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Electrocatalytic Properties of Molybdenum and Tungsten Alloys in the Hydrogen Evolution Reaction

Valeriy Kublanovsky and Yuliya Yapontseva

Abstract

The search for new electrode materials which are able to intensify the currently used process for the electrolytic production of pure hydrogen is an important scientific and technical problem. Promising materials for making electrodes or for the modification of currently used nickel cathodes are alloys of iron subgroup metals with molybdenum or tungsten, which show a higher catalytic activity in the hydrogen reduction reaction compared with pure nickel or cobalt and have a high corrosion resistance in aggressive media. The present chapter demonstrates that the catalytic, magnetic, and corrosive properties of coatings depend not only on the chemical composition of the alloy but also on its phase composition and morphology so that even coatings having the same chemical composition, but obtained under different conditions, possess different properties. Thus, by changing the electrolyte composition and the electrolysis parameters, one can obtain coatings with optimal set of functional properties and the distribution of metals on the surface which ensure hydrogen spillover and, hence, a high rate of the desired reaction.

Keywords: electrocatalytic activity, hydrogen evolution, electrodeposition, molybdenum, tungsten, spillover, corrosion
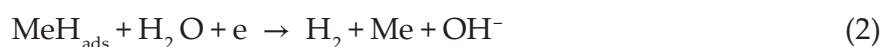
1. Introduction

The amount of energy consumed in the world has been steadily increasing in the recent decades, and the nonrenewable fossil energy sources account for over 80% of it [1]. In view of this, the search for efficient, environmentally appropriate methods for the generation of renewable energy is a vital present-day scientific problem [2]. One such promising trends is fuel cells [3, 4], the operation of which is directly bound up with the availability of high-purity hydrogen.

At the present time, the wide use of pure hydrogen is economically inexpedient in comparison, e.g., with the use of natural gas, because of the high cost of its production. The industrial method for hydrogen production by the electrolysis of alkaline aqueous solutions [5] has a number of disadvantages, such as the large expenditure of energy, low efficiency of the process, and the necessity of using noble metals as catalysts. Low carbon steel, which is corrosion-nonresistant in alkaline medium, and nickel also possess a catalytic effect in the hydrogen evolution reaction [6]; nevertheless, the problem of search for electrode materials with lower hydrogen evolution overpotential and high corrosion resistance remains vital. For instance, platinum group catalysts can be replaced by cheaper materials, such as nickel, molybdenum, and iron-chromium and iron-manganese alloys, in electrolysis in ionic liquids [7]. However, if the high cost of ionic liquids themselves is taken into account, there is no considerable reduction in the cost of materials for pure hydrogen production.

## 1.1. Hydrogen electroreduction mechanism and spillover effect

In the general form, the hydrogen electroreduction process in an alkaline medium is described by the Volmer (1)—Heyrovsky (2)—Tafel (3) mechanism with the following stages:

$$Me + H_2O + e \rightarrow MeH_{ads} + OH^- \tag{1}$$

$$MeH_{ads} + H_2O + e \rightarrow H_2 + Me + OH^- \tag{2}$$

$$2MeH_{ads} \rightarrow H_2 + 2Me \tag{3}$$

The rate of electrocatalytic reaction depends on the energy of adsorbed species, i.e., on the energy of hydrogen atoms. The plot of the exchange current density of hydrogen evolution reaction against hydrogen-metal bond energy passes through a maximum and has a volcano-like shape (**Figure 1**).

At low Me—H bond energy, the process is controlled by the discharge step, reaction (1). At very high Me—H bond energy, the process is controlled by the electrochemical desorption step, reaction (2). On nickel, cobalt, and iron, the rate-determining step changes from reaction (1) to (2) with increasing polarization. Thus, the most important parameter that determines electrocatalytic activity is the energy of bonding of adsorbed species to the catalyst [9]. When catalysts consisting of two metals are used, the formation of several alloy types, such as mechanical mixtures, solid solutions, and intermetallics is possible. From an analysis of the mechanism of electrocatalytic processes, metal-metal bond energy, and the properties of different alloy types, the authors of [9] conclude that the alloys formed by the metals that are on the different branches of the volcano plot and especially the alloys formed by d-metals with unoccupied d-orbitals (of groups IV–VI) and d-metals of group VIII with a large number of filled d-orbitals possess electrocatalytic activity.

It is known from literature that transition-metal alloys, viz. alloys of iron subgroup metals with molybdenum and tungsten, which show electrocatalytic properties with respect to
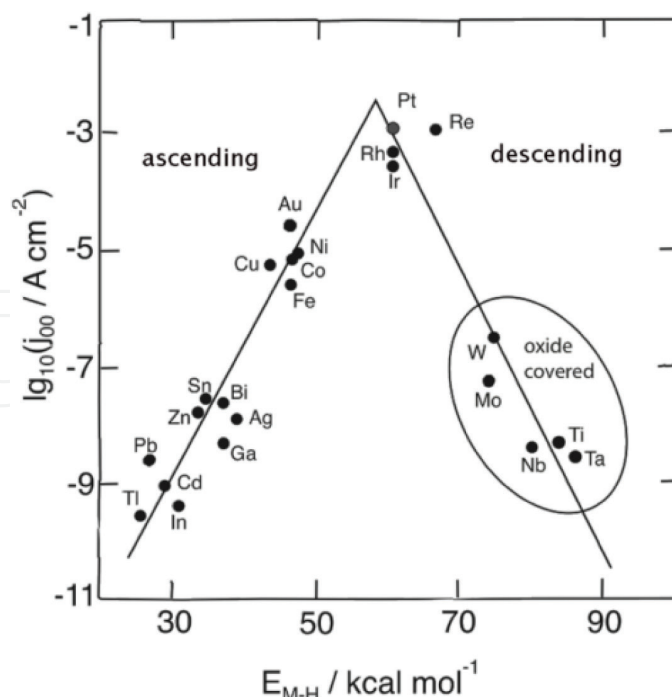
Figure 1. Dependence of the exchange current density of hydrogen evolution reaction in acid solutions against hydrogen-metal bond energy. Reprinted with permission from Ref. [8].

hydrogen reduction reaction both in acidic [10–13] and in alkaline aqueous solutions [14–17], meet these requirements, and that the use of the electrochemical method for the deposition of thin alloy coatings makes it possible to reduce the cost of electrode materials and hence the cost of produced hydrogen.

The synergetic action of alloys in comparison with individual metals is explained by researchers not only by the type of formed alloy and its chemical composition but also by the difference in the mechanism of hydrogen electroreduction on the metals, as well as by the phenomenon of interfacial diffusion of adsorbed hydrogen, hydrogen spillover. The authors of [18] showed the frequent occurrence of this phenomenon in various catalytic processes and catalyst types. Spillover is called the transport of active species, sorbed or formed on one phase, to another phase, which does not sorb and form these species. A study of the synergetic effect of alloys of cobalt and nickel with molybdenum and tungsten with allowance for hydrogen spillover was carried out in [19] for hydrodesulphurization reaction as an example, and it was suggested that different process stages occur on different catalyst phases, between which hydrogen spillover takes place. The spillover phenomenon is of great practical importance, the study of which will help to design new multiphase catalysts, where the catalytic reaction takes place by interfacial diffusion.

As applied to the alloys of molybdenum and tungsten with iron group metals, the spillover phenomenon can account for the synergetic effect of these alloys, in the case of which the discharge step on Mo(W) takes place quickly, and on Co(Ni, Fe), the electrochemical desorption step is fast. Thus, in order that this mechanism may be effected, the active centers of different nature must be at the distance from one another that makes possible the surface diffusion of hydrogen adatoms, and hence the alloy must be a solid solution or an intermetallic.

