ADVANCED CHARACTERIZATION METHODS FOR NICKEL LAYERS ELECTROCHEMICALLY DEPOSITED – REFLECTANCE OF THE FILMS

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Abstract: *Nickel was electrochemically deposited on copper substrate. The layers were studied with scanning electron microscope (SEM), composition was revealed through studies of energy dispersive of X-rays (EDX) and X-ray diffraction (XRD) and the reflectance was studied by reflectance spectroscopy.*

Keywords: *Nickel, electrodeposition, SEM, EDX, and XRD techniques, reflectance*

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 [2,3]

Decorative and functional applications development is closed by customer's demand. There are many products which have to present a particular visual aspect, and the brightness is one of the most important properties from this point of view. Achievement of a desired brightness depends by electrodeposition conditions, by receipt of the solutions and by the additives used. [10,11,12]

Materials and methods

Electrodeposition of nickel was performed at INCDFM Bucharest-Magurele Institute, in the Electrochemistry Department. A Watts bath was used, having the composition: $NiSO_4 \cdot 6H_2O$, 120g/l; $NiCl_2 \cdot 6H_2O$, 35g/l şi H_3BO_3, 35g/l. We worked at different temperatures (40-60°C).

The experimental device used to realize nickel deposition is composed by a potentiostat-galvanostat VoltaLab 40 including VoltaMaster 4 software, a thermostated electrolyze cell with a thermostate Lauda 003, magnetic shaker and thermometer to control temperature. As reference electrode it was used calomel electrode and the contra-electrode was made by electrolytic nickel.

The work mode respected the next steps in the designing of the experiments. Primary the plates of copper were cut and the thickness was measured with micrometer. Then it followed a mechanical processing of the surfaces (like polish) with emery paper and with felt. The solutions were prepared following the recipe described as above mentioned (Merk reactive substances were used). The copper plates were degreased with chloride acid (5%, temperature 65°C), washed, dried and weighing.

Before proceeds to depose nickel there were drawn the polarization curves to establish the range of values for discharging of ions in solution. During the deposition there were recorded the values for current density.

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 elucidate yet.

Results and discussions

Nickel layers electrodeposited were analized at INCDFM Bucuresti-Magurele using scanning electron mycroscopy type Zeiss EVO 20. Figure 1 and 2 present a SEM image of a sample of nickel electrodeposited at -700 mV potential, working temperature 65°C. 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.

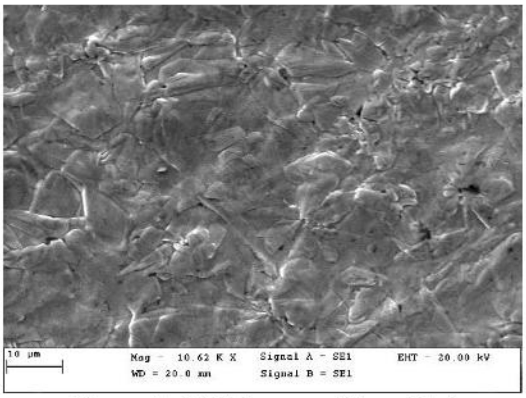

Figure 1. SEM images of the nickel electrodeposited layer from a Watts bath with addition of PVP at -700 mV potential, 65°C temperature, deposition time 10 minutes, with magnetic stirring of the electrolyte (10620X optic magnitude)

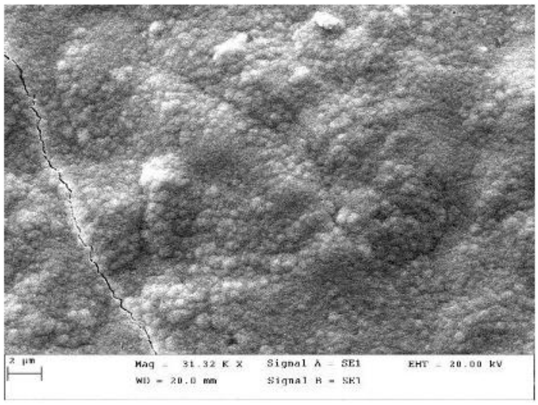

Figure 2. SEM images of the nickel electrodeposited layer from a Watts bath with addition of PVP at -700 mV potential, 65°C temperature, deposition time 10 minutes, with magnetic shaking of the electrolyte (31.320X optic magnitude)

Another type of investigations we've made there were SEM-EDX analyzes performed on Al.I. Cuza University – Iasi.
The investigation was performed by means of a SEM VEGA II LSH scanning electronic microscope manufactured by TESCAN for the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by ROENTEC Germany.

