603

Electrolytic Deposition and Anodic Oxidation of Nanostructured Fe−Ni and Fe−Co Binary Alloys

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Abstract

The synthesis of nanostructured systems based on transition metals and the investigation of their physico-chemical properties is one of the urgent problems of materials science in view of the expanding area for the application of these materials. The paper presents the results of the voltammetric study of potentiostatic electrodeposition and anodic oxidation of iron-nickel and iron-cobalt nanostructured systems with glassy carbon electrodes in various electrolytes. It was found that the electrolytic synthesis of these nanostructured systems free of oxide-hydroxide impurities can be carried out in sulphate, ammonia-tartrate and chloride media. According to the voltammetry data, the phases of solid solutions with variable composition are formed during the deposition process, and their anodic dissolution proceeds by the uniform mechanism. Metal deposition rates were compared, and an approach allowing one to calculate the compositions of electrodeposited nanostructured alloys was proposed. The capabilities of anodic and cyclic voltammetry in the characterization of nanometallic deposits were shown.

Keywords: binary systems, iron, cobalt, nickel, voltammetry, electrodeposition, anodic oxidation

INTRODUCTION

Under the conditions of the development of technologies for the synthesis of new materials, one of the promising directions is the development and optimization of the methods of electrolytic obtaining of nanostructured alloys based on the metals of iron subgroup [1−3]. The possibility of a smooth regulation of electrodeposition conditions provides broadening of the variations of alloy properties in comparison with those provided by the metallurgical and other methods of synthesis. An essential problem in this area is the investigation of the processes of the joint discharge of metal ions because numerous factors complicating interpretation of the results appear during the joint deposition of metals. The effects of the mutual influence of reactions proceeding simultaneously on the cathode are pronounced in the changes of the structure and composition of the double electric layer, inhibition (or acceleration) of reduction processes and, as a consequence, a substantial complication of the kinetics of electrochemical processes when passing from individual to joint reduction of the components [4, 5].

Complex consideration of electrode processes complicated by various kinds of interactions allows formulating recommendations for the choice of the optimal conditions for obtaining alloys. In addition, understanding of the mechanisms of electrode processes in two- and multicomponent systems is of principal importance for electrochemical analysis, for example, for one of the most popular methods, voltammetry. The parameters of voltammograms (voltage-current curves) of the oxidation of the obtained nanostructured

alloys are substantially dependent on the mutual influence of the reduction of several metals and the deposition of multiphase deposits on the cathode. In particular, this is exhibited in the shifts and/or disappearance of the phase peaks of elements or the formation of additional current peaks. It is known that voltammetry is structurally sensitive [6, 7], however, definite difficulties exist in the interpretation of the data obtained, especially if the metals under deposition are characterized by the high mutual solubility and form solid solutions. It should be taken into account that the physicochemical properties of the systems may deviate from the expected ones during the formation of nanostructured deposits because of the manifestation of nanosize effects [8−12].

Nanostructured binary iron−nickel and iron−cobalt systems are important for obtaining magnetic nanometallic materials, catalysts, metal-carbon composites and capacitor devices on this basis [4, 11−14]. Because of this, a detailed investigation of the electrochemical properties of these systems is necessary. Metal electrodes made of copper, tungsten, steel are mainly used for electrochemical synthesis; electrolytes are sulphate and chloride aqueous solutions with the addition of complex-forming agents for the creation of an optimal difference of potentials for the cathode deposition of metals and the substances governing the acidity of the medium [1−4, 15−18]. However, it is preferable to use inert electrodes made of carbon materials to exclude the interaction of metals with the substrate material and to avoid the formation of undesirable phases with a third metal. Individual and joint electroreduction and electrooxidation of iron, nickel and cobalt under these conditions require investigation due to the occurrence of crystallization hindrances and the effect of side processes of the formation of oxide and complex compounds of these metals.

The goal of the work was to study the features of the electrochemical behaviour of nanostructured binary systems Fe−Ni and Fe−Co using voltammetric methods with glass-carbon electrodes.

