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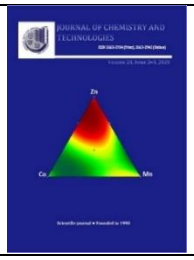

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# THE SYNTHESIS AND PHOTOCATALYTIC PROPERTIES OF THE COBALT-BASED COMPOSITES WITH REFRACTORY METALS

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## Abstract

**The possibility of electrosynthesis and control of the surface composition and morphology of the electrolytic cobalt coatings with refractory metals by varying the parameters of electrolysis has been proved. It was found that oxygen and carbon are included in the composition of the coatings as well as the main components, thus such systems can be considered as composite. The coatings deposited by pulsed current can be considered as composite materials the oxide phase for which is formed directly in the electrode process as an intermediate of incomplete reduction of tungstates and hydrolysis of zirconium (IV) salts. The topography of the films is distinguished by the presence of elliptical and spherical grains with crystallite sizes of 80 - 180 nm. On the surface of the coatings, there are hills (large grains) with a diameter of 1 - 3 μm. The fractal dimension of the surface is 2.77, which indicates the 3D mechanism of crystal growth during the formation of coatings. In terms of phase composition, composites are predominantly amorphous materials that contain nanocrystalline cobalt and the intermetallic compound $Co_3W$ and $Zr_3Co$. The study of the morphology and topography of the composite coatings surface, as well as its quantitative and phase composition, indicates the possibility of photocatalytic activity of the Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ and Co-W-$ZrO_2$ coatings. Investigation of the photodegradation of the azo dye methyl orange found that the efficiency of MO removal from the solution was 24 %, 18 %, and 10 % for 30 min of ultraviolet irradiation in the presence of Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ and Co-W-$ZrO_2$ on composite coatings, respectively. The higher photoactivity of Co-Mo-$WO_x$ composite coatings can be explained by the presence of non-stoichiometric molybdenum and tungsten oxides.**

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

# СІНТЕЗ І ФОТОКАТАЛІТИЧНІ ВЛАСТИВОСТІ КОМПОЗИЦІЙНИХ ПОКРИТТІВ НА ОСНОВІ КОБАЛЬТУ З ТУГОПЛАВКИМИ КОМПОНЕНТАМИ

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## Анотація

**Доведено можливість електросинтезу і керування складом і морфологією поверхні електролітичних покриттів кобальту з тугоплавкими металами варіюванням параметрами електролізу. Встановлено, що поряд з основними компонентами до складу покриттів включаються Оксиген та Карбон, і такі системи можуть розглядатися як композиційні. Покриття, осаджені із застосуванням імпульсного струму, можна вважати композиційними матеріалами, оксидна фаза для яких утворюється безпосередньо в електродному процесі як інтермедіат неповного відновлення вольфраматів та гідролізу солей цирконію. Топографія плівок відрізняється наявністю зерен еліптичної і сферичної форми з розмірами кристалітів 80 – 180 нм. На основній поверхні зустрічаються виступи (крупні зерна) діаметром 1 – 3 мкм. Фрактальна розмірність поверхні становить 2.77, що свідчить про 3D механізм роста кристалів при формуванні покриття. За фазовим складом композити є переважно аморфними матеріалами, які містять нанокристалічний кобальт та інтерметаліди $Co_3W$ і $Zr_3Co$. Дослідження морфології та топографії поверхні композиційних покриттів, а також її кількісного і фазового складу свідчить про можливість фотокаталітичної активності покриттів Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ і Co-W-$ZrO_2$. Дослідження фотодеструкції азобарвника метилового жовтогарячого (МО) встановлено, що ефективність видалення МО з розчину склала 24 %, 18 % і 10 % за 30 хв опромінення ультрафіолетом в присутності на композиційних покриттях Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ і Co-W-$ZrO_2$, відповідно. Вищу фотоактивність композиційних покриттів Co-Mo-$WO_x$ можна пояснити наявністю нестехіометричних оксидів Молібдену і Вольфраму.**

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*Ключові слова:* композиційні покриття; електролітичне осадження; кобальт; тугоплавкі метали; фотокаталітичні властивості.

