

PACS numbers: 68.55.J-, 81.15.Pq, 81.65.Kn, 82.45.Bb, 82.45.Hk, 82.45.Jn, 82.45.Qr

## Electrocatalytic and Corrosion Properties of CoWRe Alloys Electrodeposited from a Citrate-Pyrophosphate Electrolyte

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This work presents studies of the electrocatalytic properties of ternary CoWRe alloys during the hydrogen-evolution reaction in KOH solution and their corrosion properties in KOH, H<sub>2</sub>SO<sub>4</sub> and NaCl solutions. These alloys are electrodeposited from a citrate-pyrophosphate electrolyte with potassium-perrhenate concentrations of 0.01, 0.03, and 0.05 mol·l<sup>-1</sup>. As shown, the use of such alloys makes it possible to increase the exchange current density by an order of magnitude and reduce the hydrogen overvoltage by 150 mV compared to electrolytic cobalt. An increase in the content of rhenium in the alloy leads to an increase in the overvoltage of hydrogen evolution in alkaline solutions: both in the KOH solution and in the electrolyte for the deposition of the alloy that explains the high current efficiency when obtaining alloys' coatings. As shown, the highest corrosion resistance of such coatings with the ratio Re:W = 2:4 reaches 8.9 kΩ·cm<sup>2</sup> in NaCl solution, and in KOH solution, it is of 3.1 kΩ·cm<sup>2</sup>, and corrosion resistance increases in time.

**Key words:** cobalt, tungsten, rhenium, electrodeposition, corrosion, electrocatalysis.

У роботі представлено дослідження електрокаталітичних властивостей потрійних стопів CoWRe у реакції виділення Гідрогену в розчині KOH та корозійних властивостей цих стопів у розчинах KOH, H<sub>2</sub>SO<sub>4</sub> та NaCl. Стопи електроосадували з цитратно-пірофосфатного електроліту з концентрацією перренату Калію у 0,01, 0,03 і 0,05 моль·л<sup>-1</sup>. Показано, що використання таких стопів дає змогу на порядок збільшити густину струму

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Citation: Yu. S. Yapontseva, T. V. Maltseva, and V. S. Kublanovsky, Electrocatalytic and Corrosion Properties of CoWRe Alloys Electrodeposited from a Citrate-Pyrophosphate Electrolyte, *Metallofiz. Noveishie Tekhnol.*, **46**, No. 5: 491–505 (2024). DOI: [10.15407/mfint.46.05.0491](https://doi.org/10.15407/mfint.46.05.0491)

обміну Гідрогену та зменшити перенапругу Гідрогену на 150 мВ порівняно з електролітичним Кобальтом. Збільшення вмісту Ренію у стопі приводить до збільшення перенапруги виділення Гідрогену в лужних розчинах — як в розчині KOH, так і в електроліті для осадження стопу, що пояснює високі значення виходу за струмом під час одержання покриттів з таких стопів. Показано, що корозійна стійкість покриттів є найбільшою за співвідношення Re:W = 2:4; опір корозії сягає 8,9 кОм·см<sup>2</sup> у розчині NaCl, а у розчині KOH — 3,1 кОм·см<sup>2</sup> та з часом зростає.

**Ключові слова:** Кобальт, Вольфрам, Реній, електроосадження, корозія, електрокаталіза.

*(Received 5 October, 2023; in final version, 10 January, 2024)*

## 1. INTRODUCTION

The modern development of hydrogen fuel cell and internal combustion engine technologies creates good prospects for the development of method for the production, storage and use of eco-friendly hydrogen fuel. As was pointed out in [1–3], the increase in power consumption in the world and striving for using renewable power sources put pure hydrogen production among important and urgent tasks. The electrolytic method of hydrogen production is a highly efficient, but expensive method because of the cost of electrocatalysts based on platinum metals. Thin-layer coatings of base metal alloys can solve this problem thanks to deposition onto a cheaper metallic substrate and modifying the surface to impart the required functional properties to it.

Among the various methods of applying protective functional coatings, such as chemical deposition, thermal spraying and vapour deposition, the galvanic method occupies a special place, since it allows one to obtain coatings of a given composition and structure.

It is known that electrolytic binary refractory metals alloys with iron subgroup metals (including CoW and CoRe) exhibit electrocatalytic properties in the hydrogen evolution reaction (HER) in acidic and alkaline solutions [4–9]. The difference between rhenium alloys and alloys of other refractory metals (molybdenum and tungsten) is that the rhenium content in coatings can be varied over a very wide range (11–80 at.%), while, for tungsten alloys [9], the concentration of the refractory component at electrodeposition from similar solutions does not exceed 30 at.%. It was shown in [8] that CoRe alloys exhibit the highest electrocatalytic activity (EA) at low (20–30 at.%) and high (> 60 at.%) concentrations of refractory metal.