Table 1. Composition of a sample of nickel electrodeposited on copper substrate, from a Watts bath at -750 mV potential, 60°C, temperature, sodium lauryl-sulfate and saccharine agents added

Element	[norm. wt.-%]	[norm. at.-%]	Error in %
Nickel	72,98950	70,04394	1,95537
Copper	24,72697	21,91705	0,687472
Carbon	7,39E-09	3,47E-08	0,025
Oxygen	2,283528	8,039002	0,535272
	100	100	

The composition of the sample is presented in table 1, where it could be seen the presence of copper substrate, traces of carbon and of course, oxygen. The EDX pattern presented in figure 3.

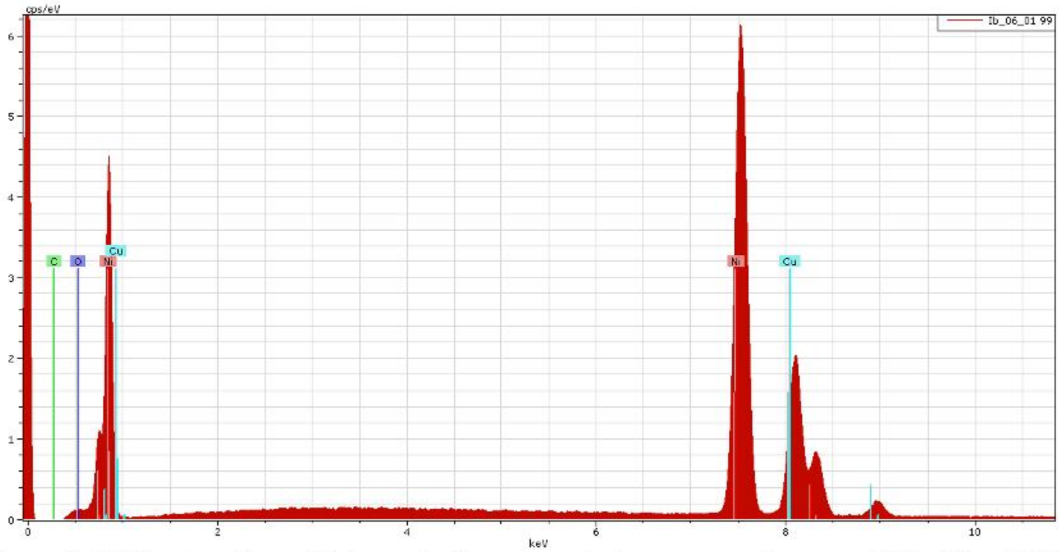

Figure 3. EDX pattern for a nickel sample electrodeposited on copper substrate at -750 mV and 60ºC

One set of measurements of the obtained samples are reflectance measurements. Brightness is a characteristic which depends by human eyes sensibility, so an objective physics parameter is reflectance. In order to measure this we used an Ocean Optics Spectrometer, doted with Spectra Suite soft, in Stefan cel Mare University, Suceava.

The reflectance is defined as a percent $(\%R_\lambda)$ relatively on the reflectance of a standard reference surface:

$$\%R_\lambda = \left(\frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda}\right) \times 100\% \quad (1)$$

where S_λ- intensity of sample at light length λ; D_λ- darkness intensity at light length λ; R_λ- reference intensity at light length λ. [2,3,5,6]

The first necessary step when it has to do reflectance measurements (generally for all types of measurements) is calibration of devices. In our case we used a mirror from spectrometer auxiliaries and we chose the value 100%.

In the next graphs there are considered samples of nickel electrodeposited on copper substrate, in the same conditions of potential and different temperatures (performed between 45°C and 65°C). As it could see, the reflectance for the lowest temperature is higher.

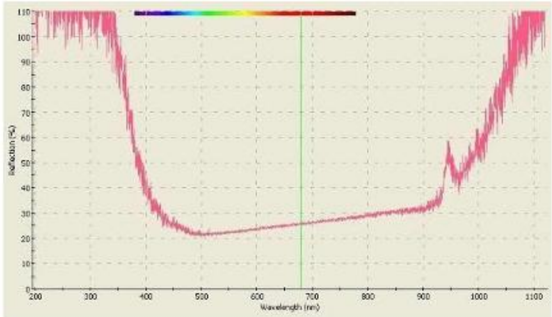

Figure 4. Graph chart recorded for a sample of nickel electrodeposited on copper substrate at -900 mV potential, temperature 45°C, time 2 minutes

