



## STUDIES ABOUT ELECTROCHEMICAL PLATING WITH ZINC-NICKEL ALLOYS

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### ABSTRACT

*The electrochemical deposition of zinc and combinations with elements of the 8<sup>th</sup> group of the Periodic System (nickel, cobalt, iron) have good properties for anticorrosive protection, compare with pure zinc. For steel pieces, these films delay apparition and formation of white and red iron oxide. We used solutions with different concentrations of zinc chloride, nickel chloride and potassium chloride. For analyze the results we utilized the optic microscope and the X-ray diffraction.*

KEYWORDS: Zn-Ni alloy, electrochemical deposition, corrosion

### 1. Preliminaries

In ordinary coating the zinc remains the principal metal for industrial applications, especially for coverage of steel products. Between the last two decades there were be applied alloys for the necessities of cover up the 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.

In the European Union there are specially efforts and laws in the way to reduce the consumption of heavy metals like cadmium and mercury. Similar ways of action there are in the world community and organizations. The heavy metals are very toxic for human organism and for the animals, because they could produce hard diseases of the central nervous system. The heavy metals remain in earth and water for a very long period, so their effect it is dangerous after a great number of years.

In the domain of anticorrosion protection cadmium is much utilized together with zinc. 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, Zn-Fe. [8], [9].

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.

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 alloys.

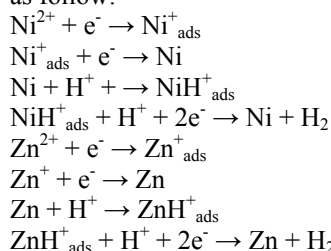
### 2. Electrochemical processes on cathode

In the experiments we deposed zinc-nickel alloys on a gold substrate which was first deposd on a glass lamella through the sputtering method. We have chosen this method to realize the analysis of the deposd layers using the X-ray diffraction (XRD).

The electrochemical reactions which are produced on cathode could be considered effectuated in two steps, as Matlosz [6],[7] describd them.

The zinc ions are deposd on their own substrate, on gold substrate used and on nickel substrate. Also, the nickel ions are deposd on their own substrate, on gold substrate and on the nickel substrate. In addition, we have to consider the secondary reactions, those where ions  $Zn^{2+}$  are combine with hydrogen to form  $ZnH^+$ , as well as ions  $Ni^{2+}$  will combine with hydrogen to form  $NiH^+$ . Those intermediary species, formed in the adsorption process, will decompose finally in metallic Zn, and metallic Ni respectively.

The electrochemical reactions could be written as follow:



Ni<sup>2+</sup> and Zn<sup>2+</sup> are dissolved as metallic ions, hydrolyzed or not. Ni<sub>ads</sub><sup>+</sup> and Zn<sub>ads</sub><sup>+</sup> which could or couldn't contain the hydroxyl group, are adsorbed univalent in intermediary reactions. Ni and Zn form the metallic layers of nickel and zinc respectively.

The kinetic of mass transfer is supposed respects the Butler-Volmer equation. In far away equilibrium conditions the anode reactions could be neglected. [2], [4].

### 3. The depositing of Zn-Ni alloys on a thin layer

#### 3.1. Experimental details

The depositing of thin films of Zn-Ni was realized electrochemically. We worked a INCDFM-Bucharest-Măgurele institute. For obtaining films with desired properties it was necessary to investigate the influence of depositing conditions (like depositing potential, the bath composition, the temperature during the depositing process, ultrasonic treatment and mechanic agitation) against structure, morphology, composition and optical, transport and magnetic properties of the layers. We tried to obtain priory uniform layers. To realize this target it was necessary to find the interval of potentials to deposit the stoichiometry composition of the alloy, searching to find the slowly as possible conditions.

We used the following compositions to prepare the electrolyte low acid for depositing of Zn-Ni alloys:

Solution I: zinc chloride 130g/l, nickel chloride 130 g/l, potassium chloride 230g/l, pH 5-6, t(°C) 24-30°C;

Solution II: zinc chloride 130g/l, nickel chloride 65 g/l, potassium chloride 230g/l, pH 5-6, t(°C) 24-30°C.