Ternary CoWRe alloys deposited from an acidic citrate electrolyte also exhibit electrocatalytic activity in HER [10, 11]. The use of ternary alloys makes it possible to arise significantly the exchange current density of hydrogen and to reduce hydrogen evolution overvoltage

compared to binary alloys. In [10, 11], the concentration of perrhenate ions was 0.01 mol/l, and the concentration of rhenium in the ternary alloy did not exceed 40%. In the present work, the concentration range of potassium perrhenate in the electrolyte for the deposition of alloys was extended in comparison with [10, 11] and amounted to 0.01–0.05 mol/l. The aim of our work was to study the electrocatalytic properties of CoWRe ternary alloys deposited from a citrate-pyrophosphate electrolyte, the use of which makes it possible to increase the rate of the electrodeposition process and obtain high-quality uniform coatings with a higher current efficiency relative to the citrate deposition electrolyte and with a high content of rhenium and tungsten in the coatings.

A technical characteristic required for the use of new electrocatalysts is their stability in aggressive medium. Therefore, it is necessary to investigate the corrosion properties of coatings in solutions, which are used to produce electrolytic hydrogen, *i.e.* KOH and H<sub>2</sub>SO<sub>4</sub>, and in a simulated corrosive NaCl solution in order that the characteristics of the materials obtained can be compared with literature data on similar materials.

Corrosion properties of electrolytic alloys Co–W in solutions of H<sub>2</sub>SO<sub>4</sub> and NaCl were studied in [12–14]. It is shown that coatings containing 17–24 at.% W have the highest corrosion resistance, which practically correspond to the composition of the Co<sub>3</sub>W intermetallic phase, as well as to the transition from the polycrystalline to amorphous structure of the coatings. It was found that the resistance of the coatings significantly changes with prolonged exposure of the sample in a NaCl solution, so after 12 hours it decreases from 7.12 kΩ/cm<sup>2</sup> to 0.97 kΩ/cm<sup>2</sup>.

One of the ways to increase the corrosion resistance of electrolytic coatings with alloys of refractory metals is the electrodeposition of ternary alloys containing two refractory metals (tungsten and molybdenum) [15, 16] with a total content for ones of 15–20 at.%. Improvement of the mechanical and electrochemical properties of such alloys in comparison with binary ones can be achieved using the pulsed electrolysis mode. It is shown that with an increase in the total content of refractory metals in CoMoW coatings, the corrosion rate decreases in an acidic medium in comparison with alloys containing only one of the refractory metals and increases in an alkaline medium due to the instability of molybdenum and tungsten oxide.

We have investigated [17] electrodeposition of ternary cobalt alloys also containing two refractory metals: tungsten and rhenium. The paper shows the dependence of the chemical and phase composition, current efficiency and microhardness of ternary CoWRe alloys on the concentration of the components of deposition electrolytes and the electrolysis mode. Since tungsten and rhenium are corrosion-resistant metals, it can be expected that electrolytic coatings with alloys of these metals will exhibit significant corrosion resistance in corrosive envi-

ronments. This work presents a study of the electrocatalytic activity and corrosion resistance of coatings obtained under the same conditions. We assume that the coprecipitation of rhenium into the ternary CoWRe alloy will improve the functional characteristics of coatings, as we showed for the CoMoRe alloy in [18].

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials and Synthesis

The electrodeposition of CoWRe alloys was carried out from citrate-pyrophosphate electrolytes containing (mol/l):  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ —0.1,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ —0.2,  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 7\text{H}_2\text{O}$ —0.2,  $\text{K}_4\text{P}_2\text{O}_7$ —0.2,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ —0.3 and  $\text{KReO}_4$  for electrolyte No. 1—0.01, No. 2—0.03 and No. 3—0.05 at pH 9.0.

Deposition was carried out in a thermostated cell at a temperature of 50°C in a galvanostatic mode using a LIPS-35 direct current source under forced convection at a magnetic stirrer rotation speed of 300 rpm. As a working electrode, a copper plate with an area of 0.25 cm<sup>2</sup> was used, on the surface of which a layer of electrolytic cobalt was deposited from an acidic sulphate-chloride electrolyte of the following composition, g/l:  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ —504, NaCl—17,  $\text{H}_3\text{BO}_3$ —45 [19] at a current density of 3 mA/cm<sup>2</sup> for an hour. The anode was a platinum wire.

### 2.2. Study of Chemical Composition and Morphology

The morphology and chemical composition of samples were studied by using a JSM-6700F field emission scanning electron microscope equipped with a JED-2300 energy-dispersive spectrometer (JEOL). Operating conditions were as follows: 20 kV accelerating voltage, 0.75 nA beam current, 1 μm beam size. Counting time for EDS analyses was 60 s. Pure W and Re were used as standards. Raw counts were corrected for matrix effects with the ZAF algorithm implemented by JEOL. Three to five spots per each sample were analysed.

