ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational program **8D05301 – «Technical Physics»**

DMITRIY SERGEEVICH DOGADKIN

PHYSICAL REGULARITIES OF STRUCTURE FORMATION AND FUNCTIONAL PROPERTIES OF CALCIUM PHOSPHATE COATINGS ON TITANIUM DURING PLASMA ELECTROLYTIC OXIDATION

The dissertation presents a comprehensive experimental and theoretical study in the field of condensed matter physics, surface physics, and biomaterials science for medical implants. The work is focused on establishing the physical regularities governing the formation of the structure and functional properties of calcium phosphate coatings on titanium produced via plasma electrolytic oxidation (PEO). At the core of the research is the investigation of the relationships between PEO process parameters, growth kinetics, microstructure evolution, phase composition, and physico-mechanical properties of coatings deposited on Ti-6Al-4V alloy substrates fabricated by selective laser melting (SLM).

Relevance of the Research Topic.

The relevance of this study stems from the urgent need to develop next-generation implants that combine superior mechanical strength with high bioactivity. Although titanium alloys are widely utilized in orthopedics and dentistry, their surfaces often exhibit limited osseointegration capability. Currently, there is a significant knowledge gap regarding the physical mechanisms governing the formation of hydroxyapatite-like phases during the PEO process, as well as the impact of applied voltage on the microstructure, phase composition, and tribomechanical properties of the resulting coatings. Addressing these issues is essential for establishing a scientific foundation for the fabrication of bioactive coatings with tailored characteristics for personalized medicine. This research aligns with the priority areas of scientific development in the Republic of Kazakhstan, specifically in biomedical materials science and additive manufacturing.

Objective of the study.

To establish the physical regularities governing the formation of the structure and functional properties of calcium-phosphate coatings on titanium during plasma electrolytic oxidation at various applied voltages, as well as to substantiate the geometric parameters of porous structures to match the biomechanical properties of implants with those of bone tissue.

Research Objectives:

1. To determine the patterns of formation of surface morphology, porosity, thickness, and structure of calcium phosphate coatings on Ti-6Al-4V alloy substrates produced by selective laser melting at various applied voltages of plasma electrolytic oxidation.
2. To identify the physicochemical mechanisms of structural and phase evolution of the formed coatings and establish patterns of formation of hydroxyapatite-like phases depending on plasma electrolytic oxidation conditions.
3. To establish relationships between plasma electrolytic oxidation parameters, the structural and phase characteristics of the coatings, and their physicomechanical properties.
4. To substantiate the criteria for selecting optimal plasma electrolytic oxidation conditions for the formation of functional coatings with a given set of properties, depending on the operating conditions of medical devices.
5. Develop a three-dimensional porous structure with target functional properties and test its biomechanical compliance with bone tissue using computer modeling and experimental analysis.

Object of study.

Calcium phosphate coatings formed by plasma electrolytic oxidation (PEO) on Ti-6Al-4V alloy substrates fabricated by selective laser melting (SLM).

Subject of study.

Physical regularities governing the formation of the structure, phase composition, elemental composition, and mechanical and tribological properties of calcium phosphate coatings as a function of the applied voltage during the PEO process.

Research methods.

Coatings were deposited using a plasma electrolytic oxidation (PEO) unit equipped with a pulsed power supply. Surface and cross-sectional morphologies were characterized via scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS). The phase composition was determined by X-ray diffraction (XRD) using Cu-Kα radiation. Fourier-transform infrared (FTIR) spectroscopy was employed to identify functional groups within the coatings. Mechanical properties (microhardness, elastic modulus) were evaluated using the instrumental indentation method and an electromechanical testing machine. Tribological tests were performed in a ball-on-disk configuration using an Al_2O_3 counterface. Additionally, finite element analysis (FEA), surrogate modeling based on artificial neural networks (ANN), and Bayesian analysis were conducted to assess the structural integrity of the implants.

