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# ELECTROCATALYTIC ACTIVITY OF NICKEL-BASED COATINGS DEPOSITED IN DES-ASSISTED PLATING BATHS CONTAINING CERIUM(III) IONS

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This paper concerns electrodeposition of coatings from electrolytes containing $NiCl_2$ (0.1 mol dm$^{-3}$) and $CeCl_3$ (0.1–0.4 mol dm$^{-3}$) salts dissolved in a deep eutectic solvent, ethaline (ethylene glycol+choline chloride). The electrochemical deposition was carried out at cathodic current densities from 1 to 5 mA cm$^{-2}$ and temperatures from 50 to 90$^0$C. It was shown that micromodification of the chemical composition of coatings with cerium occurred (no more than ~1–2.65 wt.% Ce), and the content of cerium in the coating was increased with an increase in the concentration of the Ce(III) salt in the plating electrolyte, an increase in the current density, and a decrease in the temperature. It was shown for the first time that the Ni-based electrodeposits micromodified with cerium exhibited an enhanced electrocatalytic activity in the reaction of hydrogen evolution in an alkaline medium (a decrease in the cathodic polarization by ~200–250 mV). Electrocatalytic activity correlated with the content of cerium in the coating. The enhancement of the efficiency of electrocatalysis resulting from micromodification of the chemical composition of the coatings with cerium was explained within the framework of the well-known concept of the synergistic effect of hypo-hyper-d-electronic combinations of transition metals. The use of electrolytes based on deep eutectic solvents provides additional opportunities for flexible control of the composition of deposited coatings and their electrocatalytic behavior via changes in the concentration of electrolyte components and electrolysis conditions in relatively wide intervals.

**Keywords**: electrocatalysis, hydrogen evolution reaction, electrochemical deposition, deep eutectic solvent, nickel, cerium.

### Introduction

Electrodeposited nickel coatings are widely used as electrocatalytic materials in the process of hydrogen evolution during water electrolysis [1,2]. The advantages of electrochemical catalysts of this type include relative cheapness and availability (compared to electrocatalysts based on noble metals), high electrocatalytic activity, stability, the ability to deposit and restore damaged coatings using electrolytes of different types. It is important that the electrocatalytic activity can be significantly increased by alloying nickel with a number of rare earth metals (Ce, Y, Pr, and Sm) [3,4]. Probably, the greatest interest in this context is the nickel-cerium alloy, since cerium is the most common rare earth element in the earth's crust. Electrodeposition could be one of the most convenient ways to obtain a Ni-Ce alloy, but the possibility of this method when using traditional aqueous electrolytes is limited due to the very negative electrode potential of cerium, which significantly complicates its codeposition with nickel, and the tendency of cerium ions to oxidize with the formation of the corresponding oxide $CeO_2$, which is formed in the near-electrode layer even under conditions of cathode polarization [5]. The use of non-aqueous electrolytes can largely solve these problems. In particular, it was previously established that a nickel-cerium alloy could be electrochemically deposited from an electrolyte based on the so-called deep eutectic solvents (DESs) [6]. Interest in

electrochemical systems of this type is due to significant environmental and economic advantages and special physicochemical characteristics of this new generation of ionic liquids [7]. The literature has already repeatedly reported on the potential possibilities of electrodeposition of various nickel-based electrocatalytic materials using DESs [8−10].

Among the numerous advantages of DES-based electrolytes, it should be noted the possibility of flexible control of the activity of deposited electrocatalysts via modification of their chemical composition and microstructure by introducing various alloying components into the nickel matrix. However, this advantage has not yet been fully exploited in previous studies. Thus, in particular, electrocatalytic nickel-cerium coatings deposited from DESs [6] were obtained under certain arbitrarily chosen electrodeposition conditions, and the nature of the influence of the electrolyte composition and the electrolysis parameters on the chemical composition and electrocatalytic performance of the coatings remained unclear. Therefore, the purpose of this study was to establish the influence of the concentration of cerium(III) ions in the DES-based electrolytes and deposition parameters (cathode current density and temperature) on the chemical composition, surface morphology, and electrocatalytic properties of the formed electrodeposits.

### Experimental

Electrolytes based on ethaline (a eutectic mixture of choline chloride and ethylene glycol), which is a typical representative of deep eutectic solvents, were used for the deposition of coatings. The method of preparation of ethaline did not differ from that previously described in previous publications [9−12]. Nickel(II) ions were introduced into the solution in the form of an anhydrous nickel(II) chloride salt, the electrolyte was stirred on a magnetic stirrer for 6−8 hours at a temperature of ~75$^0$C until the solid phase was completely dissolved. Next, cerium(III) ions were introduced into the electrolyte in the form of a solid salt $CeCl_3 \cdot 7H_2O$, the electrolyte was continued to be stirred on a magnetic stirrer for about 1 hour at a temperature of ~75$^0$C until the solid salt completely dissolved. To ensure the removal of excess moisture, the prepared electrolyte was heat-treated at a temperature of ~75$^0$C for several hours until the residual water content in the electrolyte was about 2−3 wt.%. The water content in the electrolyte was determined by the Fisher method.

