CONTRIBUTION ABOUT NICKEL ELECTRODEPOSITION FROM WATTS BATH WITH ADDITION OF POLYVINYLPYRROLIDONE

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Abstract: *In this work it was studied the influence of polyvinylpyrrolidone (PVP) on the nickel electroplating processes from Watts bath. PVP is a wetting agent which improves the quality of deposited layers. Its action seems to be related to the inhibition of adsorption of* $(NiOH)^+$ *species on the cathode surface. Even if there are some studies about the influence of PVP in electrochemical processes, this trend is new and our results could promote this additive for future commercial applications.*

Keywords: *nickel electrodeposition, Watts bath, polyvinylpyrrolidone, SEM technique*

Introduction

Nickel electroplating has a great commercial and industrial importance and offers a very good quality finish of surfaces. This importance is emphasized by increasing of annual global consumption of nickel, which goes to 100.000 tones. The applications of electroplating could be derived in three categories: decorative, functional and electroforming.

In the paper is studied the electrodeposition layer of Ni in the presence of polyvinylpyrrolidone as a wetting agent with SEM technique.

The electrochemical reactions on the cathode could be written generally:

$Ni^{2+} + 2e^- \rightarrow Ni$,

but the proposed mechanism is by next type:

$Ni^{2+} + H_2O \rightarrow (NiOH)^+ + H^+$

$(NiOH)^+ + e^- \rightarrow (NiOH)_{ads}$

$(NiOH)_{ads} + (NiOH)^+ + 3e^- \rightarrow 2Ni + 2OH^-$.

This mechanism was proposed after the study of inductive impedance loops with the method of electrochemical impedance spectroscopy, but all steps was not identified and elucidates yet [Bard 2001, Di Bari 2000].

Materials and methods

Nickel electro deposition was performed at INCDFM Bucharest-Magurele, in the Electrochemistry Department. It was used a Watts bath with the next composition: nickel sulfate ($NiSO_4 \cdot 6H_2O$) $240\ g \cdot L^{-1}$; nickel chloride ($NiCl_2 \cdot 6H_2O$) $45\ g \cdot L^{-1}$ and boric acid (H_3BO_3) $30\ g \cdot L^{-1}$ (Merck substances were used) [Sima 2004,2007, Sulitanu 2003]. In order to improve the properties of electrodeposited layer it was added in the Watts bath as wetting agent polyvinylpyrrolidone – 5 g. We worked at different temperatures in the range from 45°C to 65°C. The experimental device used to realize nickel electrodeposition is composed by a potentiostat-galvanostat PARSTAT 2273 Advanced Electrochemical System with special soft-ware for data processing, an electrolytic cell with thermostat Lauda 003, magnetic shaker and thermometer for temperature control. As reference electrode it was used a calomel electrode and as contra electrode was used a high purity nickel electrode. For processing the graph charts recorded during the electrodeposition it was used the soft-ware ORIGIN 7.5., specialized in complex interpretation of scientific data.

Little copper plates (approx. 2 cm^2) were cut and their thickness was measured with a micrometer. Their surface was mechanically processed with emery paper and felt. The copper plates were washed with a solution containing sulfuric acid (H_2SO_4) *98%, d=1,84 g/cm^3, 500 gL^{-1}* nitric acid (HNO_3) *d=1,42 g/cm^3, 500 gL^{-1}* and sodium chloride, *NaCl 5 g*, at 25°C temperature, for 2 minutes, then washed with distilled water, dried and weighted.

Before proceed properness to nickel electrodeposition there were drawn the polarization curves to establish the potential range for ions discharge. During electrodeposition there were registered current densities. Both potentiostatic curves and voltammogrames are useful to determine the electrochemical parameters. There were followed the change of this parameters function with concentration, temperature and composition of the deposited films [Vasilache 2008].

Results and Discussion

Figures 1 and 2 present polarization curves for those two types of solution used, Watts bath without additives and with addition of polyvinylpyrrolidone (PVP). A slowly move to the region of highest potentials is observe in the case of addition of PVP. In figures 3 and 4 there are presented cyclic voltammogrames recorded during nickel electrodeposition process without and with adding of PVP. The potential range was from +600 mV to -1200 mV, with a scanning velocity 3 mV/s (which means 180 mV/minute).

