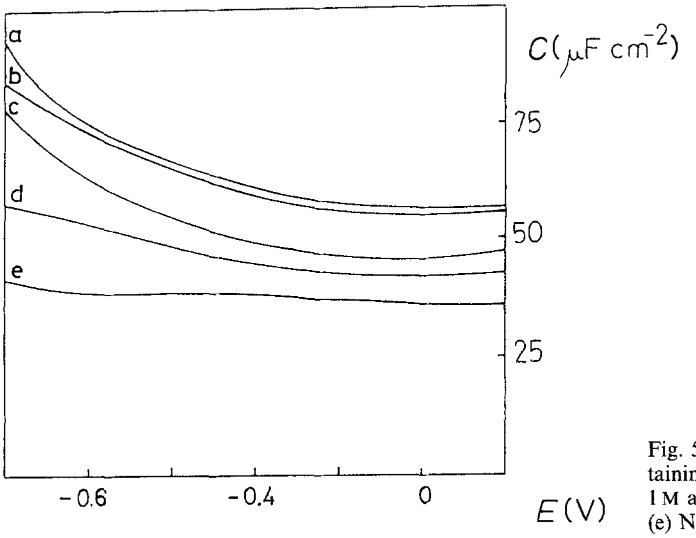

Fig. 5. Differential capacity-potential curves from solutions containing: (a) NaCl 1 M, (b) $NiCl_2$ 0.01 M and NaCl 0.98 M, (c) NaCl 1 M and 4-ethylphenol 8.0 g dm^{-3}, (d) $NiCl_2$ 0.2 M and 0.6 M, and (e) $NiCl_2$ 0.5 M. v = 10 mV s^{-1}.

tiostatic formation of a two dimensional structure by means of a nucleation and growth mechanism, progressive at low overpotentials and instantaneous at high overpotentials. The final part deviates from the theoretical curve; this effect is probably due to the proximity of the second peak. When the rising part of the second peak is analysed through a i–t^n dependence a value of $n = 2$ is obtained for all potentials, corresponding to an instantaneous three-dimensional nucleation.

The lowering of Ni(II) concentration also provokes modifications of the current-time transients (Fig. 7a). The three-dimensional growth is, in this case, retarded relative to that of two-dimensional nucleation, leading to a greater separation in the peaks for the two processes, allowing a better BFT analysis. At low overpotentials the experimental data in the reduced plot correspond to a progressive 2D-nucleation, in agreement with the results obtained at high Ni(II) concentration. Increasing the overpotential a new peak is detected previous to three-dimensional growth. This new peak approaches the first when the potential decreases. Therefore, in these experimental conditions two current peaks are observed prior to bulk deposition; these peaks may be due to the formation of two monolayers of nickel or to the deposition of two different forms of nickel.

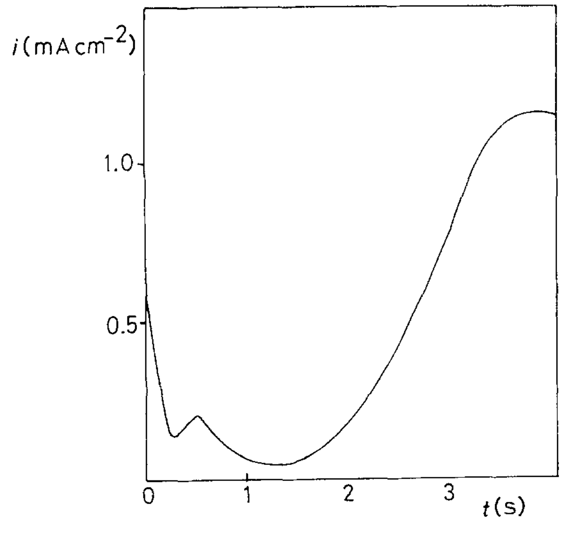

Fig. 6. Potentiostatic transient for Ni deposition from $NiCl_2$ 0.5 M at $-$1030 mV.

For three-dimensional nucleation, analysing the rising part of the transients by means of the i–t^n relation, a $2 < n < 3$ value was obtained and it is clear that three-dimensional growth of nickel centres is occurring and nucleation is instantaneous or progressive depending upon the experimental conditions. Moreover, the absence of maxima in these transients suggests that under these experimental conditions (pH 5) the deposition of the α-nickel form seems to prevail as found previously [9]. At these pH values a small amount of hydrogen is built in the deposit; the amount of H^+ ions expended during the deposition process is almost negligible as the mass controlled process does not take place until after a very long deposition time.

