N.D.Sakhnenko, M.V.Ved'*, A.V.Karakurkchi**PECULIARITIES OF COBALT CONTAINING OXIDE COATINGS FORMATION ON SILUMIN***National Technical University "Kharkiv Polytechnic Institute", 2 Kyrpychova Str., Kharkov, 61002, Ukraine***e-mail: vmv@kpi.kharkov.ua*

The process of mixed oxide coatings formation on a high-silicon aluminum alloy in a cobalt-containing pyrophosphate electrolyte by the plasma-electrolytic oxidation (PEO) method is studied. It was shown that AL25 chemical composition heterogeneity causes the consumption of a part of the anode current to homogenize the treated surface, which is reflected in minimizing the content of doping components at the initial processing stage. It was established that the growth of mixed oxides $\text{Al}_2\text{O}_3 \cdot \text{Co}_x\text{O}_y$ relative mass is a function of time with a maximum at 55 minutes. The chemical, phase composition and surface morphology of the formed oxide layer depend on the oxidation time. The catalytic component content in the surface oxides varies from 0.2 to 23.3 at.% with an increase in processing time of 10 to 60 minutes. Maximum cobalt incorporation into the oxide layer occurs at PEO of 35–50 minutes, while the silicon content in the surface layers does not exceed 2 at.%, which is favorable for the catalytic properties. The cobalt oxide, preferably Co_3O_4 , incorporation in the alumina $\alpha\text{-Al}_2\text{O}_3$ matrix is visualized by the blue-violet color steroidal surface structures in the sites of micro-arc discharges. The alumina cobalt oxide mixture layers are characterized by a developed micro-globular surface which consists of spheroid conglomerate with an average size of 1–2 microns. There are some amorphous phases in the structure of mixed oxides due to non-equilibrium PEO conditions. The set of detected factors is a prerequisite for the high catalytic properties of oxide coatings. A promising field of $\text{Al}_2\text{O}_3 \cdot \text{Co}_x\text{O}_y$ systems application is intra-cylinder catalysis in internal combustion engines.

K e y w o r d s: plasma-electrolytic oxidation, alumina matrix, cobalt oxides, catalytic activity, intra-cylinder catalysis.

INTRODUCTION. The alloys of aluminum with silicon are demanded construction materials. They are widely used in various industries: motor engineering and automotive, water and heat supply systems, etc. At present there is an intensive development of technologies for improving the operational properties of metals and alloys by modi-

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fying their surface [1,2]. One of the most demanded and promising methods is the plasma-electrolytic oxidation (PEO) of valve metals, which allows forming oxide coatings with increased mechanical, corrosion and catalytic properties [3, 4]. Among the advantages of PEO should be noted non-toxicity of used electrolytes, the simplicity and compactness of the working equipment, the lack of preliminary surface preparation stage, the possibility of processing large mass and complex geometry parts. Changing the oxidation conditions, the electrolyte qualitative and quantitative composition, the dopants nature allows varying the composition and properties of the formed oxide layers [5,6].

One of the topical directions of the practical use of oxide coatings on aluminum and alloys is catalytic redox processes, in particular, eco-friendly catalysis [7–10]. For these purposes compounds of catalytically active components are introduced in the composition of highly developed surface layers. Most often this is achieved by impregnating (precipitating) a preformed matrix of base metal oxide in solutions containing salts of dopants metals followed by heat treatment of the resulting material [11, 12]. However, this approach not only complicates and raises the cost of the technological process, but also does not allow obtaining systems with significant content of the catalytic component and high adhesion to the substrate.

At the same time, it is promising to develop a PEO technology for the formation of a highly developed carrier (base metal oxide matrix) in one process with dopants incorporation (preferably transition metal oxides) throughout the processing period due to the

implementation of electrochemical and thermo-chemical reactions in high-energy modes [13, 14]. This will provide a longer service time of the resulting catalytic material and substantially higher functional properties.

