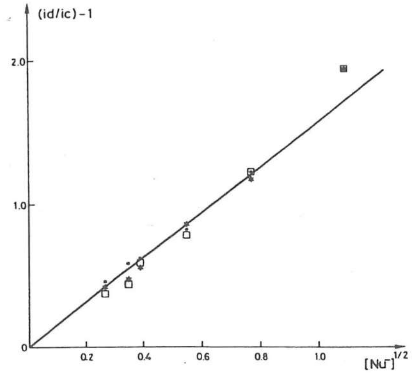

Figure 3 - A plot of the parameter $(i_d/i_c) - 1$ as a function of the square root of the nucleophile concentration.

The value of the rate constant of the substitution reaction, k_2, can be obtained from the slope of the straight line. Thus, using the value of k_1 found in the literature and equal to $8 \times 10^4\ s^{-1}$, it is found that $k_2 = 1.9 \times 10^5\ M^{-1}\ s^{-1}$.

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ELECTROCATALYTIC BEHAVIOUR OF DIFFERENT SUBSTRATES FOR THE ELECTROOXIDATION OF DMAB IN ELECTROLESS METAL DEPOSITION

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ABSTRACT - The electrooxidation of dimethylmineborane (DMAB) on specpure and electrolytic Ni and Co in succinate containing solutions of slightly acid pH has been studied by cyclic voltammetry and potential time measurements. The results have shown differences in electroactivity which can be related with surface morphologies. The study has been extended to electroless Ni-B and Co-B substrates and the electrocatalytic properties of the alloys compared to those of pure metals.

INTRODUCTION

It is usual practice to evaluate the conditions for electroless metal deposition (EMD) by the measurement of the potential evolution with time of a given substrate in the electroless solution [1]. Therefore, the substrate catalytic activity can be referred to its ability to reach the stable EMD potential. Being this critical potential closely related with the behaviour of the system substrate/reducing agent [2], the evaluation of the relative catalytic activity of different substrates can be carried out in metal ions free media.

Extensive investigation on suitable experimental conditions (presence of complexants, pH, temperature) for electroless Nickel and Cobalt deposition, using dimethylamineborane (DMAB) as reductant, was recently reported [3]. The aim of this work is to present the influence of substrate morphology on the first stages of the deposition. Considering that the process evolution is determined by the deposited first layers, the electrooxidation of DMAB on Ni-B and on Co-B is also investigated.

EXPERIMENTAL

Cyclic voltammetry and potential time measurements were carried out in adequate electrochemical cells with specpure and electrolytic metals, electroless Ni-B and Co-B working electrodes. The counter electrode was a platinum foil and electrode potentials were controlled with respect to a saturated calomel electrode by EG & G potentiostat/galvanostat model 273. Rotating electrode experiments were performed with a RDE EG & G model 616. The results were collected with a XY-t recorder.

The solutions were prepared with Analar grade reagents and de-ionised bidestilled water and specpure substrates were polished to a mirror finishing before each experiment. All measurements

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were carried out at 25 °C.

Electrolytic Ni and Co were deposited on the correspondent specpure metals from a chloride/acetate bath for Ni and from a modified sulphate/chloride solution for Co, using 2 Adm $^{-2}$ and 0.25 Adm $^{-2}$, respectively.

Electroless alloys were also plated onto specpure Ni and Co, from a bath containing metal ions, DMAB and sodium succinate. Temperatures of depositions were 40 °C for Ni-B and 55 °C for Co-B.

