ADVANCED CHARACTERIZATION METHODS FOR NICKEL AND ZINC-NICKEL ALLOY LAYERS ELECTROCHEMICALLY DEPOSITED

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Received 12 August 2011, accepted 5 November 2011

Abstract. *Nickel and zinc-nickel alloys were electrochemically deposited. 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), the reflectance was studied by reflectance spectroscopy and the hardness with a Vickers indenter device. 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 ordinary coating the zinc remains the principal metal for industrial applications, especially for coverage of steel products. In the last two decades it was registered an important increasing of application of electrodeposited alloys due to the market demand for products with high quality coatings. On the first place there are the machine buildings industry and the aerospace industry, also those for electrical components and for fixing devices. Because of fact that consumption of heavy metals has to be reduced year by year, until the total elimination, there are searching for new technologies and one of the most promised of them is that of alloys electrochemical coatings with Zn-Ni, Zn-Co and Zn-Fe.*

Keywords: *Nickel, Zinc-Nickel alloys, SEM, EDX, and XRD techniques, reflectance, Vickers hardness*

1. 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 ordinary coating the zinc remains the principal metal for industrial applications, especially for coverage of steel products. In the last two decades it was registered an important increasing of application of electrodeposited alloys due to the market demand for products with high quality coatings. On the first place there are the machine buildings industry and the aerospace industry, also those for electrical components and for fixing devices.
Because of fact that consumption of heavy metals has to be reduced year by year, until the total elimination, there are searching for new technologies and one of
the most promised of them is that of alloys electrochemical coatings with Zn-Ni, Zn-Co and Zn-Fe.[1,2,3]
The greatest automobile companies are in a continuous course for prolonging the warranty period, so their products are better and better year by year. The majority of the European factories have been changed the specifications regard the

improvement of the performances of the electrodeposited layer.
Those new economic politics are based just on the using of alloys like Zn-Ni, Zn-Co and Zn-Fe [4,5,6,7].
Out of the machine building industry there are interesting in the using of electrodeposited alloys in the field of industry for defense. The State Department of USA is asking for eliminate during the follow years of the old technologies with new technologies based on the zinc-nickel alloys [11,12,13,16].

2. Experimental

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:

$$Ni^{2+} + 2e^- \rightarrow Ni, \quad (1)$$

but the proposed mechanism is by next type:

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

$$(NiOH)^+ + e^- \rightarrow (NiOH)_{ads} \quad (3)$$

$$(NiOH)_{ads} + (NiOH)^+ + 3e^- \rightarrow 2Ni + 2OH^- \quad (4)$$

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.
The anomalous co-deposition of thin films of zinc-nickel alloys was performed electrochemically. In the way to obtain the desired properties it was necessary to search the influence of electrodeposition conditions (co-deposition potential, the bath's composition, the temperature for deposition, mechanical stirring) through the structure, morphology, composition and optical properties, transport properties and magnetic properties of layers.
The next recipes were used to prepare the low acid electrolyte for electrodeposition of zinc-nickel alloys:
The first solution: zinc chloride 130g/l, nickel chloride 130g/l, potassium chloride 230g/l, pH 5-6, t(°C) 24-30°C;
The second solution: zinc chloride 130g/l, nickel chloride 65g/l, potassium chloride 230g/l, pH 5-6, t(°C) 24-30°C.
As working electrode it was used a glass plate with a deposed gold layer, made by sputtering method (a Hummer 6 installation was used). The pH was maintained at a level between 5 and 6 naturally without adding acids, because the salts used were chlorides which through electrolytic dissociation have acid character (excepting *KCl,* which comes from a strong acid and a strong base). The work temperature was between 24°C and

30°C. As reference electrode it was used the calomel electrode directly immersed in the electrolyze cell.

The chemical reactions which occur on the cathode follow two steps, as there were described by Matlosz. Zinc ions are deposited on their own substrate, on the gold substrate and on the nickel substrate. Also, nickel ions are deposited on their own substrate, on the used gold substrate and on the zinc substrate. In addition it has to take account the secondary reactions when ions Zn^{2+} combine with hydrogen to form ZnH^{+}, in the same way ions Ni^{+} combine with hydrogen to form NiH^{+}. These intermediate species, formed in the process of adsorption, will decompose finally to form metallic *Zn* and metallic *Ni* respectively.