2. Electrocatalytic properties of nickel alloys

Nickel is the most commonly used cathode material in electrolyzers for hydrogen production [20] due to its catalytic properties, corrosion resistance in alkaline medium, and low cost. A possible way of intensifying the process and improving the required properties is electrode surface modification by molybdenum and tungsten alloys; therefore, many papers are devoted to the study of the electrodeposition and catalytic activity of NiMo and NiW alloys. For instance, the authors of [21] studied the electrodeposition of a NiMo alloy on a copper and a nickel substrate from a citrate electrolyte with pH 9.5 and a concentration ratio of the metals of 1/12. The best catalytic activity was found for a coating containing 41 wt.% molybdenum, and it was shown that the hydrogen evolution overpotential at the obtained alloy is lower compared with pure nickel in the model 1 M NaOH solution. In the study [22], a citrate electrolyte with pH 6.0 was also used, and it was shown that it is possible to deposit an alloy containing 28.5 at.% Mo, which reduces the hydrogen evolution overpotential in 8 M NaOH at 90°C from 122 to 21 mV·dec^{-1} relative to nickel. The authors of [23] found that when a SAS is added to a citrate-ammonia electrolyte for deposition, nanocrystalline coatings having catalytic activity at a molybdenum content of 19.59 at.% can be obtained. Chialvo and co-authors [24] studied the catalytic activity of thermal NiMo alloys as a function of the amount of molybdenum (0–25 at.%) and showed that the higher the Mo content, the lower the hydrogen overpotential. From an analysis of literature data, it can be concluded that there is no unambiguous dependence of electrocatalytic activity on the chemical composition of the coating; for each particular deposition electrolyte, activity is proportional to the molybdenum content, but from the comparison of a large number of papers, it becomes clear that the determining factor is electrolysis conditions, which determine the morphology, the true surface area, the presence of cracks, or an oxide phase on the alloy surface. Therefore, the catalytic properties of electrocatalytic alloys are determined experimentally in each particular case.

On the basis of investigations carried out by the authors of [25], it was concluded that molybdenum-bearing alloys are more active in the hydrogen evolution reaction in alkaline medium than tungsten-bearing alloys. When investigating the properties of Ni-Mo, Ni-W, Co-Mo, and Co-W alloys, it was also found that cobalt alloys show a higher catalytic activity than nickel alloys.

3. Electrocatalytic properties of cobalt alloys

The main characteristics of electrocatalytic activity in HER are reaction exchange current and hydrogen reduction overpotential. Therefore, the main method for studying this process is voltammetry.

3.1. Tungsten alloys

In the study [26], an investigation on the electrocatalytic properties of Co-W alloys electrodeposited from a polyligand citrate-pyrophosphate electrolyte had been carried out. The

coatings were deposited in a solution containing 0.1 mol L^{-1} of CoSO$_4$, 0.2 mol L^{-1} of Na$_2$WO$_4$, 0.2 mol L^{-1} of Na$_3$Cit (where Cit—citrate ions), 0.2 mol L^{-1} of K$_4$P$_2$O$_7$, 0.5 mol L^{-1} of Na$_2$SO$_4$ and in solutions containing SASs: 2 mL L^{-1} of water-soluble resin neonol, whose efficiency was shown when electrodepositing Co-W alloys from a citrate-ammonia electrolyte [27], and 1.5 g L^{-1} and 4.5 g L^{-1} of a nonionic SAS, OP-10 emulsifier. All experiments were performed under forced convection conditions in a current density range of 5.0–30.0 mA cm^{-2} at 50°C and electrolyte pH 8.5.

It can be seen from **Figure 2** that the composition of the coatings deposited from a citrate-pyrophosphate electrolyte is constant regardless of deposition current density and addition of SASs. All coatings containing on an average 22 at.% W, nevertheless, differ in the current efficiency of their deposition and in the morphology of the produced surface. A small increase in current efficiency for alloys is observed in the case of adding a SAS (neonol or OP-10) to the electrolyte. For instance, at 5.0 mA cm^{-2} in the presence of neonol, the current efficiency reaches 68%, and a compact, bright, adherent coating is formed. The addition of OP-10 has a noticeable effect only at a concentration of 4.5 g L^{-1}.

The addition of SASs to the electrolyte and deposition current density affects greatly the quality and morphology (**Figure 3**). For instance, in the electrolyte without additives at a current density of 5.0 mA cm^{-2}, compact bright coatings are deposited. When the current density is increased to 10.0 mA cm^{-2}, the coating becomes more stressed, and microcracks appear, and at 30.0 mA cm^{-2}, the formation of spherulites is observed. The addition of neonol makes it possible to obtain high-quality fine-crystalline deposits in a wider current density range, and the addition OP-10, on the contrary, facilitates the formation of spherulites and favors surface development.

The electrocatalytic properties of CoW coatings in the hydrogen reduction reaction were investigated by stationary voltammetry in 1.0 and 6.0 mol L^{-1} KOH solutions because KOH is used in industrial water electrolysis, and under experimental conditions, i.e., at room temperature, the solution has a maximum electrical conductivity at 28 wt.% KOH.
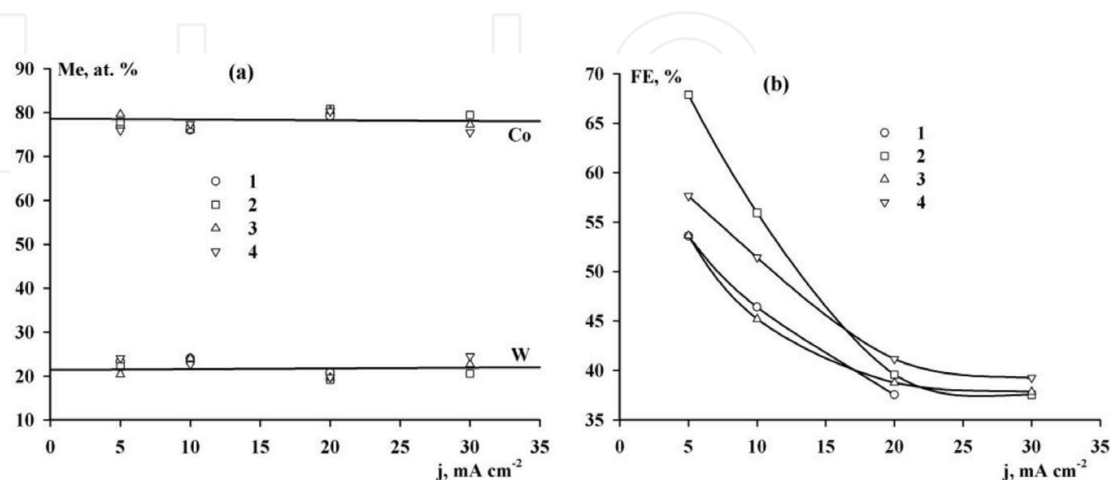

Figure 2. Dependence of the composition (a) and current efficiency (b) of Co-W alloys obtained from electrolyte: 1—without additives; 2—neonol; and 3 and 4—OP-10 (1.5 and 4.5 g L^{-1}) on the deposition current density.
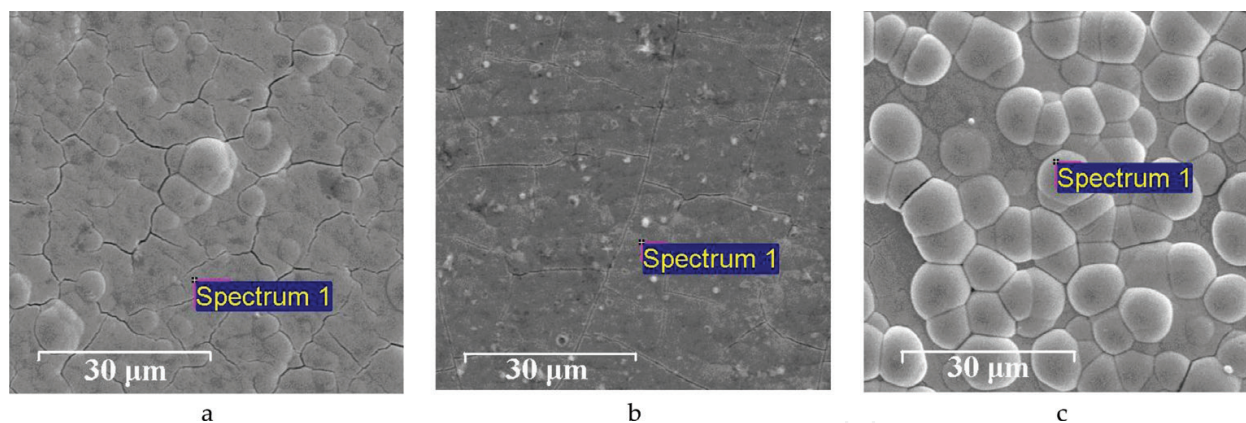
Figure 3. Microphotographs of the surface of alloys obtained from electrolytes (a) without additives and (b) neonol at a current density of 10.0 mA cm^{-2} and (c) OP-10 at 30.0 mA cm^{-2}.
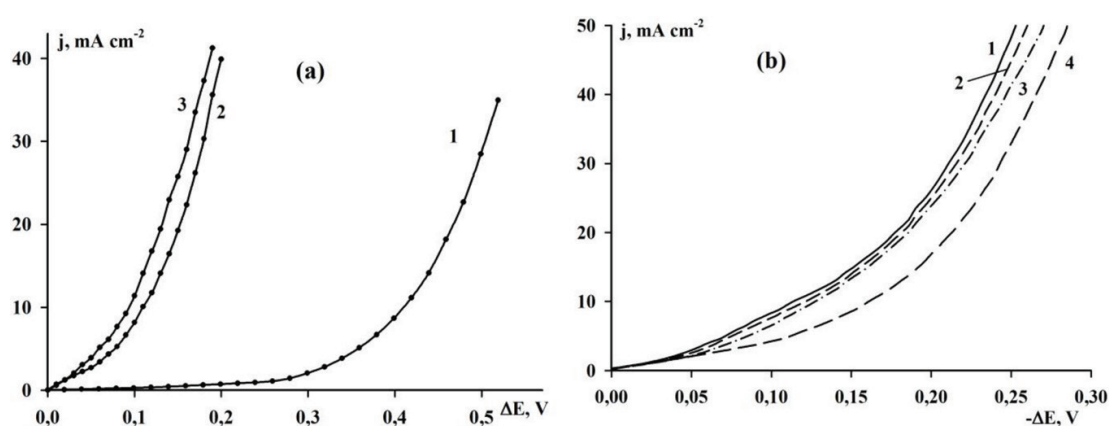
Figure 4. (a) Volt-ampere curves for the electroreduction of hydrogen in a solution of 1.0 mol L^{-1} KOH on cobalt (1) and CoW alloys (2 and 3) electrodeposited from the electrolyte without additives at 10.0 and 20.0 mA cm^{-2}, respectively. (b) Volt-ampere curves for the electroreduction of hydrogen in 6.0 mol L^{-1} KOH solution on CoW alloys, obtained from electrolytes: 1—without additives; 2—neonol; and 3 and 4—OP-10 (1.5 and 4.5 g L^{-1}) at a current density of 10.0 mA cm^{-2}.

