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COMPARISON OF THE PROPERTIES OF CoW AND CoMo ALLOYS DEPOSITED BOTH FROM ALKALINE CITRATE AND CITRATE-PYROPHOSPHATE ELECTROLYTES

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The chemical composition, current efficiency and some properties of galvanic binary CoMo and CoW alloys, deposited from both alkaline citrate and citrate-pyrophosphate electrolytes, were studied. It is shown that the main difference between mono- and polyligand electrolytes is the mechanism of the electrodeposition process and the rate of passage of limiting stages preceding the formation of an electrochemically active complex. During electrolysis in a citrate solution, the limiting step is the mass transfer of $[CoCit_2]^{4-}$ complexes, while in the citrate-pyrophosphate one, the process proceeds with kinetic control, and the hydrodynamic regime does not significantly affect the content of metals and the rate of their deposition. The use of a polyligand electrolyte makes it possible to increase the current efficiency for CoW alloys from 32.1 to 45.5% in the convective mass transfer mode and from 5.9 to 35.7% in the diffusion transfer mode. During electrodeposition from citrate-pyrophosphate electrolytes of the same composition of alloys of two different refractory metals, it was found that the current efficiency of the CoMo alloy is on average 20% higher than that of CoW. It has been found that at a close value of the content of the refractory component in X-ray amorphous alloys, the differences in the magnetic and corrosion properties of the coatings are determined by the nature of the refractory metal. Thus, during electrodeposition from a polyligand electrolyte, CoMo alloys have Ms 300–380 emu·cm^{-3} and Hc 60–72 Oe, while CoW alloys have Ms 22–45 emu·cm^{-3} and Hc 50–70 Oe. Both types of alloys are characterized by Mr/Ms – 0.2-0.3. The properties of CoW alloys deposited from a monoligand citrate electrolyte approach hard magnetic materials with Mr/Ms – 0.6–0.7.

Key words: alloy, cobalt, tungsten, molybdenum, electrodeposition.

INTRODUCTION. The study of the processes occurring during the formation of electrolytic alloys of refractory metals with metals of the iron subgroup receives much attention from researchers. First of all, that is to obtain information about the composition and structure of coatings those are deposited from solutions of various complex compositions, as well

as to determine the dependence of functional properties of the alloys on electrodeposition conditions. The functional properties of such coatings are very diverse [1, 2], but the most demanded for industry are heat resistance, hardness, and corrosion resistance [3–5].

It is known that for the formation of alloys, it is necessary to bring the precipitation potentials of two metals closer, i.e., in our case, to increase the overvoltage of cobalt precipitation due to the formation of a strong complex compound in the solution [6]. The search for new and better complexing agents for this process is associated with the impossibility of foreseeing the impact that a previously unused complexing agent or a mixture of already studied coatings will have on the composition and quality of coatings, since no correlation has yet been found between the parameters of the metal complex of the iron subgroup (size, spatial configuration, stability constant) and alloy parameters (composition, crystal structure and physicochemical properties).

The conditions for electrodeposition of binary alloys of refractory metals with metals of the iron subgroup are considered in detail by the authors of [7]. Among the electrolytes that are considered promising for the deposition of alloys with tungsten and molybdenum, one can single out citrate [8], pyrophosphate [9, 10], and alkaline polyligand electrolytes containing organic complex polyhydroxy acids (salts) with carboxyl groups; indicated by the authors of [7], alkalization of the solution with ammonia also leads to a change in the complex composition of the electrolyte. An important feature of multicomponent complex electrolytes is the possibility of the formation of polymetallic and/or polyligand complexes in the bulk of the solution, which can also significantly affect the kinetics of alloy deposition.

The citrate-pyrophosphate electrolyte proposed by us combines the advantages of citrate and pyrophosphate electrolytes and makes it possible to obtain functional coatings of the required quality with a high deposition rate. Coatings are deposited with a rather high content of refractory metal and higher values of current output compared to citrate electrolyte [11, 12]. The authors of works on the electrodeposition of binary alloys of metals of the iron subgroup with tungsten [13] showed that coatings containing 17–24 at.% tungsten have the highest corrosion resistance. This ratio of components approximately corresponds to the composition of the Co_3W intermetallic phase. Also important is the transition from the polycrystalline to the amorphous structure of the coatings, which occurs when exactly this concentration of tungsten is reached in the binary alloy.