# СИНТЕЗ И ФОТОКАТАЛИТИЧЕСКИЕ СВОЙСТВА КОМПОЗИЦИОННЫХ ПОКРЫТИЙ НА ОСНОВЕ КОБАЛЬТА С ТУГОПЛАВКИМИ МЕТАЛЛАМИ

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Аннотация

**Доказана возможность электросинтеза и управления составом и морфологией поверхности электролитических покрытий кобальта с тугоплавкими металлами при варьировании параметрами электролиза. Установлено, что наряду с основными компонентами в состав покрытий включаются кислород и углерод, и такие системы могут рассматриваться композиционные. Покрытия, осажденные с применением импульсного тока, можно считать композиционными материалами, оксидная фаза для которых образуется непосредственно в электродном процессе как интермедиат неполного восстановления вольфраматов и гидролиза солей циркония. Топография пленок отличается наличием зерен эллиптической и сферической формы с размерами кристаллитов 80 – 180 нм. На поверхности покрытий встречаются выступы (крупные зерна) диаметром 1 – 3 мкм. Фрактальная размерность поверхности составляет 2.77, что свидетельствует о 3D механизме роста кристаллов при формировании покрытий. По фазовому составу композиты являются преимущественно аморфными материалами, которые содержат нанокристаллический кобальт и интерметаллида $Co_3W$ и $Zr_3Co$. Исследование морфологии и топографии поверхности композиционных покрытий, а также ее количественного и фазового состава свидетельствует о возможности фотокаталитической активности покрытий Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ и Co-W-$ZrO_2$. Исследование фотодеструкции азокрасителя метилового оранжевого (МО) установлено, что эффективность удаления МО из раствора составила 24 %, 18 % и 10 % за 30 мин облучения ультрафиолетом в присутствии на композиционных покрытиях Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ и Co- W-$ZrO_2$, соответственно. Более высокую фотоактивнисть композиционных покрытий Co-Mo-$WO_x$ можно объяснить наличием нестехиометрических оксидов молибдена и вольфрама.**

*Ключевые слова:* композиционные покрытия; электрохимическое осаждение; кобальт; тугоплавкие металлы; фотокаталитические свойства.

## Introduction

Today, the growth rates of industrial production and economic activities result in the aggravation of the water purification problem that makes the humanity seek for innovative approaches to the ecologization of the technology park [1–3]. The sorption, destruction and separation technologies that are available today resolve the water purification problem only partially, because these require an additional neutralization and disposal of the waste accumulated on the surface of sorbents or filters during the purification process and accordingly, these are not ecologically friendly and economically sound. The photocatalytic method shows up to advantage against a background of aforementioned technologies and is characterized by an entire set of positive properties [4, 5]. The use of nanostructured thin-film materials that are based on catalytically active metals [6–8] and oxides [9–11] creates favorable conditions for the efficient solution of the problems relating to the purification of water polluted with organic pollutants and infectious agents.

The redox reactions progressing on the film surface decompose the pollutants into ecologically friendly components. The photoelectric catalysis exposed to the radiation of visible and ultraviolet ranges acts as a driving factor for these processes. Among the most promising technological approaches to the creation of nanostructured photocatalytic coatings we can distinguish the galvanic approach based on the electrochemical deposition of converted and composite coatings from electrolyte solutions [12, 13]. This method enables the variation of the composition in a wide range and hence, the physical and chemical properties of obtained coatings can also be changed. The major part of this investigation deals with the studies of the photocatalytic properties of titanium dioxide $TiO_2$ [14–16] that is one of the most extensively studied materials among transition metal oxides due to its unique photo-induced catalytic activity, its intensive interaction with water, nontoxicity, physical stability and chemical inertness. Recently, many other semiconductors such as $WO_3$, CdS, $SnO_2$, $SiO_2$, $ZrO_2$, ZnO, $Nb_2O_3$, $Fe_2O_3$, $SrTiO_3$, etc. were defined as the photocatalysts. In particular, the researchers pay a focused attention to the photoactivity of

tungsten oxide $WO_3$ [17] and zirconium oxide $ZrO_2$ [12, 18].

