

Electrochemical Researches About Influence of the Additives of Watts's Solutions on Throwing Power and Brightness

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The influence of different substances on relevant technical parameters of an electrolyte for nickel electroplating was researched. A special attention was awarded to the throwing power (TP), and also to the visual aspect, current rate and the co-deposition of the other atoms. This was realized by interpretation of registered curves during electroplating process and using a second cathode to obtain results to calculate TP with Fields' relation.

Keywords: nickel electroplating, throwing power, brightness, polarization curves

The electroplating of nickel is an intensively used process. The applications include functional coatings for protection against corrosion, for increasing the wear hardness and for decorative coatings, as brightness nickel, often in combination with chromium.

Many processes of electroplating with nickel use classical baths compositions proposed by Watts. To obtain decorative coatings on a like-mirror surface, it was developed special additive recipes, 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, even the form of the surface is irregular, and then the necessity to use an electrolyte with a good throwing power [1, 2, 4].

The empiric investigations proved that TP increase in the same time with the cathode polarization and with the conductivity of the electrolyte. These two quantities were included by Wagner in the next relation:

$$k = \chi \left(\frac{dU}{di} \right) \quad (1)$$

Wagner parameter k , which is directly proportional with TP, increases in the same manner with increasing the conductivity of the electrolyte χ and with the slope of the polarization curve (dU/di) in the same conditions [3], [9].

In the industry of electrochemical coatings TP is followed by measuring the thickness of deposited layer on cathode or a couple of cathodes connected like a function of distance through anode. The Haring-Blum cells or the Hull cells are more used for this type of experiments. The TP percent can be calculate with Fields relation:

$$TP = \frac{L - M}{L + M - 2} \times 100 \quad (2)$$

where L is the ratio of the distances between cathodes and anode and M is the ratio of deposited masses. As usual a ratio 5:1 for cathodes is used [5, 6, 9].

Recently it was found that TP increases for Watts's electrolytes by adding sodium hyposulfite. Also sodium hyposulfite is used in electroless coating with nickel because it acts as a reducer agent for nickel ions. Then

there were effectuated investigations to examine the relation between the increasing of TP and the reducer proprieties of the nickel ions and for analyzing the individual contribution of the electroplating and the electroless processes [7, 8].

Near the hyposulfite effect, there were studied the influences of the reducer agents which contain sulphur-, boron-, phosphorus-, of some organic substances, from whom it is possible to choose candidates to use for increasing TP.

Other studies were performed to find the influence of the additives about the coating aspect, co-depositing of the foreign atoms and the current efficiency.

Experimental part

The electrodeposition of nickel was effectuated at INCDFM (National Institute for Research and Developments for the Physics of Materials) București-Măgurele, in the Electrochemistry Department. It was used a Watts bath with the next composition: $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 120 g·L⁻¹; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 35 g·L⁻¹ and H_3BO_3 , 35 g·L⁻¹.

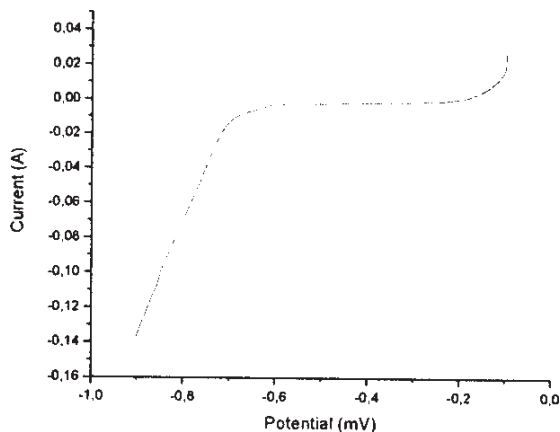
The experimental layout used to carry out the electrodeposition of nickel consisted of a potentiostat-galvanostat VoltaLab 40, with VoltaMaster 4 soft-ware, a thermostatic electrolysis cell, with a thermostat Lauda 003, a magnetic shaker and a thermometer for temperature controlling.

The value of pH was 4.5 ± 0.2 without additions. The electrolytes for brightness electroplating with nickel were obtained by adding next additives: sodium saccharine (for brightness), sodium lauryl sulfate (agent for wetting and tensional active) and gluconic acid. High purity water was used to prepare all solutions.