The purpose of the work is electrochemical synthesis, study of the composition, structure and physicochemical properties of binary alloys of cobalt with tungsten and molybdenum, depending on the complex composition of the electrolytes and the hydrodynamic regime.

EXPERIMENT AND DISCUSSION OF THE RESULT. CoW alloys were deposited from both alkaline electrolytes (solution pH 9.0): citrate (Cit) and citrate pyrophosphate (Cit-PPi), CoMo alloys were deposited from alkaline Cit-PPi electrolyte. Coatings were obtained in a thermostated cell in a galvanostatic mode using a direct current source LIPS-35 under natural convection conditions, as well as with stirring (magnetic stirrer rotation speed 300 rpm). A copper plate with an area of 1 cm^2 was used as the working electrode; platinum was the anode.

Table 1.

Composition of electrolytes for electrodeposition of alloys, mol·l^{-1}

For alloy	$CoSO_4$	Na_2WO_3	Na_2MoO_4	Na_3Cit	K_2PO_4	Na_2SO_4
CoW	0.1	0.2	–	0.2	–	0.3
CoW	0.1	0.2	–	0.2	0.2	0.3
CoMo	0.1	–	0.02	0.2	0.2	0.3

The citrate-pyrophosphate electrolyte was prepared by adding a solution of potassium pyrophosphate to an already prepared citrate electrolyte at a temperature of 70 °C. Then the pH was adjusted to a value of 9.0.

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). The operating conditions were as follows: 20 kV accelerating voltage, 0.75 nA beam current, 1 μm beam size. The counting time for EDS analyses was 60 s. Pure Co and Re were used as standards. The raw counts (Co,Kα; W,Lα; Mo,Lα) were corrected for matrix effects with a ZAF algorithm implemented by JEOL. Three to five spots per each sample were analyzed.

X-ray patterns were recorded on a diffractometer (DRON-3.0) with the Bragg-Brentano geometry and using Cu-K radiation (= 1.54183A˚) operating at 30 kV and 30 mA at a constant scan rate of 0.02–2 s^{-1}. The study of corrosion was carried out by voltammetry. These measurements were carried out using an MTech PGP-550F potentiostat-galvanostat [13] in a 1M KOH solution at a temperature of 20 ± 1 °C in a cell assembled by a working copper electrode, a silver reference electrode, and an auxiliary electrode, which is a platinum grid. Voltammetric studies of corrosion included of obtaining cathodic and anodic polarization curves with a potential sweep rate of 1.0 mV s^{-1}. As a result of the analysis of polarization measurements in the region of stationary potential (±100 mV), the corrosion resistance was calculated.

Magnetic properties of the obtained deposits were determined using a magnetometer with a vibrating sample in magnetic fields up to 2 T in SI units (20 kG in Gaussian-cgs units) at room temperature.

Fig. 1 shows the results of studying the chemical composition and current efficiency for CoW alloys and its components during electrodeposition from Cit and Cit-PPi electrolytes at a deposition current density of 10 mA·cm^{-2} both in the mode of convective mass transfer (with intensive stirring) and under conditions of natural diffusion, as well as the composition and current efficiency during the electrodeposition of CoMo alloys from Cit-PPi-electrolyte under different hydrodynamic conditions. Based on previous studies on the electrodeposition of CoW alloys from a polyligand Cit-PPi electrolyte under conditions of intensive mixing, it is known that CoW alloys contain 22–25 at. % tungsten over the entire range of deposition current densities studied [15].

