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INFLUENCE OF pH GALVANIC BATHS ON THE NICKEL DEPOSITS

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ABSTRACT

The influence of pH on cathodic and anodic current efficiency, surface quality and morphology of nickel deposit in the electrolyte solutions of the Watts bath type was investigated. Cathodic current efficiency of nickel deposit is maximum for electrolytic bath whose pH value is about 4 and decreases for an electrolytic bath with a higher pH. The deposited thickness is a significant parameter because the thickness determining may establish if the deposition corresponds to the destination 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 the pH of the bath electrolyte. The surface morphology of nickel deposit was analyzed by scanning electronic microscopy (SEM). The results showed that the structure of nickel deposits is influenced by pH of the bath. The pH increasing causes structural changes on the deposits in fine to coarse, while the electrodeposited nickel at pH 6.21 has a compact morphology with many cracks.

KEYWORDS: nickel electrodeposition, Watts bath, pH, qualitative and quantitative parameters

1. Introduction

Galvanic deposition of nickel improves a range of surface properties and size characteristics of metal or alloy support such as: corrosion and wear resistance, mechanical strength, magnetic permeability, appearance and other properties [1].

Deposits Properties and quantitative aspects of galvanic process is influenced by technological parameters such as: current density, temperature, pH, cathode or solution agitation for application, deposition time, s.a. [2].

The paper presents the effect of bath pH over the cathodic and anodic current efficiency, quality surface and morphology of nickel deposit in electrolyte solutions from bath Watts type.

2. Experimental details

2.1. Apparatus and materials

Nickel electrodeposition was carried out in a rectangular cell of size 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 cathode surface immersed in the electrolyte must be 0.6 dm^2, and the anode 0.25 dm^2, thus resulting a rate of cathode-anode rate by 2.4.

The cathode surface was prepared in advance for each electrodeposition experiment, according to the literature procedure [3].

2.2. Reagents

The nickel electrolyte of Watts bath type [4], with composition shown in Table 1 was prepared from following reagents (nickel sulphate, nickel chloride and boric acid) (INDUSTRIALCHIM, Bucharest). All solutions were prepared with bidistilate water. To adjust the pH of the electrolyte to the following study values (3.78, 5.00, 6.21) a solution of sodium hydroxide (NaOH) 0.1 N was used.

2.3. Electrolysis

All the electrodeposition experiments were carried out at a current density of 3.333 A dm^{-2} by applying current from a from a regulated power supplier (0 - 18 V, 0 - 10 A, d.c. power supply

GWINSTEK GPR-1810HD), for 20 minutes at a temperature of 30°C. A thermostatic water bath (Lauda E100) was used for maintaining invariable of electrolyte temperature. The pH of the electrolytes, before starting each experiment with a digital pH meter (Cole Parmer) was measured. After electrolysis, the cathode and anode were removed from the cells and thoroughly washed with water and dried. The cathodic and anodic respectively current efficiency were calculated from mass differences of the probes, before and after deposition ($\eta = {}^{m_p}\!/\!_{m_t}$). Where m_p is the obtained mass of the practical deposit and m_t is the theoretical mass of the deposit, what is determined by Faraday's law.

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 sulfate, $NiSO_4 \cdot 6H_2O$	292.5
Boric acid, H_3BO_3	31.5

2.4. 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.

3. Results and discussion

The hydrogen ions concentration (pH) in the electrolyte has an important role over the metal ions deposit and formation of deposits; and it is closely related to the position, in the potential series, of the metal which is deposited [3].

The more negative the standard electrode potential, the more difficult it is to deposit the indicated metal. Reactions that have a more negative standard electrode potential than hydrogen $\left(2H^+ + 2e^- \rightarrow H_2\right)$ deposit with evolution of hydrogen as a side reaction. Electrodeposition of most of the non-noble metals such as Ni, Fe, Co and Zn are accompanied by hydrogen evolution and often their electrodepositions not achieved with a current efficiency of 100%. Normally a percentage of total current is used to evolution hydrogen [5], [6], [7].