Electrochemical deposition of coatings was carried out in galvanostatic mode in a two-electrode thermostated cell (the temperature was set with an error of ±0.5$^0$C). The volume of the electrolyte was 100 ml. Cathodic and anodic spaces were not separated. Nickel anodes were used for electrolysis. Copper foil samples (disc-shaped surface with a diameter of 1.5 cm) served as cathodes. The surface of these samples was chemically degreased, etched in an aqueous solution of hydrochloric acid, rinsed, and then a layer of copper with a thickness of about 5 μm was electrochemically deposited (the electrolyte contained 250 g dm$^{-3}$ $CuSO_4 \cdot 5H_2O$ and 50 g dm$^{-3}$ $H_2SO_4$, cathode current density was 10 mA cm$^{-2}$, and the temperature was 25$^0$C ). The freshly deposited copper surface was thoroughly washed in distilled water, quickly dried in a stream of air, and used for depositing in DES-assisted electrolytes. The duration of deposition using a stabilized source of direct electric current was selected in such a way that the amount of electricity of 10 mA·h was passed. During electrolysis, the electrolyte was continuously stirred with a magnetic stirrer (500 rpm).

The weight of the deposited coatings was monitored gravimetrically, and the morphology and chemical composition of their surface were evaluated using the methods of scanning electron microscopy (SEM) and X-ray spectral electron probe microanalysis (EDX) using a Zeiss EVO 40XVP electron microscope and an Oxford INCA Energy 350 analyzer coupled with the electron microscope, respectively.

The electrocatalytic performance of the coatings was evaluated by recording the polarization curves of hydrogen evolution in an aqueous solution of 1 M NaOH at 25$^0$C. The method of electrocatalytic activity research was described in detail in a previous publication [11].

### Results and discussion

*Influence of electrolysis conditions and electrolyte composition on the chemical composition of coatings and their surface morphology*

At the first stage, the influence of the deposition temperature on the surface morphology of the coatings obtained from the electrolyte containing nickel(II) and cerium(III) salts dissolved in ethaline (Fig. 1) and their chemical composition (Table 1) was established. As can be seen, the surface of all investigated electrodeposits is built of spheroids of various sizes with a very small number of cracks and pores. As a general trend, it can be noted that an increase in temperature contributes to the formation of a more uniform surface morphology.

According to the results of EDX microanalysis, the investigated coatings contain nickel (as a dominant component), as well as cerium, carbon

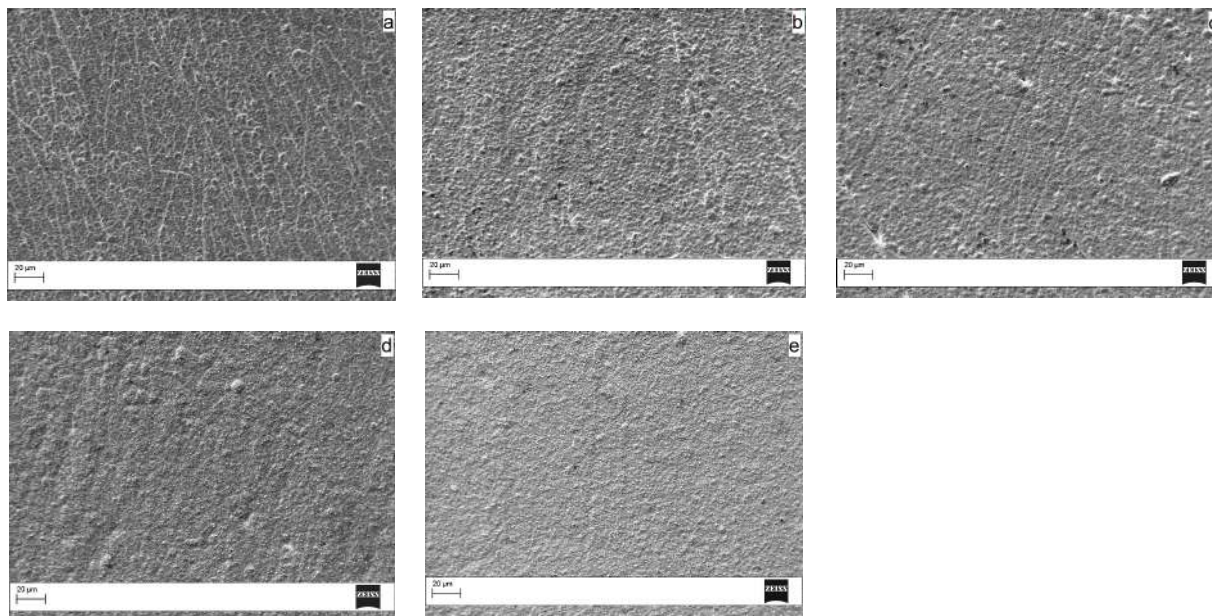*F.I. Danilov, L.S. Bobrova, L.M. Pavlenko, S.A. Korniy, V.S. Protsenko*

