

Structure and properties of electrolytic cobalt-tungsten alloy coatings

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Electrochemical synthesis mode influence on composition, structure, surface morphology and functional properties of cobalt-tungsten alloy coatings has been investigated. The high-melting element concentration range in the deposit providing the maximal level of corrosion resistance and catalytic activity both in model hydrogen evolution reaction and at hydrocarbon oxidation has been determined. Magnetic characteristics and microhardness of cobalt-tungsten alloy coating have been studied as functions of its chemical composition.

Исследовано влияние режимов электрохимического синтеза на состав, структуру, морфологию поверхности и функциональные свойства покрытий сплавами кобальт-вольфрам. Установлен диапазон содержания тугоплавкого элемента в осадке и характер поверхности, обеспечивающие максимальный уровень коррозионной стойкости и каталитической активности как в модельной реакции выделения водорода, так и при окислении углеводов. Изучены магнитные характеристики покрытия сплавом кобальт-вольфрам и его микротвердость в зависимости от химического состава.

Today, of a great importance is the task of multifunctional material development having a spectrum of characteristics such as, for instance, catalytic activity, corrosion and abrasive wear resistance, etc., that provide greater effect at a fixed resource consumption [1]. In our previous works [2, 3] aimed at electrochemical synthesis of cobalt-tungsten alloy coatings, the synergism in catalytic properties of alloy-forming components in heterogenous Red-Ox reactions has been established. Taking into consideration the fact that the properties of a catalytically active material are defined, first of all, by its surface composition and morphology, it is reasonable to use electrochemical design to synthesize a catalytic system. That technique allows managing the thin-layer film deposition not only of required thickness and composition but also of necessary phase structure and, as a result, desirable characteristics [4]. The purpose of this

work is to continue the systematic studies of interconnection between the cobalt-tungsten alloy coating and catalytic activity and surface structure and morphology thereof.

The coatings were deposited from citrate electrolyte (citric acid 0.3 M; cobalt sulfate 0.2 M; sodium tungstate 0.15 M; boric acid 0.4 M) at 333 K onto substrates of X13H17M2T steel (4–8 cm² surface area). The electrolyte acidity value in the range of pH 5–10 was controlled by sodium hydroxide addition. The coatings of 5 to 30 μm thickness were deposited using different modes: direct current of $j = 0.5...3.0$ A/dm² density, and unipolar pulse current of $j_i = 12.5$ A/dm² amplitude, the pulse and pause duration being $t_i = 2$ ms $t_p = 20$ ms. The alloy component content was varied by means of the medium hydrogen index change. The functional properties were studied for coatings synthesized under pulse mode. The chemical composition of surface

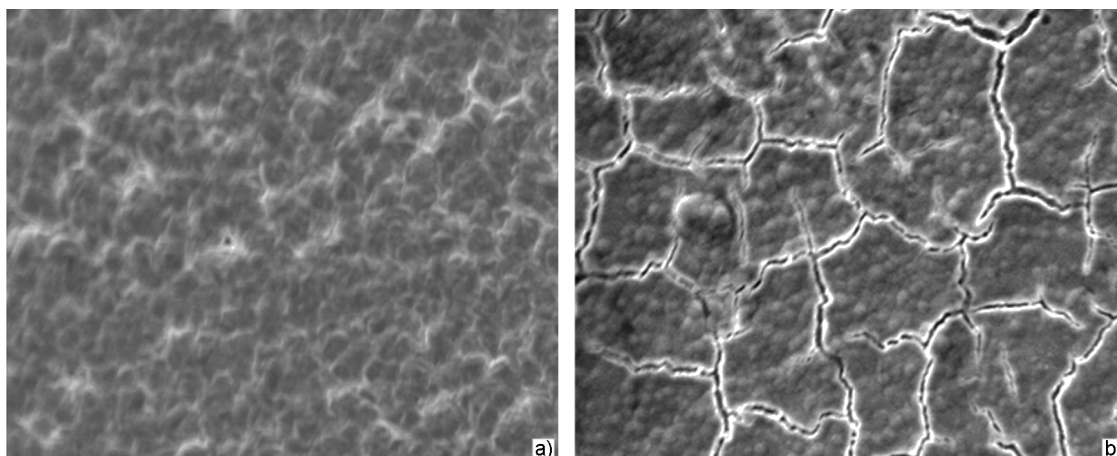


Fig. 1. Current density effect on morphology of Co-W alloy deposited under galvanostatic mode at j , A/dm²: 0.5 (a), 3.0 (b); pH 7 ($\times 2000$).