At this point, it must be emphasized that the electrochemical response of the electrode in this medium, especially in the i–t transients, is extremely sensitive to its preparation, in such a way that if the polishing process is not very accurate the monolayer of deposited nickel is not observed, although reproducible transients are obtained.

The results show that in this ethanol-water chloride medium, nickel deposits onto vitreous carbon electrodes at potentials which are dependent on Ni(II) concentration in solution. At high Ni(II) concentrations the initial deposition stages take place through the formation of a two dimensional layer followed by a complex process of nucleation and growth of three-dimensional centres. At low Ni(II) concentrations the splitting observed for the first peak in the i–t transients at high overpotentials may be related to the coexistence of two forms of electrodeposited nickel.

3.2. *Influence of 4-ethylphenol and 4-nonylphenol*

In order to analyse the influence of the alklylphenols on the nickel deposition on vitreous carbon, it is interesting to compare the electrochemical response for the electrolyte in the presence and absence of

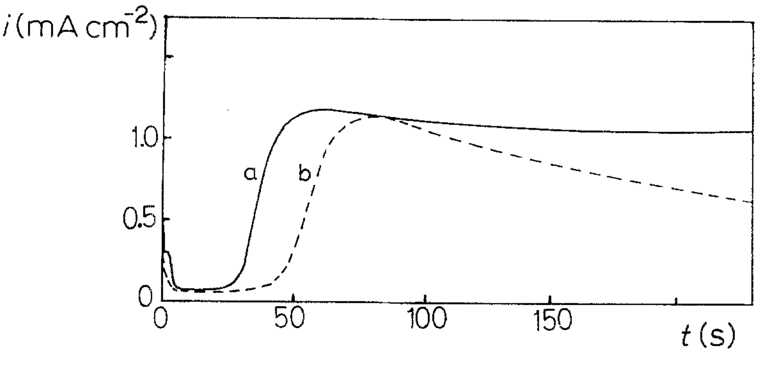

Fig. 7. Potentiostatic transient for Ni deposition for $NiCl_2$ 0.01 M and NaCl 0.98 M from $E_0 = -500$ mV to $E = -1100$ mV. (a) Free electrolyte, (b) solution containing 4-ethylphenol 8 g dm^{-3}.

additives. The nickel chloride concentration used was 0.01 M, and for 4-ethylphenol concentrations between 2.0 and 8.0 g dm^{-3} were used, whereas for 4-nonylphenol a range of 0.5–2.5 g dm^{-3} was analysed due to the lower solubility of this compound in the experimental solution.

The voltammograms obtained from solutions containing 4-ethylphenol or 4-nonylphenol show that Ni deposition is inhibited as a higher overpotential is needed to begin the deposition process (Fig. 4b). This inhibition increases with increasing additive concentration.

In the i–t transients obtained in the presence of 4-ethylphenol, monolayers of the deposit are not obtained prior to three-dimensional growth centres, showing, moreover, an induction period previous to the process, that is, nucleation is inhibited. This inhibition is similar to that observed for some organic additives in a Watts-type bath [13], but in the present case the presence of additive leads to the supression of nickel monolayer formation. As the additive concentration is increased the maximum is still well defined and the current falls more rapidly to a steady value (Fig. 7b). In all cases, the analysis of the first part of the transient shows the same i–t^n dependence as observed in the free bath; therefore, the nucleation rate is not modified by the presence of these additives.

When the 4-nonylphenol concentration in the nickel chloride solution is in the range 0.5–1.5 g dm^{-3}, for all overpotentials the i–t transients are similar to those observed in the presence of 4-ethylphenol. When the concentration is higher than 2.0 g dm^{-3} the i–t transients are similar for low overpotentials, but when the overpotential is increased the i–t transient is notably modified (Fig. 8).

In order to demonstrate the influence of organic additives on the nickel deposition process in ethanol-water medium, measurements of the differential capacity were carried out on vitreous carbon electrodes. The capacity-potential curves show that both alkyl-phenols are adsorbed on the carbon electrode (Fig. 5c).

