

Use of materials based on cobalt alloys for the eco- and energy technologies

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The possibility of electrosynthesis and control of the surface morphology and composition of electrolytic coatings from alloys of cobalt and refractory metals by varying the electrolysis parameters has been proved. It was established that the composition of the coating, along with the main components, includes oxygen and carbon, and such systems can be considered as composite materials. The coatings deposited using the pulsed current can be considered as composite materials, and their oxide phase is formed directly in the electrode process as an intermediate product of incomplete reduction of tungstates, molybdates and the hydrolysis of zirconium salts. Studies of the surface morphology and topology of the composite coatings and their quantitative and phase compositions indicate the possibility of photocatalytic activity of Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ and Co-WO_v-ZrO₂ coatings. A study of the photodegradation of azo dye methyl-orange (MO) showed that the efficiency of the removing MO from the solution was 34 %, 25 % and 14 % for 50 minutes of UV irradiation in the presence of Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ and Co-WO_v-ZrO₂ coatings. The higher photoactivity of the composite Co-MoO_x-WO_x coatings can be explained by the presence of non-stoichiometric oxides of molybdenum and tungsten.

Keywords: composite coatings, electrochemical deposition, cobalt, refractory metals, photocatalytic properties.

Використання матеріалів на основі сплавів кобальту в еко- та енерготехнологіях.
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Доведена можливість електросинтезу та контролю складу та морфології поверхні електролітичних покриттів кобальту з тугоплавкими металами при варіюванні параметрів електролізу. Встановлено, що поряд з основними компонентами до складу покриттів входять кисень та вуглець, відповідно такі системи можна вважати композиційними. У композитних матеріалах, що осадженні за допомогою імпульсного струму, оксидна фаза утворюється безпосередньо в електродному процесі як наслідок неповного відновлення вольфраматів, молібдатів та гідролізу солей цирконію. Дослідження морфології та топографії поверхні покриттів, а також їх кількісного та фазового складу вказує на можливість фотокаталітичної активності Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ та Co-WO_v-ZrO₂. Дослідженням фотодеструкції азобарвника метилового жовтогогарячого (МЖ) встановлено, що ефективність видалення з розчину становила 34 %, 25 % та 14 % протягом 50 хвилин опромінювання ультрафіолетом в присутності композитних покриттів Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ та Co-WO_v-ZrO₂ відповідно. Більш високу фотокаталітичну активність композитних покриттів Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ та Co-WO_v-ZrO₂ можна пояснити наявністю нестехіометричних оксидів молібдену та вольфраму.

1. Introduction

The cooperation between Ukraine and EC in the energy sector is aimed at the enhancement of the energy safety, competitiveness and stability that are the essential factors of the economical growth and advance on the international market [1]. It is not limited to such areas as the development of renewable energy sources, alternative fuels and electric power sources as well as the use of the principles of sustainable development and environmental protection. The contemporary economy development requires the introduction of ecologically friendly technologies that are not only efficient but are also adapted to local conditions. Thus, one of the directions for the use of electrolytic coatings is the eco-technologies that satisfy human demands for the use of natural resources with minimal damage to the environment. Eco-technology combines two branches, in particular, "eco-tools" and "eco-technologies", which that require the understanding of the structure of the ecosystem and social processes [2]. Any chemical engineering that reduces the impact on ecosystems and takes ecology as a fundamental basis, ensures the conservation of the biodiversity and sustainable development and can be considered as a form of eco-technology. The eco-technology improves economic indices while reducing environmental impact by improving selectivity efficiency, the use of materials and energy, monitoring impacts on ecological systems, development and continuous improvement of purification processes.

A large number of scientific papers have been devoted to the investigations of photocatalytically active materials due to the general urgency of the problem of the air and water purification from unwanted substances of organic origin, including the development of self-cleaning surfaces and environmentally sound disposal of toxic organic substances. This is due to the ability of photocatalysts to oxidize almost any toxic organic compounds with the release of carbon dioxide and water [3–5].

Due to their chemical resistance and property stability, titanium dioxide-based materials are of great practical importance for this application [6–9]. However, due to the peculiarities of the band structure, TiO_2 exhibits its photocatalytic properties only under the action of UV electromagnetic radiation, which makes it possible to use only about 4 % of the intensity of sunlight radiation. One of the methods to intensify

photocatalytic activity is the use of transition metal oxides in an amount of 1 to 10 mass %, which can result in a synergetic effect.