Typical reactions which may take place during the deposition of metals having a negative standard electrode potential are as follows:

$M^{+n} + ne^- \Leftrightarrow M$ Metal deposition (1)

$2H^+ + 2e^- \Leftrightarrow H_2$ Hydrogen evolution (2)

$2H_2O + 2e^- \Leftrightarrow H_2 + 2OH^-$ Water decomposition (3)

$xM^{+n} + yH_2O \Leftrightarrow M_x\left(OH\right)_y^{(xn-y)+} + yH^+$

Hydrolysis of metal ion (4)

$xM_x\left(OH\right)_y^{(xn-y)+} + \left(xn-y\right)H_2O \Leftrightarrow xM\left(OH\right)_n + \left(xn-y\right)H^+$

Precipitation of hydroxide (5)

Electrochemical reactions (2) and (3) tend to consume H$^+$ or generate OH$^-$. Hence, when they take place at the cathode, the pH of the cathode will increase. Reactions (4) and (5) tend to produce H$^+$ and will counteract the pH rise at the cathode produced by reactions (2) and (3). When the pH near the surface becomes such that hydrolysis and precipitation reactions occur, any further pH rise will be slowed by reactions (4) and (5). If the hydrolysis reaction (4) is not able to slow the pH rise, the deposit may contain hydroxide inclusions because of reaction (5).

3.1. Cathodic and anodic current efficiency

In Figure 1 the cathodic and anodic current efficiency at different pH values of nickel plating baths are shown. It is clearly observed that the cathodic current efficiency of nickel deposit is maximum for electrolytic bath whose pH value is 3.78 and for electrolytic bath pH of 5 and 6.21 it decreases.

The anodic current efficiency of nickel dissolution in electrolytic bath presenting chloride ion concentration, c_{Cl^-} = 12.0972 g/l, is 100% at pH 3.78. The anodic current efficiency of nickel dissolution at higher pH (5.00; 6.21) and at the same concentration of chloride ions, c_{Cl^-} = 12.0972 g/l decreases.

This finding means that the reactions of discharge hydroxyl ions, (OH^-), and the oxygen evolution are preferable to the dissolution process of nickel, when the solution pH is too high and / or the chloride ion concentration too [4]. Nickel anode becomes passive and the efficiency of dissolution of the anode decreases to reach near zero.

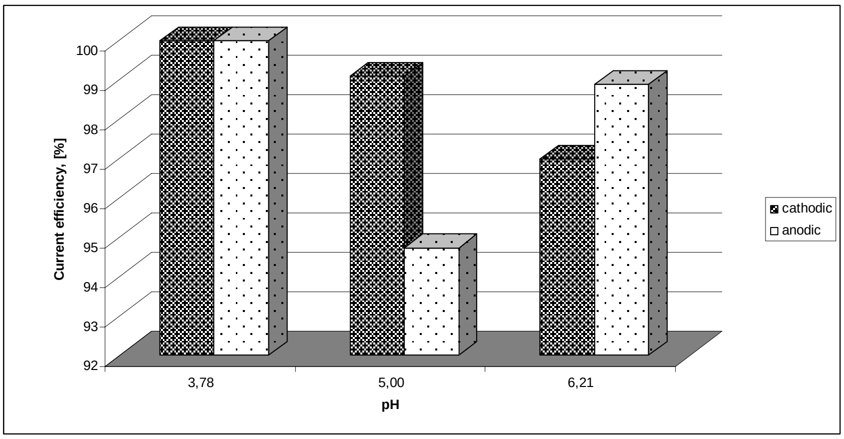


Fig. 1. *Influence of pH over cathodic and anodic current efficiency for nickel deposit on copper substrate*

3.2. Thickness of nickel electrodeposited

The measurement of the thickness of layers may determine whether the submission meets the destination application submission or not, since thickness deposit is a crucial parameter for assessing the quality of electrodeposition in order to ensure resistance galvanic coatings in different environments and climates [8], [9]. According to the values represented in Figure 2, the thickness of nickel electrodeposited in galvanic baths at pH 3.78 and 5.00 respectively are comparable.

The largest thickness was obtained for nickel plating bath pH of 6.21; but it should be noted that this layer is pulverous, brittle, with low adhesion to the substrate.

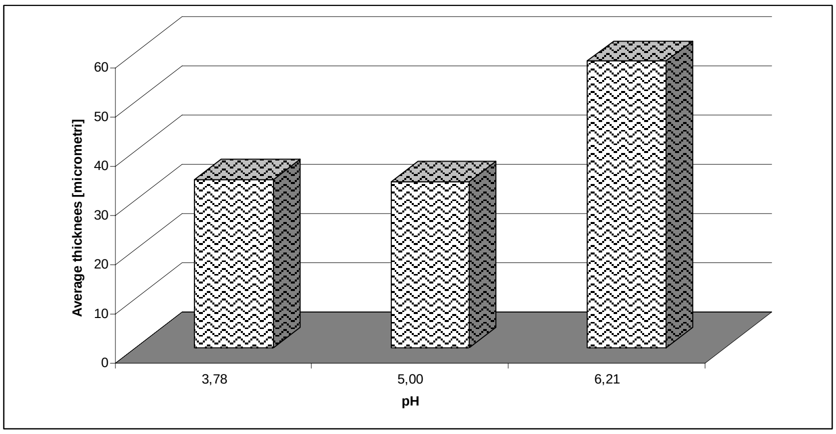


Fig. 2. *The pH influence over thickness of nickel deposit on copper substrate*

3.3. The brightness nickel coatings

The reflecting properties of the deposit is determines the degree of brightness, which defines quality decorative 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 (6):

$$\%R_\lambda = \frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda} \cdot 100\% \tag{6}$$