In this connection, the problem of the development of the methods for the electrochemical synthesis of composite coatings based on cobalt with refractory metals oxides (molybdenum, tungsten, zirconium) and the studies of their photocatalytic properties seems to be rather topical because these coatings can be applied for water purification systems and also for the combined purification of water-air mixtures.

## Experimental methods

Composite electrolytic coatings were applied onto the copper substrate, grade M0; the sample surface was prepared using a generally-accepted technique. To deposit composite Co-Mo-$WO_x$, Co-Mo-$ZrO_2$, and Co-W-$ZrO_2$ coatings biligand citrate pyrophosphate electrolytes (Table 1) were used [19, 20]. The pH factor was maintained at the level of 8 by addition of sodium hydroxide and the temperature was equal to 25 °C.

The electrolysis was carried out using the potentiostat IC-Pro in the glass cell according to the two-electrode scheme making use of radial insoluble anodes made of stainless steel of a X18H10T grade. The current density amplitude was varied in the range of 4 to 10 A/dm$^2$ 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 volumetric current density was maintained at the level of 2 A/dm$^3$.

*Table 1*

**The composition of electrolytes for deposition of cobalt-based composite coatings**

| Electrolyte composition, mol/dm$^3$ | Co-Mo-$WO_x$ | Co-W-$ZrO_2$ | Co-Mo-$ZrO_2$ |
|---|---|---|---|
| $CoSO_4$ | 0.2 | 0.15 | 0.10 |
| $Na_2WO_4$ | 0.16 | 0.02 | - |
| $Na_2MoO_4$ | 0.04 | - | 0.02 |
| $Zr(SO_4)_2$ | - | 0.05 | 0.05 |
| $Na_3C_6H_5O_7$ | 0.2 | 0.3 | 0.2 |
| $K_4P_2O_7$ | 0.4 | 0.1 | 0.1 |
| $Na_2SO_4$ | 0.5 | 0.5 | 0.5 |

A chemical composition of the obtained coatings was defined using the data of the energy dispersive spectroscopy and the electronic microprobe analyzer Oxford INCA Energy 350 (the X-ray radiation was excited by way of the sample irradiation by the electron beam with the energy of 15 keV) that was integrated into the system of scanning electron microscope (SEM). The surface morphology was studied using SEM EISS EVO 40XVP [15, 16].The images were obtained by recording secondary electrons through electron beam scanning and that allowed us to take high-resolution measurements in a wide contrast range. The images were processed using the software environment SmartSEM.

Atomic force probe microscope (AFM) NT-206 was used to study the surface topology by the contact method using the CSC-37 probe and the cantilever B with the lateral resolution of 3 nm [21, 22]. The scanning domain was fixed within 20,0 × 20,0 μm and the surface relief height was fixed with the resolution of 256 × 256 pixels. The obtained results were visualized by way of the surface reconstruction in the form of 2D and 3D-topography maps (the height is shown by a different color). The obtained AFM images were processed using the Explorer Software by analyzing average statistical amplitude parameters of the surface roughness according to the international standards, i.e. arithmetic average Ra (ISO 4287/1) that defines the surface roughness in the form of the two-dimensional arithmetic values and the mean square value Rq (ISO 4287/1) that is the defining parameter of the surface roughness. Based on the analysis data of the surface profile that was constructed along the section on topographic maps we determined the grain size, its shape and the availability of the anisotropy of the properties. All the structures show the identity of surface characteristics at different scanning sections and it enabled the extrapolation of the data to the characteristics of the tested sample on the whole.