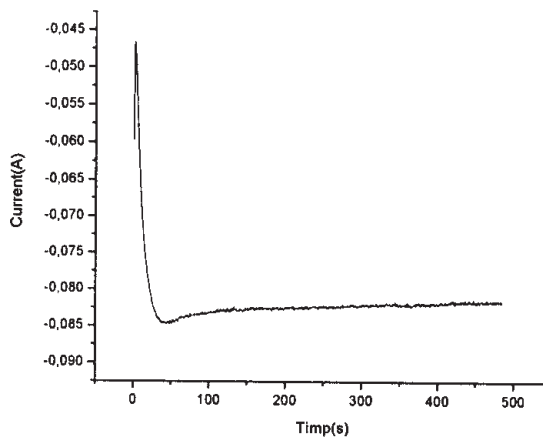
The polarization curves used to determine the Wagner parameter were measured using a thermostatic glass cell ($45-65^\circ\text{C} \pm 1^\circ\text{C}$). As working electrode it was used an electrolytic nickel electrode. A saturated calomel electrode (SCE) was used as reference electrode. All the potentials were shared after the reference electrode (SCE). The conductivity of electrolytes was measured at room temperature with a conductivity measuring apparatus.

For processing the graphs obtained from experimental recorded values it was used the software Origin 7.5, a special software used in complex interpretation of scientific data (graph charts, curves differential, surfaces integration etc.).

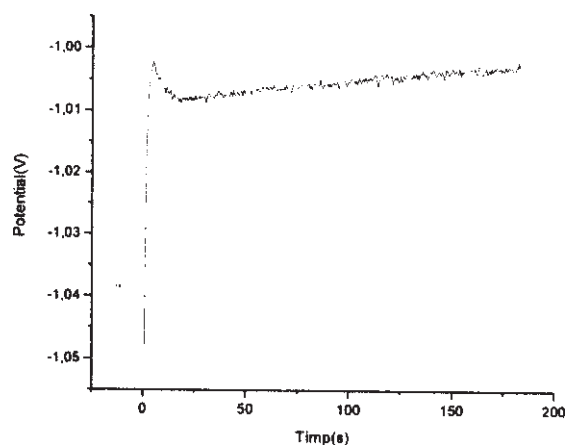
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The polarization curve for the Watts bath, for the potentials interval from -100 mV to -1200 mV and 60°C temperature



Chrono-ampere-chart recorded during nickel deposition for -900 mV potential, 60°C temperature with electrolyte shaking



Chrono-potential-chart recorded during nickel deposition for -300 mA current intensity, 60°C temperature, with electrolyte shaking



The photo corresponding for nickel electrodeposition process without additives in Watts' bath

Fig. 1. The recorded data for nickel electrodeposition without additives

Little copper plates (approx. 2 cm²) were cut and their thickness was measured with a micrometer. Their surface was mechanically processed with emery paper and felt. The solutions were prepared respecting the recipe described (chemical substances Merck were used). The little copper plates were washed with hydrogen chloride 5% la 65°C, with water, dried and weighed.

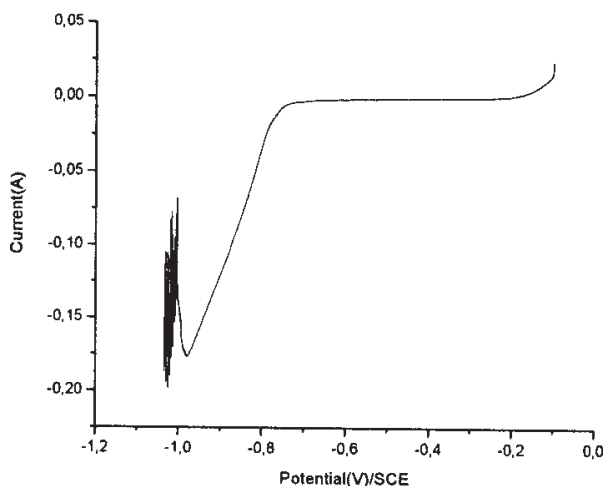
The mass of the nickel deposited were weighed before and after process. TP was calculated with equation 2.

On the way to study the visual aspect for a large interval of current densities and the medium efficiency in current, the nickel layers were deposited on a copper substrate. The electrolyte was magnetically shaken.