layers was determined by X-ray fluorescence method using portable universal spectrometer "SPRUT" as well as by analysis of characteristic X-ray spectrum obtained by energy-dispersion spectrometer INCA Energy 350. The sample surface was examined using a ZEISS EVO 40XVP scanning electron microscope. The coating corrosion resistance in media of various mineralization and pH was determined by polarization resistance method. The tests were performed in three solutions: NaOH 0.001 M (pH 11), H₂SO₄ 0.05 M (pH 3) and Na₂SO₄ 0.1 M (pH 7) [5]. The catalytic properties of electrolytic coatings differing in composition were preliminarily estimated using the exchange current (j_H^0) of hydrogen evolution model reaction from 0.001 M sulfuric acid solution under assumption of symbatic dependence of catalytic activity [6]. The experimental testing of catalytic properties was carried out using the flameless benzene oxidation reaction in a reactor under atmospheric pressure and gas flow rate w of 20,000 and 40,000 h⁻¹. The Vickers microhardness H_v of the coatings was measured by the diamond pyramid method using a PMT-3 device, loading and exposition time being 0.2 kg and 10 s, respectively. The experiment was done after 24 h aging of coatings at room temperature. The microhardness value was calculated using the well-known formula $H_v = 1854 \cdot P/d^2$, where d is the indentation diagonal, μm . The measurements were made in at least three points followed by averaging of the data obtained, confidence interval amounting $\pm 2\%$. The magnetic properties of cobalt-tungsten alloy coatings were studied at room temperature

using vibrating magnetometer in fields of -2000 to $+2000$ Oe. The instrument sensitivity was $0.1 \text{ Gs} \cdot \text{cm}^3 \cdot \text{g}^{-1}$, the measurement error $\pm 2\%$. The field lines were directed in parallel to the film surface.

Taking into account the revealed mechanism and kinetics regularities of tungsten-iron group metal co-deposition into alloys [7, 8], we concentrated attention on the electrolysis mode influence on Co-W electrolytic coating surface composition, structure and morphology. The working current value increase from 0.5 to 3.0 A/dm² in galvanostatic mode has been found to rise both deposition rate from 0.07 to 0.08 $\mu\text{m}/\text{min}$ and the high-melting element concentration in the alloy $\omega(W)$ from 20 to 37 wt. %. However, in such case, the internal stresses grow significantly, resulting in fracturing of coatings having even small (up to 3 μm) thickness (Fig. 1). Such a behavior of the system seems to be connected with the fact that new phase nucleation rate is lower than the crystal growth rate.

The nonstationary electrodeposition modes provide conditions when both nucleation and crystal growth rates become comparable to one another, thus reducing the internal stresses in coatings. The process realization in pulse mode makes it possible to apply much higher working current densities and, thereby, to achieve the coating formation speed up to 0.14–0.15 $\mu\text{m}/\text{min}$. In particular, the coatings without visible defects and cracks are formed at $j = 12.5 \text{ A}/\text{dm}^2$ (Fig. 2); however, other conditions being the same, the surface layer composition and structure depends on the solution acidity. So, coatings having $\omega(W)$ of 7 to 9 wt. % with

