

New approach to catalytic Co–W alloy electrodeposition

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The pulse electrolysis parameters (current density amplitude, frequency and on/off time ratio of pulses, pause and pulse duration) influence on cobalt-tungsten alloy deposition has been revealed. The alloy electrodeposition possibility using soluble anodes has been proved. Corrosive resistance and catalytic activity of obtained coatings have been determined.

Выявлено влияние основных параметров импульсного электролиза — амплитуды плотности тока, частоты и скважности импульсов, длительности паузы и импульса — на осаждение сплава кобальт-вольфрам. Доказана возможность реализации процесса электроосаждения покрытия с растворимыми анодами. Проведена оценка коррозионной стойкости и каталитической активности полученных сплавов.

The electrolytic Co–W alloys are known to be used as special protective coatings possessing an enhanced strength, hardness, high wear, heat and chemical resistance and improved electroerosion properties. The electrodeposition of tungsten alloys with iron group metals takes place after a film of unstable intermediates of tungsten in low oxidation states is formed in the cathode layer [1]. Such a film, from the one hand, complicates the tungsten release into the alloy, but on the other one, is its source, that is why the tungsten content in the coating decreases as the film is destroyed. Thus, it is possible to manage the alloy deposition process influencing the film development by external current polarization with varied pulse and parameters.

The study of influence of alternating and direct current parameters on the structure and physical-mechanical properties of Co–W deposits from ammonium-citrate electrolyte has shown [2] that under the same current density, the W content in the alloy during the pulse electrolysis is 10 to 15 % higher. This can be explained by the fact that the alloy formation under the pulse occurs at

considerably higher negative potentials and this the increase of refractory component content in the alloy, the alloy current efficiency being 15 to 21 %. Although there are numerous publications concerning Co and W co-deposition [3–6], information about electrochemical properties of such alloys is absent in literature, especially regarding the corrosive behavior and catalytic activity. So, the purpose of this work is to define rules of Co–W alloy electro-crystallization in the pulse, to find out the possibility of current efficiency increase and to determine optimum deposition conditions of Co–W alloys with high corrosion resistance and catalytic properties. To provide the stable work of the electrolyte stability using soluble anodes, the anodic behavior of Co and W in citrate electrolyte was studied.

The coatings were deposited from citrate electrolyte at pH = 6 in the temperature interval 293 to 333 K. The necessary pH value was provided by sodium hydroxide addition. The electrodeposition was carried out using unipolar pulse current of 19 to 910 Hz frequency (f) and on/off time ratio (Q) of 11 to 26 with platinum insoluble

anode in the amplitude density range (j_p) of 0.5 to 30 A/dm². The coatings of 5 to 9 μm thickness were electrodeposited onto steel (X13H17M2T) samples of 0.5 to 5 cm² surface area. The current yield E_c was determined by gravimetry that tungsten is in completely reduced state. The tungsten and cobalt content in the alloy were determined using a SPRUT portable X-ray spectrometer. Prior to the metal anodic polarization, the W surface was pre-activated chemically in the alkaline solution of potassium hexacyanoferrate (III) at 323 K, and that of Co, mechanically using emery paper No.0. Platinum plate was used as secondary electrode, chloride-silver as the reference one.

The corrosion tests of the alloy coatings were done by impedance spectroscopy method [7] using the alternating current bridge P-5083 in the frequency range of 0.02 to 100 kHz according to the successive substitution scheme in 0.1 M H₂SO₄ solution at room temperature. Before impedance measurements, the electrodes were held in the working solution 1 h at corrosion potential E_{cor} . The catalytic properties of electrodeposited alloys have been estimated from the exchange current value $j^0_{H_2}$ in the model reaction of hydrogen reduction from sulfuric acid solution. The cell was deoxygenated by purging with high purity argon at simultaneous work-up of solution during 30 min. The potentials were measured against the saturated mercury-sulfate reference electrode and recalculated to the hydrogen scale. The polarization was realized using a PI-50-1.1 potentiostat and PR-8 programmer, polarization measurements were registered using 2-coordinate recorder.