Several methods are available for intensifying the photocatalytic activity, and one of them is the formation of composite materials with nanoparticles of metals and semiconductors. In this case, on the one hand the lifetime of the nonequilibrium charge carriers increases partly due to the redistribution of the photogenerated charge carriers between the contacting particles, and on the other hand, the absorption edge of the composite is shifted to the visible region. In this case, the visible light is absorbed either by the nanoparticles of the modifying semiconductor or by the metal nanoparticles due to the surface plasmonic resonance. At the same time, it should be noted that the morphology of nanocomposites can have an essential effect on their properties. Thus, the development of technology for depositing photocatalytically active materials on metal carriers is an urgent scientific and practical problem. This will make it possible to create synergistic coatings with evenly distributed dopants in the main coating matrix by varying technological parameters with the subsequent use of photocatalytic eco-technologies used to treat wastewater from technogenic impurities, in particular, methyl orange azo dye. This fact determined the direction of this scientific work.

2. Experimental

Composite electrolytic coatings were applied onto the copper substrate, grade M0; the sample surface was prepared using a generally-accepted technique. To deposit the composite $\text{Co-MoO}_x\text{-WO}_x$, $\text{Co-MoO}_x\text{-ZrO}_2$ and $\text{Co-WO}_x\text{-ZrO}_2$ coatings, biligand citrate pyrophosphate electrolytes were used [10, 11]. The pH factor was maintained at the level of 8 by addition of sodium hydroxide, and the temperature was 25°C.

The electrolysis was carried out using an IC-Pro potentiostat in a glass cell according to a two-electrode scheme using radial insoluble anodes made of Kh18N10T stainless steel. The current density amplitude was varied in the range of 4 to 10 /dm², and the pulse/pause duration was 5/10 ms. The anode area to the cathode area ratio was maintained within 1:(5–7), and the volume current density was maintained at the level of 2 A/dm³.

An atomic force probe microscope (AFM) NT-206 was used to study the surface topol-

ogy by the contact method using a CSC-37 probe and a cantilever B with the lateral resolution of 3 nm [12, 13]. The scanning area was fixed within $20.0 \times 20.0 \mu\text{m}$, and the height of the surface relief was fixed with a resolution of 256×256 pixels. The obtained results were visualized by reconstructing the surface in the form of 2D and 3D relief maps (height is shown in a different color). The obtained AFM images were processed using the Explorer Software by analyzing the average statistical amplitude parameters of surface roughness in accordance with international standards: the arithmetic mean Ra (ISO 4287/1) determines the surface roughness in the form of two-dimensional arithmetic values, and the root-mean-square value R_q (ISO 4287/1) is a surface roughness parameter. Based on the analysis data of the surface profile built according to the section on the topographic map, we determined the grain size, its shape and the presence of anisotropy of properties. All the structures show the identity of the surface characteristics in different areas of the scan, which allows extrapolating the data to the characteristics of the test sample as a whole. The phase composition of the coatings was studied using the XRD method on a Siemens D500 diffractometer in the Bragg-Brentano geometry in copper radiation with a graphite monochromator. The diffraction patterns were recorded in the angular range of $2 < 2\theta < 100$ degrees with a step of 0.02 degrees at an operating voltage of 35 kV and a current of 20 mA.

Photocatalytic properties of the composite cobalt-based coatings were studied using the model reaction of the methyl orange (MO) oxidation. The studies were carried out in the thermostatic photocatalytic reactor at a temperature of 25°C with continuous stirring; the coloring agent concentration was $4.00 \cdot 10^{-2} \text{ g/dm}^3$ (C_0). A solution (pH 6.3) with plates coated by Co-MoO_x-WO_x, Co-Mo_x-ZrO₂, Co-WO_x-ZrO₂ was illuminated with a DeLux EBT-01 mercury lamp emitting soft ultraviolet. All the solutions with obtained catalysts were preliminary held in a dark place during 60 minutes to establish the adsorption equilibrium. The MO dye content in the reactor was determined at regular intervals by the photocolometric method according to [14, 15]. The studies of the MO oxidation process were carried out in parallel without the use of ultraviolet radiation.

3. Results and discussion

The studies of the surface topography of synthesized coatings using the AFM make it possible to estimate the size of grains and associates and the degree of development of the surface of the resulting coatings, which, in turn, affects the photocatalytic activity. Composite Co-MoO_x-WO_x coatings (Fig. 1(a)) are characterized by the uniformly developed globular surface; the coatings consist of spherical grains and are characterized by a sufficiently high structure density, homogeneity and uniformity with a small number of peaks up to 870 nm. It was established earlier [16] that the formation of the spheroid surface structure is due to the presence of refractory metals in the coating composition.

