

Electrodeposition kinetics and surface morphology of Ni-B-UDD composite coating

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Abstract. The article presents the results of kinetic investigations of electrodeposition of a composite electrochemical coating based on a nickel-boron alloy. Current efficiency, polarization potentiodynamic researches had shown the joint participation in the electrodeposition process of finely dispersed compounds of nickel hydroxides, poorly soluble nickel and boron compounds present in the electrolyte or formed during electrolysis, and ultradispersed diamond introduced into the electrolyte. Comparison of 2D and 3D scans of the surfaces of the formed coatings confirmed the leveling effect of additives, as well as sparingly soluble nickel and boron compounds on the structure of coatings. The proposed composite electrochemical coatings can be used instead of chrome coatings when restoring parts and units of agricultural machinery.

1 Introduction

In order to increase the level of reliability and service life of modern agricultural machinery, it is promising to use galvanic coatings with nickel, nickel-based alloys (nickel-phosphorus, nickel-boron (Ni-B)), as well as composite electrochemical coatings (CEC) based on nickel for the restoration of parts and assemblies of agricultural machinery and its alloys. The advantage of these precipitates is the method of their deposition from non-toxic electrolyte-colloids or electrolyte-suspensions in comparison with environmentally hazardous processes, such as chromium plating. In many European countries and the United States, the use of certain metals is legally prohibited [1]. In our country, environmental problems are also the subject of discussion, including at the legislative level, and on galvanic lines, this prohibition primarily concerns the processes of "hexavalent" chromium plating, which contributes to the development of alternative methods of applying protective coatings [2, 3].

In recent decades, special attention has been paid to electrodeposition of Ni-B alloys using various polyhedral additives as a boron source. Ni-B electrolytic alloys are known for their improved physical, mechanical and electrical characteristics, which makes it possible to use them instead of chrome and precious metal coatings.

The mechanisms of electrodeposition of Ni-B alloys are investigated. Studies of the effect of potassium dodeca-closo-dodecaborate additive on the kinetics of the electrodeposition of Ni-B coatings have shown that the incorporation of boron occurs by a

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chemical-catalytic mechanism, and the electrodeposition process of the Ni-B alloy is limited by diffusion. The data obtained are explained by the formation of a boron-containing complex, as well as a change in the composition of the discharging particle. The low reactivity of potassium dodeca-closo-dodecaborate does not affect the composition and structure of the resulting Ni-B coatings, which are similar to coatings with Ni-B alloys obtained with other boron-containing compounds [4].

Analyzing the known boron-containing additives in nickel-plating electrolytes, the authors of [5] believe that from the boron-containing compound of the polyhedral class (for example, decaborates, decahydroborates, dodeca-closo-dodecaborates), boron is catalytically included in the freshly deposited nickel coating by a chemical mechanism. Ni-B alloys were electrodeposited using TMAB (trimethylamine borane) as a boron source [6]. To carry out bulk electrodeposition of the Ni – B alloy, the authors recommend adding portionwise the TMAB to the electrolyte. Bulk nanocrystalline Ni-B alloys exhibit good ductility in tensile loading. The intensification of the processes of metal electrodeposition from colloidal electrolytes has been theoretically and experimentally substantiated [7].

It should be understood that the electrodeposition of coatings with a dispersed phase in the composition occurs from electrolyte-suspensions obtained by the galvanic method and containing a dispersed phase introduced into the electrolyte, or electrolyte-colloids, in which the dispersed phase is formed during preparation or electrolysis [8-9]. Analysis of many experimental data [10-12] led to the conclusion that the process of formation of CEC consists of three main stages: 1) the supply of a particle to the cathode surface; 2) fixation (adsorption, adhesion) and 3) its overgrowth by precipitating metal. There are two ways of transferring particles from the electrolyte volume to the cathode surface: natural (under the action of forces of molecular kinetic origin) and artificial (stirring, artificial sedimentation, etc.). Thus, for the successful implementation of technological solutions for the application of CEC, the most important stage of research is the study of the mechanism of the process that claims to be an alternative to chromium plating (VI).

The aim of the present research is to study the kinetic features of the electrodeposition of a CEC based on Ni-B alloy in the presence of composite additives and the morphological features of the obtained CEC.

Ultrafine diamond (UDD) was used as a dispersed phase, which was most effective on the basis of comparative studies with other composite additives, such as nanostructured zirconium diboride (ZrB_2) powder, ultrafine silicon carbide (SiC) powder [11]. Boron additive (DHBN) was used for the purpose of increasing the microhardness and wear resistance of coatings. For research used electrolyte-colloid, composition (g/l): $NiCl_2 \cdot 6H_2O$ 200, H_3BO_3 30, NH_4Cl 20, $C_7H_5NO_3 \cdot S$ 1,0, $Na_2B_{10}H_{10}$ (DHBN) 1,9; UDD 1,2; pH 3 [8], in the studies the concentration of additives and pH varied: DHBN 0-1.9; UDD 0-1.2; pH 1-3.