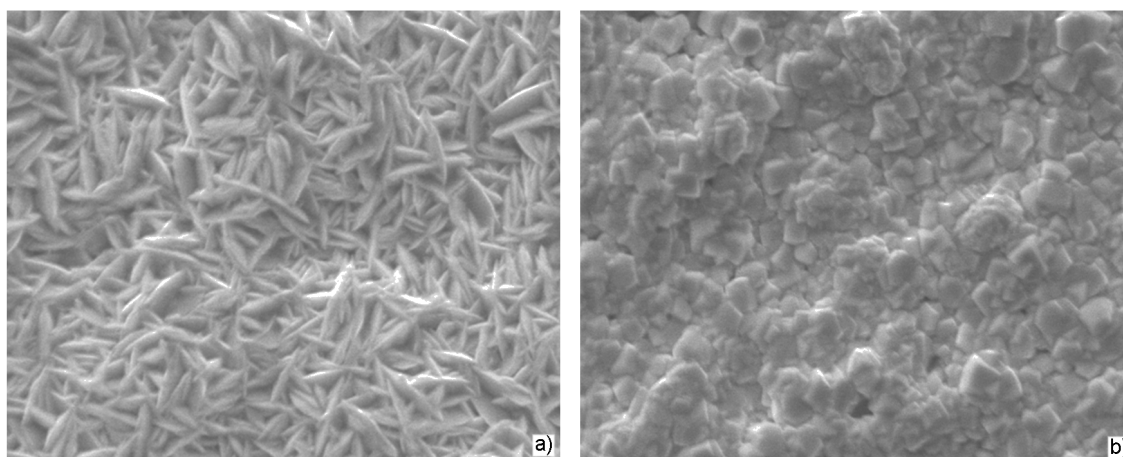


Fig. 2. Electrolyte pH effect on morphology of Co–W alloy deposited under pulse mode at pH: 5.3 (a), 7.0 (b); $j = 12.5 \text{ A/dm}^2$, $t_i/t_p = 2/20 \text{ ms}$ ($\times 5000$).

needle-plate structure are deposited from electrolyte with pH 5–5.5 (Fig. 2, a), while the pH increase to 7.0–7.05 provides enrichment in tungsten to 36–37 wt. % and formation of more fine-grained coating (Fig. 2, b). This considerable surface change probably might be associated with formation of Co_7W_6 or Co_3W intermetallic compounds (IMC) at increasing tungsten concentrations; those IMC were revealed by X-ray structure analysis and are in agreement with Co–W system state diagram [9].

For Co–W coatings with $\omega(\text{W}) = 25\text{--}35 \text{ wt. \%}$, containing IMC in the composition, both maximum hydrogen exchange current densities in model reaction and minimum ignition temperatures T_i in benzene flameless oxidation reaction have been registered (see Table). In our opinion, such effect might be explained in particular by electron density redistribution at the alloy formation resulting in over-additive increase of catalytic properties of the alloy components. Moreover, the synergism may be caused not only by high density of active centers at the catalytic layer surface but also by their arrangement configuration (Fig. 2) providing the maximum reaction ac-

celeration possible in such conditions. However, the formation of oversaturated intermetallic compound solid solution in the main metal results in a reduction of the material catalytic activity, reflecting both in j_H^0 value reduction and ignition temperature elevation (see Table). This phenomenon might be referred to increased internal stress level in electrodeposited Co–W alloys causing microcracking of the deposit, thus changing the surface morphology. The corrosion testing of Co–W alloys of various compositions testifies that the deep corrosion index k_h as a function of the tungsten concentration $\omega(\text{W})$ in the coating differs significantly for alkaline and acidic media. So, in 0.001 M H_2SO_4 solution (pH 3), the corrosion resistance increases by a factor exceeding 3 (k_h reduces from 0.13 to 0.04 mm/year) when $\omega(\text{W})$ rises from 9 to 21 wt. %, whereas in the $\omega(\text{W})$ range of 21 to 54 wt. %, the k_h value changes insignificantly. As the medium pH increases, the corrosion rate increases a little, and for alloys having $\omega(\text{W}) 20\text{--}40 \text{ wt. \%}$, k_h is almost the same for alkaline and neutral solutions. While the corrosion rate in acidic medium reduces as the tungsten content increases,

Table. Dependence of Co–W alloy coating functional characteristics on its composition