Main provisions submitted for defense:

1. Variation in the plasma electrolytic oxidation voltage allows for controlling the phase composition and properties of the coating: an increase in

voltage leads to an increase in the coating thickness from 1 to 35–37 μm and a sequential transformation of the phase composition from anatase to rutile and hydroxyapatite. The formation of a heterophase anatase-rutile structure at 250 V minimizes the elastic modulus and reduces the wear rate to $2.765\cdot10^{-4}$ $mm^3/N\cdot m$, whereas the 300 V regime is characterized by the predominance of the bioactive hydroxyapatite phase.

2. The plasma electrolytic oxidation process leads to an increase in the β-phase titanium content in the near-surface layers of the substrate, which contributes to a reduction in the effective elastic modulus of the «coating-substrate» composite from 110 to 25-35 GPa and enhances its plasticity.

3. The application of an octet cell geometry of 2 mm in size with a strut thickness of 250 μm (porosity of 80.5%, pore size of 750 μm) ensures the matching of the effective elastic modulus of the resulting structure with the mechanical characteristics of trabecular bone (1-22.3 GPa), which was confirmed by finite element modeling and empirical analysis methods.

Main results of the study:

1. A systematic investigation of PEO coatings formed at 200, 250, and 300 V was conducted. Experimental data demonstrate that at 200 V, a thin layer (~1 μm) with a grooved morphology is formed. At 250 V, the thickness increases to 3-3.5 μm with homogenous porosity. At 300 V, a sharp increase in thickness up to 35-37 μm is observed, accompanied by the appearance of cracks and delamination.

2. The optimum wear resistance was achieved at 250 V (wear rate of 2.765×10^{-4} $mm^3/N\cdot m$). At 300 V, despite the increased thickness, high porosity and micro-cracking lead to a degradation of tribological performance. The friction coefficient was found to increase from 0.50 (at 200 V) to 0.60 (at 300 V)

3. It has been proven that at 300 V, crystalline hydroxyapatite is formed with a Ca/P ratio of 1.96, which is close to the stoichiometric value (1.67). The presence of carbonate groups was confirmed, indicating the formation of carbonate-substituted hydroxyapatite, which exhibits a higher similarity to bone tissue.

4. It was shown for the first time that PEO treatment at 250 V induces a local enrichment of the β-titanium phase in the near-surface layer due to thermal cycling above the β-transus temperature followed by rapid quenching. This results in a reduction of the elastic modulus from 110 GPa (base alloy) to 80-90 GPa (at 250 V) and 25-35 GPa (at 300 V), effectively mitigating the stress shielding effect.

5. The optimized geometric parameters of the octet cell (cell size of 2 mm, strut thickness of 250 μm) enabled the fabrication of a porous scaffold with mechanical properties matched to those of trabecular bone tissue.

Scientific novelty of the obtained results:

1. For the first time, the physical regularities governing the formation of calcium phosphate coatings via PEO on SLM-fabricated Ti-6Al-4V alloy substrates have been established, revealing the pivotal role of applied voltage in the evolution of the coating's microstructure and phase composition.

2. For the first time, a comprehensive analysis of the interplay between PEO processing parameters, structural-phase states, and tribomechanical

characteristics has been conducted. It was demonstrated that the optimal balance of mechanical and tribological properties is achieved at a specific voltage of 250 V.

3. It was shown for the first time that the PEO process on SLM-produced Ti-6Al-4V substrates induces a local enrichment of the β-titanium phase, which significantly influences both the elastic modulus and the wear resistance of the resulting surface layers.

4. The physical mechanisms behind hydroxyapatite phase formation at 300 V have been elucidated, identifying the plasma-chemical reactions occurring within the discharge zone involving Ca^{2+}, PO_4^{3-} and OH^- ions from the electrolyte.

5. The geometric parameters of the octet cell for porous scaffolds were optimized to match the mechanical properties of the structure with those of trabecular bone tissue.