The analysis of the intersection profile of the surface of Co-MoO_x-ZrO₂ coatings indicates the formation of small-size conic grains of 0.2 to 0.3 μm forming crystals ranging in size from 1.5 to 3.5 μm (Fig. 1(b)). In contrast to Co-MoO_x-WO_x coatings, the histogram of orientation angles indicates the anisotropy of the properties within the entire scan area.

The surface relief and the morphology of Co-WO_x-ZrO₂ coatings are similar to those of Co-MoO_x-ZrO₂ (Fig. 1). However, it should be noted that the content of tungsten in the alloys obtained under the same electrolysis conditions is lower than in the Co-MoO_x-WO_x coatings and the zirconium percentage in the Co-MoO_x-ZrO₂ coating is reduced. A decrease in the sizes of associates (agglomerates) and the absence of the cracks in the composite electrolytic coating (CEC) can be related to the effect of tungsten on the electrocrystallization process. The obtained data confirm the change in surface characteristics with a change in the scanning range, and this fact was established for the films and coatings obtained under different conditions [17].

The use of nanostructured thin-film materials that are based on catalytically active metals and oxides creates favorable preconditions for the efficient solution of the problem of water purification from organic impurities and infectious agents [18]. The main factor of these processes is the photocatalyzation under the action of visible and ultraviolet radiation [19]. The photocatalysis process is usually described by the generic or group model [20], and its behavior is simultaneously observed in two reactions, in particular oxidation with photogenera-