EXPERIMENTAL

Investigation of electrodeposition and anodic oxidation of nanostructured systems Fe−Ni and Fe−Co was carried out by means of cyclic and stripping voltammetry using the Parstat 4000 and Versastat 3 potentiostats/galvanostats (Princeton Applied Research, США) in the three-electrode mode, and a PU-1 polarograph (Belarus). The indicator and auxiliary electrodes were glass-carbon cylindrical electrodes, the silver chloride electrode was used as a reference in a 0.1 M KCl solution which was poured in a separate cell for carrying out the measurements in all electrolytes except the chloride one. Electrolysis was carried out at a constant potential of −1.6 V, electrodeposition of metals from the surface of the indicator electrode was performed under the linearly changing potential ($v = 100$ mV/s). The glass-carbon electrodes were prepared for operation through mechanical polishing on the suspension of Al_2O_3 and etching in the diluted H_2SO_4 solution.

To prepare the solutions, twice distilled water reagents of Os. Ch. (specially pure) and Kh. Ch. (chemically pure) grades were used. Electrolytes of different types were used to obtain electrolytic Fe−Ni deposits: sulphate − 0.1 M Na_2SO_4 + H_2SO_4 (pH 2.0); chloride − 0.5 M NaCl + HCl (pH 1); ammonia-tartrate − 0.1 M $C_4H_6O_6$ + NH_4OH (pH 9.0); borate buffer − $Na_2B_4O_7$ + HCl (pH 9.2); fluoride − 0.1 M NaF (pH 9); with the addition of $Fe(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$ solutions prepared from the state standard samples (SSS) of metal ions. The range of metal ion concentrations $c(Me^{n+})$ was $(1-20) \cdot 10^{-5}$ mol/L. Measurement of solution acidity was carried out with the help of Ekotest 2000 pH-meter/ionometer (Russia).

RESULTS AND DISCUSSION

Binary iron−nickel system

In the version of individual electrodeposition, for all electrolytes indicated in Table 1 (except borate buffer), oxidation peaks were recorded both for nickel and iron. The current of oxidation peaks I_p depends on the content of metal ions in the electrolyzer. Side signals are absent from the voltage-current curves. This is the evidence that under the indicated conditions there is the possibility to obtain nanostructured Fe−Ni alloys free from oxide-hydroxide compounds.

The potentials of the peaks of iron and nickel oxidation E_p in different electrolytes are shown in Table 1. One can see that the regions of anode processes are connected with the constants of stability of complex ions [19] existing in the medium under analysis. For example, the stability of the complex ions of iron (III) increases in the sequence of ligand ions: sulphate < tartrate < fluo-

TABLE 1

Potentials of the peaks of metal oxidation E_p in different base electrolytes, mV

Metal	Borate buffer	Sulphate	Ammonia tartrate	Tetrafluoro-borate
Iron	−270	−360	−510	−850
Nickel	−	+170	−240	−290

Note. Dash means that a peak was not recorded.

ride. The peak potentials varying from −360 to −850 mV are in good agreement with this fact.

In the sulphate electrolyte, the values of current of the peaks of iron and nickel oxidation are linearly bound with the concentrations of the corresponding ions $c(Me^{n+})$ in solution (Fig. 1, *a*). A comparison between the absolute values of peak areas in the units of quantity of electricity Q and the slopes of $Q = f(c)$ dependences allows us to conclude that the rates of metal electrodeposition are equal to each other.

In the ammonia-tartrate electrolyte, the linearity of the dependence $Q = f(c)$ is observed only for nickel; in the case of iron deposition, process acceleration with an increase in $c(Fe^{3+})$ in the electrolyzer is observed (see Fig. 1, *b*). The rates of metal deposition differ substantially; in the case of joint crystallization, this will cause the deviation of the ratio of metal concentrations on the electrode surface from the corresponding ratio in solution and will require a correction of deposition conditions to obtain an alloy of definite composition.