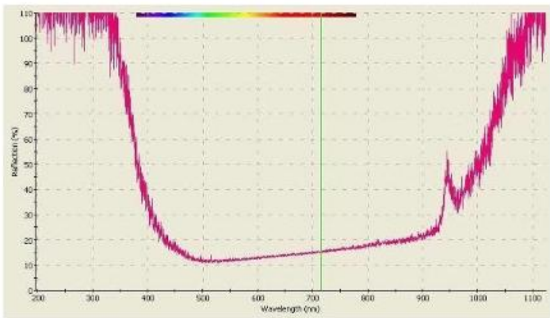

Figure 5. Graph chart recorded for a sample of nickel electrodeposited on copper substrate at -900 mV potential, temperature 55°C, time 2 minutes

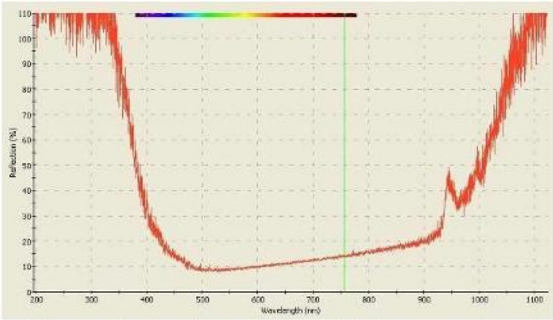

Figure 6. Graph chart recorded for a sample of nickel electrodeposited on copper substrate at -900 mV potential, temperature 65°C, time 2 minutes

For all samples of nickel electrodeposited on copper substrate at -900 mV potential and temperatures from 45°C to 65°C, we measured reflectance for all visible domains. Corresponding to wave length of 550 nm, we draw the next chart for dependence reflectance versus temperature:

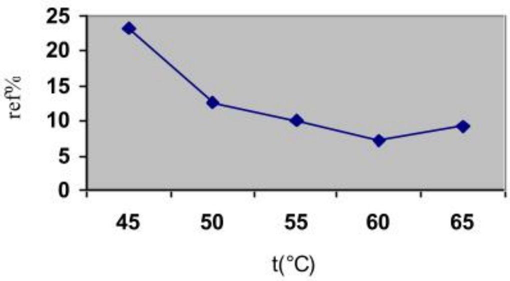

Figure 7. Reflectance vs. Temperature

Next measurements were performed for samples electrodeposited at 60ºC and different potentials (-700 mV, - 900 mV).

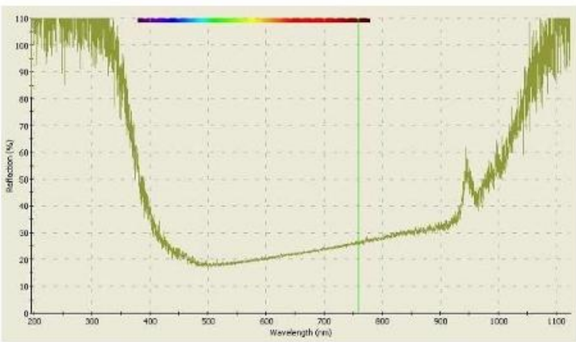

Figure 8. Graph chart recorded for a sample of nickel electrodeposited on copper substrate at -700 mV potential, temperature 60°C, time 2 minutes

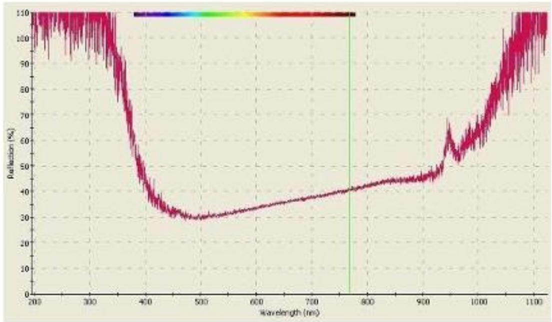

Figure 9. Graph chart recorded for a sample of nickel electrodeposited on copper substrate at -800 mV potential, temperature 60°C, time 2 minutes

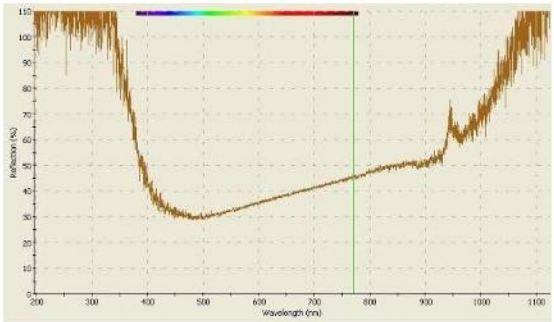

Figure 10. Graph chart recorded for a sample of nickel electrodeposited on copper substrate at -900 mV potential, temperature 60°C, time 2 minutes

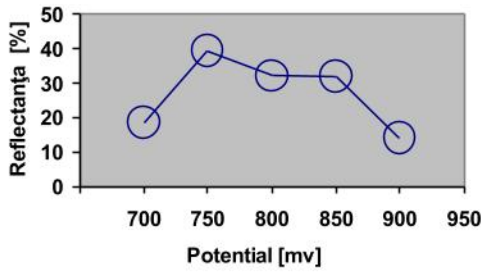

Figure 11. Reflectance vs. Potential

As it could be seen, the best reflectance was obtained at -750 mV electrodeposition potential.