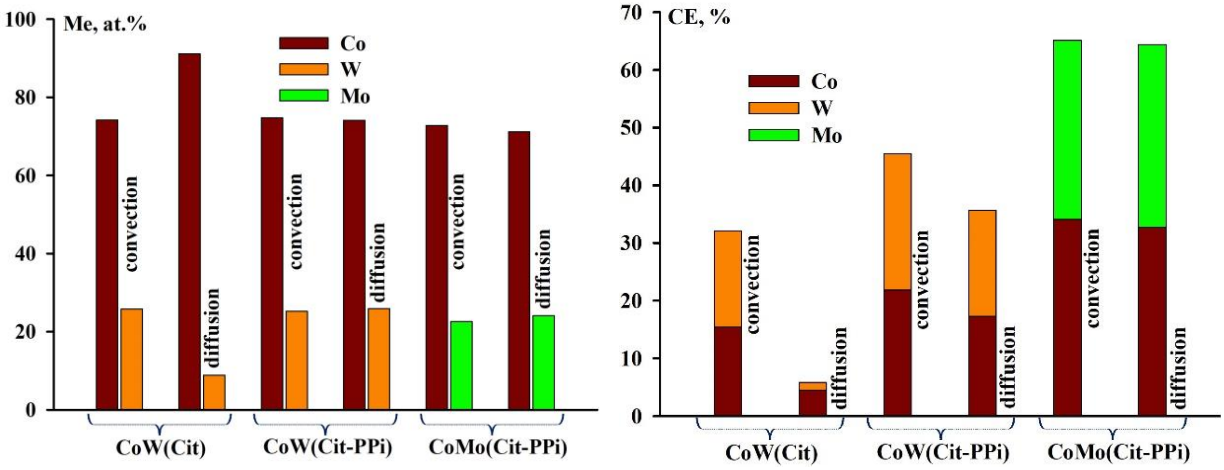

Fig. 1. Dependence of the chemical composition (a), current efficiency of the CoW and CoMo alloys, as well as their components (b) on the deposition conditions.

Let us consider the effect of intense mechanical mixing on the chemical composition and current efficiency of CoW alloys at deposition from these electrolytes. A comparison of mono- and polyligand electrolytes was carried out to demonstrate the key role of the composition of cobalt complexes on the formation of an electrolytic alloy. It is known that $[CoCit_2]^{4-}$ complexes predominate in an alkaline (pH 9.0) citrate electrolyte with a twofold excess of the ligand [16, 17]. When electrolysis is carried out in such an electrolyte, the overvoltage of cobalt evolution becomes greater than the overvoltage of hydrogen [18] so that it is not possible to obtain a coating of metallic cobalt in an amount sufficient for gravimetric determination of the current efficiency, while the deposit turns out to be loose. Probably, in an alkaline citrate electrolyte, not only tungsten, but also cobalt can't be individually reduced to metal. These metals are capable of being reduced only simultaneously with the formation of an electrolytic alloy. Since cobalt is in solution in the form of very strong complex compounds with citrate, the formation of bimetallic complexes in the volume of the solution is unlikely, but the result obtained indirectly confirms the hypothesis that reduction occurs from complex compounds formed precisely on the electrode surface [19].

During the deposition of the CoW alloy from a citrate electrolyte, the mass transfer regime has a significant effect on the composition of the resulting alloys: the tungsten content in the coating (9 at.%) and the current efficiency of the alloy (6 at.%) in the absence of forced convection are much lower than when the electrolyte is stirred (23 and 33 at.%, respectively). Based on the mechanism of induced co-deposition of the metals presented in [19], the necessary condition for the formation of electroactive complexes on the surface is the presence of $[CoCit]^-$ particles, which can be formed as a result of dissociation of the adsorbed $[CoCit2]^{4-}$ complex on the cathode surface according to equation (1):

$$[CoCit_2]^{4-} \rightarrow [CoCit]^-_{ads} + [Cit]^{3-} \qquad (1)$$

During electrodeposition from a citrate-pyrophosphate electrolyte, convection in the electrolyte has practically no effect on its chemical composition, but contributes to an increase in the current efficiency of the alloy up to 35.7%. A feature of the polyligand electrolyte is the formation of a cobalt complex $[Co(PPi)(Cit)]^{5-}$, as was shown in [20]. Thus, for the formation of the $[CoCit]^-$ complex, it is necessary to dissociate the adsorbed complex on the electrode surface according to reaction (2):

$$[Co(PPi)(Cit)]^{5-} \rightarrow [CoCit]^-_{ads} + [PPi]^{4-} \quad (2)$$

After that, in both cases, it becomes possible to form an electroactive complex according to reaction (3):

$$WO_4^{2-} + [CoCit]^-_{ads} + 2H_20 + 2\bar{e} \rightarrow \rightarrow [CoCitWO_2]^-_{ads} + 4OH^- \quad (3)$$

Taking into account the fact that the $[WO_4]^{2-}$ concentration is high, and $[CoCit]^-$ is formed directly on the surface (1), the low current efficiency in the citrate electrolyte in the natural convection mode can be explained with the diffusion of cobalt citrate complexes $[CoCit_2]^{4-}$, with the rate of reaction (1), or with a large number and insufficiently fast removal of the formed bubbles of gaseous hydrogen, blocking the active centers of the surface.

