STUDY ON THE INFLUENCE OF CURRENT DENSITY AND TEMPERATURE ABOUT ELECTRODEPOSITIONS OF NICKEL BY ELECTROLYTES OF TYPE WATTS

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Abstract: *The influence of current density and temperature on nickel electrodepositions on copper substrate from a Watts bath has been studied. Cathodic current efficiency decreases to increase current density and increases at the rise of electrolyte temperature. Thickness deposit is a decisive parameter because the determinations of the layer thickness may establish if the deposition corresponds to the destination of the application deposition or not; and the measurements were made by non-destructive physical methods. The properties of nickel deposits, brightness and hardness, are influenced by current density and temperature. The surface morphology of nickel deposit was analyzed by electronic scanning microscopy (SEM). The results showed that the structure of nickel deposits is influenced by current density and temperature. The increasing current density contribute to the fine crystallized deposits, but deposits obtained at a higher current density have the dendritic structures, while increasing temperature determines the change in the structure of deposits from fine to coarse.*

Keywords*:* *nickel electrodeposition, current density, temperature, properties, Watts bath*

Introduction

The nickel electrodeposition has known an increased interest in recent years, although it has been studied since the early 20th century, and is now a surface treatment of the most frequently used. Promoting the appearance, the life extension, and the improvement of materials performance and products in different environments, electroplating is one of the few surface-finishing processes that can satisfy the requirements of decorative and functional applications [Or'06].

Properties and structures of nickel layers are in close correlation with parameters of electroplating [Li'01], such as: electrolyte composition, pH, current and potential of depositions, temperature, mode of electrolyte agitation, time, etc.. The significant differences in the structure and the properties of nickel electrodepositions may be produced by modifications in electroplating's parameters.

Normally, a percentage of the total current is used to hydrogen evolution reaction, which is an undesirable reaction during the nickel galvanization because the nickel electroplating is not achieved with a current efficiency of 100% [Ho'87], [Ho'86], [Do'69], [Fl'84], [Ho'79], [Pu'96] and because the hydrogen is included in the nickel deposit, increasing the internal stress and the production of porous deposits.

This paper presents the influence of current density and temperature on cathodic and anodic current efficiency, quality surface and morphology of nickel deposit in electrolyte solutions of Watts bath type.

Experimental details

Apparatus and materials

Nickel electrodeposition was carried out in a rectangular cell of 13.9 cm x 12.5 cm x 10 cm made from Plexiglas, which corresponds to a volume of 1.75 l. The cathode [made by 99.98% purity copper, having the following dimensions (h x L x l): 8.0 cm x 9.8 cm x 0.1 cm] and the anode [made by 99.7% purity nickel, having the following dimensions (h x L x l): 10.0 cm x 4.0 cm x 0.3 cm] which fitted cell electrolysis was fixed so that it shows the following surfaces immersed in electrolyte: 0.6 dm^2 and respectively 0.25 dm^2.

The cathode surface was prepared in advance for each electrodeposition experiment, according to the literature procedure [On'80].

Reagents

The nickel electrolyte of Watts bath type [Ba'00], with composition shown in Table 1 was prepared from pure technical reagents (nickel sulphate, nickel chloride and boric acid) (INDUSTRIALCHIM, Bucharest). The diluted solution of sodium hydroxide (NaOH) was used to adjust the pH electrolyte at value of 4.00. All solutions were prepared with bi-distillated water.

Table 1. The chemical composition of Watts electrolytic bath for nickel electroplating

Chemical composition	Quantity (g/L)
Nickel chloride, $NiCl_2 \cdot 6H_2O$	40.5
Nickel sulphate $NiSO_4 \cdot 6H_2O$	292.5
Boric acid, H_3BO_3	31.5

Electrolysis

For each experiment were used 2400 coulomb of electricity by applying current from a regulated power supplier (0 - 18 V, 0 - 10 A, d.c. power supply GWINSTEK GPR-1810HD). A thermostatic water bath (Lauda E100) was used for maintaining invariable the electrolyte temperature. After electrolysis, the cathode and anode were removed from the cells and thoroughly washed with water and dried. The cathodic and respectively anodic current efficiency were calculated from the weight gained by the electrodes following electrolysis.

Deposit examination

The average thickness of metallic layer, [μm], was calculated taking into consideration 7 local values of cathode thickness after electrodeposition, as against the standard comparison thickness. The measurements of the above mentioned thickness were carried out using a PosiTector 6000 - DeFesko Analyzer, based on non-destructive physical method.

