Studies Concerning Nickel Electrodeposition from Watts bath with Addition of Polyvinyl Pyrrolidone (PVP)

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This work is a study about the influence of polyvinyl pyrrolidone (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 electroplating, polyvinyl pyrrolidone, polarization curves, SEM-EDX techniques

In nickel electroplating processes additives are intensively used, because they permit to achieve a better quality and improve physical, chemical and mechanical properties. Polyvinyl pyrrolidone (PVP) is a relative new used agent and acts like a wetting agent.

Many processes of electroplating with nickel use classical baths compositions proposed by Watts. In order to obtain decorative coatings on mirror-like surfaces, there were developed special recipes with aditives containing organic substances such as surfactants, brightness agents and leveling agents. The current efficiency is almost 100% for a large current densities interval. Anyway, it is difficult to obtain a uniform layer thickness distribution because of the non-uniformity of the current density. For the majority of applications it is necessary a thickness as good as it is possible, which could be achieved using additives carefully selected [1, 2].

Experimental part

Nickel electrodeposition was performed at INCDFM Bucuresti-Magurele, at the Electrochemistry Department. It was used a Watts bath with the following composition: nickel sulphate ($NiSO_4{\cdot}6H_2O$) $240\ g \cdot L^{-1}$; nickel chloride ($NiCl_2{\cdot}6H_2O$) $45\ g \cdot L^{-1}$ and boric acid (H_3BO_3) *30* (Merck reagents were used). In order to improve the properties of electrodeposited layer 5 $g{\cdot}L^{-1}$ of polyvinyl pyrrolidone, as wetting agent, were added in the Watts bath. The experiments were fulfilled at different temperatures, in the range from 45°C to 65°C. The experimental device used to realize nickel electrodeposition was composed by a potentiostat-galvanostat PARSTAT 2273 Advanced Electrochemical System with special software for data processing, an electrolytic cell with Lauda 003 thermostat, magnetic stirrer and thermometer for temperature controlling. As reference electrode it was used a calomel electrode and as counter electrode was used a high purity nickel electrode. For processing the data recorded during the electrodeposition it was used the software ORIGIN 7.5., appropriated for 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 sulphuric acid (H_2SO_4) *98%, d=1,84 g/cm*^{3}*, 500 ;* nitric acid (HNO_3) *d=1.42* g/*cm*^{3}*, 500 l* and sodium chloride, *NaCl 5 g*, at 25°C temperature, for 2 min, then washed with distilled water, dried and weighted.

Before a proper proceeding 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 voltamogrames were used to determine the electrochemical parameters. There were followed the change of this parameters function with concentration, temperature and composition of the deposited films [3 - 7].

Results and discussions

Figures 1 and 2 show polarization curves for those two types of used solutions, Watts bath without additives and with addition of polyvinyl pyrrolidone (PVP). A slow move to the region of highest potentials was observed in the case of addition of PVP.

Figures 3 and 4 present the cyclic voltamograms recorded during nickel electrodeposition process without and with addition of PVP. The potential range was from +600 mV to -1200 mV, with a scanning velocity 3 mV/s (which means 180 mV/min). In order to establish the scanning velocity it must be taken in consideration that a too high velocity doesn't permit a reaction of the electrochemical system (the processes will not be quasi-static) and a too slow one will increase too much the time for the experiments.

Comparing the two voltamograms recorded it can be concluded that additives increase the level of process reversibility because their action is to inhibit the nucleation, which leads to a slower rate of the deposition process and so to a better 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:

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

The cyclic voltamogram showed in figure 4 corresponds to the situation of a bath with additives (PVP) and it can be

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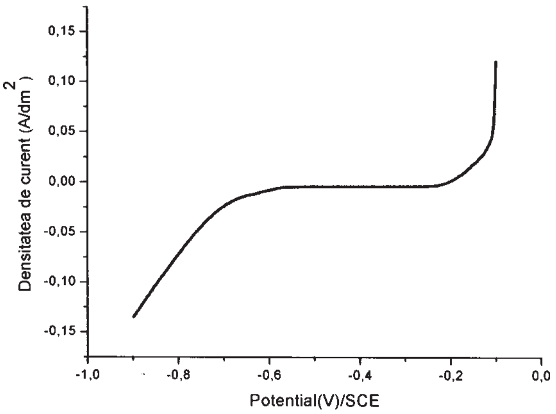

Fig.1. Polarization curve for a Watts bath for the potential range from -100 mV to -1200 mV, 65°C temperature, with magnetic shaking of the electrolyte

