

ELECTROLYTIC PRODUCTION AND CHARACTERIZATION OF NI-CO-P AND NI-W-P LAYERS

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ELEKTROLYTICKÁ PRÍPRAVA A CHARAKTERIZÁCIA NI-CO-P A NI-W-P VRSTIEV

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Abstrakt

V galvanostatických podmienkách pri prúdovej hustote $j_{dep} = 0.200 \text{ A}\cdot\text{cm}^{-2}$ boli pripravené Ni-P, Ni-Co-P a Ni-W-P vrstvy. Fázové zloženie vrstiev bolo určené rtg. difrakčnou fázovou analýzou a chemické zloženie sa analyzovalo atómovou absorpčnou spektrometriou. Pre charakterizáciu priečnej i povrchovej morfológie vrstiev bola použitá metalografická, stereoskopická a tunelová mikroskopia a taktiež profilograf typu Talysurf. Použitím voltametrickej metódy bolo študované správanie sa vrstiev v procese vylučovania vodíka a kyslíka z $5 \text{ mol}\cdot\text{dm}^{-3}$ roztoku KOH. Bolo zistené, že prídavok kobaltu a wolfrámu do Ni-P matrice vedie k tvorbe vrstiev s veľmi vyvinutým povrchom. Takéto vrstvy môžu byť použité pre elektródové materiály v elektrochémií.

Abstract

Ni-P, Ni-Co-P and Ni-W-P layers were obtained in galvanostatic conditions, at the current density $j_{dep} = 0.200 \text{ A}\cdot\text{cm}^{-2}$. The X-ray diffraction method was used to determine phase composition of the layers and the atomic absorption spectrometry was applied to specify their chemical composition. A metallographic, stereoscopic and tunneling microscope and also form Talysurf-type profilograph were used for cross-section and surface morphology characterization of the layers. The behaviour of obtained layers was investigated in the processes of hydrogen and oxygen evolution from $5 \text{ mol}\cdot\text{dm}^{-3}$ KOH solution, using voltammetry method. It was ascertained that, introduction of cobalt or tungsten into Ni-P matrix, lead to obtain the layers about very developed surface. Thus obtained layers may be useful in application as electrode materials in electrochemistry.

Keywords: Amorphous Ni-P matrix, cobalt, tungsten, electrolytic layers.

1. Introduction

Properties of nickel coatings are well known. Their wide application is a result of specific properties of nickel, which exhibit good corrosion resistance in aggressive solutions and also high catalytic activity for many electrochemical processes, in particular for the hydrogen

and oxygen evolution reaction. In order to improve the utilization of these materials and to enhance their electrocatalytic activity, various methods of their modifications could be applied, allowing to obtain materials with very developed, rough or porous electrode surface [1-6].

This study was undertaken in order to obtain the Ni-P layers, containing an additional alloying component (cobalt or tungsten) in an amount of ensuring obtained amorphous structure.

The aim of this work was to determine surface morphology and cross-section image of Ni-P, Ni-Co-P and Ni-W-P layers, their phase and chemical composition and also to evaluate their suitability as electrode materials for electrolytic hydrogen and oxygen evolution in 5 mol·dm⁻³ KOH solution.

2. Materials and experimental methods

In order to obtain Ni-P layer the following electrolyte was prepared (g·dm⁻³): NiSO₄ · 7H₂O - 28, NH₄Cl - 5, H₃BO₃ - 9, CH₃COONa - 8, NaH₂PO₂ · H₂O - 32, C₆H₅O₇Na₃ · 2H₂O - 29.

In order to obtain Ni-Co-P layer the following electrolyte was prepared (g·dm⁻³): NiSO₄ · 7H₂O - 28, CoSO₄ · 7H₂O - 84, NH₄Cl - 5, H₃BO₃ - 9, CH₃COONa - 8, NaH₂PO₂ · H₂O - 32, C₆H₅O₇Na₃ · 2H₂O - 29.

In order to obtain Ni-W-P layer the following electrolyte was prepared (g·dm⁻³): NiSO₄ · 7H₂O - 13, Na₂WO₄ · 2H₂O - 68, NH₄Cl - 50, NaH₂PO₂ · H₂O - 32, C₆H₅O₇Na₃ · 2H₂O - 200.