The direct current density increase 333 K results in a sharp increase of the alloy current yield, but almost does not influence its chemical composition (Fig. 1); the coating looking as a gray mat layer. The solution temperature lowering down to 293 K causes the E_c drop down to 20 % at tungsten content in the alloy increasing to 30 %. The pulse electrolysis at that temperature does not change the E_c value considerably, and the dependence of tungsten content in the alloy on the pulse amplitude has a maximum at 10 A/dm² (mass fraction $\omega(W) = 27\%$). Thus, it can be concluded that without heating the alloy E_c is rather low, the tungsten content being high, but there is no difference between coatings obtained in static or pulse regime. At the electrolyte temperature 333 K, the unipolar pulse frequency decrease under the same

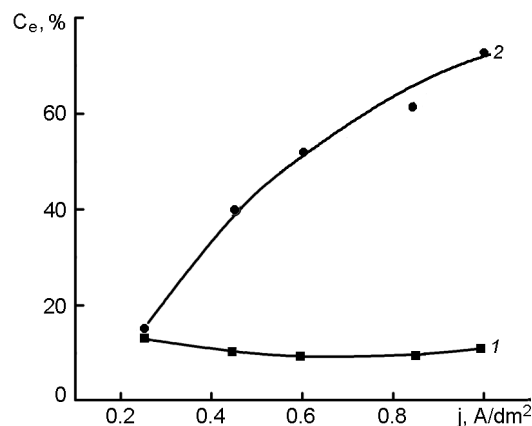


Fig.1. Effect of cathode direct current density on current efficiency C_e (2) and tungsten content $\omega(W)$ (1) in Co-W alloy.

on/off time ratio and simultaneous amplitude increase provides an enhanced E_c of the Co-W alloy (Fig. 2a).

According to [8], high-frequency pulse current slows down the cathode layer alkalization as compared to the low-frequency polarization regimes. When the pulse duration increases, the alloy E_c grows, unlike the tungsten content, since, in our opinion, the hydrogen evolution process is intensified in such conditions. When the pause time reduces, the alloy E_c drops at large current amplitude values, while at low ones, it increases. In addition, the pause time increase results in increasing tungsten content at any current density, that is like to be connected with the chemical reduction of tungsten intermediate compounds by adsorbed hydrogen atoms as a component of multistage process of tungsten (VI) reduction [9].

The dependence of tungsten content in the alloy on the current frequency shows a minimum at $f = 90$ Hz, while current density amplitude decrease results in increasing $\omega(W)$ in the alloy (Fig. 2b). As the pulse current on/off time ratio increases, tungsten content in the alloy grows as well, and the greater is the pulse amplitude (at duration 2 ms), the more significant is that influence. By pulse parameters, it is established that tungsten content in the alloy is in inverse proportion to the pulse duration. It follows from the dependence of tungsten content in the alloy on the current density amplitude and the pulse on/off time ratio (Q) that Q does not influence practically the $\omega(W)$ value, except for the $Q \rightarrow 0$ region. In this region, tungsten content in the alloy

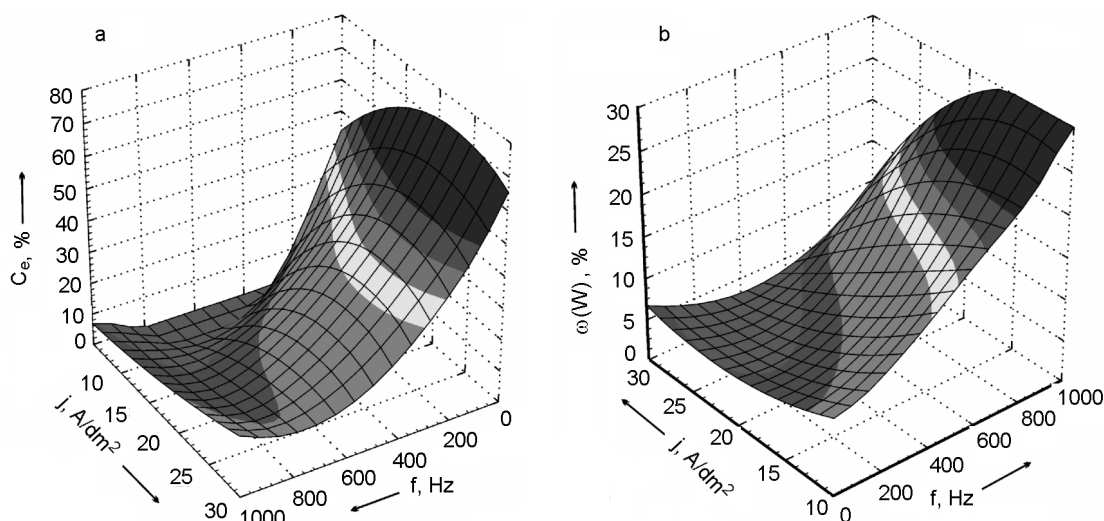


Fig. 2. Effect of pulse current amplitude and frequency E_c (a) and tungsten content $\omega(W)$ (b) in Co–W alloy.