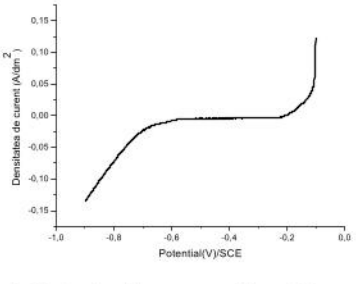

Figure 1. Polarization curve for a Watts bath for the potential range from -100 mV to -1200 mV, 65°C temperature, with magnetic shaking of the electrolyte

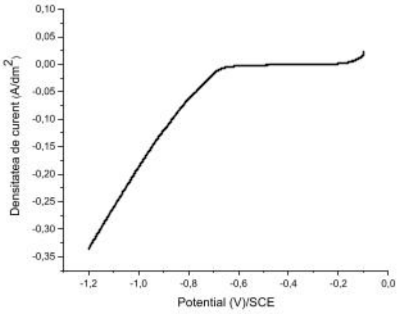

Figure 2. Polarization curve for a Watts bath with PVP adding for the potential range from -100 mV to -1200 mV, 65°C temperature with magnetic shaking of the electrolyte (ORIGIN 7.5).

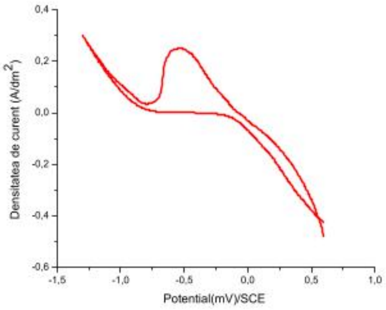

Figure 3. Cyclic voltammetry for a Watts bath without additives in the range from 600 mV to -1200 mV, with a scanning velocity of 3 mV/s

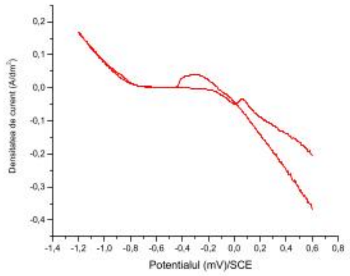

Figure 4. Cyclic voltammetry for a Watts bath with PVP in the potential range from 600 mV to -1200 mV, with a scanning velocity of 3 mV/s

In order to establish the scanning velocity it has to take care about the fact that a too higher velocity doesn't permit a reaction of the electrochemical system (the processes will not be quasi-static) and a slowest one will increase too much the time for the experiments.

Comparing the two voltammogrames recorded it can conclude that additives increase the level of process reversibility because their action is to inhibit the nucleation, a slowest rate of the deposition process and so one a good quality of the deposited layer. For a Watts bath without additives there is an intense pick for the value of current density of 0,24 A/dm^2 and a potential of -500 mV. This fact is due to adsorption of species $(NiOH)^+$, a confirmation of the next mechanism

$$\begin{aligned}
&Ni^{2+} + 2e^- \rightarrow Ni, \\
&Ni^{2+} + H_2O \rightarrow (NiOH)^+ + H^+, \quad (1) \\
&(NiOH)^+ + e^- \rightarrow (NiOH)_{ads}, \\
&(NiOH)_{ads} + (NiOH)^+ + 3e^- \rightarrow 2Ni + 2OH^-.
\end{aligned}$$

The cyclic voltammograme showed in figure 4 corresponds to the situation of a bath with additives (PVP) and it can be observe that the pick corresponding to the species $(NiOH)^+$ is more reduced as intensity and it was moved to a potential of approximate -300 mV. The cause of this behavior is that PVP decreases the adsorption of $(NiOH)^+$ on the cathode surface. Also in figure 4 it can be observe a superposition of the curves between the potentials from -400 mV to -1200 mV, as a proof of a high level of reversibility of the electrochemical reactions for this range of potentials. Figures 5, 6, 7 and 8 present the evolution of current density versus time during the electrodeposition of nickel, using a Watts bath without additives, for different discharge potentials, -800 mV, -900 mV, -1000 mV and -1100 mV respectively, in the same condition of working temperature (65°C), and with magnetic shaking of the electrolyte solution.

