Electrodeposition and Electrooxidation of Bimetallic Systems Co–Ni and Cu–Ni

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Article info	Abstract
	By means voltammetry method the characteristics of the electrodeposition and anodic oxidation processes of Cu, Ni, Co and Cu–Ni, Co–Ni were investigated in ammoniacal buffer supporting electrolyte using graphite electrode. The quantity, maximum currents and potentials of anodic peaks on the voltammetric curves in the case of binary system are defined by the ratio of metal ions concentration and electrodeposition procedure. The changes in the peaks parameters were attributed to the formation of bimetallic solid solutions with various contents of the components. It was shown that the result of coelectrodeposition of two metals on an inert substrate is determined not only the nature of the components of binary systems Co–Ni and Cu–Ni, but also features of the phase composition of bimetal in nano-state.

1. Introduction

The use of different carbon materials, both compact and with high surface area, in order to create metal-carbon composites, which serve as catalysts in chemical and electrochemical reactions, supercapacitor electrode materials and magnetic information carriers, might be quite promising. Particularly important in that context is the formation of bimetallic thin film or nanoisland systems containing metals with excellent magnetic and catalytic properties – copper, cobalt and nickel. Despite the fact that carbon materials have a very successful combination of properties, such as chemical resistance, high overpotential of hydrogen and oxygen evolution, electrolytic methods of deposition transition metals to the carbon substrates are rather poorly developed. This is especially the case in multi-component systems. The studies that have been carried out in that field mainly concern the peculiarities of electrodeposition of copper, nickel and cobalt from sulphate-citrate [1–3], chloride and boric [4, 5] electrolytes, using metal electrodes, vitreous carbon and glassy carbon [6–12].

Problems regarding electrochemical deposition of binary metallic systems on an inert surface are related to energy difficulties occurring in the formation of active sites required for crystallization of a new phase in the cathodic reduction process. A relevant problem yet to be solved is the development of control methods for structural and phase characteristics of electrolytic deposits, especially nanosized (2D-film structure, nanoislands), based on the study of the dependence of anodic oxidation parameters on phase composition, in combination with physical methods (atomic emission spectroscopy, X-ray photoelectron spectroscopy).The aim of this work is to investigation of the electrolytic deposition and subsequent anodic dissolution of binary systems Co–Ni and Cu–Ni using graphite substrate.

2. Experimental

The electrochemical measurements were performed in a three-electrode cell using a voltammetric analyser PU-1 with «GRAFIT» interfacial module. The working electrode was disk from impregnated graphite ($S = 1.5$ cm^2), the counter electrode – glassy carbon cylinder and the reference electrode – Ag/AgCl/0.1 M KCl. Before each experiment working and counter electrode surfaces were polished down to polishing cloths, thoroughly washed with pure water and transferred to the electrochemical cell. Chemicals used were sulfates of copper (II), cobalt (II) and nickel (II), 0.1 M NH$_4$Cl + NH$_4$OH (supporting electrolyte), all of analytical grade. All solutions were prepared with double-distilled water.

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Electrodeposition of binary systems Co–Ni, Cu–Ni was carried out in potentiostatic mode from electrolytes with various ratios of metal ions at the potential of the limiting diffusion current in the two methods: the first – in conditions of preliminary surface modification by adatoms one of the components (variant $Me_1{\rightarrow}Me_2$ and vice versa) within the following electrochemical step: 1–voltammetric (VA) scanning in the pure ammoniacal buffer electrolyte, potential window $(-1.6 \div +1.0)$V; 2 – adding of the Me_1 ions, electrodeposition at -1.6 V (15–120 s) and VA-scanning in the same window; 3 – adding of the Me_2, coelectrodeposition of both metals and registration of anodic voltammetric curve. The second method was simultaneous deposition of metals, in this case both Me_1 and Me_2 ions were added at the step 2. During this process the solution stirred with magnetic stirrer. Anodic oxidation was carried out in the same electrolytic cell in the potentiodynamic mode, scan rate – 100 mV/s.

3. Results and Discussion

The main factor determining the electrolytic films characteristics is the composition of supporting electrolyte and the electrode surface morphology. The criterion for the correctness of the choice of optimal composition of the electrolyte, is a metal oxidation peak on the voltammogramm obtained after the electrodeposition, stability of peak parameters and a linear relationship between the peak current and the concentration of metal ions. Based on the chemical properties of the objects successful results can be expected in the complexing buffer media, accordingly, in this study the supporting electrolyte was 0.1 M NH_4Cl+NH_4OH. Under these conditions, the electrochemical behavior of each component of the system was previously studied, and then the electrodeposition and anodic oxidation of binary systems Cu–Ni, Co–Ni.