The electrochemical reactions which occur could be written as follow:

$$Ni^{2+} + e^{-} \rightarrow Ni^{+}_{ads} \quad (5)$$

$$Ni^{+}_{ads} + e^{-} \rightarrow Ni \quad (6)$$

$$Ni + H^{+} + \rightarrow NiH^{+}_{ads} \quad (7)$$

$$NiH^{+}_{ads} + H^{+} + 2e^{-} \rightarrow Ni + H_2 \quad (8)$$

$$Zn^{2+} + e^{-} \rightarrow Zn^{+}_{ads} \quad (9)$$

$$Zn^{+} + e^{-} \rightarrow Zn \quad (10)$$

$$Zn + H^{+} \rightarrow ZnH^{+}_{ads} \quad (11)$$

$$ZnH^{+}_{ads} + H^{+} + 2e^{-} \rightarrow Zn + H_2 \quad (12)$$

Ni^{2+} and Zn^{2+} are dissolved as metallic ions, hydrolyzed or not. Ni^{+}_{ads} and Zn^{+}_{ads} which could or not to contain hydroxyl group are monovalent adsorbed in intermediate reactions. *Ni* and *Zn* are the metallic deposits of nickel and zinc respectively.

3. Results and Discussion

The nickel layers electrodeposited were analized at INCDFM Bucuresti-Magurele using scanning electron mycroscopy type Zeiss EVO 20. Figure 1 presents 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 [14,15].

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.

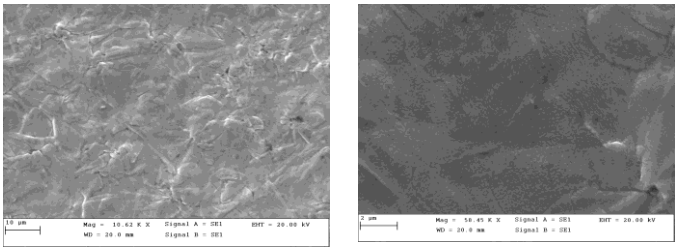

Figure 1. SEM images of the nickel electrodeposited layer from a Watts bath with addition of PVP at -700 mV potential, 65°C temperature, deposition time 10 minutes, with magnetic shaking of the electrolyte (SEM-Zeiss EVO 20 device)

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 suface:

$$\%R_\lambda = \frac{S_\lambda \text{x } D_\lambda}{R_\lambda \text{x } D_\lambda} \times 100\% \quad (13)$$

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. 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%. For the next example we considered two samples of nickel electrodeposited on copper

substrate, both in the same conditions, excepting temperature, one of them performed at 45°C and the other at 65°C. As it could see, the reflectance for the lowest temperature is higher.

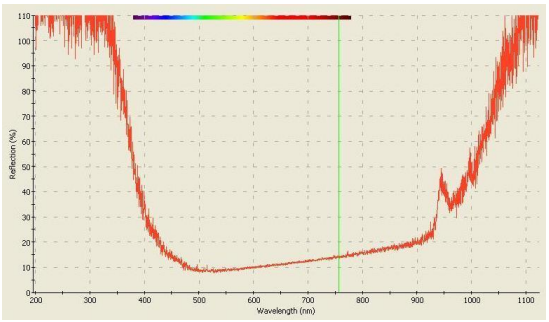

Figure 2. Graph chart recorded for a sample of nickel electrodeposited on copper substrate at -900 mV potential, temperature 65°C, time 2 minutes

For all samples of nickel electrodeposited on copper substrate at -900mV 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:

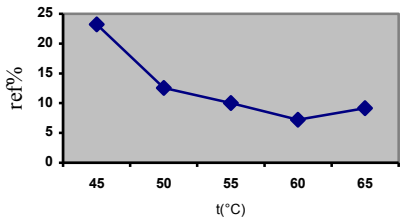

Figure 3. Reflectance vs. Temperature

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. 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 -750mV 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	

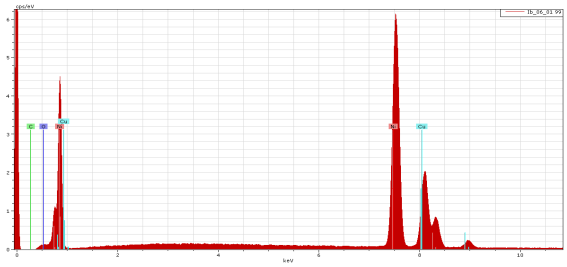

Figure 4. EDX pattern for a nickel sample electrodeposited on copper substrate at -750 mV and 60°C

Analyzing the X-ray diffraction specter of a zinc-nickel alloy electrodeposited on gold substrate, there were found the next elements (table 2)

The pick corresponding to (111) plane of nickel was found at an angle of $2\theta=44°36'$, and those corresponding to (111) plane of zinc at an angle of $2\theta=38°12'$. This analyze confirms too, the formation of zinc-nickel alloy. The deposited metals crystallize in cubic with centered faces. So, for nickel, the values for axes are (in Ångstrom) $a=3,52380$, $b=3,52380$ and $c=3,52380$ with all angles equals of 90°, and for zinc the dimensions are $a=b=c=2,4730$, with the same angles of 90°.