The brightness of metallic cover, [%], was carried out using the HR 4000 CG-UV-NIR, Ocean Optics Inc., Dunedin, FL, a miniature spectrometer, based on reflection property of the electrodeposed metallic layer. A tungsten halogen light source (UV-VIS-NIR Light Source DH-2000, Mikropack) was used for this study. The light from Light Source DH-2000 was conveyed to the sample through an optical fibre (QP400-0.25-SR/BX, Ocean Optics Inc., Dunedin, FL) and an array of 7 optical fibres (QR400-7-SR-BX, Ocean Optics Inc., Dunedin, FL).

The hardness of metallic cover, [HV], was carried out using a Shimadzu, HMV – 2T, micro-hardness analyzer, having the loading weight F = 490,3 mN (HV -0,05) and load duration of 15 s respectively.

The deposit surface morphology was examined by scanning electronic microscopy (SEM) using a Tescan microscope and a composition microanalysis was performed with Bruker probe adapted at an electron microscope.

Results and discussion

Stability of nickel plating bath

Figure 1 shows a typical spectrum of reagents in the electrolyte composition of the nickelating and the electrolyte-type nickel Watts baths in wavelength range from 300 to 1100 nm. It may be noted that the absorption spectrum of solutions of nickel: 2 - nickel chloride (40.5 g/l $NiCl_2 \cdot 6H_2O$), 3 - nickel sulfate (292.5 g/l $NiSO_4 \cdot 6H_2O$), 4 - mixture (40.5 g/l $NiCl_2 \cdot 6H_2O$, 292.5 g/l $NiSO_4 \cdot 6H_2O$) and 5 - Watts bath (40.5 g/l $NiCl_2 \cdot 6H_2O$, 292.5 g/l $NiSO_4 \cdot 6H_2O$, 31.5 g/l H_3BO_3) shows the presence of four peaks at 400 nm, 656.17 nm, 719.97 nm and 1005.06 nm and absorption spectrum of the solution: 1 - boric acid (31.5 g/l H_3BO_3) show no absorption maximum. These results confirm the absorption spectrum of the aquo - ligand complex $\left[Ni(H_2O)_6\right]^{2+}$ [Su'75], which is characterized by large bands of low intensity, typical transitions of d - d transitions. The similar spectra were obtained in the absence and presence of different concentrations in the boric acid. It can be inferred from these results that nickel is complexed by water and not by boric acid. The species predominant, in the solution mixed with high concentrations of nickel, are the aquo – cations: $\left[Ni(H_2O)_6\right]^{2+}$, $\left[Ni(H_2O)_6\right]^{2+}Cl^-$ and $\left[Ni(H_2O)_6\right]^{2+}SO_4^{2-}$, and the complexes of nickel chloride and sulphate should not occur according to the nickel speciation diagram in aqueous solutions [Ji'96], i.e. for pH range of 0–5.5 of chloride and sulphate salts solutions, the predominant species is the aquo - complex $[Ni(H_2O)_6]^{2+}$. By registering minute by minute throughout the deposition process, the absorption spectra for Watts bath was observed that the shape of spectra did not change. It may be inferred that the predominant species, $\left[Ni(H_2O)_6\right]^{2+}$ aquo - cations, by the nickel plating bath is stable during and after deposition.

