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Material Science Research India Volume 03, No. (1) 39-42 (2005)

INVESTIGATION OF ELECTROCHEMICAL BEHAVIOUR OF ORGANIC ADDITIVES USED IN ELECTROPLATING OF NICKEL

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(Received, March 22, 2005)

ABSTRACT

Production of nickel layers with consistently quality requires precise control and analytical methods. Aside from the inorganic components of the electrolyte, the organic additives are of critical importance for the properties of the nickel deposits produced. We have investigated the electrochemical behaviour of some of these additives by voltammetric methods as CV, DPP methods on electroplating nickel Watt's bath. We have observed that wetting agent is not electroactive, but it shifts the peak potential of nickel ions towards a more negative potential. Other additives as purifier, brightening and ductility enhancing agents are electroactives, but in more negative than nickel ions.

Key words :- voltammetry, electroplating, organic additives, irreversible system, peak potential.

INTRODUCTIO

The conditions used for electrodeposition of metals and alloys are very important[1-12] because they influence the mechanical and physical properties of deposits[13-16]. In this regard some organic additives are very effective[17-21]. We were interested to investigate the electrochemical behaviour of some additives such as wetting, brightening, purifier and ductility enhancing agents used in Watt's bath, separately, and then together. The effects of these compounds on electrochemical behaviour of Ni^{2+} ions were also studied by voltammetric methods.

2. EXPERIMENTAL

Voltammetric studies were performed with a polarecord 747 VA Stand and 746 VA trace analyzer (Metrohm, Swiss), using Ag/AgCl/KCl 3M as a reference electrode and a DME as working electrode. All chemicals were of analytical grade (Merck) and organic additives were commercial products. Solutions were prepared with distilled water, and experiments were conducted at 25°C. Watt's nickel electrolytic bath contains nickel ions (40-58 $g.l^{-1}$), boric acid (35-45 $g.l^{-1}$), chloride ions (35-50 $g.l^{-1}$) and pH = 4-5. Blank solution was an aqueous solution of KCl 0.075M. 0.1M $NiSO_4$ was used as a stock solution. In studying the electrochemical behaviour of Ni^{2+} ions or organic additives, and also the effects of these compounds on Ni^{2+} ions, successive addition of 0.1 ml of stock solutin to 20 ml of blank solution was employed.

3. RESULTS AND DISCUSSION

In this work, the electrochemical behaviour

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Table 1. Electrochemical behavior and analytical results for Ni^{2+} and organic additives in Watt's electrolytic bath.

specimen	method	Epc* / V	Analytical results (calibration curve)
	CV	-1.01	Y = 596.96 X + 0.282, R = 0.9999
Ni^{2+}	DPP	-1.01	Y = 1172.2 X + 0.344, R = 0.9994
	ASV	-1.12	Y = 176.94 X + 0.064, R = 0.9991
Brightner	CV	-1.09, -1.44	–
	DPP	-1.05, -1.43	Y = 8.4357 X, R = 0.9958
Ductile	CV	-1.85	–
	DPP	-1.83	Y = 6.1357 X, R = 0.9939
Purifier	CV	-1.53	–
	DPP	-1.51	Y = 4.85 X - 0.0017, R = 0.9939

Wetting Nonelectroactive, it only shifts peak potential of Ni^{2+}, by about -0.3 volt

* peak potentials were obtained versus Ag / AgCl / KCl 3M electrode

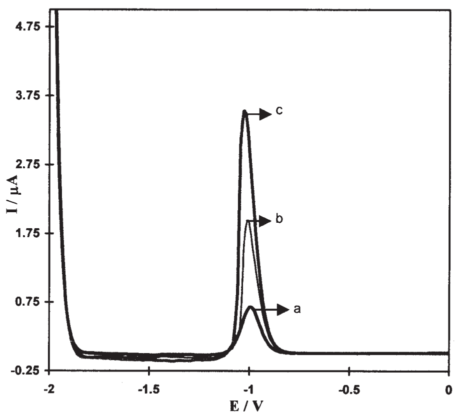

Figure 1. Differential pulse polarogram of a) 0.1, b) 0.2, c) 0.3 ml of Ni^{2+} solution (0.1 M).

