BORIC ACID AND ADDITION ROLE IN NICKEL PLATING BATH COMPOSITION

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Abstract

The use of the boric acid as buffer substance and of the organic additions in the nickel plating bath composition plays a favorable part in obtaining bright smooth and dense deposits.

Rezumat

În vederea obţinerii unor straturi lucioase, netede şi compacte, utilizarea acidului boric ca substanţă tampon şi a adaosurilor organice în compoziţia băilor de nichelare au un rol favorabil.

Résumé

L'utilisation de l'acid borique comme substance tampon et des additions organiques dans la composition des bains galvaniques ont un rôle favorable pour obtenir des couches brillantes, lisse et compactes.

Nickel electroplating electro-chemistry is studied extensively since two goals are aimed at by nickel coatings: protection of the base metal against corrosion and decorative/design surface finishing. [ONI,80], [TRI,01]

Decorative-protecting nickel coatings are used to finish automobile, motorbike, bike parts, in the medical, consumer good and tool technique, in diverse apparatus, etc.

Functional coatings are used to increase hardness, abrasion and wearing resistance, including the thick deposits for electro-forming from the polygraphic industry, deposits to protect some plants in the chemical industry (sometimes catalytically too), as well as to overhaul some worn-out or wrongly made parts.

Another functional use of nickel plating is to protect temporarily steel with thick layers of over 120μm in view of forging (to avoid decarburizing of the superficial steel layer). [MAR,84]

Nickel electroplating, irrespective of the aim in view, is carried out by low acid electrolytes (pH=3 … 5). These electrolytes are simple salt solutions which metal content is provided by a nickel salt (table 1).

Electrolytes Role in the Nickel Plating Bath Composition:

1. *Nickel salts* (Nickel sulphate, $NiSO_4 \cdot 7H_2O$; Nickel sulphamate $Ni(NH_2SO_3)_2$; Nickel fluoroborate $Ni(BF_4)_2$) provide the most part of nickel ions. In solutions of nickel salts, the nickel ions are present under the form of bivalent ions. The nickel ion is reduced to cathode. The process may be described by the following reaction:

$$Ni^{2+} + 2e^- \rightarrow Ni^0$$

2. *Nickel chloride* ($NiCl_2 \cdot 6H_2O$): improves anodes dissolution, by diminishing the overvoltage and increasing the electrolyte conductivity. Concentration decrease of Cl^- ions that takes place inside the cathode film should be avoided, as it causes “burning” of deposits. This is carried out by permanent correction of Cl^- ions concentration in baths. [GRÜ,05]

3. *Boric acid* (H_3BO_3): stabilizes the electrolyte p H. In practice it was noticed that in the absence of a buffer substance, at common temperatures, deposits become brittle and porous. The boric acid role in nickel plating has been demonstrated by the scientists: Y. Tsuru, M. Nomura and F.R. Foulkes, who studied the following two phenomena: hydrogen simultaneous discharge with the nickel ion and measurement of internal stress from the nickel layers, during high speed electrodeposition at limiting

current density of the nickel ion, in sulphamate baths which concentration in boric acid is different. [TSU,02]

Table 1. Types of Nickel Plating Baths and Working Conditions

ELECTROLYTES AND CONDITIONS	TYPES OF NICKEL PLATING BATHS			
	- sulphate-based (Watts Bath)	- chloride-based	- sulphamate-based	- tetrafluoroborates - based
Nickel sulphate, $NiSO_4 \cdot 7H_2O$	250 ... 310 g/	-------	-------	------
Nickel sulphamate, $Ni(NH_2SO_3)_2$	-------	-------	300 ... 400 g/l	------
Nickel fluoroborate, $Ni(BF_4)_2$	-------	-------	------	80 ... 100 g/l
Nickel chloride, $NiCl_2 \cdot 6H_2O$	50 ... 60 g/l	300 g/l	5 ... 15 g/l	15 g/l
Boric acid, H_3BO_3	40 ... 45 g/l	30 g/l	30 ... 40 g/l	10 g/l
Temperature	40 ... 70°C	55°C	20 ... 60°C	50°C
Maximum current density	3 ... 10 A/dm^2;	1 ... 10 A/dm^2	5 ... 20 A/dm^2	20 A/dm^2
pH range	3,0 ... 4,0	about. 3,8	3,5 ... 4,5	3,0

The boric acid concentrations in nickel sulphamate baths are shown in table 2, and the nickel sulphamate concentration ($Ni(NH_2SO_3)_2$) is constant 1,55 M.