In previous studies, a rather complicated mechanism of reactions in working solutions during the oxidation of valve metals and the feasibility of using a complex of electrolytes based on diphosphate for PEO of AL25 alloy were shown [15, 16]. As catalytically active components, based on physical and chemical properties, manganese and cobalt were selected. It was found that the ratio of cobalt and ligand concentration affects the oxidation process parameters and allows forming coatings with varying content of the catalytically active component. For further research, the composition of the electrolyte was selected, which allows oxide layers enriched in the catalytically active component to be formed with a higher surface development degree [17].

The purpose of this work is to investigate the effect of the oxidation time on the composition, phase structure and morphology of mixed aluminum and cobalt oxide coatings to select the optimal parameters for catalytic materials formation.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Oxide coatings were formed on rectangular samples of cast aluminum alloy AK12M2MgN (AL25). The chemical composition of silumin, wt. %: Si, 11.5–13.0; Cu, 1.5–3.0; Ni, 0.8–1.3; Mg, 0.8–1.3; Mn, 0.3–0.6; Fe < 0.8; Zn < 0.5; Ti < 0.2; Pb < 0.1; Sn < 0.02; Cr < 0.2. Working area for the formation of oxide coatings was 0.2 dm². The surface of samples for coatings applica-

tion was prepared by grinding with subsequent degreasing, washed with water, and dried at 30 °C. The samples were oxidized in an electrolyte of the composition, mol/dm³: 0.4 K₄P₂O₇ and 0.1 CoSO₄. PEO was conducted in the galvanostatic mode at a current density of 3–5 A/dm² using an industrial stabilized power source B5-50 (Ukraine), an electrolytic cell with forced cooling and stirring, an ammeter and a voltmeter. Coatings were formed under cooling and mixing the electrolyte and controlling the process parameters. The temperature of the working solutions was maintained in the range of 20–25 °C. The sparking voltage US was 115–120 V, the formation voltage was controlled to be UF = 140–160 V.

The chemical composition of the coatings was determined by an energy-dispersive spectrometer INCA Energy 350. The surface morphology of the coatings was studied using a scanning electron microscope ZEISS EVO 40 XVP. X-ray diffraction analysis was performed on an X-ray diffractometer DRON-2 in monochromatic CoK_α radiation (λ = 1,7902 Å). The phase identification was performed by comparing the interplane spacing (*d*, Å) and the relative intensities of the experimental curve with the data of the PCPDFWIN electronic file system.

The catalytic properties of the oxide systems were studied in the oxidation of carbon(II) oxide to carbon(IV) oxide. The studies were conducted on a laboratory bench in a tubular flow reactor made of silica glass with a coaxially wound heating coil. The initial mixture of air and carbon(II) oxide with a concentration of 1.0 vol. % was fed to a reactor with a volume of 1.5 · 10⁻² dm³ at a rate of 1.5 dm³/h. The reactor tem-

perature was gradually increased from 20 to 450 °C at a rate of 1 °C/s. The CO concentration at the inlet and outlet of the reactor was recorded using Dozor signaling-analyzing devices. The catalytic activity was evaluated by the following parameters: the initial temperature of the oxidation process (the ignition temperature, *T_i*) and the conversion extent (*X*, %). The extent of conversion was calculated by the following equation:

$$X = \frac{c(\text{CO})_i - c(\text{CO})_f}{c(\text{CO})_i} \cdot 100\%,$$

where *c*(CO)_{*i*} and *c*(CO)_{*f*} are the initial and final concentrations of carbon(II) oxide, %.

