A STUDY REGARDING THE MONITORING OF THE NICKEL BATHS pH

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Abstract: *In order to achieve the optimal performances of the electroplating process it is necesary a attentive monitoring of the electrolytes pH. The bulk pH in the Watts bath electrolyte was measured during the nickel plating process. The boric acid was the buffer agent used because it is the most used agent in the nickel plating baths, it is efficient for the pH to stabilize in the catodic film and smooth and ductile platings are obtained in its presence. To determine the pH, the potentiometric method was used, employing a glass pH electrode.*

Keywords: *nickel electrodeposition, boric acid, pH, monitoring of pH.*

Introduction

Nickel deposition is one of the commonest electroplating processes, because the deposition characteristics are easily controlled by varying the composition and the operational parameters of the electrolytic bath. The nickel amount spent for the electrodeposition procedures represent approximately 12% of the world's total consumption [Ba'94]. The electrodeposition of nickel often does not proceed with 100% current efficiency. The balance of the current is consumed normally in hydrogen evolution. Because of this hydrogen evolution, the hydrogen ion is depleted in the electrolyte near the cathode surface. Therefore, the pH of the electrolyte near the cathode surface is always higher than that in the bulk electrolyte [Ji'95]. The recently deposited nickel layer acts as a catalyst for the evolution of hydrogen, since it causes a drop in the overvoltage of process [Su'06].

In the aqueous solutions the hydrogen will always evolve if the overall deposition current is high enough; the hydrogen can result not only from H_3O^+ (at the limit concentrations) but also from water [Ma'84].

The hydrogen evolution reaction may be considered to consist of two steps: hydrogen adsorption onto the electrode M, combined with the first electron transfer (reaction 1a), followed by the electrochemical desorption and the transfer of the second electron (1b):

$$\begin{aligned} &a)\ M(e) + H_3O^+ + e^- \rightarrow MH_{(ads)} + H_2O \\ &b)\ MH_{(ads)} + H_3O^+ + e^- \rightarrow M + H_2 + H_2O \end{aligned} \qquad (1)$$

Many studies have been devoted to the mechanism of the hydrogen evolution reaction (such as those of Tafel, Volmer, Heyrovský, Parsons, Gerischer, Horiuti, Okamoto, Brockris). This mechanism is influenced by many parameters, mainly by the material and the state of the electrode surface, the applied potential, and the current density [Šu'06]. The influence of the hydrogen obtained at the catode on the structure of a metallic layer is often observed and is, also, very complex. The hydrogen can be adsorbed more easily on certain crystalline plans and it can block them so that the metal will develop preferentially on others. The developement of a selective orientation of the deposition crystals can sometimes be ascribed to the preferential adsorbtion of the hydrogen onto some sides.

The hydrogen can also diffuse in the metal and change its mechanical features and this phenomenon is known as "hydrogen embrittlement" [Ma'84].

There are three basic factors that can suppress the increase of the cathode surface pH. The first factor is the mass transfer rate of hydrogen ions towards the cathode surface.The reduced thickness of the diffusion layer brought about by the vigorous agitation will prevent rising to a large extent the cathode surface pH. The second factor is the proton donating pH buffers, such as boric acid, or the bisulfate ion. The third factor is the hydroxyl-consuming pH buffers, such as: $Ni(OH)^+$; $Ni_4(OH)_4^{4+}$. As the cathode surface pH increases, the following equilibria will shift to the right to generate more protons [Ji'95]:

$$HSO_4^- \rightarrow SO_4^{2-} + H^+ \quad (2)$$

$$Ni^{2+} + H_2O \rightarrow NiOH^+ + H^+ \quad (3)$$

$$4Ni^{2+} + 4H_2O \rightarrow Ni_4(OH)_4^{4+} + 4H^+ \quad (4)$$

$$Ni^{2+} + 2H_2BO_3 \rightarrow Ni(H_2BO_3)_2 + 2H^+ \quad (5)$$

$$Ni^{2+} + NH_4^+ \rightarrow Ni(NH_3)^{2+} + H^+ \quad (6)$$

When the supply of hydrogen ions is unable to meet the depletion rate, the cathode surface pH will rise; the solution becom alkaline by replacing the H_3O^+ ions and eventually lead to the formation of insoluble $Ni(OH)_2$ on the cathode surface, because the solubility products of the nickel hydroxide and, thus, its precipitation are overtaken.