Table 2. Sulphamate Baths with different boric acid concentrations put into study [TSU,02]

BATH NUMBER	1	2	3	4	5
Nickel sulphamate concentration, $Ni(OSO_2NH_2)_2$	1,55 M	1,55 M	1,55 M	1,55 M	1,55 M
Boric acid concentration, H_3BO_3	0	0,08 M	0,16 M	0,49 M	0,81 M
pH	4,0	4,0	4,0	4,0	4,0

From the experimental data obtained, the researchers were able to represent graphically the potential variation depending on partial current density for the nickel ions, wherein one may estimate the limiting current density for these ions (figure 1).

This curve indicates the fact that the process presents usually a Tafel slope of $-0{,}12 \times 10^{-1}$ V and the limiting current density for the nickel ions in bath 5 is between the range 20 - 25A/dm^2. The same value of $-0{,}12 \times 10^{-1}$ V of Tafel slope was obtained by Epelboin (1971) for the Watts bath. [EPE,71]

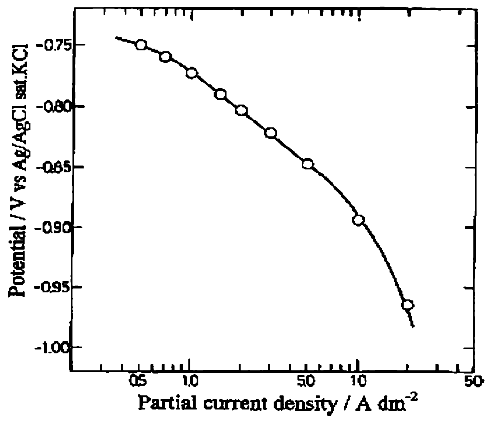

Fig. 1: Potential variation (without taking into account the potential fall caused by internal electrolyte resistance) depending on the current density of nickel ion for the deposition of the latter one. [TSU,02]

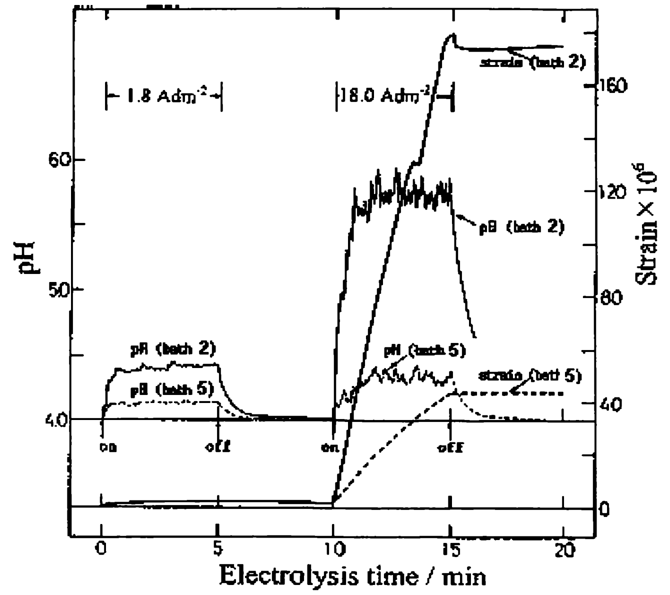

Fig. 2: The relation between the solution pH at 0,1 mm from the electrode surface and the internal stress of the deposited nickel layers in bath 2 (0,08 M H_3BO_3) and in bath 5 (0,81 M H_3BO_3) [TSU,02]

Figure 2 shows the relation between the solution pH (measured dynamically during the electroplating process) at a distance of 0,1mm from the nickel cathode surface and the internal stress evolved in the deposited nickel layers in bath 2 (0,08 M H_3BO_3) and in bath 5 (0,81 M H_3BO_3).