The phase composition of the coatings was studied using the method of X-ray structure analysis and the diffractometer Siemens D500 (Bragg-Brentano's geometric layout) under the copper radiation with the graphite monochromator. The diffractograms were recorded in the angular range of 2 <2θ <100 °C with the pitch of 0.02 at the operating voltage of 35 kV and the 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 the continuous mixing; the coloring agent concentration was equal to $4.00 \cdot 10^{-2}$ g/dm$^3$ ($C_0$).The solution (pH 6.3) with Co-Mo-$WO_x$, Co-Mo-$ZrO_2$, Co-W-$ZrO_2$ coated plates was illuminated with the mercury lamp DeLux EBT-01 radiating a soft ultraviolet. All the solutions with obtained catalysts were preliminary held in the dark place during 60 minutes to establish the adsorption equilibrium.

The content of the MO coloring agent in the reactor was determined over equal time intervals using the photocolorimetric method according to [11, 12]. The studies of the MO oxidation process were carried out simultaneously using no ultraviolet radiation.

## Results and discussion

The photocatalysis is usually described by the group model in which at least the two reactions occur simultaneously, in particular the oxidation reaction with the photogeneration of the holes and the reduction reaction with the photogeneration of the electrons [23].

An enhanced activity of nanosized photocatalysts can be explained by a high degree of the material dispersion, i.e. the number of atoms on the surface or on crystal faces is comparable with the number of atoms inside. In addition, as the particle size of semiconducting photocatalysts approaches several nanometers, the electron wavelength becomes comparable with the crystal size. In this case, the charge carriers are viewed at the quantomechanical level as the particles in the box whose size is defined by crystal sizes. Such nanosized particles of the solid matter in which quantum effects are manifested are called *Q*-particles [24, 25]. Hence, the surface morphology and topology are considered to be an important factor that has an effect on the photocatalytic activity of nanocomposite materials.

The analysis data of the surface morphology and its composition obtained for the samples with cobalt-based composite coatings are indicative of the fact that a definite amount of carbon and oxygen was detected in addition to basic components, i.e. cobalt, molybdenum, tungsten and zirconium (Fig. 1). It should be noted that the oxygen content is increased with an increase in the content of refractory components in the coatings. An increased content of molybdenum in the Co-Mo-$ZrO_2$ coating contributes to the formation of the uniform microglobular surface (Fig.1 b, d) and the availability of zirconium provides a decreased cracking of the coatings (Fig.1 b, c). Such systems are viewed as composite electrolytic Co-W-$ZrO_2$, Co-Mo-$ZrO_2$ and Co-Mo-$WO_x$ coatings due to a considerable amount of oxygen in the composition that is related to the incomplete reduction of tungstate-ions and zirconium hydrolysis (IV) and also the nonuniform distribution of alloy components on the surface.