Practical significance.

The results of this study are of significant practical value for the development of technological protocols for forming bioactive calcium phosphate coatings on titanium alloy implants fabricated via selective laser melting (SLM).

The significance of the findings lies in their potential application for:

- The development of patient-specific titanium implants with enhanced osseointegrative properties achieved by forming hydroxyapatite-containing coatings through PEO;
- The optimization of PEO parameters to produce coatings with tailored structural-phase characteristics and mechanical properties suited for specific clinical applications;
- The fabrication of implants with an adjustable elastic modulus (ranging from 25 to 110 GPa) by combining additive manufacturing and PEO modification, effectively mitigating the stress shielding effect;
- Implementation in orthopedics, dentistry, and maxillofacial surgery for the treatment and replacement of bone defects of various etiologies.

Reliability and validity of the obtained results.

The reliability of the results is ensured by a rigorous and systematic approach to the experimental studies and the application of complementary structural and elemental analysis techniques (SEM-EDS, XRD, and FTIR). The validity is further supported by the use of state-of-the-art certified equipment, the high reproducibility of the experimental data, and their consistency with findings reported in both national and international peer-reviewed literature.

Compliance with scientific development directions or state programs.

The experimental results of this dissertation were obtained within the framework of the Targeted Funding Program « Development and Implementation of Competitive Science-Based Technologies to Ensure Sustainable Development of the Mining and Metallurgical Industry of the East Kazakhstan Region» (Grant No. BR24992854), Targeted Funding Program «Development of technology for manufacturing prototypes of domestic medical instruments and medical devices»

(Grant No. BR24992786). The research was conducted at the Physics Center of the D. Serikbayev East Kazakhstan Technical University (EKTU) and aligns with the priority areas of scientific development of the Republic of Kazakhstan, specifically in the fields of biomedical materials science and additive manufacturing.

Doctoral candidate's personal contribution to each publication:

Sagidugumar A., Dogadkin D., Turlybekuly A., Kaliyev D. Calcium Phosphate Coatings Deposited on 3D-Printed Ti–6Al–4V Alloy by Plasma Electrolytic Oxidation // Coatings. 2024.

Contribution: Conceptualization and definition of research objectives; development of PEO coating protocols; conducting experimental studies on microstructure, phase composition, and properties; analysis and synthesis of the obtained data; and drafting the manuscript.

Dogadkin D., Sagidugumar A., Kaliyev D., Dmitriev N., Kozhakhmetov Y. The Role of Signal Waveforms in Plasma Electrolytic Oxidation // Coatings. 2025.

Contribution: Literature review; conducting tribological testing and subsequent data analysis; interpretation of results; writing and technical editing of the manuscript.

Beisekenov N., Azamatov B., Sadenova M., Dogadkin D., Kaliyev D. Data-Driven Design and Additive Manufacturing of Patient-Specific Lattice Titanium Scaffolds for Mandibular Bone Reconstruction // Journal of Functional Biomaterials. 2025.

Contribution: Participation in finite element analysis (FEA); analysis of numerical simulation results; discussion of the findings and preparation of high-quality visualizations/figures.

Dogadkin D., Azamatov B., Alapati S., Kaliyev D., Rudenko S., Sadenova M., Dmitriev N. Integrated Experimental and Computational Analysis of SLM-Fabricated Ti6Al4V Octet-Truss Scaffolds for Bone Tissue Engineering // Materials. 2026.

Contribution: Conceptualization and definition of research objectives; development of research methods; conducting experimental studies on microstructure, phase composition, and mechanical properties; analysis and synthesis of the obtained data; participation in finite element analysis (FEA); analysis of numerical simulation results; discussion of the findings; preparation of high-quality visualizations/figures; and drafting the manuscript.