As working electrode we used a glass lamella having a gold thin layer deposited using sputtering method (using a Hummer 6 installation). The pH level was maintained between 5 and 6 naturally without adding acids, because the salts were chlorides which produce after electrolytic dissociation have acid character (excepting KCl, salt of a strong acid and a strong base). The working temperature was between 24°C and 30°C.

To realize a good adhesion it was used the next method. The glass lamella was first polished, then gold plated in sputtering installation. We made some proves with bright glass, but the result was negative because all the gold was dissolved in solution.

As reference electrode it was used the calomel electrode immersed directly in the electrolytic cell.

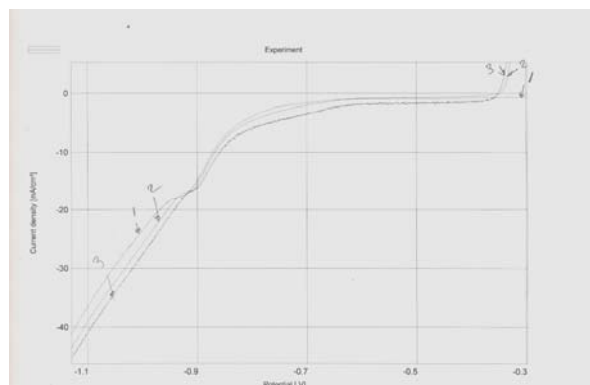
#### 3.2. Methods and technique used, instruments, equipments and software

The electroplated layer of Zn-Ni alloy was made using a potentiostat-galvanostat Voltalab and software Voltmaster.

The measurement of structural and morphological properties of the films was realized using the optical microscope of the INCDFM institute and the XRD installation of Mechanics Faculty, University Ștefan cel Mare-Suceava.

#### 3.3. Results and discussions regard the electroplating with Zn-Ni alloys

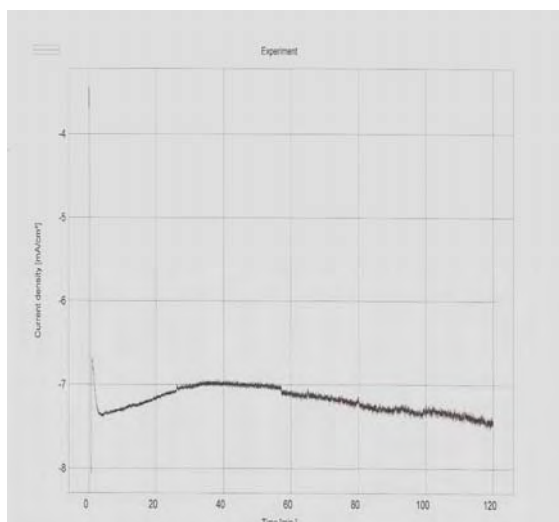
Figure 1 shows the polarization curves for electroplating with Zn-Ni alloys on Au substrate. At the beginning the current density grows insignificant with potential, due to the fact of electronic clouds around the electrodes and due to the thermal agitation which opposed to the ordinate movement of the ions in solution. Then is a passing portion followed by a linear portion when the current density grows with the potential. It is the time when the electrolytic cell is like an ohmic resistor, so the polarization curve shows clearly the constant ratio between potential and current density.



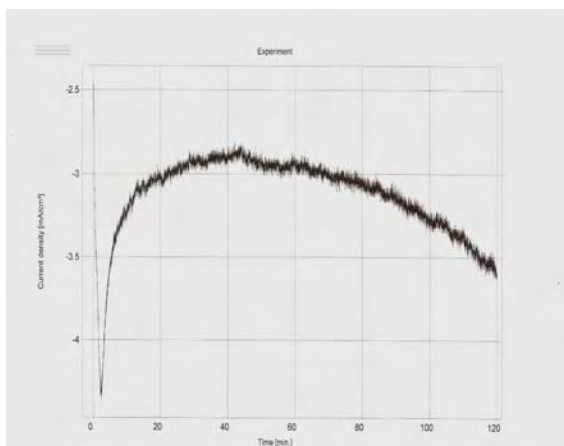
**Fig.1.** Polarization curves: 1- deposited on Au, 2- deposited on Zn-Ni alloy, 3- deposited on Zn-Ni alloy.