RESULTS and DISCUSSION

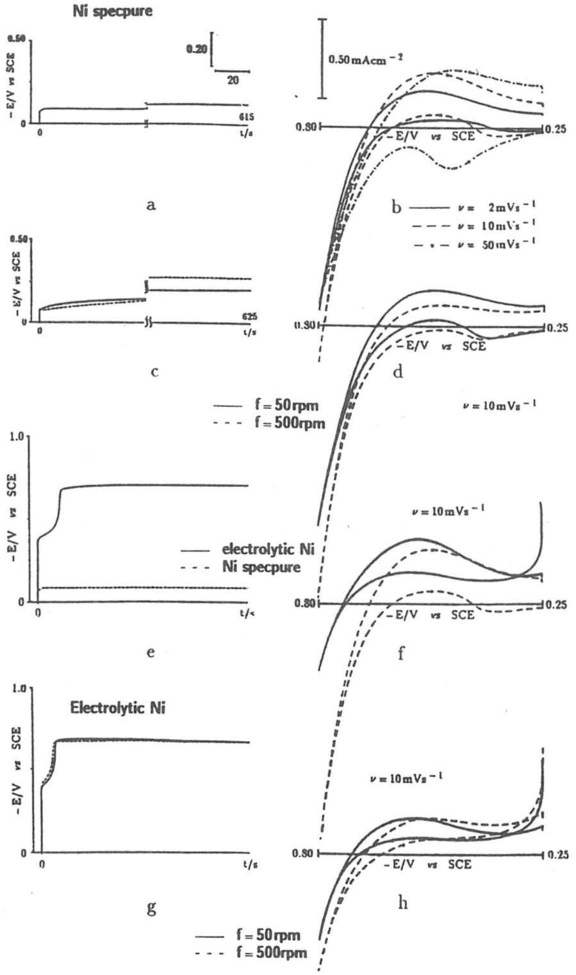

Fig. 1 - Evaluation of catalytic activity of Ni substrate in 0.1 M DMAB + 0.2 M $(C_2H_2NaO_2)_2$ pH = 4.5, T = 25 °C

Ni specpure appears to be non catalytic for the electrooxidation of DMAB since the open circuit potential in metal ions free media does not reach the correspondant value to the deposition (fig. 1a) in useful time. However (fig. 1b), when the potential of the electrode is controlled and swept on the cathodic direction, the conditions for the interaction substrate /reducing agent can be reached; the adsorption and subsequent oxidation of DMAB occur, illustrated by the presence of the anodic peak on the cathodic scan. As the sweep rate, increases, the peak occurs at more negative values showing that the processes are potential and time dependent [3].

The effect of electrode rotation is complex, enhancing the acess of DMAB to the interface but diminishing the "residence time" for an effective adsorption. This is clearly evident in figure 1c (higher open circuit

potential value) and figure 1d (lower anodic peak current) and Ni specpure remains non-catalytic.

When the substrate is electrolytic deposited Ni there is a different behaviour as can be observed in figures 1e and 1f.

The deposition potential is attained in approximately 10 s and an increase in the peak current is also noticeable. This easier interaction between substrate and reductant is also responsible for the lower transition time to reach the required potential when the substrate is rotated (fig. 1g). The effect is not clearly revealed in the voltammetric curves (fig. 1h), but the oxidation occurs at lower cathodic potentials.

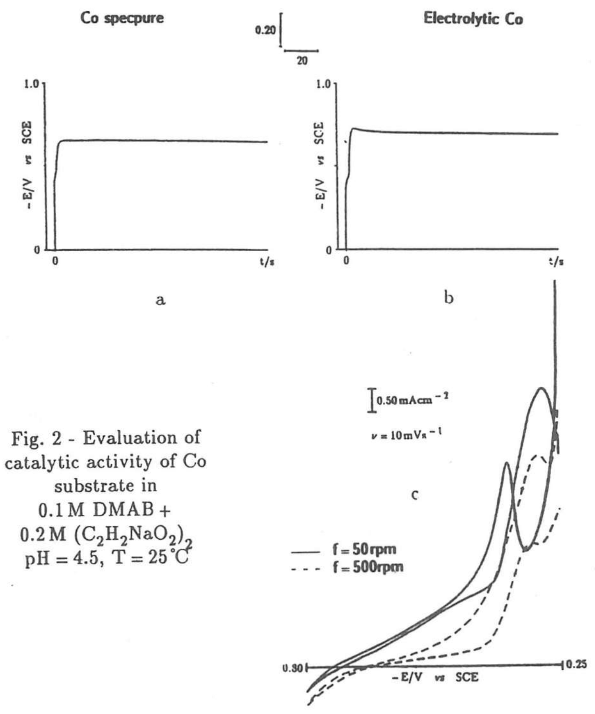

Fig. 2 - Evaluation of catalytic activity of Co substrate in 0.1 M DMAB + 0.2 M $(C_2H_2NaO_2)_2$ pH = 4.5, T = 25 °C

In the case of Co, a strong catalytic ability, is noted, non-dependent of its origin. Short and similar transition times were observed for both - specpure and electrolytic substrates - figures 2a and 2b.

The voltammetric response of electrolytic Co shows an identity of the oxidation potential in both scans, when the electrode rotates at high speed - figure 2c.

