STUDIES REGARDING NICKEL ELECTRODEPOSITION FROM WATTS BATH WITH ADDITION OF POLYVINYLPYRROLIDONE AND SODIUM SACCHARINE

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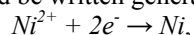email: _g.gutt@usv.ro, sandu_i03@yahoo.com, violetav@usv.ro_

ABSTRACT

This paper is based on some studies about the influence of polyvinylpyrrolidone (PVP) and sodium saccharine as far as concern their influence on the nickel electroplating processes from Watts bath. PVP is a wetting agent which improves the quality of deposited layers. Sodium saccharine is a leveling agent which improves adherence and brightness of the deposited layers. PVP actions through the inhibition of adsorption of (NiOH)$^+$ species on the cathode surface. Sodium saccharine controls crystals growth on the electro-crystallization process. Our results are able to promote using of these additives for future commercial applications. SEM-EDX techniques and optical microscopy were used with the aim to emphasize the uniformity, the continuality and the micro-structural granularity of the electrodeposited layers,, correlated with chemical composition and metallic brightness, through absorption spectroscopy.

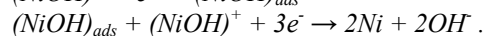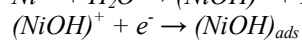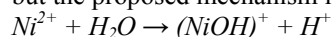KEYWORDS: nickel electrodeposition, Watts bath, polyvinylpyrrolidone, sodium saccharine, SEM-EDX technique

1. Introduction

Nickel electroplating is an important way to fight against corrosion. With the aim to obtain layers with a superior quality or aspect, there are used many additives for specific purposes. Sodium saccharine is one of these and it has been used by decades. PVP is a new one and is less studied. This work reports studies regarding the nickel electrodeposition in the presence of sodium saccharine and 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.

2. Experimental details

It was used a Watts bath with the following composition: nickel sulphate ($NiSO_4 \cdot 6H_2O$) *240 gL^{-1}*; nickel chloride ($NiCl_2 \cdot 6H_2O$) *45 gL^{-1}* and boric acid (H_3BO_3) *30 gL^{-1}* (Merck reactants were used). In order to improve the properties of electrodeposited layer it was added in the Watts bath as wetting agent polyvinyl pyrolidone – 5 g. We worked at different temperatures in the range from 45°C to 65°C. The experimental device used to realize nickel electrodeposition consists by a potentiostat-galvanostat PARSTAT 2273 Advanced Electrochemical System with special soft-ware for data processing, an electrolytic cell with thermostat, 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, specialized in complex interpretation of scientific data. Small surface 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 voltamogrames 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.

3. Results and discussions

Figures 1 and 2 present polarization curves for those two types of solution used, Watts bath without additives and with addition of polyvinyl pyrolidone (PVP). A slowly move to the region of highest potentials is observe in the case of addition of PVP.
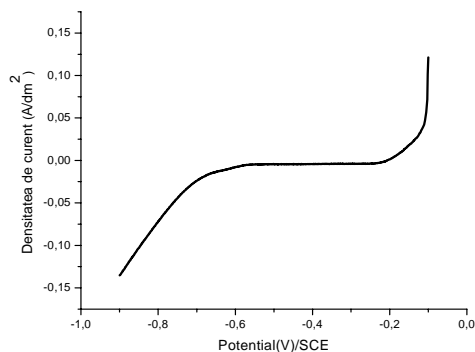

Fig.1. *Polarization curve for a Watts bath for the potential range from -100 mV to -1200 mV, 65°C temperature, with magnetic stirring of the electrolyte.*
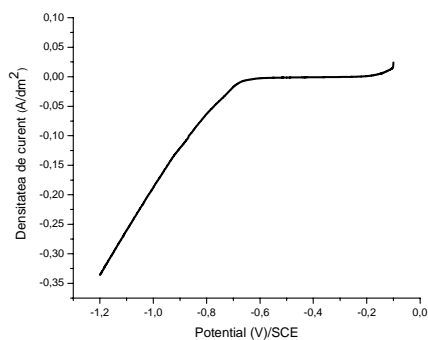

Fig.2. *Polarization curve for a Watts bath with PVP adding for the potential range from -100 mV to -1200 mV, 65°C temperature with magnetic stirring of the electrolyte.*