Figure 4a shows a considerable decrease in hydrogen overpotential on CoW alloys relative to electrolytic cobalt. For instance, at the current density of 30.0 mA cm^{-2}, the overpotential decreases by 360 mV. As one would expect, a higher electrocatalytic activity is observed for the coating with more developed surface with spherulites morphology.

Figure 4b shows the effect of SASs added to an electrolyte for the deposition of CoW alloys on their electrocatalytic properties in a solution analogous to industrial electrolyte for hydrogen production. It can be seen that in this particular case, the addition of SAS rather has adverse effects, i.e., smoothing the surface during electrodeposition improves the mechanical and corrosive properties of the coating, but reduces its true surface area.

3.2. Molybdenum alloys

In the study [28], cobalt and Co-Mo alloys were deposited from a citrate-pyrophosphate electrolyte, proposed earlier [29], with the different concentration ratio of the metals in the

solution: [Co]:[Mo] = 20:1; 10:1: 5:1; 1:1 in a current density range of 10–100 mA cm^{-2} at 50°C. The studies of hydrogen electroreduction on Co-Mo alloys were carried out in solutions with different mineralization and pH, viz. 0.01 mol L^{-1} H$_2$SO$_4$; 0.5 mol L^{-1} Na$_2$SO$_4$; and 1.0 mol L^{-1} KOH. The voltammetric measurements for the determination of the kinetic parameters of hydrogen reduction were made at 25°C. The current-potential curves were recorded under potentiostatic conditions with a step of 20 mV. Before each experiment, argon was passed through the solution for 30 min.

In order to show clearly the catalytic effect of the alloy in comparison with an individual metal, current-potential curves of hydrogen reduction on pure cobalt deposited from a citrate-pyrophosphate electrolyte at a current density of 30 mA cm^{-2} and a temperature of 50°C have been obtained.

Figure 5 shows current-potential curves of hydrogen electroreduction in an acidic, an alkaline, and a neutral medium on electrolytic cobalt cathodes and cathodes made of Co-Mo alloys electrodeposited at the same current density and temperature.

Because of differences in electroreduction mechanism at different pH values, the lowest hydrogen evolution overpotential on cobalt is observed in an acidic medium and the highest in a neutral medium, as is the case with the dependence obtained for a mercury electrode and described in [30]. In the case of cobalt cathode, the coefficient *b* of the Tafel portion of the polarization curve for the acidic, alkaline, and neutral media was 0.122, 0.142, and 0.125 V, and the exchange current density was 1.93, 4.59 × 10^{-2} and 6.31 × 10^{-3} mA cm^{-2}, respectively.

Figure 5 shows a considerable decrease in hydrogen evolution overpotential on the alloy. For instance, at the current density of 10 mA cm^{-2}, the overpotential value in the alkaline medium is lower by over 200 mV.

The plots shown in **Figure 6** have been obtained on alloys electrodeposited at different current densities of 10–100 mA cm^{-2}. The abscissa of the figure gives the ratio of the amounts of the metals in the alloy, and not the exact percentage because of the peculiarities of EDX
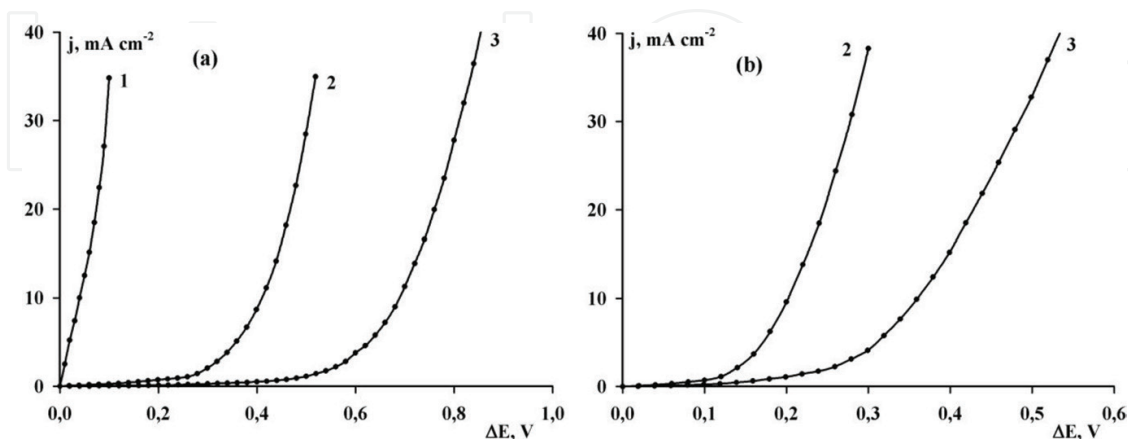
Figure 5. Stationary current-potential curves of the electroreduction of hydrogen evolution on electrolytic cobalt (a) and Co-Mo alloys (b) with the ratio [Mo]/[Mo] + [Co] = 0.33 electrodeposited at the current density 30 mA cm^{-2}, in media with different pH: 1—H$_2$SO$_4$, 2—KOH, and 3—Na$_2$SO$_4$.
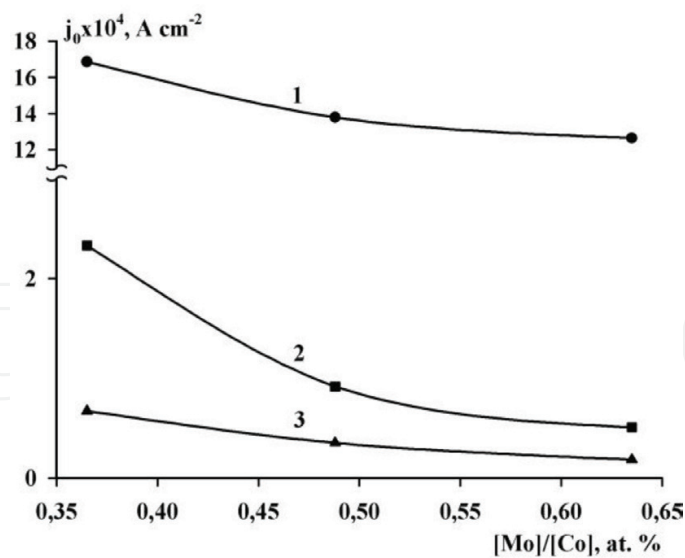
Figure 6. Dependence of the exchange current densities of the hydrogen electroreduction reaction on the ratio of molybdenum to cobalt in alloys electrodeposited at current densities of 10, 30, and 100 mA cm^{-2} from the solution with a [Co]:[Mo] ratio of 1:1 in various media: 1—H_2SO_4, 2—KOH, and 3—Na_2SO_4.

analysis, in which the coating surface layer, on which a large amount of oxygen and carbon are adsorbed. The adsorbed light elements can be removed by polishing the surface or treating it with argon ions. Both in this and in the initial case, the ratio of the metals in the alloy remains constant, as was shown in [17], with a coating depth of up to 100 nm. Thus, the ratio of molybdenum and cobalt in the surface layer, determined by EDX analysis, corresponds to the volumetric chemical composition of the alloy.