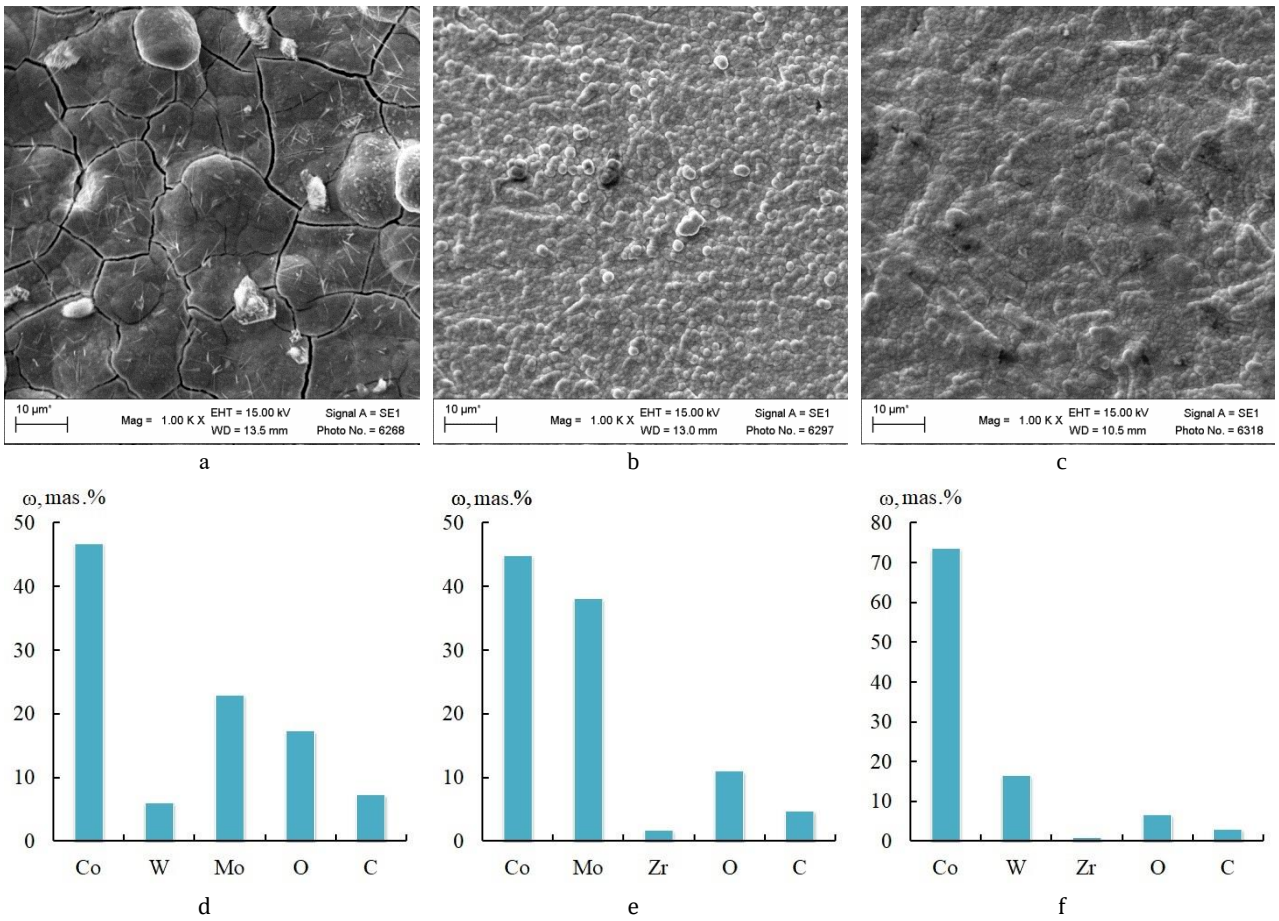


**Fig. 1. Morphology (a, b, c) and composition (d, e, f) of composite coatings Co-Mo-$WO_x$ (a, d), Co-Mo-$ZrO_2$ (b, e) and Co-W-$ZrO_2$ (c, f)**

The coating surface topography analysis gives sufficiently exhaustive information on the adsorption capacity. In the material science, the roughness acts as a surface quality characteristic and it depends on the material treatment method. When depositing galvanic coatings, this parameter reproduces a degree of the substrate roughness and it is a regular result of a mechanism of the nucleation process on the substrate made of the other metal and the crystal growth during the alloy formation [26, 27]. The atomic-force microscopy data analysis (Fig. 2) is indicative of that the composite Co-Mo-$WO_x$ coatings differ by a more globular and more branched surface in comparison with the coatings containing zirconium oxide (Co-Mo-$ZrO_2$, Co-W-$ZrO_2$) in their composition. At the same time, the latter show a greater height difference.