2 Materials and Methods

Electrolytes were prepared on distilled water using reagents from Aldrich, chemically pure grade. To intensify mass transfer, as well as to distribute dissolved substances and suspended particles in the volume of the solution, the electrolyte was stirred using an electric magnetic stirrer. The current efficiency of metal, alloy, nickel-based CEC, as well as the hydrogen current efficiency were determined by the coulometric method. Polarization measurements were carried out using an Elins P-8nano potentiostat in a potentiodynamic mode at a potential change rate of 1 mV/s. The research was carried out in a three-electrode electrochemical cell at a temperature of 20° C. The working electrode was a flat nickel plate with an area of 0,01 dm². The non-working surface of the plate was insulated with an epoxy compound. The surface of the electrode under study was prepared according to the generally accepted procedure: the electrode was cleaned and polished to a

mirror finish, degreased with Viennese lime, activated with a 10% hydrochloric acid solution, washed in distilled water, placed in an electrochemical installation and kept to a steady-state potential. The auxiliary electrode was nickel; the reference electrode was silver chloride electrode. All potentials in the polarization dependences are given relative to the normal hydrogen electrode.

Morphological studies of electroplated coatings were obtained by the semi-contact method on a PHYWE atomic force microscope.

3 Results and discussion

A current efficiency of more than 100% is the most important characteristic of electrolytes containing fine particles (both introduced into the electrolyte and formed during electrolysis) involved in electrode processes [7]. Figure 1a shows the dependences of the current efficiency of (1) nickel and (2) hydrogen on the electrode potential in the electrolyte of the optimal composition for obtaining a wear-resistant nickel-boron-UDD ECC at pH 3, but in the absence of DHBN and UDD additives. Taking into account the confidence interval, the total current efficiency does not exceed 100%.

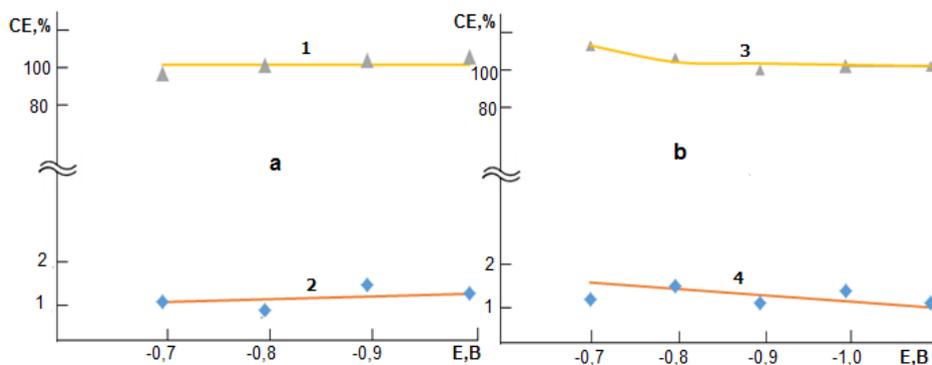


Fig. 1. Dependences of the current efficiency of nickel (1), CEC Ni-B-UDD (3) and hydrogen (2,4) on the electrode potential, obtained in an electrolyte of optimal composition. Temperature 20°C, concentration of additives, g/l: a - DHBN 0, UDD 0; b - DHBN 1,9, UDD 1,2.

In the same electrolyte, but already in the presence of the corresponding concentrations of DHBN and UDD (Figure 1b) at potentials of 0.59 V and 0.69 V, the CEC current efficiency is 11% and 105%, respectively.

We explain the results of these studies by the inclusion in the cathode deposit of fine particles introduced into the electrolyte, as well as the inclusion of both non-decomposed colloidal nickel compounds and poorly soluble nickel and boron compounds.