### 2.3. Study of the Alloys Properties in the Hydrogen Evolution Reaction

Voltammetric measurements of the electrocatalytic properties of alloys in the hydrogen evolution reaction were carried out in a solution of 1.0 mol/l KOH under natural convection conditions in a thermostated cell with separated cathode and anode spaces at a temperature of 20°C. To obtain the  $j$ - $E$  dependences, a ПИ-50-1.1 potentiostat and a ПП-8 programmer were used. Stationary polarization curves were obtained in potentiostatic mode with a step of 20 mV.

## 2.4. Corrosion Measurements

The study of corrosion was carried out by impedance spectroscopy and voltammetry using the AUTOLAB system (GPSTAT 20 + FRA) with the GPES 4.9 software in solutions, mol/l: 0.01—H<sub>2</sub>SO<sub>4</sub>, 3.5% NaCl, 1.0—KOH; at a temperature of 20 ± 1°C in a cell assembled according to a three-electrode circuit with a saturated silver-chloride reference electrode and an auxiliary electrode in the form of a platinum grid. All potentials in this work are given relative to a saturated hydrogen electrode. Cathodic and anodic polarization curves were obtained with a potential task rate of 1.0 mV/s. Analysing the data of polarization measurements in the stationary potential region (± 100 mV), the resistances and corrosion currents were calculated. The electrochemical impedance spectra were recorded after keeping the sample in a corrosive solution for 10 minutes for the potential to reach a steady—state value. The voltage was applied sinusoidally with amplitude of 5 mV. The spectra have been obtained in a frequency range of 5.0 kHz—20 MHz. The parameters of the corrosion process have been determined from an analysis of the spectra obtained.

## 3. RESULTS AND DISCUSSION

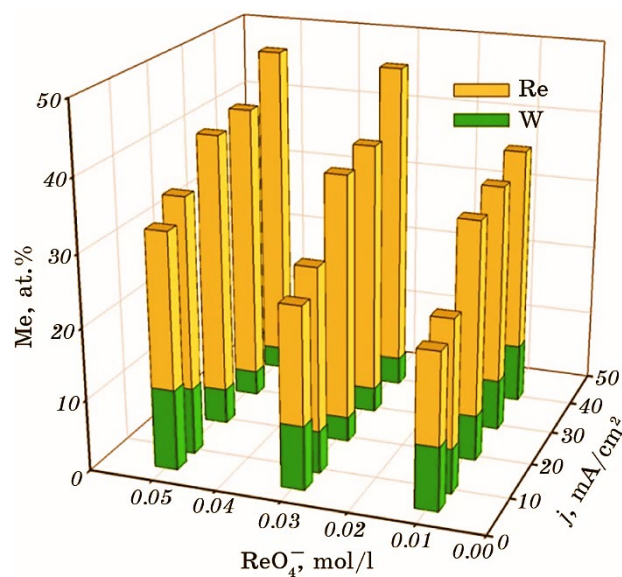
### 3.1. Chemical Composition and Morphology

Figure 1 shows the effect of the deposition current density and rhenium ion concentration in the solution on the rhenium and tungsten content of alloys (the residue is cobalt). It can be seen that the amount of refractory metals in coatings under experimental conditions is not over 47 at.%, *i.e.*, the basic metal in the alloy is cobalt. The rhenium content of the coating increases with current density and potassium perrhenate concentration from 13 at.% to 44 at.%, and the tungsten content decreases from 11 at.% to 3 at.%.

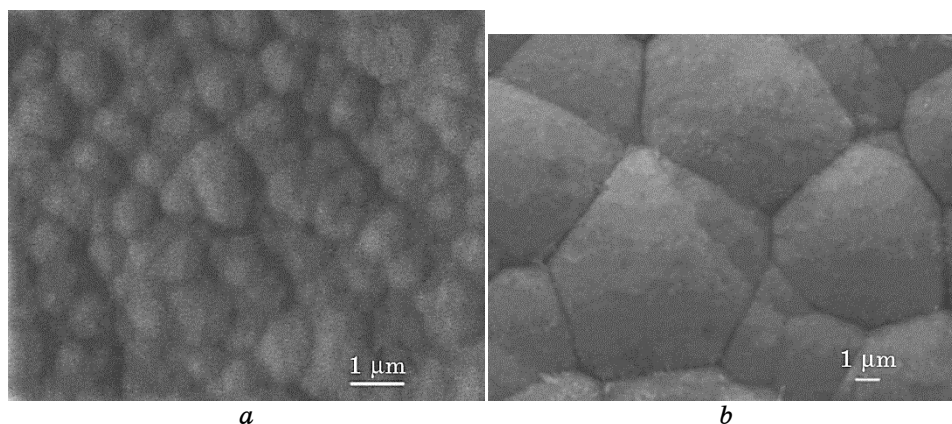
The electrolysis conditions and electrolyte composition have the same synchronous effect on the morphology of coatings, *i.e.*, when the deposition current density and rhenium ion concentration in the solution are increased, the size of surface agglomerates increases by two orders of magnitude from 0.1 μm to 10 μm. Figure 2 shows micrographs of coatings having the greatest differences: minimum rhenium content and a current density of 5 mA/cm<sup>2</sup> (*a*) and high rhenium content and a current density of 30 mA/cm<sup>2</sup> (*b*).