The studies demonstrate that the chronograms of operating voltage (formation curves) and voltage change (trend) during oxidizing silumin in the electrolyte 0.4 mol/dm³ K₄P₂O₇, 0.1 mol/dm³ CoSO₄ at different current densities have a classic form (fig. 1) consisting of characteristic regions [18, 19]. The first prespark region I (fig. 1, *a*) corresponds to the formation of silumin components in the oxides phase and voltage increases linearly with time. In the second prespark region II, the change in the operating voltage is influenced by the opposite processes of growth and destruction of oxide layers, which affects the reduction in *dU/dt*. Moreover, with increase in current density, the formation rate exceeds the dissolution rate and *dU/dt* is higher (fig. 1, *b*).

The third section (fig. 1, III) corresponds to the transition of the PEO process to the sparking mode due to the phase oxides breakdown. Not only electrochemical, but also thermochemical reactions occur in the spark zone, associated with water thermolysis and with the participation of

electrolyte components. The sparking

Fig. 1. Formation curves (a) and voltage trend (b) at oxidation current density, A/dm²: (1) 3, (2) 5, (3) 10.

voltage increases with increasing current density, and it is at this stage that the probability of dopants inclusion in the aluminum oxide matrix increases. The time of sparking decreases from 6 to 1 min with increase in current density i over the studied interval.

Sparking voltage in all cases is 120–125 V. Sparking intensity in the oxidation process is quite high. Region IV of formation curves is associated with sparking to microarc regime transition. The final formation voltage depends on the initial current density of PEO. For $i = 3\text{--}5$ A/dm² UF is 160–170 V and enables conducting the process of PEO treatment within 15 min or longer. At the current density of 10 A/dm² UF does not exceed 160 V. The oxidation process rapidly goes through all stages and from the 4th minute enters the arc mode. In this case, PEO of the alloy after 8 min is impractical; the formed coating is destroyed under the influence of arc discharges.

Figure 2 shows the morphology and chemical composition of the silumin surface oxidized at a current density of 3 A/dm² in different regions of the formation curve (time of oxidation). Due the local dissolution of alloying components in regions I and II particularly silicon content in surface layers is reduced by 3–4 at.% in comparison with its percentage in silumin. The transition from the juvenile surface to the developed alumina structure with a large number of irregular shaped inclusions (Fig. 2 a) is observed. At this stage, there is almost no incorporation of additional components into the oxide layer.

The sparking initiation (luminescence) is visualized by the appearance of a small sparks that evenly cover the surface to be treated, which characterizes the beginning of electrolyte components incorporation into the surface layers (fig. 2, b). On SEM images, it is possible to identify a significant number of crater-like small apertures with fused edges. The content of silicon in the surface layer is reduced by almost two

Fig. 2. Morphology and chemical composition of the surface, at.% : *a* – prespark (regions I and II), Al – 33.5, O – 56.0, Si – 10.5; *b* – sparking (region III) Al – 33.5, O – 56.7, Si – 6.5, Co – 3.3, *c* – microarc (region IV), Al – 33.3, O – 55.2, Si – 2.5, Co – 9.0; magnification $\times 500$.

times and is not more than 5 at.%. In this case, the content of cobalt gradually increases to 3.3 at.%.

Under the conditions of constant current density, the oxidation process almost instantaneously goes into the micro-arc mode: there is an enlargement of sparks with decrease in their number, the burning of micro-arc discharges occurs at the corners (projections) of the specimen and is accompanied by a characteristic cracking due to the "collapse" of gas vapors in micro-discharge channels. In places of burning sparks appear spheroid islands of characteristic blue-violet color, typical for the incorporation of cobalt. During processing, the number of such island structures significantly increases, they are combined, agglomerated and form mosaic structures (fig. 2, *c*).

The mixed cobalt oxides formation is also evidenced by the chemical composition analysis at different sites of the sample surface. The spheroids and agglomerated structures exhibit a range of 5.0–23.3 at.% (Co),

on the valley of the sample cobalt percentage is about 14.5 at.%. For the silicon content there is a reverse dependence: on the hills Si does not exceed 2.0 at.%, and on the valley it is 5.0 at.% throughout the processing period.

The influence of current density is sufficiently evident in the change of surface morphology of oxide coatings obtained during 15 min. (fig. 3).