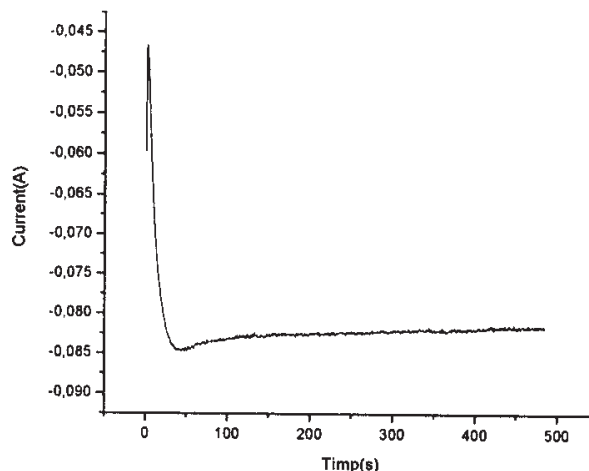
The investigations were performed with the optic microscope Zeiss DSM 982 Gemini.

Results and discussions

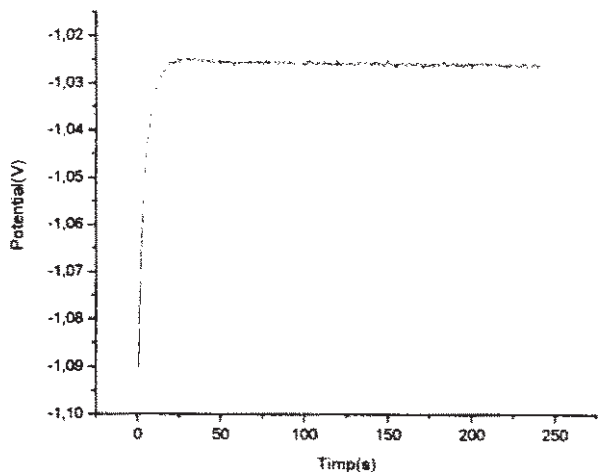
The polarization curves, the chrono-potential-charts and the chrono-ampere-charts are represented in figures 1-4.



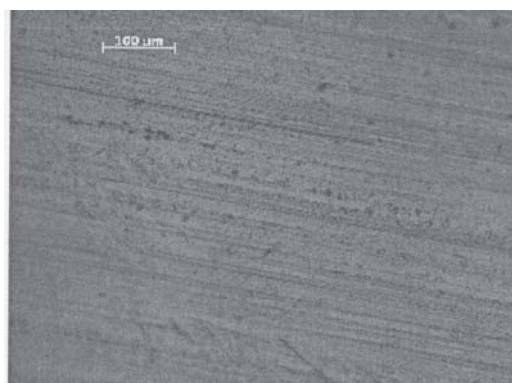
The polarization curve for the Watts bath with sodium saccharine, for the potentials interval from -100 mV to -1200 mV and 60°C temperature



Chrono-ampere-chart recorded during nickel deposition from Watts' bath with sodium saccharine, for -850 mV potential, 60°C temperature with electrolyte shaking

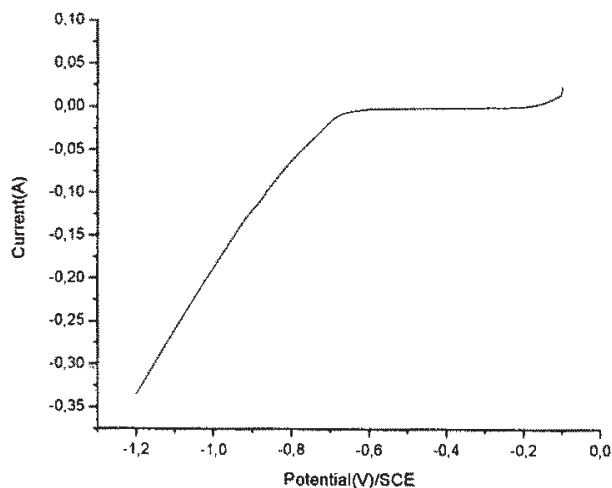


Chrono-potential-chart recorded during nickel deposition from Watts' bath with sodium saccharine, for -200 mA current intensity, 60°C temperature, with electrolyte shaking