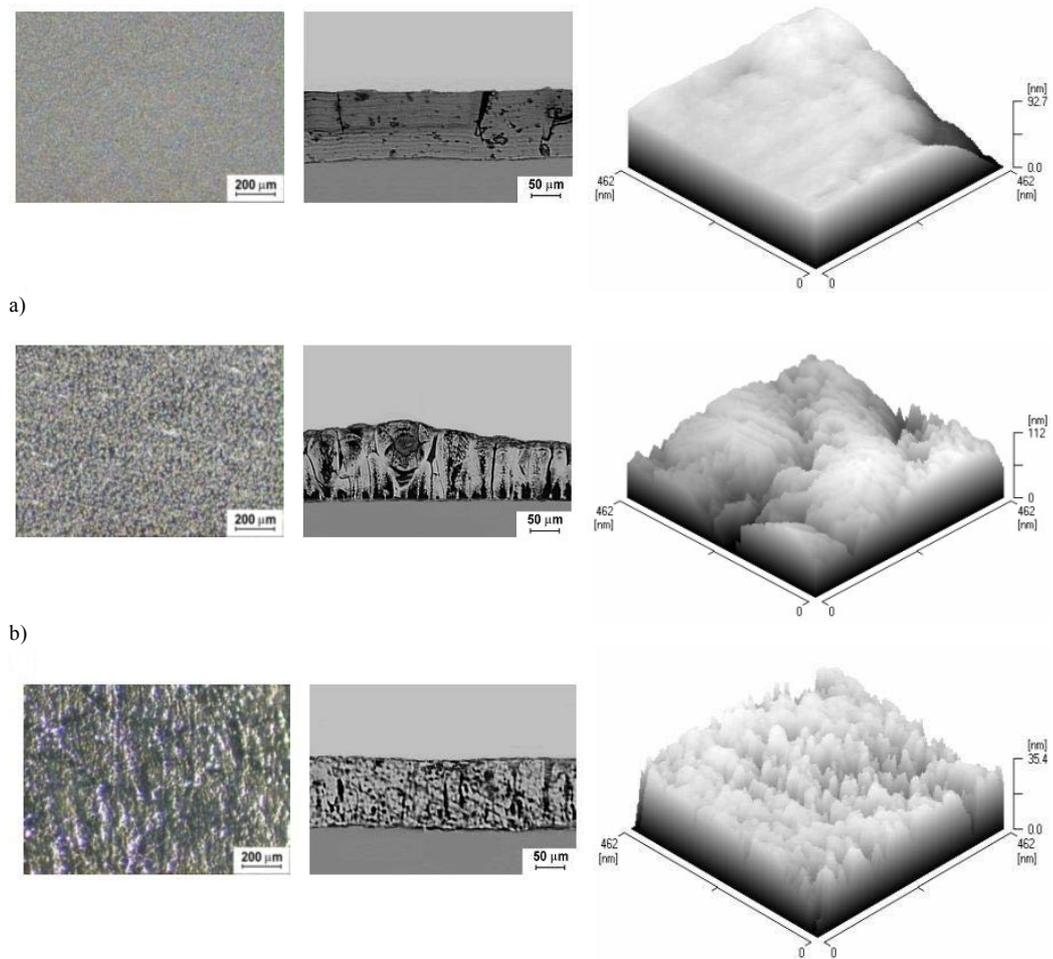
The electrodeposition process was conducted in galvanostatic conditions at the current density 0.200 A·cm⁻². The layers were deposited on a copper plate with a surface area of 1 cm² [1,2].

Surface morphology of obtained layers was determined by stereoscopic microscope Nikon SMZ-2T (mag. 196x), tunneling microscope and form Talysurf-type profilograph. Cross-section of obtained layers was determined by metallographic microscope Nikon ALPHAPHOT-2 YS2 (mag. 320x). Structural investigations were conducted by X-ray diffraction method using Philips diffractometer and CuK_α radiation ($U = 40$ kV, $I = 20$ mA). The chemical composition of the layers was determined by the atomic absorption method using a Perkin-Elmer spectrometer. The layers were dissolved in nitric and hydrofluoric acids, transferred into a measuring flask and diluted to 100 cm³. Finally, after appropriate dilution they were analysed for particular elements.

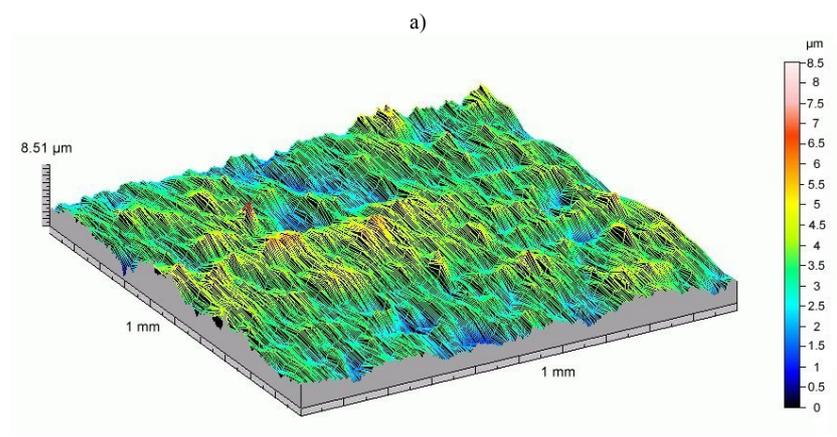
Investigations of electrolytic hydrogen and oxygen evolution on the prepared layers were conducted in a three-electrode cell using voltammetry method. These measurements were carried out in 5 mol·dm⁻³ KOH solution and using Autolab[®] electrochemical system.