When comparing alloys of two refractory metals, it should also be noted that the current efficiency of the CoW alloy is lower than that of the CoMo alloy during convective mass transfer in a polyligand electrolyte and even lower at deposition in a monoligand electrolyte. Such a difference may be due to the nature of the refractory metal, its concentration in the electrolyte, and its electrocatalytic activity in the hydrogen evolution reaction. It was shown in [21] for the electrodeposition of CoMo alloys that an increase in the concentration of molybdate ions in a solution and a change in the ratio of metal concentrations from Co: Mo = 5:1 to Co: Mo =1:1 leads to a significant decrease in the current efficiency of the alloy. Therefore, based on the analogy of the properties and deposition processes of these metals, it can be assumed that with a 10-fold excess of tungstate ions compared to the content of molybdate ions (in deposition electrolytes), a decrease in the current efficiency of the CoW alloy is also possible.

On fig. 2 shown that the CoW coating deposited from the Cit electrolyte under natural convection conditions is smoother and has almost no spherulites. Coatings deposited from a polyligand electrolyte are more stressed and cracked.

The main problem of electrolytic alloys of molybdenum is significant internal stresses in coatings, which lead to cracking [22, 23]. To solve this problem, several options have been proposed: the addition of surfactants [24, 25], the usage of pulsed electrolysis [26], the selection of fundamentally different deposition electrolytes [27], and the use of a constant magnetic field [28, 29].

Comparing the cracking of CoMo coatings deposited at a current density of 10 $mA \cdot cm^{-2}$ in natural and forced convection, we can draw a similar conclusion that a coating growing at a slower rate is less stressed. On the diffraction patterns shown in Fig. 3, it is shown that, regardless of the mass transfer regime and the complex composition of electrolytes (for the CoW alloy), all coatings are X-ray amorphous. When the same amount of electricity is passed, the CoW coatings from the alkaline citrate electrolyte, which are released with a small current efficiency, are deposited in a small thickness,

and therefore, sharp peaks related to copper can be seen in the diffraction pattern. Only for the CoMo alloy deposited from the Cit-PPi electrolyte, a peak of the Co_3Mo intermetallic compound is observed. The broad peak observed for all samples in terms of the diffraction angle also corresponds to the formation of Co_3Mo and Co_3W intermetallic compounds.