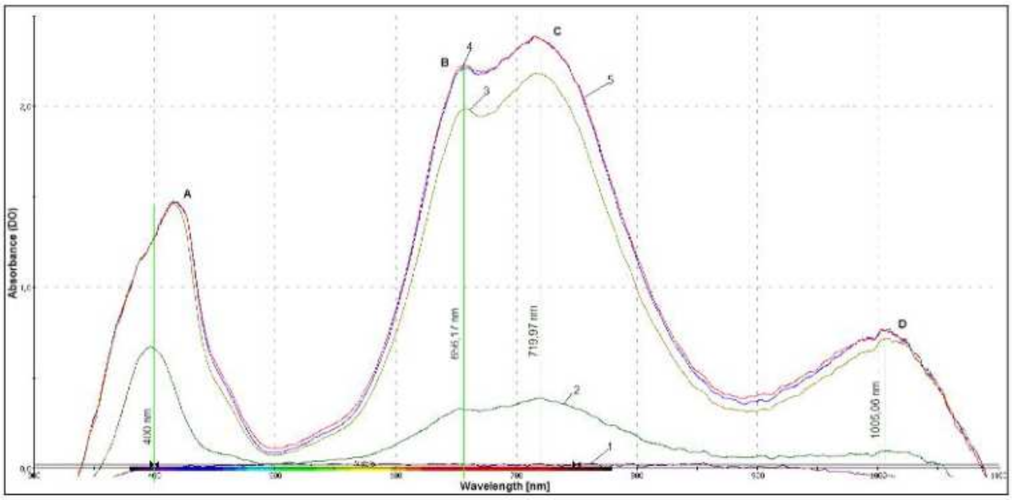


Figure. 1. Overlapping spectra of UV - VIS - NIR range for the following solutions:
1) 31.5 g/l H_3BO_3, 2) 40.5 g/l $NiCl_2 \cdot 6H_2O$, 3) 292.5 g/l $NiSO_4 \cdot 6H_2O$, 4) mixture (40.5 g/l $NiCl_2 \cdot 6H_2O$, 292, 5 g/l $NiSO_4 \cdot 6H_2O$), 5) Watts bath (40.5 g/l $NiCl_2 \cdot 6H_2O$, 292.5 g/l $NiSO_4 \cdot 6H_2O$, 31.5 g/l H_3BO_3)

Cathodic and anodic current efficiency

The influence of current density and temperature on cathodic and anodic current efficiency for the nickel deposit and the dissolution of nickel respectively are shown in Figure 2.

The data indicate that the cathodic current efficiency depends greatly on current density. The increased current density leads to a decrease in cathodic current efficiency for deposition of nickel from electrolytes with pH = 4 and the concentration of nickel ions $c_{Ni^{2+}}$ = 75.3205 g/l. This effect is due to increasing concentration polarization, but at the same time due to increase specific reaction discharging hydrogen [Fi'83], [Sc'**].

The increasing temperature from 15 to 45 °C the cathodic current efficiency increases, meaning that the minimization of the concentration polarization is aided by increasing bath temperature, which favors the nickel deposit.

Nickel anode becomes passive and the efficiency of anode dissolution is near zero, when the reactions of discharge hydroxyl ions, (OH^-), and the oxygen evolution are preferable to the dissolution process of nickel, i.e. when the solution pH is too high and / or the chloride ion concentration too low [Ba'00]. The anodic current efficiency for dissolution of nickel in the practical conditions of electroplating (c_{Cl^-} = 12.0972 g/l, pH = 4) is always 100% . This means that the anodic current efficiency is not affected by increasing current density and temperature of electrolyte bath.

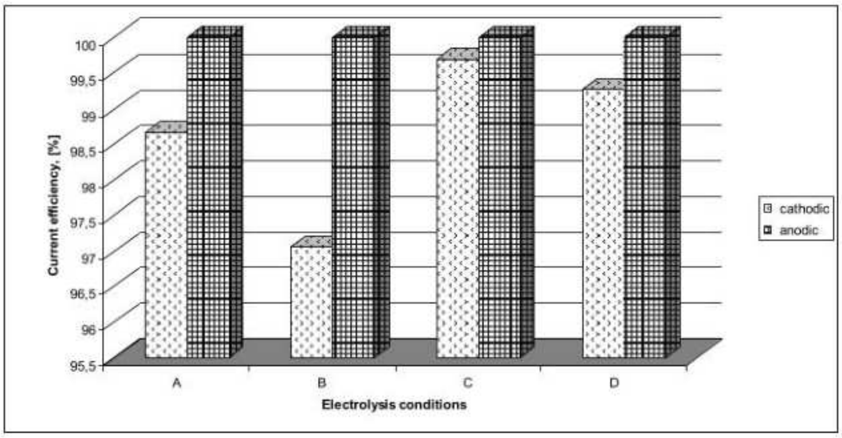


Figure 2. Cathodic and anodic current efficiency for nickel deposit on copper substrate in the following electrolysis conditions: A) 1.666 A/dm^2, 15 °C, B) 5A/dm^2, 15 °C, C) 1.666 A/dm^2, 45 °C, D) 5 A/dm^2, 45 °C

The thickness of nickel electrodeposits

The thickness deposited is a crucial parameter for evaluating the quality of an electrodeposition in order to ensure the resistance of galvanic coatings in different environments and climates; the determinations of thickness may determine whether the deposit corresponds the destination application or not [Ba'00a], [Ro'02].

According to the electrodeposed nickel layer thickness values represented in Figure 3, the low current densities lead to thick deposits of nickel. Nickel bath temperature increase leads to a decrease in the thickness of the deposited layer (Figure 3).

