

# The influence of addition of sulfate ionic liquid precursors on the electrochemical properties of the electrodeposited nickel coatings

Marek BARANIAK, Jarosław WOJCIECHOWSKI – Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznań, Poland; Juliusz PERNAK – Institute of Chemical Technology and Engineering, Poznan University of Technology, Poznań, Poland; Grzegorz LOTA\* – Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznań, Poland

Please cite as: CHEMIK 2016, 70, 9, 497–502

## Introduction

One of the most often used processes of an electrolytic metal deposition on steel and alloy components surfaces is nickel plating. The nickel coatings show both protective and decorative features. As a result of a reaction occurring on the cathode, divalent nickel ions from the salt solution are reduced, i.e. are discharged to the metallic form [1, 2]. The mechanism of this process has been described with two models:

- nickel ions, by electrostatic interaction, are attracted by the negatively charged electrode and, after taking a specific place in its crystalline structure, are reduced to the metallic form,
- firstly, in the near-electrode layer, nickel cation is reduced and then the atom is incorporated in the crystalline structure of the formed layer [2].

The nickel electrodeposition process may be conducted using a few different types of baths. The most popular are Watts-type baths that contain nickel sulfate, nickel chloride, boric acid, and organic additives that affect the kinetics of the electrolytic process of nickel reduction and on the mechanical and decorative properties of the obtained coatings. These additives are often divided into type I and type II additives in the literature. Both types are added to Watts-type bath at different concentrations [1, 2]. An example of the type I additive is saccharine, which serves as a carrier and reducer of the stresses occurring in the coating crystalline layer in the nickel electroplating bath [3–5]. Type II additives are commonly known as brighteners. The mechanism of their incorporation in the newly formed crystalline structure of the nickel coating has a significant impact on the current efficiency of the conducted electrolytic process and on the size of the formed crystals of the reduced nickel [6–8]. The type II additives include quaternary ammonium salts containing a nitrogen atom with a concentrated positive charge of an ion pair in their structure [9–11]. In this case divalent nickel cations, which are present in the solution in the form of borate complexes  $[\text{Ni}(\text{H}_2\text{BO}_3)_{n/2}]^{2+}$ , additionally form ions pairs with ammonium cation. In such a case, an ammonium salt serves as a catalyst and inhibitor of two competitive reactions, i.e. nickel and hydrogen reduction [8].

The paper presents the effect of additions of sulfate ionic liquid precursors (type II precursors) on the protective properties of nickel coatings electrodeposited from Watts-type baths. The corrosion properties of the obtained nickel coatings were tested by means of electrochemical techniques.

## Methods

The coatings were deposited on the AISI 1018 steel. 30 mm disks were cut out from the steel and cleaned mechanically using abrasive paper with granulation 2500, degreased chemically in a solution containing  $15 \text{ g dm}^{-3}$  NaOH and  $30 \text{ g dm}^{-3}$   $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$  (298 K, 10 minutes), and rinsed with distilled water. Then, the chemical etching process in HCl solution ( $1 \text{ mol dm}^{-3}$ , 298 K, 5 minutes) was conducted, the disks were rinsed again with distilled water and placed in the Watts-type bath for nickel electroplating without drying at the following composition:  $250 \text{ g dm}^{-3}$   $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $30 \text{ g dm}^{-3}$   $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $40 \text{ g dm}^{-3}$   $\text{H}_3\text{BO}_3$ . The pH of this bath was 4.3–4.4. The addition of ionic liquid precursor was  $500 \text{ mg}$  in  $1 \text{ dm}^3$  of the bath. Figure 1 presents a general formula for two series of ionic liquid precursors studied, whereas Table 1 presents arranged substituent lengths and samples designations.