In the PEO process, cobalt incorporation into oxide layers occurs in the form of drop-shaped and spherical inclusions of blue-purple color (fig. 3, *a*). With increase in oxidation current density from 3 to 5 A/dm², their number increases, they form mosaic structures and evenly cover the entire sample surface (fig. 3, *b*). The resulting ceramic-like coating has high adhesion to the substrate. Oxidation of samples at 10 A/dm² leads to cobalt incorporation in the form of voluminous islet structures (fig. 3, *c*). Given a quite rapid transition of PEO to the arc mode, there is a tendency to these inclusions

Fig. 3. Surface morphology of $\text{Al}_2\text{O}_3 \cdot \text{CoO}_x$ coatings, obtained at different current densities, A/dm^2 : (a)3; (b)5; (c)10; magnification $\times 500$.

peeling off from the substrate.

The results of the X-ray diffraction analysis exhibit difference between the silumin samples oxidized in a pyrophosphate solution and in an electrolyte with cobalt sulfate addition (fig. 4).

There are lines associated only with $\alpha\text{-Al}_2\text{O}_3$ and Si on XRD patterns of samples treated in a cobalt-free solution. And the shape of XRD patterns for mixed oxide systems substantially changes which confirms the incorporation of Co_3O_4 oxides into the alumina matrix. The intensity of the cobalt oxide lines depends on the quantitative composition of the surface layer. The X-ray diffraction pattern also revealed a wide halo at angles of $2\theta \sim 10\text{--}30^\circ$ reflecting amorphous structure.

Testing the oxide system in the model reaction of carbon(II) oxide conversion to CO_2 showed (table) that their activity (both ignition and complete conversion (T_c) temperature) is similar to platinum catalyst and is much better than the parameters of

alumina.

Pilot tests of mixed oxides deposited on the surface of the combustion chambers piston of an ICE, showed that the coating of $\text{Al}_2\text{O}_3 \cdot \text{CoO}_x$ allows ones to reduce NO_x emissions by 10 % and CO ones by 15–18 % in forced diesel engine operating modes. This is due to the lower the ignition temperature of the air-fuel mixture on the surface of $\text{Al} | \text{Al}_2\text{O}_3 \cdot \text{CoO}_x$ catalyst composed of mixed oxides with developed surface.

The heterogeneity of the chemical composition and a significant amount of doping components in silumin in comparison with pure aluminum result in differences in the technological parameters of PEO [20]. This is due to the consumption of a certain amount of anode current at the initial oxidation stage to homogenize the alloy surface. The higher the operating current the faster the alloy components oxidize from the surface in the alkaline environment in the presence of pyrophosphate. The surface becomes chemically homogeneous and phase alumina

is formed. The latter serves as a matrix for the incorporation of catalytically active cobalt in the sparking region of PEO. The reflection of this is a change in the chemical composition and morphology of the surface of the sample in different sections of the voltage chronogram.

Considering the competing processes of formation and dissolution of phase oxide at

Fig. 4. XRD patterns for oxidized silumin and mixed oxide coatings. The composition is similar to fig. 2, *b*.

Table 1

Characteristics of CO conversion to CO₂

Material	Metal, at. %	T_i , K	T_c , K
Pt	100	490	570
Al Al ₂ O ₃	30.8	595	670
Al Al ₂ O ₃ ·CoO _x	8.7	505	580

the initial oxidation stage, the actual growth of the mass of the oxide layer is observed only in the micro-arc mode with a gradual

increase and a maximum of 55 minutes of processing. The optimal time interval, based on the results obtained, is the oxidation of AL25 within 30–55 minutes. In the studied conditions, the micro-arc PEO regime is maintained quite long, which leads to a uniform increase in the thickness of the oxide layer with increasing processing time.

