

Hydrogenation and cracking of nickel coatings electrodeposited in the presence of brighteners

M. Monev

Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.11, Sofia 1113, Bulgaria

Received October 9, 2015; Revised November 3, 2015

During cathodic polarization in an acidic media containing hydrogenation-enhancing additives, nickel absorbs large quantities of hydrogen and a new crystal phase, nickel hydride is formed. The investigation of the phase transformation of electrodeposited nickel into nickel hydride under cathodic charging showed that the organic compounds 1,4-butyne-1,3-diol and saccharine, both being typical representatives of two classes of additives for nickel electrolytes, which are usually added in order to improve the properties of the layers such as their appearance, internal stresses, *etc.*, contribute to a more complete phase transformation of nickel into nickel hydride. This is assisted by the fine structure of the nickel deposits with a higher density of defects as well as the incorporated compounds containing sulphur as a product of electrochemical transformation of the saccharine. The type of the additives influences both the tendency of the nickel layers to form cracks and the shape of the cracks.

Key words: electrodeposition; nickel coatings; cathodic hydrogenation; nickel hydride; X-ray diffraction; crack formation.

INTRODUCTION

During cathodic polarization in acidic media containing hydrogenation-enhancing additives, nickel absorbs large quantities of hydrogen [1]. A new crystal phase, nickel hydride (β -NiH_x, where $0.7 \leq x \leq 0.8$) with a f.c.c. lattice is formed, the lattice parameter being approximately 6% larger than that of nickel [2]. For a very short time strongly stressed layers are formed [3] that lead to lasting structural alterations - broadening of the grain boundaries [4], crushing of the crystallites [5], formation of cracks [6].

In a previous X-ray analysis it has been established that the conversion of nickel into nickel hydride in bright nickel electrodeposits is more complete than that of matt ones obtained from an additive-free electrolyte [7]. The hydride phase is unstable and disintegrates under normal conditions. In contrast to matt coatings where the disintegration follows an equation inherent to first-order reactions [8], the disintegration of the hydride phase in the bright coatings is not so a fast process and it begins after a certain period of time after the end of hydrogenation [7]. When the hydrogenation is over above a certain degree, a process of crack formation in the bright nickel deposits starts [9]. The cracking process proceeds at a rate which offers a possibility for a direct observation of the initiation and

propagation of the cracks by using a metallographic microscope. A part of the cracks shows a shape close to that of the Archimedes spiral [10].

However, bright coatings can be obtained in the presence of at least two organic additives – each one of the two classes of additives for nickel electrodeposition [11]. In the present work the effect of saccharine and 1,4-butyne-1,3-diol - typical representatives of the two classes of additives on the process of phase transformation, as well as on the subsequent cracking of the nickel coatings after the end of cathodic hydrogenation was investigated.

The study of the process of phase transformation and hydrogen induced cracking can be also of interest for the water electrolysis. Nickel electrodes are widely used in the electrochemical technologies for hydrogen production [12]. With long-term electrolysis in alkaline solution, energy efficiency losses at the nickel cathodes are established, which is manifested in increase in the hydrogen overvoltage at constant cell current [13]. According to one of the hypotheses, such a behavior is associated with the formation of hydride at the nickel cathode surface [14]. In order to reduce the energy consumption, a large number of studies are focused on electrodeposition of new electrode materials on the base of nickel for alkaline as well as for acidic medium (Proton exchange membrane (PEM) hydrogen generators work at very low pH values) [15]. Lowering of the hydrogen overvoltage is reached by increase of the catalytic activity (modification of nickel by incorporation of

To whom all correspondence should be sent:
E-mail: monev@ipc.bas.bg

metallic/non-metallic compounds, including such, containing sulfur [16-18]) and/or by increase of the active surface area of the electrodes. However, the modification of the elemental composition and/or the structure changes the susceptibility of the electrode to hydrogenation, as well. Consequently, the question about the stability of the electrodes in acidic media arises also in the case, where inorganic materials like solid acids or a composite material based on them, containing S, Se, P, As (hydrogenation-enhancing compounds) are used in order to extend the working window of PEM [19].