### 3.2. Properties of Alloys in the Hydrogen Evolution Reaction

Figure 3 shows the voltammetric dependences of hydrogen evolution in



**Fig. 1.** Dependence of the percentage of refractory metals in CoWRe alloys on the deposition current density and potassium perrhenate concentration in the electrolyte.



**Fig. 2.** Surface morphology of CoWRe alloys electrodeposited from electrolyte No. 1 at current densities of 5.0 mA/cm<sup>2</sup> (a) and No. 3 at 30.0 mA/cm<sup>2</sup> (b) (reprint from [17]).

a KOH solution on CoWRe alloys electrodeposited from electrolytes Nos. 1–3 in the current density range of 5–30 mA/cm<sup>2</sup>.

To compare the effect of the chemical composition of coatings on their electrocatalytic properties, the figure shows the voltammetric

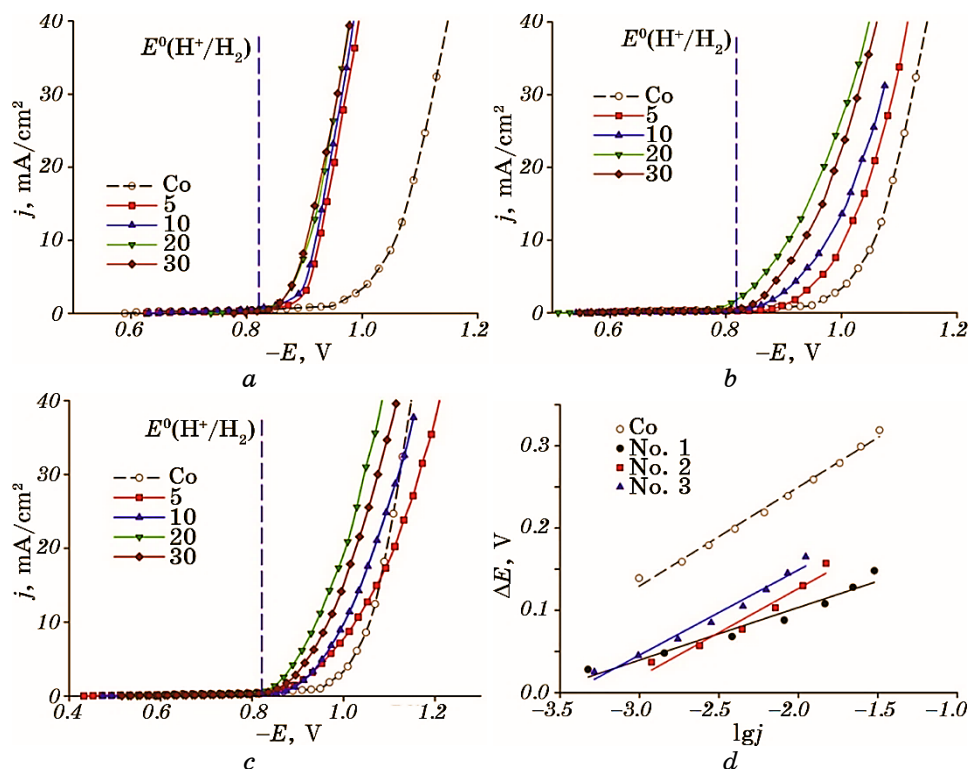


Fig. 3. Voltammetric curves of hydrogen electroreduction on CoWRe alloys electrodeposited from electrolytes No. 1 (a), No. 2 (b), No. 3 (c) and the Tafel section for Co and alloys deposited at 20 mA/cm<sup>2</sup> (d).

characteristic for a pure electrolytic cobalt cathode deposited from an acidic sulphate electrolyte.

The presented dependences show that an increase in the electrodeposition of potassium perrhenate in the solution, and, consequently, the amount of rhenium in the alloy, leads to a significant change in the properties of the coatings. Thus, in comparison with pure cobalt, the coatings obtained from electrolyte No. 1 exhibit good electrocatalytic properties; the coatings deposited from electrolyte No. 2 only slightly reduce the overvoltage of hydrogen evolution, and the properties of the coatings obtained from electrolyte No. 3 are comparable to those of cobalt. The figure also shows that the best electrocatalytic properties are exhibited by coatings deposited at 20 mA/cm<sup>2</sup>. For these alloys Fig. 3, *d* shows the Tafel sections, and it can be seen from data the best catalyst is alloy, deposited from electrolyte No. 1.

To determine the kinetic parameters of the hydrogen evolution reaction, all experimental dependences were rearranged in semi-logarithmic

coordinates. Previously, we found significant differences in the value of the hydrogen exchange current density on the surface of electrolytic cobalt [20, 21]. Under the conditions of our experiment for cobalt, the Tafel slope is 120 mV, which indicates that the limiting stage of sum reaction is the transfer of the first electron, *i.e.*, the Volmer reaction, and the logarithm of the hydrogen exchange current density is of  $-4.08$ .