The adsorption of 4-alkylphenol compounds on vitreous carbon electrodes is responsible for the shift of the deposition process to the more negative potentials observed in the voltammetric curves, for the disappearance of the monolayer and for the induction period observed in the i–t transients prior to the nucleation of three dimensional growth centres. It seems that the two dimensional structure is only formed when the nickel complex can be directly adsorbed on the carbon surface, but when the adsorbed additive is present this deposition process is hindered and deposition begins with the formation of a three-dimensional structure. However, this adsorption does not fully explain the posterior inhibition observed in the i–t transients at times greater than t_m (time corresponding to maximum in i–t curve). Therefore it was decided to study the behaviour of these organic compounds on a carbon electrode, modified by the presence of electrodeposited nickel, in order to obtain information about their influence when the electrode is nickel coated.

After depositing nickel for a controlled time at a potential corresponding to three-dimensional growth,

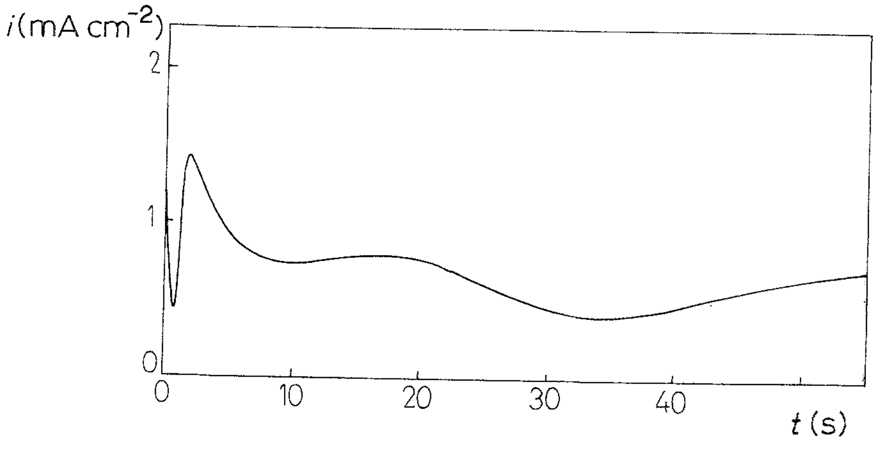

Fig. 8. Potentiostatic transient for Ni deposition for $NiCl_2$ 0.01 M NaCl 1 M and 4-nonylphenol 2.5 g dm^{-3}. $E_0 = -500$ mV to $E = -1220$ mV.

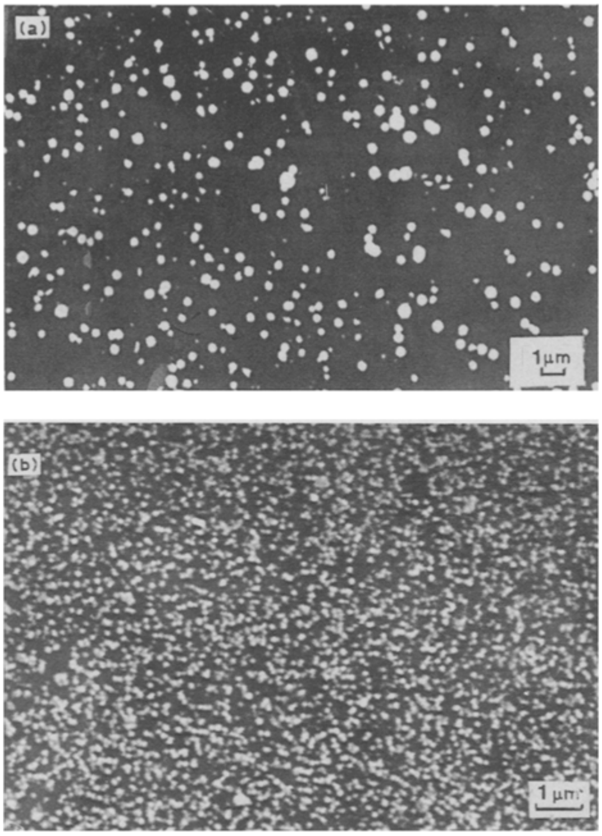

Fig. 9. Scanning electron microscopy of surfaces produced by nickel deposition from solutions containing 0.01 M $NiCl_2$ + 0.98 M NaCl during 60 s. (a) Free electrolyte at − 1000 mV, (b) with 4-ethyl phenol at − 1110 mV.

the electrode was transferred to a blank solution (NaCl 1.0 M) or a blank with the additive solution and the current-potential or capacity-potential curves were recorded.

The voltammetric study showed that with this modified electrode the hydrogen evolution was catalysed with respect to the vitreous carbon electrode. Moreover additive reduction processes were not observed at potentials previous to the hydrogen evolution, so that the inhibition observed at times greater than t_m cannot be due to additive reduction.