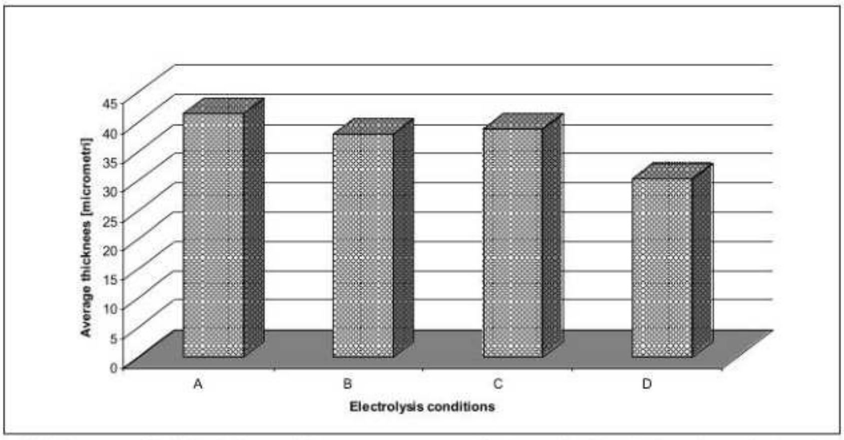


Figure. 3. The thickness of nickel deposition on copper substrate in the following electrolysis conditions: A) 1.666 A/dm^2, 15 °C, B) 5A/dm^2, 15 °C, C) 1.666 A/dm^2, 45 °C, D) 5 A/dm^2, 45 °C

The brightness of the nickel coat

The degree of brightness depends on the reflecting properties of deposits and it defines the quality of decorative galvanic coatings. The reflection was done as a relative percent ($\%R_\lambda$) from the reflection of standard reference substance STAN-SSH (STAN-SSH High-reflectivity Specular Reflectance Standard, Ocean Optics Inc.), according to the equation (1):

$$\%R_\lambda = \frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda} \cdot 100\% \qquad (1)$$

Where: S_λ - the intensity of sample at λ wavelength, D_λ - the black intensity of sample at λ wavelength, R_λ - the intensity of standard reference substance at λ wavelength.

The reflections measurements were carried out at the wavelengths, where the visual sensibility is maximum: 420 nm (blue), 534 nm (green) and 564 nm (red) [17], taking into consideration 3 points from the electrode surface. The brightness value of metallic cover corresponding to the graphic representation is the average of these 9 reflection values.

According to the data represented in Figure 4, the highest value of reflecting property for the deposit obtained by electrolysis conditions (1.666 A/dm^2, 15 °C) was obtained; and the lowest value (matt nickel) has a deposit obtained under the conditions of electrolysis D.

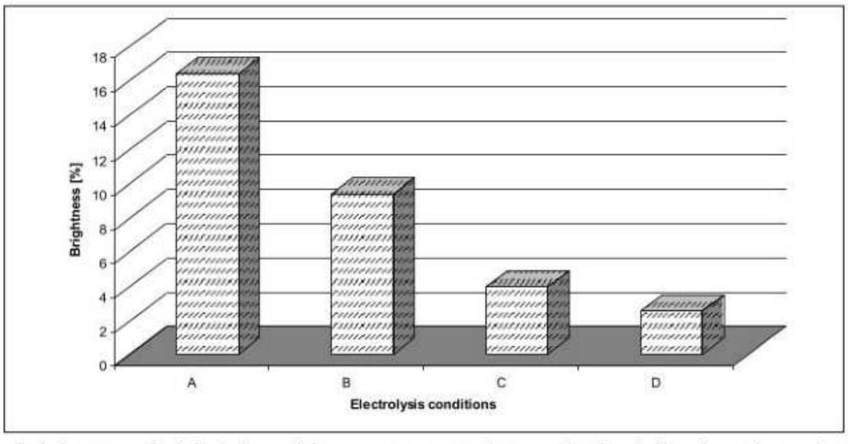


Figure 4. The brightness of nickel deposition on copper substrate in the following electrolysis conditions: A) 1.666 A/dm^2, 15 °C, B) 5A/dm^2, 15 °C, C) 1.666 A/dm^2, 45 °C, D) 5 A/dm^2, 45 °C

Hardness of nickel electrodepositions

The current density, temperature and electrolyte composition greatly influences the hardness. The change in hardness as a function of current density is passing through a maximum of a curve; the increase in the electrolyte temperature it usually causes decreased in hardness, this behavior is closely related to the influence that the temperature exerts on the structure [Fi'83].