It was established for the joint deposition of iron and nickel that the anode voltage-current curves recorded in the sulphate, ammonia-tartrate and fluoride electrolytes exhibit a number of common phenomena: the formation of the sole oxidation peak, with its current and potential depending on the ratio of metal concentrations (see Fig. 1, 2).

A regular change of the potential of the total peak with the variation of the $c(Fe^{3+})/c(Ni^{2+})$ ratio was detected. The direction of the change in the potential of oxidation peak is determined by the electrochemical properties of the metals: if a more active metal (iron) is introduced, then E decreases; if a more inert metal (nickel) is introduced, E increases Fig. 3). According to the phase diagram [20], when alloyed, iron and nickel form solid solutions within a broad concentration range, so the changes observed in the voltage-current curves may be interpreted as a transition from the phases of pure iron and nickel to the phase of the solid solution with variable composition. It should be stressed that the only peak in the voltage-current curves for nano-structured systems is the evidence in favour of the fact that the anodic oxidation proceeds according to the mechanism of the uniform dissolution of the solid solution phase, which implies the simultaneous transition of both components of the binary system into solution.

Results of the investigation of the electrochemical behaviour of the binary Fe−Ni system in the solution of sodium tetrafluoroborate correspond at
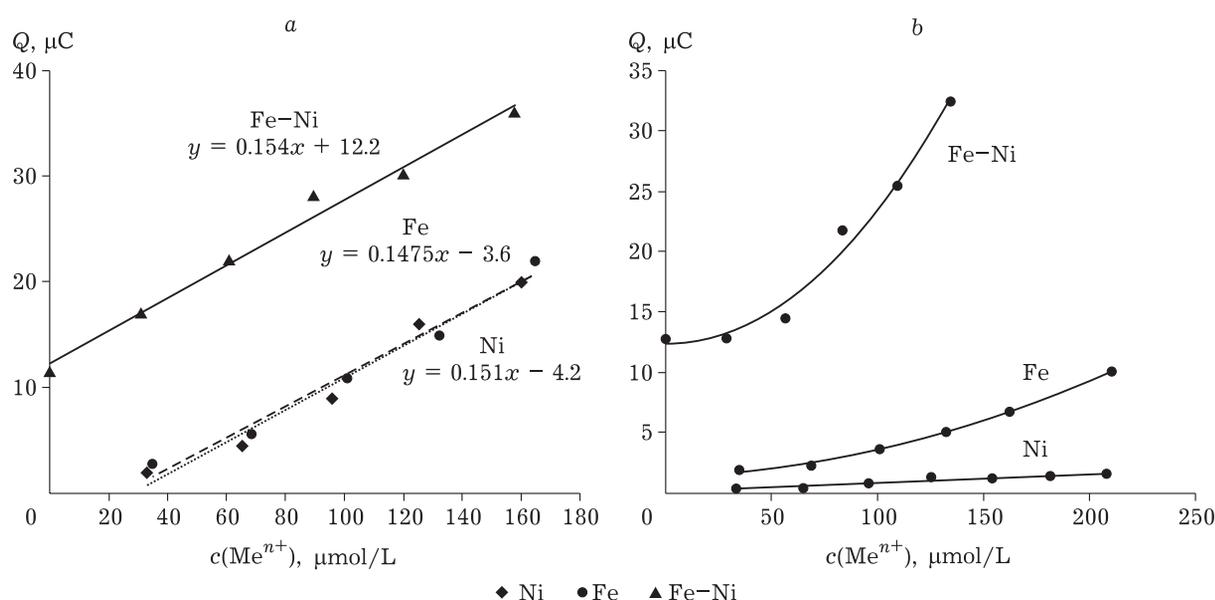
Fig. 1. Dependences of the currents of oxidation peaks in the units of the quantity of electricity Q for Fe, Ni and the Fe−Ni system on the concentration of metal ions in the sulphate (*a*) and ammonia-tartrate electrolyte (*b*). In the system Fe−Ni $c(Fe^{3+})$, 10^{-4} mol/L: 1.3 (*a*), 3 (*b*).
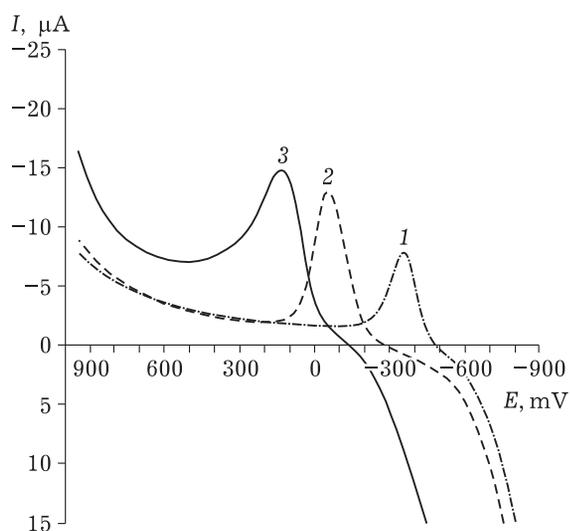
Fig. 2. Anodic voltage-current curves of the oxidation of nano-structured deposits of Fe and the binary Fe−Ni system deposited from the sulphate electrolyte; $c(Fe^{3+}) = 6 \cdot 10^{-5}$ mol/L, $c(Ni^{2+})$, 10^{-5} mol/L: 0 (*1*), 6 (*2*); 9 (*3*).