$\omega(\text{W})$ in alloy, wt. % (electrolyte pH)	Corrosion rate k_h , mm/year		Hydrogen exchange current density $-\lg j_H^0$ [A/cm^2] (pH 3)	Ignition temperature T_i , $^\circ\text{C}$	Microhardness H_v
	pH 3	pH 11			
7 (4.0)	0.112	0.167	4.85	215	394
21 (5.1)	0.033	0.089	4.18	–	479
34 (5.7)	0.025	0.081	4.22	160	513
53 (7.3)	0.009	0.124	4.67	220	676

in alkaline and neutral media the $k_h = f[\omega(W)]$ dependences show a pronounced minimum: in the $\omega(W)$ range of 10 to 50 wt. %, k_h diminishes from 0.15 to 0.07 mm/year and then increases to 0.12 mm/year. That character of the dependence could be explained by acidic properties of tungsten oxide films. The high level of internal stresses in electrodeposited Co–W alloys might result in microcracks causing the corrosion rate sharp increase at tungsten concentrations $\omega(W) > 40$ wt. %.

In synergetic Co–W alloys, not only catalytic activity in redox reactions is typically improved, but also the physico-mechanical properties. The Co–W coating microhardness H_v amounts 400 to 700, whereas for the alloy forming components $H_v(\text{Co}) = 130$, $H_v(\text{W}) = 350$. The application of pulse mode electrolysis provides an increased coating microhardness by 15 % on average, the alloy composition being the same. The microhardness of electrolytic chrome coatings amounts 700 to 850, depending on the preparation conditions, while the technology thereof requires the use of carcinogenic Cr(VI) compound solutions. This allows us to offer the Co–W alloys as an alternative for chrome hard coatings, since electrolytes for depositing these alloys are safer for the environment.

The magnetic properties of Co–W alloy coatings were estimated basing on coercive force, saturation magnetization and residual magnetization (Fig. 3). For films under consideration, it is possible to attain the coercive force H_c in the range of 150 to 160 Oe at $\omega(W)$ up to 20 wt. % (Fig. 3, curve 1). Under these conditions, the saturation magnetization σ_S and residual magnetization σ_R are reduced from 107 to 80 $\text{Gs}\cdot\text{cm}^3\cdot\text{g}^{-1}$ and from 39 to 37 $\text{Gs}\cdot\text{cm}^3\cdot\text{g}^{-1}$, respectively. Such characteristics allow to offer these films as information carriers in data storage devices.

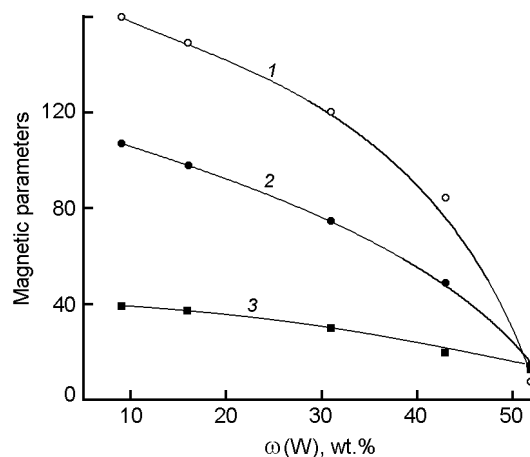


Fig. 3. Co–W alloy composition effect on its magnetic characteristics: coercive force, Oe (1); saturation magnetization (2) and residual magnetization, $\text{Gs}\cdot\text{cm}^3\cdot\text{g}^{-1}$ (3).

The characteristics mentioned above for Co–W alloys allow to propose these coatings as corrosion resistant and catalytic active ones, possessing favorable magnetic properties as well as microhardness close to that of chrome coatings, thus being suitable as an alternative for the latter.

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Структура та властивості електролітичних покриттів сплавом кобальт-вольфрам

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Досліджено вплив режимів електрохімічного синтезу на склад, структуру, морфологію поверхні та функціональні властивості покриттів сплавами кобальт-вольфрам. Визначено діапазон вмісту тугоплавкого елемента у покритті та відповідний характер поверхні, які забезпечують максимальний рівень корозійної стійкості та каталітичної активності як у модельній реакції виділення водню, так і під час спалення вуглеводнів. Вивчено магнітні характеристики сплаву кобальт-вольфрам та його мікротвердість в залежності від хімічного складу покриття.