

ABSTRACT

of dissertation for the Philosophy Doctor (PhD) degree on 6D072300 -

"Technical Physics" specialty

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"Study of the structure and physical and mechanical properties of detonation coatings based on aluminum and zirconium oxides"

The dissertation work is devoted to the optimization of the process of detonation spraying of coatings based on aluminum and zirconium oxides in order to improve their tribological and mechanical characteristics, as well as experimental studies of the influence of technological parameters of detonation spraying on the formation of the structural-phase state and physical and mechanical properties of coatings. In particular the structure, phase composition, microhardness, nanohardness, corrosion resistance, wear resistance, abrasive resistance, erosion resistance and heat resistance of aluminum oxide coatings were studied depending on the technological parameters of spraying (shot frequency, barrel filling volume) and on the temperature of subsequent thermal annealing. A method has been developed for applying a gradient coating of aluminum oxide, which has high hardness, wear resistance and adhesive strength.

The relevance of the study.

In modern mechanical engineering, an important role is given to the surface of materials, the state of which affects the performance properties of machine parts and tools. During the operation of machine parts, tools and technological equipment, the surface layers are exposed to the most intense impact. Currently, to improve the physical and mechanical properties of the surface of metals and alloys, protective coatings are used that have high physical and mechanical characteristics: hardness, resistance to wear and aggressive environments, low thermal and electrical conductivity, etc., which can significantly increase the life time and parts reliability. For the manufacture of protective coatings that meet a wide range of the above requirements, ceramics based on aluminum and zirconium oxides are widely used. Aluminum and zirconium oxides have properties characteristic of ceramics, but at the same time they have the strength of metals. Coatings based on aluminum and zirconium oxides have a high chemical and thermal stability, therefore they are of great practical interest, they are usually applied to metals to improve their corrosion resistance in high-temperature aggressive environments.

To obtain coatings based on aluminum and zirconium oxides, the methods of anodizing, thermal oxidation (TO), gas thermal spraying (GTS), microarc oxidation (MAO), etc. are widely used. Among them, the most promising is the method of gas thermal spraying, which allows solving the problems of protecting individual parts and entire structures from wear, corrosion, overheating, exposure to aggressive media, etc. There are many works devoted to obtaining coatings based on oxides using the technology of plasma, flame and detonation spraying, which are related to gas-thermal spraying methods.

Aluminum oxide forms several polymorphic varieties, or forms, having the same chemical composition, different crystal lattice structure and, therefore,

different properties. During heat treatment, aluminum oxide occurs $\alpha \rightarrow \gamma$ transformation. When heated, zirconia undergoes destructive phase changes. Therefore, the study of the formation structural-phase states of coatings from Al_2O_3 and ZrO_2 , depending on the type and mode of thermal spraying, is of great interest.

In order to obtain coatings from aluminum oxide by plasma, flame and detonation spraying methods, $\alpha\text{-Al}_2\text{O}_3$ is usually used as the initial powder. At the same time, the obtained coating practically consists of $\gamma\text{-Al}_2\text{O}_3$ in the case of flame spraying of corundum ($\alpha\text{-Al}_2\text{O}_3$), while plasma and detonation spraying form two-phase coatings consisting of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. But the obtained coatings have the main phase $\gamma\text{-Al}_2\text{O}_3$, which has a relatively loose structure and much lower compactness, hardness, abrasive and corrosion resistance than $\alpha\text{-Al}_2\text{O}_3$. It is possible to improve the physical and mechanical properties of aluminum oxide coatings by increasing the proportion of $\alpha\text{-Al}_2\text{O}_3$ in the composition of the coatings. And the improvement of the physical and mechanical properties of ZrO_2 coatings is also possible by selecting the optimal spraying parameter. Usually, to improve the physical and mechanical properties of Al_2O_3 and ZrO_2 coatings, volume or surface heat treatments are used. However, this increases the complexity of the process of obtained coatings and is not economically feasible. Therefore, one of the main tasks of improving the physical and mechanical characteristics of Al_2O_3 and ZrO_2 gas-thermal coatings is to optimize the spraying process. And this is possible with detonation spraying, which is distinguished by the pulsed nature of the spraying process and is carried out using a gas explosion to accelerate and heat the particles of the sprayed powder material. During detonation spraying, the powder material melts and under the influence of a shock wave, moves to the substrate at high speed, forming a coating on its surface. High speed is an important factor in the formation of the structure, physical and mechanical characteristics of the coating.