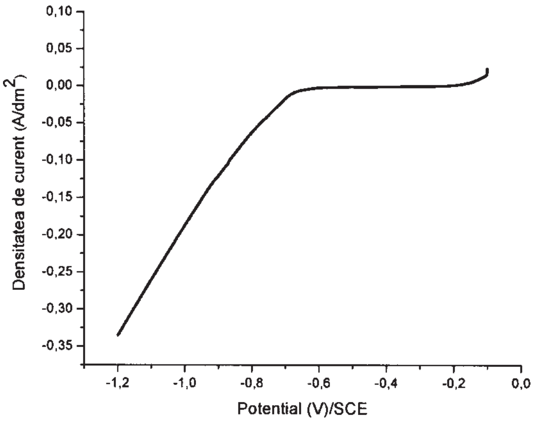

Fig.2. Polarization curve for a Watts bath with PVP adding for the potential range from -100 mV to -1200 mV, 65°C temperature with magnetic shaking of the electrolyte

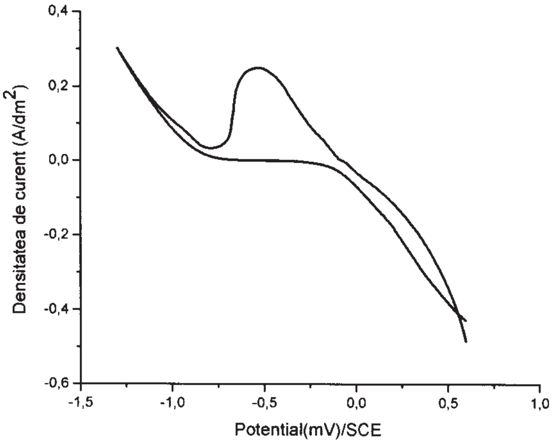

Fig.3. Cyclic voltametry for a Watts bath without additives in the range from 600 mV to -1200 mV, with a scanning velocity of 3 mV/s

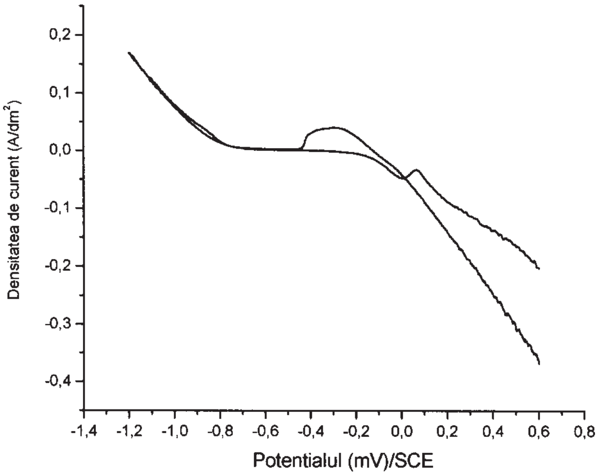

Fig.4. Cyclic voltametry for a Watts bath with PVP in the potential range from 600 mV to -1200 mV, with a scanning velocity of 3 mV/s

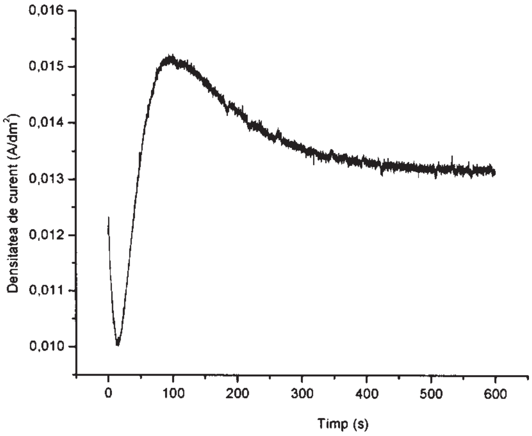

Fig.5. Chronoamperogram chart recorded during nickel electrodeposition from a Watts bath, at -800 mV potential, 65°C temperature, with magnetic stirring of the electrolyte

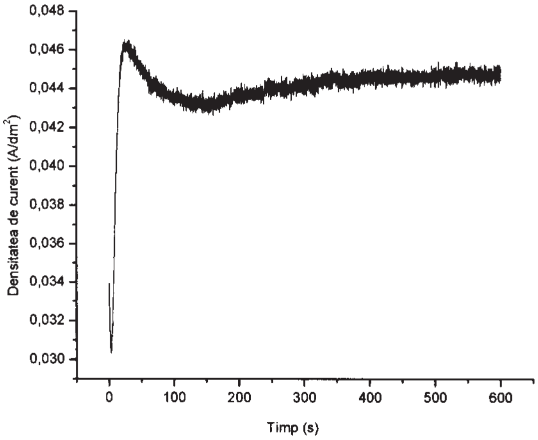

Fig.6. Chronoamperogram chart recorded during nickel electrodeposition from a Watts bath, at -900 mV potential, 65°C temperature, with magnetic stirring of the electrolyte

observed 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 it can be observed 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 from a Watts bath without additives, for different discharge potentials, -800 mV, -900 mV, -1000 mV and -1100 mV respectively, in the same conditions of temperature (65°C), and with magnetic stirring of the electrolyte solution.