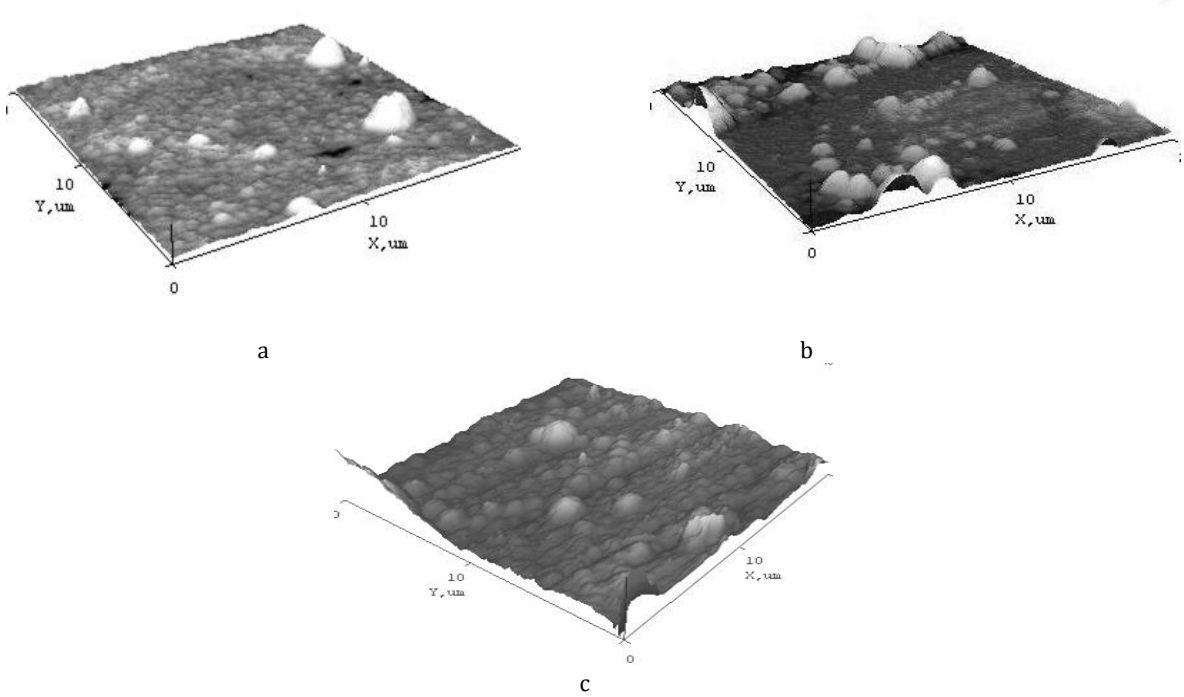


**Fig. 2. 3D-maps of surfaces Co-Mo-$WO_x$ (a), Co-W-$ZrO_2$ (b) and Co-Mo-$ZrO_2$ (c)**

Based on the research data of the surface morphology and topography of composite coatings and also of its quantitative and phase compositions we can assume that these can manifest a photocatalytic activity.

Alongside with the formation of the branched globular surface the phase composition of coatings can turn out to be an important factor that has an effect on coating properties and in particular on the photocatalytic activity because it conditions the surface distribution of active acceptor centers. The $CoMoWO_x$ and $CoMoZrO_2$ coating samples (Fig.3a, c) represent the amorphous substance and in this case spike transients that are observed on X-ray patterns (Fig.3 a, c) correspond to those of the copper substrate. The CoW $ZrO_2$ sample (Fig.3b) also gives the X-ray pattern of the amorphous substance that shows the lines of nanocrystalline cobalt and the $Co_3W$ and $Zr_3Co$ intermetallides present in small amounts.

When the coating surface is exposed to the ultraviolet radiation, the catalyst photoexcitation process occurs due to the formation of the electrons and holes that either directly interact with coloring agent molecules or initiate the formation of OH radicals that have a high reactivity. Hence, the MO destruction process occurs with the intensive solution discoloration.

It was established that the composite Co-Mo-$WO_x$ coating obtained by way of pulsed electrolysis from the citrate-pyrophosphate electrolyte has a higher degree of photoactivity in comparison to zirconium-containing composites that were deposited under the same conditions. Based on the research data of the MO photodestruction (Fig. 4 a) it was established that the efficiency of MO removal from the solution made up 24 %, 18 % and 10 % during the thirty minutes in the presence of composite Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ and Co-W-ZrO coatings, accordingly. To study the kinetics of the MO photodestruction under the action of light in the presence of obtained photocatalysts we constructed the dependences of $\ln(C/C_0) = f(t)$.