Ovari and Rotinyan [Ov'70] measured the cathode surface pH using a microglass pH electrode during nickel electrodeposition under the following conditions: the concentration range of 0.25 ÷ 2 M $NiCl_2$, the temperature of 55°C and the pH in the acid region of 0.75 ÷ 2.5. They found that the surface pH was always higher than the bulk pH if the bulk pH was above 1.5 units. They claimed that the surface pH increased initially with increasing curent density; however, it did not increase further when the current density reached a certain level.

Kun şi Chan [Ku'83] have estimated the reliability of surface pH measurements during nickel electrodeposition using electrochemical techniques, which had, anyway, some drawbacks associated with the effect of gas bubbles and the current flow. The most convenient technique was to use a pH-sensing electrode, such as black Pt/H_2, Pt - quinhydrone, Sb_2O_3/Sb and the glass pH electrodes. The glass pH electrode was used the most, and among the new techniques the one based on the use of an optically-transparent electrode together with a U.V. – visible indicator is difficult to achieve.

A useful technique for measuring the surface pH consits of the use of a flat-bottom glass pH electrode juxtaposed with a fine gold gauze cathode [De'90], [De'93], [Ro'87], [Ro'90]. Deligianni şi Romankiew [De'90] descovered that a higher nickel concentration and the presence of the boric acid resulted in a lower surface pH. Using a rotating pH electrode, they observed that the surface pH decreased continuously with the increasing of the rotation speed.

The purpose of this study was to monitor the Watts bath electrolyte pH both at the half distance between the two electrodes and at a 0.5 mm distance from the catodic surface. We analysed the effect of the bath pH on the catodic current efficiency.

Materials and methods

Boric acid and nickel salts stock solutions were prepared with analytical-grade reactives from Merck.

The final concentrations have been adjusted by an appropriate dilution with water, in 0.1425 – 1.425 mol·l^{-1} the range for nickel and in 0.0566 – 0.566 mol·l^{-1} the range for boric acid.

After preparation, the solutions were stored in polyethylene flasks at the room temperature. Table 1 shows the bath composition and the plating conditions used for the experiment.

Table 1 The bath composition and the plating

Chemicals	**Concentration**
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	0.17038 mol·l^{-1}
Nickel sulphate ($NiSO_4 \cdot 6H_2O$)	1.11276 mol·l^{-1}
Boric acid (H_3BO_3)	0.50946 mol·l^{-1}
Temperature	35°C
Current cathodic density	1.0745 A·dm^{-2}

The pH determination has been made with an Oakton pH 1100 pH-meter (Eutech instruments) with a glass pH electrode that has a common composition (Orion).

During the electrolysis, the bulk pH and the solution pH were recorded respectively, at every 5 minutes, at a 0.5 mm distance from the electrode surface and in a 250 ml electrolyte cell charge.

Results and discussion

The pH variation according to the nickel ions' concentration in the mixed solution of chloride and nickel sulphate without boric acid and to the nickel ions' concentration in the mixed solution with boric acid, respectively, at 20°C is presented in Figure 1. The mixed solution pH without boric acid varies according to the concentration in the range 4.701 and 3.31 and the pH varies in the presence of the boric acid in the range 4.701 and 3.158.

The function of the boric acid during the nickel electrodeposition is a controversial subject. The conventional view is that boric acid serves as a pH buffer. However, it has been claimed that boric acid serves as a homogeneous catalyst and lowers the overpotential of nickel deposition [Ho'85], [Ho'87], [Ho'86], [Ho'79]. It has been reported [Ti'77] that there is a complex forming between nickel and borate ions in the mixed on chloride and sulphate solutions, according to the reaction 7:

$$Ni^{2+} + 2H_2BO_3 \rightarrow Ni(H_2BO_3)_2 + 2H^+ \qquad (7)$$

Another interesting point concerning the buffering capacity of boric acid is the effect of an electric field. It was found that the equilibrium's dissociation constant of the boric acid near the cathode surface is substantially lager than the corresponding value in the bulk electrolyte [Ma'70], [Ji'95].