The figures 2 (a) and (b) shows the way of variation in time of current density in the case of those two solutions described above.

The decreased of the current density appears like a normal fact in electrochemical cover processes because in time the concentration of ions (and those of all components) in solution decrease and the number of charge transporters are smaller and smaller with time. There is also an initial period when the current density increase for a time. It is the period of advance of the electrochemical reactions, when the chaotic movement of the thermal agitation is progressively surpassed by the ordinate movement of the charge transporters in the electric field created by those two electrodes.



a) solution I

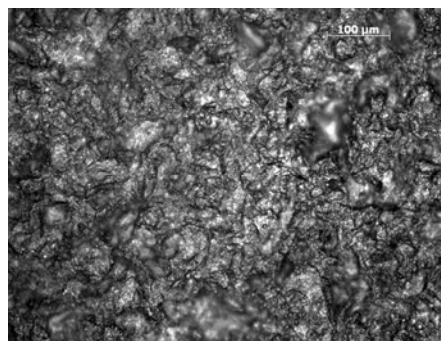


b) solution II

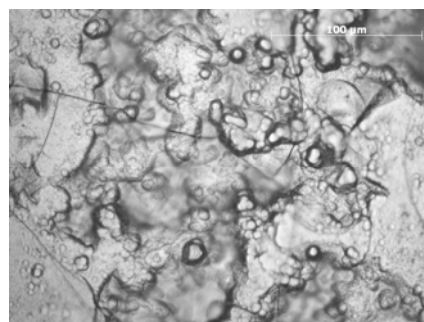
**Fig.2.** The current registered during the depositing of Zn-Ni alloy for 2 hours, at 30°C temperature.

The figures 3 and 4 represent photos of the surfaces covered with Zn-Ni alloys at 30°C temperature for two hours, but at different potentials. As it can see, in the first case (figure 3) the deposited has a better quality.

In figure 4 it could be observe micro-crashes in the deposited material. It was working at -1000mV potential. Micro-crashes could be explained through internal stress (mechanical) which appears and due to the fact that the increase of potential conduce to increasing also of the velocity of the ions in interaction with the cathode. Also the processes of dissolution of the electrode are much intense.



**Fig.3.** Microscopic photo of deposited Zn-Ni alloy at -850 mV, for 2 hours, at 30°C temperature.



**Fig.4.** Microscopic photo of deposited Zn-Ni alloy at -1000mV, for 2 hours, at 30°C temperature.

#### 4. The optimization of the process of electroplating with Zn-Ni alloy

On the way to optimize the process of electrochemical plating with Zn-Ni alloy, we shall use the results of the table and a method for optimization of Taguchi [1] type.

We shall take as factors which have to be controlled the next quantities:

- solution type: (1)solution I, (2) solution II
- discharge potential: (1) -850mV, (2) -900mV, (3) -1000mV, (4) -1100mV

The intensity of current will be measured and the efficiency of electroplating process will be calculated. We shall construct a matrix of the experiment, as it follows:



**Table 1.** The matrix of the experiment of electroplating with Zn-Ni alloy

No	Controlled factors		Measured values	
	Potential	Solution	Current	Efficiency
1	1	1	7	53
2	2	1	14	37.6
3	3	1	21	35.55
4	4	1	35	35.55 (**)
5	1	2	3	38.5
6	2	2	6	22.7
7	3	2	15	22.8
8	4	2	13	(**)
The average of the values				35.025

In the calculus of the average value of the efficiency we don't take in consideration the values with (\*\*) because these correspond with the cases when the alloy exfoliates. If it calculates the medium effect of every factor then it will obtain for the first solution:

$$(53+37.6+35.55)/3=42.05$$

and for the second solution:

$$(38.5+22.7+22.8)/3=28.$$

It could be observed that the first solution (those noted I) permit to obtain a greater efficiency compare to the second solution (those noted II).