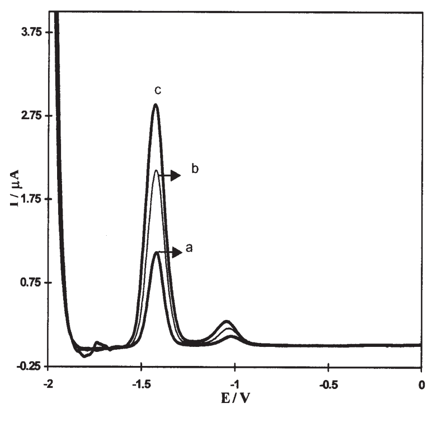

Figure 2. Differential pulse polarogram of a) 0.1, b) 0.2 c) 0.3 ml of brightening solution.

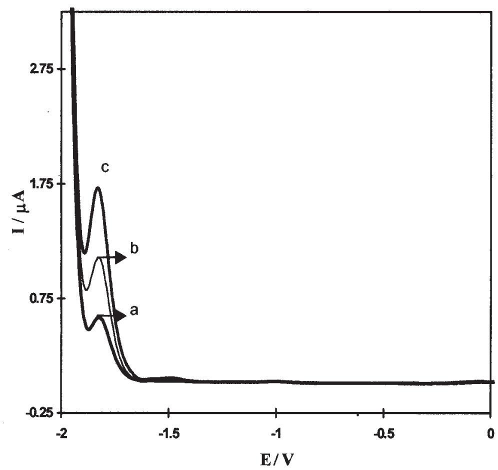

Figure 3. Differential pulse polarogram of a) 0.1, b) 0.2, c) 0.3 ml of ductility enhancing solution

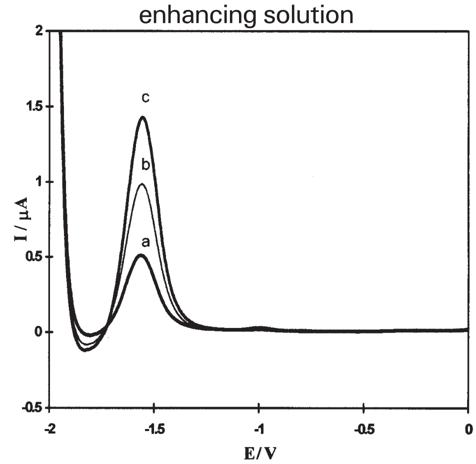

Figure 4. Differential pulse polarogram of a) 0.1, b) 0.2, c) 0.3 ml of purifier solution

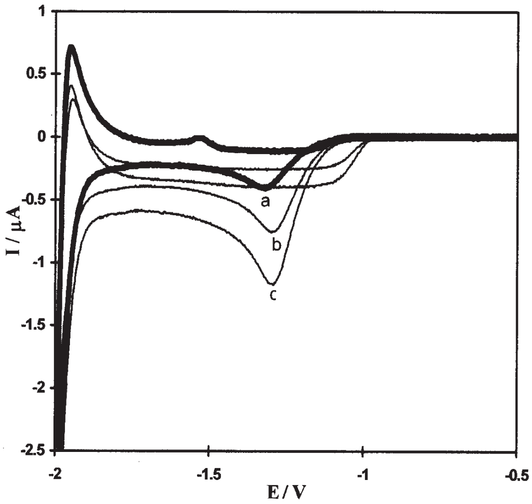

Figure 5. Cyclic voltammogram of 0.2 ml wetting solution + a) 0.1, b) 0.2, c) 0.3 ml Ni^{2+} solution