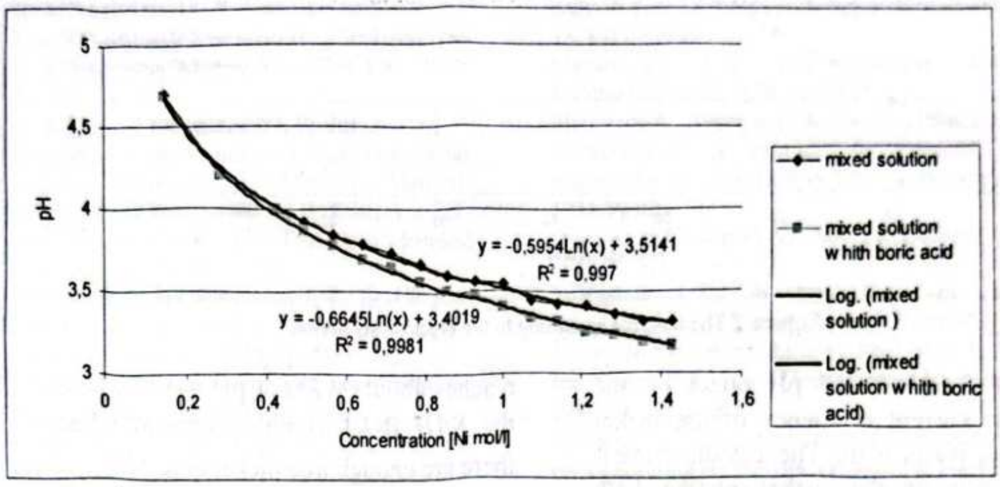

Figure 1 pH according to the nickel ions' concentration and that of the boric acid in the solution.

To clarify the functions of the boric acid in the nickel-containing solutions, starting by the simplest case, a series of pH/$NaOH$ titrations on free boric acid (5 ÷ 40 $g \cdot l^{-1}$) solutions in the presence and absence of 2M $NaCl$ solution at 25°C were performed. There are altogether four ionic species which may form through equilibrium reactions as follows [Ba'76], [Ji'95]

$$H_3BO_3 + H_2O \xrightarrow{Q_{11}} B(OH)_4^- + H^+$$

$$2H_3BO_3 \xrightarrow{Q_{21}} B_2O(OH)_5^- + H^+$$

$$3H_3BO_3 \xrightarrow{Q_{31}} B_3O_3(OH)_4^- + H^+ + 2H_2O$$

$$4H_3BO_3 \xrightarrow{Q_{42}} B_4O_5(OH)_4^- + 2H^+ + 3H_2O$$

The calculations made by using the equilibrum constants from the literature [Ba'76] indicated that multistep dissociation of boric acid could happen as the pH went up to 13. However, interestingly, only the first-step dissociation was obvious at pH up to 13 from the pH titration results [Ji'94], [Ji'95].

Figure 2 shows the bulk pH evolution in time in the electrolysis process, for 60 minutes, for four nickel plating baths with different amounts of boric acid. In the case of the bath with the highest boric acid concentration, a pH increament through first 30 minutescould be observed, then, it is maintained constant at about 4.3. While the boric acid content in the initial solution is decreasing, the pH is increasing slower. The monitoring of the solution pH at 0.5 mm distance from the catodic surface led to values very close to those of the bulk pH measured at the half distance between the two electrodes.

These results show that in the start period of the electrolysis, the pH is increasing, then it stabilizes around a certain value. This shows the involvement of a certain type of reciprocal interaction between the boric acid and the nickel ions complex – borate ions, $Ni(H_2BO_3)_2$ - formed during the electroplating process.