3. Results and discussion

All Ni-P, Ni-Co-P and Ni-W-P layers electrolytically deposited, show good adhesion to the substrate. The Ni-P layer is silver – grey in colour and Ni-Co-P and Ni-W-P layers are silver – grey with a metallic shine. The presence of cobalt and tungsten in the Ni-Co-P and Ni-W-P layers, changes the heterogeneity of the surface and increases the number of interfaces between nickel and cobalt or tungsten. The thickness of all layers is about 100 μm. For comparison, in work presented surface topography is in the nano- and millimetric scale. In the both cases the Ni-Co-P layer was characterized by higher elevations on the surface in comparison to the Ni-W-P and Ni-P layers. It was found that the presence of cobalt or tungsten in the Ni-P matrix distinctly enlarged the real surface of the layers, in particular in the case of the Ni-Co-P layer (Fig.1,2).



a) b) c)
 Fig.1 Surface morphology, cross-section image and surface topography in the nanometric scale of Ni-P (a), Ni-Co-P (b) and Ni-W-P (c) layers.



a)

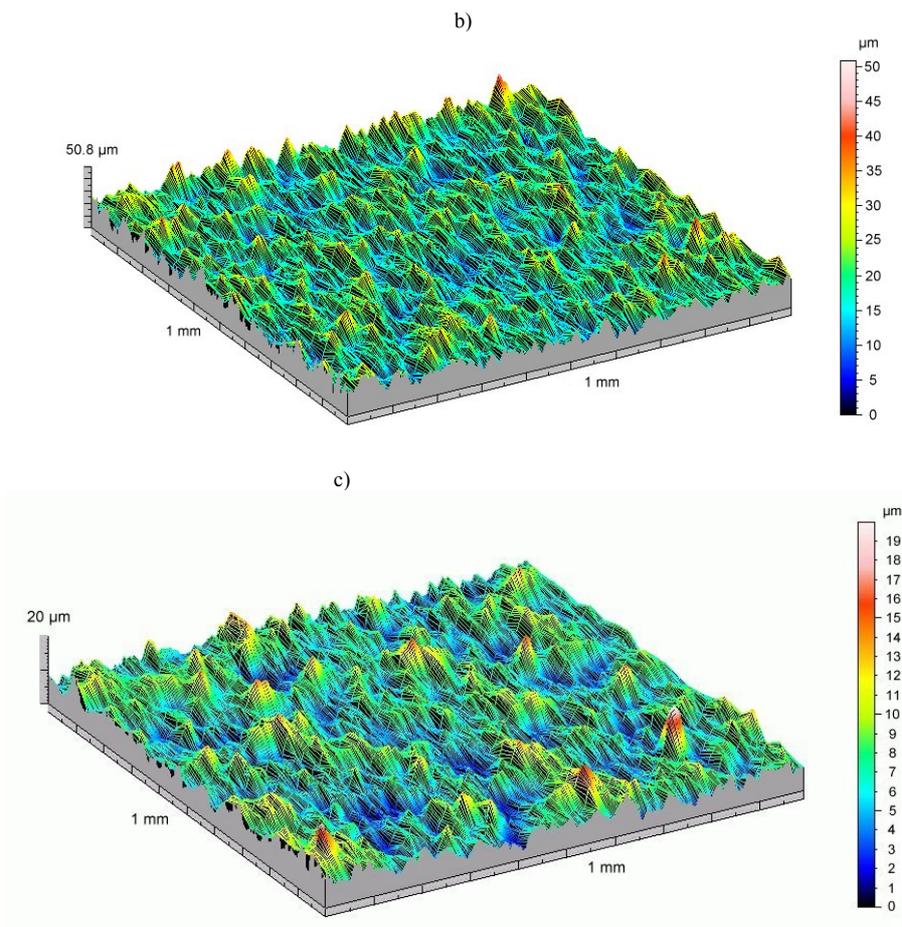


Fig.2 Surface topography in the millimetric scale of Ni-P (a), Ni-Co-P (b) and Ni-W-P (c) layers.