It is noticeable that the change in the chemical composition of the formed oxide coatings can be traced in the change in the morphology of the surface layers in the variation of the time of PEO treatment. The incorporation of cobalt into the surface layers substantially changes their morphology and causes the formation of bulk structures with a high specific surface. With increase in the processing time from 15 to 20 minutes, the morphology of the samples surface varies from the characteristic alumina barrier structure to a highly developed mosaic one if cobalt is incorporated in the alumina matrix. This is due to a growth of the oxide layer thickness and an increase in the cobalt content in the sparking mode. PEO treatment for 30–55 minutes leads to the consolidation of the formed ceramic-like coatings and the formation of the structure of bulk spheroids. With increase in processing time of up to 60 minutes, the surface of the coating becomes almost uniform due to the "healing" of the protrusions and defects, as well as the inclusion of a significant amount of phosphates in the surface layers. The obtained results are in full accordance with the kinetic laws and allow us to determine the rational time of PEO for the application of oxide coatings of a given composition and morphology.

The peculiarities of the phase structure of obtained oxide coatings in combination

with a developed surface and a high cobalt content are a prerequisite for their high catalytic properties. The catalytic activity of mixed oxide systems can be attributed to several factors. Firstly, it is a high affinity of non-stoichiometric cobalt oxides to oxygen and the corresponding decrease in the activation energy of O=O double bond breakdown. Secondly, the developed micro globular surface of oxide systems is characterized by a large number of catalytic centers and provides an increase in the number of elementary collisions and interactions.

CONCLUSIONS. $\text{Al}_2\text{O}_3 \cdot \text{Co}_3\text{O}_4$ mixed oxide coatings with a cobalt content of up to 23.3 at.% were obtained on a high-silicon aluminum alloy AL25 by one-stage plasma-electrolytic oxidation in a cobalt-containing pyrophosphate electrolyte. It has been established that the surface concentration of Si in mixed coatings is two to three times lower than that in the processed alloy. The ratio of cobalt and oxygen in the coatings is non-stoichiometric; the content of cobalt in mixed oxides increases with increasing current density and operating time. With increase in the cobalt content the surface morphology varies from uniformly rough to micro-globular with relatively large spheroids. The resulting oxide systems have a developed surface with a large number of catalytic centers, consisting of spheroids and toroidal structures that alternate between themselves. The application of $\text{Al}_2\text{O}_3 \cdot \text{Co}_3\text{O}_4$ coatings on to the surface of combustion chambers helps to save fuel and improves the ecological characteristics of internal combustion engines, which can therefore be recommended for use in gas neutralization systems and in-cylinder catalysts for ICE.

ОСОБЛИВОСТІ ФОРМУВАННЯ КОБАЛЬТ ВМІСНИХ ОКСИДНИХ ПОКРИТТІВ НА СИЛУМІНІ

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Вивчено процес формування змішаних оксидних покриттів на висококремністому алюмінієвому сплаві у кобальтвмісних пірофосфатних електролітах методом плазмо-електролітичного окислення (ПЕО). Показано, що гетерогенність хімічного складу АЛ25 обумовлює необхідність витрати частини анодного струму на гомогенізацію поверхні, що відбивається в мінімізації змісту легуючих компонентів на початковій стадії обробки. Встановлено, що зростання відносної маси змішаних оксидів $\text{Al}_2\text{O}_3 \cdot \text{Co}_x\text{O}_y$ є функцією часу з максимумом, що припадає на 55 хв. Хімічний, фазовий склад і морфологія поверхні утвореного оксидного шару залежать від часу окислення. Вміст каталітичного компонента в поверхневих оксидах змінюється від 0,2 до 23,3 %ат. при збільшенні часу обробки від 10 до 60 хвилин. Максимальне включення кобальту в шар оксиду відбувається при ПЕО 35–50 хвилин, в той час як вміст кремнію в поверхневих шарах не перевищує 2 %ат., що сприятливо для каталітичних властивостей. Включення оксиду кобальту Co_3O_4 у матрицю $\alpha\text{-Al}_2\text{O}_3$ візуалізується стереїдними поверхневими структурами синьо-фіолетового кольору, які переважають у місцях мікродугових розрядів. Шар змішаного оксиду алюмінію і оксидів кобальту характеризується розвинутою мікроглобулярною поверхнею, що складається з конгломератів сфероїдів із середнім розміром 1-2 мкм. У