The anodic VA – curves obtained for individual metals show the presence of oxidation peaks of cobalt and nickel phases at potentials -490 mV and -420 mV. It should be noted that the oxidation of copper occurs in two stages at $E_p = -40$ and $E_p = -240$ mV. The absolute amount of the metal phase on the electrode surface in each case linearly related to the concentration of metal ions in the electrolytic cell (Fig. 1).

Therefore, the electrodeposition proceeds no complicated side reactions and selected experimental conditions can be used for electrolytic synthesis of deposits of copper, cobalt, nickel and their binary systems. Comparing the slope of $I - c(M^{2+})$ and $Q - c(M^{2+})$ plots, we can conclude that the

deposition rate decreases in the series: Co>Cu>Ni.

In these conditions reduction of metal ions, apparently, occurs from ammonia complexes in accordance with the scheme:

$$Me(NH_3)_n^{2+} + 2e \rightarrow Me^0 + nNH_3$$
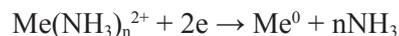
3.1. Binary system Co–Ni

Anodic voltammetric (VA) curves for Co-Ni deposits obtained in the first methods ($Me_1{\rightarrow}Me_2$) demonstrate the formation of one metal phase during electrodeposition. At any ratio $c(Co^{2+}):c(Ni^{2+})$ the single anodic peak is observed (Figs. 2 and 3) independently of the sequence of components addition. The peak parameters depend on the concentration ratio, time of deposition and scan rate. An increase in the nickel content results in a significant increasing in the peak potential, on the contrary – the addition of cobalt causes a gradually shift of the peak to the more negative position.

Voltammetric curves obtained at various times of simultaneous electrodeposition of both metals are shown on the Fig. 4. During the anodic oxidation of system Co-Ni with equiatomic components ratio on the VA curves was observed only one current peak for all considered times of cathodic deposition. Thus, the oxidation picture qualitatively similar to the one described above.
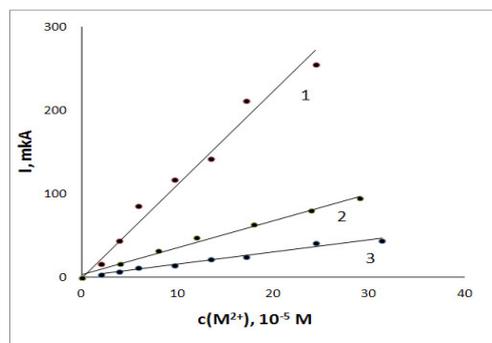

Fig.1. Dependence of the anodic oxidation currents on metal ions concentrations: Co^{2+} (1), Cu^{2+} (2), Ni^{2+} (3).
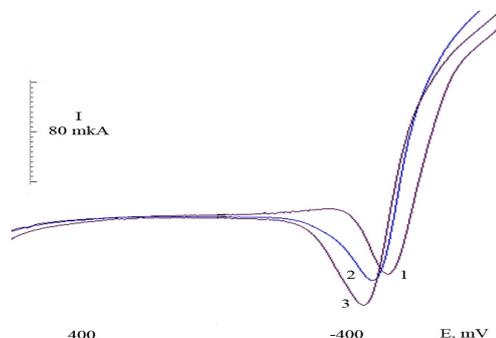

Fig. 2. Anodic VA curves for Co→Ni deposits obtained at concentrations: $c(Co^{2+}) = 5\cdot10^{-5}$ M (1), $c(Ni^{2+})$, 10^{-5} M: $1 - 0$; $2 - 1$; $3 - 2$.
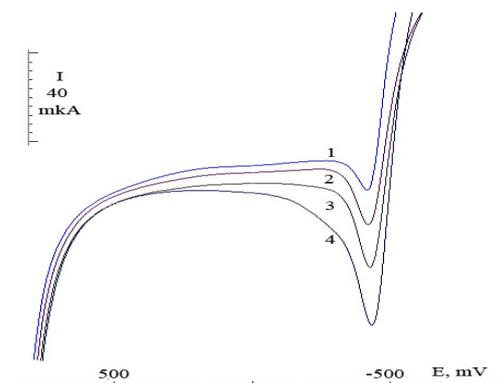
Fig. 3. Anodic VA curves for Ni→Co deposits obtained at concentrations: c (Ni^{2+}) = 0.9·10^{-4} M, c (Co^{2+}), 10^{-5} M: 1 – 0; 2 – 1; 3 – 2; 4 – 4.
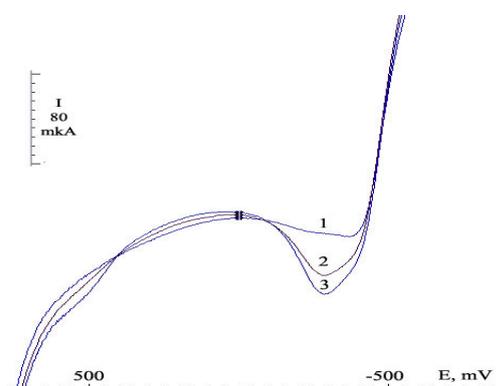