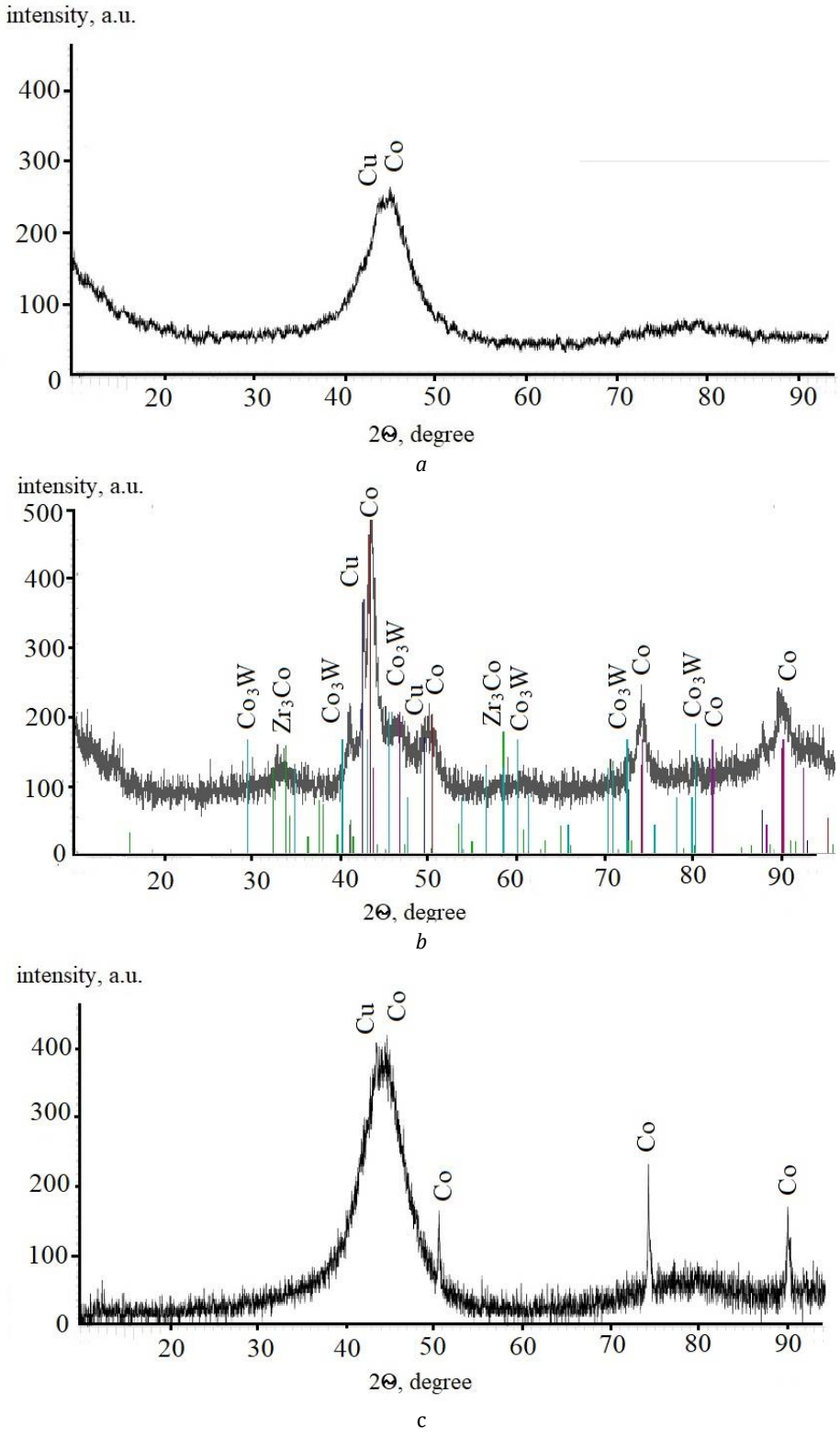


**Fig. 3. X-ray patterns of composite coatings Co-Mo-$WO_x$ (a), Co-W-$ZrO_2$ (b) and Co-Mo-$ZrO_2$ (c)**

The slope of the linearized dependence (Fig. 3, b) defines the speed constant $k$ that is equal to $1.06 \cdot 10^{-2}$ $min^{-1}$, $0.80 \cdot 10^{-2}$ $min^{-1}$ and $0.47 \cdot 10^{-2}$ $min^{-1}$ for Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ and Co-W-$ZrO_2$, accordingly (Fig. 4, b). A higher photoactivity of the composite Co-Mo-$WO_x$ coatings can be explained by the availability of the two nonstochiometric molybdenum and tungsten oxides that can form mobile radical oxygen-containing particles under the action of UV radiation with the branched microglobular surface.