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) [10], 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 (Figure 3).

The highest value of reflecting property of the nickel deposit was obtained at bath pH 3.78; and the lowest (matt deposition) have a deposit obtained from bath pH 5.00. Nickel deposit in electrolyte with pH of 6.21 was a higher brightness than the deposit from bath pH of 5.00, but because the nickel deposit obtained from electrolyte with pH 6.21 is pulverous with many cracks (Figure 5), we can say that the value of the reflecting property contributes and brightness substrate.

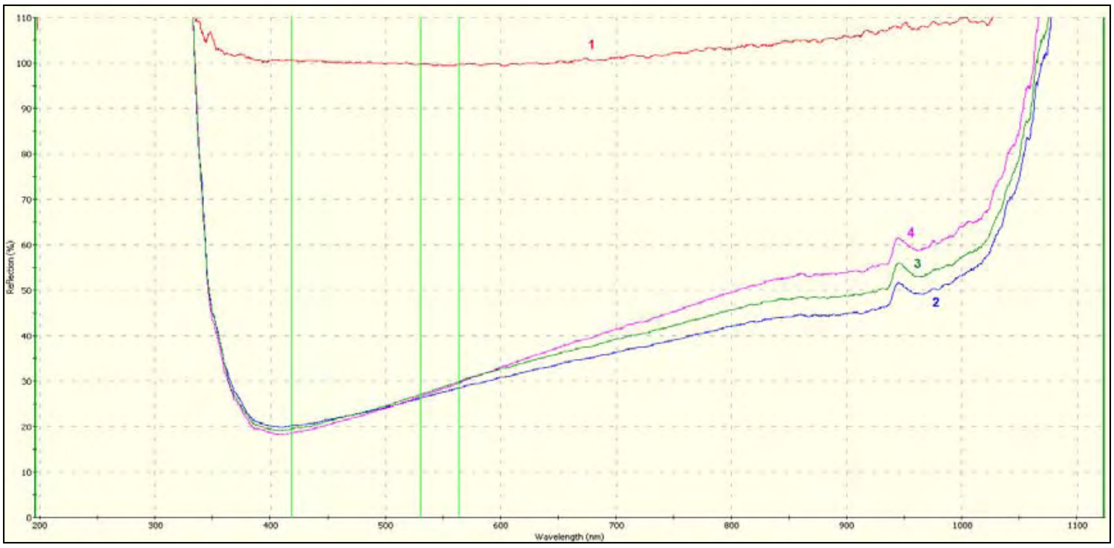


Fig. 3. *The reflection as function of wavelengths for: 1 - standard reference substance STAN-SSH, 2, 3, 4 - nickel deposit from pH 3.78 on copper substrate in 3 points of the electrode surface*