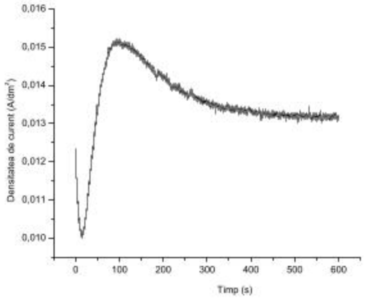

Figure 5. Chronoamperograme chart recorded during nickel electrodeposition from a Watts bath, at -800 mV potential, 65°C temperature, with magnetic stirring of the electrolyte (ORIGIN 7.5)

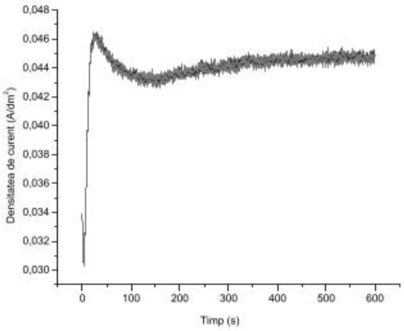

Figure 6. Chronoamperograme chart recorded during nickel electrodeposition from a Watts bath, at -900 mV potential, 65°C temperature, with magnetic stirring of the electrolyte. (ORIGIN 7.5)

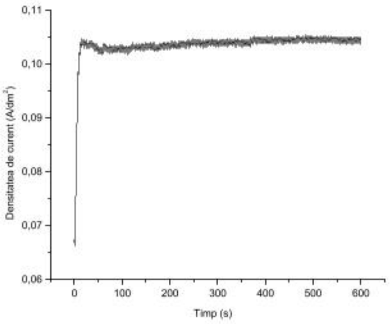

Figure 7. Chronoamperograme chart recorded during nickel electrodeposition from a Watts bath, at -1000 mV, 65°C temperature, with magnetic stirring of the electrolyte.

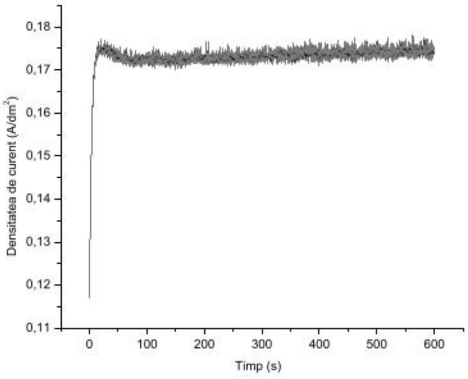

Figure 8. Chronoamperograme chart recorded during nickel electrodeposition from a Watts bath, at -1100 mV potential, 65°C temperature, with magnetic stirrinng of the electrolyte.

Figures 9, 10 and 11 show the evolution of current density versus time during the electrodeposition of nickel from a Watts bath with polyvinyl pyrrolidone for potentials of -800 mV, -900 mV and -1100 mV, using a work temperature of 65°C. All the chronoamperograme charts were recorded and performed using the soft-ware ORIGIN 7.5.

Analyzing the chronoamperograme charts recorded at nickel electrodeposition without additives it can observe that current density increases in the same manner with working potential, because Ohm's law is valid also for the electrochemical processes.

If we compare the chronoamperograme charts recorded during electrodeposition without additives and during electrodeposition with additives (PVP), in the second case a decrease of current density can be observed. This decrease of current density is as a consequence of inhibition of adsorption processes of species $(NiOH)^+$ and decreasing in growing nickel crystals on the cathode surface. For electrodeposition with PVP also the Ohm's law is valid, because the current densities increase in the same manner with potential.

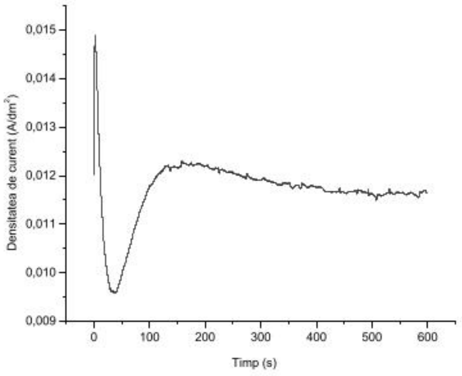

Figure 9. Chronoamperograme chart recorded during nickel electrodeposition from a Watts bath with addition of PVP, at -800 mV potential, 65°C temperature, with magnetic stirring of the electrolyte.

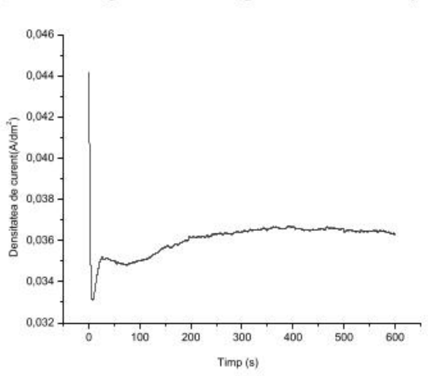

Figure 10. Cronoamperograme chart recorded during nickel electrodeposition from a Watts bath with addition of PVP, at -900 mV potential, 65°C temperature, with magnetic stirring of the electrolyte.