A number of theoretical models are known from the literature [13-15], which predict the process of formation of CEC and their composition, however, they are largely idealized; do not rely on experimental data. Therefore, of interest are the experimental data obtained in the study of the features of the electrodeposition of CEC. To investigate the effect of DHBN, UDD on the process of forming a composite coating, polarization studies were carried out and the obtained polarization characteristics were studied. Figure 2 a, b shows the polarization dependences obtained in solutions with different concentrations of UDD, but in the absence of DHBN at pH 1 and 3. In electrolytes not containing dispersed diamond particles (Figure 2 a, b, curves 3, 6) limiting currents in the area of working current densities is not observed. In our opinion, this shows that colloidal compounds of nickel hydroxides are rather finely dispersed, and the system is not monodisperse, therefore, limiting reduction currents are not recorded. When UDD is added to the solution, it can be

assumed that additional mechanical activation causes coagulation of some colloidal particles of nickel hydroxides. The appearance of limiting reduction currents (Figure 2 a, b, curves 4, 5), which have higher values when the maximum concentration of UDD is added, corresponds to an increase in the concentration of dispersed compounds of nickel hydroxides.

A decrease in polarization upon the addition of UDD to the electrolyte at pH 3, as well as an increase in the productivity of electrolytes containing a diamond additive, is apparently explained by the participation of UDD particles in additional mixing of the difficult-to-stir part of the diffusion layer together with colloidal nickel compounds.

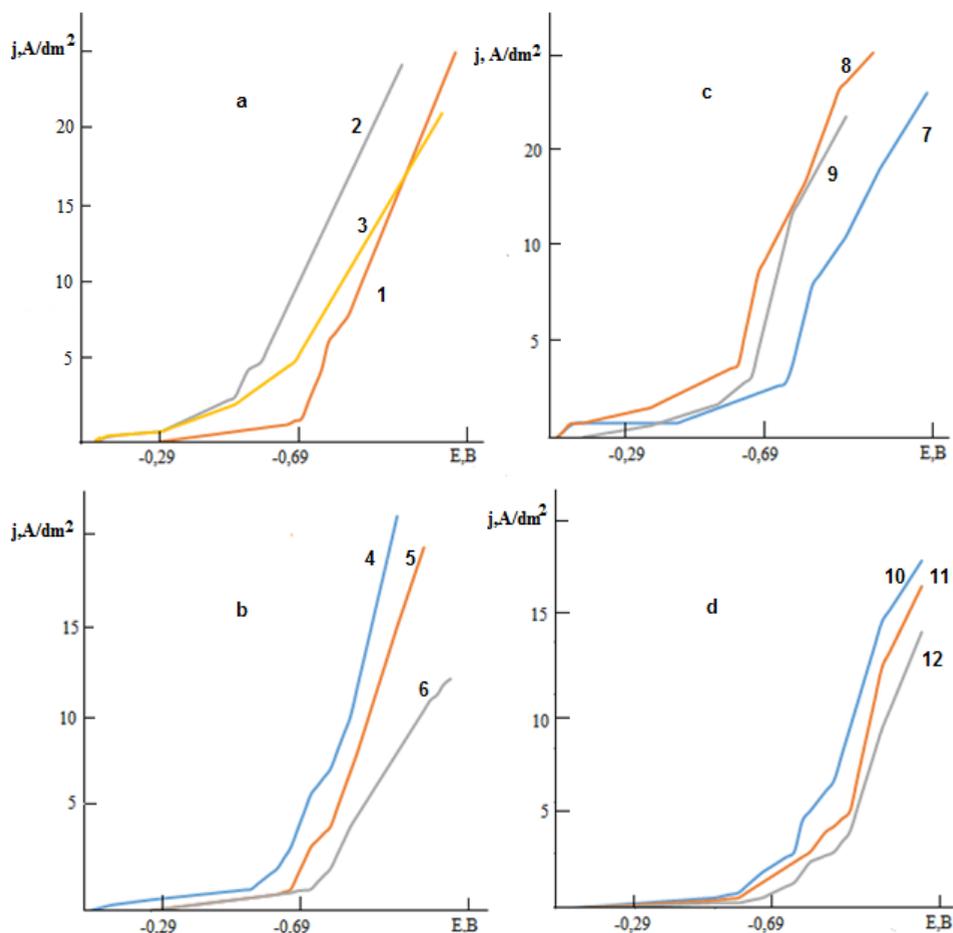


Fig. 2. Potentiodynamic polarization dependences obtained in an electrolyte of optimal composition, temperature 20°C. DHBN concentration, g/l: **0**, a - pH 1, b pH 4; concentration of DHBN, g/l: **1,9**, c - pH 1, g - pH 4. Concentration of UDD, g/l: **1,22** - 1, 4, 7, 10; **0,05** - 2, 5, 8, 11; **0** - 3, 6, 9, 12.