In figures 3 and 4 there are presented 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/minute). 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.
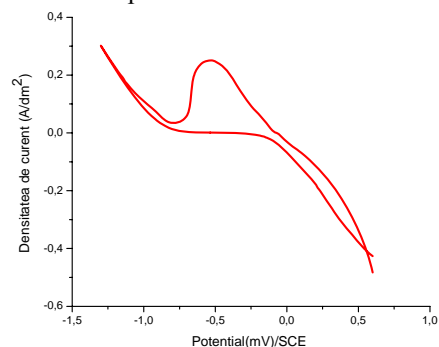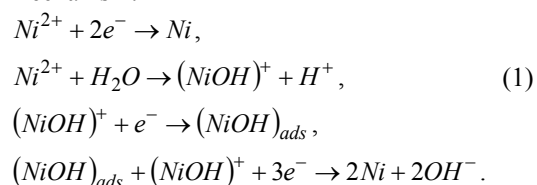

Fig.3. *Cyclic voltametry for a Watts bath without additives in the range from 600 mV to -1200 mV, with a scanning velocity of 3 mV/s*
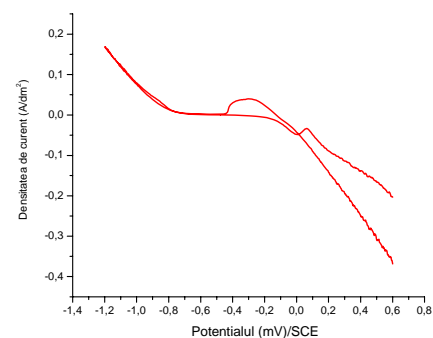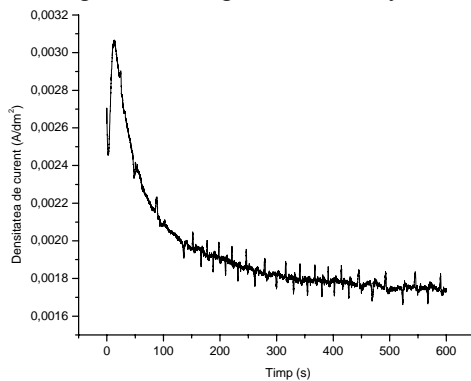

Fig.4. *Cyclic voltametry for a Watts bath with PVP in the potential range from 600 mV to -1200 mV, with a scanning velocity of 3 mV/s*
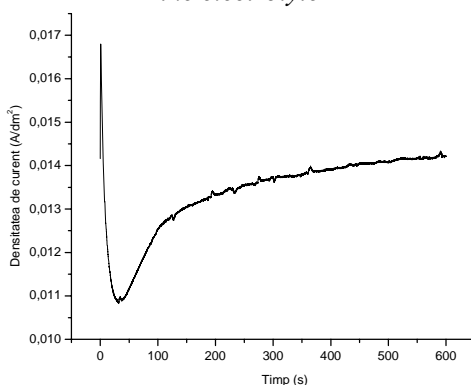
Comparing the two voltamograms recorded it can conclude that additives increase the level of process reversibility because their action is to inhibit the nucleation, a slowest rate of the deposition process and so one a good quality of the deposited layer. For a Watts bath without additives there is 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 following mechanism:

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

$$Ni^{2+} + H_2O \rightarrow (NiOH)^+ + H^+, \qquad (1)$$

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

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

The cyclic voltamograme shown 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 approximately -300 mV. The cause of this behaviour 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.

electrodeposition in the same manner with the increasing of the potential, a predictable fact due to the Ohm's law. An interesting behavior could be sign comparing the charts recorded for -700 mV and -800 mV working potential. In the first case there is a gentle decreasing of the current density while for the second there is a gentle increasing of the current density.

For highest potentials (-900 mV and -1000 mV) there is signed a stabilization of the current density during electrodeposition process.