In the case of ternary alloys, a much more complex picture is observed. Based on the Sabatier principle and volcano-like dependence, rhenium is the closest metal to platinum in terms of the Me-H bond energy and hydrogen exchange current density, and also belongs to the group of metals that are characterized by the limiting stage of electrochemical desorption (Heyrovsky reaction), as well as for platinum [22]. In the presence of rhenium, the coefficient  $b$  changes significantly and for alloys deposited from electrolyte No. 1 is 78–72 mV, for coatings deposited from electrolyte No. 2 is 107–96 mV, and for No. 3 is 129–103 mV with increasing current density of alloy deposition.

When analysing the experimental data, several factors should be taken into account: an increase in the degree of surface coverage with atomic hydrogen as the cathodic polarization increases; oxides of tungsten and rhenium are always present on the surface of alloys of these metals, formed as a result of contact with air, as well as in case of incomplete electroreduction of salts of these metals in solution, while part of the formed hydrogen atoms can be spent on the reduction of these oxides; the ability of rhenium to absorb hydrogen. These factors contribute to a change in the surface of the alloys and the experimental results obtained. The authors of [23] performed calculations of the kinetic parameters of different stages of hydrogen electroreduction taking into account such changes and came to the conclusion that a high content of rhenium on the surface can lead to the fact that the Volmer and Heyrovsky reactions can proceed with comparable rates, which is why Tafel slope is 60–80 mV. The authors of [24] came to a similar conclusion. However, the value of the coefficient  $b$  in our case cannot serve as an unambiguous proof of a change in the reaction mechanism; the changes can also indicate that the experimental data are distorted precisely due to the mentioned changes in the alloy surface.

If we assume that the mechanism of hydrogen electroreduction does not change, then the Volmer reaction, which is the limiting stage for metals of the iron group (including cobalt), occurs quickly and reversibly on the surface of tungsten and rhenium, and the reaction of electrochemical desorption, on the contrary, is limiting for refractory metals and reversible for cobalt. Thus, to create effective electrocatalysts, it is necessary to take into account that there should be metal atoms on the surface, on which an electrochemical reaction occurs at a high rate (refractory metals W, Re, Mo) and the amount of these atoms should be sufficient for the possibility of surface diffusion of hydrogen



adatoms (spill over effect). However, a large number of refractory metal atoms leads to a decrease in the number of cobalt atoms, on which the stage of electrochemical desorption rapidly occurs to remove hydrogen from the surface and the rate of the entire process decreases.

Despite the generality of the mechanism of hydrogen evolution, the refractory metals W, Re, and Mo differ significantly in their properties, while the common thing is that to achieve the electrocatalytic effect, the amount of refractory metals (one or two at the same time) must be in the range of 10–30 at. %.

The dependence of the exchange current density for cobalt and CoWRe alloys (Fig. 4, *a*) shows that the use of ternary alloys makes it possible to reduce  $j_0(\text{H}_2)$  by an order of magnitude compared to pure cobalt when the rhenium content in the alloy is 6–10 times more than the content of tungsten. However, in this case, it is necessary to take into account the differences in the value of the coefficient  $b$  for different coatings. Regardless of the reasons for these differences (change in the mechanism or change in surface properties), the exchange current density calculated for different values of  $b$  cannot be compared with each other and unambiguously judge the magnitude of the electrocatalytic effect; therefore, Fig. 4, *b* shows a similar dependence for hydrogen overvoltage. This dependence shows that the use of alloys deposited from electrolyte No. 1 can reduce the hydrogen overvoltage by 150 mV and the more rhenium is in the deposition electrolyte and in the coating, the less this effect becomes.

When comparing the dependences of the electrocatalytic properties of coatings in a KOH solution and the current efficiency of alloys during their electrodeposition from a citrate-pyrophosphate electrolyte [14] on their chemical composition, it can be seen that during the ca-

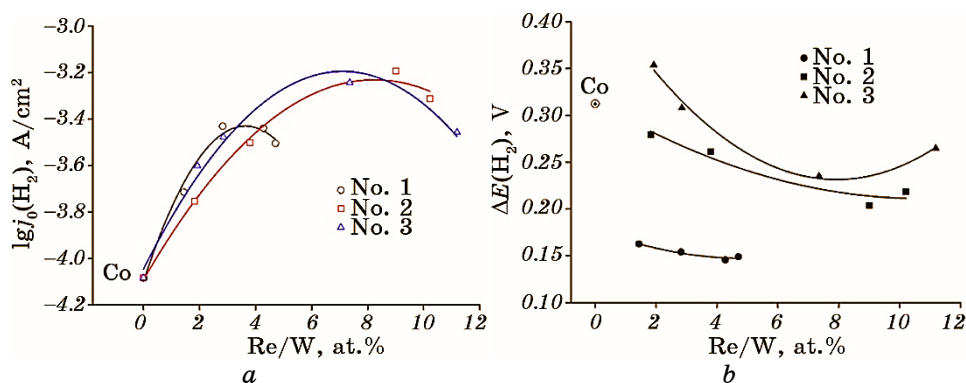


Fig. 4. Dependence of the hydrogen exchange current on CoWRe alloys deposited from electrolytes 1–3, respectively (*a*) and hydrogen overvoltage at 30 mA/cm<sup>2</sup> (*b*) on the ratio of refractory metals in the alloy.