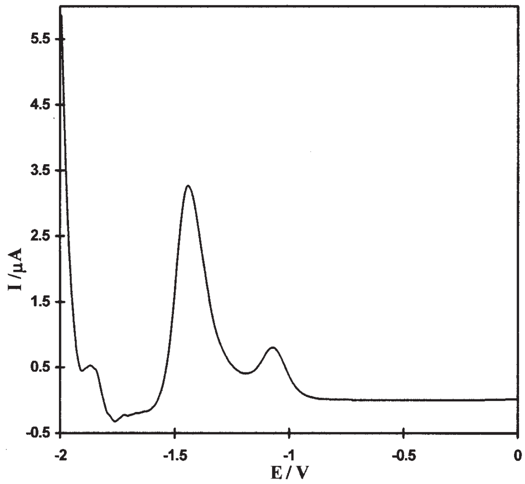

Figure 7. Differential pulse polarogram of mixture of additives with Ni^{2+}.

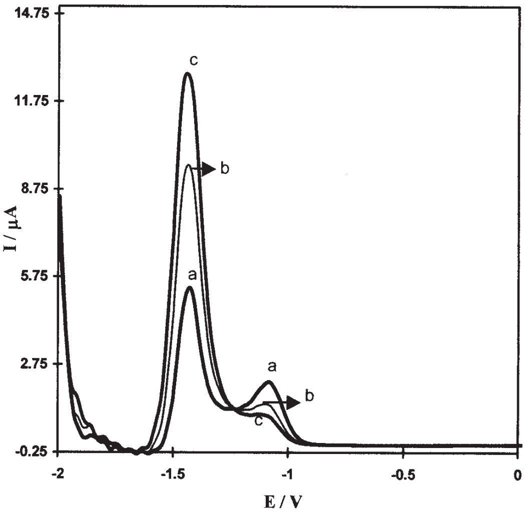

Figure 6. The second peak in brightening is higher than the first and the first coincides on peak current of Ni^{2+}.

of Ni^{2+} in Watt's electrolytic bath , By CV, DPP, and ASV (anodic stripping voltammetry) methods, in absence of organic additives, and also, electrochemical behaviour of each organic additive, by CV and DPP methods were studied separately. In separate experiments, the effect of each additive on Ni^{2+} behaviour, and vice versa, and at last the effects of all additives together on Ni^{2+} behaviour, were studied. In Fig. 1 to 4, DPP voltamograms of Ni^{2+}, brightening, purifier and ductility enhancing agents are presented. In table (1), we have focused, on these results and also, analytical information about determination of these additives in the presence of Ni^{2+}. Our results show that the Ni / Ni^{2+} system presents an irreversible behaviour, with Ep_c =-1.01, -1.01 and -1.12 V, in CV, DPP, and ASV, separately, in Watt's bath. Also, we observed that the wetting agent is not electroactive, but it changes the peak potential of Ni^{2+} by about -0.3 volt, figure (5), and this shift has not an inconvenient effect on Ni^{2+} electrochemical behaviour, because boric acid will be reduced in more negative potential.

Other additives, such purifier and ductility enhancing agents are electroactive at Ep_c = -1.53 and -1.85 respectively, in CV and DPP methods, whereas the brightening enhancing agent presents two peaks at potentials -1.09 and -1.80 volts that do not have equal height peak currents . The second peak is relatively much higher than the first, and also, the first peak coincides on peak current of Ni^{2+}, figure

(6). Also, by studying calibration curve, the end column of table (1), it is possible to measure the concentration of electroactive additive by DPP method. Finally, we have studied the presence of all additives, together, with Ni^{2+}, and we have observed that the peak potentials of all compoundsdoes not change in this condition, Figure (7).

4. CONCLUSIONS

Our results prove that Ni^{2+} and organic additives like brightening, purifier and ductility enhancing agents are electroactives, and they present an irreversible behaviour in Watt's electrolytic bath, and also, their peak potentials are more negative than Ni^{2+}. The additive like wetting agent is not electroactive but its presence changes peak potential of Ni^{2+}, by about -0.3 volt . Finally, this shift does not makes an inconvenient effect, because boric acid will be reduce in more negative potential.

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