That apparent strange behavior recorded for -800 and -900 mV could be promoted by secondary reactions of hydrogen evolution and $(NiOH)^+$ complex, as follows:

$$Ni^{2+} + H_2O \rightarrow (NiOH)^+ + H^+$$
$$(NiOH)^+ + e^- \rightarrow (NiOH)_{ads}$$

Fig.5. Chrono-amperograme recorded during nickel electrodeposition from a Watts bath with addition of PVP and sodium saccharine, at -700 mV and 65 °C, with magnetic stirring of the electrolyte
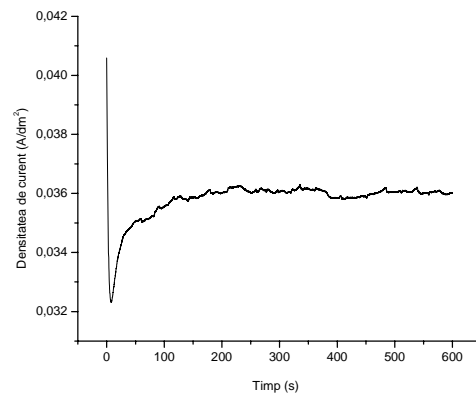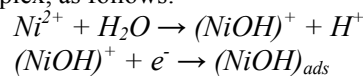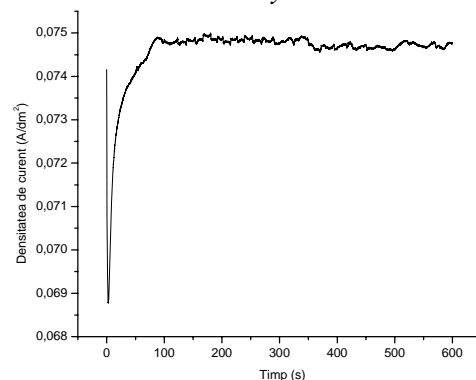

Fig.7. Chrono-amperograme recorded during nickel electrodeposition from a Watts bath with addition of PVP and sodium saccharine, at -900 mV and 65 °C, with magnetic stirring of the electrolyte

Fig.6. Chrono-amperograme recorded during nickel electrodeposition from a Watts bath with addition of PVP and sodium saccharine, at -800 mV and 65 °C, with magnetic stirring of the electrolyte

Fig.8. Chrono-amperograme recorded during nickel electrodeposition from a Watts bath with addition of PVP and sodium saccharine, at -1000 mV and 65 °C, with magnetic stirring of the electrolyte

From these charts there could be observe an increasing of the current density during

Some simple calculus for electrostatic resistance of the cell gives values which decrease with the increasing of deposition potential, a fact that

proves that for high potentials there is a decreasing on the rate of secondary reactions.

$$R_{700} = \frac{0,700}{0,0018} = 388\,\Omega \cdot dm^2 \; ,$$

$$R_{800} = \frac{0,800}{0,014} = 57,14\,\Omega \cdot dm^2 \; ,$$

$$R_{900} = \frac{0,900}{0,036} = 25\,\Omega \cdot dm^2 \; ,$$

$$R_{1000} = \frac{1,000}{0,075} = 13,33\,\Omega \cdot dm^2$$

Another fact that is easy to observe is stabilization of the current density during electrodeposition for the when there are used high working potentials (-900 mV and -1000 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.

Figures 9, 10, 11 and 12 show the evolution of current density versus time during the electrodeposition of nickel from a Watts bath without additives, for -700 mV, -800 mV, -900 mV and -1000 mV, and 65°C working temperature. All the chrono-amperograme charts were recorded and performed using the soft-ware ORIGIN 7.5.
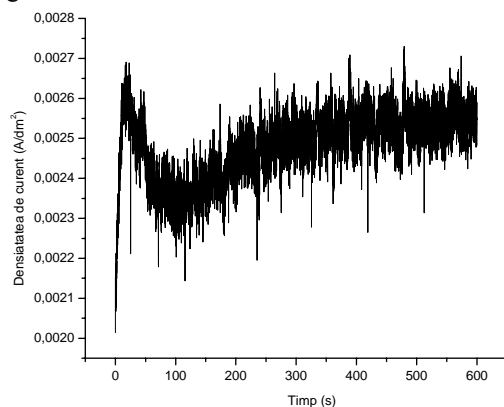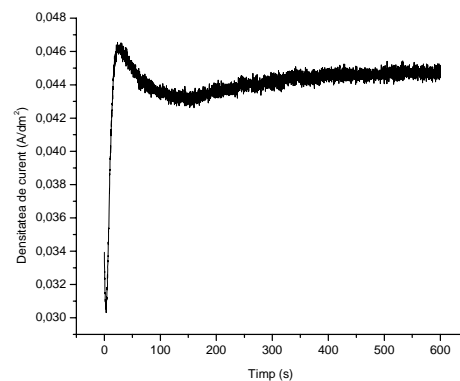
Fig.9. *Chrono-amperograme recorded during nickel electrodeposition from a Watts bath withot additives, at -700 mV and, 65 ℃, with magnetic stirring of the electrolyte.*