A deposit of matte nickel obtained from a Watts bath has a hardness of about 200-250 HV and a bright nickel layer deposited from a bath containing brightness agents has a higher hardness from HV 500-600 [Sa'74].

As seen in Figure 5 the hardness of the deposit obtained under A electrolysis conditions were more than 250 HV, with the highest value. This high value can be explained on the basis of layer thickness, which in these conditions of electrolysis presents the greatest thickness of deposit. It should be noted that the deposit obtained under conditions of electrolysis D has a higher hardness value at a smaller thickness than that obtained under the conditions of electrolysis B and that has a greater thickness.

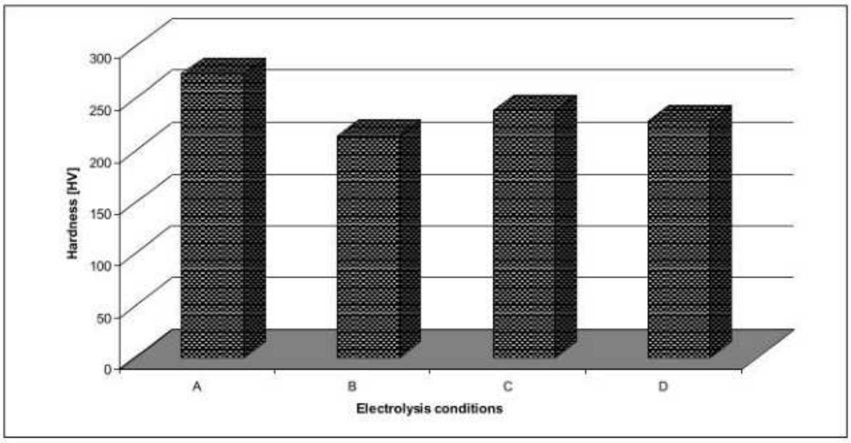
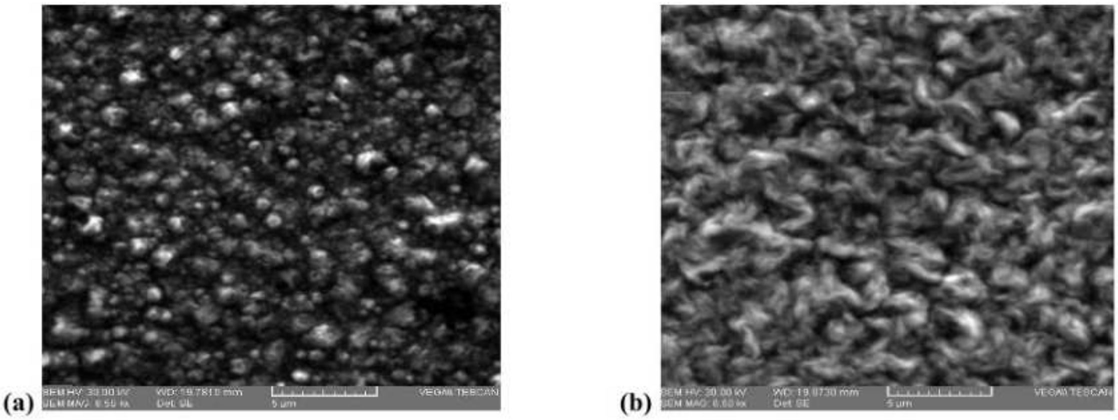


Figure 5. The hardness of nickel deposition on copper substrate in the following electrolysis conditions: A) 1.666 A/dm², 15 °C, B) 5A/dm², 15 °C, C) 1.666 A/dm², 45 °C, D) 5 A/dm², 45 °C

Morphology of surface

The studied nickel deposits are deposits in the form of compact layer, continuous, smooth and adherent to the substrate. Figure 6 (a, b, c and d) presents the surface morphology of nickel deposits obtained by scanning electron microscopy.