Fig. 4. Anodic VA curves for Co–Ni deposits obtained at simultaneous deposition time: 1) 15 s, 2) 30 s, 3) 45 s; at concentrations: c(Co^{2+}) = 9·10^{-5} M, c(Ni^{2+}) = 2·10^{-5} M.
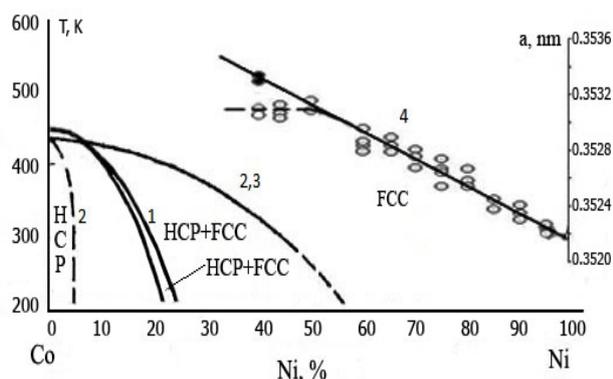

Fig. 5. Phase digram of the binary system Co-Ni (low temperature area) – 1, 2 and fragment of PD of nanosized system (3) with dependence of lattice parameter on composition (4) [15].

At the same time, the deposition of the components from the solution richer in cobalt leads to the formation of the complex-shaped peaks in the anodic stage (Fig. 4). Each of these peaks, to a first approximation, are the result of the superposition of two peaks. Upon that peak potentials differ

significantly from oxidation potentials of the individual cobalt and nickel phases. The linear dependence of the peak currents on the deposition time are an indication of the quantitative cathodic reduction of metal ions.

As is known, the oxidation peak potential correlates with thermodynamic stability of the metal phase at the electrode surface, in the case of electrolytic alloys – with the mixing energy (ΔG_{mix}). This value depends on the crystallographic structure and molar fractions of the components in the alloy [11].

Will discuss the obtained results taking into consideration the phase composition data for the system Co–Ni in the macroscale and nanosized states. Information about the phase diagrams (PD) of macroscale equilibrium system Co-Ni for the low temperatures region is controversial (Fig. 5, according [14, 15]). It is typical for many phase diagrams (not only metal systems) because of the difficulties in reaching the equilibrium state at low temperatures.

Phase diagrams of nanosized polymetals are different noticeably than that for the corresponding PD of macroscale equilibrium systems. The main differences of a general nature are discussed in [16–17]. According to these data, in the nickel-rich compositions field a solid solution based on the FCC lattice of nickel is formed with a lower limit of nickel solubility (according to different sources), it is shown in Fig. 5. There are also two-phase field and cobalt-rich solid solution field, the boundaries of which for a «massive» system at low temperatures can not be regarded as firmly established. For nanosized systems they are also identified with certain error. Based on the characteristics of the observed anodic processes, compositions according Figs. 2–4, there is reason to be attributed to solid solutions rich in cobalt and nickel, respectively (i.e. FCC and HCP fields of PD).

In point of fact, on the VA curves corresponding to these compositions, there is the single symmetric peak, which is shifted gradually (for high Co:Ni ratio) from the cobalt oxidation field to the nickel oxidation field with increasing nickel content. Conversely, in the nickel-reach compositions an increasing in cobalt content results in the peak displacement to the more negative potentials, where the oxidation of cobalt occurs. The observed phenomenon may be related to the changes in the mixing energy at change of the solid solution composition [11, 18]. The simultaneous oxidation of the components of the electrolytic deposit with constant and equal rates is a condition for the realization of this process. This is confirmed by the observed dependence of the charge under the peak (quantity of electricity) on the components concentrations (Figs. 6 and 7). It is interesting to note that the dependences

