The electrochemical behavior of nanostructured binary systems based on transition metals

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Abstract. By means cyclic and anodic linear sweep/stripping voltammetry methods the electrochemical behavior of bimetallic electrolytic nanoalloys and nanostructured powders Cu–Cd, Ni–Cd, Fe–Co, Fe–Ni was investigated in acidic (chloride, sulfate) and ammonia buffer media with the glassy carbon and carbon paste electrodes. The conditions (supporting electrolytes, concentrations of metal ions, voltammetric parameters) of the electrochemical synthesis and voltammetric characterization of the binary systems were established.

1. Introduction

Investigation of physicochemical properties of nanostructured (NS) bimetallic systems, finding of interrelation these properties with morphology and phase composition is an urgent problem in the field of new materials synthesis, as well as in the development of fundamental concepts of materials science. The binary systems based on the transition metals (Cu, Cd, Ni, Fe, Co) are widely used in the manufacturing of chemical and electrochemical reactions catalysts, magnetic devices, biomedical nanoparticles [1-5].

Electrochemical methods are known to be economical and available for the synthesis of the bimetallic systems, including Cu(Ni)-Cd and Fe-Ni(Co) [6-10]. In addition, the electrochemical analysis, for example, a combination of cyclic (CV) and anodic sweep/stripping linear voltammetry (ASLV), allows to obtain the unique information not only about the elemental and phase composition [10-13], but also about the spatial arrangement of the phases [14, 15]. In this respect voltammetry is able to compete with the known structure analysis techniques. The voltammetric methods are characterized by the highest sensitivity and provide the ability to detect the response of single nanoparticles placed on the surface of the electrode or present in the electrolyte. At the same time, an implementation of the voltammetric analysis requires thorough selection of experimental conditions, such as background electrolyte, cell design, working electrode material, sequence of stages during registration of VA curves. The above-mentioned transition metals are electrochemically active; however, the occurrence of anodic oxidation – cathodic reduction processes with their participation is accompanied by the formation of oxide-hydroxide compounds and catalytic hydrogen evolution, which significantly complicates the electrochemical experiment. In this paper we report and discuss the electrochemical behavior of the bimetallic systems Cu-Cd, Ni-Cd, Fe-Co, Fe-Ni in the form of electrolytic nanoalloys and nanostructured powders to identify suitable parameters for their electrochemical synthesis characterization.
2. Experimental

The CV and ASLV electrochemical measurements were performed in a three-electrode cell using potentiostat/galvanostat Parstat 4000. The working and counter electrodes were the glassy carbon cylinders (l = 15 mm, d = 2 mm) and the reference electrode – Ag/AgCl in 0.1 M KCl. Before experiment working and counter electrode surfaces were polished down to polishing cloths, etching in 5 M H2SO4, thoroughly washed with pure water and transferred to the electrochemical cell. Chemicals used were CuSO4, NiSO4, CoSO4, FeSO4, supporting electrolytes: 0.1 M 0.1 M NH4Cl + 0.1 M NH4OH (pH 9.8), 0.1 M Na2SO4 + H2SO4 (pH 1.5–2.0); 0.1 M KCl + HCl (pH 1.5–2.0); 0.075 M Na2SO4 + 0.025 M KCl + H2SO4 (pH 1.5) all of analytical grade. All solutions were prepared with double-distilled water. pH measurements were carried out using pH-meter Expert 001.

The electrodeposition of the nanoalloys Cu–Cd, Ni–Cd, Fe–Ni, Fe–Co was carried out in the potentiostatic conditions from the supporting electrolytes with various ratios of the metal ions concentrations (1·10⁻³ – 1·10⁻⁴ M) at –1.6 V, time of the deposition was 2 – 5 min. 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. The Cu–Cd powders were prepared by means electrolysis with glassy carbon cathode and graphite anode, electrolyte was 0.08 M CuSO4 + 0.4 M CdSO4 in various ratio with additives of 0.1 M H2SO4 at i = 0.1 A/cm², E = 4 V.

Nanostructured Ni–Cd, Fe–Ni, Fe–Co powders synthesized according to the procedure of chemical reduction given in [3, 19] were cleaned by water or etching agents and then were immobilized on the surface of the working electrode (glassy carbon or carbon paste, fabricated from chemical pure graphite powder and paraffine oil). Powder X-ray diffraction (XRD) data were recorded by diffractometer DRON 2 (Cu Kα).

3. Result and Discussion

Preliminary the conditions for the formation of a reproducible CV and/or ASLV signal linearly dependent on the concentration of the metal ions into the electrolyzer were chosen for each metal.

The simple acidic (sulfate and chloride) or complexing and having a buffer effect media (ammonia buffer solution) were used as background electrolytes. It is shown that all the mentioned electrolytes can be used for the electrodeposition and characterization of the Cu-Cd, Ni-Cd systems. The investigation of Fe-Ni, Fe-Co systems is possible only in the sulphate electrolyte with pH not more than 2. Under these conditions the parameters of the anodic peaks and the relative electrodeposition rates of each metal were determined.