In the alloys deposited from an electrolyte with the concentration ratio [Co]:[Mo] = 1:1, the amount of molybdenum decreases and the exchange current density of the hydrogen reduction reaction increases with increasing deposition current density, which can be accounted for in terms of the value which the surface morphology and the true electrode area have, as was shown in [17]. **Figure 7** shows surface micrographs of alloys electrodeposited at two current densities of 10 and 100 mA cm^{-2}. It can be seen that at a low current density, smooth, fine-crystalline, and
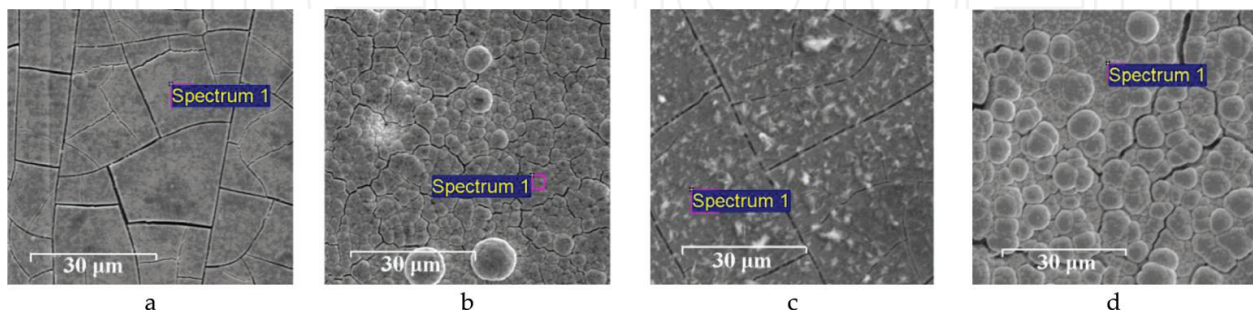

Figure 7. The morphology of Co-Mo alloys precipitated from electrolytes [Co]:[Mo] = 1:1 (a and b) and [Co]:[Mo] = 5:1 (c and d) at current densities of: a and c—10 mA cm^{-2}; b and d—100 mA cm^{-2} and the ratio of metals [Mo]/[Mo] + [Co] equal to 0.39, 0.27, 0.28, and 0.21, respectively.

bright coatings are deposited in spite of the presence of microcracks. Increasing the deposition current density to 100 mA cm^{-2} results in the formation of spherulites and considerable surface development. This regularity is observed for all investigated solutions.

The conclusion that the electrocatalytic activity decreases with increasing refractory metal content may contradict papers, published earlier, on the properties of Co-Mo coatings [17, 14]. However, attention should be called on how the coating composition was changed. There are several ways of influencing the chemical composition of alloys, viz. changing the electrolyte composition and pH, temperature, current density, hydrodynamic regime, etc. For instance, in the study [14], a change in alloy composition is achieved by changing both deposition current density and electrolyte composition and in the study [17], by changing pH and, hence, the concentration ratio of different complex species that are able to be discharged to form an alloy. Thus, it is impossible to obtain a rigorous dependence of catalytic activity on the composition of coating deposited under different conditions, because the electrolysis conditions influence not only chemical but also phase composition, which in turn influences the properties of the alloy as a whole.

The effect of change in the composition of the solution for alloy electrodeposition on the electrocatalytic properties is clearly seen in **Figure 8**, which shows current-potential curves of hydrogen electroreduction on cobalt and alloys deposited at a current density of 30 mA cm^{-2} from electrolytes containing different sodium molybdate concentrations. It is seen from the figure that the highest hydrogen evolution overpotential is observed on cobalt deposits and the lowest on the alloy deposited from the electrolyte with [Co]:[Mo] = 10:1. The kinetic parameters of hydrogen electroreduction in an alkaline medium are presented in **Table 1**.

The difference in the value of hydrogen exchange current on alloys with the same chemical composition is seen in **Figure 9**.
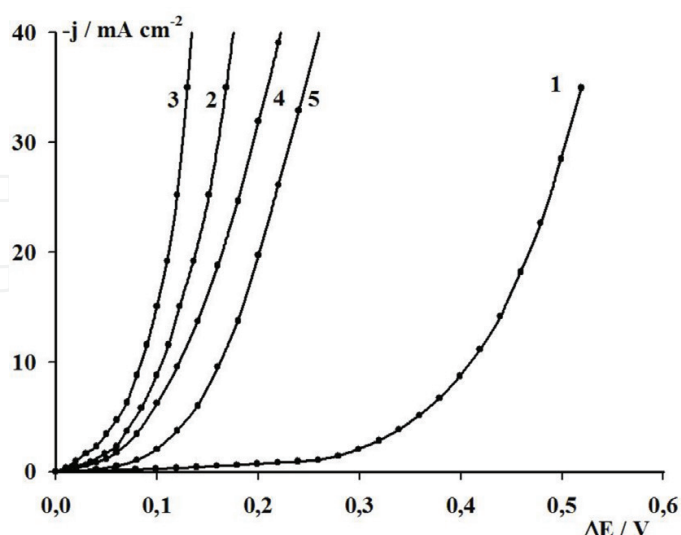

Figure 8. Polarization curves obtained in KOH solution on cobalt (1) and Co-Mo alloys with the ratio of metals [Mo]/[Mo]+[Co] equal to (2)—0.11, (3)—0.19, (4)—0.23, and (5)—0.33, respectively, electrodeposited at 30 mA·cm^{-2} from electrolytes [Co]:[Mo] = 20:1, 10:1, 5:1, 1:1, respectively.

Electrolyte	$j_{dep.}$ (mA cm^{-2})	E_0 (V)	a	b	j_0 (mA cm^{-2})	[Mo]/([Mo] + [Co])*
Co	30	−0.821	0.190	0.142	4.59×10^{-2}	—
[Co]:[Mo] = 20:1	10	−0.910	0.181	0.134	4.46×10^{-2}	0.22
	30	−0.985	0.038	0.077	3.21×10^{-1}	0.11
[Co]:[Mo] = 10:1	10	−0.940	0.125	0.091	9.23×10^{-2}	0.25
	20	−1.005	0.045	0.058	1.67×10^{-1}	0.23
	30	−1.025	0.025	0.056	3.58×10^{-1}	0.19
[Co]:[Mo] = 5:1	10	−0.920	0.130	0.155	1.25×10^{-1}	0.28
	30	−0.980	0.050	0.062	1.56×10^{-1}	0.23
	100	−1.000	0.035	0.053	2.19×10^{-1}	0.21
[Co]:[Mo] = 1:1	10	−0.900	0.189	0.146	5.08×10^{-2}	0.39
	20	−0.935	0.110	0.089	5.81×10^{-2}	0.37
	30	−0.980	0.083	0.080	9.17×10^{-2}	0.33
	40	−0.965	0.069	0.077	1.27×10^{-1}	0.30
	100	−1.010	0.043	0.068	2.33×10^{-1}	0.27

Here, $j_{dep.}$ is the current density of alloy deposition; E_0 is the stationary potential of the alloy in a KOH solution; a and b are coefficients in the Tafel equation; and j_0 is hydrogen exchange current density.

*The ratio of the metals was calculated based on their atomic fraction in alloys.