Sagidugumar A.N., Dogadkin D.S., Azamatov B.N., Turlybekuly A., Rudenko S.O. Calcium phosphate coating formed on titanium scaffold by plasma electrolytic oxidation // Bulletin of Karaganda University. Physics Series. 2022.

Contribution: Experimental synthesis of coatings; participation in XRD and mechanical data analysis; discussion of results; and drafting the manuscript.

Sagidugumar A.N., Turlybekuly A., Dogadkin D., Pogrebnjak A.D., Kantay N., Sadibekov A. Phase transformations during the doping of zinc chloride and silver nitrate into calcium phosphates // Bulletin of Karaganda University. Physics Series. 2022.

Contribution: Participation in the analysis of phase transformations; data interpretation; writing and critical editing of the article.

Publications:

1. Sagidugumar A., Dogadkin D., Turlybekuly A., Kaliyev D. Calcium Phosphate Coatings Deposited on 3D-Printed Ti–6Al–4V Alloy by Plasma Electrolytic Oxidation // Coatings. 2024. Vol. 14. No. 6. P. 696. Q2 (Materials Science, Coatings & Films), IF: 2.8. DOI: 10.3390/coatings14060696
2. Dogadkin D., Sagidugumar A., Kaliyev D., Dmitriev N., Kozhakhmetov Y. The Role of Signal Waveforms in Plasma Electrolytic Oxidation // Coatings. 2025. Vol. 15. No. 1. P. 36. Q2 (Materials Science, Coatings & Films), IF: 2.8. DOI: 10.3390/coatings15010036
3. Beisekenov N., Azamatov B., Sadenova M., Dogadkin D., Kaliyev D. Data-Driven Design and Additive Manufacturing of Patient-Specific Lattice Titanium Scaffolds for Mandibular Bone Reconstruction // Journal of Functional Biomaterials. 2025. Vol. 16. No. 9. P. 350. Q1 (Engineering, Biomedical), IF: 4.8. DOI: 10.3390/jfb16090350
4. Dogadkin D., Azamatov B., Alapati S., Kaliyev D., Rudenko S., Sadenova M., Dmitriev N. Integrated Experimental and Computational Analysis of SLM-Fabricated Ti6Al4V Octet-Truss Scaffolds for Bone Tissue Engineering // Materials. 2026. Vol. 19. № 8. P. 1646. Q1 (Materials Science, General Materials Science), IF: 3.2. DOI: 10.3390/ma19081646
5. Sagidugumar A.N., Dogadkin D.S., Azamatov B.N., Turlybekuly A., Rudenko S.O. Calcium phosphate coating formed on titanium scaffold by plasma electrolytic oxidation // Bulletin of Karaganda University. Physics Series. 2022. Vol. 106. No. 2. P. 32–36. DOI: 10.31489/2022Ph2/32-36 (The journal is indexed in the list of the Committee for Quality Assurance (CQASHE RK)).
6. Sagidugumar A.N., Turlybekuly A., Dogadkin D., Pogrebnjak A.D., Kantay N., Sadibekov A. Phase transformations during the doping of zinc chloride and silver nitrate into calcium phosphates // Bulletin of Karaganda University. Physics Series. 2022. Vol. 106. No. 2. P. 18–23. DOI: 10.31489/2022Ph2/18-23 (The journal is indexed in the list of the Committee for Quality Assurance (CQASHE RK)).
7. Patent of the Republic of Kazakhstan for Utility Model No. 9325 «Trabecular cage for interbody spondylosis». Published July 5, 2024.

Scientific Presentation and Validation of the Results:

The main findings of the dissertation research were presented and discussed at the following scientific events:

- The International Conference «Advanced Materials Manufacturing and Research: New Technologies and Methods (AMM&R 2021)» (February 19, 2021, Ust-Kamenogorsk, Kazakhstan).

- The International Conference «The 25th Conference on Process Integration, Modelling, and Optimisation for Energy Saving and Pollution Reduction (PRES’22)» (September 5–8, 2022, Bol, Croatia).