thodic process on the alloy surface in an alkaline medium, these dependences have opposite tendencies. That is, the ability of the coating to reduce the hydrogen evolution overpotential is manifested not only in the KOH solution, but also in the process of the formation of the alloy itself in a weakly alkaline deposition electrolyte. With an increase in the concentration of potassium perrhenate in the electrolyte, and hence an increase in the amount of rhenium in the coating (electrolytes Nos. 1–3), the value of the current efficiency, and, consequently, the rate of deposition of alloys, increases markedly and at a rhenium content of 35–45 at.% reaches the maximum value under experimental conditions 93%. This value of the current efficiency of the CoWRe ternary alloy is not typical for the electrodeposition of alloys of refractory metals with metals of the iron subgroup and can be explained precisely by the properties of ternary alloys in the hydrogen evolution reaction, which is a side and undesirable reaction during alloy electrodeposition, and a target reaction in a KOH solution. Thus, the formation and growth of an alloy capable of electrocatalysis of a hydrogen reaction leads to a significant decrease in the current efficiency during its production, which is observed for coatings deposited from electrolyte No. 1. On the contrary, the alloys deposited from electrolyte No. 3 have a high overvoltage of hydrogen evolution and therefore they themselves are released with the highest current efficiency up to 93%.

### 3.3. Corrosion Studies

It is known that each of the refractory metals (tungsten and rhenium) has a high corrosion resistance. In this case, as was shown in Ref. [8], the corrosion resistance of a binary electrolytic alloy is an intermediate value between the corrosion resistances of pure metals. For ternary alloys [11], a difference was shown in the corrosion resistance of crystalline and x-ray amorphous coatings. So, crystalline coatings are formed at a low content of rhenium in the alloy (up to 20–25 at.%). As the rhenium content increases, a transition to x-ray amorphous (nanocrystalline) alloys is observed. During electrodeposition from acidic citrate solutions [11], crystalline coatings are formed at deposition current densities of 20–40 mA/cm<sup>2</sup> and have the highest corrosion resistance. Nanocrystalline coatings demonstrate lower corrosion resistance in all studied corrosive solutions. In this work, we studied the influence of the chemical composition and conditions of electrodeposition from polyligand electrolytes of the CoWRe ternary alloy on the corrosion resistance of coatings in media with different pH. The study of the corrosion properties of alloys of refractory metals in a KOH solution is of great importance, since these materials are considered by modern researchers as the most promising electrocatalysts for producing pure hydrogen. In electrolyzers, both acidic and alkaline electrolytes are used to produce

hydrogen, but the use of KOH solutions has become more widespread precisely because of the greater corrosion resistance of the electrodes.

The current–voltage curves of corrosion of CoWRe alloys (deposited at the same current density of  $10 \text{ mA/cm}^2$ ) in a solution of KOH, NaCl,  $\text{H}_2\text{SO}_4$  and the dependence of the specific corrosion resistance on the ratio of rhenium and tungsten concentrations in coatings during corrosion in a NaCl solution are shown in Fig. 5. Figure 5, *a* shows the difference in potentials and corrosion currents in various corrosion solutions, as well as in the behaviour of alloys during anodic polarization. This deposition current density was chosen because the coatings obtained under these conditions have the most corrosion resistant. Experimental current–voltage dependences for samples obtained at other current densities have a similar form and therefore are not shown in the figure.

A feature of corrosion of coatings in an alkaline solution is the presence of a dissolution peak before reaching the limiting current. This behaviour is associated with the dissolution of one of the phases on the alloy surface, which begins at anodic polarization of  $\approx 300 \text{ mV}$  from the corrosion potential and is probably related to the dissolution of the component that is least stable in an alkaline environment, namely, cobalt. The current–voltage curves show that the potential of the corrosion process shifts to the negative side with an increase in the current density of the deposition of coatings, which is explained by a change in their chemical composition, in particular, an increase in the amount of rhenium in the alloy. The corrosion resistance of the studied coatings is quite high, more than  $3 \text{ k}\Omega\text{-cm}^2$  (Table 1), and the optimal ratio of refractory metals for corrosion protection in an alkaline environment is  $\text{Re}:\text{W} = 3\text{--}4$ . Obviously, the corrosion characteristics depend not only on the chemical, but also on the phase composition.