Fig. 1. SEM microphotographs of the surface of coatings deposited from an electrolyte containing 0.1 M Ni(II) and 0.2 M Ce(III) in ethaline at the cathodic current density of 5 mA cm$^{-2}$ at different temperatures ($^0$C):
a − 50, b − 60, c − 70, d − 80, and d − 90

T a b l e  1

**Effect of electrodeposition temperature on the chemical composition of coatings deposited from an electrolyte containing 0.1 M Ni(II) and 0.2 M Ce(III) in ethaline at the cathodic current density of 5 mA cm$^{-2}$**

| Electrodeposition temperature, $^0$C | Content of the chemical element in the coating, wt.% | | | |
|---|---|---|---|---|
| | Ni | Ce | C | O |
| 50 | 90.74 | 1.66 | 3.35 | 4.25 |
| 60 | 92.46 | 0.70 | 4.04 | 2.79 |
| 70 | 92.98 | 0.16 | 4.21 | 2.65 |
| 80 | 93.20 | 0.18 | 4.34 | 2.28 |
| 90 | 94.68 | 0.00 | 3.27 | 2.05 |

and oxygen. As the temperature increases, there is a decrease in the content of cerium in the coatings, and at 90$^0$C cerium is practically absent in the coating (according to EDX data). It should be noted that the content of cerium did not exceed ~1.7 wt.%, so the determination of cerium was carried out almost at the limit of the sensitivity of the method used. However, there is no doubt that the obtained data well reflect the main trends of changes in the content of cerium when the electrochemical deposition conditions are changed.

Note that, considering the very low content of cerium in the formed electrodeposits, in this case it is correct to speak not so much about classical electrochemical alloying as about micromodification of the coating chemical composition with cerium.

The introduction of carbon and oxygen into coatings deposited from solutions based on deep eutectic solvents was previously observed when depositing nickel [13] and chromium [14]. The source of carbon and oxygen in the coatings is obviously the organic components of the electrolyte. It follows from the obtained data that an increase in temperature leads to a decrease in the oxygen content in the coating. As for the carbon content, it is not possible to follow a clear trend of change of its content with temperature, and it is at the level of approximately 3.3−4.3 wt.%.

An increase in the content of cerium in the electrodeposits with a decrease in temperature is a desirable effect, taking into account the literature data on the positive effect of doping with cerium on electrocatalytic activity [3,4]. However, lowering the temperature of the electrolyte based on DES results in a significant increase in the viscosity of the electrolyte and a decrease in its electrical conductivity, which are extremely negative phenomena. Considering these circumstances, further experiments were conducted at the electrolyte temperature of 50$^0$C.

At the next stage of the work, the influence of the current density and the concentration of cerium(III) salt in the solution on the deposition of coatings was investigated. Figure 2 shows the influence of the concentration of cerium(III) ions in the electrolyte and the cathodic current density on the surface morphology of the coatings deposited

from ethaline-based electrolytes at a constant temperature. For comparison, an SEM image of the surface morphology of a nickel coating deposited from an electrolyte containing no cerium(III) salt is shown (Fig. 2,a). Note that the last coating was deposited from an electrolyte containing 0.25 M Ni(II) and at the current density of 1 mA cm$^{-2}$, since when the concentration of nickel(II) ions is reduced to 0.1 M and the current density is increased, it is not possible to obtain a compact coatings with satisfactory adhesion to the substrate. As can be seen, the «nickel» coating exhibits the presence of
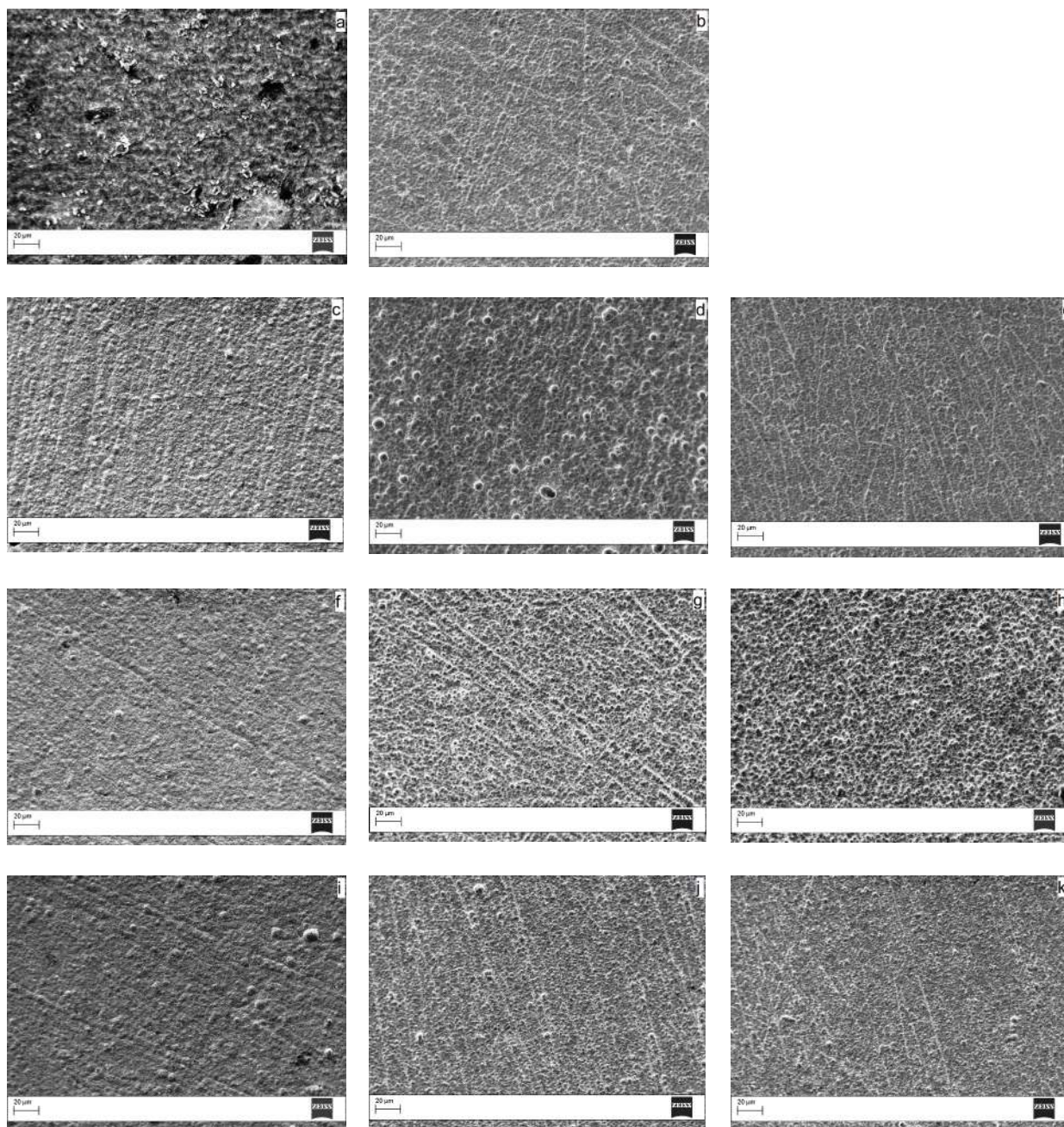