The Ni-P layer contains about 80% of nickel and about 20% of phosphorus. XRD investigations show that the Ni-P layer is an amorphous. This may be concluded from the presence of wide reflex on the diffraction pattern of this layer in the range of diffraction angles characteristic for (111) and (200) reflexes of nickel. The Ni-Co-P layer contains about 45% of nickel, about 11% of phosphorus and about 44% of cobalt. The Ni-W-P layer contains about 68% of nickel, about 12% of phosphorus and about 20% of tungsten. XRD investigations show that the Ni-Co-P and Ni-W-P layers are an amorphous structure like the Ni-P layer. The absence of sharp reflexes of cobalt or tungsten does not prove unequivocally that this phase is absent in the layer. This component may be built in the layer but in the amorphous form (Fig.3).

The behaviour of thus obtained layers was investigated in the processes of hydrogen and oxygen evolution from alkaline solution. The results obtained were used to estimate the ability of given materials to facilitate hydrogen and oxygen evolution in $5 \text{ mol} \cdot \text{dm}^{-3}$ KOH solution.

For hydrogen and oxygen evolution processes the potentiodynamic curves showed that the enlarged real surface of the Ni-Co-P layer evokes an increase in the current density in comparison with values observed for the Ni-W-P and Ni-P layers (Fig.4a,b).

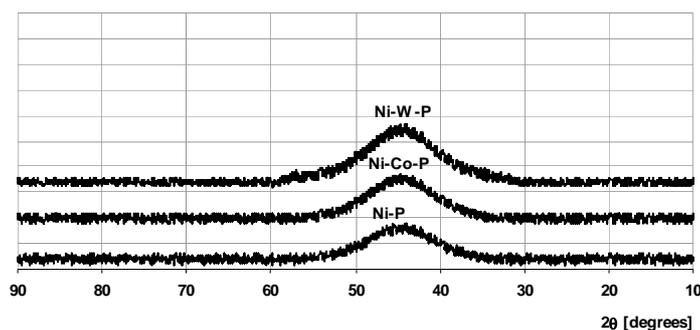


Fig.3 X-ray diffraction pattern for the Ni-P, Ni-Co-P and Ni-W-P layers.

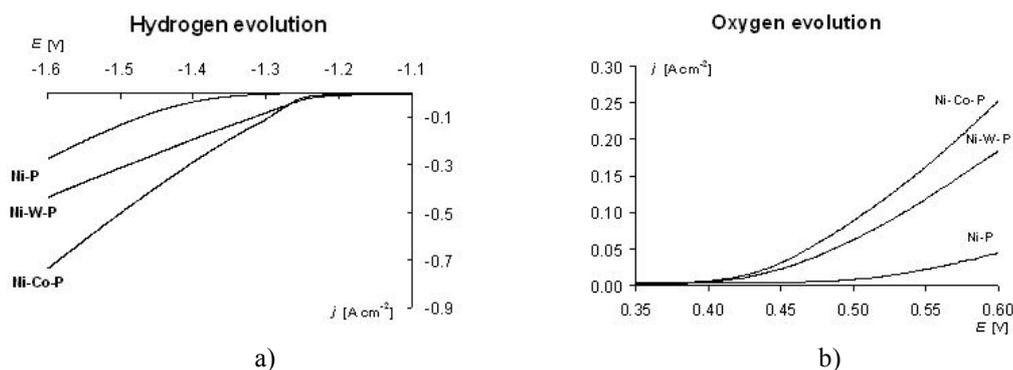


Fig.4 Potentiodynamic curves $j = f(E)$ obtained in $5 \text{ mol} \cdot \text{dm}^{-3}$ KOH solution, for hydrogen (a) and oxygen (b) evolution reaction.

4. Conclusions

Electrolytic layers Ni-Co-P and Ni-W-P are formed of both amorphous matrix and amorphous metallic ingredient. Presence of cobalt or tungsten in the Ni-Co-P or Ni-W-P layers causes an increase in the real surface area of the layers, in particular in the case of the Ni-Co-P layer. This layer is characterized by enhanced electrochemical activity for the hydrogen and oxygen evolution in $5 \text{ mol} \cdot \text{dm}^{-3}$ KOH solution compared to Ni-W-P and Ni-P layers.

It was ascertained that, introduction of cobalt or tungsten into Ni-P matrix, lead to obtain the layers about very developed surface. Thus obtained layers may be useful in application as electrode materials in electrochemistry.

Acknowledgements

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Literature

- [1] Popczyk M., Bajdur W.: Galvanotechnik, 3(90) (1999) 662.
- [2] Popczyk M., Budniok A.: Archives of Material Science, 4(22) (2001) 261.
- [3] Karimi R., Shervedani A., Lasia J.: Electrochem. Soc., 145 (1998) 2219.
- [4] Karimi - Shervedani, A. Lasia, J. Electrochem. Soc., 144 (1997) 2652.
- [5] Lu G., Evans P., Zangari G.: J. Electrochem. Soc., 150(5) (2003) A551.
- [6] Kupka J., Budniok A.: J. Appl. Electrochem., 20 (1990) 1015.