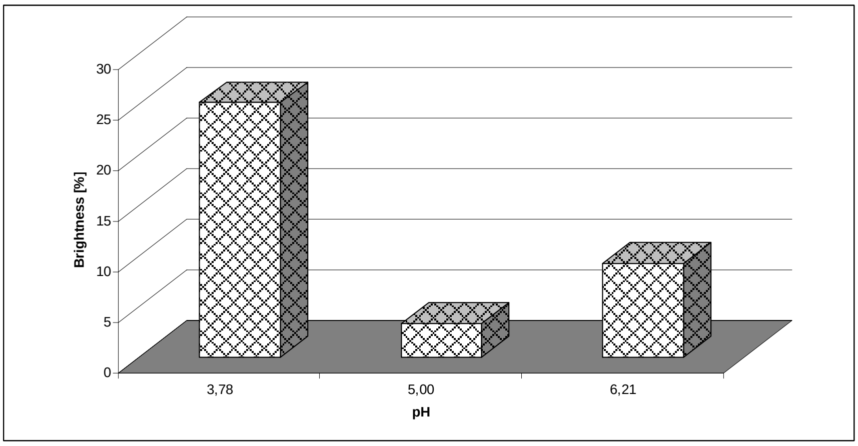


Fig. 4. *The pH influence over brightness of nickel deposit on copper substrate*

3.4. Electrodepositions hardness of nickel

The study results on the effect of electrolytes pH over the hardness of nickel deposits from Watts type bath is presented in Figure 4. the hardness obtained for layers deposited in an electrolytic baths pH of 3.78 and 5.00 respectively are comparable; while the layer of nickel electrodeposited in bath pH of 6.21 has a hardness around 500 HV [11], [12]. The nickel coating is about twice as hard, and this high hardness, were assigned according to some authors, the formation of basic compounds in the cathode film [3] or by others, increases the amount of hydrogen included in the deposit [13].

Indentation hardness in electrodeposited Ni films obtained from electrolyte with pH 6.21 is shown in Figure 5, and also can be observed many cracks in the layer.

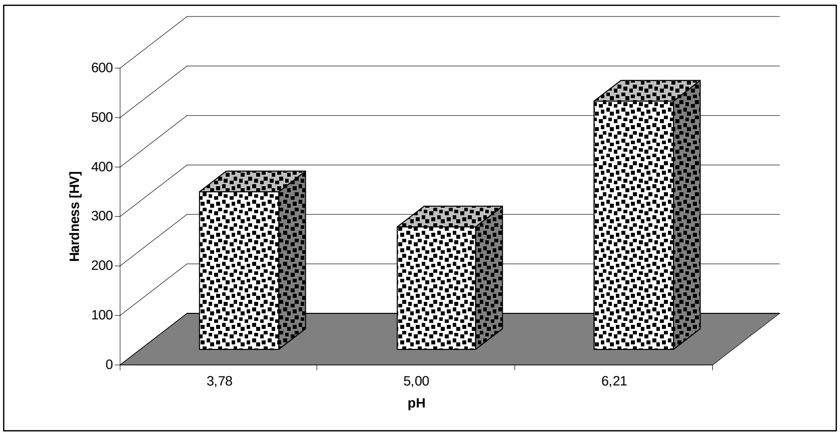


Fig. 4. *The pH influence over hardness of nickel deposit on copper substrate*

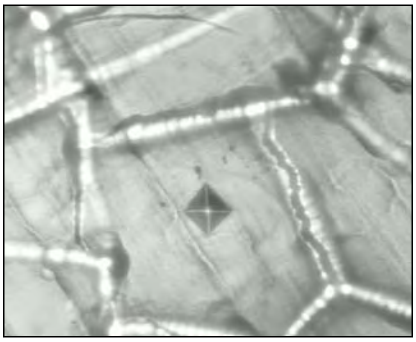


Fig. 5. *Indentation hardness in electrodeposited Ni films on Cu substrate at*
$i = 3.333$ (A/dm^2), $T = 30$ ºC and $pH = 6.21$

3.5. Surface morphology

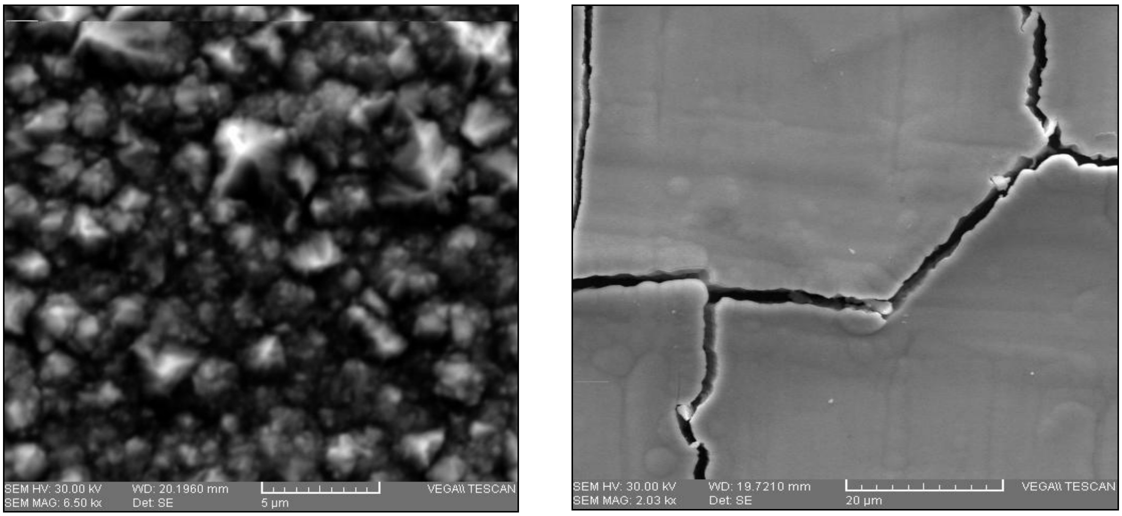
The deposits obtained from electrolyte baths whit pH of 3.78 and 5.00 respectively are adherent to the substrate, smooth, compact and coherent at examination with the naked eye; while nickel layer electrodeposition in bath pH of 6.21 is not compact, it has numerous cracks and gently exfoliating. In Figure 6a are present the morphology surface of nickel deposits obtained by scanning electron microscopy. The surface morphology of the deposit showed a smooth surface like the accumulation of fine spherical deposits (Figure 6 a) in case a bath pH value of 3.78. If can be seen, the entire surface of the deposit, growing crystals surrounded by smaller crystals uniformly distributed [14]. The deposit obtained at pH 6.21 has a compact morphology with many cracks (Figure 6 b).