Subsequently, we studied the joint influence of UDD and DHBN on the process of CEC formation (Figure 2, c, d). In the area of obtaining high-quality precipitation, the appearance of two limiting currents was recorded, and in solutions only with DHBN (Figure 2, c, d, dependences 7, 8, 10, 11). In the process of electrolysis, the following processes are possible (Figure 2 c, d, dependences 8-12): 1) reduction of colloidal compounds of nickel hydroxides, which in the presence of a boron-containing additive (DHBN) become more stable and do not coagulate when adding the highest concentration of a composite additive (UDD) due to hydrophobic interactions (first limiting current); 2)

reduction concentration of sparingly soluble nickel and boron compounds near at the cathode (second limiting current). Composite diamond additive has the greatest effect on the formation of the colloidal system in solutions with pH 3 (Figure 2 d, dependences 10, 11). In electrolytes containing UDD there are decrease in polarization and increase productivity. Apparently, this is explained by the participation of the composite additive in the formation of a mobile pore system at the cathode surface and additional mixing of the near-electrode layer together by colloidal compounds of nickel hydroxides. The occurrence of limiting currents in solutions without DHBN (Figure 2 a, b, dependences 1,2,4,5) and in electrolytes containing DHBN (Figure 2 c, d, dependences 8-12) is probably explained by the values of the potentials of uncharged nickel surface. At the potentials of occurrence of limiting currents from -0,65 V to -0,85 V (Figure 2 a, b, curves 2-5), the surface of the nickel cathode carries a negative charge. However, in the region of potentials slightly distant from the potential of the uncharged nickel surface, the forces of chemical affinity can retain diamond particles, which, apparently, are negatively charged.

With a further decrease in the surface potential, the particles can be displaced from the electrode surface and desorbed. Let us analyze the results of kinetic studies in electrolytes containing DHBN and UDD. In the potential range from -0,77 V to -0,87 V, the forces of chemical affinity can retain both boron-containing anions and diamond particles, which, when the potential is shifted to the negative side, are desorbed and removed from the surface (Figure 2, c, d, dependences 7, 8,10,11).

These data are experimentally confirmed by the results of analyzes of the UDD and boron content in the coating. It was shown that an increase in the diamond content both in the electrolyte and in the coating led to an increase in the proportion of boron inclusion in the cathode deposit, which is explained by the adsorption of DHBN or its sparingly soluble compounds on diamond particles and their joint inclusion in the galvanic deposit.

Using the Gwyddion program the data of morphological studies of the obtained coatings were analyzed (Figure 3).

In accordance with the results of atomic force microscopy by 2D and 3D visualization, it was found that in the electrolyte without additives (coating - nickel) the average roughness is 5,63 μm , the peak height is 0,26 μm ; in electrolyte with the addition of DHBN (coating - Ni-B alloy), the average roughness is 3 microns, the peak height is 0,074 microns; in electrolyte with DHBN and UDD additives (Ni-B-UDD coating) the average roughness is 2.5 μm , the maximum peak height is 0,066 μm .

These studies show the leveling effect of the additives used, as well as sparingly soluble compounds of nickel, nickel and boron, on the structure of precipitates.

4 Conclusions

According to the carried out kinetic studies, it was established joint participation in the formation of the investigated type of galvanic coatings from colloidal compounds of various compositions: finely dispersed compounds of nickel hydroxides, poorly soluble compounds of nickel and boron formed in the electrolyte solution during its preparation. and/or during electrolysis, as well as ultrafine diamond introduced into the electrolyte as a composite additive. The study of the morphology of coatings of various compositions showed a smoothing effect of the additives used and the resulting compositions on the structure of the coatings.