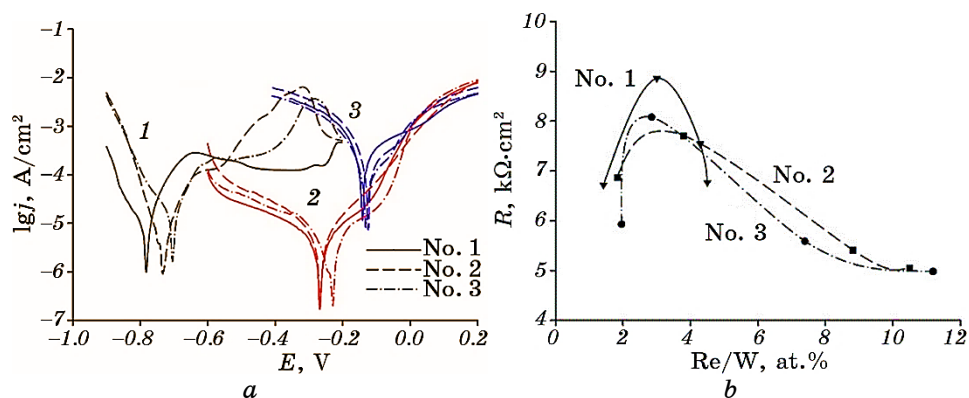


Fig. 5. Voltammetric curves of corrosion of CoWRe alloys, deposited at  $10 \text{ mA/cm}^2$ , in a KOH (1), NaCl (2),  $\text{H}_2\text{SO}_4$  (3) solution (*a*) and dependencies of corrosion resistance on Re/W concentration ratio.

**TABLE 1.** Potential ( $E$ ), current ( $j$ ) and resistance ( $R$ ) of corrosion represented for alloys deposited at 10 mA/cm<sup>2</sup>.

Electrolyte/Alloy	Corrosion media	$E_{\text{corr}}$ , V	$j_{\text{corr}} \cdot 10^5$ , A/cm <sup>2</sup>	$R$ , k $\Omega$ ·cm <sup>2</sup>
No. 1/76Co18Re6W	1 M KOH	-0.783	1.6	3.14
No. 2/71Co23Re6W	1 M KOH	-0.734	2.0	2.49
No. 3/64Co27Re9W	1 M KOH	-0.705	2.7	1.35
No. 1/76Co18Re6W	3.5% NaCl	-0.267	0.6	8.86
No. 2/71Co23Re6W	3.5% NaCl	-0.266	0.8	7.71
No. 3/64Co27Re9W	3.5% NaCl	-0.228	0.7	8.08
No. 1/76Co18Re6W	0.01 M H <sub>2</sub> SO <sub>4</sub>	-0.142	20.0	0.29
No. 2/71Co23Re6W	0.01 M H <sub>2</sub> SO <sub>4</sub>	-0.125	18.3	0.32
No. 3/64Co27Re9W	0.01 M H <sub>2</sub> SO <sub>4</sub>	-0.131	15.9	0.37

In our work [17], the results of x-ray phase analysis of alloys deposited from electrolyte No. 2 at various current densities were presented, and it was shown that the peak of the crystalline phase is observed only in the case of deposition at a low current density of 5 mA/cm<sup>2</sup>, *i.e.*, with a low content of rhenium in the alloy. This peak was attributed to the W<sub>0.8</sub>Re<sub>0.2</sub> intermetallic compound. Our further studies show that the peak at the same values of  $\Theta$  also corresponds to a solid solution of rhenium in cobalt; the value of  $\Theta$  is due to the deformation of the crystal lattice of cobalt during the formation of a solid solution, since the radius of the rhenium atom is larger than that of cobalt. Thus, the high values of the corrosion resistance of coatings deposited at low current densities can be due to the formation of a solid solution of rhenium in cobalt and a tungsten-rhenium intermetallic compound during electrodeposition. Alloys obtained at current densities > 10 mA/cm<sup>2</sup> are x-ray amorphous and it is not possible to determine their exact phase composition by this method.

A study of the corrosion of CoWRe alloys in sulfuric acid shows that, regardless of the chemical composition of the coatings and the electrolysis mode, the current-voltage curves for all the obtained samples practically coincide. The corrosion potential of all samples varies in a narrow range of 40 mV and shifts to the positive side with an increase in the rhenium content. Studies show that the obtained coatings have the least resistance in sulfuric acid, which is explained by the ability of refractory metals, which should provide corrosion resistance, to dissolve in an acidic environment with the formation of tungstic and perrhenic acids. The highest corrosion resistance under these conditions was obtained up to 370  $\Omega$ ·cm<sup>2</sup>.

During corrosion in a NaCl solution, two regions of limiting currents are observed on the anodic branch of the polarization curves, and

the potential for reaching the second limiting current ( $E \approx 0.2$  V) does not depend on the composition of the alloy and the corrosion potential. Therefore, it can be assumed that the first limiting current is of a diffusion nature and is associated either with the delivery of a depolarizer or with the removal of reaction products from the surface, and the second is with the formation of oxide compounds on the surface. However, the oxide film is not dense and cannot protect the coating due to surface activation in the chloride solution, so further dissolution occurs at a constant rate, the same for all coatings. In Figure 5, *b*, it can be seen that there is an area of optimal ratio of components, at which the highest corrosion resistance is observed. Therefore, to protect against corrosion in a chloride solution, the content of rhenium in the coating should be 2–4 times higher than that of tungsten. Such a ratio of refractory components is formed during electrodeposition at low current densities of 5–10 mA/cm<sup>2</sup>. Similar results were obtained both in alkaline and acid corrosive solutions.