The considered binary systems can be divided into two types, in accordance with a predominant phase organization: the systems forming intermetallic compounds (IMC) – Cu-Cd, Ni-Cd, or solid solutions – Fe-Co, Fe-Ni.

By means voltammetry method for the NS electrolytic system copper - cadmium in the chloride media was found that the binary nanoalloy on the electrode surface consists of several phases. Anodic dissolution of this alloy is accomplished by the formation of up to four additional current peaks on the voltammograms in the potential region between the oxidation peaks of pure copper and pure cadmium phases (Figure 1A). Table 1 shows the peak potentials for the chloride electrolyte. Most probably, each additional peak corresponds to a single IMC phase of a constant composition, since the peak potential does not depend on the ratio of the metal concentrations (excluding peak at –186 mV). Similar conclusions were reached by V.D. Jovič et al [12], who investigated the behavior of this system in 0.01 – 0.1 M CuSO4, 0.2M CdSO4, 10⁻³ M H2SO4, 0.5 M Na2SO4.
Table 1. The anodic peak potentials for the Cu-Cd electrolytic nanoalloys in comparison with the partial Gibbs energy of the IMC formation; 0.1 KCl + 0.1M HCl (pH 2), c(Cu\(^{2+}\)) = 1\(\cdot\)10\(^{-5}\) M, c(Cd\(^{2+}\)) = 4\(\cdot\)10\(^{-5}\) M.

| Ep, mV | Cd  | I   | II  | III | IV\(^a\) | Cu  |
|-------|-----|-----|-----|-----|---------|-----|
|       | -670| -640| -485| -386| -186 ÷ -150 | +23; +370 |
| IMC   | Cd\(_3\)Cu | Cd\(_8\)Cu\(_5\) | Cd\(_3\)Cu\(_4\) | CdCu\(_2\) |
| \(\Delta G_{f}^{298}(\text{Cd})\), kJ/mol | -0.84 | -8.49 | -6.98 | -11.69 |

\(\text{a}\) Peak potential depends on the cadmium concentration

Figure 1. Anodic voltammograms obtained for the Cu-Cd electrolytic nanoalloys on glassy carbon (A) and NC Cu-Cd powders (B) on carbon paste electrode in the chloride media: 0.1 M KCl + HCl (pH 2). c(Cu\(^{2+}\)) = 1\(\cdot\)10\(^{-5}\) M (A). The ion concentration ratios are shown in the graphs.

Using a mercury film electrode an ASLV analysis of the electrolyte after partial anodic dissolution of the copper-cadmium nanoalloys was carried out. It is established that anodic dissolution of the IMCs occurs through the selective oxidation of a more electroactive component (cadmium), because copper ions are not detected in the solution up to a scanning potential of -100 mV. The values of partial Gibbs energy of the IMC formation [16] suggest that the selective dissolution of cadmium from the IMC in the process of the anodic potential sweep and, accordingly, the formation of the IMC peaks occurs in the sequence: Cd\(_3\)Cu \(\rightarrow\) Cd\(_8\)Cu\(_5\) \(\rightarrow\) Cd\(_3\)Cu\(_4\) \(\rightarrow\) CdCu\(_2\).
The total amount of the IMCs in the NS electrolytic alloy is linearly related to the concentrations of copper and cadmium ions in the electrochemical cell. Each phase is characterized by the intrinsic existence region in the ion concentrations; however, it is not possible to bring these data into correlation with the fields of the phase diagram, apparently due to the non-equilibrium conditions of the alloy formation.

The XRD analysis of the NS powders Cu-Cd obtained by “massive” electrodeposition of the components confirmed the presence of the intermetallic compounds CuₓCdᵧ (Figure 2) [17]. However, the overlapping of the reflexes did not allow to establish the exact composition of the intermetallicides in the powder samples, since the observed in the region 39.2 – 40.2 deg. peak corresponds to the several IMCs (CdCu₂, Cd₅Cu₃ and Cd₄Cu₃) at once. The peak asymmetry at large angles (40.5 deg.), arising from an increase in the amount of cadmium, implies the formation of an IMC Cd₄Cu.

The anodic linear voltammetry shows a commonality of the electrochemical properties of the electrolytic and nanopowder bimetallic alloys, which consists in the formation of oxidation peaks of intermetallic compounds CuₓCdᵧ in the same potential fields (Figure 1b). A distinctive feature of the powder systems is the wider peaks on the anodic voltammograms, probably, due to a diffusion limitation and, consequently, their greater overlapping. Furthermore, based on the number of peaks it must be taken into account, that the phase composition of powders is not so rich.

