ABSTRACT

of the thesis «**Development of a technology for applying protective coatings of plasma electrolytic oxidation on the surface of aluminum alloys**» submitted for the degree of Doctor of Philosophy (PhD) in the specialty 8D07103 - «Materials Science and Engineering»

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The purpose of the thesis is development of energy-efficient technologies for obtaining protective coatings via pulsed current modes in the PEO process in order to ensure optimal structural characteristics on the surface of aluminum alloys.

Research objectives and their place in the performance of research work

1. Conducting a systematic and in-depth study to determine the optimal electrolyte composition for the fast coating growth on the surface of the AA2024 alloy via using a unipolar PEO current source.

2. Study of the role of various silicon-containing particles with different sizes and types (SiO_2 and Si_3N_4) in a phosphate-based electrolyte on the formation and composition of coatings. Study of corrosion-, and wear-resistance of coatings.

3. Obtaining coatings on the surface of various aluminum alloys Al-Cu and Al-Si. Study the effect of the chemical composition of the initial alloys on the formation and composition of coatings.

4. Optimization of the processing parameters in the PEO bipolar mode. Study of the microhardness of the obtained coatings.

5. Study of the influence of the chemical stability of the silicate electrolyte on the technological process in the bipolar current PEO mode.

Research methods

Research was carried out using modern equipments from certified laboratories at the KazNRTU named after K.I. Satbayev (Laboratory of Engineering), Helmholtz-Zentrum hereon (Institute of Surface Sciences, Geesthacht, Germany). During the experimental research work, a number of advanced methods and equipment were used. In particular, a laboratory unit for plasma electrolytic oxidation and a sample preparation complex (grinding and polishing unit), pH meter (691, Metrohm), conductivity measurements (SevenMulti, Mettler Toledo), thickness gauge (MiniTest 2100, Elektro Physik), optical microscopy (OLYMPUS BX53M), scanning electron microscope (TescanVega3SB) with an energy dispersive spectrometer system (EDS eumeX), laser scanning confocal microscope (LSM 800, ZEISS) X-ray diffraction measurements (XRD, D8 Advance, BrukerAXS), glow discharge optical emission spectroscopy (GD-Profiler 2, HORIBA), synchrotron PETRA III (DESY), tribotester with oscillating motion (TRIBOtechnic), microhardness meter STEP-100 Anton-Paar, potentiostat (Gamry) were used. During the PEO process, the oxidation voltage as a function of the treatment time was recorded, using a data acquisition system SignaSoft 6000 (Gantner Instruments). The surface characteristics were evaluated using software «ImageJ» as well.

The main provisions (proven scientific hypotheses and other conclusions that are new knowledge) to be defended

1) An electrolyte composition with a content of hydroxides (2 g/l), silicates (12-24 g/l) and phosphates (12-24 g/l) is proposed, which leads to an increase in the coatings growth rate and an improvement in the density and uniformity of PEO layers on the surface of the AA2024 alloy. The use of an optimal electrolyte composition at a low current density of 50 mA/cm^2 contributes to energy savings of up to 31% during the process.

2) The onset of soft sparking in bipolar PEO treatment leads to a high coating growth and an increase in the energy efficiency of the process. Under conditions of soft sparking, stable voltage after its reduction results in energy savings of up to 44% at a current density of 100 mA/cm^2 in an electrolyte containing silicates and phosphates at 24 g/l.

3) The chemical stability of silicate electrolytes affects the PEO process. As the number of treatments increases, the electrolyte conductivity decreases, and its chemical and phase composition changes.

Description of the main research results

During the scientific research, the following scientific results were obtained:

1) The composition of an electrolyte with a low hydroxide content (2 g/l), with a silicate and phosphate content at 12-24 g/l, has been optimized, which increases the growth rate of coatings and improves the density and uniformity of PEO layers.

2) It was found that energy savings in the unipolar PEO treatment mode are associated with a mixed electrolyte composition with a concentration of silicates and phosphates equal to 18-24 g/l when using a relatively low current density (50 mA/cm^2). A higher rate of coating growth when using an optimal electrolyte composition can reduce the processing time if a certain thickness is required. However, proper cost and environmental impact analysis of highly concentrated electrolytes is a complex process and must be performed for specific components/applications.

3) A variety of phases, coating thicknesses and final voltages as a function of electrolyte compositions was observed. With high final voltages (over 470 V) for coatings produced in mixed electrolytes with low concentrations of hydroxide, silicate or phosphate (2 and 6 g/L), γ-Al_2O_3 crystalline phase predominates in the PEO layer composition. However, only a low efficiency of coating growth can be reached. High silicate-phosphate contents (18-24 g/L) in mixed electrolytes with low final voltages of about 360 V results in a fully amorphous PEO layer and significantly increases coating thickness.

4) A relatively low coating growth rate, with dominating inward layer growth in hydroxide-, and phosphate-based electrolytes was observed. Si-based electrolytes contribute to preferential outward growth of the PEO coatings, where the deposition from the electrolyte and Al oxidation processes simultaneously occur. The thickening of the coatings mainly depends on the rapid deposition of bath compounds from Si-based electrolytes.