Table 2
Identified elements after X-ray diffraction analyze for a sample of zinc-nickel alloy electrodeposited at -1100 mV potential and 30°C temperature

Identified element	d_{hkl} (Å)	Crystalin plane
Zn	CFC-2,4730	(111)
Au	CFC-4,07860	(222)
KCl	CFC-6,29170	(222)
$Zn_5(OH)_8Cl_2 \cdot H_2O$	Rombic-6,3400;6,3400;23,6600	(111)
Ni	CFC-3,52380	(111)
Ni	CFC-3,52380	(220)
$(Ni(OH)_2)(NiOOH)$	Rombic-3,0710;3,0710;23,2000	(222)

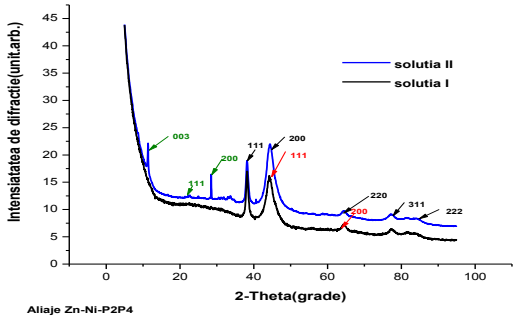

Figure 5. X-ray diffractogramme recorded for a Zn-Ni alloy co-deposited on gold substrate a) from solution I, b) form solution II

Another type of measurements was those of micro-hardness. The experiments were performed in Stefan cel Mare University – Suceava. For different conditions we found the next results for Vickers micro-hardness:

Table 3
Results of micro-hardness measurements for some samples of nickel electrodeposited on copper substrate

Sample	Deposition potential (mV)	Temperature (°C)	Force (N)	HV
26	700	60	0.050	62.1
27	750	60	0.050	71.2
28	800	60	0.050	76.6
29	850	60	0.050	78.6
30	900	60	0.050	68.7

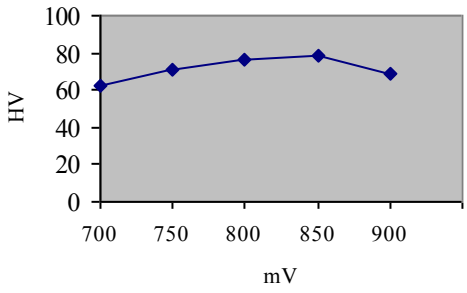

Figure 6. Micro-hardness vs. deposition potential

It was observed that micro-harness increases directly with deposition potential, but when it is surpassing a limit, will follow a decrease of the micro-hardness. This is again a result confirmed by other studies.

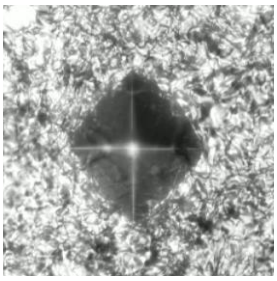

Figure 7. Photo of hardness indent for nickel deposited on copper substrate from a Watts bath with addition of PVP, at -1000 mV potential and 65°C temperature (Shimadzu HMV)

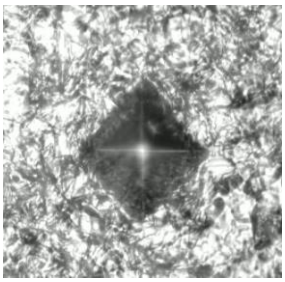

Figure 8. Photo of hardness indent for nickel deposited on copper substrate from a Watts bath with addition of PVP, at -900 mV potential and 65°C temperature (Shimadzu HMV)

4. Conclusion

The deposited Ni and Zn-Ni alloys 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.

5. Acknowledgment

This paper was supported by the project "Progress and development through post-doctoral research and innovation in engineering and applied sciences– PRiDE - Contract no. POSDRU/89/1.5/S/57083", project co-funded from European Social Fund through Sectorial Operational Program Human Resources 2007-2013.

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