These results are similar those obtained by other researchers and it is easy to see that the best reflectance (and brightness, of course) is obtained for the lowest temperature. For higher than 60°C temperatures the brightness increases again, but economic efficiency of the process is lowest, because it is necessary to spend heat for increasing the temperature of the electrochemical cell [14,15].

Conclusion

The electrodeposited Nickel layers are important in technique. To obtain the stoichiometric composition it has to follow carefully the values of the physical and chemical parameters.

The quality of the deposed could be controlled through the electrolyte concentration, discharge potential and the working temperature.

The analyses SEM-EDX and XRD confirm that the zinc-nickel alloys were formed. Also it is confirmed that the percents of those two metals in the deposed alloy depend of working conditions.

Conditions to obtain desired properties like hardness and brightness were established [16,17,18]

Acknowledgements

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References

1. Bajat, J.B., Maksimovic, M.D., Radovic, G.R., *Electrochemical deposition and characterization of zinc-nickel alloys deposited by direct and pulse current*, J. Serbian Chemical Society. 67 (8-9), 2002, p. 625-634

2. Bard, A., J., *Electrochemical Methods. Fundamentals and Applications,* John Wiley and Sons, New-York, 2001

3. Di Bari, G., *Electrodeposition of Nickel, Modern Electroplating, Fourth Edition,* John Wiley and Sons, Inc. New-York, 2000

4. Cui, C., Q., Lee, J., K., Electrochemistry Acta 40, p. 1653, 1996

5. Firoiu, C., Tehnologia proceselor electrochimice, Editura Didactică şi Pedagogică, Bucureşti, 1983

6. Grünwald, E., *Tehnologii moderne de galvanizare în industria electronică şi electrotehnică*, Editura Casa Cărţii de Ştiinţă, Cluj-Napoca, 1995

7. Grünwald, E., Mureşan, L., Vermeşan, G., Vermeşan, H., Culiuc, A., *Tratat de galvanotehnică,* Editura Casa Cărţii de Ştiinţă, Cluj- Napoca, 2005

8. Holm, M., O·Kofe, T., *Journal of Applied Electrochemistry,* 30, p. 1125-1132, 2000

9. Mohanty, U., S., Tripathy, B., C., Das, S., C., Mistra, V., N., *Metallurgical and Materials Transactions B,* Vol.36b, p. 737, 2005

10. Mitoşeriu, O., Iticescu, C., Cârâc, G., *Revista de Chimie, Bucureşti,* 55, nr.7, p. 525- 529, 2004

11. R. Valotkiene, K. Leinartas, D. Virbalyte, E. Juzeliunas, *Chemija (Vilnius),* 4, T12, p. 236, 2001

12. Paunovič, M., Schlesinger, M., and Weil, R., *Fundamental Considerations, Modern Electroplating, Fourth Edition,* John Wiley and Sons, Inc. New-York, 2000

13. Tripathy, B., C., Singh, P., Muir, D., M., Das, S., C., *Journal of Applied Electrochemistry,* 31: 301-305, 2001

14. Vasilache V., *Contribution about nickel electrodeposition from Watts bath with addition of Polyvinylpyrolidone*, Annals of the Suceava University - Food Engineering Year VIII, No.1, 2009, pg.15-19, Suceava

15. Vasilache, V., Gutt, Gh., Vasilache, T., *Electrochemical researches about influence of the additives of Watts's s solutions on throwing power and brightness*, Revista de Chimie, Bucureşti, 59, 2008

16. Vasilache, V., Gutt, S., Gutt G., Vasilache T, Filote C., Sandu I, *Studies of hardness for the electrodeposited nickel from Watts Baths with addition of polyvinyl pyrrolidone (PVP)*, Revue Roumaine de Chimie, 2009, 54(3), 245-248

17. Vasilache, V., *Contribuţii la optimizarea proceselor de depunere galvanică a nichelului şi a aliajelor de nichel folosite în construcţia de maşini*, Teza de doctorat, Suceava, 2008

18. Vasilache V., Gutt S., Gutt G., Vasilache T, Sandu I., Sandu G.I., *Ditermination of the Dimension of Cristalline Grains of Thin Layers of Zinc - Nickel Alloys Electrochemically Deposited,* Metalurgia International, vol.XIV(2009), no.3, p.49-53.