5) It has been revealed that the incorporation of various sizes and types of silicon-based particles in the coating formation process is associated with locally high discharge temperatures. The addition of SiO_2 nanoparticles to the phosphate electrolyte showed high uptake and chemically active incorporation of SiO_2

nanoparticles into the coating, with the formation of mixed phases of mullite ($Al_2O_3 \cdot nSiO_2$) along with γ-Al_2O_3. However, the local discharge temperature during PEO (final voltage 485 V) was insufficient for the formation of silicate phases when using micro-sized SiO_2 and nanoscale Si_3N_4 particles in a phosphate electrolyte due to their large size or chemical stability.

6) It is shown that the formation of coatings on different substrates (Al-Cu and Al-Si) contributes to the production of coatings with different compositions and characteristics. It was found that the coating obtained on the surface of the Al-Cu alloy has a high growth rate. The PEO process was characterized by a lower efficiency of coating formation on the Al-Si surface. It is revealed that achieving the same final voltage of 480 V is essential due to the importance of high local temperatures and effective discharge energy during PEO processing for the formation of silicon-containing phases on various substrates.

7) It is revealed that the soft sparking mode in bipolar PEO treatment leads, along with a high coating growth rate of, to an increase in the energy efficiency of the process. High energy savings are achieved under soft sparking conditions at a stable voltage after its reduction in an electrolyte with a concentration of silicates and phosphates equal to 24 g/l.

8) It was found that in the case of coatings obtained in a silicate electrolyte (18 g/l), a discharge voltage of at least 400 V is required to onset of soft sparking mode when using current densities of 50 and 100 mA/cm2, whereas for coatings obtained in a silicate-phosphate electrolyte (24 g/l) a discharge voltage of at least 300 V is required.

9) It has been experimentally established that thin coatings obtained in a phosphate electrolyte (18 g/l) with a predominance of the γ-Al_2O_3 phase have a high microhardness compared to thick coatings formed in an electrolyte containing silicates and silicate-phosphates (18-24 g/l) under soft sparking conditions in the bipolar PEO treatment regime.

10) It has been established that the chemical stability of the silicate compositions of electrolytes affects the PEO process. It was found that with an increase in the number of treatments, the electrical conductivity decreases, and the chemical and phase composition of the electrolyte changes.

Substantiation of the novelty and importance of the obtained results

The importance for carrying out this research work is due to the high energy consumption of the PEO process and low oxidation productivity, which limit the wide range of applications of this method in mass production. The main scientific problem, the development of which is devoted to the dissertation work, is the creation of technological and scientific foundations for surface treatment of aluminum alloys by plasma electrolytic oxidation.

The novelty of the topic is the development of energy-efficient technologies for obtaining protective coatings on the surface of aluminum alloys in order to ensure high process performance and improve their structural characteristics.

Compliance with scientific development directions or government programs

The dissertation work was carried out within the framework of an international project FUNCOAT H2020-MSCA-RISE-2018 («Development and design of new multifunctional PEO coatings», 823942), and during an overseas research internship at the Institute of Surface Sciences (Geesthacht, Germany), and is also a continuation of the applicant's research as the head of the grant financing project of the Ministry of Education and Science of the Republic of Kazakhstan "Zhas Galim" IRN: AP25795409 (2025-2027) on the topic "Study of surface modification of aluminum alloys by plasma electrolytic oxidation".

The contribution of the doctoral student to the preparation of each publication The phD student's personal involvement in obtaining scientific results consists in developing a plan and conducting experiments, performing theoretical and experimental research, as well as discussing and summarizing the data obtained. Based on the materials of the dissertation, 4 publications have been published, including *2 articles in an international peer-reviewed scientific journal included in the Scopus database and the Web of Science*:

1. **G. Yeshmanova**,C. Blawert, M. Serdechnova, D.C.Florian Wieland, M. St arykevich, E. Gazenbiller, D. Höche, D. Smagulov, M.L. Zheludkevich Effect of electrolyte composition on the formation of PEO coatings on AA2024 aluminium alloy, Surfaces and Interfaces 44 (2024) 103797 (*Q1, 82%, IF 6.2*), https://doi.org/10.1016/j.surfin.2023.103797.

2. **G. Yeshmanova**, C. Blawert, M. Serdechnova, M. Starykevich, T. Wu, U. Kakimov, V. Kasneryk, T. Shulha, D. Smagulov, M.L. Zheludkevich Influence of different Si sources on plasma electrolytic oxidation coating formation, morphology and composition, Journal of Alloys and Compounds 1036 (2025) 181845 (*Q1, процентиль 91%, IF 6.3*) https://doi. org/10.1016/j.jallcom.2025.181845

1 article in publications recommended by the Committee for Quality Assurance in Science and Higher Education of the Republic of Kazakhstan, included in the Web of Science database:

Yeshmanova G., Smagulov D., Blawert C. Plasma electrolyte oxidation technology for obtaining protective coatings of aluminum alloys, Kompleksnoe ispolzovanie mineralnogo sirya 2021 2(317) 78-93. https://doi.org/10.31643/2021/6445.21.

Proceedings of international scientific and practical conferences:

1. **Yeshmanova G.**, Smagulov D., Obtaining protective coatings on the surface of aluminum alloys by plasma electrolytic oxidation, Proceedings of the II International Conference in Memory of Academician E.G. Boos (ICHEPMS – 2024), February 15-16, 2024, Satbayev University, Almaty.