Fig. 2. SEM microphotographs of the surface of coatings deposited from electrolytes containing 0.1 M Ni(II) (b−k) in ethaline at different concentrations of cerium(III) salt in the electrolyte and different current densities: b − 0.1 M Ce(III), 3 mA cm$^{-2}$; c − 0.2 M Ce(III), 1 mA cm$^{-2}$; d − 0.2 M Ce(III), 3 mA cm$^{-2}$; e − 0.2 M Ce(III), 5 mA cm$^{-2}$; f − 0.3 M Ce(III), 1 mA cm$^{-2}$; g − 0.3 M Ce(III), 3 mA cm$^{-2}$; h − 0.3 M Ce(III), 5 mA cm$^{-2}$; i − 0.4 M Ce(III), 1 mA cm$^{-2}$; j − 0.4 M Ce(III), 3 mA cm$^{-2}$; and k − 0.4 M Ce(III), 5 mA cm$^{-2}$. a − coating deposited from an electrolyte containing no added cerium(III) salt at the concentration of nickel(II) ions of 0.25 mol dm$^{-3}$ at the current density of 1 mA cm$^{-2}$. The temperature in all cases is 50$^{0}$C

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asymmetric crystallites of various sizes; there are also a significant number of pores. The introduction of Ce(III) salts into the composition of the plating electrolyte contributes to the formation of a more uniform spheroid surface morphology, in which pores and cracks are almost absent. At the same time, no clear patterns of changes in surface morphology can be observed with increasing current density and concentration of cerium(III) salt in the electrolyte.

The influence of the Ce(III) salt concentration and the cathodic current density on the chemical composition of the formed coatings is given in Table 2.

In all cases, the dominant component in the coating is nickel, the content of which, depending on the composition of the electrolyte and deposition conditions, ranges from ~72 to 92 wt.%. It is interesting that the lowest nickel content was observed when deposited from an electrolyte that does not contain added cerium(III) salt at all. At the same time, the coating contains a high amount of carbon and oxygen, which probably determines the formation of a very defective surface morphology. The introduction of a cerium(III) salt into the electrolyte containing nickel(II) chloride dissolved in ethaline results in a micromodification of the coating chemical composition with cerium (no more than 2.65 wt.%), which is accompanied by a significant increase in the nickel content and a decrease in the carbon and oxygen contents.