In complete solution (with the presence of metal ions) the evolution of the open circuit potential of Ni specpure - figure 3a (solid line) - reveals that it is apparent the weak activity of this substrate. In spite of the higher transition time - approximately 150 s - the deposition process occurs. This can be explained in analogy with hipophosphite ion (another reducing agent), which is more reactive when it works like a ligand in the coordination sphere of a particular complex ion, than in metalic ions free media [4].

As soon as thin films of Ni-B (on Ni specpure) are formed - figure 3a (dashed line) - the oxidation of the reductant occurs more easily than on specpure Ni which comproves the autocatalytic capacity of these Ni alloys. Since electroless deposition produces a clean surface without oxides or hydroxides, its morphology is likely more adequate for a faster deposition of the subsequent electroless films.

The catalytic ability of Co for the electrooxidation of DMAB and subsequent deposition of Co-B in complete solution is illustrated by figure 3b. Short and similar transition times for both substrates - Co specpure and electroless Co-B - were expected from the known catalytic behaviour of that metal for hydrogenation / dehydrogenation processes [2].

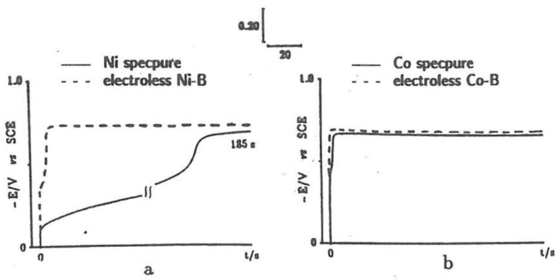

Fig. 3 - Behaviour of nickel for electroless metal deposition in
$0.1\,M\ NiSO_4 + 0.1\,M\ DMAB + 0.2\,M\ (C_2H_2NaO_2)_2$ (a)
$0.1\,M\ CoSO_4 + 0.1\,M\ DMAB + 0.2\,M\ (C_2H_2NaO_2)_2$ (b)
pH = 4.5, T = 25°C

CONCLUSION

The onset of electroless metal deposition, using DMAB as reducing agent can be strongly influenced by the substrate morphology. The effect is more pronounced for metals presenting weak interaction with the reductant, being nickel a typical example. Although the catalytic effect of the metalic ions in solution on the electrooxidation of DMAB must be taken into account, differences in structure and non-metallic content between first and subsequent electroless deposited layers are to be expected for platings occurring on the electrodeposited or the bare metal.

For substrates with high catalytic activity for EMD, as is the case of Cobalt, the influence of the underlaying morphology on the deposited layers properties is more difficult to establish. It will justify a detailled investigationon the voltammetric behaviour, since the DMAB oxidation process was seen to be well descriminated by measurements carried out on electrodes under rotation.

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ON THE ELECTROCHEMICAL SYNTHESIS OF POLY - 3 - METHYLTHIOPHENE

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Electronic polymers such as polypirrole, polyaniline and polythiophene, have been under active study [1-3] due to the interest in the numerous applications of these materials and to enhance the understanding of fundamental aspects.

Although considerable literature exists on the charge transport in polymeric systems [4] only recently emphasis has been given to the influence of the preparation conditions on the properties exhibited by these materials [5,6].

Conducting polymers can be synthesized easily by electrochemical oxidation of respective monomers / olygomers in solution. The deposition mechanism is poorly understood likely due to different growth processes imparted by certain potential / current conditions.

With the aim of correlating morphological and redox behaviour differences with the potentiostatic and galvanostatic conditions used to grow conducting polymer films on metal electrodes, in the present work poly-3-methylthiophene films have been synthesized by electrochemical oxidation of the monomer in a three electrode two compartment cell consisting on a specpure Pt working disk electrode (Ø = 670 μm), a Pt foil counter electrode and a saturated calomel reference. The solution was 0.6 mol dm^{-3} 3-methylthiophene in 0.2 M $LiClO_4$/acetonitrile, deaerated before each experiment by purified nitrogen bubbling for, at least, 15 min. The growth has been carried out either potentiostatically, in the range 1.24 - 1.29V (vs SCE) with a resolution of 10 mV, and galvanostatically, imposing a current density in the range 0.4 - 1.2 mA cm^{-2} with a resolution of 0.2 mA cm^{-2}. In all experiments it was used 60 mC cm^{-2} total charge density.