Currently, there are no exact methods for calculating the technological parameters of detonation spraying that fully allow predicting the properties of ceramic and metal-ceramic coatings, including coatings made of aluminum and zirconium oxides. Therefore, the technological parameters that determine the properties of detonation coatings were determined experimentally.

In connection with the foregoing, the topic of the dissertation work is devoted to the improvement of the detonation spraying method in order to obtain coatings from aluminum and zirconium oxides with high tribological and mechanical characteristics, as well as experimental studies of the influence of technological parameters of detonation spraying on the formation of the structural-phase state and physical and mechanical properties coatings from aluminum oxide and zirconium seems to be relevant.

The purpose of the dissertation work is a study of the influence of technological parameters of detonation spraying on the formation of the structural-phase state and physical and mechanical properties of detonation coatings based on aluminum and zirconium oxides.

To achieve this goal, the following **tasks** were solved:

- comparative study of structural and phase changes, tribological properties, hardness, adhesive strength and corrosion resistance of oxide coatings obtained by detonation spraying;

- to study the effect of heat treatment on the structure and properties of coatings based on aluminum and zirconium oxides obtained by detonation spraying;

- to investigate the effect of the shot frequency during detonation spraying on the structure and properties of aluminum oxide coatings;

- to study the effect of the degree of filling the detonation gun barrel with an explosive mixture on the formation of the structural-phase state, mechanical and tribological properties of aluminum oxide coatings;

- to develop a method for detonation spraying of gradient coatings with high mechanical and tribological characteristics.

Object of study: aluminum and zirconium oxide coatings obtained by detonation spraying.

The subject of the study is a technological parameter of detonation spraying, a feature of the formation of the structure and properties of coatings from oxides of aluminum and zirconium before and after heat treatment.

Research methods. According to the tasks set, the following analysis methods were used: scanning electron microscopy (SEM); energy dispersive X-ray microanalysis (EDS); X-ray diffraction analysis (XRD); measurements of nanohardness, microhardness, tests for wear resistance, heat resistance and corrosion resistance.

Scientific novelty of the work:

- for the first time, systematized experimental data were obtained on the effect of technological parameters (shot frequency, barrel filling degree) of detonation spraying on the structure, phase composition, mechanical and tribological properties of aluminum oxide coatings;

- it has been established for the first time that a decrease in the degree of filling the detonation gun barrel with an explosive mixture leads to an increase in the volume fraction of the $\alpha\text{-Al}_2\text{O}_3$ phase in coatings, and thereby an increase in microhardness and wear resistance;

- a new method has been developed for obtaining a graded coating of aluminum oxide by gradually reducing the degree of filling the detonation gun barrel with an explosive mixture. This method makes it possible to obtain a coating having a structure in which the $\alpha\text{-Al}_2\text{O}_3$ phase increases from the substrate to the surface. The obtained gradient coating has high hardness, wear resistance and adhesive strength.

The main provisions for defense:

1. As a result of heat treatment at temperatures of 1200 °C in detonation coatings of aluminum oxide, consisting of $\gamma\text{-Al}_2\text{O}_3$ with a small amount of $\alpha\text{-Al}_2\text{O}_3$, structural-phase transformations occur with the formation of a large amount of $\alpha\text{-Al}_2\text{O}_3$, which leads to an increase in their hardness to 46% and wear resistance up to 40%. After heat treatment at 1000°C, the microhardness of the ZrO_2 coating increases by 25%.

2. When applying aluminum oxide coatings by detonation spraying, a decrease in the degree of filling of the detonation barrel with an explosive mixture from 68 to 53% leads to an increase in the volume fraction of the α -Al₂O₃ phase and, thereby, an increase in microhardness by ~1.5 times and a decrease in wear intensity by ~2.5 times.

3. Detonation spraying of corundum powder (α -Al₂O₃) by gradually reducing the degree of filling of the detonation gun barrel with an explosive mixture from 68 to 53% makes it possible to obtain an aluminum oxide coating having a gradient structure, in which the α -Al₂O₃ phase increases from the substrate to the surface.

Scientific and practical significance of the work.

The results of the performed research have significant scientific and practical value. In this work, a comparative study of the structural-phase and physical-mechanical properties of oxide coatings based on aluminum and zirconium oxides obtained by the detonation method was carried out, as well as a comprehensive experimental study of the effect of technological parameters of continuous detonation spraying on the structural-phase state and physical-mechanical properties of the oxide- aluminum coatings contributes to the further development of detonation spraying technology and can be used in the process of obtaining coatings from powder materials based on aluminum oxide with improved functional properties.