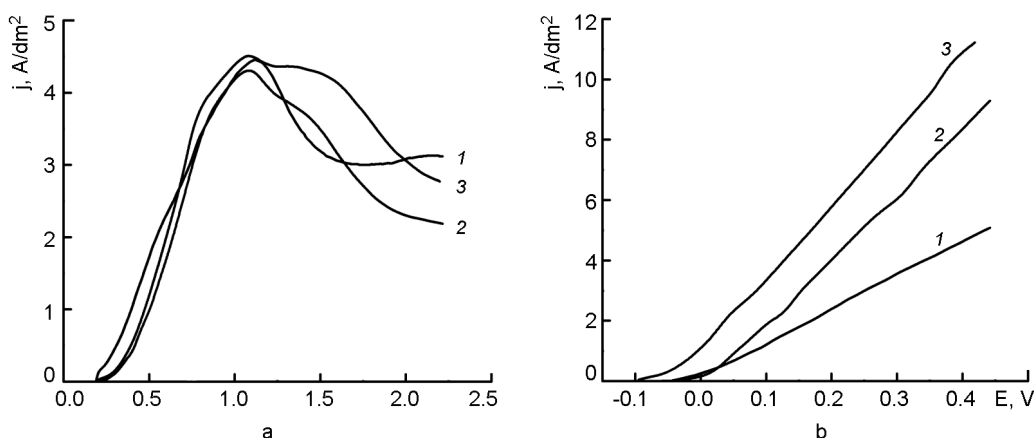
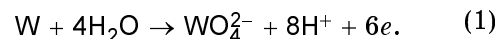


Fig. 3. Anodic polarization dependences of W (a) and Co (b) in electrolytes of composition, mol/l: citric acid – 0.3 (1); citric acid – 0.3, CoSO_4 – 0.2 (2); citric acid – 0.3, CoSO_4 – 0.2, Na_2WO_4 – 0.1 (3). Potential scanning rate is 20 mV/s.

grows for all current density amplitude values on/off time ratio reduces, while in the region of high current densities, there is an extreme of $\omega(W)$. The consideration of the response surface cuts testifies that dependence of the alloy E_c on the on-off time ratio shows an extreme character, in particular, as the on/off time ratio increases, the function passes through a maximum at $j = 12.5 \text{ A/dm}^2$, while at $j = 30 \text{ A/dm}^2$, it increases monotonously. The coating electrodeposition at frequency variation and constant current density amplitude has demonstrated that the permissible maximum amplitude in the low frequency region (18 to 85 Hz) is 25 A/dm^2 , since the coatings become cracked at higher values. As the frequency increases, the maximum cathode current

density grows. Thus, the study results provide a basis for electrochemical deposition of catalytically active and corrosion resistant Co–W alloy coatings, their composition and property control by electrolysis parameter variation. Anodic polarization dependences for tungsten in citrate electrolyte (Fig. 3a) testify that in the potential range 0.3 to 1.1 V active metal dissolution occurs, probably according to reaction:



Tungsten passivation in citrate acid solution, in our opinion, is a result of WO , WO_2 and W_2O_5 oxide formation on its surface. When cobalt sulfate is added to citric acid solution, a current decrease in the passive state is observed, which is likely associated

with cobalt oxide (III) formation having a higher resistivity as compared to tungsten oxides. When sodium tungstate is added, the wave in the passive region become more pronounced, and this fact allows to suppose that in the presence of WO_4^{2-} ions the chemical reduction of cobalt occurs [9]. The study results allow to conclude that it is possible to carry out the Co–W alloy electrodeposition process using soluble tungsten anode in the anodic current density range 1 to 2 A/dm². Consideration of cobalt anodic polarization dependence in citrate electrolyte (Fig. 3b) exhibits a region of active metal dissolution, and addition of both CoSO_4 and Na_2WO_4 increases the rate of that process. The experiments have shown that in the current density range of 0.8 to 1.5 A/dm², anodic current efficiency amounts about 100 %.