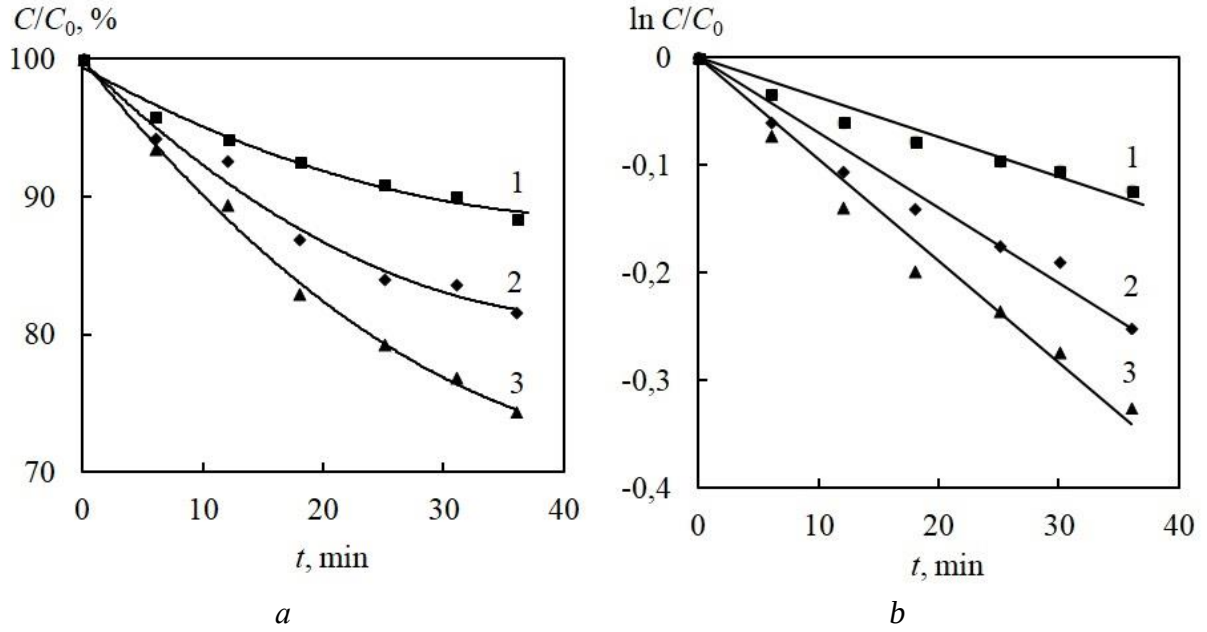


**Fig. 4. Change in methyl orange concentration with time of UV irradiation on composites: Co-W-$ZrO_2$ (1); Co-Mo-$ZrO_2$ (2); Co-Mo-$WO_x$ (3)**

## Conclusions

Hence, cobalt-based composite coatings were deposited from the citrate-pyrophosphate electrolyte and these are characterized by microcrystallinity and a sufficiently high degree of the surface development. The composite coatings that contain zirconium oxides in their composition are characterized by a relatively high height difference.

It was shown that the contact masses of Co-Mo-$WO_x$, Co-Mo-$ZrO_2$ and Co-W-$ZrO_2$ coatings are photocatalytically active in the methyl orange destruction reaction when exposed to UV-radiation and in this case Co-Mo-$WO_x$ coatings have a higher catalytic activity in comparison with Co-Mo-$ZrO_2$ and Co-W-$ZrO_2$ coatings and can be comparable with converted titanium oxide coatings. The obtained data are indicative of the possibility of the creation of photocatalytic converters and the mixed composite materials formed on the metal carriers can be used for the sewage water treatment to remove organic aromatic compounds.

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