4. Conclusions

1. The cathodic current efficiency is maximum for electrolytic bath whose pH value is about 4 and decreases for an electrolytic bath with a higher pH.

2. Properties of nickel deposits, brightness and hardness are influenced by the pH of the bath electrolyte.

3. Surface morphology of nickel deposit was analyzed by scanning electronic microscopy (SEM). Results showed that the structure of nickel deposits is dependent on bath pH. The increasing pH causes deposits structural changes from fine to coarse; while nickel electrodeposited at pH 6.21 has a compact morphology with many cracks.



a) b)

Fig. 6. *Surface morphology of nickel deposit obtained from electrolytic baths with pH: a) 3,78; b) 6.21*

References

[1]. Oriňáková R, Turoňová A., Kladeková D., Gálová M., Smith R. M. - *Recent developments in the electrodeposition of nickel and some nickel-based alloys,* Journal of Applied Electrochemistry, (2006) **36**:957–972

[2]. Marinescu A., Andonianţ Gh., Bay E. - *Tehnologii electrochimice şi chimice de protecţie a materialelor metalice,* Editura Tehnică, Bucureşti, 1984;

[3]. Oniciu, L., Grűnwald, E. - *Galvanotehnica*, Editura Ştiinţifică şi Enciclopedică, Bucureşti, 1980

[4]. di Bari G. - *Modern Electroplating*, Fourth Edition, Edited by Mordechay Schlesinger and Milan Paunovic © 2000 John Wiley & Sons. Inc, New York, 2000

[5]. Deligianni H., L. Romankiw T. - I*n situ surface pH measurement during electrolysis using a rotating pH electrode, IBM* J. Res. Develop., 37, 2, 1993

[6]. Ji J., Cooper W.C., Dreisinger D.B., Peters E. - *Surface pH measurements during nickel electrodeposition*. Journal of Applied Electrochemistry (1995), **25** (7), 642–650.

[7]. Vasilache V., M Poroch – Seriţan M., Gutt Gh. - *Contributions on elaboration of a material balance, an energetic balance and an optimization way for nickel cover process*, Conferinţa Ştiinţifică UgalMat 2007, vol. II, 383 - 388

[8]. di Bari G. A. - *International Nickel Inc.,* Saddle Brook, N.J.; www.inco.com, electroplating solutions, Nickel Plating, Metal Finishing, Volume 98, Issue 1, Ianuary 2000, p. 270 - 288, wwwscience direct.com

[9]. Rose I., Whittington C. - *Nickel Plating Handbook,* OMG Finland Oy, 2002, nickel.sales@omgi.com, www.omgi.com;

[10]. http://ro.wikipedia.org/wiki/Culoare

[11]. Doi T., MizumotoK., Tanaka S., Yamashita T. - *Bright Nickel Plating from Nickel Citrate Electroplating Baths*, Metal Finishing, 2004, 26 - 35

[12]. Doi T., MizumotoK., Tanaka S., Yamashita T. - *Effect of Bath pH on Nickel Citrate Electroplating Bath*, Metal Finishing, 2004, 104 – 111

[13]. Firoiu C. - *Tehnologia proceselor electrochimice*, Editura Didactică şi Pedagogică, Bucureşti, 1983

[14]. LI Chao-qun, LI Xin-hai, WANG Zhi-xin, GUO Hua-jun - *Nickel electrodeposition from novel citrate bath*, Trans. Nonferrous Met. SOC. China, **17** (2007) 1300-1 306, www.csu.edu.cnlysxb.