Obviously, the corrosion characteristics largely depend on the crystal structure of the alloy. In the case of ternary CoWRe alloys deposited from both acidic citrate and polyligand citrate pyrophosphate electrolytes, alloys with a pronounced crystal structure and containing a small amount of rhenium have the highest corrosion resistance. At the same time, the ratio of refractory metals in the alloy is also important, where Re:W = 2–4 is optimal. The corrosion properties of coatings are also directly related to the electrocatalytic properties in the hydrogen evolution reaction. With an increase in the content of rhenium in the alloys due to an increase in the concentration of perrhenate ions in the solution or an increase in the deposition current density, the electrocatalytic properties of the alloys in HER deteriorate, *i.e.*, the overvoltage of hydrogen evolution increases. In the case of corrosion processes, this means that the depolarizer recovery rate decreases. Since the corrosion process takes place without access to oxygen, the only possible depolarizer is hydrogen. Decreasing the recovery rate of the depolarizer reduces correspondingly the rate of the corrosion process as a whole.

When assessing the possibility of using coatings as electrocatalysts, information on the corrosion stability of the material in time is needed. The authors of [14] showed that in the case of binary CoW alloys, the corrosion resistance in the simulated corrosive solution decreases within 12 hours by a factor of over 4. The KOH solution, which is mainly used to produce pure hydrogen, is still more aggressive, and this rapid loss of stability of electrodes is inadmissible. Using electrochemical impedance spectroscopy, we have studied the behaviour of a ternary CoWRe alloy deposited from electrolyte No. 3 at a current density of 10 mA/cm<sup>2</sup> in a KOH solution during 24 hours (Fig. 6).

Figure 6 shows a fivefold increase in corrosion resistance within 24 hours. This behaviour shows a gradual slow surface passivation owing

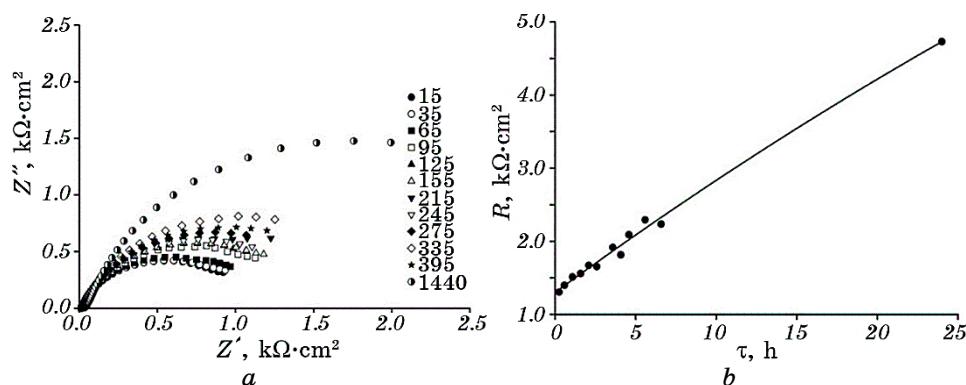


Fig. 6. Electrochemical impedance spectra (a) (the holding time in the solution is given in the figure in min.) and the time dependence of corrosion resistance (b).

to the formation of refractory metal oxide compounds.

#### 4. CONCLUSION

The properties of alloys in the hydrogen evolution reaction in a KOH solution depend on the rhenium content in the coatings. Thus, an increase in the amount of rhenium in the precipitate leads to a significant increase in the overvoltage of hydrogen evolution, which affects negatively on the process of obtaining hydrogen in a KOH solution, but positively on the process of growing the precipitate in an electrodeposition solution and makes it possible to obtain an alloy with a current efficiency of up to 93%, which is not characteristic for the electrodeposition of binary alloys of this type with molybdenum and tungsten.

Ternary CoWRe alloys deposited from a citrate-pyrophosphate electrolyte have high corrosion resistance, especially in neutral (up to 8.9  $\text{k}\Omega\cdot\text{cm}^2$ ) and alkaline media (up to 3.1  $\text{k}\Omega\cdot\text{cm}^2$ ). Corrosion resistance of coatings increases by 4 times during exposure of samples in an alkaline solution for one day. The highest corrosion resistance in all investigated solutions is possessed by coatings electrodeposited at current densities of 5–10  $\text{mA}/\text{cm}^2$  and containing 25–35 at.% of refractory elements.

This work was performed with the financial support of the National Academy of Sciences of Ukraine within the state budget theme ‘Finishing processing of materials in order to give them unique functional properties’ (0123U100650).

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