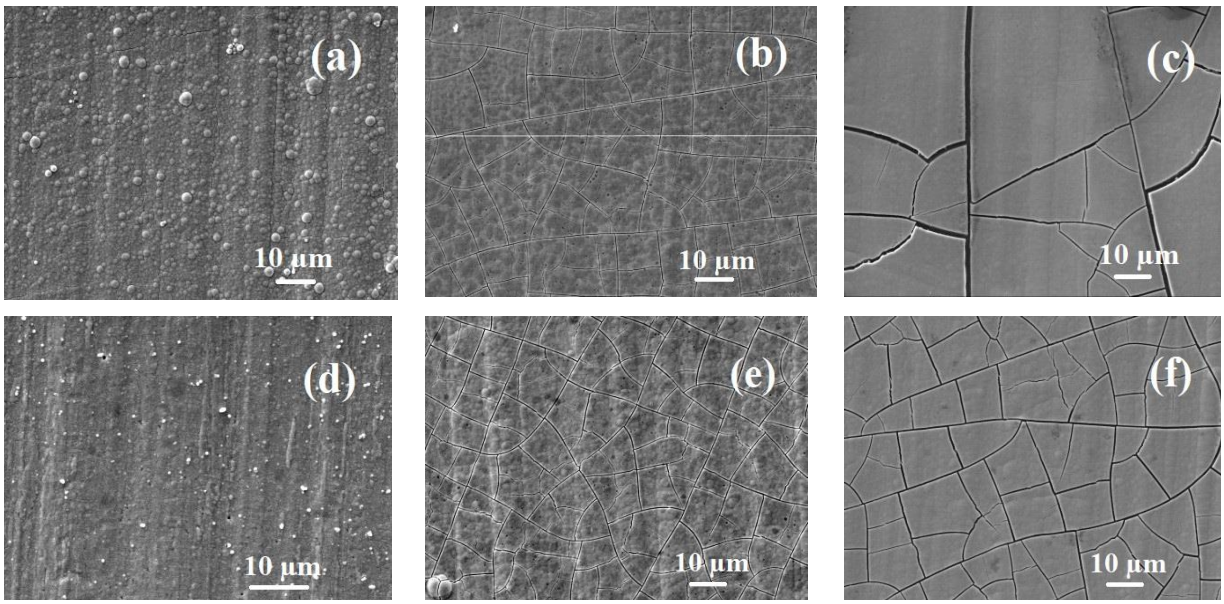

Fig. 2. Surface morphology of CoW alloy coatings deposited from Cit (a, d) and Cit-PPi (b, e) electrolytes, as well as CoMo alloys (c, f) in the convective mass transfer mode (a, b, c) and without mixing (d, e, f).

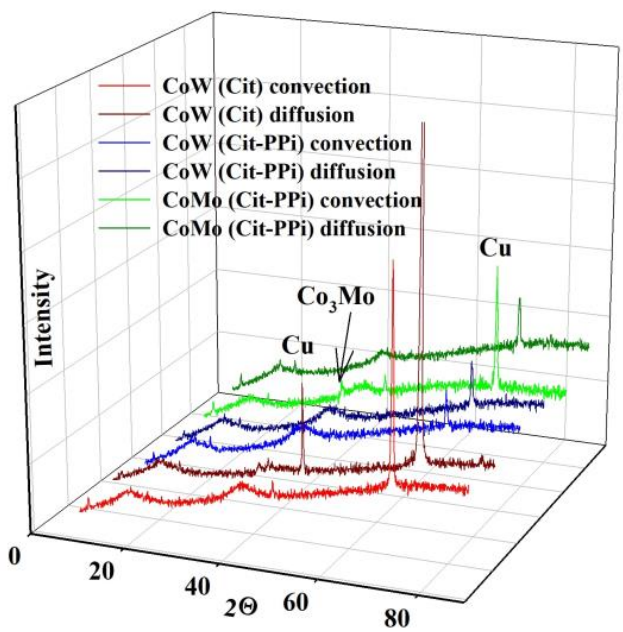

Fig. 3. X-ray diffraction patterns of CoW and CoMo alloys coatings deposited from Cit and Cit-PPi electrolytes under various mass transfer conditions.

The dependences obtained in the study of the influence of the mass transfer mode and the conditions of deposition of coatings by tungsten and molybdenum alloys with cobalt on their magnetic properties are shown in Fig. 4. It can be seen from the results that, despite the similarity of the chemical composition and structure, the coatings deposited from electrolytes of different complex compositions have fundamentally different magnetic properties.

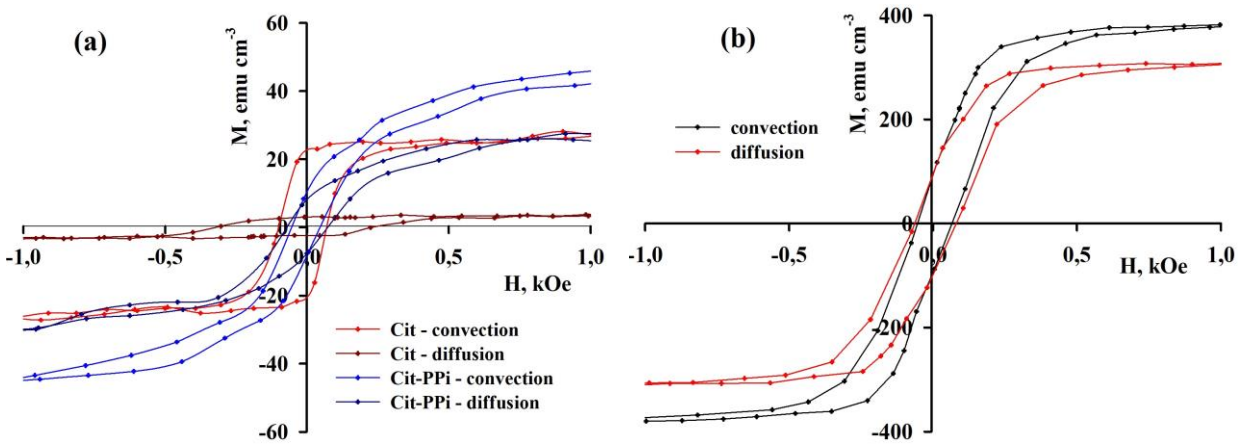

Fig. 4. Magnetic hysteresis loops for CoW(a) and CoMo(b) alloys.