$Q = f(c_M)$ proved sensitive to the deposition methods (sequence of component addition). The increasing complexity of anodic peaks and curves $Q = f(c_{Co})$ may be associated with two-phase structure of the systems having the corresponding compositions.
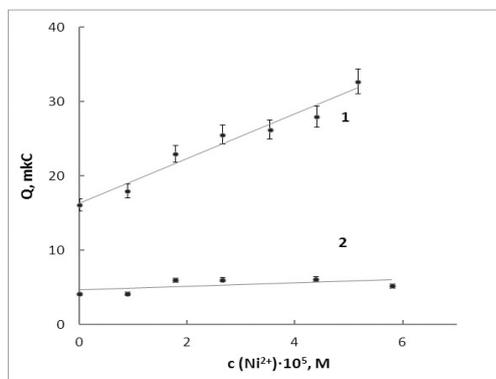

Fig. 6. Dependence of the quantity of electricity under anodic peak on Ni^{2+} concentration for Co→Ni deposits obtained from solutions containing $c(Co^{2+})$, 10^{-5} M: 1–13; 2–5.
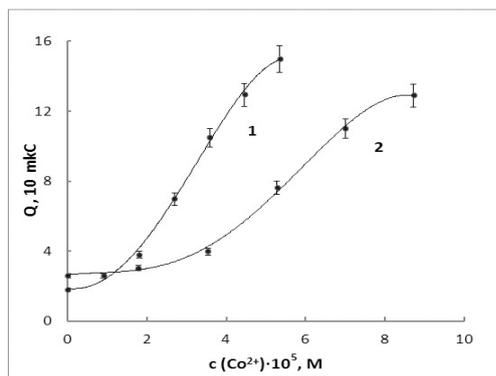

Fig. 7. Dependence of the quantity of electricity under anodic peak on Co^{2+} concentration for Ni→Co deposits, obtained from solution containing $c(Ni^{2+})$, 10^{-5} M: 1–9·; 2–13.

3.2. Binary system Cu–Ni

Anodic VA curves for the electrolytic deposits Cu–Ni reached in nickel obtained by means the first deposition method are shown on Figs. 8 and 9. These curves differ markedly from the one obtained for the Co–Ni oxidation. The study of the structural and phase characteristics of the nanosized (NS) powders Cu-Ni [17] showed a significant difference between its PD and PD of macroscale equilibrium system (Fig. 10). Nanosized Cu-Ni powders synthesized by means chemical reduction with hydrazine-hydrate in almost the entire composition field contain two phases of FCC none equilibrium solid solutions with the dependence of the lattice

parameter on the composition shown in Fig. 11. The results of voltammetric studies represent these features of PD Cu-Ni.

VA for individual copper oxidation with two peaks corresponding to the two-step oxidation $(Cu^0 \rightarrow Cu^+ \rightarrow Cu^{2+})$ transformed in a complicated manner during binary system oxidation. The «main» peak $(Cu^0 \rightarrow Cu^+)$ is not observed, the «bimetallic» peak $(E_p \approx -390$ mV) gradually shifts towards negative potentials and at 84% Ni this peak is approaching the pure nickel peak position (Fig. 8). Coming from opposite direction peak shift at the position corresponding to the nickel oxidation to more positive potentials is observed with increasing copper content (Fig. 9). Noted changes in the peak position at a variation ratio of the components provide a basis for attributing it to the oxidation of the solid solution rich in nickel. According to this feature the system under consideration corresponds to the PD of the nanosized (but not macroscale) Ni-Cu. A comparison with the phase composition of nanosized powder shows that we observe the electrochemical oxidation of the non-equilibrium solid solution rich in nickel.
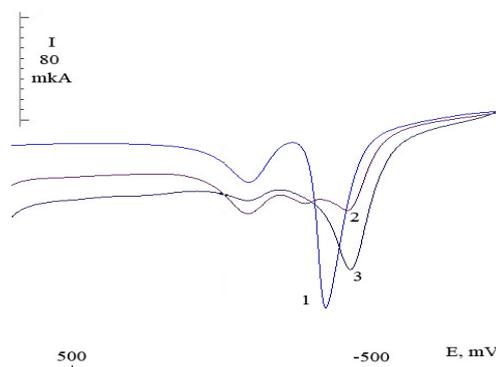