Fig. 3. Dependences of the potentials of oxidation peaks in the binary Fe−Ni system on the concentration of nickel ions in the sulphate (*1*) and ammonia tartrate (*2*) electrolytes; $c(Fe^{3+}) = 6 \cdot 10^{-5}$ mol/L.

the qualitative level to the main results obtained in the sulphate and ammonia tartrate electrolytes: a change of the peak potential and an increase in its absolute value are observed under variation of the ratio of metal ion concentrations. In this case, problems involve poor repeatability of peak parameters, which is likely to be connected with the changes in the composition of the base electrolyte due to its hydrolysis.

Under the conditions of the joint electrodeposition of Fe and Ni from the sulphate electrolyte, the linearity of the dependences of *I* and *Q* on the concentration of metal ions is conserved (see Fig. 1, *a*). Comparing their slopes we may conclude that the mutual effect of the parallel processes for nickel andiron is absent, most probably because of the practical equality of the rates of metal deposition. In addition, the so-called induction period, which is necessary for the formation of crystallization centres on the electrode surface, is excluded. An inverse effect is observed in the solution of 0.1 M $C_4H_6O_6$ + NH_4OH: dependences obtained for the binary system have essentially different parameters (see Fig. 1, *b*).

Equal rates of iron and nickel deposition in the sulphate electrolyte, assuming the uniform anodic oxidation, allow us to determine the content of each metal in the binary phase. As a result of calculations, the dependence of half-peak potential $E_{1/2}$, mV (as a value weakly dependent on the concentration) on the molar fraction of the metal $x(Me)$ was plotted (Fig. 4).

One can see that the potential of the half-peak of uniform oxidation of the binary Fe−Ni alloy is connected with the molar fractions of the components *via* a dependence which is close to linear, and this fits within the theoretical notions on the effect of composition on the energy of alloy formation [6]. The resulting dependence may be used to determine the composition of nano-structured Fe−Ni alloys and to calculate thermodynamic parameters for similar systems. It is difficult to carry out the indicated procedure of calculation of the contributions from each metal into the total peak for the ammonia tartrate electro-
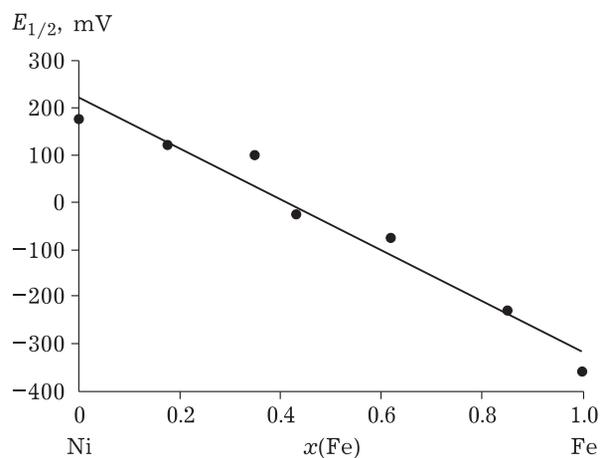
Fig. 4. Dependence of the potential of half-peak of the oxidation of binary Fe−Ni alloy on the molar fraction of Fe in the electrolytic nano-structured Fe−Ni system deposited from the sulphate electrolyte.