Table 1. Kinetic parameters of hydrogen reduction reaction in a 1 mol L^{-1} KOH.
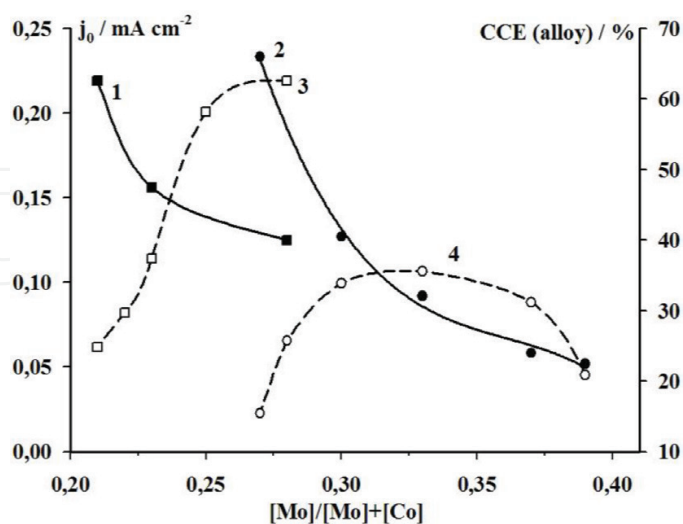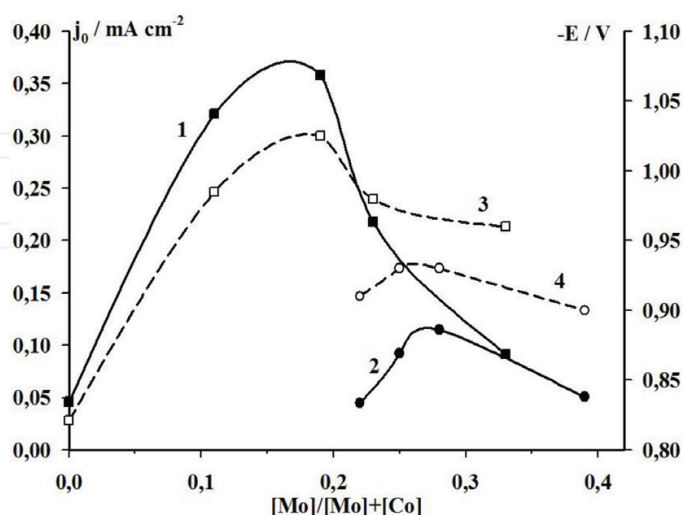

Figure 9. The dependence of the exchange current of the hydrogen reduction in a 1.0 mol L^{-1} KOH solution (1 and 2) and the current efficiency (3 and 4) of the Co-Mo alloys electrodeposited in the electrolytes [Co]:[Mo] = 5:1 and [Co]:[Mo] = 1:1 on the ratio of metals in the alloy.

In **Figure 9**, attention should be called on how the current efficiency of the deposition of the alloy and its electrocatalytic activity correlate with each other. In spite of the fact that the current efficiency was measured for a citrate-pyrophosphate electrolyte for deposition, this electrolyte is a weakly alkaline salt solutions, in which the alloys that are formed also exhibit electrocatalytic activity against the parallel cathodes process, with hydrogen electroreduction; therefore, the plots shown in **Figure 9** are of antibate character. Therefore, alloys, electrodeposited at high current densities up to 100 mA cm^{-2} and having the highest catalytic activity (for all deposition electrolytes) are deposited with the lowest current efficiency.

From the obtained data, it can be concluded that in the case of Co-Mo alloys electrodeposited from citrate-pyrophosphate electrolytes, the hydrogen exchange current decreases for each particular electrolyte with increasing amount of molybdenum in the alloy. However, in a series of electrolytes with the different concentration ratio of the discharging metals, the alloys that differ greatly in chemical composition can have the same electrocatalytic activity; this can be seen in **Figure 10**, which shows values of hydrogen exchange currents and stationary potentials for alloys deposited at the same current density, but from different electrolytes.

An extreme form is typical both of the plots of hydrogen exchange current density vs. the ratio of the alloy components and of the stationary potential values of the alloy in the KOH solution.

Thus, the optimal electrolyte for the making of electrocatalytic Co-Mo alloys is the electrolyte with a cobalt and molybdenum concentration ratio of 10:1, which occupies an intermediate position in the series of investigated solutions; so, increasing or decreasing the concentration of sodium molybdate and hence of molybdenum in the alloy results in the deterioration of the catalytic properties of the coating.

Figure 10. The dependence of the exchange current (1 and 2) and the stationary potential (3 and 4) in the KOH solution on the molybdenum and cobalt ratio in alloys deposited at current densities, mA cm^{-2}. 1: 3—30; and 2: 4—10.

It is known [10] that the electrocatalytic activity of electrode material can be increased by several ways, e.g., by increasing the true working surface area of the catalyst, viz. by making the catalyst not in the form of a continuous film, but in the form of nanofibers [31]. The true surface area must be estimated when fabricating continuous alloy coatings, as this was done in [17]; it should be noted, however, that the factor of surface development is not determining in the ascertainment of the causes of the electrocatalytic activity of the materials under investigation. Another important factor is the nature of the metals comprising the alloy, which was shown in [25], but the physicochemical properties of one metal do not account for the synergetic effect in the use of alloys. The phenomenon that describes most reliably the synergetic action of two or more metals is spillover effect, which was described in [10–12]. Since hydrogen evolution occurs on Co and Mo with different rate-determining steps, as was said above, the occurrence of hydrogen spillover makes it possible to bring about a fact reaction (1) on molybdenum atoms and a rapid electrochemical desorption (2) on cobalt atoms.

Because of this, the synergetic effect of the alloy will manifest itself when the atoms are arranged in an optimal manner to perform sequential reaction steps. This is possible when the alloy is an intermetallic, an amorphous phase, or solid solutions with nanosized crystals.

When we attempted to investigate the coatings obtained by us by X-ray phase analysis, we have not obtained somewhat well-defined peaks of phases, i.e., the coatings were either very fine-crystalline, below the device sensitivity level, or amorphous. However, different properties (e.g., corrosion or magnetic properties) of Co-Mo alloys of the same composition have also been obtained by us earlier. Their phase composition has been studied by us by stripping analysis and shown in [32].

4. Corrosion properties

Some of the main characteristics of modern catalytic materials are not only their activity in the desired reaction but also mechanical strength and corrosion resistance in aggressive media; therefore, the comprehensive investigation of the physicochemical properties of the electrode material is an important scientific and technical problem.

4.1. Tungsten alloys

In the study [26], the corrosion characteristics of electrolytic Co-W alloys deposited from a citrate-pyrophosphate electrolyte in 3.5% NaCl and 6 mol L^{-1} KOH solutions at 25°C have been determined by EIS and stationary voltammetry (**Figure 11**).

The impedance hodographs obtained at a stationary potential in a corrosive medium can be described by a circuit comprising the ohmic resistance of the solution, charge transfer (corrosion) resistance, and a constant phase element. The corrosion parameters calculated in accordance with this equivalent circuit are listed **Table 2**.

The coating deposited at a current density of 5.0 mA cm^{-2} has the highest corrosion stability because in the region of kinetic control of electrochemical reaction, most fine-crystalline
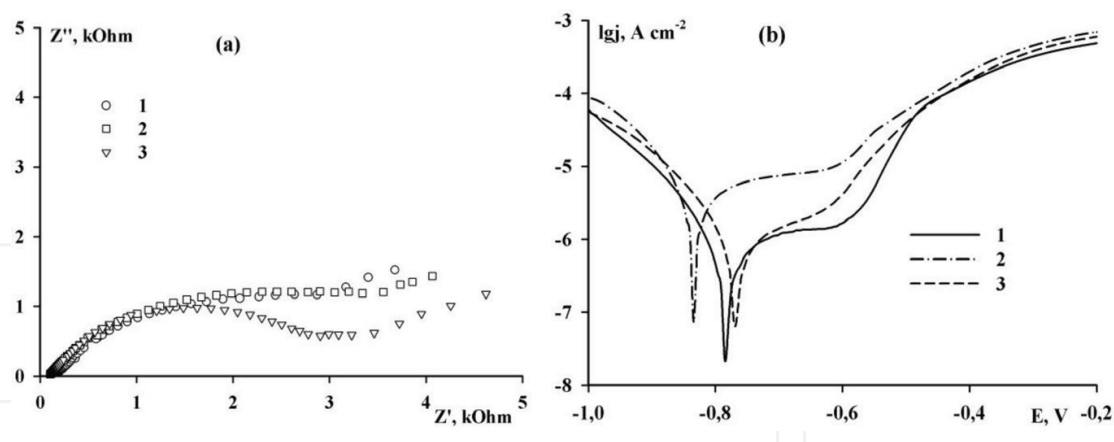
Figure 11. Electrochemical impedance spectra (a) and current-potential curves (b) obtained in the case of corrosion of coatings electrodeposited from a citrate-pyrophosphate electrolyte at the current densities mA cm^{-2}: 1—5.0; 2—10.0; and 3—20.0.

and compact deposits are formed. Since the chemical composition of the coatings deposited from a citrate-pyrophosphate electrolyte is almost constant, the dependence of polarization resistance on deposition current density can be attributed to a difference in surface morphology and the appearance of microcracks on increasing the deposition current. On the whole, the corrosion rate of the obtained alloys is comparable with that in an analogous solution of electrolytic chromium deposited from Cr(III) and Cr(VI) baths in the study [33] (**Figure 12**).

The parameters of the corrosion process, determined by the electrochemical impedance method, have been calculated on the basis of an equivalent circuit comprising the ohmic resistance of the solution, corrosion resistance, a constant phase element, and Warburg impedance (**Table 3**).