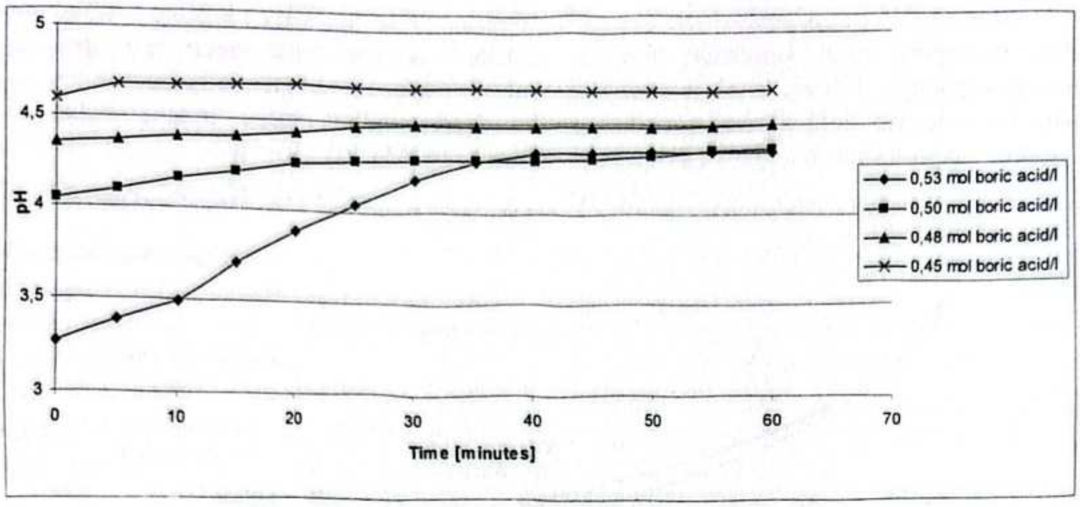

Figure 2 The bulk pH according to the electrolysis period

Figure 3 shows the pH effect on the catodic current efficiency of the nickel plating Watts bath. The catodic current efficiency of the nickel plating bath reaches about 94.2% at pH = 4.6, where the $Ni(H_2BO_3)_2$ complexes prevail when there are enough free nickel ions, Ni^{2+}.

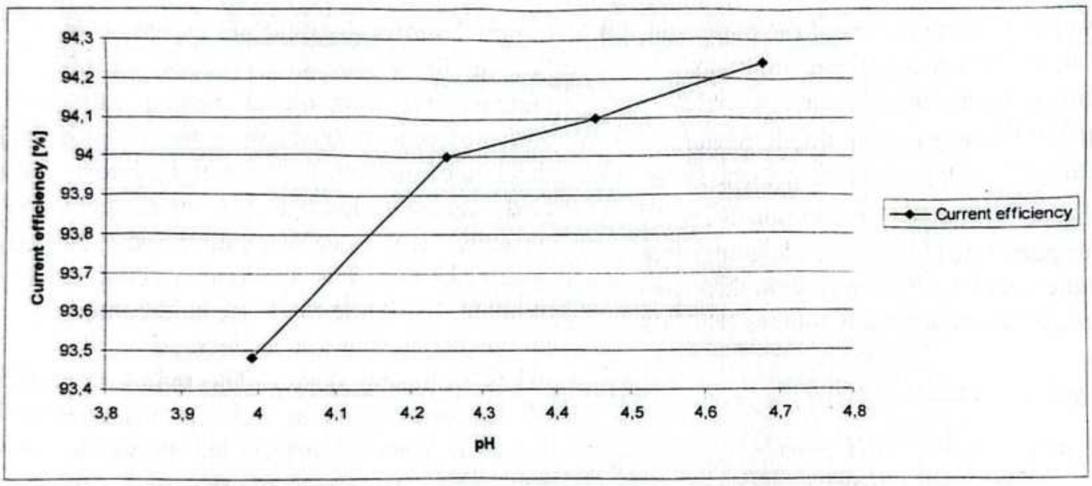

Figure 3 Relation between cathode curent efficiency and bath pH.

The information above shows that the presence of the boric acid at an ideal concentration in the nickel plating bath is decisive.

The introduction of an adequate monitoring strategy would allow a more efficient control of the bath composition, optimizing the plating characteristics.

Conclusions

1. Monitoring the pH is an important link in the control of the quality of the galvanic processes in order to obtain qualitative depositions.
2. Most of the studies regarding the stabilization mechanism of the pH both in the nickel plating baths and in the catodic film were made on the Watts baths that contain the boric acid as a buffering agent.
3. The involvement of a certain reciprocal interaction between the boric acid and the nickel ions complex – borate ions , $Ni(H_2BO_3)_2$ - formed during the

deposition process is indicated by the pH stabilization around a certain value, after a certain period of time from the beginning of the process.

In case of the baths that were studied around a 3.9 – 4.7 pH range, high efficiencies of catodic current were obtained.

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