Table 2.

Magnetic hysteresis parameters of CoW and CoMo alloys.

Parameter	CoW-Cit		CoW-Cit-PPi		CoMo-Cit-PPi	
	stirring	diff.	stirring	diff.	stirring	diff.
Ms, emu·cm^{-3}	30	3.8	45	22	380	300
Hc, Oe	85	275	50	70	72	60
Mr/*Ms*	0.73	0.61	0.20	0.37	0.25	0.32

First of all, it should be noted that the saturation magnetization of molybdenum alloys Ms (300–380 emu cm^{-3}) is an order of magnitude higher than that of tungsten alloys. Such alloys reach saturation magnetization in low strength fields, have a relatively low coercive force (60–72 Oe), and are classified as magnetically soft materials in terms of their properties. In addition, the saturation magnetization of all coatings obtained by mixing is significantly higher than for alloys deposited under natural diffusion conditions. For CoW alloys, there is also a difference between the properties of coatings deposited from electrolytes of different complex compositions. For example, the coatings obtained in the Cit electrolytes are distinguished by a significantly higher coefficient of loop rectangularity, i.e., their properties are close to those of hard magnetic materials. Particularly distinguished is the alloy deposited under natural convection and having the lowest tungsten content, the

properties of which are closest to those of pure cobalt.

The magnetic properties of electrolytic cobalt depend on its crystal structure [30] and, consequently, on the conditions of deposition and composition of electrolytes. The coercive force of cobalt coatings varies over a wide range: from 15 Oe for amorphous films to 380 Oe for coatings with an hcp structure and a preferred (002) orientation. The high coercive force and the rectangular shape of the hysteresis loop indicate that coatings with the crystal lattice of hcp are deposited from the citrate electrolyte, but the size of the crystals (2–3 nm) does not make it possible to accurately identify and confirm this assumption by XRD.

The corrosion resistance of coatings deposited at current density of 10 mA·cm^{-2} in a corrosion solution of 1M KOH are presented in table. 3.

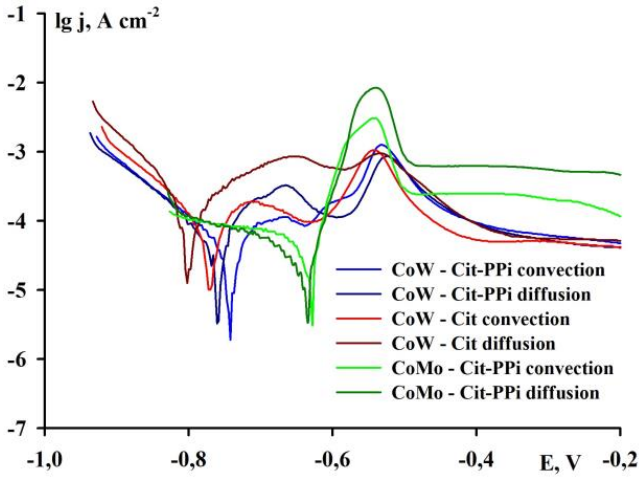

Fig. 5. Voltammetric curves of corrosion of alloys in a solution of 1M KOH.

Table 3.

Corrosion resistance of coatings with CoW and CoMo alloys.

Parameter	CoW-Cit		CoW-Cit-PPi		CoMo-Cit-PPi	
	stirring	diff.	stirring	diff.	stirring	diff.
-*E*, В	-0.772	-0.801	-0.742	-0.760	-0.627	-0.637
-lgj_{corr}, А·см$^{-2}$	4.9	4.1	4.6	4.5	4.7	4.9
R, кОм·см^2	3.6	0.9	3.0	2.4	3.3	3.6

It can be noted that during the deposition of alloys from polyligand electrolytes, the mass transfer regime has practically no effect on the corrosion resistance of the alloys. In terms of their corrosion resistance, alloys deposited from the same electrolyte, but in different hydrodynamic conditions, are very similar to each other. The only exception is the coating containing the least amount of refractory component and being the least corrosion resistant. It should also be noted that tungsten alloys are more prone to passivation in an alkaline solution than molybdenum alloys.