EXPERIMENTAL

Nickel coatings of thickness approximately 20 μm were deposited onto mechanically polished copper substrates from electrolyte containing: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ - 280 g l^{-1} , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ - 50 g l^{-1} and H_3BO_3 - 30 g l^{-1} . Current density of 5 A dm^{-2} , pH 4.0-5.0, deposition temperature of 55 $^\circ\text{C}$ and air agitation of the bath were used. Saccharine up to concentration of 1.0 g l^{-1} and 1,4-butyndiol up to concentration of 0.2 g l^{-1} were added to this electrolyte either separately or in a combination. Immediately after deposition and rinsing, the samples were subjected to hydrogenation in a 1N H_2SO_4 solution containing selenious acid (H_2SeO_3). The conditions of each hydrogenation procedure are given in the figure captions.

After rinsing with distilled water and ethyl alcohol the hydrogenated samples were studied by X-ray analysis with Co K_α X-rays. The volume fraction of the hydride phase (M_{NiH}) was calculated by means of the formula proposed in [7]:

$$M_{\text{NiH}} = \frac{(I_{hkl})_{\text{NiH}}}{(I_{hkl})_{\text{NiH}} + (I_{hkl})_{\text{Ni}}}$$

The integral intensities of the Ni line 111 ($(I_{hkl})_{\text{Ni}}$) and Ni-H line 111 ($(I_{hkl})_{\text{NiH}}$) were measured by oscillating the goniometer of the X-ray diffractometer within the range of $47^\circ \leq \theta \leq 55^\circ$.

The samples were examined for cracking by a metallographic microscope using a magnification of 120 x.

RESULTS

Formation and disintegration of nickel hydride

The X-ray analysis of samples, deposited from electrolytes containing individual brighteners shows that in both cases the tendency towards hydrogenation increases with increase of their concentration the effect being more expressed in the presence of 1,4-butyndiol in the electrolyte

(Fig. 1). The successive addition of both brighteners leads to an increase in their activity, and almost a total transformation of the nickel coating into a hydride phase is achieved for a short time (Fig. 2). According to the previous investigations, the saccharine activity could be related to deposition of fine-grained coatings [20] and to incorporation of disintegrated products containing sulphur [21]. The addition of 1,4-butyndiol also causes a decrease of the crystallites size [20, 22] as well as an increase of the value of microdeformations [20]. Moreover, the 1,4-butyndiol stimulates the incorporation of sulphur when both saccharine and 1,4-butyndiol are added in the electrolyte [11].

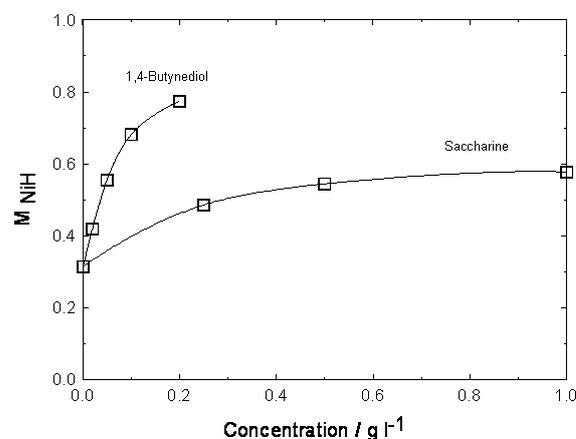


Fig. 1. Volume fraction of hydride phase as a function of brighteners' concentration at separate addition to the nickel electrolyte. Hydrogenation conditions: 1n H_2SO_4 + 10 mg l^{-1} H_2SeO_3 , 15 mA cm^{-2} (1.5 A dm^{-2} cathodic current density), 30 min.

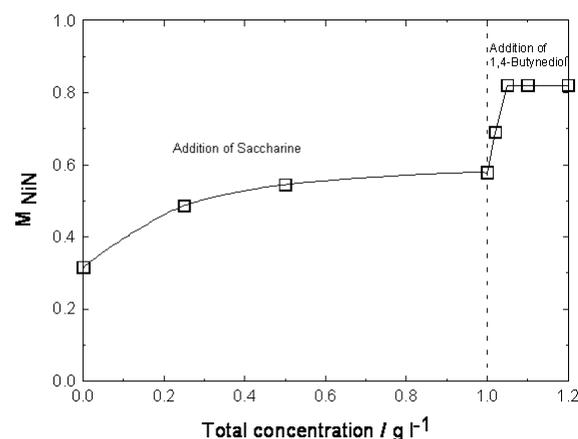


Fig. 2. Volume fraction of hydride phase as a function of brighteners' concentration at successive addition to the nickel electrolyte. Hydrogenation conditions: 1n H_2SO_4 + 10 mg l^{-1} H_2SeO_3 , 15 mA cm^{-2} , 30 min.