(a) **(b)**

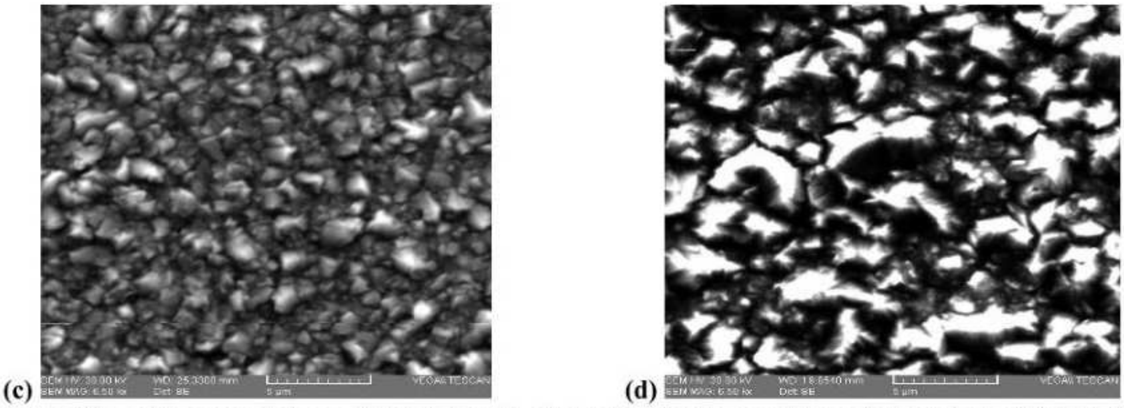


Figure 6. The surface morphology of nickel deposit obtained under the conditions of electrolysis: **(a)** A) 1,666 A/dm^2, 15 ºC; **(b)** B) 5 A/dm^2, 15 ºC; **(c)** C) 1,666 A/dm^2, 45 ºC; **(d)** D) 5 A/dm^2, 45 ºC

Increasing current density contributes, usually, to obtain fine crystallized deposits through the cathodic polarization growth. However, the current density cannot be increased over a certain value without any negative influence on the quality of deposits. At too high current densities due to the considerable decrease in the concentration of metal ions in the solution layer near the cathode, the deposits obtained were of dendritic appearance [Fi'83]. Thus, for the same temperature at current density of 1.666 A/dm^2 fine crystallized deposits were obtained (Figure 6a and Figure 6c), while deposits have a dendritic appearance at the current density of 5 A/dm^2 (Figure 6b and Figure 6d).

A comparison of figures 6a to 6c and figures 6b to 6d is observed that the structure of deposits becomes coarse with increasing temperature. This action is explained by decreasing the concentration polarization and the electrochemical polarization.

Composition microanalysis of nickel deposits

Figure 10 and Figure 11 show that the composition microanalysis of nickel deposits has been achieved with the Bruker probe adapted at electron microscope. For all the conditions of electrolysis, the results of microanalysis determinations showed that deposits of nickel were made on copper substrate. Figure 11 shows the distribution of compact continuous nickel deposited on the copper substrate surface.

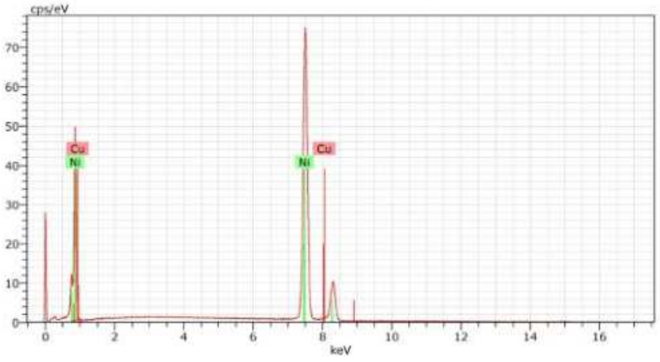


Fig. 10. Microanalysis composition of nickel deposits

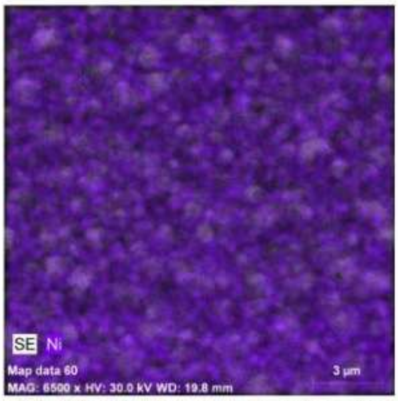


Fig. 11. Distribution of nickel deposited on copper substrate surface under conditions of electrolysis A) 1,666 A/dm^2, 15 ºC

Conclusions

The cathodic current efficiency decreases when the current density increases and increases when rising electrolyte temperature.

The properties of nickel deposits, the brightness and hardness, are influenced by current density and temperature.

The surface morphology of nickel deposit was analyzed by scanning electronic microscopy (SEM). The results showed that the structure of nickel deposits is dependent on the effect of electrodeposition variables, such as: the current density and temperature. The increasing current density contributes to obtain the fine crystallized deposits, but in too high current density deposits they have a dendritic appearance, while the increasing temperature results in a coarse structure of deposits.

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