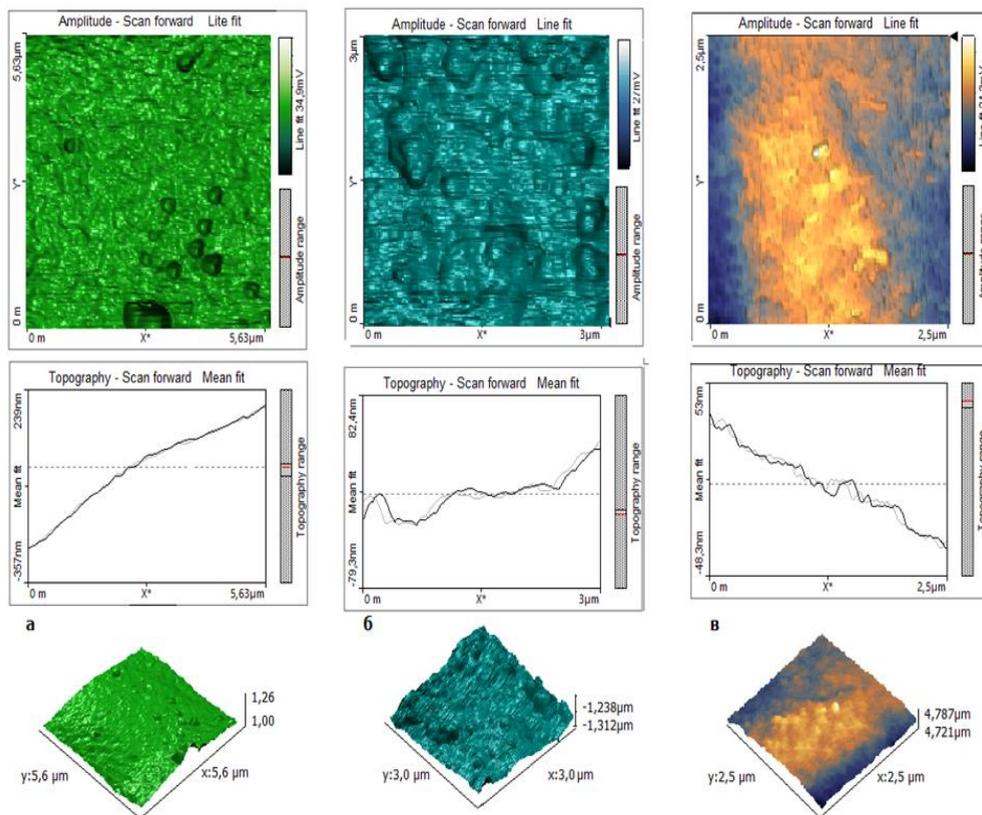


Fig. 3. Results of morphological analysis of coatings obtained from electrolyte-colloid of optimal composition at the following concentrations of additives, g/l: a - DHBN 0, UDA 0; b - DHBN 1,9, UDD 0; DHBN 1,9, UDD 1,2.

The study of the morphology of coatings of various compositions showed a smoothing effect of the applied and formed compositions.

References

1. V.T. Jelinek, *Galvanotekhnika i obrabotka poverkhnosti* **1**, 4-10 (2018) doi: 10.47188/0869-5326_2018_26_1_4
2. N.A. Polyakov, *Russian journal of electrochemistry* **9**, 858-872 (2016) doi:10.1134/S1023193516090081
3. V. Tseluikin, A. Yakovlev, *Russian Journal of Applied Chemistry* **5**, 614-619 (2019) doi: 10.1134/S1070427219050057
4. V. Rogozhin, E. Anan'eva, A. Abramov, *Russian Journal of Applied Chemistry* **9**, 1552-1555 (2016) doi:10.1134/S1070427216090251
5. E. Anan'eva, V. Rogozhin, V. Osmanov, M. Mikhaleenko, *Russian Journal of Applied Chemistry* **6**, 823-828 (2019) doi:10.1134/S1070427219060120
6. I. Matsui, N. Omura, T. Yamamoto, Y. Takigawa, *Surface and Coatings Technology* **15**, 411-417 (2018) doi: 10.1016/j.surfcoat.2018.01.041
7. L. Degtyar, I. Zhukova, V. Mishurov, *Materials Science Forum* **945**, 682-687 (2019) doi: 10.4028/www.scientific.net/MSF.945.682

8. L. Degtyar, I. Zhukova, V. Mishurov, *Materials Science Forum* **992**, 652-657 (2020) doi: 10.4028/www.scientific.net/MSF.992.652
9. L. Degtyar, I. Zhukova, V. Mishurov, E. Shubina, and V. Kovko, *E3S Web Conf.* **175**, 6 (2020) doi: doi.org/10.1051/e3sconf/202017505010
10. V.D. Jović, U.Č. Lačnjevac, B.M. Jović, *Modern Aspects of Electrochemistr*, 1-84 (2014) doi:10.1007/978-1-4939-0289-7_1
11. Z. Abdel Hamid, *Metallurgical Engineering* **1**, 29-42 (2014) doi: 10.14355/me.2014.0301.04
12. A. Martínez-Hernández, F. Manríquez-Guerrero, J. Torres et al., *Electrodeposition of Composite Materials*, 130-143 (2016) doi:10.5772/61858
13. A. Vakhrushev, E. Molchanov, A. Fedotov, *MATEC Web of Conferences* **242**, 01005 (2018) doi: 10.1051/matecconf/201824201005
14. H. Zhou, N. Du, L. Zhu, J. Shang, Zh. Qian, X. Shen, *Electrochimica Acta* **1**, 157-167 (2015) doi:10.1016/j.electacta.2014.10.122
15. N. Acet, D. Eroglu, *Journal of The Electrochemical Society* **2**, 31-36 (2018) doi: 10.1149/2.0451802jes