The corrosion studies, carried out by us, of CoW alloys in a 6.0 mol L^{-1} KOH solution showed that the corrosion resistance in a concentrated KOH solution (**Figure 12**) is two order of magnitude lower than in a model NaCl solution; nevertheless, the coatings can be considered corrosion proof. It was noted that the coatings obtained for the experiment are of the worst quality in comparison with others, since they are intermediate at the transition from fine crystalline to spherulite deposits. The deposits of these two types are dense and smooth, and only at 10.0 mA cm^{-2}, the largest number of cracks is observed, which accordingly affects the properties of coatings; nevertheless, the coatings have a low corrosion rate and are passivated in alkaline solution.

	j (mA cm^{-2})	W (at.%)	R (kOhm cm^{-2})	R$_p$ (kOhm cm^{-2})	E$_{corr}$ (V)	J$_{corr}$ × 10^5 (A cm^{-2})
1	5.0	23.3	18.0	41.2	−0.782	1.35
2	10.0	24.0	18.8	6.9	−0.834	8.53
3	20.0	20.8	12.8	16.6	−0.786	5.24

Here, j is alloy deposition current density; W is tungsten content, at.%; R is corrosion resistance determined by the impedance method; R$_p$ is corrosion resistance determined by voltammetry; E$_{corr}$ is corrosion potential; and j$_{corr}$ is corrosion current density.

Table 2. Corrosion parameters of alloys in a 3.5% NaCl solution.
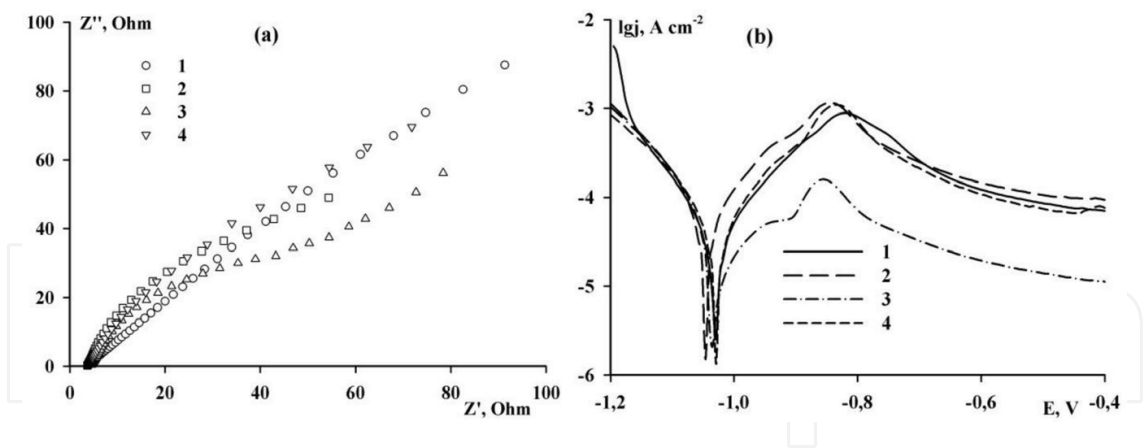
Figure 12. Spectra of electrochemical impedance (a) and current-potential curves (b), obtained in the case of corrosion in a 6.0 mol L^{-1} KOH solution, for coatings electrodeposited at a current density of 10.0 mA cm^{-2} from electrolytes 1—no additives; 2—neonol; 3 and 4—OP-10 (1.5 and 4.5 g L^{-1}).

Electrolyte	W (at.%)	R (kOhm cm^{-2})	R$_p$ (kOhm cm^{-2})	E$_{corr}$ (V)	J$_{corr}$ × 10^3 (A cm^{-2})
1	24.0	0.92	0.58	−1.03	0.84
2	23.7	0.46	0.37	−1.05	0.11
3	24.0	0.34	0.40	−1.04	0.17
4	22.6	0.40	0.48	−1.03	0.12

Table 3. Corrosion parameters of alloys in a 6 mol L^{-1} KOH solution.

4.2. Molybdenum alloys

To determine the corrosion properties of electrolytic Co-Mo alloys in the study [34], the coatings were deposited from a citrate-pyrophosphate electrolyte with different concentration ratios of the metals: [Co]/[Mo] = 1/1 and [Co]/[Mo] = 5/1. The aim of the authors was a large percentage of a component having ferromagnetic properties, i.e., cobalt. To fabricate cobalt-rich alloys, electrolytes with low sodium molybdate content and, hence, with small amount of molybdenum in the coating are used.

As is seen from **Figure 13**, the amount of molybdenum in the alloy electrodeposited from an electrolyte at [Co]/[Mo] = 5/1 decreased relative to the alloy deposited from an electrolyte with [Co]/[Mo] = 1/1; in this case, however, no direct proportionality between the molybdenum content of the alloy and solution is observed. For instance, the concentration ratio of molybdate and cobalt in the electrolyte was 0.2 and changed from 0.4 to 0.27 in the coating. The amount of cobalt in the deposit changes only slightly on increasing the current density, but the percentage of nonmetallic impurities, mainly oxygen, increases, which affect the internal stresses in the deposit. Nevertheless, this change in the concentration ratio of the metals in the solution leads to a great increase in current efficiency for the alloy at low current densities (**Figure 13b**). Thus, it can be stated that in terms of the cobalt content of the alloy, the most optimal conditions for the deposition of magnetic coatings are current densities of 10–50 mA cm^{-2}.
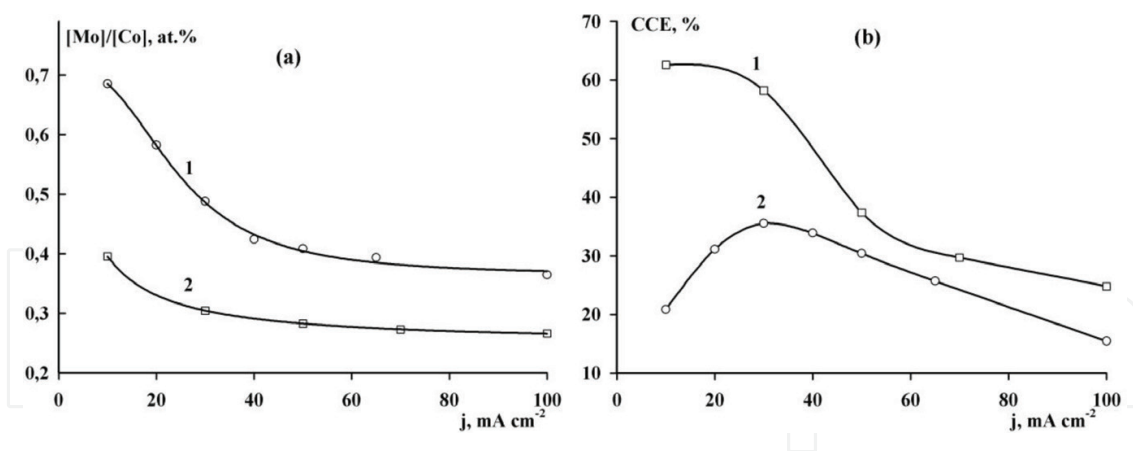
Figure 13. Dependence of the ratio of the metals content (a) and current efficiency (b) for alloys electrodeposited from electrolytes with a concentration ratios [Co]/[Mo] = 1/1 and [Co]/[Mo] = 5/1 on current density.

The corrosion test of the obtained coatings was carried out in a sulfate-chloride solution. The calculation of corrosion resistance from electrochemical impedance data has been performed on the basis of an equivalent circuit comprising the ohmic resistance of the solution, charge transfer resistance, and a constant phase element.

Alloy samples electrodeposited from an electrolyte with [Co]/[Mo] = 5/1 with increasing current density, i.e., with decreasing molybdenum content (**Figure 13**, curve 2), and an alloy electrode-posited from an analogous citrate electrolyte containing no pyrophosphate at 30 mA cm^{-2}, have been investigated. **Figure 14** and **Table 4** show no clear correlation between the molybdenum content of the alloy and corrosion resistance. Besides, the coatings deposited from solutions with the same ratio of the metals in the presence and absence of pyrophosphate are similar in anticorrosion properties despite the difference in their chemical composition.