The same behavior could be observe like for the situations of electrodeposition with addition of PVP and sodium saccharine.
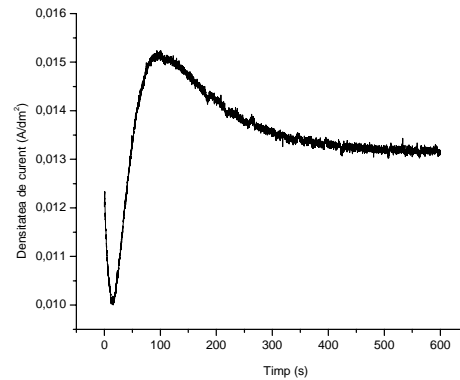
Fig.10. *Chrono-amperograme recorded during nickel electrodeposition from a Watts bath without additives, at -800 mV and 65℃, with magnetic stirring of the electrolyte*

Fig.11. *Crono-amperograme recorded during nickel electrodeposition from a Watts bath without additives, at -900 mV and 65 ℃, with magnetic stirring of the electrolyte.*
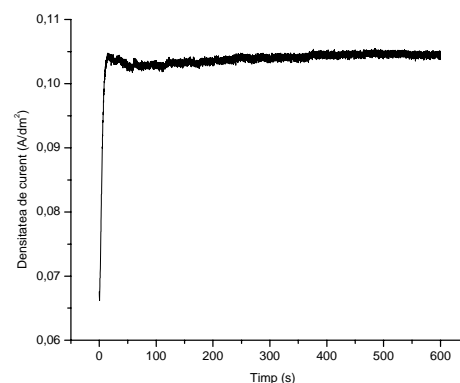
Fig.12. *Chrono-amperograme recorded during nickel electrodeposition from a Watts bath without additives, at -1000 mV and 65 ℃ temperature, with magnetic stirring of the electrolyte.*

For electric resistance it was found

$$R_{700} = \frac{0,700}{0,0025} = 280\,\Omega \cdot dm^2 \quad,$$

$$R_{800} = \frac{0,800}{0,0135} = 59,25\,\Omega \cdot dm^2 \quad,$$

$$R_{900} = \frac{0,900}{0,036} = 20,45\,\Omega \cdot dm^2 \quad,$$

$$R_{1000} = \frac{1,000}{0,075} = 9,615\,\Omega \cdot dm^2$$

The values are lower than in case of bath with additives, so additives increase the ohmic resistance of the cell. Figure 13 presents a SEM image of a sample of nickel electrodeposited at -700 mV and 65°C, from a Watts bath with addition of PVP and sodium saccharine. 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.
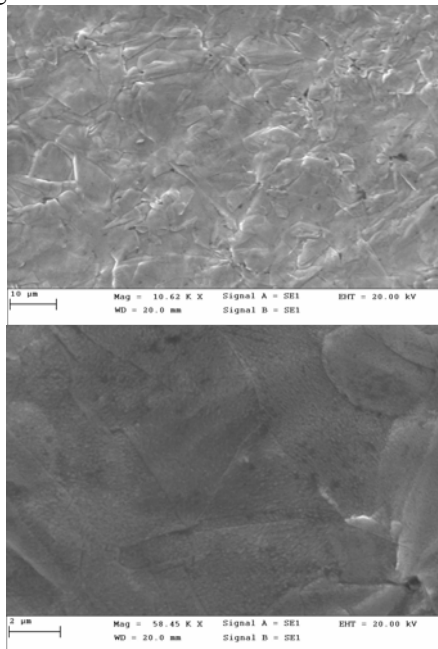
***Fig.13.** SEM images of a nickel electrodeposited layer from a Watts bath with addition of PVP and sodium saccharine at -700 mV, 65°C and deposition time 10 minutes, with magnetic stirring of the electrolyte*

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.

4. Conclusions

The polyvinyl pyrolidone and sodium saccharine as addition agents in Watts bath for nickel electroplating permit to achieve layers with good properties and a good quality of the final product. PVP actions in manner to inhibit the adsorption of ions $(NiOH)^+$. Even it is a new way for study the results are about to confirm that it can be used for commercial applications.

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