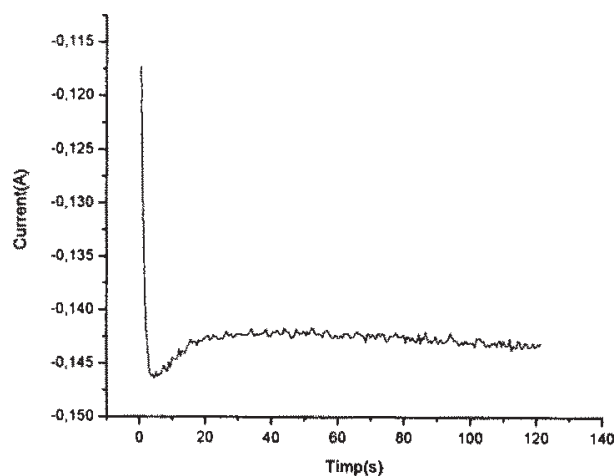


The photo corresponding for nickel electrodeposition process with sodium saccharine in Watts' bath

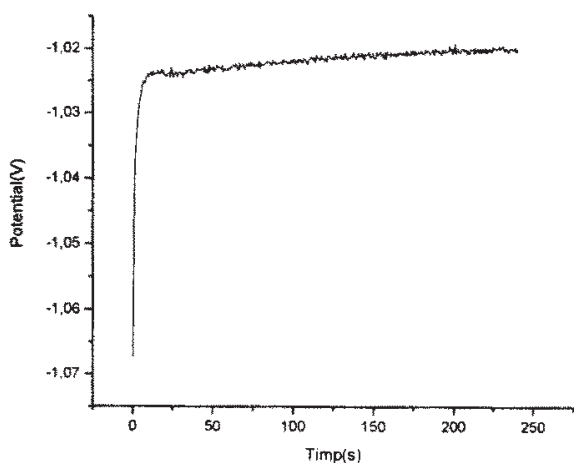
Fig. 2. The recorded data for nickel electrodepositing with adding of sodium saccharine



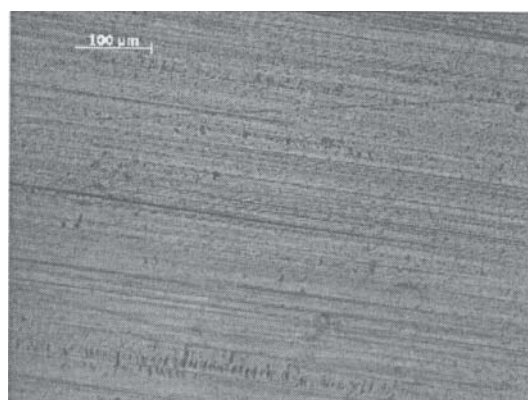
The polarization curve for the Watts bath with sodium lauryl sulfate, for the potentials interval from -100 mV to -1200 mV and 60°C temperature



Chrono-ampere-chart recorded during nickel deposition from Watts' bath with sodium lauryl sulfate, for -900 mV potential, 60°C temperature with electrolyte shaking

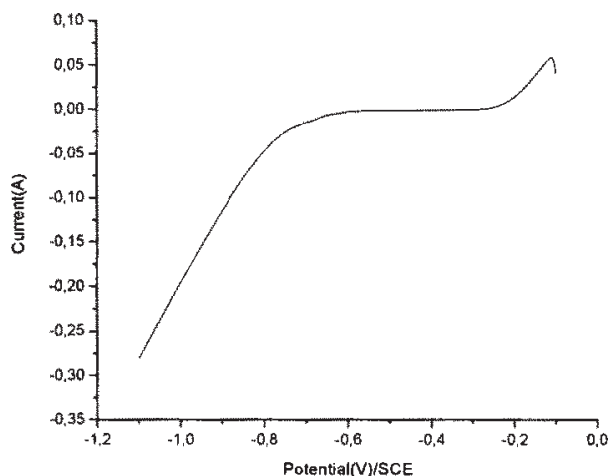


Chrono-potential-chart recorded during nickel deposition from Watts' bath with sodium lauryl sulfate, for -200 mA current intensity, 60°C temperature, with electrolyte shaking