The capacity-potential curves reveal significant adsorption of additives on Ni/vitreous carbon electrodes, being more pronounced for 4-nonylphenol at the same concentration. This adsorption may explain the fall observed in the i–t transient when the phenols are present in the solution. When nickel is deposited on the electrode, the additives are able to adsorb onto the electrodeposited metal, hindering further deposition processes. As expected, this inhibition is more pronounced at higher additive concentration.

It seems that the adsorption ability of the alkylphenols on the substrate is related to their chain length. From this assumption it follows that the phenolic derivative used in the present bath [1, 2] will produce greater inhibition of the process in accordance to its greater adsorption.

The shape of the transients at a 4-nonylphenol concentration of 2.5 g dm^{-3} and high overpotentials (Fig. 8) suggest that the deposit formation takes place via a multilayer mechanism (layering), similar to that observed in other experimental conditions for nickel deposition [13].

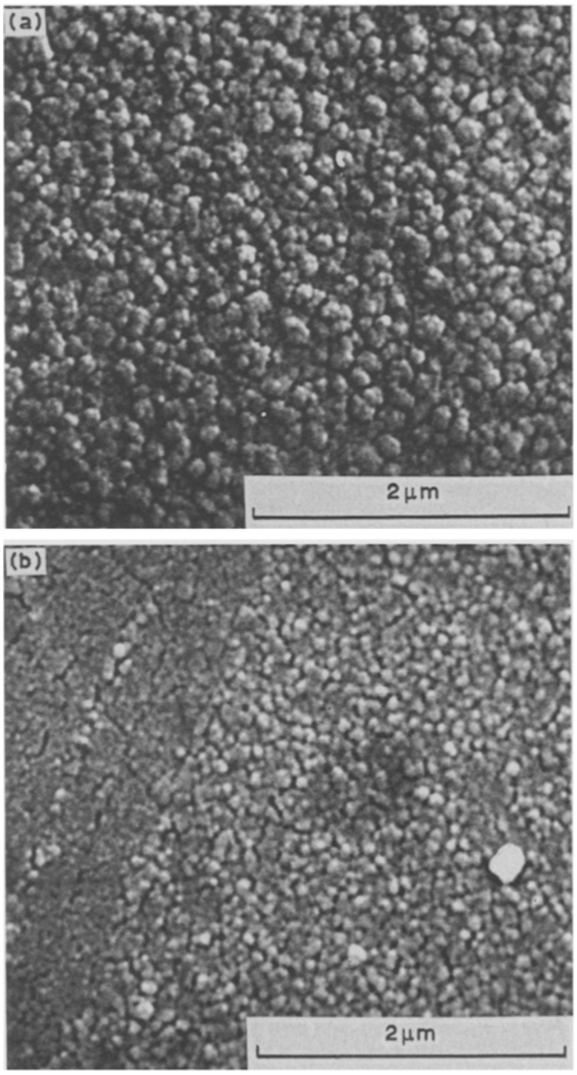

Fig. 10. Comparison of scanning electron microscopy of surfaces produced by nickel deposition at − 1130 mV for 200 s. (a) Deposition in 0.01 M $NiCl_2$ + 1 M NaCl; (b) Deposition in the same solution containing 1.5 g dm^{-3} 4-nonylphenol.

3.3. *Scanning electron microscopy*

Scanning electron microscopy (SEM) was used to examine the morphology of the deposits. When the additive is not present, isolated crystals of variable size are observed, exhibiting cubic symmetry (Fig. 9a). With additive the crystals are smaller (Fig. 9b), resulting in fine-grained deposits (Fig. 10). This size reduction is more pronounced on increasing the additive concentration and alkyl-phenol chain length, results which are in agreement with those obtained for the differential adsorption of these compounds.

These kinds of additive appear to act as grain refiners and levelling agents, effects which are similar to those observed for the phenolic derivative used in previous zinc-nickel deposition studies [1].

However, in the presence of such additives cracking of the deposit is observed (Fig. 10b), indicating that such a deposit is highly stressed.

The results show that the compounds used in this work modify the first stages of the nickel deposition process, leading to a significant inhibition, including the disappearance of the nickel monolayer. This influence results in an increase in deposit uniformity, but also involves stressing the deposit, a factor that could necessitate the use of an additive combination to obtain a suitable deposit.

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