CONCLUSIONS.

– The composition of cobalt complexes in solution plays a key role in the formation of electroactive particles on the cathode. In a polyligand electrolyte, the deposition of metals proceeds with kinetic control, regardless of the presence or absence of mechanical mixing. The deposition rate of alloys under these conditions is much higher, with a slight increase in the cracking of the coatings, which is typical for such alloys.

– In alkaline citrate electrolyte, the hydrodynamic regime has the greatest influence on the chemical composition and current efficiency of CoW alloys. Thus, the amount of tungsten in the alloy during stirring increases 3 times, and the current efficiency of the alloy increases 6 times compared to natural convection mode.

– All obtained coatings are X-ray amorphous and it is not depend on the conditions of deposition and the content of the refractory component

– Given the close chemical composition and structure of the coatings, the differences in magnetic and corrosion properties can be attributed to the influence of the nature of the refractory metal: for example, molybdenum alloys are magnetically soft materials, and tungsten alloys are close to magnetically hard.

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ПОРІВНЯННЯ ВЛАСТИВОСТЕЙ СПЛАВІВ CoW ТА CoMo, ОСАДЖЕНИХ ІЗ ЛУЖНОГО ЦИТРАТНОГО ТА ЦИТРАТНО-ПІРОФОСФАТНОГО ЕЛЕКТРОЛІТІВ

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У роботі вивчено хімічний склад, вихід за струмом, властивості бінарних сплавів CoMo та CoW, що осаджені з лужного цитратного (Cit) та цитратно-пірофосфатного (Cit-PPi) електролітів. Показано, що основна відмінність моно- та полілігандних електролітів полягає у механізмі процесу та швидкості проходження лімітуючих стадій, що передують утворенню електрохімічно активного комплексу. При електролізі в цитратному розчині лімітуючою стадією є масоперенесення комплексів $[CoCit_2]^{4-}$, а в цитратно-пірофосфатному – процес проходить із кінетичним контролем, завдяки чому гідродинамічний режим незначно впливає на вміст металів та швидкість їхнього осадження. При цьому покриття сплавами, які осаджуються з меншою швидкістю, є менш тріщинуватими та напруженими.

Незалежно від режиму масопереносу та комплексного складу електролітів покриття сплавами є рентгеноаморфними. Широкий пік, що спостерігається для всіх зразків за величиною кута дифракції, відповідає утворенню інтерметалідів Co_3Mo та Co_3W.

Знайдено, що при близькому значенні вмісту тугоплавкого компонента в рентгеноаморфних сплавах відмінності в магнітних та корозійних властивостях покриттів визначаються природою тугоплавкого металу. Намагніченість насичення сплавів молібдену Ms (300–380 emu·cm^{-3}) є значно вищою, ніж сплавів вольфраму. Такі сплави досягають намагніченості насичення в полях малої напруженості, мають відносно низьку коерцитивну силу (60–72 Oe) та за своїми властивостями належать до магніто-м'яких матеріалів. Крім цього, намагніченість насичення всіх покриттів, отриманих при перемішуванні, є значно вищою, ніж для сплавів, осаджених за умов природної дифузії. Для сплавів CoW також спостерігається відмінність між властивостями покриттів, що осаджені з електролітів різного комплексного складу. Так, покриття, отримані в Cit-електроліті, відрізняються значно більшим коефіцієнтом прямокутності петлі, тобто за своїми властивостями наближаються до магнітотвердих матеріалів. Особливо виділяється сплав, що був осаджений за умов природної конвекції та має найменший вміст вольфраму, властивості якого найбільш близькі до властивостей чистого кобальту. За своєю корозійною стійкістю сплави, що осаджені з одного електроліту, але в різних гідродинамічних режимах, є дуже схожими між собою. Виняток становить лише покриття, що містить найменшу кількість тугоплавкого компонента та є найменш корозійностійким. Слід зазначити, що сплави вольфраму більше схильні до пасивації в лужному розчині, ніж сплави молібдену.

Ключові слова: сплав, кобальт, вольфрам, молібден, електроосадження.

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