Table 2

**Influence of Ce(III) salt concentration and cathodic current density on the chemical composition of coatings deposited from an electrolyte containing 0.1 M Ni(II)\* at the temperature of 50⁰C**

| Ce(III) salt concentration, mol dm⁻³ | Cathodic current density, mA cm⁻² | Content of the chemical element in the coating, wt.% | | | |
|---|---|---|---|---|---|
| | | Ni | Ce | C | O |
| 0 | 1 | 72.14 | – | 6.75 | 21.11 |
| 0.1 | 3 | 91.62 | 1.00 | 3.64 | 3.74 |
| 0.2 | 1 | 92.05 | 0.51 | 4.01 | 3.42 |
| | 3 | 92.63 | 1.17 | 3.26 | 2.95 |
| | 5 | 90.74 | 1.66 | 3.35 | 4.25 |
| 0.3 | 1 | 92.02 | 0.50 | 4.11 | 3.37 |
| | 3 | 91.85 | 1.74 | 2.55 | 3.85 |
| | 5 | 89.69 | 1.95 | 2.44 | 5.92 |
| 0.4 | 1 | 92.54 | 0.59 | 3.67 | 3.20 |
| | 3 | 91.56 | 1.56 | 3.02 | 3.86 |
| | 5 | 89.79 | 2.65 | 2.79 | 4.77 |

Note: * − when the coating was deposited from an electrolyte containing no added cerium(III) salt, the concentration of nickel(II) ions was 0.25 mol dm⁻³.

An increase in the concentration of cerium(III) salt leads to a natural increase in the content of cerium in the coating. Some deviation from this dependence, which can be observed for isolated values given in Table 2, are probably related to the above-mentioned fact that the content of cerium is actually on the margin of error of its determination. The trend towards an increase in the content of cerium in the coating is more clearly visible with an increase in the deposition current density. It is interesting that changes in the content of cerium and carbon in the electrodeposits when changing certain conditions of deposition are antibatic: an increase in the content of cerium, as a rule, is accompanied by a corresponding decrease in the content of carbon. For oxygen introduced into the coating, such a tendency is not noticeable.

It is important to note that the data on the content of cerium in the coating deposited from an electrolyte based on ethaline, obtained in this work, differ significantly from the results of a previous study [6]. In that work, with an electrolyte containing 0.2 M CeCl₃ and 0.1 M NiCl₂ dissolved in ethaline, the authors managed to produce electrocatalytic coatings containing approximately 85% Ce and 15% Ni, while in our study at the same concentrations of cerium and nickel chloride salts, the content of Ce in the coating did not exceed 2.65 wt.%. Such a difference is obviously caused by the difference in other conditions of the electrodeposition process. In particular, the electrolyte used in study [6] additionally contained 0.2 M NH₄Cl and 0.5 M H₃BO₃. Besides, electrolysis was carried out at the temperature of 25⁰C and the current density of 10 mA cm⁻². In our experiments, under such conditions, it was not possible to obtain compact electrodeposits on the cathode. Even at the temperature of 50⁰C and continuous stirring of the electrolyte (500 rpm), powdery and spongy coatings poorly bonded to the substrate were formed during electrolysis at current densities greater than 5 mA cm⁻², probably as a result of reaching the maximum current density. However, at current densities up to 5 mA cm⁻², it was possible to obtain compact coatings with good adhesion to the copper substrate. As shown below, the introduction of a very small amount of cerium into the coating under such conditions was sufficient to ensure satisfactory electrocatalytic activity.

*Influence of electrolysis conditions and electrolyte composition on the electrocatalytic properties of deposited coatings in the reaction of hydrogen evolution*

In order to evaluate the electrocatalytic behavior of coatings micromodified with cerium, the

polarization curves of hydrogen evolution reaction were obtained in an aqueous solution of 1 M NaOH using the deposited coatings as cathode materials. As expected, all recorded polarization dependences had an exponential character, typical of hydrogen evolution in a sufficiently concentrated alkaline aqueous solution. Figure 3 shows a series of polarization dependences registered for coatings deposited at different temperatures (50−90⁰C). As can be seen, the highest polarization of the cathodic process is observed on the coating deposited from an electrolyte that does not contain cerium salt at all. Micromodification of the coating chemical composition with cerium contributes to a significant decrease in cathodic polarization (shift of the polarization curve towards more positive potentials by approximately 300 mV at the deposition temperature of 50⁰C). The strongest electrocatalytic effect is observed for the coating deposited at the lowest temperature used (50⁰C). An increase in temperature leads to a gradual weakening of the electrocatalytic effect. However, even at the temperature of 90⁰C, when, according to EDX spectra, the coating does not contain cerium at all (Table 1), the polarization of hydrogen evolution is still somewhat lower than when using a coating deposited from an electrolyte that does not contain added cerium(III) salt. Probably, in this case, the chemical composition of the coating is micromodified and cerium is introduced into it (at a level lower than the sensitivity of the detection method), which is reflected accordingly on the electrocatalytic performance.

The effect of strengthening the electrocatalytic action resulted from the micromodification of the chemical composition of the electrodeposits with cerium can be illustrated very clearly on a series of polarization curves of hydrogen evolution on coatings deposited from electrolytes with different Ce(III) salt content (Fig. 4). As can be seen, there is a noticeable shift of the curves in the direction of lower cathodic polarization with an increase in the concentration of cerium(III) salt.