Figures 9, 10 and 11 show the evolution of current density versus time during the electrodeposition of nickel from a Watts bath with addition of polyvinyl pyrrolidone for potentials of -800 mV, -900 mV and -1100 mV, and 65°C temperatures. All the chronoamperogram charts were recorded and performed using the software ORIGIN 7.5.Analyzing the chronoamperogram charts recorded during nickel electrodeposition from solutions without

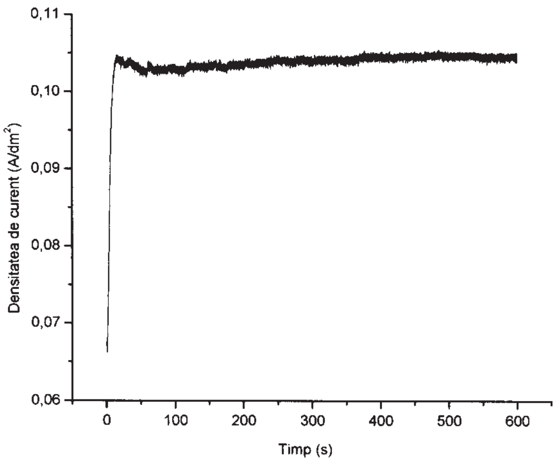

Fig.7. Chronoamperogram chart recorded during nickel electrodeposition from a Watts bath, at -1000 mV , 65°C temperature, with magnetic stirring of the electrolyte

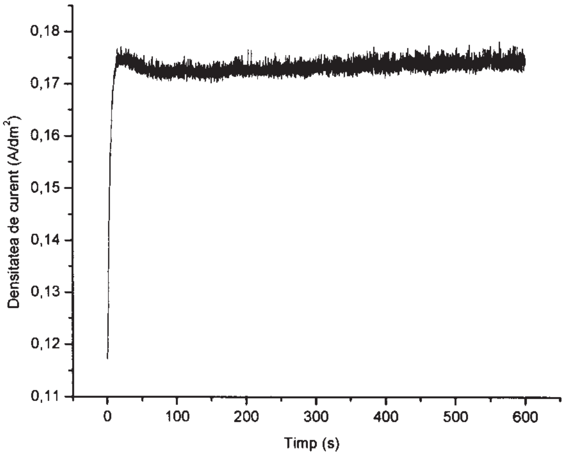

Fig.8. Chronoamperogram chart recorded during nickel electrodeposition from a Watts bath, at -1100 mV potential, 65°C temperature, with magnetic stirring of the electrolyte

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 chronoamperogram 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 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.

Another fact easy to observe is the stabilization of the current during electrodeposition for the case of use of high working potentials (-1000 mV and -1100 mV respectively, figs. 7, 8). This fact could be a logical consequence of masking of the secondary reactions by the main 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 acts like an ohm-type resistor. Of course, if the 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. In our experimental situations, the deposition time was 10 min, so it can be considered that there is not a significant modification in concentration of ions in electrolyte.

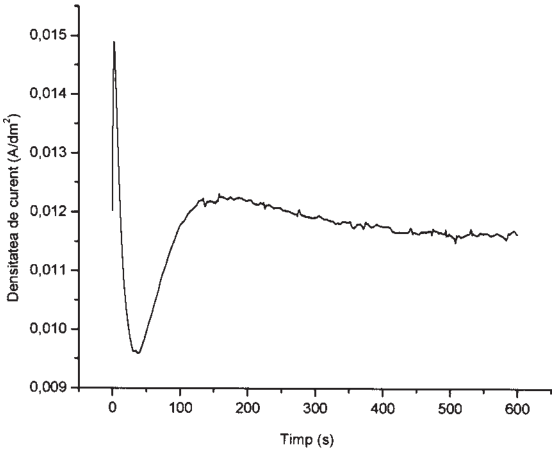

Fig.9. Chronoamperogram chart recorded during nickel electrodeposition from a Watts bath with addition of PVP, at -800 mV potential, 65°C temperature, with magnetic stirring of the electrolyte