The developed method for obtaining gradient coatings from aluminum oxide can be used to improve the performance of steel products exposed to wear and corrosion.

The developed method is protected by utility model patents "Method of applying a detonation coating" (No. 6204 published on July 2, 2021) and "Method of applying a detonation coating on metal surfaces" (No. 6665 published on November 12, 2021). An act of implementation without economic effect of the results of the dissertation work into the production of LLP "PF "BEST" (Act No. 285, 07.12.2021 year, Ceramic factory) was received.

Connection of the dissertation topic with research projects. The dissertation work was carried out in the laboratory "Surface Engineering and Tribology" and the National Scientific Scientific Laboratory for Collective Use of the East Kazakhstan University named after Sarsen Amanzholov (Ust-Kamenogorsk, Kazakhstan) and at the faculty "Basic Engineering Training" of the East Kazakhstan Technical University named after Daulet Serikbaev (Ust-Kamenogorsk, Kazakhstan).

Research work was carried out as part of the implementation of the following projects of grant and program-targeted financing:

No. BR05236748 "Research and development of innovative technologies for obtaining wear-resistant materials for engineering products" with funding from the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan, contract No. 197 dated 16.03.2018;

With grant funding of scientific research by the Committee of Science the Ministry of Science and Technology of the Republic Kazakhstan on the topic

"Improving the wear resistance and corrosion resistance of centrifugal pump impeller blades by applying detonation multilayer coatings", state registration No. AP09058615, 2021-2023 years.

Personal contribution of the author. The author's personal contribution consists in the search and analysis of literary periodicals devoted to the topic of the dissertation research. Together with scientific consultants, the goals and objectives of the study were determined, methods for studying oxide coatings were selected. The author of the dissertation was directly involved in the preparation of samples, studied the phase composition, surface morphology, measured the microhardness and nanohardness of the surface and the depth of the obtained oxide coatings, as well as in discussing the results and writing publications. The analysis of the results obtained and the formulation of the main conclusions were carried out jointly with scientific consultants.

The degree of validity and reliability of the results obtained in the work. The validity and reliability of the results obtained in the work is ensured by the originality and clarity of the problem statement, the choice and use of well-tested experimental research methods, the volume and statistics of experimental data. The research results have been publicly tested: published in scientific journals, reported and presented by the author at national and international conferences.

Approbation of dissertation work. The materials of the dissertation research were presented and tested at the following scientific conferences:

1. XIV-International Conference "Technologies with new materials: Powder metallurgy, composite materials, protective coatings, welding" (Minsk, Belarus, 2020);
2. XVIII-International IUPAC Symposium Macromolecular-Metal Complexes (Moscow, 2019);
3. VI-International scientific and technical conference "Creativity of youth - innovative development of Kazakhstan" East Kazakhstan State Technical University. D. Serikbaeva (Ust-Kamenogorsk, 2020);
4. VII-International scientific and technical conference "Creativity of youth - innovative development of Kazakhstan" East Kazakhstan Technical University named after D. Serikbaev (Ust-Kamenogorsk, 2021);
5. Advanced materials manufacturing and research: new technologies and techniques (AMM&R2021) international conference to be hosted virtually by D.Serikbayev East Kazakhstan technical university (Ust-Kamenogorsk, 2021).

Moreover, the main results of the dissertation work were reported and discussed at scientific seminars of the Department of Physics, at joint scientific seminars of the Faculty of Basic Engineering Training of the East Kazakhstan University. D. Serikbaev, as well as at scientific seminars of the research center "Surface Engineering and Tribology" of the East Kazakhstan University S.Amanzholov.

Articles. In total, 15 scientific articles were published on the topic of the dissertation, of which:

- 6 articles in scientific publications approved by the Committee for Quality Assurance in Science and Higher Education of the MOHEAS RK;

- 2 articles in journals included in the international information resources Web of Science Core Collection (ClarivateAnalytics) and Scopus, in particular: “Coatings” (Q2) and “Materials Research Express” (Q4);

- 5 articles and abstracts of reports in collections of materials of international conferences;

- 2 patents of the Republic Kazakhstan for a utility model.

Structure and scope of the dissertation work. The dissertation consists of an introduction, four chapters, conclusion and list of references, total 152 pages, 76 figures, 19 tables, 283 list of references, 6 appendixes.