структурі змішаних оксидів присутні аморфні фази через нерівноважні умови ПЕО. Скупність описаних факторів – передумова високих каталітичних властивостей оксидних покриттів. Перспективною сферою застосування систем $\text{Al}_2\text{O}_3 \cdot \text{Co}_x\text{O}_y$ є внутрішньоциліндровий каталіз у двигунах внутрішнього згорання.

К л ю ч о в і с л о в а: плазмо-електролітичне оксидування, матриця оксиду алюмінію, оксиди кобальту, каталітична активність, внутрішньо-циліндровий каталіз.

ОСОБЕННОСТИ ФОРМИРОВАНИЯ КОБАЛЬТ - СОДЕРЖАЩИХ ОКСИДНЫХ ПОКРЫТИЙ НА СИЛУМИНЕ

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Изучен процесс формирования смешанных оксидных покрытий на алюминиевом сплаве АЛ25 в кобальтсодержащем пирофосфатном электролите методом ПЭО. Показано, что гетерогенность химического состава АЛ25 обуславливает необходимость затраты части анодного тока на гомогенизацию поверхности на начальной стадии обработки. Установлено, что рост относительной массы смешанных оксидов $\text{Al}_2\text{O}_3 \cdot \text{Co}_x\text{O}_y$ является функцией времени с максимумом, приходящимся на 55 мин. Химический, фазовый состав и морфология поверхности сформированных оксидных слоев зависят от времени ПЭО. Содержание Со в поверхностных слоях изменяется от 0,2 до 23,3 % ат. при увеличении времени обработки с 10 до 60 мин. Слой смешанных оксидов $\text{Al}_2\text{O}_3 \cdot \text{Co}_x\text{O}_y$ характери-

зуется развитой микроглобулярной поверхностью. В структуре смешанных оксидов присутствуют аморфные фазы из-за неравновесных условий ПЭО. Совокупность описанных факторов является предпосылкой высоких каталитических свойств оксидных покрытий. Перспективная область их применения – внутрицилиндровый катализ в двигателях внутреннего сгорания.

К л ю ч е в ы е с л о в а: плазменно-электролитическое оксидирование, матрица оксида алюминия, оксиды кобальта, каталитическая активность, внутрицилиндровый катализ.

REFERENCES

1. Glazoff M.V., Zolotarevsky V.S., Belov N.A. *Casting Aluminum Alloys*. (Oxford: Elsevier, 2007).
2. Dong H. *Surface Engineering of Light Alloys: Aluminium, Magnesium and Titanium Alloys*. (Elsevier, 2010).
3. Malyshev V.N., Zorin K.M. Features of Microarc Oxidation Coatings Formation Technology in Slurry Electrolytes. *Appl. Surf. Sci.*, 2007. **254** (5): 1511.
4. Gupta P., Tenhundfeld G., Daigle E.O., Ryabkov D. Electrolytic plasma technology: Science and engineering – An overview. *Surf. Coat. Technol.* 2007. **201** (21): 8746.
5. Rogov A.B., Slonova A.I., Shayapov V.R. Peculiarities of iron-containing microplasma coating deposition on aluminum in homogeneous electrolyte. *Appl. Surf. Sci.* 2012. **261**: 647.
6. Borisov A.M., Krit B.L., Lyudin V.B., Morozova N.V., Suminov I.V., Apelfeld A.V. Microarc oxidation in slurry electrolytes: A review. *Surf. Eng. Appl. Electrochem.* 2016. **52** (1): 50.