Under normal conditions, the nickel hydride phase is unstable (Fig. 3). Coatings, deposited from electrolyte containing only saccharine disintegrate

immediately when the hydrogenation is over. Obviously, the incorporation of sulphur in the coatings as a product of electrochemical transformation of the saccharine facilitates not only the hydrogenation of nickel layers but also the desorption of the hydrogen after the end of hydrogenation. Coatings, deposited from electrolyte containing both brighteners exhibit a retarded disintegration and the time of delay increases with increasing butyndiol concentration (Fig. 4).

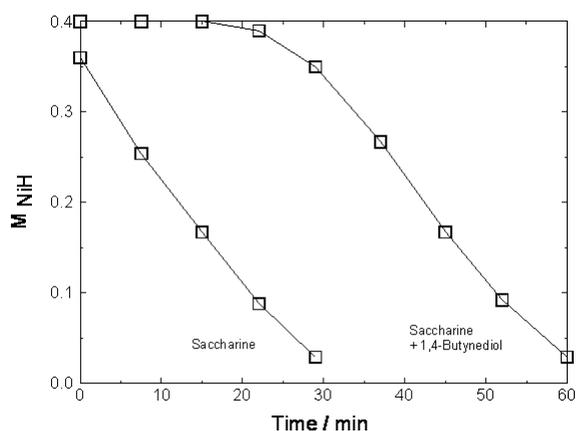


Fig. 3. Disintegration of hydride phase at a room temperature as a function of the type of the nickel coating. Hydrogenation conditions: 1n H₂SO₄ + 1 mg l⁻¹ H₂SeO₃, 2.5 mA cm⁻², 40 min.

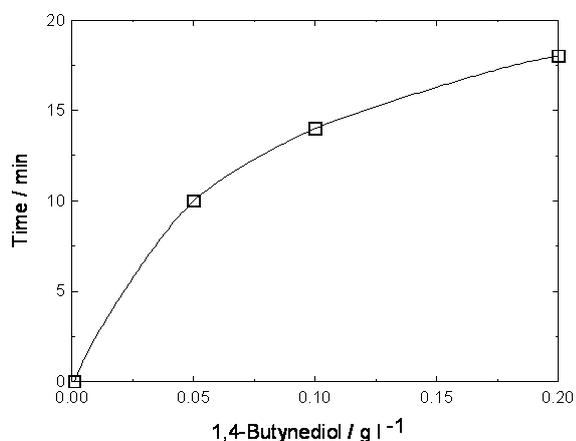


Fig. 4. Time of delay of hydride phase disintegration as a function of 1,4-butynediol concentration in electrolyte containing 1 g l⁻¹ saccharine. Hydrogenation conditions: 1n H₂SO₄ + 1 mg l⁻¹ H₂SeO₃, 15 mA cm⁻², 30 min.

A smaller delay of hydride phase disintegration is observed in coatings obtained from an electrolyte containing only butyndiol. The influence of 1,4-butynediol on the disintegration of the hydride phase could be seen in several directions. The addition of 1,4-butynediol leads to deposition of coatings with a fine structure, showing a higher density of defects [20] and by this way, favourable conditions are created for stronger absorption of the

hydrogen into the nickel matrix. It is known that the defects and grain boundaries are sites which could act as H traps [23, 24]. Moreover, a largest quantity hydrogen is absorbed in the coatings obtained from an electrolyte containing both brighteners. The bright nickel coatings occlude hydrogen in amounts exceeding those needed for hydride phase formation [21, 25], and this phase visibly begins to disintegrate only after desorption of a portion of the occluded hydrogen.

Cracking of the hydrogenated nickel coatings

The metallographic study of samples subjected to cathodic hydrogenation indicates that cracking of the coatings is not observed when they are produced in an additive-free electrolyte. The hydrogenation degree of such coatings is considerably low [7, 21] and obviously, the internal stresses are not so high in order to cause cracks. The coatings produced in electrolyte containing only saccharine didn't show a tendency for cracking. These coatings are strongly hydrogenated and this effect is confirmed by the great alteration of the internal stresses during the cathodic hydrogenation [21]. However, cracks are not formed and this is probably due to the internal stresses which after the end of cathodic hydrogenation (followed by the hydrogen desorption) remain in the range of compressive stresses as are the own stresses of these coatings after deposition [21]. Cracks of an irregular shape are formed after hydrogenation of coatings, deposited from electrolyte containing only 1,4-butynediol. The spiral type of cracking begins to appear when the deposits are obtained from an electrolyte containing both brighteners (Fig. 5a). This occurs under "mild" hydrogenation. Ununiform cracking after "mild" hydrogenation shows that the hydrogenation doesn't run uniformly, both on the surface and in the bulk of the bright coatings. A regular net of cracks is formed after a strong hydrogenation of the coatings obtained from electrolyte containing both brightening additives [9, 10].