The anticorrosion resistance of Co-Mo coatings is usually associated with the percentage content of molybdenum in them as a more corrosion-resistant metal, and the magnetic properties
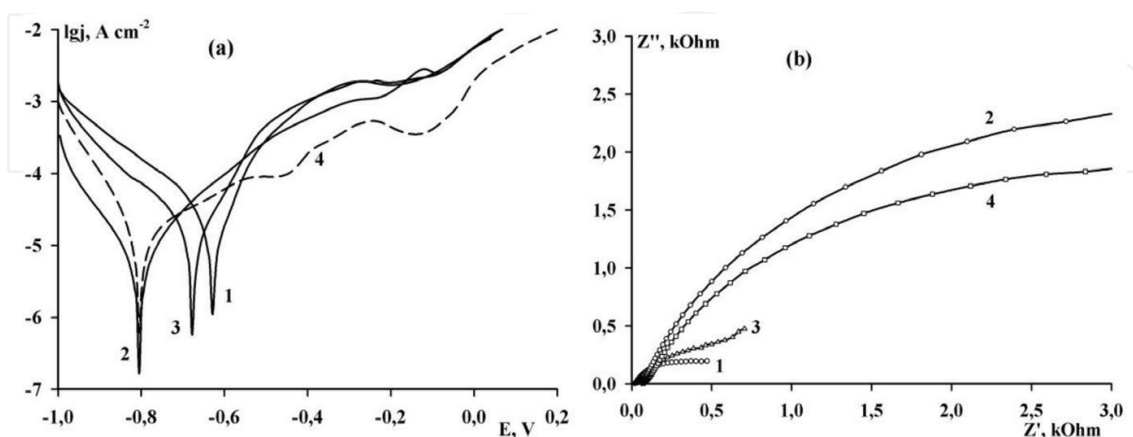
Figure 14. Stationary current-potential curves (a) and electrochemical impedance spectra (b) of the corrosion of alloys deposited from polyligand electrolyte (1–3) and a citrate electrolyte (4) at the deposition current densities, mA cm^{-2}: 1—10; 2 and 4—30; and 3—50.

Electrolyte	j (mA cm^{-2})	Mo (at.%)	R (Ohm)	R$_p$ (Ohm)	E$_{corr}$ (V)	J$_{corr}$ (A cm^{-2})
Citrate-pyrophosphate	10	21.5	5.05×10^2	2.97×10^3	−0.627	3.58×10^{-4}
	30	17.4	5.71×10^3	1.77×10^4	−0.804	829×10^{-6}
	50	16.0	7.02×10^2	3.55×10^2	−0.677	6.40×10^{-4}
Citrate	30	23.9	4.57×10^3	8.06×10^3	−0.804	2.83×10^{-5}

Here, j is deposition current density.

Table 4. Dependence of the corrosion parameters of Co-Mo alloys on alloy composition.

of coatings—with a cobalt content as a metal with ferromagnetic properties. However, the functional properties of coatings can depend not only on the chemical composition of the alloy but also on its phase composition, morphology, thickness, porosity, and other factors.

When studying the corrosion and magnetic properties of Co-Mo coatings [32] deposited from a citrate-pyrophosphate electrolyte, it was found that for the coatings obtained under different electrolysis conditions and having the same chemical composition, the corrosion stability and magnetic parameters are different; it was suggested that the properties of the alloy largely depend on its phase composition.

In the study, the corrosion and magnetic properties of coatings with same Mo content of the alloy (21.2 at.%), deposited from a citrate-pyrophosphate electrolyte under different electrolysis conditions, have been investigated. The corrosion stability of the coatings was studied in a solution containing 7 g L^{-1} Na$_2$SO$_4$ and 7 g L^{-1} NaCl at pH 6.0 and 24 ± 1°C (**Table 5**). The magnetic properties (**Table 6**) of the obtained deposits were determined by means of a vibrating sample magnetometer in fields of up to 20 kOe at room temperature (**Table 5**).

The magnetic characteristics of such Alloys are also given. Their calculated values are listed in **Table 6**. The main criteria for evaluating the properties of soft-magnetic materials are low coercive force, low remanent magnetization and high saturation magnetization, as well as the ability to reach saturation magnetization in low intensity fields. It is evident from **Table 6** that the largest saturation magnetization values—927 Gs were obtained at a magnetic field intensity of 3 kOe for the alloys deposited from an electrolyte with a ratio of 5:1. For the coatings deposited from an electrolyte with ratio of 1:1, no saturation magnetization is observed even at 20 kOe; the maximum value obtained under experimental conditions for alloys deposited at 25° and 50°C was 113 and 290 Gs, respectively. Thus, it can be concluded that the alloy deposited from an electrolyte with the concentration ratio of the metals [Co]/[Mo] = 5/1. We assumed that such a difference in functional properties for the coatings having the same chemical composition may be due to a difference in their phase composition.

Deposition electrolyte	j (mA cm^{-2})	t (°C)	R$_p$ (Ohm)	E$_{corr}$ (V)	J$_{corr}$ (A cm^{-2})
[Co]/[Mo] = 1/1	30	25	2.71×10^3	−0.804	8.44×10^{-5}
[Co]/[Mo] = 1/1	40	50	9.82×10^2	−0.808	2.54×10^{-4}
[Co]/[Mo] = 5/1	10	50	2.97×10^3	−0.627	3.58×10^{-4}

Table 5. Corrosion properties of alloys having the same chemical composition (21.2 at.% Mo).

Deposition electrolyte	j (mA cm^{-2})	t (°C)	H (Oe)	M_R (Gs)	M_S (Gs)
[Co]/[Mo] = 1/1	30	25	155	5.0	113
[Co]/[Mo] = 1/1	40	50	117	20.0	290
[Co]/[Mo] = 5/1	10	50	102	252	927

Here, H is coercive force, M_R is remanent magnetization, and M_S is saturation magnetization.

Table 6. Magnetic properties of alloys having the same chemical composition (21.2 at.% Mo).

To study the phase composition, the electrochemical method of linear stripping voltammetric analysis (LSVA) was used [35]. An advantage of this method, besides simplicity, is the possibility to follow the dissolution dynamics of the alloy. Before the stripping analysis, a 0.5 μM thick layer of Co or Co-Mo alloys were deposited onto the working electrode from a citrate-pyrophosphate electrolyte with the concentration ratios of the metals [Co]/[Mo] = 1/1 and [Co]/[Mo] = 5/1 at a current density of 10–100 mA cm^{-2} and a temperature of 25 and 50°C.

The electrolyte for the anodic dissolution of the obtained alloy deposits must meet the following requirements: it must have a high electrical conductivity, be nonaggressive toward the coating, and not cause spontaneous chemical dissolution. In this electrolyte, an electrochemical side reaction paralleling the anodic dissolution of the deposit under investigation must be ruled out. The use of various acids as working solutions was considered inexpedient since the electrochemical process in such electrolytes is paralleled by the chemical dissolution of the coating under analysis. Alkaline solutions are unsuitable for use as working electrolytes because of passivation processes on the surface of samples under investigation. The optimal solution for the anodic dissolution of coatings under investigation is NaCl solution, which makes it possible to obtain on the current-potential curves clear peaks corresponding to the dissolution potentials of the various phases of the alloy. The stripping analysis of coatings was performed in a 0.5 M NaCl solution at 25°C on a rotating disk electrode at a rotational speed of 774 rpm.