A qualitatively similar situation is observed during the investigation of the nickel-cadmium electrolytic nanoalloys and NS powders. According to the phase diagram [21] IMCs NiCd, NiCd₂ and solid solutions riched in nickel are formed in the Ni-Cd system, it should be noted that IMC Ni₃Cd was detected [3] in the NS powders produced via chemical co-reduction of salts. In this case, the ALSV data show, that at the electrodeposition in the sulfate-chloride electrolyte several binary phases of variable composition are formed, since the potentials of their anodic peaks (E_{Cd} = –710 mV, E_{I} = –550 mV, E_{II} = –450 mV, E_{III} = –310 mV, E_{IV} = –200 mV, E_{Ni} = –110 mV) depend on the ratio of the concentrations of nickel and cadmium (Figure 3A). There are no individual phases of nickel and cadmium in the binary samples; it can be explained by the formation of solid solutions in a wider concentration range than in the Cu-Cd electrolytic system.

The phase composition of thin nickel-cadmium films depends on the type of supporting electrolyte; in ammonia buffer the electrodeposition occurs at a faster rate than in a sulphate-chloride one; apparently, this determines a larger amounts of phases in the first case [7].

It was proved that the voltammetric study (CV or ASLV) of the nanostructured nickel-cadmium powders is not realized without ammonium etching of the samples (2M NH₄OH water solution was used). Oxide-hydroxide layers present as impurities in the nanopowders reduce electrical conductivity and prevent obtaining of the correct results (Figure 3C). In the other side the voltammetric analysis can be used for the detection the oxygen-containing compounds in the nanostructured alloys.
The electrochemical response of metal phases in the oxygen pure nanopowders (Figure 3B) correlates with the X-ray diffraction data [3]. With an increasing in cadmium content from 6 to 60%, the total peak of the binary phase oxidation \( E = -0.17 \pm -0.25 \) V is shifted to the field of more negative potentials, and then an appearance of a peak at \(-0.77\) V supposedly corresponding to the IMC NiCd\(_5\) oxidation is observed. The change in the phase composition of the NS powder was studied during successive CV scans, as well as when performing cathodic reduction, which lead to degradation of the initial powder structure and the appearance of a cadmium peak at the potential of \(-0.85\) V. The voltammetric technique we developed has been used in the investigation of the chemical reduction mechanism which realized during the synthesis of the nanostructured powders Ni-Cd [18].

The electrochemical response of the NS electrolytic alloys Fe-Ni and Fe-Co in the sulfate electrolyte has a number of common features, consisting in the regular shift of an anodic peak of the first metal when the second metal is added into the system and in the increasing of the single anodic peak current (Fig.4). It should be noted that the direction of the peak shift is determined by the electrochemical properties of metals: if the more active metal is added, the peak potential decreases, if the more “noble” one is increased.

According to the phase diagrams and the results obtained by X-ray diffraction for the NS powders [19, 20], the components of the Fe-Ni and Fe-Co systems form solid solutions in a wide range of concentrations, therefore, the changes observed on the voltammetric curves can be interpreted as a transformation of the pure components phases to the phases of solid solutions having the variable composition. As can be seen in Figure 4 C, when the solid solution is enriched with one of the components, a regular change in the peak potential takes place. The obtained dependence can be used to determine the relative content of metals in the nanostructured systems using the voltammetric data.

The presence of a single anodic peak on the VA curves indicates that the oxidation of the solid solution phase in each case occurs according to a simultaneous mechanism. The dependences of an electricity amount under the peaks on the concentrations of metal ions in the binary systems leads to the same conclusions. Additionally, it was found that in the sulfate medium during the deposition of nickel (or cobalt) in the presence of iron, so-called “induction period” needed for the formation of metal crystallization centers on the inert electrode surface is excluded.

The nanostructured Fe–Co, Fe–Ni powders are characterized an increased tendency to oxidation; therefore, only the peaks of oxide-hydroxide phases were observed on the voltammetric curves.
Preliminary preparation of the powders did not lead to the desired results; further experiments are meant to be used in an argon glove box.

![Anodic voltammograms obtained for NS Fe-Ni (A) and Fe-Co (B) electrolytic nanoalloys on glassy carbon electrode in the sulfate media: 0.1 M Na$_2$SO$_4$ + H$_2$SO$_4$ (pH 2), the dependence of the peak potential on the Ni$^{2+}$ concentration (C), c(Fe$^{3+}$): 8·10$^{-5}$ M (A, C); 12·10$^{-5}$ M (B).](image)

**Figure 4.**

4. Conclusion
The electrochemical response of nanostructured bimetallic systems Cu– Cd, Ni–Cd, Fe–Co and Fe–Ni by means voltammetric methods (CV and ASLV) can be used in the investigation of their physico-chemical characteristics such as phase and elemental composition, spatial phase arrangement, stability to the oxidation, etc. The acidic sulfate (for Fe–Co, Fe–Ni, Cu–Cd, Ni–Cd), acidic chloride (pH 1.5 – 2.0) and ammonia buffer electrolytes (for Cu–Cd, Ni–Cd) are suitable for electrochemical synthesis and voltammetric characterization of the bimetallic electrolytic nanoalloys and nanostructured powders.

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