The polarization curves of the hydrogen evolution process, recorded on electrocatalytic materials electrodeposited from electrolytes of different compositions and under different electrolysis conditions, and processed in the coordinates of the Tafel equation, allowed calculating the corresponding Tafel constants, transfer coefficients, and exchange current densities (Tables 3 and 4)[1].
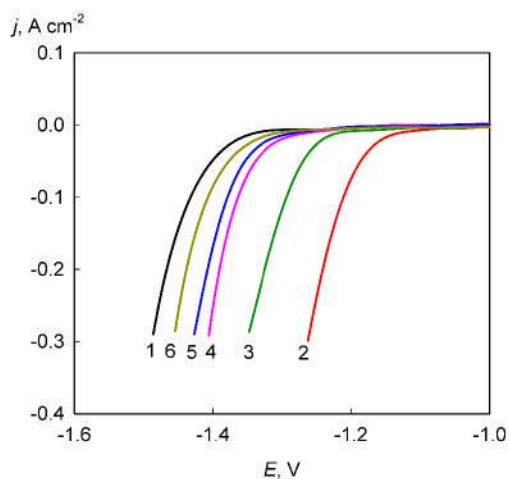


Fig. 3. Polarization curves of hydrogen evolution in an aqueous solution of 1 M NaOH on coatings deposited from an electrolyte containing 0.1 M Ni(II) and 0.2 M Ce(III) in ethaline at the cathodic current density of 5 mA cm⁻² at different temperatures (⁰C): 2 − 50; 3 − 60; 4 − 70; 5 − 80; and 6 − 90. Curve 1 corresponds to a coating deposited from an electrolyte containing no added cerium(III) salt at the concentration of nickel(II) ions of 0.25 mol dm⁻³ at the current density of 1 mA cm⁻²
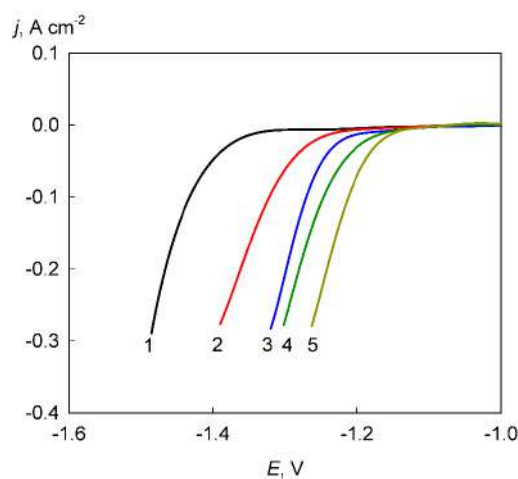
Fig. 4. Polarization curves of hydrogen evolution in an aqueous solution of 1 M NaOH on coatings deposited at the cathodic current density of 5 mA cm⁻² and the temperature of 50⁰C from an electrolyte containing 0.1 M Ni(II) and a variable concentration of Ce(III) in ethaline: 2 − 0.1 M; 3 − 0.2 M; 4 − 0.3 M; and 5 − 0.4 M. Curve 1 corresponds to a coating deposited from an electrolyte containing no added cerium(III) salt at the concentration of nickel(II) ions of 0.25 mol dm⁻³ at the current density of 1 mA cm⁻²

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[1] Polarization curves of hydrogen evolution obtained on samples deposited at different current densities, the kinetic data for which are given in Table 4, are not provided in the article.

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Table 3

**Kinetic parameters of the hydrogen evolution reaction in an aqueous solution containing 1 M NaOH when using electrocatalytic coatings deposited at different temperatures from an electrolyte containing 0.1 M Ni(II) and 0.2 M Ce(III) in ethaline at the cathode current density of 5 mA cm$^{-2}$**

| Electrodeposition temperature, $^0$C | Kinetic parameters | | | |
|---|---|---|---|---|
| | Tafel constants | | exchange current density, $j_0$, A cm$^{-2}$ | transfer coefficient $\alpha$ |
| | –a, V | –b, V dec$^{-1}$ | | |
| 50 (without Ce(III))* | 0.635 | 0.213 | $1.04 \cdot 10^{-3}$ | 0.28 |
| 50 | 0.249 | 0.089 | $1.66 \cdot 10^{-3}$ | 0.66 |
| 60 | 0.363 | 0.110 | $5.06 \cdot 10^{-4}$ | 0.54 |
| 70 | 0.481 | 0.137 | $3.08 \cdot 10^{-4}$ | 0.43 |
| 80 | 0.443 | 0.106 | $6.48 \cdot 10^{-5}$ | 0.56 |
| 90 | 0.628 | 0.230 | $1.85 \cdot 10^{-3}$ | 0.26 |

Note: * – this line shows data for a coating deposited from an electrolyte containing no added cerium(III) salt, the concentration of nickel(II) ions was 0.25 mol dm$^{-3}$ and the deposition current density was 1 mA cm$^{-2}$.