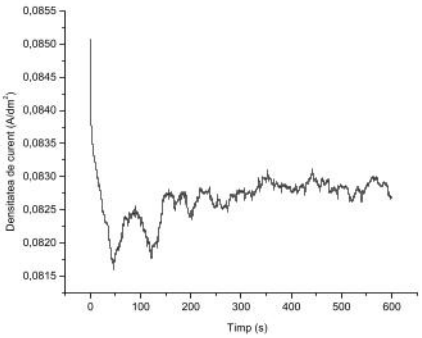

Figure 11. Chronoamperograme chart recorded during nickel electrodeposition from a Watts bath with addition of PVP, at -1100 mV potential, 65°C temperature, with magnetic stirring of the electrolyte.

Another fact that is easy to observe is the stabilization of the current during electrodeposition for the case of using high working potentials (-1000 mV and -1100 mV respectively, figures 7, 8). This fact could be a logical consequence of covering of the secondary reactions by principal electrochemical reactions, discharging of Ni^{2+} ions, and stabilizing of electrodynamics equilibrium in all the mass of the electrolyte, especially on the electrodes surface.

The Nernst diffusion layer is stabilized and the entire electrolyte is closer than an ohm-type resistor. Of course if deposition time is very long, a slowest decreasing of current density will be observe because the concentration of ions in solution will decrease due to the deposited metal. But in our experimental situations the deposition time was 10 minutes, so it can be considered that there is not a significant modification in concentration of ions in electrolyte.

The nickel layers electrodeposited were analyzed at INCDFM Bucuresti-Magurele using scanning electron microscopy type Zeiss EVO 20. Figure 12 presents a SEM image of a sample of nickel electrodeposited at -700 mV potential, working temperature 65°C, from a Watts bath with addition of PVP. In the first image which has the resolution 10620X it can be observed the steps of electro-crystallization, and also the micro-pores produced by hydrogen evolution. In the image having the resolution 58450X, it can be seen a micro-pore in the right-down-corner. Both images present a uniform covered surface, a good quality of the deposited layer.

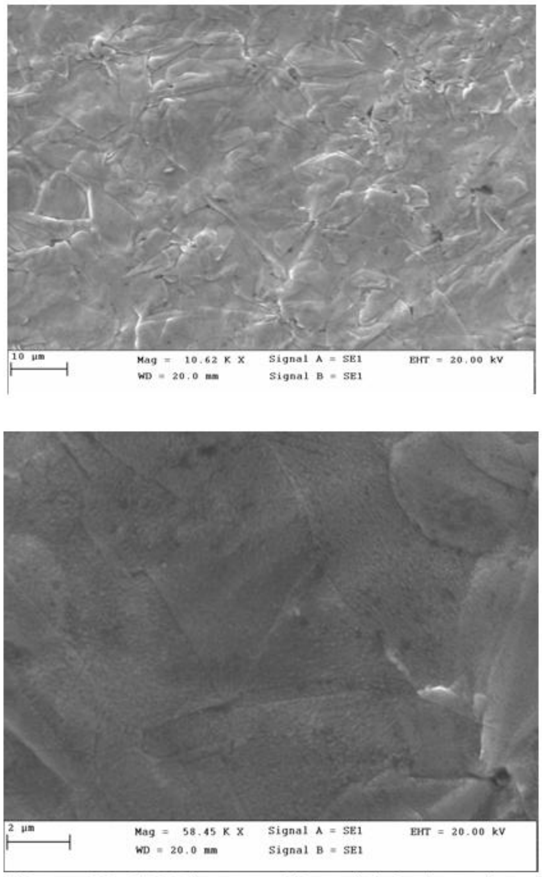

Figure 12. SEM images of the nickel electrodeposited layer from a Watts bath with addition of PVP at -700 mV potential, 65°C temperature, deposition time 10 minutes, with magnetic stirring of the electrolyte (SEM-Zeiss EVO 20 device)

Conclusions

The polyvinylpyrrolidone as additive (wetting agent) in Watts bath for nickel electroplating proves good properties of electrodeposited layers and a good quality of the final product. It actions in manner to inhibit the adsorption of ions $(NiOH)^+$. Even it is a new way for study the results are close to confirm that it can be used for commercial applications.

Acknowledgments

Prof. Dr. Ioan Sandu, Al.I. Cuza University of Iasi: researcher. Dr. Ionut Enculescu, INCDFM Bucuresti-Magurele, researcher. Dr. Cristian Teodorescu

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