lyte because there is no information on the partial rates of metal deposition at the given concentrations of their ions in the electrolyte.

Binary iron—cobalt system

Investigation of the electrochemical behaviour of the binary system Fe−Co was carried out in the sulphate, fluoride and chloride electrolytes. Deposition from the fluoride electrolyte resulted in the formation of a multicomponent deposit which included a number of oxygen-containing cobalt and iron compounds as revealed by means of anodic voltammetry. A complicated picture of anodic oxidation was recorded: in addition to the peaks related to the oxidation of the metal phase, additional peaks with current depending on metal ion concentrations were observed in the cyclic voltage-current curves.

Side processes were not observed in the sulphate and chloride electrolytes. The peaks of iron and cobalt oxidation during individual electrodeposition were recorded at −420 and −10 mV in the sulphate electrolyte, respectively, and at −270 and −90 mV in the chloride electrolyte, respectively. One can see that the use of the chloride electrolyte allows one to bring the potentials of the oxidation-reduction processes substantially closer to each other. A comparison of I_p of metal oxidation allows us to conclude that the rate of iron deposition

both in sulphate and in chloride electrolytes is almost two times as high as the rate of cobalt oxidation (for example, in the sulphate electrolyte $I_p = 5.0c(Co^{2+}) - 4.1$, $I_p = 8.8c(Fe^{3+}) - 12$, while in the chloride electrolyte in the case of equal concentrations the ratio $I_p(Co)/I_p(Fe) = 45 : 84$).

A characteristic feature of the peak of cobalt oxidation in the sulphate medium is the change of its shape and a substantial shift of E_p to negative values with an increase in $c(Co^{2+})$. This fact may be explained by a decrease in the activation energy of the anode process as a result of the modification of electrode surface under the conditions of consecutive registration of voltage-current curves. For the chloride electrolyte, no phenomena of this kind were observed.