In some cases, probably due to improper preliminary processing of the substrate, the cathodic hydrogenation doesn't cause crack formation but blistering. Formation of bubbles is observed after cathodic hydrogenation of the coatings, deposited in the presence of saccharine (Fig. 5b). In coatings, deposited from electrolyte containing both brighteners, circle peelings are removed from their surface because these coatings are more brittle (Fig. 5c). The same circle peelings were also observed on the surface of zinc coatings,

obtained from zincate electrolytes in the presence of certain brighteners [26]. This effect could be connected with a hydrogenation of the iron substrate in the initial stages of the process when the rate of hydrogen reaction is much higher than that of the zinc electroreduction. The formation of bubbles as well as the removal of circle peelings from the surface of the coatings were observed after a certain period of time after the end of hydrogenation of nickel as well as after the deposition of zinc. The form and the time for appearance of blistering indicate that centres of internal stresses are created because of the ununiform hydrogenation and/or of the redistribution of the hydrogen after ending up the hydrogenation.

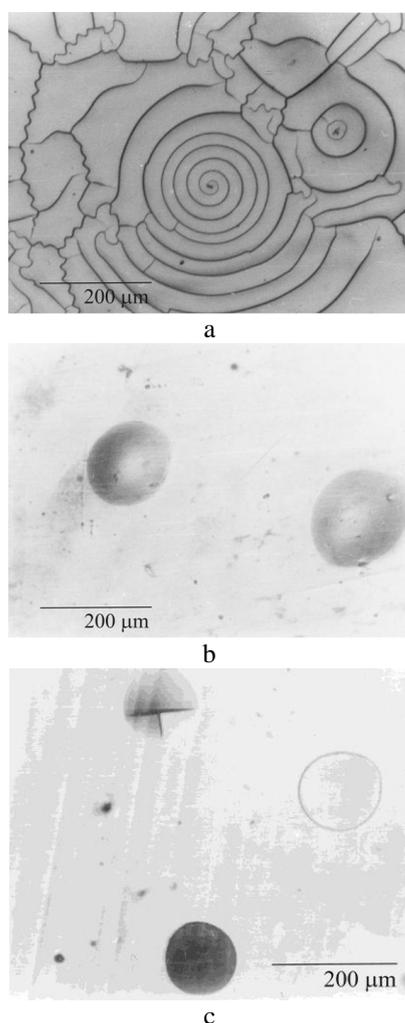


Fig. 5. Hydrogen induced structural alterations in nickel coatings: a - cracking after cathodic hydrogenation of coatings deposited from electrolyte containing both brighteners; b - blisters, formed after cathodic hydrogenation of a coating deposited from electrolyte containing saccharine; c - circles, peeled after cathodic hydrogenation of a coating deposited in the presence of both brighteners.

CONCLUSION

Both additives in the nickel electrolyte - 1,4-butynediol and saccharine contribute to a more complete phase transformation of nickel into nickel hydride. This is assisted by the fine structure of the nickel deposits with a higher density of defects as well as the incorporated compounds containing sulphur as a product of electrochemical transformation of the saccharine.

The delay of the hydride phase disintegration is related to the influence of 1,4-butynediol on the coating structure, the effect being more enhanced in combination with saccharine.

Cracking of the coatings, as a result of cathodic hydrogenation, is not observed when they are produced in an additive-free electrolyte or in an electrolyte containing saccharine. Concentric and spiral cracks are formed only in coatings, deposited from an electrolyte containing both brightening additives. It could be suggested, that this is related to the influence of three factors: formation of strain regions in the nickel deposits, as a result of irregular hydrogenation; various mechanical properties of the layers due to the influence of the additives and adhesion of the layers to the substrate.

Acknowledgement: The present studies were performed with the kind support of Fund "Scientific Research" (Research Project X-484) and Deutsche Forschungsgemeinschaft (Research Project 436 BUL 113/97).