Initially a deposition of a preliminary nickel layer of 1.8 μm thickness has been made, at a current density of 1,8 A/dm^2, then the pH solution and internal stress measurement resulted from the deposition that took place at a plating current density of 18,0 A/dm^2. During the electroplating in bath 5, which has a high concentration of boric acid (0,81 M), the pH near to the electrode surface remained close to volumetric solution value of 4,0; whereas , for bath 2 which contains 0.08 M only boric acid , the pH adjacent to the electrode surface has increased rapidly at a value of almost 5,75, at the same time precipitating also the nickel hydroxide ($Ni(OH)_2$). [TSU,99]

Raub (1993) states that nickel hydroxide precipitation in the Watts bath starts at a solution pH of 5,0 and up to 5,6 which afterwards varies around this value, releasing at the same time hydrogen bubbles on the electrode surface [RAU,93]

The stress resulted in the nickel layer deposited in bath 2 is four times higher than that evolved in the nickel layer deposited in bath 5.

The hydroxyl ion produced during the hydrogen releasing process through the reaction:

$$H_2O + e^- \longrightarrow \frac{1}{2} H_2 \uparrow + OH^-$$

sustain the general observations according to which, the higher the solution pH is, the higher the internal stress from the metallic coating is. In the case of bath 2, though the pH in the electrolyte solution volume was kept at a low value of 4,0, the high value of almost 6 of the pH adjacent to electrode surface indicates the presence of hydrogen formation in high quantity and consequently, explains the significant increase of internal stress that may be noticed in the deposited nickel layer.

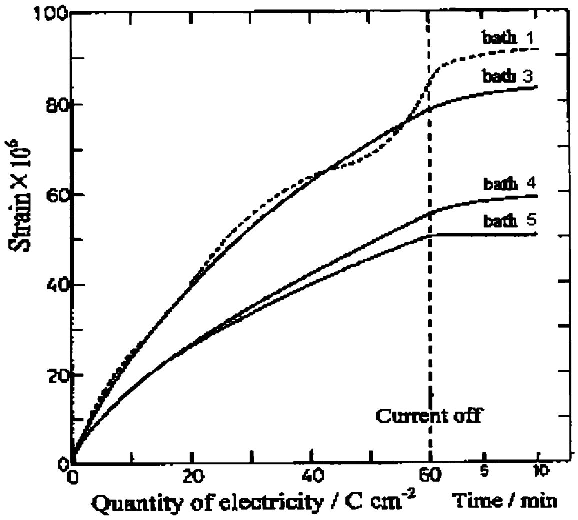

Fig. 3: The Effects of the Boric Acid Concentration upon internal stress in nickel layers deposited at 18,0 A/dm^2. [TSU,02]

On the other hand, as it was shown above, a high concentration of boric acid in the electroplating bath may inhibit hydrogen release during nickel electroplating. As seen in the case of bath 5, the adjacent pH to the electrode surface could not significantly increase above the pH volumetric value of 4,0. It results that the boric acid in high concentration is able to inhibit the formation of hydrogen bubbles on the electrode surface, thus formation of high stresses in the deposited layers being avoided and therefore the deposited nickel layers do not deform. [TSU,02]

Figure 3 shows the way the internal stress varies in the electrodeposited nickel layers in electroplating nickel baths, which boric acid concentration varies, at a current density of 18,0 A/dm^2. At boric acid concentrations of $\geq$ 0,16 M (baths 3, 4 and 5) the internal stress increased slightly at the same time as the total quantity of electricity which went through the circuit for a cycle term. However, in the case of bath 1, which does not contain boric acid, the internal stress has increased in a unpredictable way, a fluctuating one as compared to that noticed in the case of baths containing boric acid. [TSU,02]

4. Besides the basic salts, the electroplating electrolytes contain also other organic substances-additions (brightness addition; leveling substances; tension-active and complexion substances) which have the role to change favorably the features of electroplated deposits (corrosion resistance, hardness, brightness) depending on the coating use.