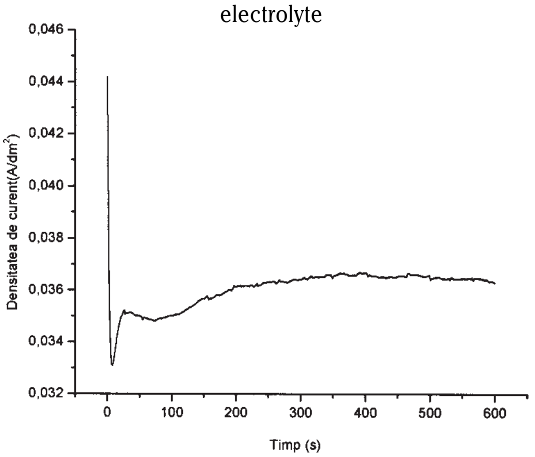

Fig.10. Cronoamperogram chart recorded during nickel electrodeposition from a Watts bath with addition of PVP, at -900 mV potential, 65°C temperature, with magnetic stirring of the electrolyte

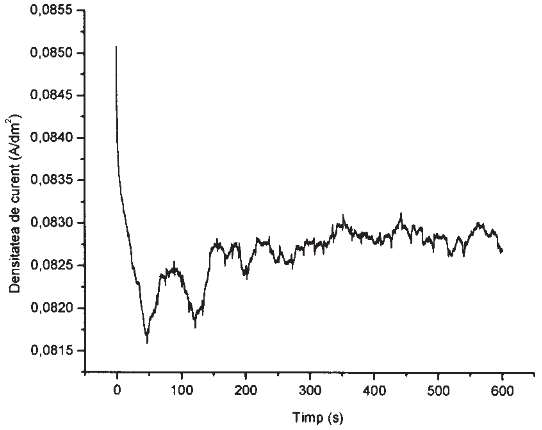

Fig.11. Chronoamperogram chart recorded during nickel electrodeposition from a Watts bath with addition of PVP, at -1100 mV potential, 65°C temperature, with magnetic stirring of the electrolyte

The electrodeposited nickel layers were analized at INCDFM Bucuresti-Magurele using a Zeiss EVO 20 scanning electron mycroscopy type.

Figure 12 presents a SEM image of a sample of electrodeposited nickel at -700 mV potential, temperature 65°C, from a Watts bath with addition of PVP. In the first image which has the resolution 10620X there 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

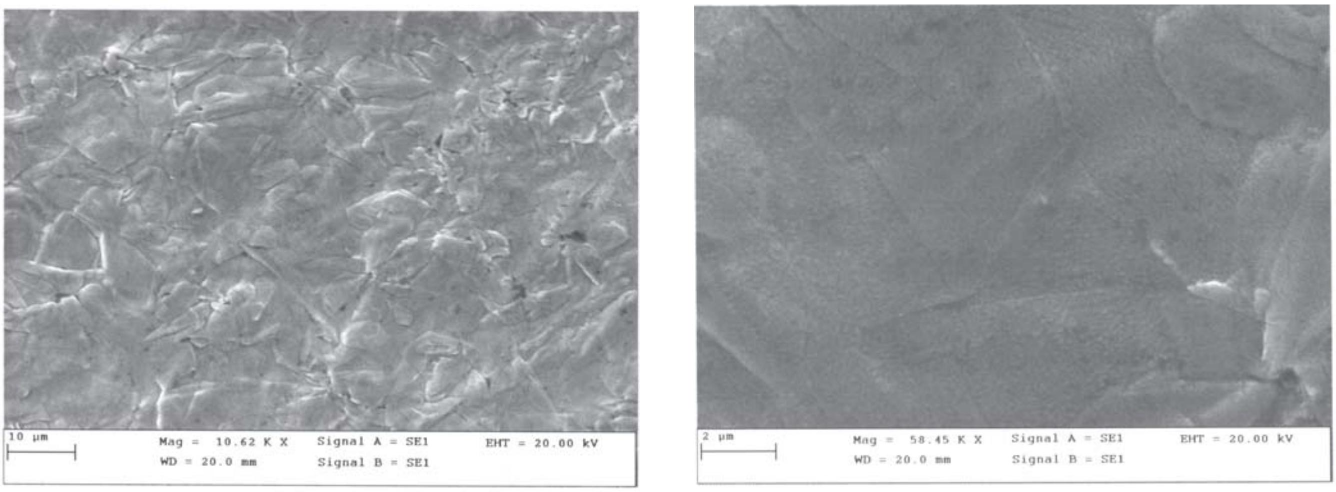

Fig.12. SEM images of the nickel electrodeposited layer from a Watts bath with addition of PVP at -700 mV potential, 65°C temperature, deposition time 10 min, with magnetic stirring of the electrolyte (SEM-Zeiss EVO 20 device)

in the right-down-corner. Both images present a uniform covered surface, a good quality of the deposited layer [8].

Conclusions

The polyvinyl pyrrolidone as addition agent in Watts bath for nickel electroplating proves good properties of electrodeposited layers and a good quality of the final product. It actions inhibiting the adsorption of ions $(NiOH)^+$. Even it is a new additive, less studied, the results could confirm that it can be used for commercial applications.

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Manuscript received: 30.07.2007