Fig. 8. Anodic VA curves for Cu→Ni deposits obtained at concentrations: $c(Cu^{2+})$, 10^{-4} M: 1 – 1,1; $c(Ni^{2+})$, 10^{-4} M: 1 – 0; 2 – 2; 3 – 6.
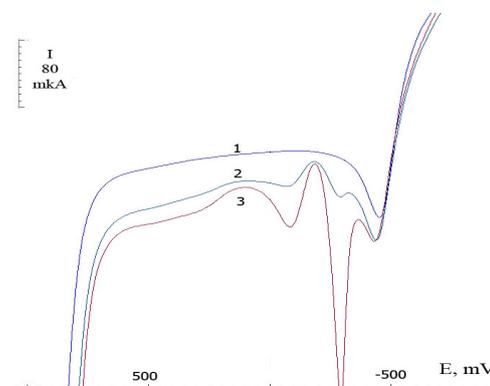

Fig. 9. Anodic VA curves for Ni→Cu deposits obtained at concentrations: $c(Ni^{2+})$, 10^{-4} M: 1 – 3; $c(Cu^{2+})$, 10^{-5} M: 1 – 0; 2 – 2; 3 – 4.
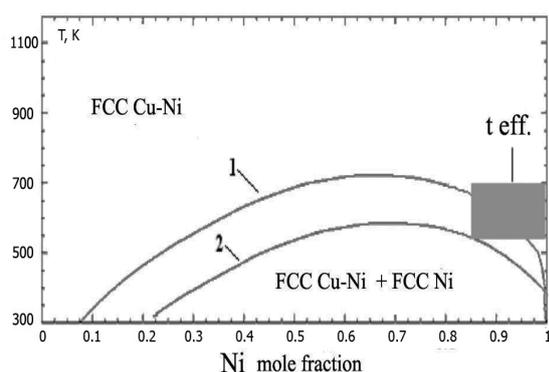
Fig. 10. Variants (1, 2) of low temperature fields of Cu–Ni phase diagram and effective temperature area for nano-sized bimetal.
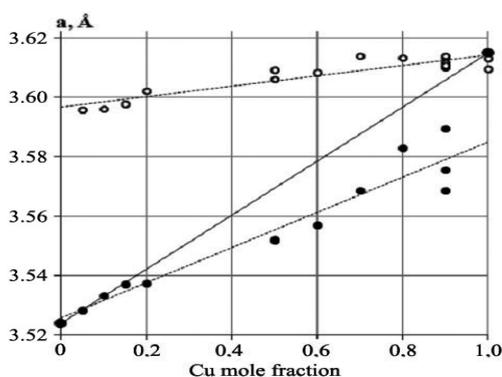

Fig. 11. Dependence of Ni (●) and Cu (○) phases lattice parameters on the system composition.

The idea of the similarity of the system under consideration and Cu-Ni system studied in [17] is based on similar methods of the synthesis: electro-chemical reduction under nonequilibrium conditions (in present work) and liquid-phase chemical reduction [17].

Processes occurring in the field of –80 mV and –270 mV, probably refer to the oxidation of na-noscale nonequilibrium Cu-Ni solid solution rich in copper, however, they occur by more complicated way. First of all, implementation of one of the oxidation stages at a potential more positive than the oxidation potential of pure copper is non-trivi-al. It can be assumed that a significant increase of the oxidation potential $Cu^0 \rightarrow Cu^+$ is associated with the formation on the electrode surface of extreme-ly nanosized particles of copper-rich solid solution with the values of the electron work function great-er than the values for large particles. It is a known effect [19] found for nanoscale structures, which, in principle, should increase the potentials of the anode processes. This fact may also explain the slightly asymmetry of the anodic oxidation peaks of solid solution phase rich in nickel. The lower effect values for nickel phase may be related to a larger size of crystallites. For all the above compositions, the results show perspectivity of use electrochemi-cal approach (combined analysis of processes in the cathode and anode cycles) for the investigation of phase composition of nanosized multicomponent metallic systems obtained by electrodeposition. The solution to this problem is of considerable interest because the use of most other methods encounters great difficulties because of nanoscale dimentionali-ty of the objects. At the same time, the development of this approach requires extensive experiments.

4. Conclusions

It was shown that the result of coelectrodeposition of two metals on an inert substrate is determined not only the nature of the components of binary systems Co–Ni and Cu–Ni, but also features of the phase composition of bimetal in nano-state. By comparing with PD NS Co–Ni systems it was shown that in the field of solid solutions formation the shift for a single peak of bimetal oxidation is observed during a vari-ation ratio of the components. The oxidation peak of nonequilibrium, nickel-rich solid solution NS Cu–Ni previously detected by XRD is transformed in a similar way. The peak observed in the more positive field than the oxidation potential of copper was sup-posedly attributed to oxidation of extremely nano-sized particles of copper-rich solid solution.

Acknowledgements

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