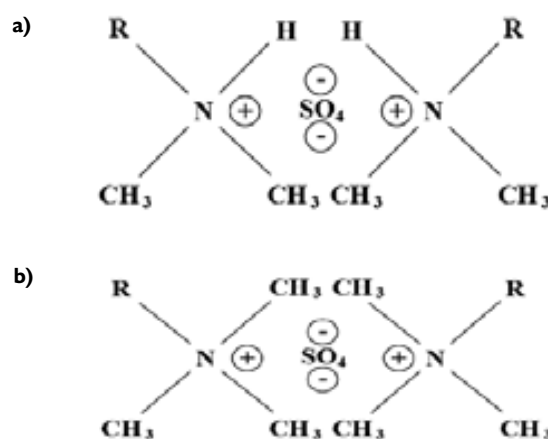


Fig. 1. (a) General formula of the ionic liquid type I precursor, (b) General formula of the ionic liquid type II precursor

Table 1

Ionic liquid precursors used in Watts type bath

Name of ionic liquid precursor additive abbreviation	Type	Alkyl substituent	Sample designation
Di(hexyldimethylammonium) sulfate C6I	I	R = C <sub>6</sub>	P01
Di(hexadecyldimethylammonium) sulfate C16I	I	R = C <sub>16</sub>	P02
Di(hexyltrimethylammonium) sulfate C6II	II	R = C <sub>6</sub>	P03
Di(hexadecyltrimethylammonium) sulfate C16II	II	R = C <sub>16</sub>	P04
No addition			P05

\*Corresponding author:  
Grzegorz LOTA – Ph.D., D.Sc., (Eng.), e-mail: grzegorz.lota@put.poznan.pl

Table 2

Corrosion potentials and corrosion current densities values

Sample	$E_{\text{cor}}$ vs SCE (V)	$j_{\text{cor}}$ ( $\mu\text{A cm}^{-2}$ )
P01	-0.515	4.428
P02	-0.366	2.324
P03	-0.655	1.626
P04	-0.513	7.830
P05	-0.446	5.067

All the ionic liquid precursors were synthesised at the Department of Chemical Technology of the Institute of Chemical Technology and Engineering at Poznan University of Technology. The cathode deposition was conducted for 7 minutes. Current density, which was determined based on Hull cell tests, was  $4.95 \text{ A dm}^{-2}$ . 99% pure nickel was used as an anode. Then, the samples were rinsed with distilled water and dried.

The nickel-coated samples were subjected to electrochemical tests in a vessel in the three-electrode system. Platinum was used as an auxiliary electrode, with a saturated calomel electrode as a reference electrode. The tests were conducted at ambient temperature. 3.5% NaCl solution was used as an electrolyte. It is often used in corrosion tests to represent the external factors. Prior to the commencement of tests, the auxiliary electrode was degreased with acetone and then washed with distilled water using an ultrasonic washer. Electrochemical tests were conducted using the potentiostat/galvanostat VMP3 Biologic, France.

At the first stage, the changes of equilibrium potential of the tested electrode were measured for open circuit for 240 minutes. Then, a linear polarization test was performed in the range  $\pm 0.250 \text{ V}$  in relation to equilibrium potential with a potential changing rate of  $0.0002 \text{ V s}^{-1}$ . EC-Lab Software® was used to determine tangents to the obtained curves. The intersection point of these tangents was used to determine potential values and corrosion current density.

## Results

Figure 2(a) presents the curve of equilibrium potential changes as a function of time at open circuit conditions, and Figure 2(b) presents the changes of voltammetric curves in the semi-logarithmic scale.

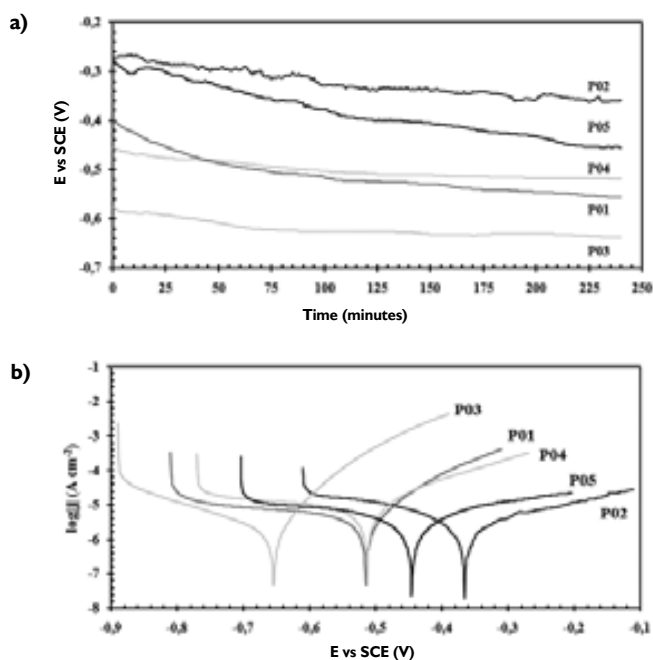


Fig. 2. (a) Potential monitoring at open circuit conditions measurement, (b) Linear polarization measurement