The electrochemical behaviour of the binary Fe−Co system is completely similar to that for the Fe−Ni system: An increase in $c(Fe^{3+})$ also leads to an increase and regular shift of the initial oxidation peak to lower potential values (Fig. 5, 6). With an increase in cobalt content, E_p increases, which is explained by the formation of the solid Fe−Co solution. The latter fact is in agreement with the data reported in [21], obtained for nano-structured Fe−Co powders. The only current peak on the voltammograms is the evidence of the fact that the anodic dissolution of the solid solution phase in the sulphate and chloride media occurs uniformly.
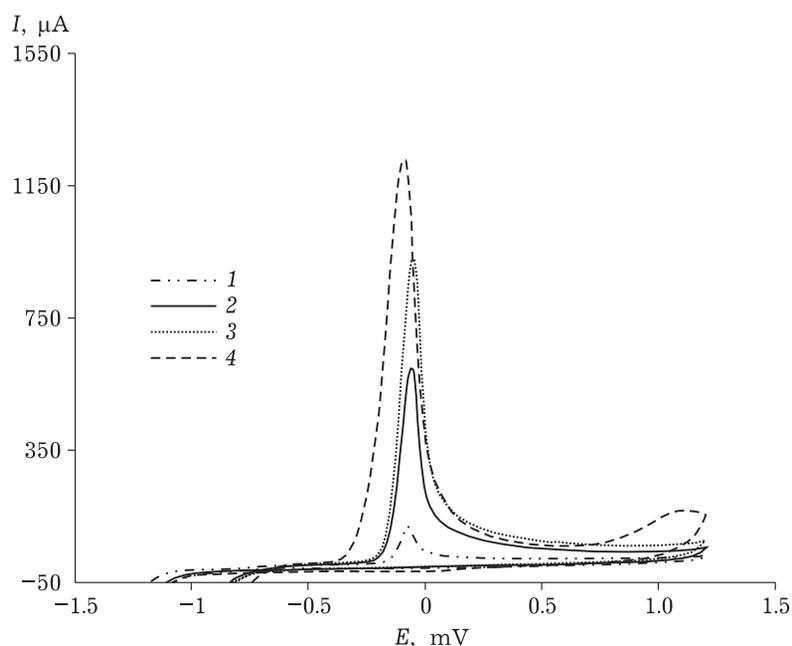
Fig. 5. Cyclic voltammetric curves recorded for the binary Fe−Co system in the chloride electrolyte. $c(Co^{2+})$, 10^{-4} mol/L: 2 (*1*), 3 (*2*), 4 (*3, 4*); $c(Fe3+)$, 10^{-4} mol/L: 0 (*1−3*), 4 (*4*).

$E_{1/2}$, mV
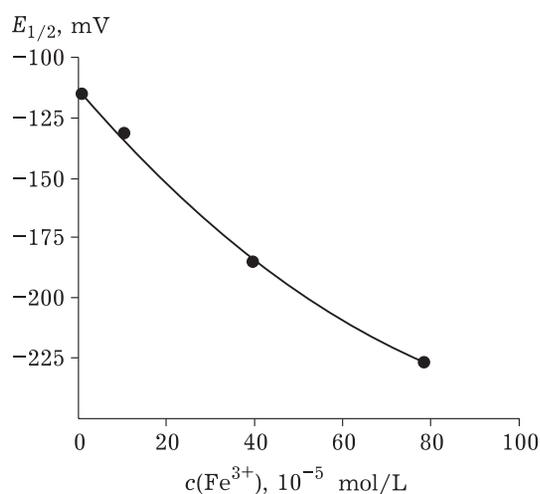
Fig. 6. Dependence of the potential of the half-peak of binary Fe−Co alloy oxidation on the concentration of iron ions, $c(Co^{2+}) = 4 \cdot 10^{-4}$ mol/L.

It is necessary to stress that at a definite relation between component concentrations depending on the initial concentrations of the metals to be deposited, the Fe−Co system stops to be single-phase and is transformed into the two-phase version. In addition, more electronegative peak of current is recorded in this situation. The potential of the additional peak is almost equal to the potential of the peak of iron oxidation. It is possible that under the experimental conditions the possibility of coexistence of the binary phase of the solid iron-cobalt solution and the individual phase of pure iron is implemented (taking into account the high mutual solubility of the components, most probably, layer-by-layer deposition of the phases differing from each other in composition takes place). This may be the reason why the dependences of the current of the total peak on the concentration of metal ions deviate from the linearity.

CONCLUSION

The features of the electrochemical behaviour of nanostructured binary iron-nickel and iron-cobalt systems in the electrolytes differing from each other in nature were investigated. It was demonstrated that the regularities of the anodic oxidation of the systems under consideration during the joint electrodeposition are independent of electrolyte type and have a number of common features manifested in the change of the potential of oxidation peak and a regular increase in the value of anodic peak with the variation of components ratio, which is a sign of the formation of a

solid solution of variable composition. Anodic oxidation of the electrolytic phases occurs uniformly, that is, both components pass into solution simultaneously. For the electrodeposition of nanostructured Fe−Ni and Fe−Co alloys free of oxide-hydroxide impurities, it is recommended to use sulphate, ammonia tartrate and chloride electrolytes.

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