Attention is drawn to a sufficiently large spread of the values of the transfer coefficient of the hydrogen evolution reaction (in the range from 0.28 to 0.66). At first glance, such changes could indicate certain changes in the electrochemical reaction mechanism. However, as a first approximation, it can be assumed that the transfer coefficients approach the «traditional» value of 0.5, which in the case of the reaction of electrochemical hydrogen evolution from alkaline solutions on transition metals is usually associated with the slow Volmer stage (i.e. electrochemical reduction of hydrogen from water molecules, accompanied by formation of adsorbed hydrogen atoms on the surface) [10,11]. In our opinion, the observed deviations of the transfer coefficient from its «theoretical» value (0.5) are rather related not to changes in the mechanism of the electrochemical reaction, but to changes in the adsorption conditions resulting from the micromodification of the coating chemical composition with cerium. Indeed, a change in the state of the surface due to the introduction of cerium can cause certain changes in the adsorption parameters of water molecules and hydrogen atoms, which leads to a corresponding change in the apparent values of the transfer coefficient. It is this, first of all, that causes irregularities in the trends in the value of exchange current densities with a gradual change in certain electrocatalyst deposition conditions, since values of $j_0$ were calculated by extrapolating the Tafel dependence to zero polarization using the equation $\log j_0 = -\dfrac{a}{b}$.

Therefore, the Tafel constant «a» is a more reliable value in this case that can characterize the electrocatalytic properties of the coatings.

Table 4

**Kinetic parameters of the hydrogen evolution reaction in an aqueous solution containing 1 M NaOH when using electrocatalytic coatings deposited at the temperature of 50$^0$C at different contents of Ce(III) salt and at different current densities***

| Ce(III) salt concentration, mol dm$^{-3}$ | Cathodic current density, mA cm$^{-2}$ | Kinetic parameters | | | |
|---|---|---|---|---|---|
| | | Tafel constants | | exchange current density, $j_0$, A cm$^{-2}$ | transfer coefficient, $\alpha$ |
| | | –a, V | –b, V dec$^{-1}$ | | |
| – | 1 | 0.635 | 0.213 | $1.04 \cdot 10^{-3}$ | 0.28 |
| 0.1 | 3 | 0.417 | 0.132 | $6.81 \cdot 10^{-4}$ | 0.45 |
| 0.2 | 1 | 0.392 | 0.134 | $1.20 \cdot 10^{-3}$ | 0.44 |
| | 3 | 0.321 | 0.100 | $5.99 \cdot 10^{-4}$ | 0.59 |
| | 5 | 0.248 | 0.089 | $1.66 \cdot 10^{-3}$ | 0.66 |
| 0.3 | 1 | 0.388 | 0.148 | $2.35 \cdot 10^{-3}$ | 0.40 |
| | 3 | 0.299 | 0.106 | $1.53 \cdot 10^{-3}$ | 0.56 |
| | 5 | 0.364 | 0.141 | $2.62 \cdot 10^{-3}$ | 0.42 |
| 0.4 | 1 | 0.320 | 0.113 | $1.44 \cdot 10^{-3}$ | 0.52 |
| | 3 | 0.254 | 0.098 | $2.49 \cdot 10^{-3}$ | 0.61 |
| | 5 | 0.218 | 0.098 | $5.99 \cdot 10^{-3}$ | 0.60 |

Note: * – when the coating was deposited from an electrolyte containing no added cerium(III) salt, the concentration of nickel(II) ions was 0.25 mol dm$^{-3}$.

It follows from the obtained data that the coatings deposited from the electrolyte without added cerium(III) salt have the lowest electrocatalytic activity (the highest absolute value of the Tafel constant «a»). With an increase in the concentration of Ce(III) salt in the electrolyte, a decrease in the temperature, and an increase in the cathodic current density, in general, there is a tendency to a decrease in the absolute value of the Tafel constant «a», which means an increase in the electrocatalytic activity of the coating as an electrode material. It is important that the observed changes in electrocatalytic behavior correlate well with changes in the content of cerium in the coating when varying one or another factor that determines the electrodeposition conditions (Tables 1 and 2): the more cerium the coating contains, the higher its activity as an electrocatalyst. Therefore, micromodification of the coating chemical composition with cerium is the main reason for the increase in electrocatalytic activity in the reaction of hydrogen evolution in an alkaline environment. Correlations between the content of other elements introduced into the coating (carbon and oxygen) are not observed.

It is interesting to note that the decrease in the polarization of hydrogen evolution when a small amount of cerium (up to 2.65 wt.%) is introduced into a nickel-based coating is comparable, and in some cases even greater, than the effect observed in work [6] when a coating with very high content of cerium (85%) was deposited. The obtained data indicate a significant prospect of changing the electrocatalytic behavior of coatings by including a very small amount of alloying components in their composition (i.e. via micromodification) and confirm the need for careful selection of electrolysis conditions to ensure the highest electrocatalytic effect.

The found effect of a significant increase in electrocatalytic activity resulting from micromodification of the chemical composition of the deposited films with cerium is well consistent with known ideas about the synergistic effect of enhancing electrocatalysis within the concept of hypo-hyper-d-electronic combinations of transition metals [15]. Indeed, it was noted in the literature that the combination of $d^8$-orbitals of Ni and $d^1$-orbitals of Ce should lead to the formation of an electronic structure that promotes higher electrocatalytic activity [4]. In our work, it was shown for the first time that such a synergistic effect can be observed even with a very small content of an alloying additive (cerium) in the alloy.