Figure 2(a) shows large variability of equilibrium potentials depending on the bath used. It is recommended that the equilibrium potential is shifted towards more positive values, which results in a better inhibition of the corrosion process occurring – on the component surface under thermodynamic equilibrium conditions [12]. Figure 2(a) indicates that Sample P02, in comparison with Sample P05, is the only one that shows corrosion-inhibiting properties. In case of the voltammetric curves, the most positive corrosion potential was also observed for Sample P02. Table 2 presents the determined values of corrosion current densities ( $j_{\text{cor}}$ ) and corrosion potentials ( $E_{\text{cor}}$ ).

Based on the obtained results, we may conclude that the best anti-corrosive properties, in comparison to the sample obtained using a normal Watts-type bath without any organic additives (P05), are exhibited by Sample P02, as it has the most positive corrosion potential and the lowest corrosion current density. The low corrosion current density value for Sample P03 seems a bit surprising, as it has the most negative value of a corrosion potential. It is probably the result of the underestimation of the corrosion current by the program algorithm due to the shape of the voltammetric curve.

As already mentioned in the Introduction, the mechanism of electrolytic nickel deposition in the presence of type I and II additives involves the formation of complexed systems in the solution, on the one hand, and the selective adsorption of compounds on the substrate material surface on the other. In the analysed case, it may be noted that ionic liquid precursors with longer carbon chains in the substituent (C16I and C16II) exhibited better electrochemical properties than analogous systems with shorter ones (C6I and C6II). This may indicate the increase in the surface hydrophobicity and/or the formation of a less porous layer (by e.g. the formation of complex ion pairs and thus more uniform coatings). This is shown by the better corrosive resistance of coatings obtained from the solutions of protic ionic liquid precursors in comparison to their aprotic homologs.

## Summary

The conducted electrochemical studies indicated a significant impact of the used ionic liquid precursors as additives to the Watts-type baths on the corrosive properties of the obtained coatings. Among the tested ionic liquid precursors, the improvement of anti-corrosive properties was observed for a Watts-type bath containing di(hexadecyldimethylammonium) sulfate. The type of substituents and their quantity play an important role. Among the tested Watts-type bath additives it was found that sulfate protic ionic liquid precursors exhibit better anti-corrosive properties than their aprotic equivalents containing  $\text{CH}_3$  groups. Moreover, the improvement of corrosion resistance increases with the increase in the carbon chain length. This is probably due to the formation of complexed ionic pairs in the salt solution and the obtaining of a very tight nickel coating. Despite that, in comparison to the coatings electrodeposited from Watts-type bath without any additives, a nickel layer with better anti-corrosive properties was produced only in one case, i.e. from a solution containing di(hexadecyldimethylammonium) sulfate.

The authors would like to gratefully acknowledge the financial support from the Ministry of Science and Higher Education, project no. 03/31/DSBP/0313

## Literature

- Schlesinger M., Paunovic M.: *Modern Electroplating*. John Wiley & Sons 2010.
- Rekć W.: *Galwanotechnika*. Wydawnictwo Politechniki Poznańskiej 1992.
- Nakamura Y., Kaneko N., Watanabe M., Nezu H.: *Effects of saccharin and aliphatic alcohols on the electrocrystallization of nickel*. Journal of Applied Electrochemistry 1994, 24, 227–232.
- Mockute D., Bernotiene G.: *The interaction of additives with the cathode in a mixture of saccharin, 2-butyne-1,4-diol and phthalimide during nickel electrodeposition in a Watts-type electrolyte*. Surface and Coatings Technology 2000, 135, 42–47.
- Mockute D., Bernotiene G., Vilkaite R.: *Reaction mechanism of some benzene sulfonamide and saccharin derivatives during nickel electrodeposition in Wat-*