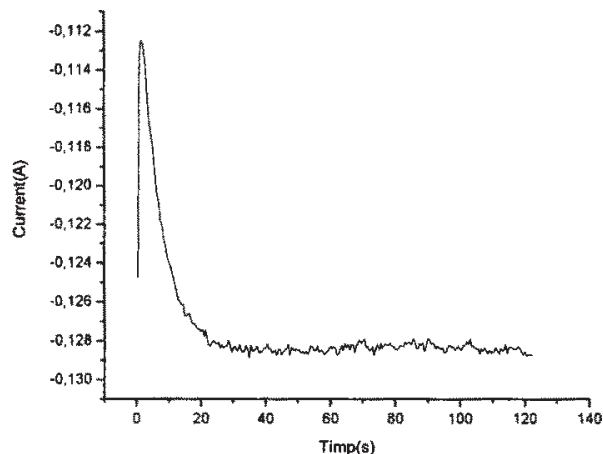


The photo corresponding for nickel electrodeposition process with sodium lauryl sulfate in Watts' bath

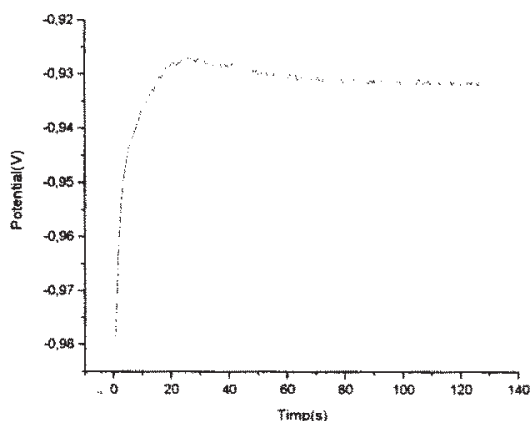
Fig. 3. The recorded data for nickel electrodepositing with adding of sodium lauryl sulfate



The polarization curve for the Watts bath with sodium saccharine and sodium lauryl sulfate, for the potentials interval from -100 mV to -1200 mV and 60°C temperature



Chrono-ampere-chart recorded during nickel depositing from Watts' bath with sodium saccharine and sodium lauryl sulfate, for -900 mV potential, 60°C temperature with electrolyte shaking



Chrono-potential-chart recorded during nickel deposition from Watts' bath with sodium saccharine and sodium lauryl sulfate, for -150 mA current intensity, 60°C temperature, with electrolyte shaking



The photo corresponding for nickel electrodeposition process with sodium saccharine and sodium lauryl sulfate in Watts' bath

Fig. 4. The recorded data for nickel electrodeposition with adding of sodium saccharine and sodium lauryl sulfate

Throwing power and the visual aspect

For those 4 samples we calculated from the polarization curves the ratio dU/di and found the next values were found:

Condition for electrodeposition	the slope dU/di (Ω/dm^2)
electrodeposition without additives	1666.66
electrodeposition with sodium saccharine	677.966
electrodeposition with sodium lauryl sulfate	1777.77
electrodeposition with sodium lauryl sulfate and sodium saccharine	1142.85

Table1
MEASURED VALUES OF THE MASSES OF CATHODES AND THE CALCULATED TP

samples	1. without additives		2. with sodium saccharine		3. with sodium lauryl sulfate		4. with sodium saccharine and sodium lauryl sulfate	
	initially	finally	initially	finally	initially	finally	initially	finally
$m_{cath1}(g)$	2,1681	2,1892	1,1578	1,1670	1,0899	1,1044	1,1717	1,1811
$m_{cath2}(g)$	2,1782	2,2259	1,1311	1,1819	1,0743	1,1096	1,1992	1,2285
TP	44,23%		18,08%		47,12%		30,71%	

These useful values to determine Wagner parameter are in Ω/dm^2 because we have determined and recorded the current density. With the help of electrolyte conductivity it is possible to calculate the Wagner parameter (1). From the slopes dU/di can be seen that by adding sodium lauryl sulfate a greater TP is obtained, and in the case of adding sodium saccharine the TP is smallest. This fact is close to the brightness effects visually determined with the optical microscope.

We've determine then the values of TP with Fields' relation (2), but it has to mention that we used an electronic balance with 4 decimals. So the results occurred greater errors compare with the case of using an electrochemical balance.

Conclusions

As it can be observed a good correlation between calculated values with Fields' formula and those close to Wagner parameter was obtained. For the deposit with sodium saccharine it was obtained the best brightness qualitative appreciated, visually, but also with the optic microscope. The lowest value for TP was obtained for the solution with sodium saccharine, too. This expected fact confirms the mechanism of action for a brightness agent, which functions like an inhibitor for the crystals growing. Also it's a knowing fact that from solutions deposited at

lowest temperatures can be obtained a better brightness compared with solutions deposited at highest temperature.

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