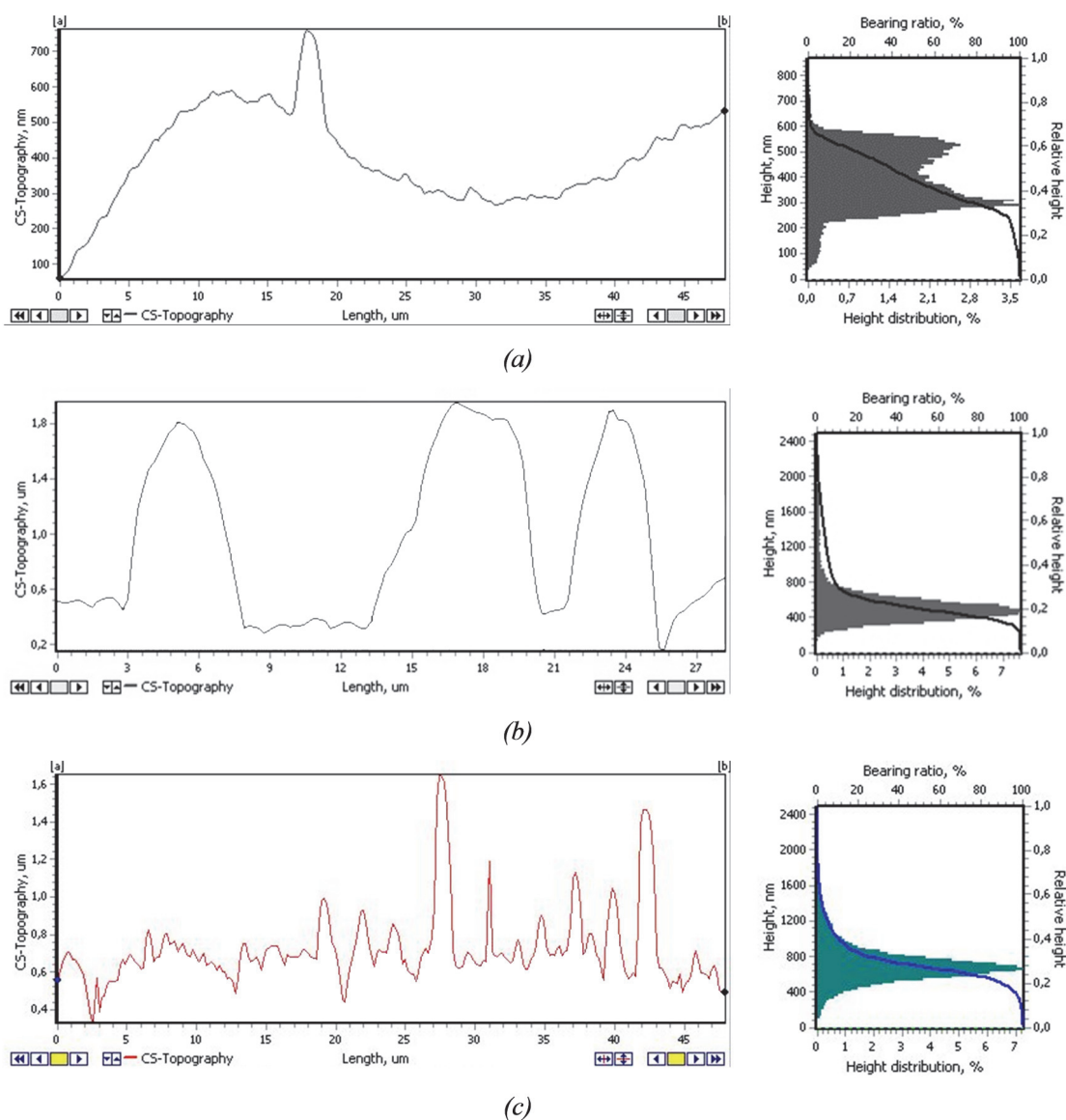


Fig. 1. Surface relief profiles of CEC: Co-MoO_x-WO_x (a), Co-MoO_x-ZrO₂ (b), Co-WO_x-ZrO₂ (c). Scan area is 48 × 48 μm.

tion of holes and reduction with photogeneration of electrons. The intensified activity of nanosize photocatalysts can be explained by the high degree of dispersity of materials, i.e., the number of atoms on the crystal surface or its faces can be comparable to the number of atoms located inside. In addition, as the particle size of semiconductor photocatalysts approaches several nanometers, the electron wavelength becomes comparable to the crystal size. In this case, charge carriers are considered at the mechanical quantum level as particles whose dimensions are determined by the size of the crystal. The nanosize particles of the solid substance that show quantum effects are called the Q-particles [21].

The ultraviolet irradiation of the coating surface results in the catalyst photoexcitation process due to the formation of electrons which either directly interact with dye molecules or initiate the formation of highly reactive radical ions. Hence, we observe the process of degradation of methyl orange (MO) with intense discoloration of the solution.

Since the azo dye contains nitrogen and sulfur compounds, as a result of deep photocatalytic oxidation, not only carbon (IV) oxides and water are formed, but also NH₄⁺, SO₄²⁻, H⁺ [22] ions; this follows from the general equation

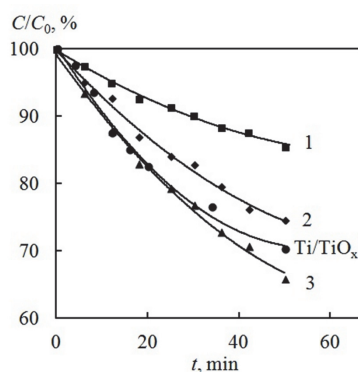
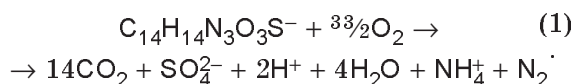


Fig. 2. Chronograms of the concentration of azo dye methyl orange as a function of the UV exposure of photocatalysts: titanium oxide, Co-WO_x-ZrO₂ (1); Co-MoO_x-ZrO₂ (2); Co-MoO_x-WO_x (3).



The photocatalytic oxidation of the MO water solution proceeds with the participation of O₂^{•-}, HO₂^{•-} radicals under the action of UV-radiation; its initial phase is characterized by the breaking of bonds in the dye molecule near the azo group with the formation of nitrogen N₂. Further oxidation results in the formation of dealkylated derivatives which are converted into carbonic and aliphatic acids through many reactions with complete mineralization of the substrate, i.e. formation of CO₂ and H₂O.

Data on the change in concentration in the model reaction of photodegradation of the azo dye methyl orange in the absence of a photocatalyst showed that these changes amount to 3 % during 60 minutes of UV irradiation.

It was established that the composite Co-MoO_x-WO_x coatings formed from the citrate — pyrophosphate electrolyte using the pulsed electrolysis have a higher photoactivity in comparison to the zircon composites formed under similar conditions. Based on the research data on the methyl-orange degradation (Fig. 2) we established that the efficiency of removing the methyl orange from the solution was 34.1 %, 25.4 % and 14.5 % for Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ and Co-WO_x-ZrO₂, respectively, after 50 minutes of UV irradiation with CEC. At the same time, the oxidation of the azo dye methyl orange on the titanium oxide over the same period of time was 29 %.