- ts-type electrolyte. *Surface and Coatings Technology* 2002, 160, 152–157.
6. Mohanty U. S., Tripathy B. C., Singh P., Das S. C.: *Effect of pyridine and its derivatives on the electrodeposition of nickel from aqueous sulfate solutions. Part I: Current efficiency, surface morphology and crystal orientation.* *Journal of Applied Electrochemistry* 2001, 31, 579–583.
  7. Mohanty U. S., Tripathy B. C., Singh P., Das S. C.: *Effect of pyridine and its derivatives on the electrodeposition of nickel from aqueous sulfate solutions part II: Polarization behaviour.* *Journal of Applied Electrochemistry* 2001, 31, 969–972.
  8. Ciszewski A., Postuszny S., Milczarek G., Baraniak M.: *Effects of saccharin and quaternary ammonium chlorides on the electrodeposition of nickel from a Watts-type electrolyte.* *Surface and Coatings Technology* 2004, 183, 127–133.
  9. Franklin T. C., Darlington J., Fierro R.: *Ion pairing as a method of controlling the composition of electrodeposited alloys.* *Journal of the Electrochemistry Society* 1986, 133, 893–896.
  10. Franklin T. C., Narayanan T. S. N. S.: The effect of blocking additives on the electrodeposition of cadmium. *Journal of the Electrochemical Society* 1996, 143, 2759–2764.
  11. Franklin T. C., Williams T., Narayanan T. S. N. S., Guhl R., Hair G.: *A comparison of the effects of ion pairing and blocking additives on electrodeposition of zinc and cadmium.* *Journal of the Electrochemical Society* 1997, 144, 3064–3066.
  12. Baszkiewicz J., Kamiński M.: *Korozja materiałów.* Oficyna Wydawnicza Politechniki Warszawskiej 2006.

Marek BARANIAK – Ph.D., (Eng.), has graduated from the Faculty of Chemical Technology, Poznan University of Technology. In 2002 he got a doctor's degree of chemical sciences in the chemical technology. He is an senior researcher at the Institute of Chemistry and Technical Electrochemistry of Poznan University of Technology. Research interests: chemical technology, electrochemistry.  
e-mail: marek.baraniak@put.poznan.pl, phone: + 48 61 665 21 58

Jarosław WOJCIECHOWSKI – M.Sc., (Eng.), has graduated from the Faculty of Chemical Technology, Poznan University of Technology. In 2013, he received his M.Sc., (Eng.) academic degree. He is currently a Ph.D. student at Interdisciplinary Doctoral Studies "Materials Science" at the Institute of Chemistry and Technical Electrochemistry at the same university.  
e-mail: jaroslaw.g.wojciechowski@doctorate.put.poznan.pl,  
phone: +48 61 665 21 58

Professor Juliusz PERNAK – Ph.D., D.Sc., (Eng.), has graduated at Silesian University of Technology, Faculty of Chemical Technology. From 1971 to today he employed at the Poznan University of Technology Department of Chemical Technology. Details on [www.juliusz.pernak.com.pl](http://www.juliusz.pernak.com.pl).  
e-mail [juliusz.pernak@put.poznan.pl](mailto:juliusz.pernak@put.poznan.pl), phone: +48 61 6653682

\*Grzegorz LOTA – Ph.D., D.Sc., (Eng.), graduated from Faculty of Chemical Technology, Poznan University of Technology, in 2001. He obtained his Ph.D. degree (chemical sciences) at the same faculty in 2005. In 2012 he received D.Sc. also at the same faculty. He is currently employed by Institute of Chemistry and Technical Electrochemistry Poznan University of Technology and Institute of Non-Ferrous Metals, Division in Poznan Central Laboratory of Batteries and Cells. Scientific interests: electrode materials for chemical power sources, electrochemical capacitors, Li-ion batteries, Ni-MH and fuel cells batteries.  
e-mail: grzegorz.lota@put.poznan.pl, phone: + 48 61 6652158