Figure 15 shows a current-potential curve of the dissolution of freshly deposited cobalt (curve 1) in a 0.5 M NaCl solution. The observed dissolution peaks are traditionally attributed to the complex phase structure of metals and alloys, but their number depends on the electrolyte in which dissolution is performed [35]. The plot of cobalt dissolution current vs. potential exhibits three peaks, which we further use in order to distinguish the peaks of dissolution of the alloy from the peaks of cobalt dissolution. The figure shows plots except the oxygen and chlorine evolution curve. It can be seen that in the case of dissolution of alloys, the magnitude of the peaks and their number are different. For instance, for the alloys deposited from an electrolyte with the same concentration ratio of the metals, the magnitude of peak 1 is the same, but besides it, only one large peak is observed for the alloy obtained at 50°C and 40 mA cm^{-2}, whereas two peaks are observed for the alloy obtained at 25°C and 30 mA cm^{-2}. However, for the alloy deposited from an electrolyte with lower molybdate content, the magnitude of peak 1 is much larger than for other alloys. Based on the potentials of the peaks, the known cathodic quantity of electricity, the phase diagram of the double layer, and stoichiometry, it can be suggested that peaks 1 and 3 relate to cobalt dissolution and peak 2 to the dissolution of a solid solution of the chemical compound CoMo in cobalt.
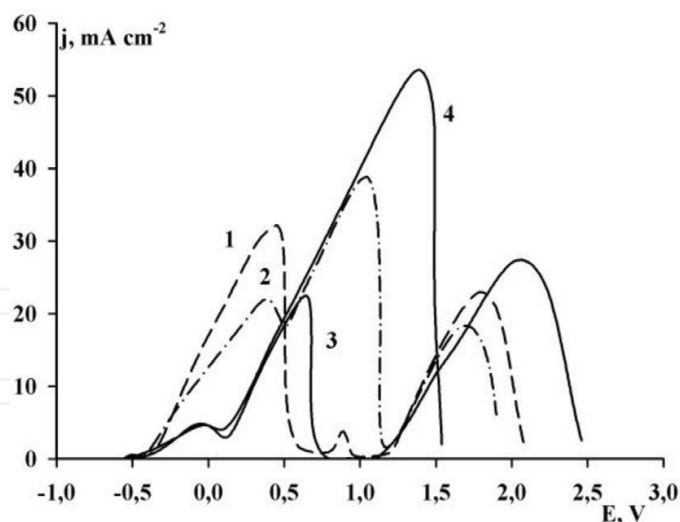
Figure 15. Anodic dissolution curves for pure cobalt (curve 1) and Co-Mo alloys (21.1 at.% Mo) deposited under the following conditions: 2—Co:Mo = 5:1, 50°C, 10 mA cm^{-2}; 3—Co:Mo = 1:1, 25°C, 30 mA cm^{-2}; 4—Co:Mo = 1:1, 50°C, 40 mA cm^{-2}.
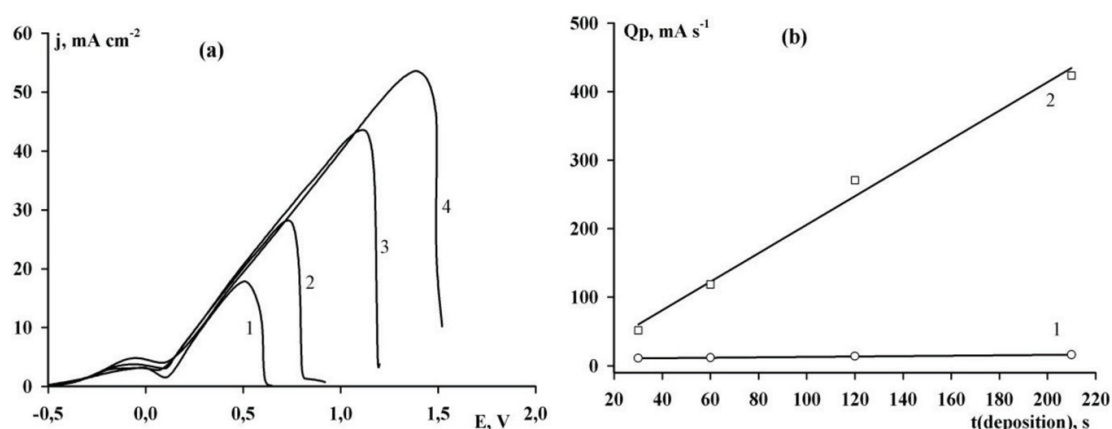
Thus, the alloy deposited from an electrolyte containing a small amount of molybdate contains a larger amount of cobalt bound into neither a chemical compound nor a solid solution; this can explain the 200 mV shift of the corrosion potential of this alloy to positive values, i.e., cobalt is a more electropositive metal than molybdenum, as well as the improvement of the magnetic properties of the alloy. The increase in peak 2 indicates an increase in the percentage of the molybdenum-rich phase, which results in the improvement of the corrosion properties of alloys.

Stripping analysis of alloys deposited from an electrolyte with [Co]/[Mo]=1/1 at different current densities is shown in **Figure 16**. It is seen from the figure that for the coatings obtained at lower deposition current densities 10–20 mA cm^{-2}, three dissolution peaks are observed. For the alloys deposited at 30 and 40 mA cm^{-2}, only two dissolution peaks are observed. The magnitude of peak 1 remains unchanged, and it can be assumed to correspond to the amount of cobalt that is directly on the electrode surface, i.e., dissolution of the less corrosion-resistant component than the alloy takes place, and since the electrode geometry does not change, the quantity of electricity for dissolution remains constant too. In the remaining alloy phase at different current densities, different redistribution of cobalt between the solid solution and the free α-phase takes place.

To study the alloy formation process, anodic polarization curves have been obtained for Co-Mo alloys deposited from an electrolyte with [Co]/[Mo] = 1/1 under the conditions corresponding to the maximum current efficiency: a current density of 30 mA cm^{-2} and at temperature of 50°C [36]. The coatings were deposited during 30, 60, 120, and 210 s (**Figure 17**). All current-potential curves of the dissolution of Co-Mo alloys exhibit two peaks. As one would expect, the quantity of electricity for the dissolution of the solid solution increases linearly with deposition time. We failed, however, to determine the order of deposition of the components; using this method, it is impossible to either confirm or refute the hypothesis that cobalt deposits first, which catalyzes later the reduction of molybdenum. Under our experimental conditions, an alloy phase which grows uniformly with increasing deposition time is present in the alloy even within a deposition time of 30 s.
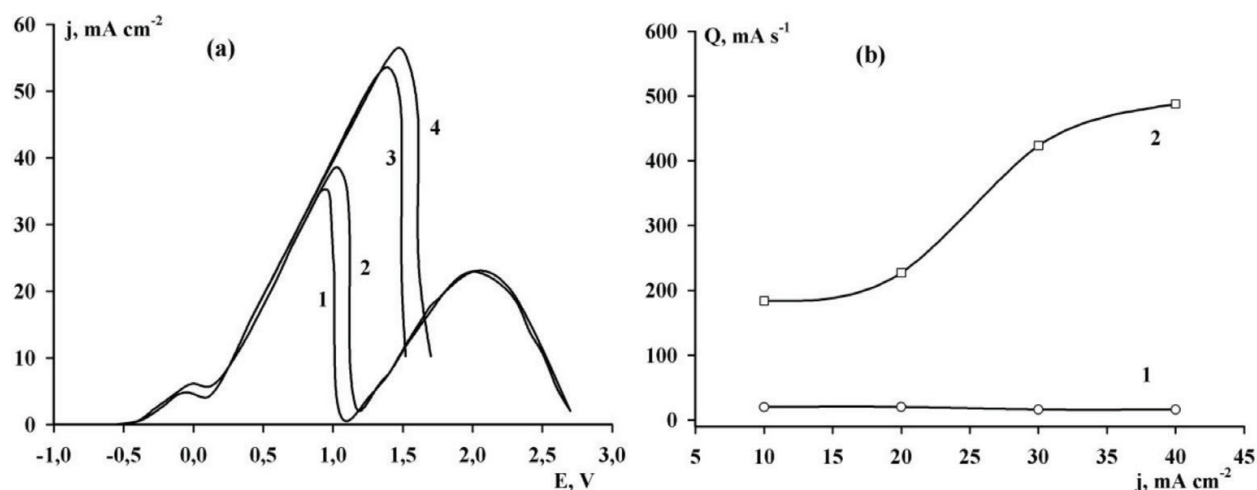
Figure 16. (a) Anodic current-potential curves of the dissolution of Co-Mo alloys deposited from an electrolyte at [Co]/[Mo] = 1/1 at 50°C at different current densities, mA cm^{-2}: 1—10, 2—20, 3—30, 4—40 and (b) The magnitude of anodic dissolution peaks.

Figure 17. (a) Anodic current-potential curves of the dissolution of Co-Mo alloys deposited from an electrolyte with [Co]/[Mo]=1/1 at 30 mA·cm^{-2} and 50°C at different deposition time, s: 1—30, 2—60, 3—120, 4—210. (b) The magnitude of the anodic dissolution peaks: 1—the first peak, and 2—the second peak.

5. Conclusions

Electrolytic alloys of molybdenum and tungsten with iron subgroup metals possess catalytic properties in the hydrogen evolution reaction and can be used as a coating which improves the properties of exiting nickel cathodes.

For each particular electrolyte and particular deposition conditions, the activity of the alloy and its corrosion stability increase with the amount of molybdenum, but the comparison of data obtained by different authors does not give a clear correlation.

The properties of alloys depend not only on their chemical composition but also on their phase composition. The alloy containing the same amount of molybdenum, but fabricated under different conditions, has different corrosion and magnetic properties.

The amorphous and nanocrystalline structure of electrolytic alloys makes hydrogen spillover possible, which greatly accelerates the hydrogen reduction process in alkaline electrolytes.

Electrolytic coatings of refractory metals alloys have a wide range of physicochemical properties. Controlling the electrolysis modes allows precipitating and accurately controlling the chemical and phase composition of the coatings, and hence producing corrosion-resistant materials for soft magnetic materials, electrocatalysts, and wear-resistant coatings.

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