7. Lukiyanchuk I.V., Rudnev V.S., Tyrina L.M. Plasma electrolytic oxide layers as promising systems for catalysis. *Surf. Coat. Technol.* 2016. **307** (Part C): 1183.
8. Rudnev V.S., Lukiyanchuk I.V., Vasilyeva M.S., Medkov M.A., Adigamova M.V., Sergienko V.I. Aluminum- and titanium-supported plasma electrolytic multicomponent coatings with magnetic, catalytic, biocide or biocompatible properties. *Surf. Coat. Technol.* 2016. **307**(Part C): 1219.
9. Sakhnenko N., Ved M., Bykanova V. Characterization and photocatalytic activity of $Ti/Ti_nO_m \cdot Zr_xO_y$ coatings for azo-dye degradation. *Func. Mater.* 2014. **21**: 492.
10. Sakhnenko N., Ved M., Karakurkchi A., Galak A. A study of synthesis and properties of manganese-containing oxide coatings on alloy VT1-0, *East-Europ J Enterpr Technol.* 2016. **3** (5(81)): 37.
11. Rakoch A.G., Khokhlov V.V., Bautin V.A., Lebedeva N.A., Magurova Yu.V., Bardin I.V. Model concepts on the mechanism of microarc oxidation of metal materials and the control over this process. *Protection of Metals.* 2006. **42** (2): 158.
12. Rudnev V.S., Yarovaya T.P., Nedorozov P.M., Mansurov Yu.N. Wear-resistant oxide coatings on aluminum alloy formed in borate and silicate aqueous electrolytes by plasma electrolytic oxidation. *Protection of Metals and Physical Chemistry of Surfaces.* 2017. **53**: 466.
13. Rogov A.B. Plasma electrolytic oxidation of Al1050 aluminium alloy in homogeneous silicate-alkaline electrolytes with edta4-complexes of Fe, Co, Ni, Cu, La and Ba under alternating polarization conditions. *Mater. Chem. Phys.* 2015. **167**: 136.
14. Dudareva N.Yu., Abramova M.M. The Structure of Plasma-Electrolytic Coating Formed on Al-Si alloys by the Micro-Arc Oxidation Method. *Protection of Metals and Physical Chemistry of Surfaces.* 2016. **52** (1): 128.
15. Boguta D.L., Rudnev V.S., Yarovaya T.P., Kaidalova T.A., Gordienko P.S. On Composition of Anodic-Spark Coatings Formed on Aluminum Alloys in Electrolytes with Polyphosphate Complexes of Metals. *Russ. J. Appl. Chem.* 2002. **75** (10): 1605.
16. Wang P., Li J.P., Guo Y.C., Yang Z., Wang J.L. Ceramic coating formation on high Si containing Al alloy by PEO process. *Surface Engineering.* 2016. **32** (6): 428.
17. Ayday A., Durman M., Growth Characteristics of Plasma Electrolytic Oxidation Coatings on Aluminum Alloys. *Acta Physica Polonica A.* 2015. **127** (4): 886.
18. Yar-Mukhamedova G.Sh., Ved M.V., Karakurkchi A.V., Sakhnenko N.D., Mixed alumina and cobalt containing plasma electrolytic oxide coatings. *IOP Conference Series: Materials Science and Engineering.* 2017. **213**: 012020.
19. Sakhnenko N.D., Ved M.V., Karakurkchi A.V. *Nanoscale Oxide PEO Coatings Forming from Diphosphate Electrolytes.* In: Fesenko O., Yatsenko L. (eds.) Nanophysics, Nanomaterials, Interface Studies, and Applications. NANO 2016. Springer Proceedings in Physics. 2017. **195**: 159.
20. Ved' M.V., Sakhnenko N.D., Karakurkchi A.V., Myrna T.Yu. Functional mixed cobalt and aluminum oxide coatings for environmental safety. *Func. Mater.* 2017. **24** (2): 303.

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