## Aktualności z firm

### News from the Companies

Dokończenie ze strony 499

#### Startuje Inkubator Innowacyjności+

Inkubator Innowacyjności+ to program, który wspiera proces zarządzania wynikami badań naukowych i prac rozwojowych, w szczególności w zakresie komercjalizacji. Program wspiera promocję osiągnięć naukowych, zwiększa ich wpływ na rozwój innowacyjności oraz wzmacnia współpracę między środowiskiem naukowym a otoczeniem gospodarczym. Inkubator zakłada dofinansowanie podmiotów – uczelni, spółek celowych – które mogą też utworzyć konsorcja. Konsorcja jako takie są przez program premiiowane i oznacza to, że ich dofinansowanie może wynieść maksymalnie 3 mln PLN, podczas gdy pojedynczych wnioskodawców do 2 mln PLN. O przyznaniu dofinansowania w ramach programu Inkubator Innowacyjności+ decyduje szereg czynników, podmioty muszą spełnić określone warunki, np. zgłoszenie co najmniej 15 wynalazków lub wzorów użytkowych, krajowych lub zagranicznych. Podmioty muszą również być w stanie zapewnić wkład własny na poziomie minimum 20% wnioskowanej kwoty. Zaraz po otrzymaniu dofinansowania każdy z podmiotów ma obowiązek utworzyć radę lub komitet inwestycyjny – tak powstały organ będzie się zajmował monitorowaniem i ewaluacją działań realizowanych w ramach projektu, których czas trwania nie może przekroczyć 31 stycznia 2019 r. (kk)

(<http://www.nauka.gov.pl/>, 29.08.2016)

#### Ponad 24 mln PLN do wzięcia przez polskich doktorów

Ponad 24 mln PLN na realizację innowacyjnych projektów badawczych mogą otrzymać młodzi doktorzy z Polski i z zagranicy, którzy wezmą udział w programach: FIRST TEAM, HOMING i POWROTY, ogłoszonych przez Fundację na rzecz Nauki Polskiej. Wnioski moż-

na zgłaszać do 17 października br. We wszystkich trzech programach o dofinansowanie ubiegać mogą się młodzi doktorzy: do pięciu lat po doktoracie, niezależnie od narodowości. Przedmiotem projektów, realizowanych obowiązkowo we współpracy z partnerem naukowym, mogą być przełomowe w skali międzynarodowej prace badawczo-rozwojowe o dużym znaczeniu dla gospodarki i społeczeństwa.

Pula środków przeznaczonych na drugi konkurs w programie FIRST TEAM wynosi aż 14 mln PLN. Dzięki niemu młodzi badacze otrzymają środki na założenie pierwszego zespołu. Finansowanie może sięgać nawet 2 mln PLN i zostać przyznane na trzy lata z możliwością przedłużenia o jeden rok. Badania mogą być realizowane w jednostkach naukowych, przedsiębiorstwach albo konsorcjach naukowo-przemysłowych w Polsce.

Program HOMING to z kolei propozycja dla osób, które chcą wrócić z zagranicy do pracy naukowej w Polsce. Na drugi konkurs FNP zamierza przeznaczyć łącznie 8 mln PLN. W ramach programu można zdobyć grant w wysokości ok. 800 tys. PLN na projekt o charakterze stażu podoktorskiego. Finansowanie może zostać przyznane na dwa lata, bez możliwości przedłużenia. Projekty mogą być realizowane w jednostkach naukowych lub przedsiębiorstwach.

Natomiast badacze, którzy na wczesnym etapie swojej kariery zawodowej przerwali prowadzenie prac badawczo-rozwojowych z powodu pracy w innym sektorze gospodarki lub ze względu na rodzicielstwo, mogą się ubiegać o grant w wysokości do ok. 800 tys. PLN w programie POWROTY. Projekty mogą być realizowane w jednostkach naukowych lub przedsiębiorstwach. W konkursie można zdobyć łącznie 2,4 mln PLN. (kk)

(<http://naukawpolsce.pap.pl/>, 22.08.2016)

Dokończenie na stronie 511