Now we shall calculate the effect of the discharge potential and we shall find for the value of -850mV:

$$(53+38.5)/2=45.75.$$

For the value -900mV it will find immediately

$$(37.6+22.7)/2=30.15,$$

and for 1000mV we shall have

$$(35.55+22.8)=29.175.$$

As here it points to the problem of optimization in finding the better energy efficiency, and how it is seeing immediately that the efficiency decrease with the discharge of the potential, it is clearly that the most opportune value is that of -850mV, through the values chose for the experiment. As a matter of fact for this value it was obtain the better quality of the deposited.

Through those two solutions used for study, the solution I permitted to obtain the better efficiency and a good quality of deposited alloy.

### 5. The EDX analysis of deposited

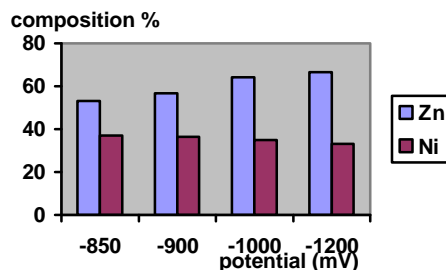
In the University Ștefan cel Mare Suceava we analyzed the probes of Zn-Ni alloys with the apparatus Ray-ny Shimadzu EDX 720 in the material characterization laboratory. It could be observe that the Zn-Ni alloy it is co deposited in all the cases. The percents of zinc and nickel differs function of solution which was used in electroplating process and function of discharge potential used.

The results of analysis were written in table 2 and 3 and then we represent the graph of the composition of the alloy function of potential in the case of those two solutions with composition described above.

Together with zinc and nickel the analysis EDX found other chemical elements, but in reduced percent, as K, Ca and Fe.

**Table 2.** The composition of Zn-Ni alloys function of potential (solution I)

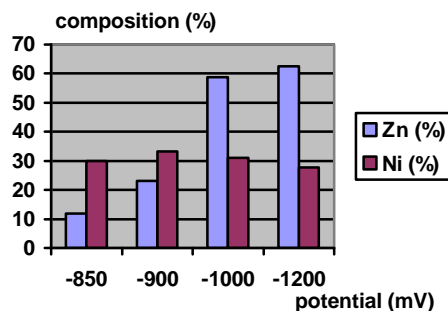
Potential (mV)	-850	-900	-1000	-1200
Zn (%)	53.206	56.717	64.321	66.423
Ni (%)	36.93	36.359	35.035	33.120



**Fig. 5.** The dependence of composition of Zn-Ni alloy co-deposited function of discharge potentials for the solution I; the deposited were effectuated at -850mV, -900mV, -1000mV and -1200mV

**Table 3.** The composition of Zn-Ni alloys function of potential (solution II)

Potential (mV)	-800	-900	-1000	-1200
Zn (%)	11.832	23.017	58.710	62.496
Ni (%)	29.949	33.338	31.127	27.818



**Fig. 6.** The dependence of composition of Zn-Ni alloy co-deposited function of discharge potentials for the solution II; the deposited were effectuated at -850mV, -900mV, -1000mV and -1200mV



As it could be seen in all analysis effectuated, the Zn-Ni alloys were formed in all deposited layers. The ratio for those two metals differs function of work conditions (discharge potentials). Of course these conditions could be chosen after the criteria of using the final product, sorting the parameters in the way to obtain the desired alloy in the desired percents. It will modify the concentration of the solution in the electrolytic bath also in function of the scope.

## 6. Conclusions

The deposited of Zn-Ni alloys are important in technique. Following Brenner [3] definition, the electroplating of the system of Zn-Ni alloys is an anomalous co-deposition. So the co-deposition is possible only in particular experimental conditions.

To obtain the stoichiometric composition it has to follow carefully the values of the physics-chemic parameters.

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

The surface for deposited also has to be finished with care because it is important.

The analyses XRD confirm that the zinc-nickel alloys were formed. Also it is confirmed that the

percents of those two metals in the deposited alloy depend of working conditions.

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