### Conclusions

Ii was stated for the first time that nickel-based coatings can be micromodified by introducing a small amount of cerium (up to 2.65 wt.%) into them via electrochemical deposition from an electrolyte based on a eutectic mixture of choline chloride and ethylene glycol containing dissolved nickel(II) and cerium(III) chlorides. Under the used conditions of electrolysis, compact coatings were formed that are well bonded to the copper substrate. It was shown that the presence of even a small amount of cerium in the electrodeposit is sufficient for a significant increase in the electrocatalytic activity of the coatings when they are used as electrode materials in the reaction of cathodic evolution of hydrogen in an aqueous solution of 1 M NaOH. In particular, in some cases, the cathodic polarization of hydrogen evolution was decreased by ~200−250 mV, and the calculated exchange current density increased approximately 6 times compared to the electrocatalyst electrochemically deposited in the absence of cerium(III) ions in the plating electrolyte. The amount of cerium introduced into the coating increases with an increase in the concentration of Ce(III) ions in the electrolyte, an increase in the current density, and a decrease in the temperature. A correlation is observed between the electrocatalytic activity and the content of cerium in the coating. The use of an electrolyte based on DES makes it possible to flexibly influence the electrocatalytic characteristics of the formed electrocatalysts by changing the concentration of cerium(III) salt in the deposition electrolyte, temperature and current density within wide limits.

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**ЕЛЕКТРОКАТАЛІТИЧНА АКТИВНІСТЬ ПОКРИТТІВ НА ОСНОВІ НІКЕЛЮ, ОСАДЖЕНИХ З ЕЛЕКТРОЛІТІВ НА ОСНОВІ DES, ЩО МІСТЯТЬ ІОНИ ЦЕРІЮ(III)**

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Досліджено закономірності електроосадження покриттів з електролітів, що містять розчинені солі NiCl$_2$ (0.1 моль/дм$^3$) і CeCl$_3$ (0.1−0.4 моль/дм$^3$) в низькотемпературному евтектичному розчиннику ethaline (етиленгліколь+ +холін хлорид) при катодних густинах струму від 1 до 5 мА/см$^2$ та температурах від 50 до 90$^0$C. Показано, що відбувається мікромодифікування хімічного складу покриттів за рахунок впровадження церію (не більше ~1−2.65 мас.%), причому вміст церію в покритті зростає при підвищенні концентрації солі Ce(III) в електроліті для осадження, збільшенні густини струму та зниженні температури. Уперше показано, що гальванопокриття на основі Ni, мікромодифіковані церієм, проявляють підвищену електрокаталітичну активність у реакції виділення водню в лужному середовищі (зменшення катодної поляризації на ~200−250 мВ). Електрокаталітична активність корелює з вмістом церію в покритті. Підсилення ефективності електрокаталізу при мікромодифікуванні хімічного складу покриття церієм пояснюється у рамках відомої концепції про синергетичний ефект при гіпо-гіпер-d-електронну комбінацію перехідних елементів. Використання електролітів на основі низькотемпературних евтектичних розчинників надає додаткові можливості для гнучкого керування складом осаджених покриттів і їх електрокаталітичною поведінкою за рахунок зміни концентрації компонентів електроліту і умов проведення електролізу в широких інтервалах.

**Ключові слова**: електрокаталіз, реакція виділення водню, електрохімічне осадження, низькотемпературний евтектичний розчинник, нікель, церій.

## ELECTROCATALYTIC ACTIVITY OF NICKEL-BASED COATINGS DEPOSITED IN DES-ASSISTED PLATING BATHS CONTAINING CERIUM(III) IONS

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This paper concerns electrodeposition of coatings from electrolytes containing $NiCl_2$ (0.1 mol dm$^{-3}$) and $CeCl_3$ (0.1−0.4 mol dm$^{-3}$) salts dissolved in a deep eutectic solvent, ethaline (ethylene glycol+choline chloride). The electrochemical deposition was carried out at cathodic current densities from 1 to 5 mA cm$^{-2}$ and temperatures from 50 to 90$^0$C. It was shown that micromodification of the chemical composition of coatings with cerium occurred (no more than ~1−2.65 wt.% Ce), and the content of cerium in the coating was increased with an increase in the concentration of the Ce(III) salt in the plating electrolyte, an increase in the current density, and a decrease in the temperature. It was shown for the first time that the Ni-based electrodeposits micromodified with cerium exhibited an enhanced electrocatalytic activity in the reaction of hydrogen evolution in an alkaline medium (a decrease in the cathodic polarization by ~200−250 mV). Electrocatalytic activity correlated with the content of cerium in the coating. The enhancement of the efficiency of electrocatalysis resulting from micromodification of the chemical composition of the coatings with cerium was explained within the framework of the well-known concept of the synergistic effect of hypo-hyper-d-electronic combinations of transition metals. The use of electrolytes based on deep eutectic solvents provides additional opportunities for flexible control of the composition of deposited coatings and their electrocatalytic behavior via changes in the concentration of electrolyte components and electrolysis conditions in relatively wide intervals.

**Keywords**: electrocatalysis; hydrogen evolution reaction; electrochemical deposition; deep eutectic solvent; nickel; cerium.

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