The alloy functional properties have been estimated by the corrosive resistance and catalytic activity in hydrogen reduction model reaction. With increasing tungsten content in the alloy, the random corrosion potential E_{cor} of Co–W coating is shifted towards the positive direction, thus indicating its increasing corrosive resistance.

The alloy chemical resistance was tested by impedance spectroscopy method. In experimental impedance hodographs of Co–W alloy coatings, the frequency characteristics in complex surface $1/\omega C_S - R_S$ describe satisfactorily a part the circle with center located below the abscissa axis. It follows from the impedance theory [10] that a substituting equivalent scheme of parallel connected capacity and resistance may correspond to such hodograph. The semicircle center displacement below the axis of active impedance component R_S is usually explained by influence of electrode roughness and its surface heteroresistance [11]. The tungsten content increase in the alloy to 20 % results in enlarged semicircle diameter, i.e. corrosion resistance (Fig. 4), followed by stabilization of R_p . The further consideration of hodographs has permitted to improve the equivalent scheme of electrode substitution and to describe it.

The hodograph shape for the electrode with cobalt coating ($\omega(\text{W}) = 0$) is substantially different. In the low-frequency range, the experimental points form a line with the slope angle about 45°. Impedance of such an electrode can be simulated by the Ershler-Rendls equivalent scheme that describes a mixed kinetics. In such case, the resistance R_p decreases by two orders (see Fig. 4), and

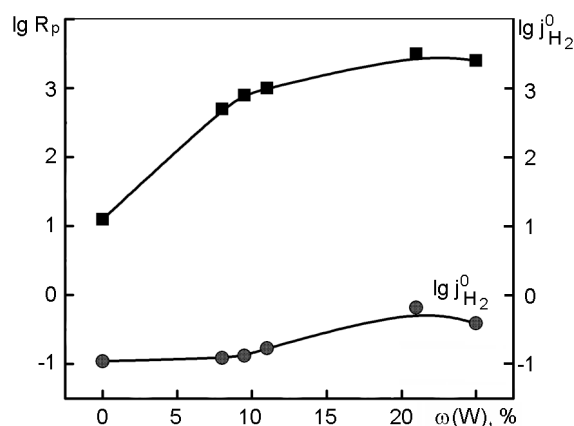


Fig. 4. The alloy tungsten content influence on corrosion resistance R_p and hydrogen exchange current density $j_{H_2}^0$.

the capacity C_1 obtained from the dependence $C_p - 1/\omega R_p$ grows to 260 $\mu\text{F}/\text{cm}^2$. This abnormally high C_p can be explained, probably, by coating surface degradation resulting in the coating complete dissolution within 3 h. The essential difference in hodograph for Co and Co–W deposits with the varied refractory metal content allows to state that tungsten codeposition changes the nature of electrochemical reactions and the formation of corrosion-resistant electrolytic Co–W alloy takes place.

The catalytic activity of obtained alloys in hydrogen evolution reaction increases with rising tungsten content (Fig. 4). The synergism effect is observed in this case, i.e. hydrogen exchange current density on the alloy exceeds its values for the alloy-forming components.

To conclude, the effect of main pulse electrolysis parameters (current density amplitude, pulse frequency and on/off time ratio, the pulse and pause duration) on cobalt-tungsten alloy composition and its current efficiency has been determined. The regimes providing the coatings with predetermined contents of the alloy-forming components have been identified. The Co–W alloy deposition possibility using soluble Co and W anodes has been proved, the current density interval preferred to carry out the process has been determined. The alloy corrosion stability explored using the impedance spectroscopy method answers completely to electrochemical kinetics laws and is defined by the alloy-forming component contents and increases in proportion with the tungsten content. The Co–W alloy catalytic activity has been established to exceed

its values for the alloy-forming components as a result of synergism effect. The study has proved the possibility of cobalt-tungsten alloy deposition with satisfactory high current efficiency and predictable high level of anticorrosion and catalytic properties.

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Новий підхід до електроосадження каталітичного сплаву Co–W

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Встановлено вплив основних параметрів імпульсного електролізу — амплітуди густини струму, частоти та скважності імпульсів, тривалості паузи та імпульсу — на процес осадження сплаву кобальт-вольфрам. Доведено можливість реалізації процесу електроосадження покриття з розчинними анодами. Проведено оцінку корозійної стійкості та каталітичної активності отриманих сплавів.