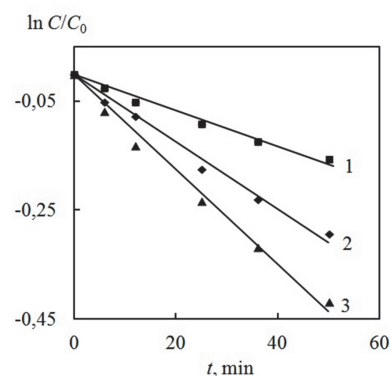


Fig. 3. Chronograms of the concentration of azo dye methyl orange as a function of the UV exposure of photocatalysts: Co-MoO_x-WO_x (1), Co-MoO_x-ZrO₂ (2), Co-WO_x-ZrO₂ (3).

To study the MO photodegradation kinetics under the action of light in the presence of the formed photocatalysts we plotted $\ln(C/C_0) = f(t)$ dependences. A linear character of the dependences indicates the first order reaction of the photocatalytic oxidation of MO. The slope of the linear curve (Fig. 3) determines the reaction rate constant k that was $1.08 \cdot 10^{-2} \text{ min}^{-1}$, $0.87 \cdot 10^{-2} \text{ min}^{-1}$ and $0.49 \cdot 10^{-2} \text{ min}^{-1}$ for Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ and Co-WO_x-ZrO₂, respectively. The higher value of the photocatalytic activity of composite coatings can be explained by the presence of two nonstoichiometric oxides of molybdenum and tungsten which are capable of forming mobile radical oxygen-containing particles on the developed microglobular surface under the action of the UV-radiation.

In the model reaction of the degradation of azo dye methyl orange, the Co-MoO_x-WO_x composite coatings exhibited high catalytic activity; this makes it possible to recommend these coatings for wastewater treatment plants to remove organic aromatic compounds in a pilot plant for photocatalytic wastewater treatment (Fig. 4).

4. Conclusions

It has been established that the contact masses of electrolytic composite coatings Co-MoO_x-WO_x, Co-MoO_x-ZrO₂ and Co-WO_x-ZrO₂ exhibit high photocatalytic activity in the reaction of azo dye destruction under the action of the UV-radiation; moreover, the Co-MoO_x-WO_x coatings have a higher catalytic activity compared to Co-MoO_x-ZrO₂ and Co-WO_x-ZrO₂ coatings and can be comparable with conversion titanium oxide coatings. The obtained data in-

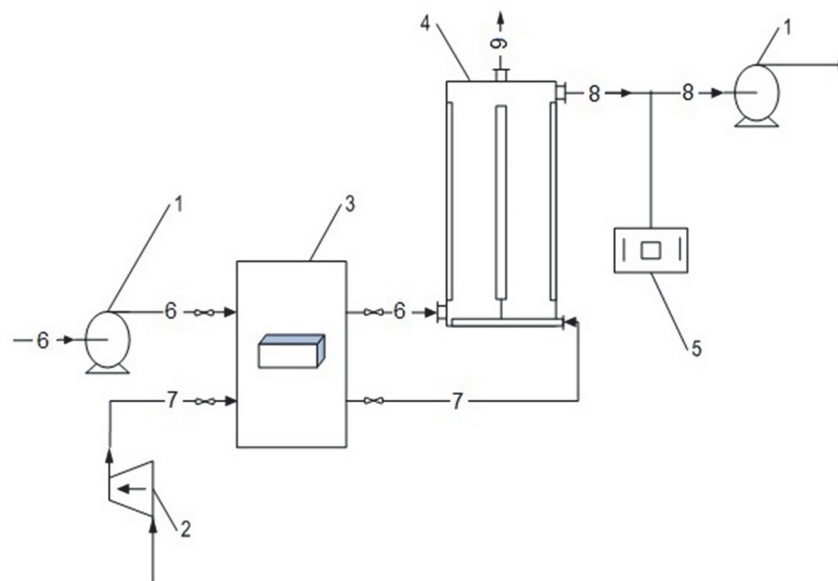


Fig. 4. Scheme of an installation designed for industrial wastewater treatment from organic aromatic compounds: 1 — pump, 2 — compressor, 3 — flow meter, 4 — reactor with the photocell and lamp and 5 — sampler. Technological streams: 6 — contaminated production wastewater, 7 — compressed air, 8 — treated wastewater, 9 — exhaust gases.

dicade the possibility of developing photocatalytic converters using mixed composite materials formed on metal carriers and used to treat wastewater from organic aromatic compounds.

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