REFERENCES

1. B. Baranowski, M. Smialowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim., Geol. Geogr.*, **7**, 663 (1959).
2. A. Janko, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **8**, 131 (1960).
3. Z. Szklarska-Smialowska, M. Smialowski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **6**, 427 (1958).
4. A. Janko, P. Michel, *C.R. Acad. Sci.*, **251**, 131 (1960).
5. A. T. Sanzharowski, O. S. Popova, *Zh. Prikl. Khim.*, **34**, 2120 (1961).
6. A. Janko, A. Szummer, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **14**, 885 (1966).
7. St. Rashkov, M. Monev, I. Tomov, *Surface Technology*, **16**, 203 (1982).
8. A. Janko, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **10**, 617 (1962).
9. St. Rashkov, M. Monev, N. Atanassov, *Surface Technology*, **17**, 309 (1982).
10. M. Monev, St. Rashkov, R. Kaishev, *Surface Technology*, **17**, 315 (1982).
11. Yu. Yu. Matulis, *Blestjashtie elektroliticheskie pokritija*, Vilnius, Mintis, 1969.
12. K. Zeng, D. Zhang, *Prog. Energy Combust. Sci.*, **36**, 307 (2010).

13. H. E. G. Rommal, P. J. Moran, *J. Electrochem. Soc.*, **132**, 325 (1985).
14. D. M. Soares, O. Teschke, I. Torriani, *J. Electrochem. Soc.*, **139**, 98 (1992).
15. E. Navarro-Flores, Zh. Chong, S. Omanovic, *J. Mol. Catal. A: Chem.*, **226**, 179 (2005).
16. J. I. Krjukov, S. F. Chernishov, A. G. Pshenichnikov, L. I. Altentaller, I. P. Naumov, J. S. Lapin, N. P. Kuznecov, *Elektrochimija*, **29**, 504 (1993).
17. N. A. Assuncao, M. J. Giz, G. Tremiliosi-Filho, E. R. Gonzalez, *J. Electrochem. Soc.*, **144**, 2794 (1997).
18. Y. Tie-chui, L. Rui-di, Zh. Ke-chao, *Trans. Nonferrous Met. Soc. China*, **17**, 762 (2007).
19. A. Goñi-Urtiaga, D. Presvytes, K. Scott, *Int. J. Hydrogen Energy*, **37**, 3358 (2012).
20. N. Atanassov, Hr. Bozhkov, St. Rashkov, *Surface Technology*, **17**, 291 (1982).
21. M. Monev, M. E. Baumgärtner, O. Loebich, Ch. J. Raub, *Metalloberfläche*, **45**, 2 (1991).
22. I. Tomov, M. Monev, *J. Appl. Electrochem.*, **22**, 262 (1992).
23. A. Atrens, D. Mezzanote, N. F. Fiore, A. Genshaw, *Corros. Sci.*, **20**, 673 (1980).
24. R. M. Latanision, M. Kurkela, *Corrosion-Nice*, **39**, 174 (1983).
25. P. Ch. Borbe, F. Erdmann-Jesnitzer, W. Schoebel, *Z. Metallkd.*, **71**, 227 (1980).
26. M. Monev, L. Mirkova, I. Krastev, Hr. Tsvetkova, St. Rashkov, W. Richtering, *J. Appl. Electrochem.*, **28**, 1107 (1998).

НАВОДОРОДЯВАНЕ И НАПУКВАНЕ НА НИКЕЛОВИ ПОКРИТИЯ ЕЛЕКТРООТЛОЖЕНИ В ПРИСЪСТВИЕ НА БЛЯСЪКООБРАЗОВАТЕЛИ

М. Монеv

Институт по физикохимия, Българска академия на науките, ул. Акад. Г. Бончев, Бл. 11, 1113 София

Постъпила на 9 октомври, 2015 г.; коригирана на 3 ноември, 2015 г.

(Резюме)

При катодна поляризация в кисела среда, съдържаща стимулиращи наводородяването добавки, никелът абсорбира значителни количества водород и се образува нова кристална фаза, никелов хидрид. Изследването на фазовото превръщане на електроотложен никел в никелов хидрид при катодно наводородяване показва, че органичните съединения 1,4-бутиндиол и захарин, типични представители на два класа добавки за никелови електролити, които обичайно се използват за подобряване на свойствата на покритията като външен вид, вътрешни напрежения и др., допринасят за по-пълното превръщане на никела в никелов хидрид. Това се дължи на по-фината структура на никеловите отложения с по-висока плътност на дефекти, както и на включенията, съдържащи сяра като продукт от електрохимичното превръщане на захарина. Добавките оказват влияние както върху склонността на никеловите слоеве към напукване, така също и върху вида на пукнатините.