Research on finding some additions as good as possible which behave identically even if the working conditions vary, led to the fact that at present one may find on the market hundreds of brightening agents for the bright nickel plating process (table 3). Some of these brightening agents have high cost, and their use is quite difficult because, except the proper agent, also contain activating and wetting agents. [GUT,85]

Table 3. Different organic substances used as additions at improving the features of electroplated nickel deposits

No.	ADDITION AND ITS ROLE	BIBLIOGRAPHY
1.	*Strato lux* - a brightening agent that has a maximum of brightness with temperature and concentration, optimum values being at 35 – 40^{0}C and concentration of 0,25 - 0,75 g/l;	[GUT,85]
2.	*Rotor lux* – a brightening agent specific to rotative plants, has maximum values at concentrations of 0,5 g/l and 0,7 g/l at temperatures between 30 - 35^{0}C, fact explainable since in the rotative plants one operates with lower temperatures, as the boric acid dissolves due to continuous electrolyte agitation;	[GUT,85]
3.	*Soda saccharine* – a brightening agent with wide use in nickel deposits, presents a maximum of brightness at temperatures between 35 - 40^{0}C, optimum values being for concentrations of 3 – 7 g/l;	[GUT,85]
4.	*Naphtalene-disulphonic acid* – a brightening agent with a medium of brightness slightly lower than the other brightening agents;	[GUT,85]
5.	*Sulpho-semi-carbaside derivatives* - improve significantly the quality of the electroplated nickel producing mirror-bright surfaces with fine crystals.	[MIL,93]
6.	*2-butyne-1,4-diol* and *sulphonic derivatives (sodium benzene sulphonated, sodium benzene sulphinated* and *sulphosalicyl acid)* - block the nickel electro-crystallization in Watts bath by absorption on the cathode surface.	[GAO,99]
7.	*Pyridine* and its *derivatives (2-picoline* and *4-picoline)* – act as anticorrosive substances and brightening agents (in electrotechnics), and as leveling agents (in chemical industry). These additives act as brightening and leveling agents in the following order: 4-picoline>2-picoline>pyridine.	[DUB,93], [KIR,82], [YAD,93] [MOH,01]
8.	*Cumarin*- in quantities of about 0,6 g/l has a high leveling effect, but has also an inconvenient - its decomposition products (melylotic acid, o-hydroxyphenol , propanol, and so on) influence negatively the mechanical characteristics of deposition (elongation, tearing values are significantly decreased, the leveling effect diminishes, and the deposit appearance gets worse);	[GRÜ,05]
9.	*Sodium lauryl-sulphate, alcohol-ether-sulphates,* as well as the *substituted anyl-sulphonates* – wetting additions used to avoid "pitting";	[GRÜ,05]
10.	*1,4-butyndiol* - addition of leveling effect. These additions increase cathode polarization of nickel deposits. Adjust nickel deposition by the fact that nickel plates especially in the surface pits, leveling simultaneously the inequalities of the base metal.	[GRÜ,05]

Conclusions:

- The characteristics of nickel deposits are slightly influenced by the basic electrolyte, but instead are strongly influenced by the boric acid presence, as well as organic additions.
- The boric acid inhibits hydrogen release during high speed nickel electrodeposition from the nickel electroplating bath close to the limiting current density of nickel ions diffusion. Consequently, the pH adjacent to the metal deposition surface is kept at close to that of the volumetric solution, so that the noxious effects of the deposited hydrogen on the development of high internal stresses in the nickel deposits are greatly reduced.
- The organic additions influence significantly the characteristics of nickel deposits. The characteristics of nickel electroplating electrolytes with brightening depend greatly on exploitation parameters that can be modified in relatively close limits; some additions allow enlargement of the brightening field.

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